

A. STUDY OF THE OXIDATIVE DEGRADATION OF
2,2,3,4,5-PENTAPHENYL-3-CYCLOPENTENONE BY VARIOUS OXIDANTS
AND
B. [1,5]-SIGMATROPIC PHENYL REARRANGEMENTS IN 2- AND/OR 5-
(p- or m-SUBSTITUTED PHENYL)-1,3,4-TRIPHENYL-2,4-CYCLOPENTADIEN-1-OLS:
ELECTRONIC EFFECTS AT THE MIGRATION TERMINUS

by

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(ABSTRACT)

A Hammett series comprised of seven 2- and/or 5-(p- or m-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ols was prepared and the ratio of the two-product mixture resulting from their thermal [1,5]-sigmatropic phenyl rearrangements was determined. In this system phenyl could migrate toward either of two positions, and the effect of the substituents upon the direction of migration was investigated to determine the extent of electronic effects in this neutral sigmatropic rearrangement. The results of these rearrangements are used to discuss the proposed transition state for phenyl rearrangements in the pentaphenylcyclopentadienol system. A strictly neutral transition state is proposed.

In addition, the oxidative degradation of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one by various oxidants was investigated. This substrate was found to be inert to all the reagents examined, with the exception of diacetyl chromate. The action of this oxidant upon the substrate produced an equimolar mixture of benzil, benzophenone, and benzoic acid in an overall yield of 40 to 42 percent.

DEDICATION

For Boo, Amy and Jason

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INTRODUCTION

The thermally induced isomerization of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one has been shown by Youssef and Ogliaruso¹ to be an example of a [1,5]-thermally allowed sigmatropic phenyl rearrangement. Investigation into the possibility that the rearrangement could be sensitive to electronic effects was undertaken by Perfetti,² who examined the kinetics of the rearrangement of five 3,4-bis-(p-substituted phenyl)-1,2,5-triphenyl-2,4-cyclopentadienols. The rates of isomerization were found to be nearly identical and a linear free energy relationship was not observed. Subsequent study into the kinetics of the 1-(p-substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols by Oldaker² indicated no significant rate differences among eight members of a Hammett series at the temperatures investigated.

The conclusion of these investigations into the electronic nature of phenyl migration in this system, and the crux of this dissertation, was the characterization of electronic effects at the migration terminus. A Hammett series of 2- and/or 5-(p- or m-substituted phenyl) cyclopentadienols were synthesized and isomerized. The migration of phenyl in this system can take two directions, therefore two products could be formed, and it was the effect of the substituents on this product distribution that was studied. The relative proportions of these structural isomers is an indication of the nature of the electronic effects at the migration terminus.

The kinetic series studied by Oldaker² was followed simply by infrared spectroscopy (disappearance of the hydroxyl peak), since only one product was formed; however, the series examined herein produces two structural isomers. Complicating this investigation was the fact that the two-product mixture could not be physically separated by chromatographic techniques. Therefore, it was proposed that a quantitative method for the oxidative degradation of the isomerization products be determined. It was expected that this system would give clean oxidation to easily characterizable secondary products, which would indicate the ratio of the primary (isomerization) products to each other. The amount of effort and time that was dedicated to this aspect of the study justified its elevation to a complementary role to the main study, and as such is presented in its own historical, experimental, and discussion section of this dissertation.

The syntheses leading to the compounds of interest, the approach to the problem of determining the product ratios, and the results of the rearrangements are presented herein.

SECTION A. HISTORICAL

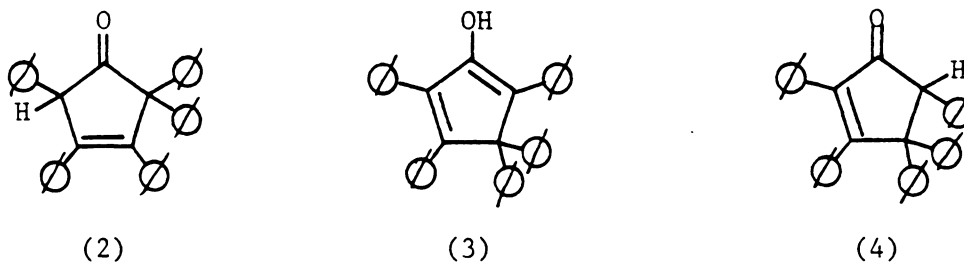
In the course of our studies of electronic effects in the [1,5]-sigmatropic phenyl rearrangement of polyphenylated carbinols^{1,2,3,4,5} it became necessary to determine a method for the oxidative degradation of products of the general type (1).



(1), $X \neq Y$

X and/or Y = *p*-MeO, *p*-Me, *m*-MeO, H, *p*-Cl, *p*-Br

In 1943, the prototype for such a series, 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2), was oxidized by Allen and VanAllan,⁶ although at that time they believed the compound to be a mixture of structures (3) and (4).

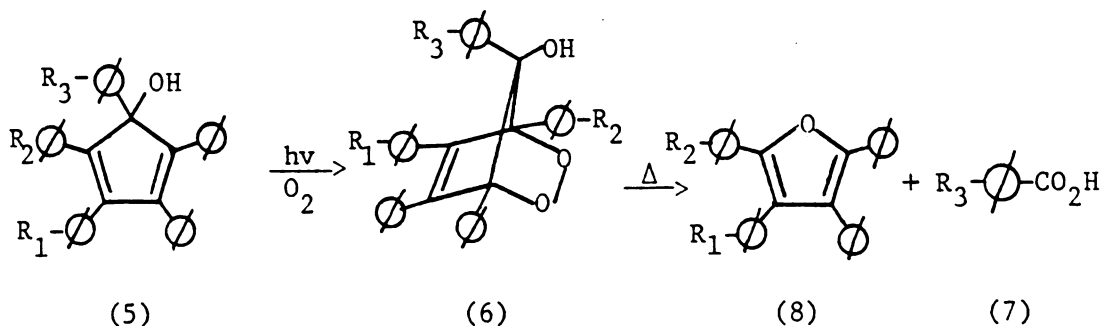


Allen and VanAllan's proposed structures were corrected by Dufraisse, et al.⁷ and later confirmed by Youssef and Ogliaruso¹ to be structure (2). Allen and VanAllan, attempting to prove the proposed structures

(3) and (4) oxidized the compounds with chromium trioxide using acetic anhydride as solvent. The reported products were benzoic acid (yield not given) and benzophenone (60%). They eliminated the correct structure, (2) from consideration by the non-production of benzil.

Allen and VanAllan's work represents the only reported oxidation of the parent compound (2). The closely related compound 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (5, $R_1=R_2=R_3=H$) (from which (2) may be obtained via [1,5] sigmatropic phenyl rearrangement) has been the subject of oxidative studies.^{8,9}

Photooxidation was reported by Dufraisse, et al.,⁸ and Rio and Ranjon⁹ to produce the photooxide (6).

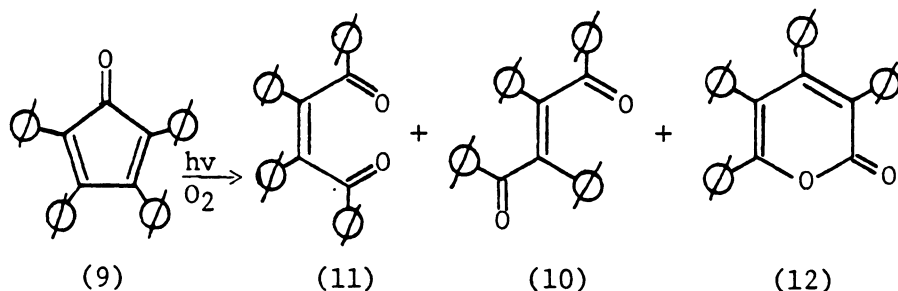


This photooxide, upon heating, decomposed to an aromatic acid, (7), and a furan, (8). The intermediate photooxides were stable and could be isolated.

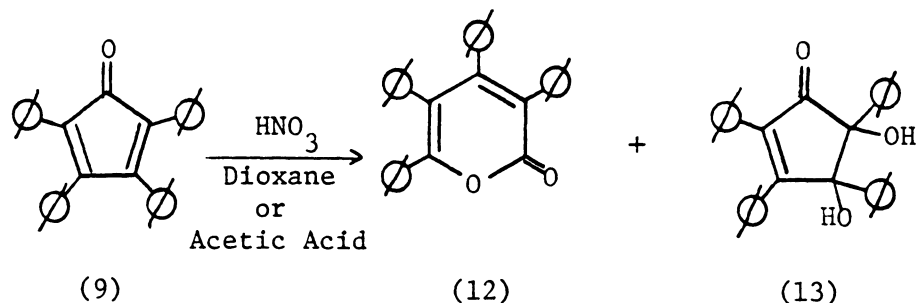
A considerably greater amount of work has been directed toward the oxidation of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (tetra-cyclone (9)). This compound is the substrate from which (4) is prepared, via Grignard reaction with phenylmagnesium bromide. The

first reported oxidation of (9) was by Dilthey and Quint¹⁰ using either lead dioxide or nitric acid. The structure of the product was not given.

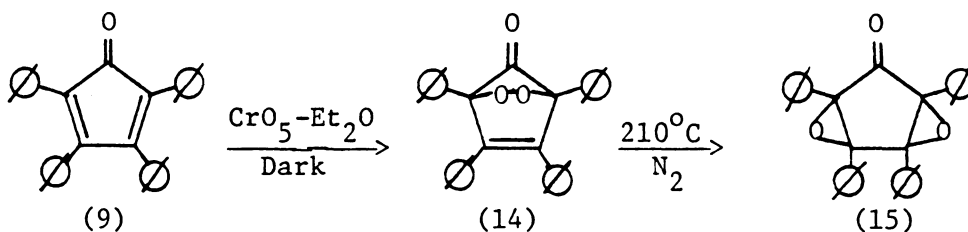
Photooxidation of (9) has been reported.^{11,12} Coan et al.¹¹ found that oxidation of (9) by irradiation in the presence of oxygen produced trans-dibenzoyl silbene (10), while Bikales and Becker¹² reported that in addition to (10), cis-dibenzoylstilbene (11) and tetraphenyl-2-pyrone (12) were also produced.



In 1954, Yates¹³ reported that heating tetracyclone (9) with nitric acid and dioxane or acetic acid on a steam bath produced both tetraphenyl-2-pyrone (12) and 2,3-dihydroxy-2,3,4,5-tetraphenylcyclopenten-4-one (13).



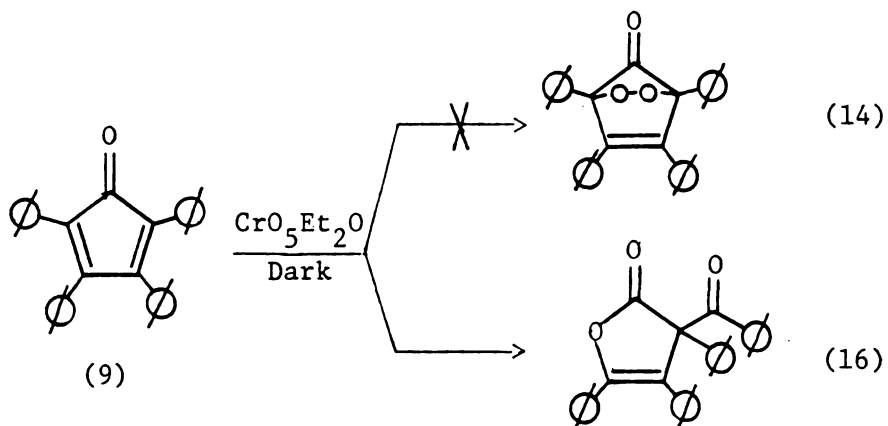
Chan¹⁴ made the initial report of the oxygenation of tetracyclone by diperoxychromium(VI) oxide etherate ($\text{CrO}_5 \cdot \text{Et}_2\text{O}$) to yield tetracyclone endo-peroxide (14).



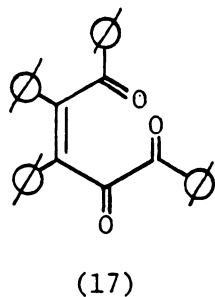
The yield is essentially quantitative, and the compound is stable at low temperature (-5°C). Pyrolysis at 210°C under nitrogen afforded a mixture of products from which the diepoxy-ketone (15) was isolated in ten percent yield.

Subsequently, however, Chan¹⁵ reevaluated the reactions and reported inability to prepare the earlier claimed peroxide. Instead, a comparison of the product of the action of $\text{CrO}_5 \cdot \text{Et}_2\text{O}$ on (9) with a pure sample of keto-lactone (16) indicated they were identical. The earlier assignment was attributed to similarity of spectral data and contamination by some peroxidic material. Chan also found that (16) could be prepared in 80 percent yield by oxidation of (9) with chromium trioxide in acetic acid, and stated that:

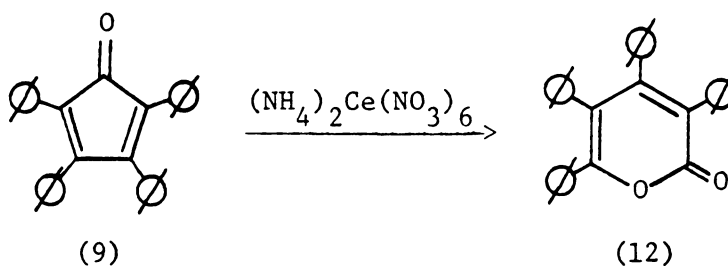
It is a distinct possibility, although not proven in this work, that chromic acid, formed by degradation of the pentoxide, is responsible for the formation of (16).



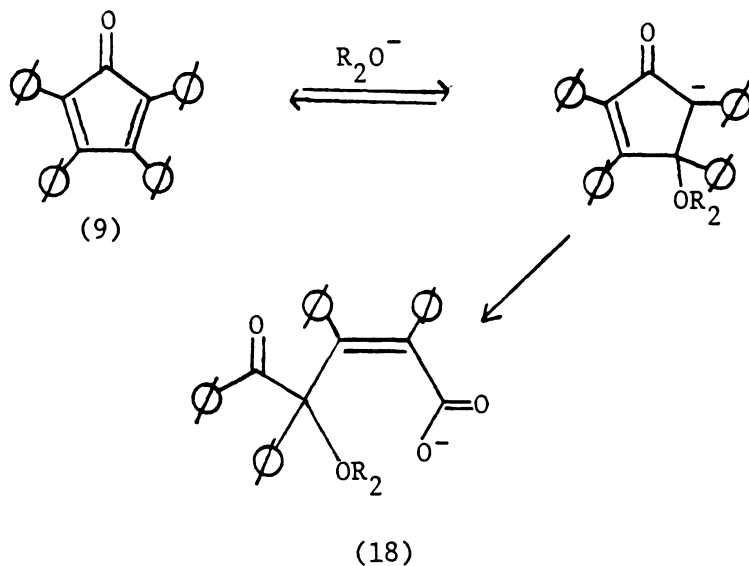
The trione (17) was suggested as a reasonable intermediate.



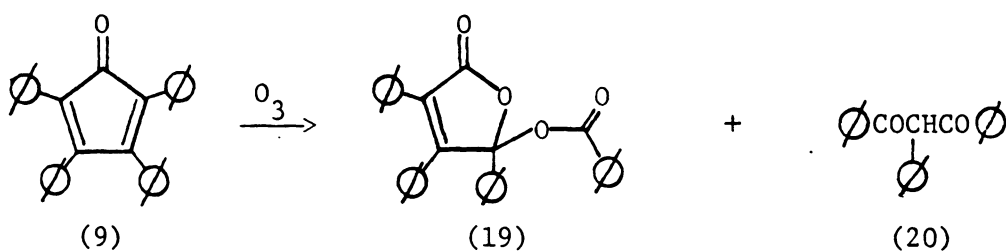
Tetracyclone has been oxidized by ceric ammonium nitrate to give a 71 percent yield of the pyrone (12).



Autoxidation of (9) under basic conditions was reported by Muckensturm¹⁷ to give (18). The first step is Michael addition of base, giving a carbanion which is autoxidized.



Finally, in 1981 Bailey¹⁸ investigated the oxidation of tetra-cyclone by ozone. Two compounds were isolated, in yields of 56 percent of (19) and 32 percent of (20).



Both products could be accounted for based on initial 1,2- addition of ozone to one of the double bonds followed by rearrangements of peroxidic intermediates. The possibility of 1,4- addition was not

ruled out. All efforts to isolate intermediates failed.

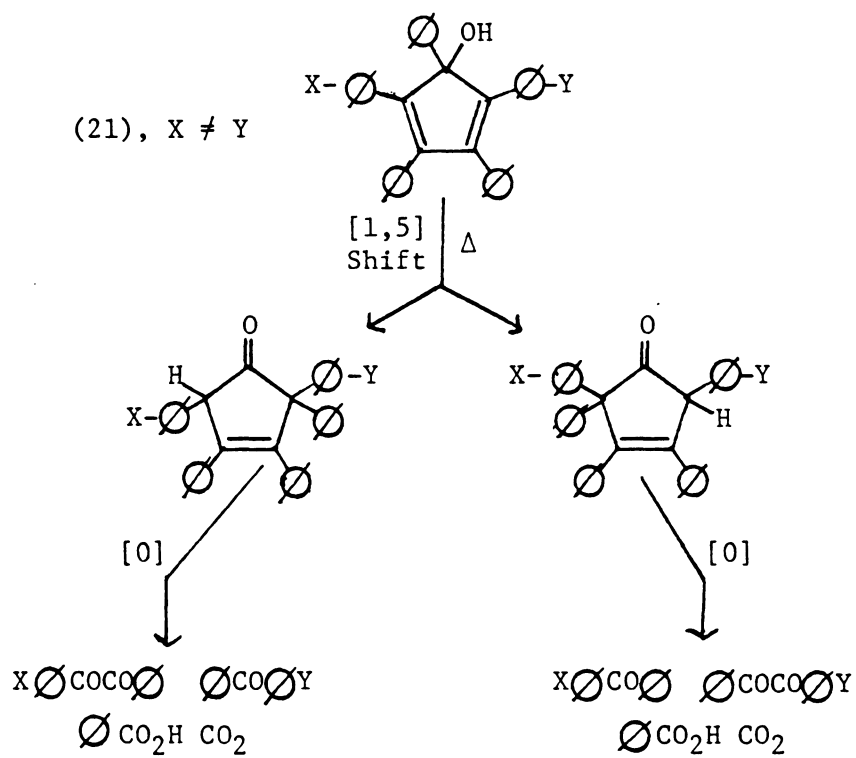
In summary, while a variety of oxidizing agents have been examined for the closely related compound tetracyclone (9) and pentaphenylcyclopentadienol (5), only Allen and VanAllan's work on 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2) precedes this dissertation.

The goal of this research was two-fold; first, to reexamine the initial work by Allen and VanAllan, and secondly to examine the action of a variety of oxidants on (2). The hope was that a quantitative method could be determined for the oxidative degradation of this prototype, which could then be applied to the substituted cases (1) in order to assign their structures.

In Section B of this dissertation a series of 2- and/or 5-(p- or m-substituted phenyl) alcohols was thermally rearranged, to give a mixture of products. If a method could be found to oxidatively cleave the ring bonds of the parent compound, and then applied to the substituted cases, a mixture of substituted benzils and benzophenones would be produced which could be correlated to the original (isomerization) product distribution (see Scheme 1).

This section describes the action of various oxidants on 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one. Also described is the gas chromatographic method developed for separation of mixtures of substituted benzils and benzophenones.

SCHEME 1



X and/or Y = p-MeO, p-Me, m-MeO, H, p-Cl, p-Br

SECTION A. EXPERIMENTAL

Reactions and Syntheses Required for the Oxidation Study

Oxidative Studies

The evaluations of prospective oxidative systems for the oxidative degradation of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one were performed as follows. The degradation product mixture (minus the aqueous base-soluble components) was transferred to a 10 or 25ml volumetric flask and brought up to volume with chloroform. These samples were injected into a Varian 1200 series gas chromatograph. This chromatograph was equipped with a flame ionization detector, and flow rates were set at approximately 30ml/min. helium, 30ml/min. hydrogen, and 300ml/min. air. The column used was a 6' x 1/8" stainless steel column packed with a liquid loading of 5% OV-275 on a stationary support of Chromosorb W. For the evaluations of oxidations of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one, the column was operated isothermally at 215°C, the detector maintained at 240°C, and the injector at 210°C. For evaluations of the product mixtures resulting from oxidation of the rearrangement products (see experimental, section B), these same conditions were employed with the exception of the cases where 4-methoxybenzil was an expected product, these being run with the column temperature programmed from 215°C to 235 or 240°C at a rate of 2° per minute. Peaks were recorded on a Linear 10mV recorder and the height multiplied by the width at half-height¹⁹ taken as a measure of concentration.

Calibration curves were constructed for benzil and benzophenone as follows. A set of standards [1.0%, 2.5%, 5.0%, and 10% (molar basis)] for both compounds were prepared. Three 2.0ul injections were made for each concentration and the peak height multiplied by width at half-height averaged and plotted versus concentration or grams of compound. Following construction of the calibration curves, the oxidation products were injected, and the amount of benzil or benzophenone present in the sample determined by comparing the value of the peak height multiplied by width at half-height to the calibration curve values. Representative calibration curves for benzil and benzophenone can be found in Appendix A.

Preparation of Mono-Substituted Benzils

The results of these reactions are summarized in Table 1.

A. 4-Bromobenzil

Into a 500ml, three-necked, round-bottom flask was placed 32g (0.24 mole) of anhydrous aluminum chloride and 100mls of carbon disulfide. The flask was seated in an ice bath and equipped with a magnetic stirring bar and reflux condenser. To this was added 31.4g (0.2 mole) of bromobenzene, followed by dropwise addition of 37.1g (0.24 mole) of phenylacetyl chloride over 15 minutes. The solution was stirred in the ice bath for one hour, then three hours at room temperature. Next, the reaction mixture was poured onto 200g of ice and 100g of concentrated hydrochloric acid. The carbon disulfide layer and aqueous layer were separated, and the aqueous layer extracted with 100mls of benzene which was combined with the carbon disulfide layer. The organic phase was washed with 100mls of water, dried with anhydrous magnesium sulfate, and filtered to yield a red-green solution. This solution was stripped on a rotary evaporator to yield a dark, thin liquid which solidified upon standing. Next, it was transferred to a crucible and trituated with 30mls of petroleum ether (b.p. 30-60°C), which extracted a green colorant. The remaining paste was dissolved in 20mls of benzene, filtered, and stripped on a rotary evaporator to yield 36.2g (0.1316 mole, 65.8%) of crude 4-bromodesoxybenzil as a yellow oil. The product was not purified further, but was oxidized by the following procedure to 4-bromobenzil.

Into a 250ml, three-necked, round-bottom flask was placed 24.4g (0.088 mole) of crude 4-bromodesoxybenzil, 44g (0.50 mole) of dioxane, 10.76g (0.097 mole) of selenium dioxide, and 1.76g (0.097 mole) of water. The reaction mixture was refluxed for 5.5 hours, then filtered hot to remove selenium metal. The selenium was washed with 20mls of hot dioxane, then the dioxane solution was stripped on a rotary evaporator to yield 24.8g (0.0858 mole, 97.4%) of crude 4-bromobenzil as a brown oil. The crude product was crystallized from aqueous ethanol to yield 23.6g (0.085 mole, 96.5%) of yellow powder, mpt. 85.0-86.0°C [lit. mpt. 86.5°C]²⁰

B. 4-Methoxybenzil

Into a 500ml, three-necked, round-bottom flask equipped with stirring bar and reflux condenser was placed 100mls of carbon disulfide and 32.0g (0.24 mole) of anhydrous aluminum chloride. The flask was cooled by means of an ice bath, and 21.6g (0.20 mole) of anisole was added to the mixture with stirring. A dropping funnel charged with 37.1g (0.24 mole) of phenylacetyl chloride was fitted to one side-neck and slow addition begun. After one hour in the ice bath, the reaction mixture was stirred for an additional hour at room temperature, then poured onto 200g of ice and 100g of concentrated hydrochloric acid. Two layers were present, a lower carbon disulfide layer (blue-green) and an upper aqueous layer. The layers were separated, the carbon disulfide layer washed with 100mls of water, and the aqueous phases discarded. The carbon disulfide phase was filtered to remove a small

amount of an insoluble white sediment, then stripped on a rotary evaporator to yield approximately 20-25mls of a red-green liquid. This solidified overnight, was then transferred to a crucible, and trituated with a small amount of petroleum ether (b.p. 30-60°C) which removed a blue colorant. The remaining solid was a light tan powder, mpt. 72.5-74.5°C [lit. mpt. 74-75°C],²¹ weighing 27.7g (0.1226 mole, 61.2%). This material was not purified further, and 20.0g (0.088 mole) was oxidized to 4-methoxybenzil by the following procedure.

Into a 100ml, three-necked, round-bottom flask was placed 20.0g (0.088 mole) of crude 4-methoxydesoxybenzil, 44g (0.50 mole) of dioxane, 10.76g (0.097 mole) of selenium dioxide, and 1.76g (0.097 mole) of water. The reaction mixture was refluxed for eight hours, and washed with 15mls of hot dioxane. The dioxane was removed on a rotary evaporator to yield 21.0g (0.0875 mole, 99.4%) of a yellow oil contaminated with red particles. The oil was chromatographed on a 2.5cm x 4.0cm column packed with neutral alumina using chloroform as eluent in an attempt to remove the particles of selenium metal. The eluate was stripped to yield 20.2g (0.084 mole, 95.6%) of a yellow oil. The oil was crystallized from a minimum amount of boiling chloroform. After standing overnight, large bright yellow crystals had formed but there were also a few tiny specks of selenium present. The product was dissolved in hot 80 percent ethanol and filtered while hot through

a büchner funnel. Spontaneous crystallization of the filtrate occurred, and the filtrate was cooled in an ice bath to yield 18.37g (0.0764 mole, 86.8%) of product in the form of yellow needles, mpt. 61.5-63.0°C. [lit. mpt. 61.5-63.0°C]²²

C. 4-Chlorobenzil

Into a 1000ml, three-necked, round-bottom flask equipped with reflux condenser and magnetic stirring bar was placed 64.0g (0.48 mole) of anhydrous aluminum chloride and 200mls of carbon disulfide. To this was added 45.0g (0.4 mole) of chlorobenzene followed by drop-wise addition of 74.2g (0.48 mole) of phenylacetyl chloride through an addition funnel. The reaction mixture was seated in an ice bath, and stirred for 1.5 hours, then gently heated for four hours. When the evolution of hydrogen chloride had ceased (four hours) the reaction mixture was poured onto 400g of ice and 200g of concentrated hydrochloric acid. The carbon disulfide layer was separated from the aqueous layer, and washed with two 100ml portions of water. The water extracts were combined with the aqueous layer, then extracted with two 100ml portions of benzene which was combined with the carbon disulfide. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 73.0g (0.316 mole, 79.1%) of crude 4-chlorodesoxybenzil as a brown oil. The crude 4-chlorodesoxybenzil was not purified further, but was oxidized by the following procedure to 4-chlorobenzil.

Into a 250ml, three-necked, round-bottom flask equipped with reflux condenser and stirring bar was placed 40.56g (0.176 mole) of crude 4-chlorodesoxybenzil, 88g (1.0 mole) of dioxane, 21.5g (0.194 mole) of selenium dioxide, and 3.52g (0.194 mole) of water. The reaction mixture was stirred and refluxed for 22 hours. The dioxane solution was filtered while hot to remove selenium metal, the selenium washed with 20mls of hot dioxane, and the filtrate stripped on a rotary evaporator to yield 40.4g (0.165 mole, 93.8%) of a product as a brown oil. The oil was dissolved in hot 80 percent ethanol, and filtered while hot to remove residual selenium. The filtrate crystallized, producing 36.7g (0.150 mole, 85.4%) of product in the form of yellow powder, mpt. 73.5-75.0°C. [lit. mpt. 73°C]²³

D. 4-Methylbenzil

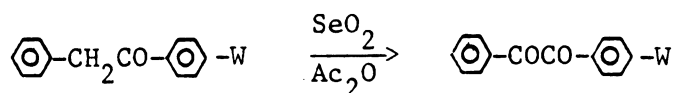
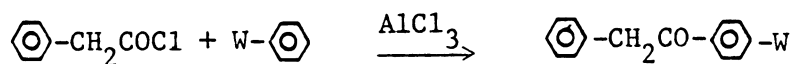
Into a 500ml, three-necked, round-bottom flask equipped with reflux condenser and stirring bar was placed 92g (1.01 mole) of toluene, and 37.5g (0.28 mole) of anhydrous aluminum chloride followed by drop-wise addition of 77g (0.50 mole) of phenylacetyl chloride. The mixture was stirred in an ice bath for two hours followed by one hour of refluxing. Next, the solution was poured onto 250g of ice and 100mls of concentrated hydrochloric acid. The organic and aqueous phases were separated, and the aqueous phase extracted with three 100ml portions of ether. The ether was combined with the organic phase and washed with 50mls of ten percent sodium carbonate, then three 100ml portions of ether. The organic solution was dried with anhydrous

magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 39.0g (0.185 mole, 37%) of a brown oil which solidified, and was triturated with petroleum ether to yield a yellow-brown powder. The crude 4-methyldesoxybenzil was oxidized by the following procedure to 4-methylbenzil.

Into a 100ml, three-necked, round-bottom flask was placed 20.0g (0.09 mole) of crude 4-methyldesoxybenzil, 22.2g (0.2 mole) of selenium dioxide, 70mls of glacial acetic acid, and 3.6g (0.2 mole) of water. The flask was equipped with a magnetic stirring bar and reflux condenser. Heat was applied via a heating mantle and the solution refluxed overnight. The following morning the reaction mixture was poured onto 100g of ice, then extracted with three 100ml portions of benzene. The benzene extracts were combined, then washed twice with 50mls of ten percent sodium carbonate followed by three 50ml portions of water. The organic solution was filtered while hot through a büchner funnel to remove residual selenium metal. The filtrate was stripped on a rotary evaporator to yield crude 4-methylbenzil, which was vacuum distilled (128-130°C @ 2.5mm Hg) to yield 40.2g (0.179 mole, 35.9%) of pure product as a yellow liquid. [lit. b.p. 136-140°C @ 3mm Hg]⁷³

TABLE 1

Preparation of 4-Substituted Benzils



Phenyl Substituent (W=)	4-Substituted Benzil (W=)	Yield (%)	Mpt. (°C)	Boiling Point (°C)
Cl	p-Cl	74.2	73.5-75.0 lit. 73.0 ²³	
Br	p-Br	61.0	85.0-86.0 lit. 86.5 ²⁰	
MeO	p-MeO	53.2	61.5-63.0 lit. 61.5-63.0 ²²	
Me.	p-Me	35.9		128-130 @ 2.5mm Hg lit. 136-140 @ 3mm Hg ⁷³

Oxidation of 2,2,3,4,5-Pentaphenyl-3-Cyclopenten-1-one

The results of these reactions are summarized in Table 2.

A. Via Potassium Permanganate in Crown Ether

I. Using a 2:1 Molar Ratio of Oxidant to Substrate

Into a 500ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 0.924g (0.002 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one and 25mls of benzene. Through an addition funnel was added 0.632g (0.004 mole) of potassium permanganate dissolved in 100mls of benzene by use of 1.49g (0.004 mole) of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 ether). The purple solution of oxidant decolorized upon contact with dissolved substrate, resulting in a final solution colored dark green-brown. The reaction mixture was stirred at room temperature for 21 hours. The following day the solution was filtered, removing a small amount of dark brown precipitate (MnO_2) and yielding a yellow filtrate. The filtrate was extracted with two 25ml portions of five percent sodium carbonate to remove any acidic organic compounds. The organic solution was dried with anhydrous magnesium sulfate, filtered and stripped on a rotary evaporator to yield 2.04g of an oil. An infrared spectrum of the oil indicated a major carbonyl band at 1760cm^{-1} , the frequency of the carbonyl stretch of the substrate. Two smaller bands appeared at 1735 and 1670cm^{-1} . Gas chromatographic analysis of the oil (as described at the beginning of the experimental section) indicated no benzil or benzophenone. Acidification of the carbonate

extract was followed by extraction with two 25ml portions of benzene and two 25ml portions of chloroform. This organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.11g of a yellow oil whose infrared spectrum contained none of the major bands of an infrared spectrum of benzoic acid. The oils were not analyzed further.

II. Using a 6:1 Molar Ratio of Oxidant to Substrate

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 0.948g (0.006 mole) of potassium permanganate dissolved in 100mls of benzene by use of 2.23g (0.006 mole) of 18-crown-6 ether. Dropwise addition of 0.462g (0.001 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one dissolved in 50mls of benzene was begun with stirring. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was filtered to remove a brown precipitate (MnO_2), then the precipitate was washed with 100mls of five percent sodium hydroxide to remove any organic acids. This aqueous solution was combined with a 100ml, five percent sodium carbonate extraction of the organic layer. The aqueous phase was acidified with ten percent hydrochloric acid, then extracted with two 50ml portions of benzene which were dried with anhydrous magnesium sulfate, filtered and stripped on a rotary evaporator to yield 0.18g of a light yellow oil whose infrared spectrum did not match that of benzoic acid. The original organic phase was washed with 100mls of water, then dried with anhydrous magnesium sulfate to yield 2.33g of a

bright yellow oil. The oil was analyzed by gas chromatography (as described at the beginning of the experimental) which indicated no benzil or benzophenone. The oils were not further analyzed.

B. Via Permanganate/Sodium Periodate

I. Using 33% Tertiary Butanol as Solvent

Into a 500ml, three-necked, round-bottom flask was placed 0.462g (0.001 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one suspended in 100mls of a 50 percent (v/v) aqueous solution of t-butanol. The solution was stirred by a magnetic stirring bar, and 100mls of a stock oxidant solution [2.086g (0.0098 mole) of sodium periodate, 0.0395g (0.00025 mole) of potassium permanganate, and 100mls water] was added, followed by 85mls of t-butanol giving a final solution of 33 percent (v/v) t-butanol. The reaction mixture was stirred at room temperature for 24 hours, by which time the solution had become cloudy pink. The pH was maintained at approximately 7-8 throughout the reaction period by addition of small amounts of potassium carbonate. At the end of the reaction period, excess oxidant was destroyed by addition of sodium sulfite, and the reaction mixture allowed to stand overnight. The solution was acidified to pH 3 with ten percent hydrochloric acid, then extracted with two 100ml portions of benzene and one 100ml portion of chloroform. The organic extracts were combined, then extracted with three 50ml portions of five percent sodium carbonate. The aqueous extracts were washed once with 25mls of benzene, which was returned to the organic phase. The organic phase was dried with anhydrous

magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.496g of a yellow oil whose infrared spectrum had major bands (1760cm^{-1} , 1720cm^{-1}) corresponding to the substrate unconjugated ketone, (2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one) and its conjugated counterpart, 2,2,3,4,5-pentaphenyl-2-cyclopenten-1-one. Fractional crystallizations gave 0.145g (0.0003 mole, 31.3%) of a powder, mpt. $167-171^{\circ}\text{C}$ [lit. mpt. for conjugated isomer: $169-170^{\circ}\text{C}^1$], with major IR band at 1720cm^{-1} . Crystallization of the filtrate gave 0.113g (0.0024 mole, 24.5%) of a powder, mpt. $185-188^{\circ}\text{C}$ [lit. mpt. for unconjugated isomer: $194-195^{\circ}\text{C}^1$], with major IR band at 1760cm^{-1} . The remaining filtrate was stripped on a rotary evaporator to an oil which was analyzed by gas chromatography. No benzil or benzophenone was found by gas chromatographic analysis. The original carbonate extract was now acidified to pH 3 with ten percent hydrochloric acid, then extracted with 50mls of benzene and 50mls of ether which were combined, then washed with 20mls of water. This organic phase was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.007g of a brown oil, whose infrared spectrum did not contain any bands corresponding to benzoic acid. The oils were not analyzed further.

II. Using 65% Pyridine as Solvent

Into a 500ml, three-necked, round-bottom flask was placed 0.462g (0.001 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one dissolved in 25mls of pyridine. To this was added 150mls of a stock oxidant solution

[3.129g (0.0146 mole) of sodium periodate, 0.119g (0.00075 mole) of potassium permanganate, and 150mls of water] followed by 250mls of pyridine making a final solution of 65 percent pyridine. Upon addition of the oxidant, the temperature of the solution rose slightly above ambient to 33°C. Potassium carbonate was added periodically to maintain the pH at approximately 7.5-8.5. The reaction mixture was stirred for 24 hours at room temperature, then quenched with sodium bisulfite to destroy excess oxidant. The aqueous pyridine solution was extracted with three 100ml portions of benzene and the benzene extracts combined. The benzene solution was extracted with 100mls of ten percent sodium carbonate, then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.236g of an oil which had a major infrared band at 1760cm^{-1} corresponding to that of the substrate. The oil was analyzed by gas chromatography which indicated that no benzil or benzophenone was present. The carbonate extract was acidified with ten percent hydrochloric acid, then extracted with two 25ml portions of benzene which were combined, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.245g of an oil. Infrared spectroscopy indicated no bands corresponding to benzoic acid. The oils were not further analyzed.

III. Using 75% Acetone as Solvent

Into a 500ml, three-necked, round-bottom flask was placed 2.086g (0.00975 mole) of sodium periodate, 0.0395g (0.00025 mole) of potassium permanganate, and 75mls of water. The flask was equipped with a

magnetic stirring bar and reflux condenser. Stirring was initiated, and 2.00g (0.00433 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one dissolved in 125mls of acetone added dropwise through an addition funnel over five minutes. There was a slight rise in the temperature of the solution from ambient (22°C) to 27°C. The purple solution contained a white suspension (substrate), and an additional 100mls of acetone was added to aid dissolution but the suspension remained. The pH was maintained at approximately 7-8 by periodic addition of potassium carbonate. The reaction mixture was stirred at room temperature for 24 hours, at which time the flask held a slightly pink solution, white suspension, and orange-red oil. Excess oxidant was destroyed by addition of sodium bisulfite, then the solution was acidified with ten percent hydrochloric acid to a pH of 3. The reaction mixture was extracted with four 100ml portions of ether, and the ether combined. The ether solution was extracted with four 100ml portions of ether, and the ether combined. The ether solution was extracted with four 100ml portions of ten percent sodium carbonate, the aqueous extracts combined, and the ether dried with anhydrous magnesium sulfate. The ether solution was filtered and stripped on a rotary evaporator to yield 1.69g of a gold brown oil. Analysis of the oil by gas chromatography indicated a peak occurring at the retention time for benzophenone which calibration curves established at less than 1.0% production. No benzil was present. The carbonate extracts were acidified to pH of approximately 3 with ten percent hydrochloric acid, then extracted with two 100ml portions of benzene and two 100ml portions of

ether. The extracts were combined and dried with anhydrous magnesium sulfate, filtered and stripped on a rotary evaporator to yield 0.008g of a brown tar with an acrid odor. Infrared spectroscopy indicated that none of the major bands of benzoic acid were present. The oils were not further analyzed.

C. Via Potassium Potassium Permanganate/Sodium Periodate in Crown Ether

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar was placed 100mls of benzene, 0.948g (0.006 mole) of potassium permanganate, and 2.232g (0.006 mole) of 18-crown-6 ether. To the purple solution was added 6.42g (0.03 mole) of sodium periodate, followed by 0.462g (0.001 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one dissolved in 25mls of benzene. The reaction mixture was stirred at room temperature for 24 hours, then filtered to remove a brown precipitate (MnO_2). The filtrate remained purple. The filtrate was treated with sodium bisulfite to destroy the potassium permanganate, and the solution decolorized. The organic solution was extracted with four 50ml portions of sodium carbonate, then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 2.18g of a light yellow oil. Analysis of the oil by gas chromatography revealed no benzil or benzophenone. The carbonate extracts were acidified to pH of approximately three, then extracted with three 100ml portions of benzene. The benzene extracts were combined, dried with anhydrous magnesium sulfate, and

stripped on a rotary evaporator to yield 0.06g of a brown oil whose infrared spectrum contained none of the major bands of benzoic acid. The oils were not further analyzed.

D. Via Chromium Trioxide in 90% (v/v) Acetic Acid (0.002M in H₂SO₄)

Into a 500ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 200mls of a 0.002M sulfuric acid in 90 percent (v/v) acetic acid solution and 1.2g (0.012 mole) of chromium trioxide. To this was added 0.924g (0.002 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one partially dissolved in 50mls of the solvent system described above. The reaction mixture was stirred at room temperature for 24 hours. The reaction mixture was transferred to a separatory funnel with 100mls of water and extracted with two 100ml portions of benzene and 100mls of ether. The organic extracts were combined, then extracted with three 100ml portions of five percent sodium carbonate. The organic solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 1.097g of an oil that was analyzed by gas chromatography, which indicated no benzil or benzophenone was produced. The carbonate extracts were combined and acidified with ten percent hydrochloric acid to pH of approximately 3, then extracted with four 50ml portions of benzene. The benzene was washed once with 25mls of water, then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.016g of a brown oil which contained none of the major infrared bands of benzoic acid. The

oils were not further analyzed.

E. Via Chromium Trioxide in 70% Sulfuric Acid

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 75mls of 70 percent sulfuric acid and 1.2g (0.012 mole) of chromium trioxide. To the stirred solution was added 0.924g (0.002 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one partially dissolved in 25mls of 70 percent sulfuric acid. The reaction mixture was stirred at room temperature for 24 hours, then poured into 50mls of cold water and extracted with two 100ml portions of benzene followed by two 100ml portions of ether. The organic extracts were combined, washed once with 20mls of water, then extracted with three 100ml portions of five percent sodium carbonate solution. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.754g of an oil which was analyzed by gas chromatography. No benzil or benzophenone was present. The carbonate extracts were combined, the pH adjusted to approximately three with ten percent hydrochloric acid, then extracted with two 100ml portions of benzene. The benzene extract was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.010g of a brown oil whose infrared spectrum contained none of the major bands of benzoic acid. The oils were not further analyzed.

F. Via Chromium Trioxide in Acetic Anhydride at 85-95°C for 24 Hours

Into a 250ml, three-necked, round-bottom flask equipped with stirring bar and reflux condenser was placed 4.0g (0.04 mole) of chromium trioxide and 100mls of freshly distilled acetic anhydride. To the stirred solution was added 2.31g (0.005 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one, which immediately dissolved. The reaction mixture was maintained at 85-95°C for 24 hours. The green reaction mixture was then poured onto 100mls of water, then extracted with three 100ml portions of benzene followed by 100mls of ether. The organic solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 2.32g of an orange gum which was analyzed by gas chromatography to contain 0.355g [0.00195 mole, 39% of the amount which theoretically should be produced (see discussion)] of benzophenone and 0.418g (0.002 mole, 39.8% of the amount which theoretically should be produced) of benzil. The infrared spectrum was complex and contained other major carbonyl bands. Column chromatography was not effective in isolating any of the other reaction products present in the gum. The carbonate extracts were combined, acidified to pH of approximately three with ten percent hydrochloric acid, then extracted with two 100ml portions of benzene. The benzene extracts were dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.238g (0.0019 mole, 39.0% of the amount which should theoretically be produced) of an oil whose infrared spectrum matched that of benzoic acid. The oil was dissolved in boiling water, filtered, then the filtrate allowed to cool slowly.

This produced 0.146g (0.0012 mole, 24.0%) of white needles, mpt. 121.0 - 122.5°C. [lit. mpt. for benzoic acid, 122°C].²⁵ The products were not further analyzed.

G. Chromium Trioxide/Acetic Anhydride Control Run on an Equimolar Mixture of Benzoic Acid, Benzophenone, and Benzil at 85-90°C for 22 Hours

Into a 500ml, three-necked, round-bottom flask was placed 160mls of acetic anhydride and 6.0g (0.06 mole) of chromium trioxide. The flask was equipped with a magnetic stirring bar and reflux condenser. To the stirred solution was added 1.82g (0.01 mole) of benzophenone, 2.10g (0.01 mole) of benzil, and 1.22g (0.01 mole) of benzoic acid. The reaction mixture was maintained at 85-90°C for 22 hours then extracted with two 100ml portions of benzene followed by 100mls of ether. The organic extracts were combined, washed once with 20mls of water, then extracted with four 100ml portions of five percent sodium carbonate. The organic solution was then dried with anhydrous magnesium sulfate, filtered, and stripped to yield 4.03g of a yellow oil which crystallized on standing. The yellow solid was dissolved in chloroform and analyzed by gas chromatography. The product was found to contain 1.61g (0.0089 mole, 89% recovery) of benzophenone, and 2.0g (0.0095 mole, 95% recovery) of benzil. These products accounted for 3.61g (89.3%) of the weight of the product. The carbonate extracts were acidified with ten percent hydrochloric acid to pH of approximately three, then extracted with two 100ml portions of benzene, and the

benzene extracts combined, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.784g (0.0064 mole, 65% recovery) of a white powder whose infrared spectrum matched that of benzoic acid. The powder was recrystallized from a minimum amount of boiling water to yield 0.574g (0.00574 mole, 57.4%) of white needles, mpt. 121-122°C [lit. mpt. for benzoic acid, 122°C].²⁵ The products were not further analyzed.

H. Via Chromium Trioxide/Acetic Anhydride at 85-95°C for 1.5 Hours

Into a 500ml, three-necked, round-bottom flask was placed 5.0g (0.0108 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one and 250mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. To the stirred solution was added 6.49g (0.0649 mole) of chromium trioxide. The reaction mixture was maintained at 85-95°C for 1.5 hours, then poured onto 300mls of ice water. The reaction mixture was extracted with three 100ml portions of benzene, and the aqueous layer discarded. The benzene extracts were combined, then extracted with three 100ml portions of five percent sodium carbonate. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 4.08g of a brown oil which was analyzed by gas chromatography. The product was found to contain 0.747g (0.0041 mole, 38.0% of the amount that theoretically should be produced) of benzophenone, and 0.873g (0.00416 mole, 38.5% of the amount that theoretically should be produced) of benzil. These products account for 1.61g (39.7%) of the

weight of the oil produced. The carbonate extract was acidified to pH of approximately three with 35mls of ten percent hydrochloric acid, then extracted with three 100ml portions of benzene, and the benzene extracts combined. The benzene solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.35g (0.0028 mole, 26.5% of the amount that theoretically should be produced) of an orange powder whose infrared spectrum matched that of benzoic acid. The products were not further analyzed.

I. Chromium Trioxide/Acetic Anhydride Control Run on an Equimolar Mixture of Benzoic Acid, Benzophenone, and Benzil at 80-95°C for 1.5 Hours

Into a 1000ml, three-necked, round-bottom flask was placed 2.27g (0.0108 mole) of benzil, 1.97g (0.0108 mole) of benzophenone, and 1.32g (0.0108 mole) of benzoic acid and 210mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. To the stirred solution was added 10.5g (0.105 mole) of chromium trioxide. The reaction mixture was maintained at 80-95°C for 1.5 hours, then poured onto 300mls of water. The aqueous mixture was extracted with three 100ml portions of benzene and two 50ml portions of benzene and two 50ml portions of chloroform, and the organic extracts combined and extracted with three 60ml portions of five percent sodium carbonate. The organic layer was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 3.93g of a brown oil. The oil was analyzed by gas chromatography

and found to contain 1.78g (0.0098 mole, 90.7% of the recovery) of benzophenone, and 2.08g (0.0099 mole, 92.0% recovery) of benzil. These products account for 98.2 percent of the weight of the oil. The carbonate extracts were acidified to pH of approximately three with ten percent hydrochloric acid, extracted with two 100ml portions of benzene and 50mls of ether, and the organic extracts combined. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped to yield 0.78g (0.0064 mole, 59.3% recovery) of a tan powder whose infrared spectrum matched that of benzoic acid. The powder was recrystallized from a minimum amount of boiling water to yield 0.27g (0.0022 mole, 20.5%) of a white powder, mpt. 122-123°C. A second crop of off-white powder was obtained weighing 0.45g (0.0037 mole, 34.1%) and having a melting point of 119-121°C [lit. mpt. of benzoic acid, 122°C].²⁵ The products were not analyzed further.

J. Via Chromium Trioxide/Acetic Anhydride at 80-95°C for 0.75 Hours Followed by Work-Up and Re-Oxidation

Into a 500ml, three-necked, round-bottom flask was placed 5.0g (0.0108 mole) of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one and 250mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. To the stirred solution was added 5.4g (0.054 mole) of chromium trioxide. The reaction mixture was maintained at 80-95°C for 0.75 hours, then poured onto 200mls of ice/water, and extracted with two 100ml portions of benzene followed by 100mls of chloroform. The organic layers were combined, then extracted with

three 50ml portions of five percent sodium carbonate. The organic phase was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 5.1g of a brown oil. The oil was analyzed by gas chromatography and found to contain 0.806g (0.00443 mole, 41.0% of the amount which theoretically should be produced) of benzophenone, and 0.948g (0.0045 mole, 41.8% of the amount which theoretically should be produced) of benzil. The carbonate extracts were combined, acidified to pH of approximately three with ten percent hydrochloric acid, then extracted with three 100ml portions of benzene. The benzene extracts were combined, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a tan solid which was recrystallized from a minimum amount of boiling water, producing 0.307g (0.0025 mole, 23% of the amount which theoretically should be produced) of benzoic acid as a white powder, mpt. 121-122°C [lit. mpt. for benzoic acid, 122°C²⁵]. The infrared spectrum of the powder was identical to that of benzoic acid. Next, the organic oil from the above oxidation (without the benzoic acid fraction) was subjected to the above procedure a second time. The results of gas chromatographic analysis were 0.796g (0.0043 mole, 40.5%) of benzophenone and 0.93g (0.0044 mole, 41.0%) of benzil. The carbonate extract, however, afforded an additional 0.425g of tan powder which was recrystallized from boiling water to yield an additional 0.18g (0.00147 mole, 13.7%) of benzoic acid (mpt. 120-120.5°C) for a total yield of benzoic acid of 0.487g (0.004 mole, 36.9%).

K. Oxidation of 2-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one Via Chromium Trioxide/Acetic Anhydride at 80-95°C for 1.5 Hours

Into a 1000ml, three-necked, round-bottom flask was placed 6.43g (0.0643 mole) of chromium trioxide and 200mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. To the stirred solution was added 4.01g (0.00804 mole) of 2-(p-chlorophenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one. The solution was maintained at 80-95°C for 1.5 hours, then poured onto 100mls of cold water and extracted with four 50ml portions of benzene and two 50ml portions of ether. The organic extracts were combined and extracted with three 60ml portions of five percent sodium carbonate. The organic phase was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 3.6g of a brown oil. Gas chromatographic analysis of the oil revealed 0.65g (0.003 mole, 37.3% of the amount which theoretically should be produced) of 4-chlorobenzophenone, and 0.724g (0.00345 mole, 42.9% of the amount which theoretically should be produced) of benzil. The carbonate extracts were acidified with ten percent hydrochloric acid to pH of approximately three, then extracted with two 100ml portions of benzene. The organic extract was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a brown powder which was recrystallized from a minimum amount of boiling water to yield 0.17g (0.0014 mole, 17.3%) of benzoic acid, mpt. 120-121°C. [lit. mpt. 122°C]²⁵

TABLE 2

Oxidation Trials

<u>Substrate</u>	<u>Oxidant</u>	<u>Conditions</u>	<u>% Benzo- phenone</u>	<u>% Benzil</u>	<u>% Benzoic Acid</u>
Parent Ketone	KMnO ₄	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /(3X)	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	65% Pyridine, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	33% t-Butanol, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	75% Acetone, 24 hrs, R.T.	<1	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	CrO ₃	90% AcOH, 0.002M H ₂ SO ₄	----	----	----
Parent Ketone	CrO ₃	70% H ₂ SO ₄	----	----	----
Parent Ketone	CrO ₃	Ac ₂ O, 1.5 hrs, 80-95°C	38.0	38.5	24.0 [¶]
Control Mix [†]	CrO ₃	Ac ₂ O, 1.5 hrs, 80-90°C	90.2	92.0	57.4 [¶]
Control Mix [†]	CrO ₃	Ac ₂ O, 20 hrs, 85-90°C	89.0	95.0	26.5 [¶]
Parent Ketone	CrO ₃	Ac ₂ O, 50 min(2X), 80-90°C	41.0	41.8	54.6 [¶]
1-Chloro Ketone*	CrO ₃	Ac ₂ O, 1.5 hrs, 80-95°C	37.3(C1)	42.9	36.9 [¶]
Parent Ketone	CrO ₃	Ac ₂ O, 24 hrs, 85-95°C	39.0	39.8	17.3 [¶]

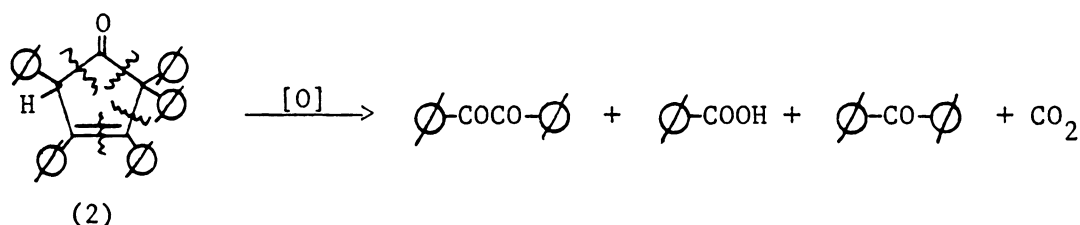
*2-(p-chlorophenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one

†Equimolar mixture of Benzil, Benzoic Acid, and Benzophenone

¶Recrystallized Yield

SECTION A. RESULTS AND DISCUSSION

The goal of this study was to evaluate the action of prospective oxidizing agents on 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2), with the hope that one oxidizing agent could be found which would quantitatively cleave the ring bonds to produce the easily characterizable products benzil, benzophenone, and benzoic acid.



If this could be accomplished, then the oxidant could be used to solve the problem of analysis of the two-product mixture²⁶ produced by thermal isomerization of 2- and/or 5-(*p*- or *m*-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ols (21) (see Scheme 1). Oxidation in this case would produce benzoic acid and carbon dioxide regardless of the substitution pattern, and in addition, a mixture of substituted benzils and benzophenones.

Thus, before beginning the oxidations it became necessary to develop a chromatographic method for separation not only of benzil and benzophenone, but also for the anticipated substituted analogs. Of the column packings evaluated for this separation, gas chromatography using a 6' x 1/8" stainless steel column packed with 5% OV-275 on

Chromosorb W proved to be nearly ideal, with only two compounds unresolved (bromobenzophenone and benzil) of the twelve in the study. Representative chromatograms are given in Figures 1 and 2.

With an analytical method now developed for evaluation of the oxidations, the question became one of choosing prospective oxidants. The paucity of reported oxidations of the parent ketone (2) has already been demonstrated in the historical section of this dissertation. Only one reported oxidation exists, that of Allen and VanAllan,⁶ whose original work on the rearrangements in the cyclopentadienol system was corrected by Youssef and Ogliaruso¹ in 1972, leading to the development of an extensive study of electronic effects in the sigma-tropic rearrangement of this system.^{1,2,3,4,5} Ironically, evidence will be presented in this dissertation that products other than those described in Allen and VanAllan for the action of chromic acid on ketone (2) were found by this author. My apologies for the continued abuse they have suffered at the hands of our group.

For the closely related compound, tetracyclone (9), oxidations with ozone,¹⁸ ceric ammonium nitrate,¹⁶ chromium pentoxide-etherate,^{14,15} nitric acid,¹⁰ and photooxidation¹¹ have all been reported. However, in addition to cleavage products, these oxidants exhibit a propensity toward producing ring-closure secondary products such as (12) and (19).

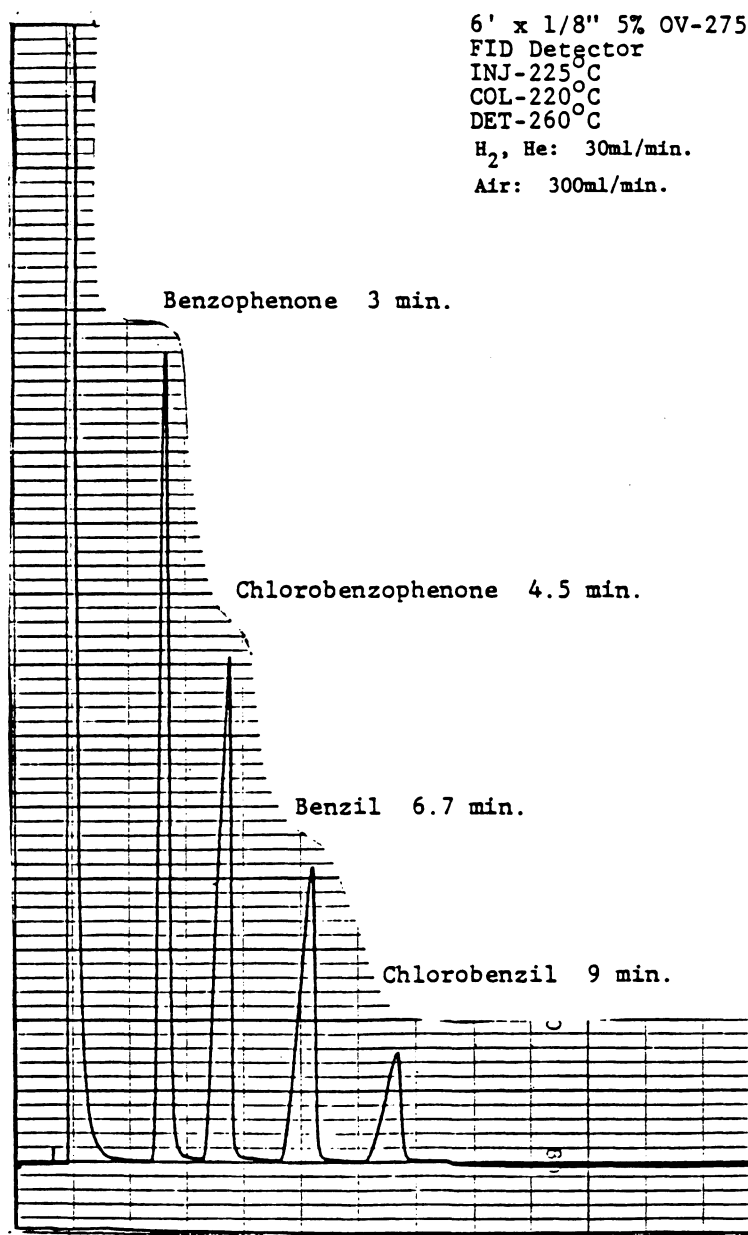


FIGURE 1. Chromatogram of Benzil
Chlorobenzophenone, Benzil and Chlorobenzil

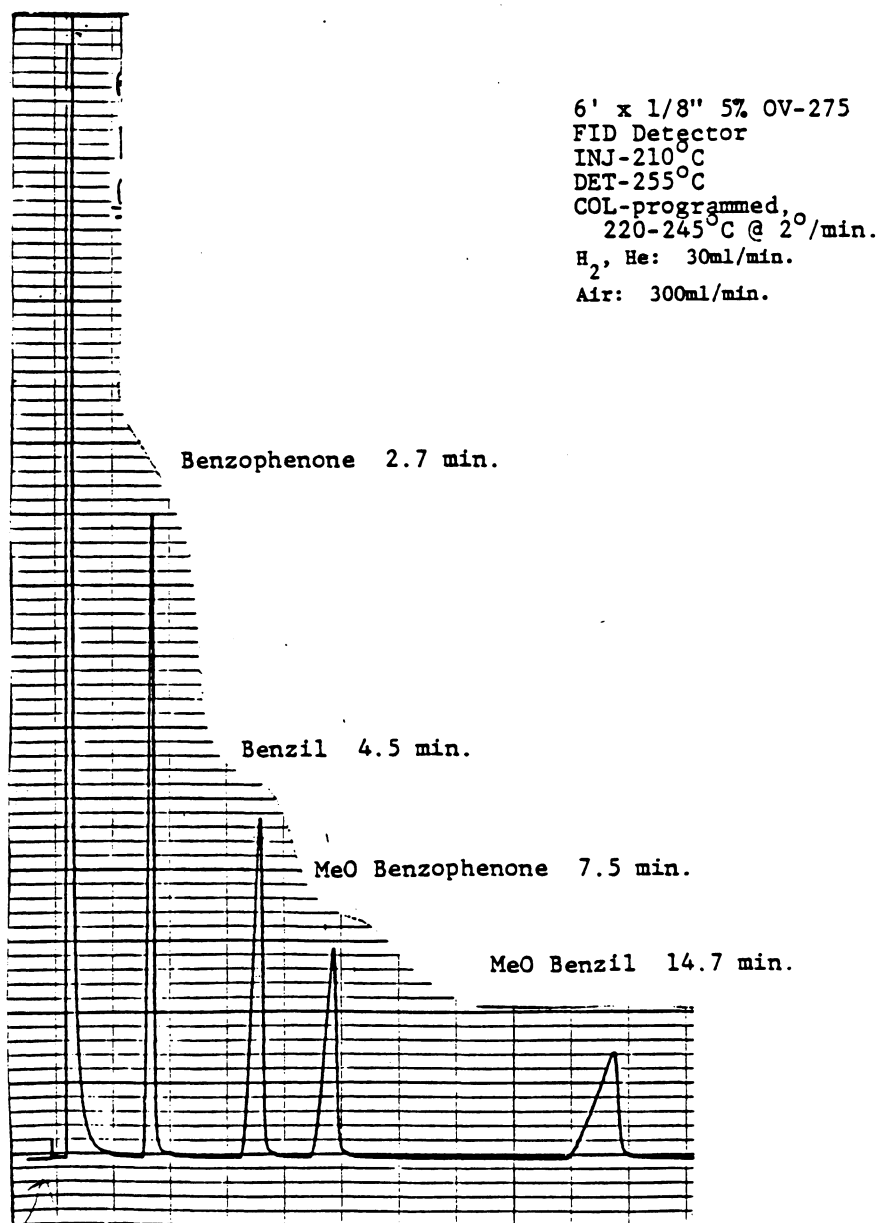
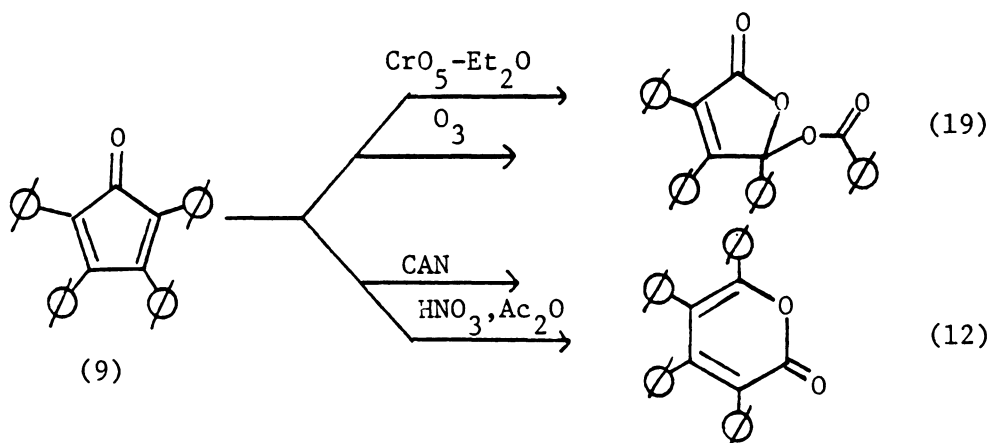
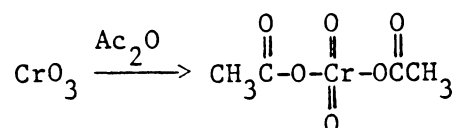
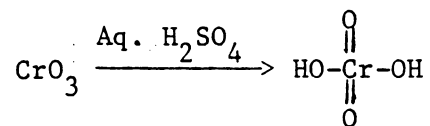


FIGURE 2. Chromatogram of Benzophenone, Benzil
Methoxybenzophenone and Methoxybenzil



Whether this phenomenon would be observed in the compound of interest (2) was unknown. It was decided that the best approach would be to reexamine the single reported oxidation of (2) by Allen and VanAllan, who used chromic trioxide in acetic anhydride (diacetyl chromate), and to examine oxidizing agents which had not been reported for the related systems, tetracyclone (9) and pentaphenylcyclopentadienol (5). The oxidants chosen were, in addition to chromic anhydride, potassium permanganate, and potassium permanganate/sodium periodate (Lemieux-von Rudloff reagent).^{27,29,29,30} Variations in the ratio of oxidant to substrate and changes in solvent were tested. In addition, changing the solvent in the case of chromium trioxide also changes the actual specie present, i.e., chromium trioxide in acetic anhydride produces diacetyl chromate as the oxidizing agent. In aqueous sulfuric acid,





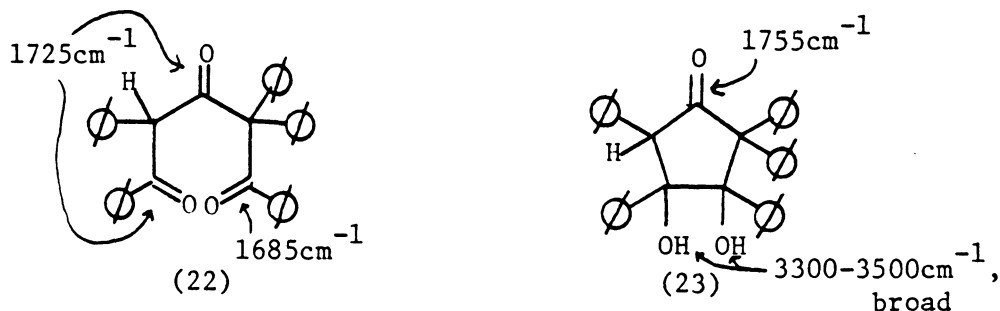
the actual oxidant present is chromic acid. These species differ in the type of products produced, even though Cr(VI) is the oxidant in both cases.

Since the ultimate goal of this study was to effect quantitative cleavage of the ring bonds of parent ketone (2) to yield benzophenone, benzil and benzoic acid, the evaluation of oxidants was approached in the following manner. In order to standardize the oxidations as much as possible, the parameters of 24 hours reaction time and room temperature were used, except in the case of diacetyl chromate, where the attempt was made to reproduce the conditions of Allen and VanAllan.⁶ Since these authors reported very little as to reaction conditions, varied temperature runs were made with this reagent. It was found that the products in this case were unchanged even when comparing runs from room temperature to approximately 90°C, which was the upper limit evaluated.

After quenching, each reaction mixture was extracted with benzene to remove the organic compounds, followed by extraction with sodium carbonate to remove possible acids, such as the expected benzoic acid. The organic oil was analyzed by the outlined procedure, and if no benzil or benzophenone were produced, the products were not analyzed further, with the exception of taking an infrared spectrum. The results

of the evaluation of the various oxidants are summarized in Table 2.

The reaction of potassium permanganate with the substrate produced no benzil or benzophenone. Crown ether,³³ known for its ability to solubilize salts in organic solvents, was used to effect a homogenous reaction mixture. This reaction was run with varying amounts of permanganate, but none of the expected cleavage products were produced. Permanganate oxidation of double bonds and ketones has been proposed to proceed via cyclic manganate esters which can decompose to give epoxides, glycols, or cleavage products. The infrared spectrum from the action of permanganate on (2) suggests that a mixture of (22) and (23) may be present, with the bands present assigned as



indicated. The infrared is given in Figure 3. The alkyl C-H stretching is from the crown ether.

Oxidation by the Lemieux-von Rudloff reagent was also ineffective. This reagent was described by Lemieux and von Rudloff^{27,28,29,30} as effective at cleaving unsaturated sites in a wide variety of aliphatic alcohols, polyols, aldehydes, acids, ketones, ethers, and esters. As can be seen from Table 2, the parent ketone (2) is inert to the reagent. None of the expected cleavage products were formed. The possibility exists that mutual insolubility is the critical consideration. The

TABLE 2

Oxidation Trials

<u>Substrate</u>	<u>Oxidant</u>	<u>Conditions</u>	<u>% Benzo- phenone</u>	<u>% Benzil</u>	<u>% Benzoic Acid</u>
Parent Ketone	KMnO ₄	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /(3X)	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	65% Pyridine, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	33% t-Butanol, 24 hrs, R.T.	----	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	75% Acetone, 24 hrs, R.T.	<1	----	----
Parent Ketone	KMnO ₄ /NaIO ₄	Crown Ether/Benzene, 24 hrs, R.T.	----	----	----
Parent Ketone	CrO ₃	90% AcOH, 0.002M H ₂ SO ₄	----	----	----
Parent Ketone	CrO ₃	70% H ₂ SO ₄	----	----	----
Parent Ketone	CrO ₃	Ac ₂ O, 1.5 hrs, 80-95°C	38.0	38.5	24.0 [¶]
Control Mix [†]	CrO ₃	Ac ₂ O, 1.5 hrs, 80-90°C	90.2	92.0	57.4 [¶]
Control Mix [†]	CrO ₃	Ac ₂ O, 20 hrs, 85-90°C	89.0	95.0	26.5 [¶]
Parent Ketone	CrO ₃	Ac ₂ O, 50 min(2X), 80-90°C	41.0	41.8	54.6 [¶]
1-Chloro Ketone*	CrO ₃	Ac ₂ O, 1.5 hrs, 80-95°C	37.3(Cl)	42.9	36.9 [¶]
Parent Ketone	CrO ₃	Ac ₂ O, 24 hrs, 85-95°C	39.0	39.8	17.3 [¶]

*2-(p-chlorophenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one

†Equimolar mixture of Benzil, Benzoic Acid, and Benzophenone

¶Recrystallized Yield

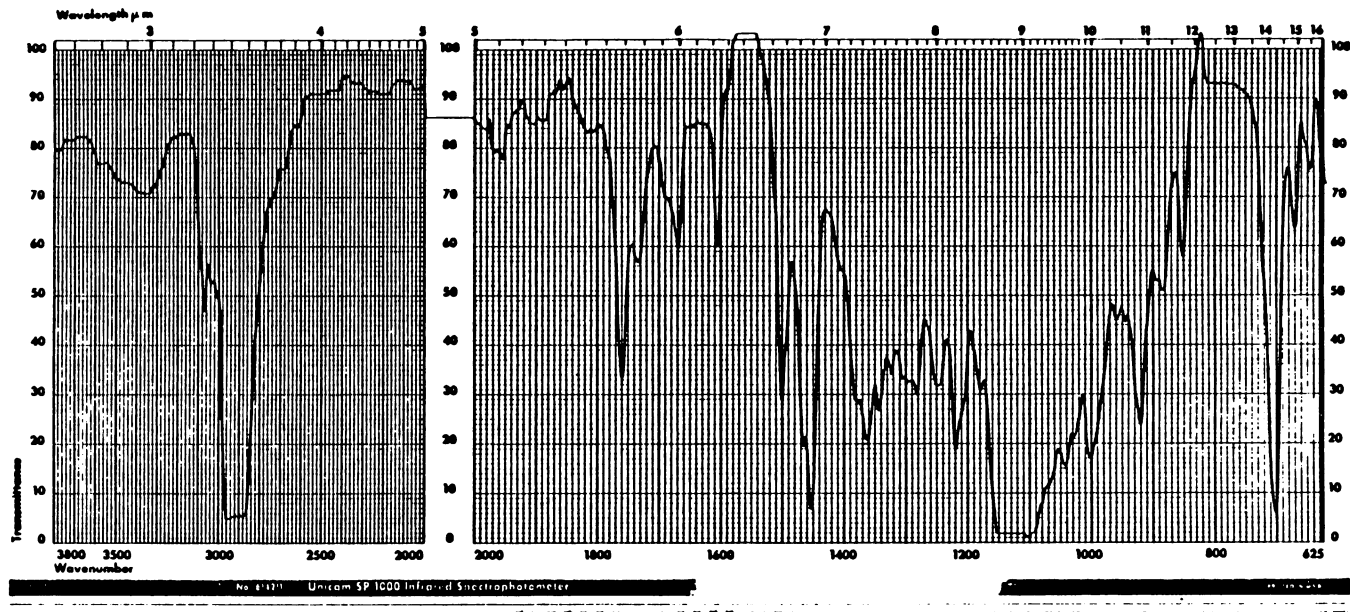
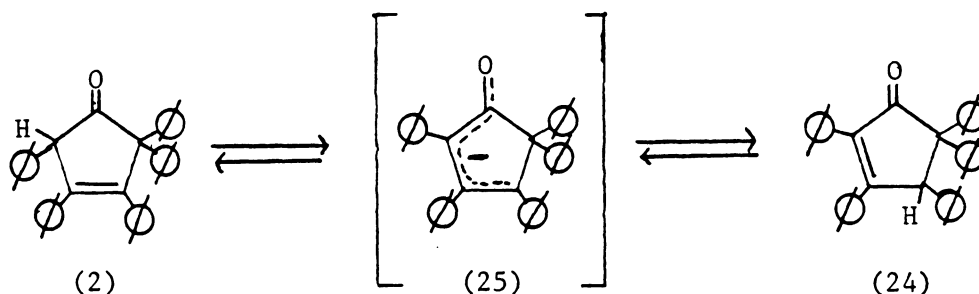


FIGURE 3. Infrared Spectrum of Reaction Mixture from Oxidation of Parent Ketone with KMnO_4 /Crown Ether in Benzene

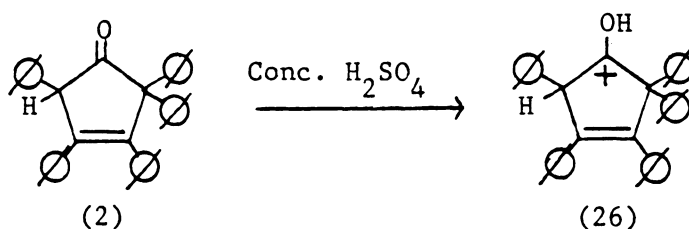
oxidant requires aqueous solutions maintained at a pH of approximately 7-8, and the ketone (2) is poorly soluble in such an environment. Solvent systems used were 33 percent tertiary butanol, 65 percent pyridine, and 75 percent acetone. The pH is maintained between seven and ten by periodic addition of potassium carbonate. This pH is required for the system to operate as designed, i.e., only catalytic amounts of permanganate are needed, since the periodate constantly regenerates it from the manganate state. The permanganate produces glycols and hydroxy ketones which are cleaved by action of the periodate. The infrared spectrum of the oil resulting from the action of this reagent on (2) in 33 percent tertiary butanol contained bands at 1760cm^{-1} and 1720cm^{-1} , corresponding to the carbonyl frequencies of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2), and its conjugated isomer 2,2,3,4,5-pentaphenyl-4-cyclopenten-1-one (24). Youssef and Ogliaruso⁴ have shown that (2) can be converted to (24) by the action of carbonate ion, which produces the delocalized anion (25). Thus,



it is not unexpected that (2) and (24) would be isolated from this reaction, and in fact they were (see experimental). When (2) was subjected to the same oxidant in pyridine, the infrared spectrum of

the product was identical to that of the starting material (See Figure 4). This is readily explained by the fact that no potassium carbonate was added to this reaction mixture, since the solvent maintained the pH in the desired range (7-9). Attempts to solubilize the combination of $\text{KMnO}_4/\text{NaIO}_4$ in benzene by use of 18-crown-6 crown ether also led to no benzil or benzophenone production.

Attempts to oxidize (2) using chromic acid [CrO_3 in 90 percent AcOH (0.002M in H_2SO_4), and CrO_3 in 70 percent H_2SO_4] produced no benzil or benzophenone and were not analyzed further. The possibility exists that in the high acid concentrations described above, (2) was protonated, making attack by the electrophilic chromium species impossible.



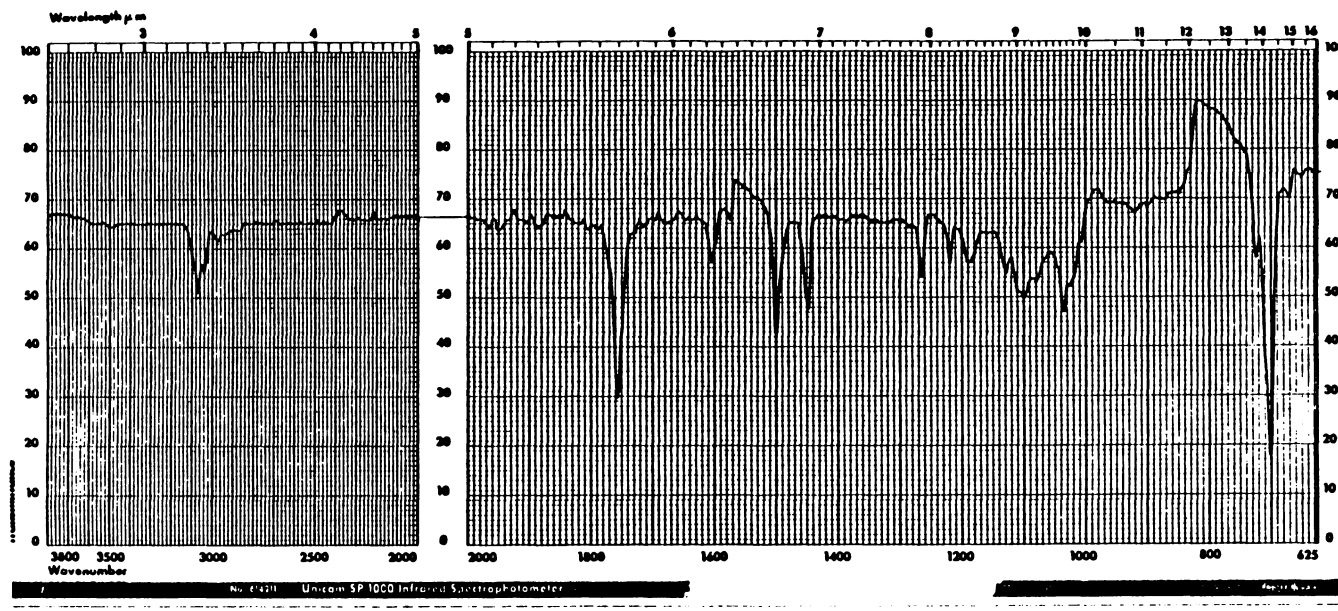
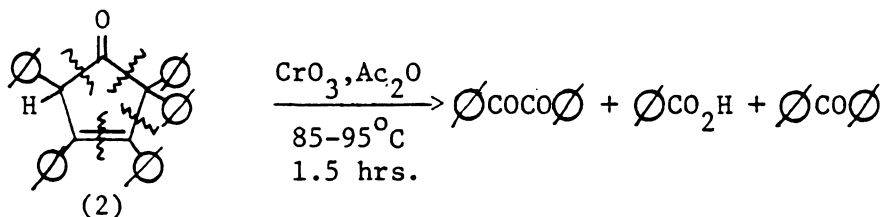


FIGURE 4. Infrared Spectrum of Reaction Mixture from Oxidation of Parent Ketone with $\text{KMnO}_4/\text{NaIO}_4$ in 65% Pyridine

on (2) consist of a 40-43 percent overall yield of a consistently equimolar mixture of benzil, benzophenone, and benzoic acid.

Initially, (2) was subjected to this oxidant at 80-95°C for 1.5 hours, conditions which consistently produced 38-40 percent overall yield of the expected cleavage products. The yields for the benzoic acid were always slightly lower than the benzil and benzophenone,



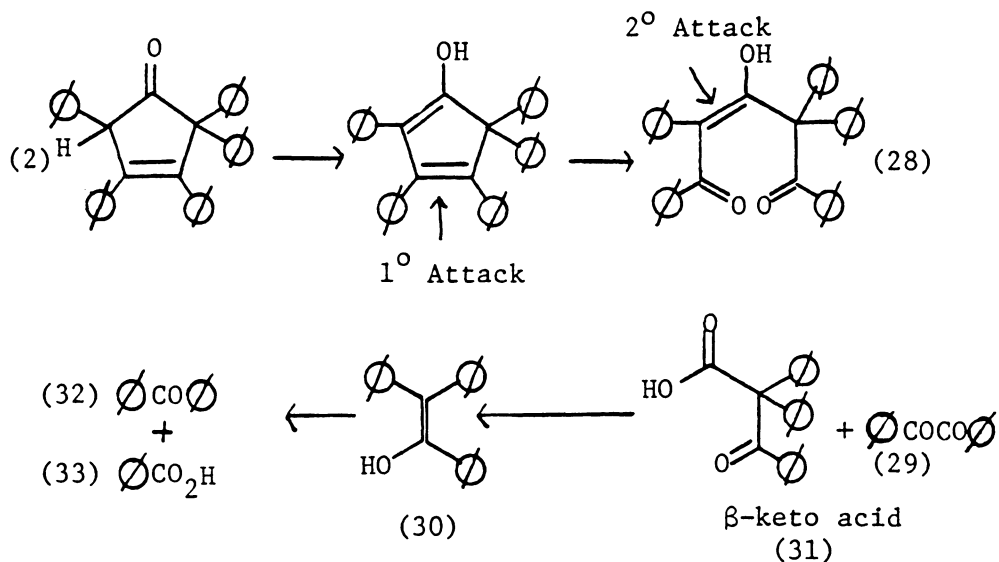
but this was due to losses in extraction and recrystallization. The fact that repetitive runs using these conditions led to the same products in the same proportions suggested the following possibilities. One, oxidative cleavage may be complete, followed by further degradation of the expected products. This possibility did not seem likely, since it would assume that benzil and benzophenone are degraded at exactly the same rate by the oxidant. This possibility was eliminated by subjecting a control mixture comprised of equimolar amounts of the three expected products to the oxidant, under identical conditions. As can be seen from Table 2, the recovery of the expected products was nearly quantitative, particularly when considering the multiple extractions involved in the work-up and the relative error (2.5%)¹⁹

of the gas chromatographic integration method employed. Thus, the consistent, moderate yield was not due to losses of the primary oxidation products. The second possibility, underoxidation of the parent ketone (2), was eliminated as a possibility by runs employing tremendous excess over the amount of oxidant theoretically required for total cleavage.

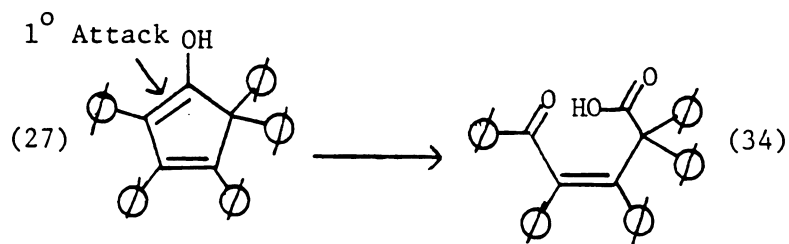
A third possibility, that perhaps some intermediate organochromium ester was resisting decomposition or that lower oxidation states of chromium were in some way inhibiting further oxidation was also eliminated. Oxidizing (2) for one-half the usual reaction time, followed by complete work-up (aqueous extractions to remove acids and chromium salts) and gas chromatographic analysis produced 40-41 percent of the expected benzil and benzophenone. The reaction mixture was then stripped and subjected to the oxidant a second time. Gas chromatographic analysis indicated (within experimental error) an identical amount of the same products (41-42%).

Oxidation with this reagent was also performed at longer reaction times (24 hours, 85-95°C), producing once again a 39-40 percent yield of benzil and benzophenone.

One plausible explanation for these experimental findings is as follows. Ketone (2) contains two sites which would undergo initial attack by the chromium oxidant, the double bond and the ketone (via enolization).^{35,36} Cleavage of the double bond first would lead to the observed products by the following route. This pathway also accounts for the equimolar production observed for these products.

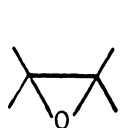


Alternatively, attack may occur first at the enolic site. Attack here, however, ultimately does not lead to cleavage products. The initial product of cleavage of the enolic site leads to (34).

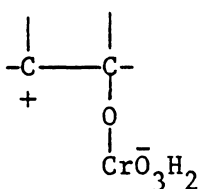


With subsequent attack at the double bond, the following ring closure product, lactone (35) becomes favored. Various investigators have proposed the following intermediates or products from the action of

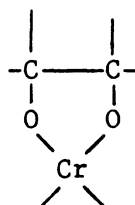
chromic acid or diacetyl chromate on olefins: epoxides (36),³⁷ carbonium ions (37),³⁸ cyclic chromium esters (38),³⁹ and for the case of tetraryl ethylenes, benzopinacol carbonate (39).⁴⁰



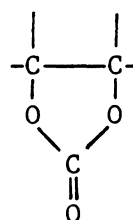
(36)



(37)

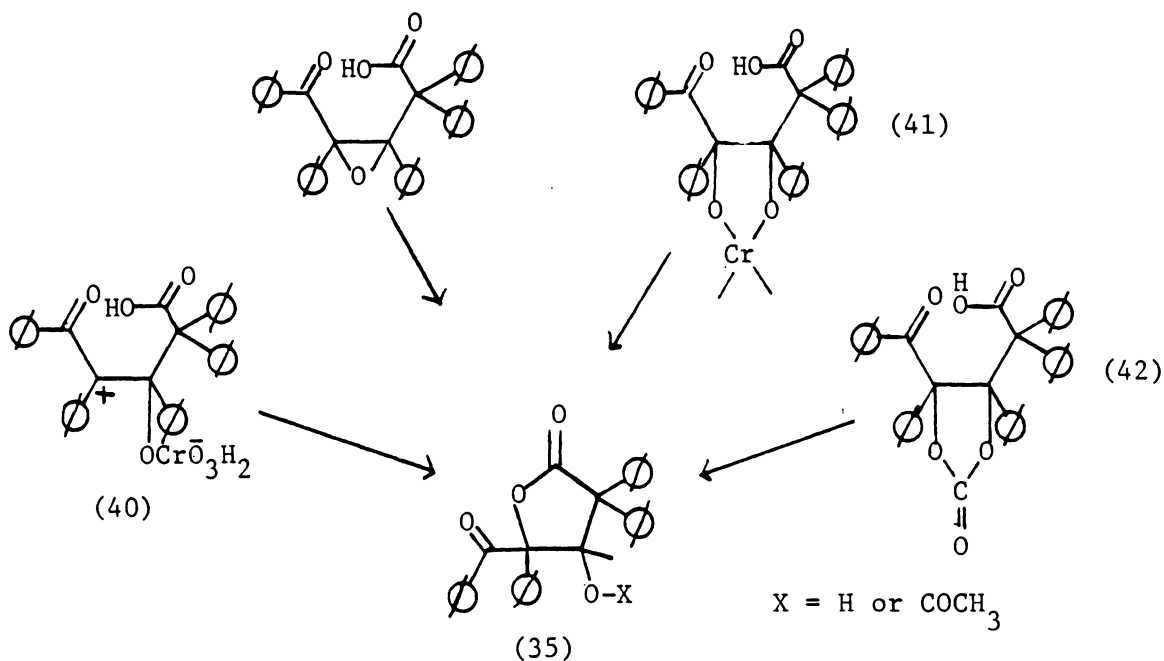


(38)

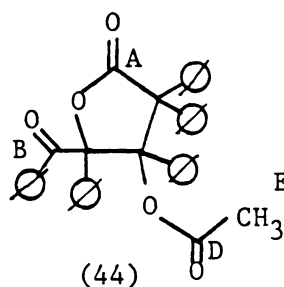
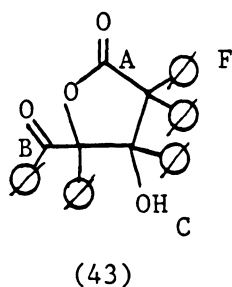


(39)

It is apparent that each of these structures bears a site well-disposed toward nucleophilic attack by the -OH of the acid moiety already present. Spontaneous ring closure is especially favorable



in this system, producing a relatively stain-free 5-membered ring, and is favorable entropically. Precedent and propensity for ring formation in the oxidation of the related compound tetracyclone has been previously demonstrated (see historical). Furthermore, γ -lactones have been found to be stable to chromium(VI) oxidation in other systems.^{40,41} Finally, column chromatography of the reaction mixture produced a series of fractions which gave the infrared spectrum shown in Figure 5. The bands may be assigned as follows and appear to be a mixture of the free hydroxy-lactone (43) and the acetylated form (44).

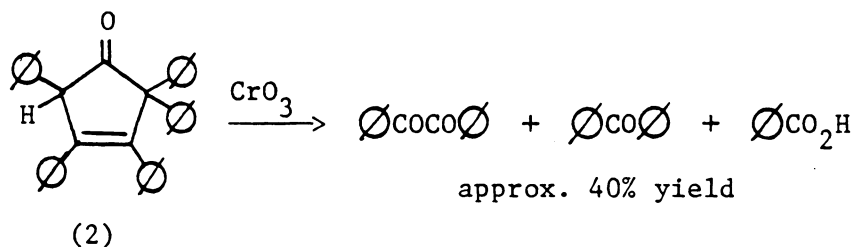


<u>Band</u>	<u>Frequency (cm⁻¹)</u>
A	1765
B	1680
C	3400-3600
D	1720
E	1380; 2900-3000
F	1450, 1500, 1580, 1600; 3000-3100

The presence of two parallel pathways for the oxidation of (2) by diacetyl chromate is consistent with the experimental data. Attack at the double bond first leads to the expected cleavage products, while initial attack at the ketonic site probably leads to γ -lactone

which is not further degraded.

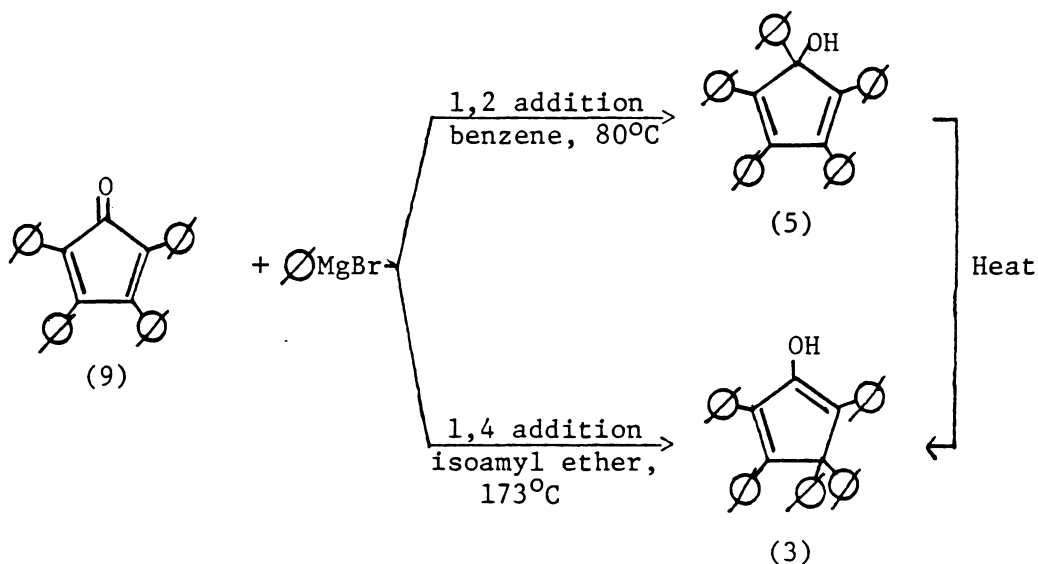
In summary, of the oxidants evaluated only chromium trioxide in acetic anhydride produced significant amounts of the desired products, in roughly 40 percent yield. In terms of the system under study, since the pattern of cleavage appears to be the desired one, i.e., produces benzils and benzophenones, the procedure could be used qualitatively to determine if indeed one, the other, or a mixture of two possible products of thermal rearrangement (Scheme 1) are produced. However, since the identity of the missing 56-58 percent has not been proven, this author would hesitate to use the oxidation to quantitate the proportions of the two.



In reference to Allen and VanAllan's earlier work, it is surprising that the presence of an equimolar amount of benzil with regard to the other two cleavage products could have escaped detection. This author presents the results of multiple oxidations of (2) with chromic anhydride as a correction of the literature.

SECTION B. HISTORICAL

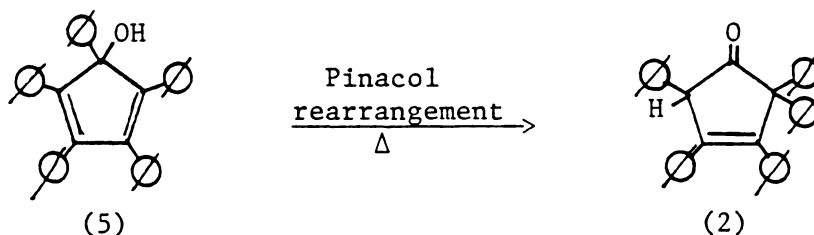
In 1943, Allen and VanAllan⁶ reported that the reaction of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (9) with phenylmagnesium bromide produced two compounds: 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (5) and 2,3,3,4,5-pentaphenyl-4-cyclopenten-1-ol (3). In refluxing benzene the product obtained is (5), as a result of 1,2- addition. When the reaction was performed at high temperature (refluxing isoamyl ether 173°C) the product obtained is (3), the result of 1,4-addition or 1,2-addition followed by thermally induced rearrangement.



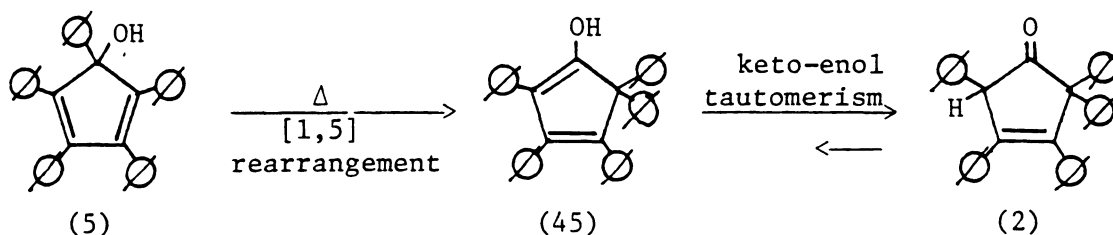
The formation of (3) from (5) reportedly occurred when the 1,2-addition product was heated in refluxing isoamyl ether, or by heating at 290-300°C in the absence of solvent.

In 1961 Dufraisse, Rio and Ranjon⁷ reexamined the thermal rearrangement in the absence of solvent, finding that the true

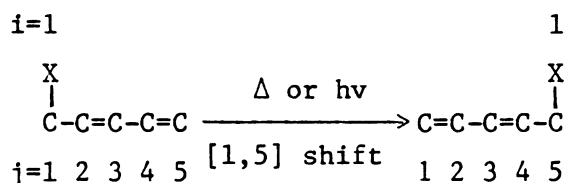
structure of the major product (two minor products are also produced) was not (3) but rather 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2). They proposed that the mechanism of formation of (2) from (5) was via pinacol rearrangement.



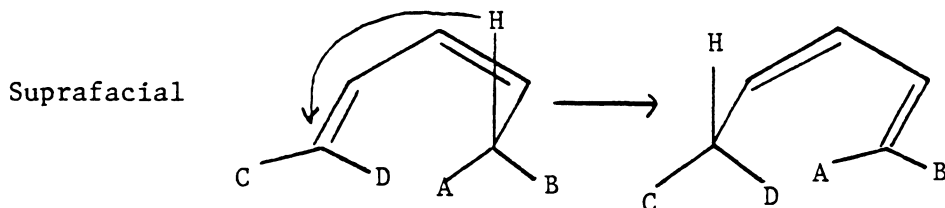
In 1972 Youssef and Ogliaruso¹ encountered the work of Allen and VanAllan. By this time, however, a new mechanistic interpretation had been made available by Woodward and Hoffman.⁴² Their theory that conservation of orbital symmetry is observed throughout the course of concerted reactions could be used to explain the formation of (2) via a thermally-induced, [1,5]-sigmatropic phenyl rearrangement. Initially formed is the enol (45) which rapidly tautomerizes to the ketone (2).

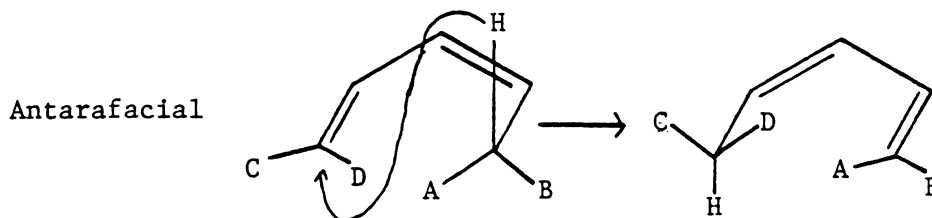


Sigmatropic rearrangements⁴² are uncatalyzed, unimolecular, single-step processes whereby a sigma bond flanked by one or more π electron systems migrates to a new position in the molecule. The rearrangements require thermal or photochemical initiation and the σ and π bond shifts occur in concerted fashion with conservation of orbital symmetry. The rearrangements are classified by two letters, i and j, set in brackets. The numbers refer to the point of attachment of the sigma bond after migration occurs, with numbering beginning at the two atoms forming the initial sigma bond.⁴²



Geometrically, there are two pathways for migration. Migration may occur with the migrating group moving along one face of the π system, denoted as a suprafacial rearrangement. Alternatively, the migrating group may move from one face of the π system to the other denoted as an antarafacial rearrangement and shown here for [1,5]-migration of hydrogen.

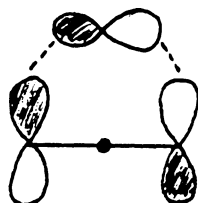
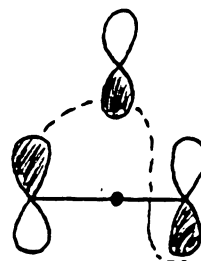




In any given sigmatropic rearrangement only one of the two pathways is allowed by the orbital symmetry rules; the other is forbidden. Whether a particular system will rearrange suprafacially or antarafacially can be determined using a modified frontier orbital approach. In this approach, the transition state is treated as if the σ bond were broken and the migrating group and π -system are free-radicals. In the transition state there is overlap between the highest occupied molecular orbital (HOMO) of one and the HOMO of the other. Each HOMO is singly occupied, and together they provide a pair of electrons.

These rules are illustrated in Figure 6. Considering a [1,3] migration of carbon, the symmetry of the HOMO of the allylic radical in the ground state (thermal rearrangement) dictates that rearrangement occurs suprafacially with inversion of configuration in the migrating group or antarafacially with retention. In the excited state (photo-chemical rearrangement) the symmetry of the HOMO is reversed and thus migration occurs antarafacially with inversion or suprafacially with retention. In reality [1,3]-antarafacial shifts are rare due to the extreme strain imposed to attain the transition state. The selection rules for neutral [1,j] thermal sigmatropic rearrangements are shown in Table 3.

HOMO (Ground State)

Suprafacial
w/inversionAntarafacial
w/retention

HOMO (Excited State)

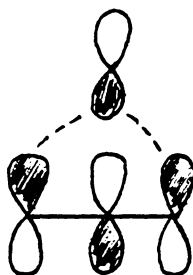
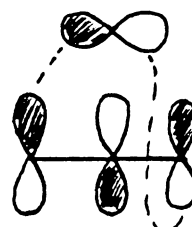
Suprafacial
w/retentionAntarafacial
w/inversion

FIGURE 6. [1,3]-Sigmatropic Shift of Carbon

TABLE 3

HOMO Selection Rules for Neutral [1,j]

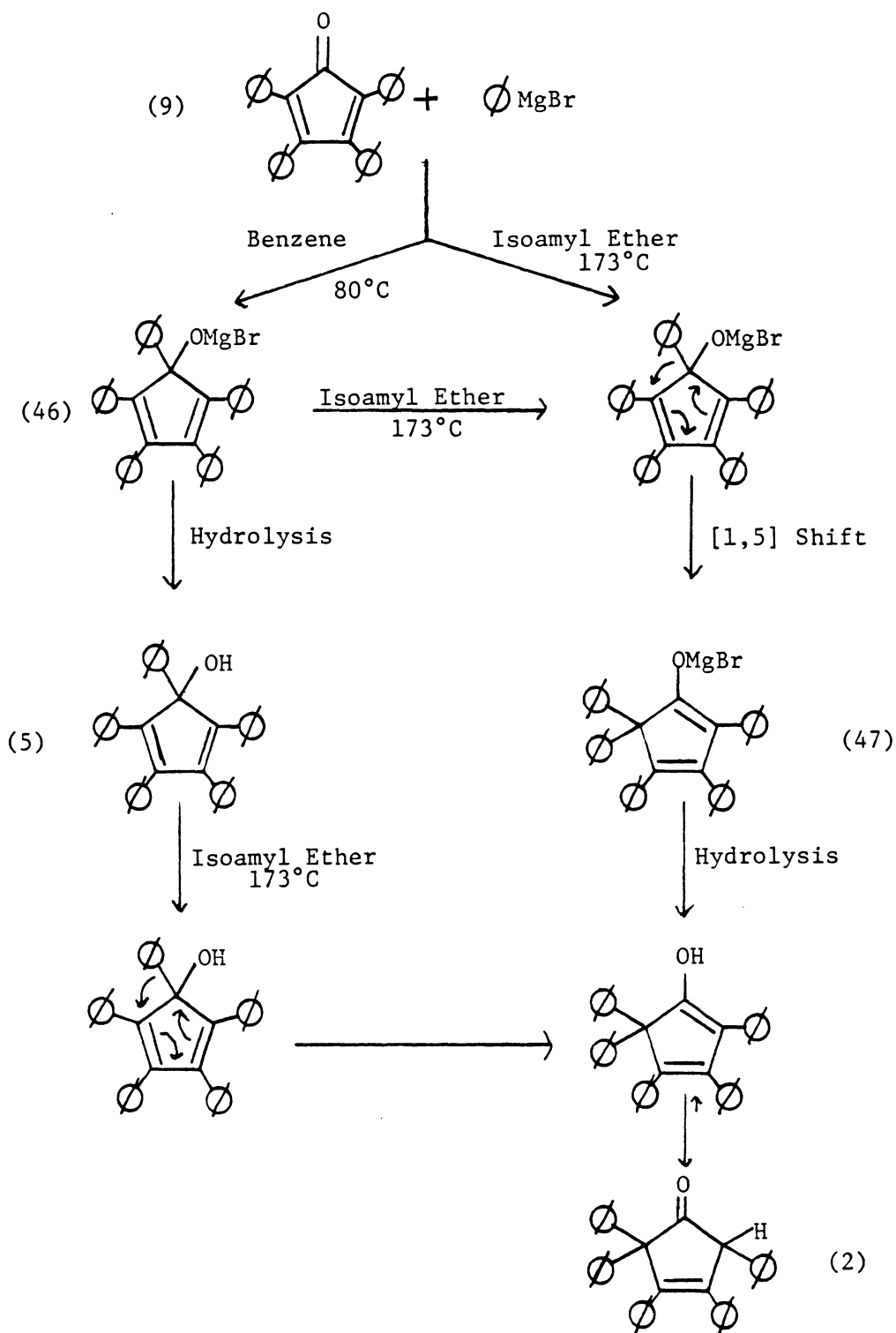
Thermal Sigmatropic Rearrangements

<u>1</u>	<u>Allowed</u>	<u>Forbidden</u>
3	antara-retention supra-inversion	antara-inversion supra-retention
5	antara-inversion supra-retention	antara-retention supra-inversion
7	antara-retention supra-inversion	antara-inversion supra-retention

In order to investigate and verify a sigmatropic rearrangement as the mechanism of the conversion of (5) to (2) the following series of reactions^{1,3} were performed. The possibility of direct 1,6- addition was eliminated by showing (5), the product of a 1,2- addition to be an intermediate. Performing the reaction in refluxing benzene produces (46), the magnesium bromide salt of (5) as a result of a 1,2- addition of the Grignard reagent. Hydrolysis of (46) produced (5), which can be isomerized to (2) by heating in refluxing isoamyl ether. Alternatively, the Grignard salt (46) can be rearranged to (47) which upon hydrolysis affords (2) also. This was the first reported instance of a thermally induced sigmatropic rearrangement of the magnesium salt of a Grignard reaction. The conclusion from the above series of reactions was that the reaction in question proceeded via 1,2- addition of phenylmagnesium bromide to (9) to produce the Grignard salt (46), which could be hydrolyzed to give the alcohol (5). The alcohol (5) when subjected to high temperature rearranges by a phenyl shift to give the enol (45) which rapidly tautomerizes to the ketone (2). These reactions are presented in a flowchart as Scheme 2.

Two other considerations had to be eliminated before the characterization of the rearrangement was complete. To establish the concertedness of the phenyl shift, the possibility of ionic pathways or free-radical pathways had to be eliminated. The ionic pathway was eliminated by refluxing (5) in both isoamyl ether ($\epsilon=2.82$)⁴³ and dimethyl sulfoxide ($\epsilon=46.6$).⁴⁴ In spite of the great difference in the dielectric constants of the solvents, the rates of isomerization

SCHEME 2



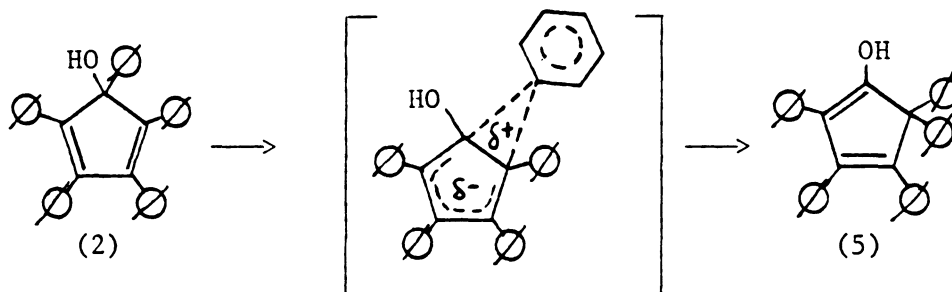
(as monitored by chromatography) were identical.^{1,3} To eliminate the free-radical pathway, (2) was refluxed in isoamyl ether with a strong stream of oxygen bubbling continuously through the solution. The yield of (4) was identical to that obtained in the absence of oxygen. The conclusion was that since the presence of a radical inhibitor (oxygen) had no effect on the yield of (4), the reaction must not be free-radical in nature. These possibilities eliminated, the reaction was characterized as a thermally induced, [1,5]-sigmatropic phenyl rearrangement. The shift is suprafacial in accordance with the Woodward-Hoffman rules.⁴²

Also in 1973, Youssef and Ogliaruso³ studied and reported the kinetics of the conversion of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (5) to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (2). These studies indicated first order dependence of rate upon reactant, consistent with a sigmatropic rearrangement. A calculated activation energy (E_a) of 36.1 ± 3.6 kcal/mol was obtained along with an entropy of activation ($\Delta S^\ddagger$) of -7.5eu. At this time the only other values for [1,5]-sigmatropic phenyl shifts were those obtained by Miller⁴⁵ in the indene system. Miller obtained values of E_a and $\Delta S^\ddagger$ of 27.2 kcal and -27.2eu, respectively.

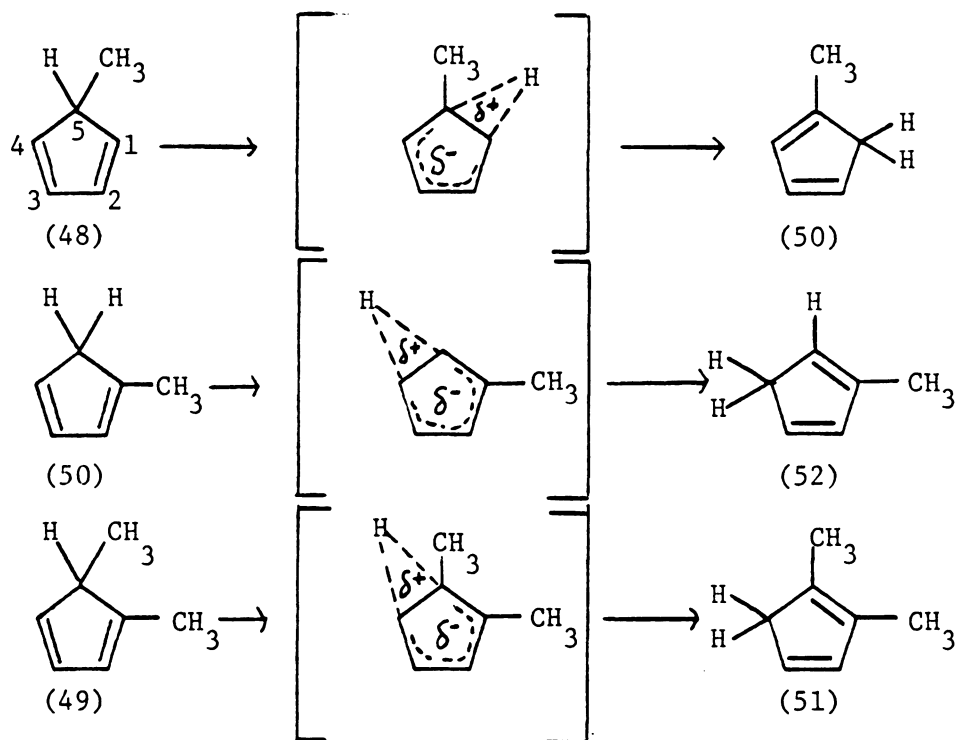
Also at this time attempts to characterize the electronic nature of sigmatropic rearrangements were being performed in other systems. McLean's studies of migration of hydrogen in cyclopentadienes,^{46,48} Miller's work on phenyl and hydrogen migration in substituted indenenes,⁴⁷ and McCullough's investigation of substituted-phenyl

migratory aptitudes in diarylindenes⁴⁹ were well under way. Furthermore, all had given indications that the sigmatropic rearrangements occurring in these cases may not truly be purely neutral, as defined by Woodward-Hoffman rules.

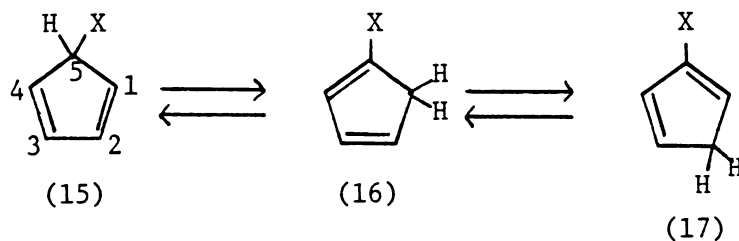
Youssef and Ogliaruso proposed a transition state similar to that proposed for sigmatropic hydrogen migration in cyclopentadienes.⁴⁸



This transition state is based in part on the studies by McLean and Haynes,⁴⁸ who investigated the [1,5]-hydrogen migrations of methyl-substituted cyclopentadienes. 5-Methylcyclopentadiene (48), 1,5-dimethylcyclopentadiene (49), and 1-methylcyclopentadiene (50) were synthesized and the rates of migration measured. It was found that the rate of rearrangement of (48) to (50) was fastest of the three, (49) to (51) proceeded at an intermediary rate, and (50) to (52) was slowest. In terms of the proposed transition state the following explanations can be applied. 5-Methylcyclopentadiene (48), with a methyl substituent only at C₅, proceeds fastest due to stabilization of the partial positive charge experienced at C₅ in the transition state. Presumably, methyl stabilizes the δ^+ by its inductive effect, and by facilitating rehybridization of the sp^3 carbon (C₅) to the more electronegative



sp^2 . In the conversion of (50) to (52), the methyl substituent lies along the π -backbone in the transition state, an area which bears a partial negative charge. In this case the electron-donating inductive effect of methyl destabilizes the transition state by exacerbating the build-up of electron density. Thus, the rate of rearrangement is the slowest of the three cases. Finally, in the conversion of (49) to (51), methyl groups situated at C_5 and C_1 exert their electronic effects on both a δ^+ and a δ^- site, effectively canceling each other and yielding an intermediary rate of rearrangement.



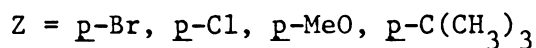
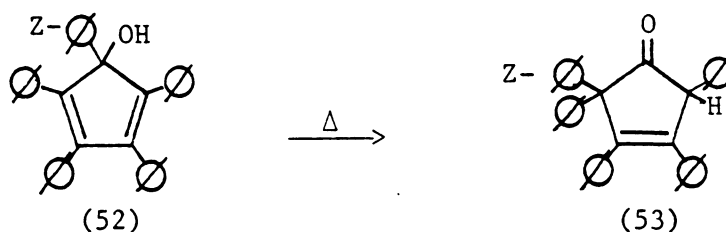
Relative Rate of Rearrangement

X=H	1.0
X=Cl	0.67
X=Br	0.64
X=I	0.17

Breslow⁵⁰ also confirmed a definite substituent effect for the [1,5]-hydrogen migration in cyclopentadiene. The rates of rearrangement of the C₅-halogen substituted cyclopentadienes were compared to the rate for the parent compound. Halogen substitution in all cases slowed rearrangement relative to the parent compound. This was consistent with the proposed transition state, since the electron-withdrawing halogen at C₅ effectively destabilizes the δ⁺ borne at that site in the transition state. The destabilizing electron-withdrawal through induction must be predominating over the ability to stabilize through π-donation via resonance.

The 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (5) system seemed especially well-suited for an investigation into the possibility that the rearrangement could be sensitive to electronic effects. Any of the phenyl rings positioned about the cyclopentadienol ring could be utilized to examine electronic effects at the carbon to which it

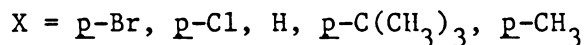
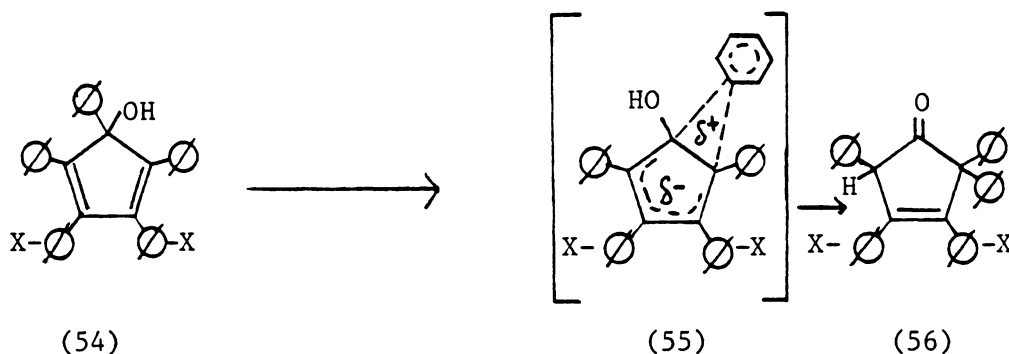
was attached by examining a Hammett series of substituents. The first site examined was C₁. Youssef^{4,5} initiated this study in which a Hammett series of 1-(p-substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols were to be synthesized, followed by isomerization. The existence (or non-existence) of a linear-free energy



relationship was to be determined by comparing the relative rates of isomerization. Youssef's initial examination of this system involved the p-bromo-, p-chloro-, p-methoxy-, and p-t-butyl- substituents. The rates of isomerization at 173° in isoamyl ether were compared to each other and to the parent compound. Unfortunately the results were inconclusive in that while the rates differed, a linear-free energy relationship was not observed.⁵¹ Furthermore, the gas chromatographic analysis employed may have affected the results, i.e. there was no way to determine if additional rearrangement had occurred while passing through the heated column.

In 1975, a liquid chromatographic method was developed by Berg, Ogliaruso, and McNair⁵² for the analysis of the alcohol/ketone reaction mixture. This enabled Perfetti,² to investigate the kinetics of

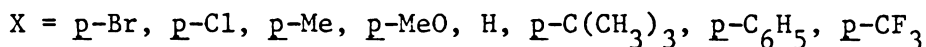
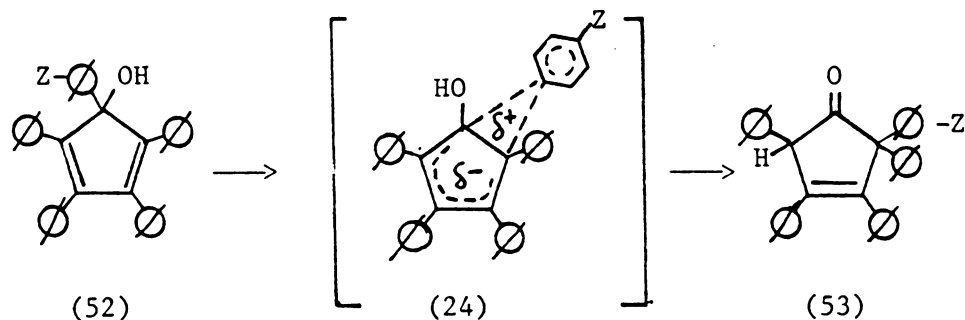
the rearrangement of the analogous series of 3,4-bis(*p*-substituted phenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ols (54) for electronic effects. In this series the substituents are located along the



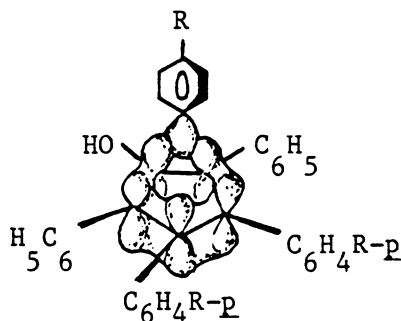
π -backbone, an area bearing a δ^- charge in the proposed transition state. Thus, electron-donating substituents would be expected to decrease the rate of rearrangement through destabilization of the transition state. Conversely, the electron-withdrawing substituents should increase the rate of rearrangement. Perfetti found that the rates were roughly the same, and no correlation of rate to a substituent's Hammett value could be made. Entropies of activation (26.5–30.3 kcal/mol) were consistent with the value obtained for the parent compound (2), (34.7 kcal/mol) and with the value reported by Miller⁴⁵ for [1,5]-phenyl shift in the indene system (27.2 kcal/mol).

Concurrently, Oldaker² was extending the series initiated by Youssef on the kinetics of the rearrangement of the 1-(*p*-substituted phenyl) alcohols (52). This study was the first to employ a Hammett linear free energy probe directly at the migration center of a true

sigmatropic rearrangement. It was believed that the electronic effects of the substituents examined would be more pronounced due to their proximity. The prediction for the effect of a particular



substituent on the rate of rearrangement in the case of series (52) is precisely the reverse of series (54). In Oldaker's series, the substituents are exerting their electronic effects upon a δ^+ charge. Thus, electron-donating substituents should increase the rate of rearrangement while electron-withdrawing substituents should slow the rate of reaction. As with Perfetti's² study, the rates were nearly identical and linear free energy correlations were not observed. The parameters employed were σ_p , σ_p^+ , σ_p^0 , σ_p^- , σ_n , and σ_m^+ . Oldaker and Perfetti's work led them to the conclusion that the originally proposed transition state was not applicable in the pentaphenylcyclopentadienol system. A transition state devoid of charge separation was consistent with their findings and they concluded the system rearranges by a truly neutral, concerted mechanism.

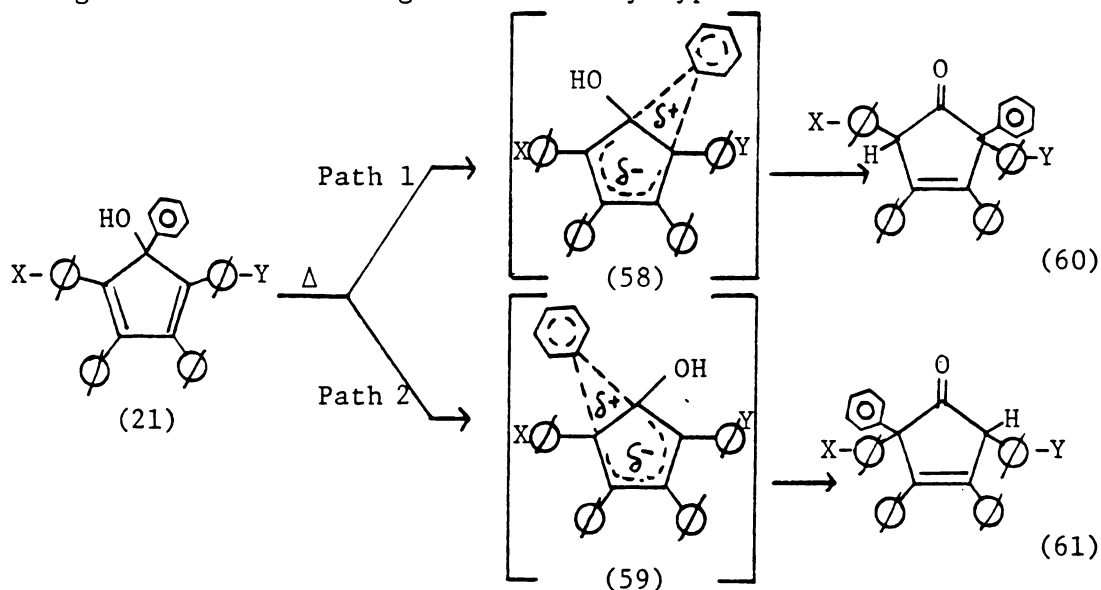


Transition State Devoid of Charge Separation²

As a final step in the characterization of the electronic nature of rearrangements in this system, the subject of this dissertation was undertaken. Specifically, is the transition state best represented as purely neutral, as concluded by Perfetti and Oldaker;² or does it resemble the partially charge-separated transition state proposed and proven for hydrogen migration in cyclopentadienes?^{46,50} The possibility certainly exists, that for unknown reasons Oldaker's and Perfetti's systems simply did not permit the electronic effects of the substituents to be observed. In Perfetti's system, the substituted phenyl rings at C₃ and C₄ can never attain the geometry required for electron transmission through resonance; the rings at C₂, C₃, C₄, C₅ assume a propeller-shaped (30°) orientation with respect to the central five-membered ring.

In order to determine which of the two representations best applies to the pentaphenylcyclopentadienol system, the following can be used as a probe. A series of 2- and/or 5-(p- or m-substituted

phenyl)-1,3,4-triphenyl-2,4-cyclopentadienols (21) were synthesized and thermally rearranged. In a system such as this, with more than one migration pathway available, substituents should interact with the transition state in a manner which would influence the direction of migration. Considering the initially hypothesized transition

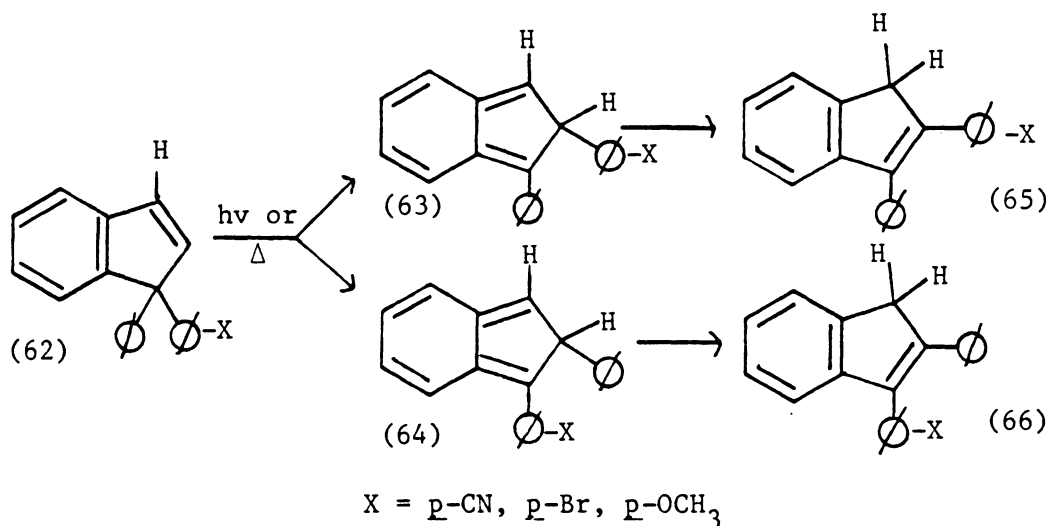


state when Y is electron-donating (p-Me, p-MeO) and X=H, pathway one leading to form (60) should be preferred since the Y-substituent is stabilizing the δ^+ in the transition state relative to unsubstituted phenyl. If the migrating phenyl group migrates toward the side where X=H, the electron-donating effect of the Y-substituent is forced to interact with a δ^- charge (Path 2), destabilizing the transition state. When Y is electron-withdrawing (p-Br, p-Cl, m-MeO) and X=H, path two is preferred since path one would produce a transition state in which the electron-withdrawing substituents would exacerbate a δ^+ charge.

These effects should be even more pronounced for the cases where $X=Br$, $Y=Me$ and $X=Cl$, $Y=MeO$, since path 1 allows the electron-donating Y -substituent to stabilize a δ^+ in the transition state, while simultaneously the electron-withdrawing X -substituent is stabilizing a δ^- charge. An attempt by phenyl to migrate by path 2 in this case would require a transition state in which both the δ^+ and δ^- charges are exacerbated by the electron effects of the substituents. The rearrangement in this system is not considered to be reversible. Therefore parallel path first order kinetics leading from reactant to the two products are observed, and therefore the product distribution ratio at $t=\infty$ is a measure also of the ratio of the relative rates of path 1 and path 2. It is this product distribution and its correlation (or lack thereof) to the Hammett values of the substituents that forms the basis of this dissertation.

If the product distribution correlates with the nature of the substituents as described above, support is given to the δ charge-separated transition state hypothesis. If no preference is shown, i.e., the product ratio is 50/50, then the strictly neutral concerted rearrangement concluded by Perfetti and Oldaker is favored. Determination of the product ratio is not a trivial matter. The original approach was by oxidative degradation as described in Section A of this dissertation. Subsequently the approach was by NMR analysis of the product mixture. This did not appear feasible at the outset of this study, but was reexamined after the technique was utilized by

McCullough⁵³ on the examination of migratory aptitudes of substituted phenyl in the indene system.



McCullough, using 100 MHz proton NMR, was surprisingly able to distinguish and quantitate the methylene signals for the product mixtures produced.

The synthesis of seven 2- and/or 5-(*p*- or *m*-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadienols followed by isomerization and analysis of the resulting product distribution form the basis of this dissertation. The synthetic pathways and approaches to the analysis of the mixtures are presented herein.

SECTION B. EXPERIMENTAL

Reactions and Syntheses

Required for the Substituent Effect Study

Melting points were determined on a Thomas-Hoover melting point apparatus and are not corrected. They were performed using open capillary tubes unless otherwise indicated.

Elemental analyses were performed with either the departmental Perkin-Elmer model 240, CHN analyzer or by Control Equipment Corporation, Lowell, Massachusetts.

Infrared spectra (IR) were taken on a Pye-Unicam model 1025 infrared spectrophotometer using the polystyrene peaks at 1583cm^{-1} and 1602cm^{-1} as a standard.

Mass spectra were obtained on a Varian MAT 112 double focusing mass spectrometer and Varian MAT 112 double focusing mass computer system equipped with a Varian data machine (620L-100) to provide hard copies of spectra at 70 eV, with a ionizing current of 70 μA . The ionization chamber was maintained at 200°C (nominal) and the inlet systems were adjusted between $100\text{--}150^{\circ}\text{C}$ as to maintain an analyzer tube pressure between 1.0 and 3.0×10^{-6} Torr. Samples were introduced into the ionization chamber using a direct inlet probe. Mass assignments were based upon high boiling PFK as a internal standard.

Nuclear magnetic resonance (NMR) spectra were obtained on either a Varian EM-390 (90 MHz) or a JEOL FX-200 (200MHz) using tetramethyl silane (TMS) as an external standard.

Preparation of Ethyl (p- or m-Substituted Phenyl)Acetates

The results of these reactions are summarized in Table 4.

A. Ethyl (p-Bromophenyl)acetate

I. Via Acid-Catalyzed Esterification

Into a 250ml, 3-necked, round-bottom flask equipped with a magnetic stirring bar and surmounted by a reflux condenser was placed 170ml absolute ethanol, 21.5g (0.1 mole) of p-bromophenylacetic acid, and 17mls of concentrated sulfuric acid. This mixture was refluxed for four hours then allowed to stand at room temperature overnight. It was then poured onto 200g of ice and extracted with three 100ml portions of ether. The ether extracts were washed with three 100ml portions of 10 percent sodium bicarbonate, followed by two 50ml portions of water, and dried with anhydrous magnesium sulfate. The ether solution was filtered and transferred to a one-liter round-bottom flask equipped with stirring bar, distillation head and condenser and distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point the remaining liquid (crude ethyl p-bromophenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 106-107°C @ 1.0mm Hg; 91-92°C @ 0.55mm Hg) to yield 18.0g (0.074 mole, 74%) of pure ethyl p-bromophenylacetate as a

clear, colorless liquid. [lit. b.p. 88-90°C @ 0.35mm Hg]⁵⁴

Analysis: M.W. (Mass Spec.) Calcd: 243.1

Found: 243

II. Via Acid-Catalyzed Azeotropic Esterification

Into a 250ml, single-neck, round-bottom flask equipped with a magnetic stirring bar was placed 75mls benzene, 50mls absolute ethanol, 10mls concentrated sulfuric acid, and 21.5g (0.1 mole) of p-bromophenylacetic acid. The flask was surmounted by a fractionating column, Dean-Stark adapter, and reflux condenser. The flask was heated via heating mantle and the solution brought to reflux. When reaction was complete (approx. 12 hrs), as indicated by cessation of production of water, the reaction mixture was poured onto 200g of ice. This aqueous solution was then extracted with three 150ml portions of ether. The ether was then washed with three 100ml portions of 10 percent sodium bicarbonate followed by two 50ml portions of water. The ether was dried with anhydrous magnesium sulfate, filtered, and transferred to a one liter, single-neck, round-bottom flask equipped with stirring bar, distillation head and condenser. The solution was distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point, the remaining liquid (crude ethyl p-bromophenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 106-107°C @ 1.0mm Hg) to yield 20.95g (0.086 mole, 86%) of pure

ethyl *p*-bromophenylacetate as a clear, colorless liquid. [lit. b.p. 88-90°C @ 0.35mm Hg]⁵⁴

Analysis: M.W. (Mass Spec.) Calcd: 243.1

Found: 243

B. Ethyl (p-Chlorophenyl)acetate

I. Via Acid-Catalyzed Esterification

Into a 1-liter, three-necked, round bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 550ml absolute ethanol, 68.0g (0.4 mole) *p*-chlorophenylacetic acid and 55ml concentrated H₂SO₄. The solution was refluxed for four hours and then allowed to stand at room temperature overnight. Next, it was poured onto 700g of ice, then extracted with three 250ml portions of ether. The ether extracts were combined and washed with 100mls of water, two 150ml portions of 10 percent sodium bicarbonate, and one 100ml portion of water. The ether was dried with magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 69.9g (0.352 mole, 88%) of a gold liquid. This was then transferred to a 250ml round-bottom flask equipped with stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 92°C @ 1mm Hg; 85.5-87.0°C @ 0.5mm Hg) to yield 64.3g (0.323 mole, 81%) of pure ethyl *p*-chlorophenylacetate as a clear, colorless liquid. [lit. b.p. 253-254°C @ 749mm Hg]⁵⁵

Analysis: M.W. (Mass Spec.) Calcd: 198.65

Found: 198

II. Via Acid-Catalyzed Azeotropic Esterification

Into a 250ml, single-neck, round-bottom flask equipped with a magnetic stirring bar was placed 75ml benzene, 50ml absolute ethanol, 10ml concentrated sulfuric acid, and 17.06g (0.1 mole) of p-chlorophenylacetic acid. The flask was surmounted by a fractionating column, Dean-Stark adapter, and reflux condenser. Heat was applied via heating mantle and the solution brought to reflux. When reaction was complete, as indicated by cessation of production of water (approx. 12 hrs), the reaction mixture was poured onto 200g of ice. This aqueous solution was extracted with three 125ml portions of ether. The ether was washed with three 100ml portions of 10 percent sodium bicarbonate followed by two 50ml portions of water. The ether was dried with magnesium sulfate, filtered, and transferred to a one-liter, single-neck, round-bottom flask equipped with stirring bar, distillation head, and condenser. The solution was distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point, the remaining liquid (crude ethyl p-chlorophenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted by Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 85.5-87.0°C @ 0.5mm Hg) to yield 18.24g (0.092 mole, 92%) of pure ethyl p-chlorophenylacetate as a clear, colorless liquid. [lit. b.p.

253-254°C @ 749mm Hg]⁵⁵

Analysis: M.W. (Mass Spec.) Calcd: 198.65

Found: 198

C. Ethyl (p-Methoxyphenyl)acetate

I. Via Acid-Catalyzed Esterification

Into a 1-liter, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 550mls of absolute ethanol, 66.4g (0.4 mole) of p-methoxyphenylacetic acid, and 55mls concentrated H₂SO₄. The solution was refluxed for four hours and then allowed to stand at room temperature overnight. Next it was poured onto 650g of ice and extracted with three 250ml portions of ether. The ether extracts were combined and washed with 100mls of water, two 100ml portions of 10 percent sodium bicarbonate, and finally 100mls of water. The ether was dried with magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 61.0g (0.314 mole, 78.6%) of a yellow liquid. The crude ethyl p-methoxyphenyl acetate was then transferred to a 250ml round-bottom flask equipped with magnetic stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 100.5-103.0°C @ 0.6mm Hg) to yield 53.7g (0.277 mole, 69%) of pure ethyl p-methoxyphenyl acetate as a clear, colorless liquid. [lit. b.p. 138-140°C @ 7mm Hg]⁵⁶

Analysis: M.W. (Mass Spec.) Calcd: 194.22

Found: 194

II. Via Acid-Catalyzed Azeotropic Esterification

Into a 250ml, single-neck, round-bottom flask equipped with a magnetic stirring bar was placed 75mls of benzene, 50mls of absolute ethanol, 12mls of concentrated sulfuric acid, and 16.6g (0.1 mole) of *p*-methoxyphenylacetic acid. The flask was surmounted by a fractionating column, Dean-Stark adapter, and reflux condenser. Heat was applied via heating mantle and the solution was brought to reflux. When reaction was complete, as indicated by cessation of production of water (approx. 12 hrs), the reaction mixture was poured onto 200g of ice. This aqueous solution was extracted with three 125ml portions of ether. The ether was washed with three 100ml portions of 10 percent sodium bicarbonate followed by one 50ml portion of water. The ether was dried with magnesium sulfate, filtered, and transferred to a one-liter, single-neck, round-bottom flask equipped with stirring bar, distillation head, and condenser. The gold solution (fruity odor, as with the other para-esters) was distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point, the remaining liquid (crude ethyl *p*-methoxyphenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted by Claisen adapter, fractionating column (15cm, crimped, evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 95-97°C @ 0.5mm Hg; 100.5-103°C @ 0.6mm Hg) to yield 17.1g (0.088 mole, 88.1%) of pure ethyl *p*-methoxyphenylacetate as a clear, colorless liquid. [lit. b.p. 138-140°C @ 7mm Hg]⁵⁶

Analysis: M.W. (Mass Spec.) Calcd: 194.22

Found: 194

D. Ethyl (m-Methoxyphenyl)acetate

I. Via Acid-Catalyzed Azeotropic Esterification

Into a 250ml, single-neck, round-bottom flask equipped with a magnetic stirring bar was placed 75mls of benzene, 50mls of absolute ethanol, 10mls of concentrated sulfuric acid, and 16.6g (0.1 mole) of m-methoxyphenylacetic acid. The flask was surmounted by a fractionating column, Dean-Stark adapter, and reflux condenser. The flask was heated via heating mantle and the solution brought to reflux. When reaction was complete (approx. 12 hrs) as indicated by cessation of production of water, the reaction mixture was poured onto 200g of ice. This aqueous solution was then extracted with three 125ml portions of ether. The ether extracts were combined and washed with three 50ml portions of 10 percent sodium bicarbonate followed by two 25ml portions of water. The ether was dried with anhydrous magnesium sulfate, filtered, and transferred to a one-liter, single-neck, round-bottom flask equipped with stirring bar, distillation head, and condenser. The solution was distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point, the remaining liquid (crude ethyl m-methoxyphenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected

to a vacuum pump and the product was distilled (b.p. 100-101°C @ 0.85mm Hg) to yield 17.10g (0.088 mole, 88%) of pure ethyl m-methoxyphenylacetate as a clear, colorless liquid. Unlike the para-esters, which all possess a fruity odor, the meta-methoxy ester is nearly odorless. [lit. b.p. 146-147°C @ 14mm Hg]⁵⁷

Analysis: M.W. (Mass Spec.) Calcd: 194.22

Found: 194

E. Ethyl (p-Methylphenyl)acetate

I. Via Acid-Catalyzed Esterification

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and surmounted by a reflux condenser was placed 170mls of absolute ethanol, 15.0g (0.1 mole) of p-methylphenylacetic acid, and 17mls of concentrated sulfuric acid. This mixture was refluxed for four hours, then allowed to stand at room temperature overnight. Next, it was poured onto 200g of ice and extracted with three 100ml portions of ether. The ether extracts were washed with three 100ml portions of 10 percent sodium bicarbonate, followed by two 50ml portions of water and dried with anhydrous magnesium sulfate. The ether solution was filtered and transferred to a one-liter round-bottom flask equipped with stirring bar, distillation head, and condenser. This ether solution was distilled at atmospheric pressure until the temperature began to rise above 80°C. At this point the remaining liquid (crude ethyl p-methylphenylacetate) was transferred to a 100ml round-bottom flask equipped with stirring bar and surmounted

by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 72.5-74.5°C @ 0.45mm Hg) to yield 13.3g (0.075 mole, 75%) of pure ethyl *p*-methylphenylacetate as a clear, colorless liquid. [lit. b.p. 124°C @ 20mm Hg]⁵⁸

Analysis: M.W. (Mass Spec.) Calcd: 178.22

Found: 178

II. Via Acid-Catalyzed Azeotropic Esterification

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar was placed 100mls of benzene, 75mls of absolute ethanol, 10mls of concentrated sulfuric acid, and 25.0g (0.166 mole) of *p*-methylphenylacetic acid. The flask was surmounted by a fractionating column, Dean-Stark adapter, and reflux condenser. The flask was heated via heating mantle and the solution brought to reflux. When reaction was complete, as indicated by cessation of production of water (approx. 12 hrs.), the reaction mixture was poured onto 250g of ice. This aqueous solution was then extracted with three 150ml portions of ether. The ether solutions were combined and washed with three 100ml portions of 10 percent sodium bicarbonate followed by two 50ml portions of water. The ether was dried with anhydrous magnesium sulfate, filtered, and transferred to a one-liter, single-neck, round-bottom flask equipped with magnetic stirring bar, distillation head, and condenser. The solution was distilled at atmospheric pressure

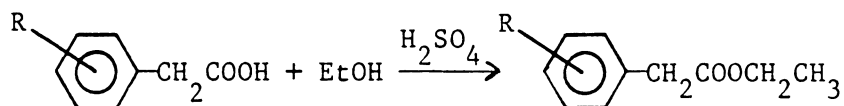
until the temperature began to rise above 80°C. At this point, the remaining liquid (crude ethyl p-methylphenylacetate) was transferred to a 100ml round-bottom flask equipped with a magnetic stirring bar and surmounted by a Claisen adapter, fractionating column (15cm, crimped, evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product was distilled (b.p. 72.5-74.5°C @ 0.45mm Hg) to yield 26.96g (0.15 mole, 91.4%) of pure ethyl p-methylphenylacetate as a clear, colorless liquid. [lit. b.p. 124°C @ 20mm Hg]⁵⁸

Analysis: M.W. (Mass Spec.) Calcd: 178.22

Found: 178

TABLE 4

Preparation of Ethyl (p- or m-Substituted Phenyl) Acetates



Ethyl Acetate R=	Acid-Catalyzed Esterification Yield (%)	Acid-Catalyzed Azeotropic Esterification Yield (%)	Boiling Point (°C)
p-Br	74.0	86.0	106-107 @ 1.0mm Hg lit: 88-90 @ 1.0mm Hg ⁵⁴
p-Cl	81.0	92.0	85.5-87.0 @ 0.5mm Hg lit: 253-254 @ 749mm Hg ⁵⁵
p-MeO	69.0	88.1	100.5-103.0 @ 0.6mm Hg lit: 138-140 @ 7mm Hg ⁵⁶
m-MeO	not performed	88.0	100-101 @ 0.85mm Hg lit: 146-147 @ 14mm Hg ⁵⁷
p-Me	75.0	91.4	72.5-74.5 @ 0.45mm Hg lit: 124 @ 20mm Hg ⁵⁸

Preparation of p- or m-Substituted Diphenylacetacetonitriles

The results of these reactions are summarized in Table 5.

A. 2-(p-Chlorophenyl)-4-Phenylacetoacetonitrile

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 60mls of absolute ethanol and 5.8g (0.25 atom) of sodium. When all the sodium had reacted, 18.9g (0.125 mole) of p-chlorophenylacetonitrile and 25.4g (0.155 mole) of ethyl phenylacetate were mixed and allowed to drip slowly into the sodium ethoxide through a dropping funnel. Addition was carried out over approximately 45 minutes, followed by three hours of refluxing. The reaction mixture was then poured onto 300g of ice and extracted with three 100ml portions of ether. The ether was combined and washed once with 50mls of ten percent sodium carbonate. The ether was then discarded, the aqueous phases combined and acidified with 18 percent hydrochloric acid to pH of approximately three. This was then extracted with four 100ml portions of ether, the ether combined and washed with 50mls of water, four 50ml portions of ten percent sodium bicarbonate, and finally 50mls of water. The ether solution was then dried with anhydrous magnesium sulfate, filtered, and stripped to yield a pale yellow shiny solid which was heated with 75mls of carbon tetrachloride to give a white precipitate. The crude yield of product was 17.1g (0.063 mole, 50.6%), melting point of 126.5-127.5°C. This was recrystallized from carbon tetrachloride (10mls per 1.5 gram of compound) to yield 15.4g (0.057 mole, 45.7%)

pale yellow-white crystals, melting point 127.5-128.5°C. [lit. mpt. 131.0-131.2°C]⁵⁹

Analysis: M.W. (Mass Spec.) Calcd: 269.75

Found: 270

B. 2-(p-Bromophenyl)-4-Phenylacetoacetonitrile

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser, and dropping funnel was placed 60mls absolute ethanol and 5.8g (0.25 atom) of sodium. When all the sodium had reacted, 24.5g (0.125 mole) of p-bromophenyl-acetonitrile mixed with 25.5g (0.155 mole) of ethyl phenylacetate was added slowly to the sodium ethoxide solution over one hour. After addition was complete, the solution was refluxed for three hours, then poured onto 300g of ice and extracted with three 100ml portions of ether. The ether was washed once with 50mls of ten percent sodium carbonate, the aqueous phases combined, and the ether discarded. The aqueous solution was acidified with 50mls of 18 percent hydrochloric acid to pH of approximately three, and extracted with four 100ml portions of ether. The ether was washed with 50mls of water, four 50ml portions of ten percent sodium bicarbonate, and finally 50mls of water. This ether solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow oil to which 100mls of carbon tetrachloride was added, resulting in a voluminous precipitation of yellowish white solid with a metallic sheen. The crude yield was 27.1g (0.0863 mole, 69%). This

was recrystallized from carbon tetrachloride (10mls per 1.5g of compound) to yield 25.3g (0.0805 mole, 64.4%) of off-white powder, melting point 124.0-125.2°C. [lit. mpt. 86-87°C]⁶⁸

Analysis: M.W. (Mass Spec.) Calcd: 314.17

Found: 314

Calcd. for $C_{16}H_{12}ONBr$: C, 61.16; H, 3.85; N, 4.45;

Br, 25.43

Found: C, 60.97; H, 3.80; N, 4.39; Br, 25.41

C. 2-(p-Methylphenyl)-4-Phenylacetoacetonitrile

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser, and dropping funnel was placed 60mls of absolute ethanol and 5.8g (0.25 atom) of sodium. When all the sodium had reacted, 16.4g (0.125 mole) of p-methylphenylacetonitrile mixed with 25.5g (0.155 mole) of ethyl phenylacetate was added dropwise over one hour. After addition was complete, the solution was refluxed for three hours, poured onto 300g of ice, and extracted with three 100ml portions of ether. The ether was washed with 50mls of sodium carbonate, the ether discarded, and the aqueous phases combined. The aqueous solution was acidified with 50mls 18 percent hydrochloric acid to pH of approximately 3, then extracted with four 100ml portions of ether. The ether was combined, washed with 50mls of water, four 50ml portions of ten percent sodium carbonate, and finally 50mls of water. This ether solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary

evaporator to yield 22.2g of an oil which precipitated a white powder from 70mls of carbon tetrachloride. This was recrystallized from carbon tetrachloride (15mls per 1.5g of compound) to yield 20.2g (0.081 mole, 65%) of white powder, melting point 111.0-112.5°C. [lit. 110.5-112.5°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 249.3

Found: 249

Calcd. for $C_{17}H_{15}ON$: C, 81.90; H, 6.06; N, 5.62

Found: C, 81.73; H, 6.10; N, 5.59

D. 2-(p-Methoxyphenyl)-4-Phenylacetoacetonitrile

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 48mls of absolute ethanol and 4.64g (0.20 atom) of sodium. When all the sodium had reacted, a mixture of 14.72g (0.10 mole) of *p*-methoxyphenylacetonitrile and 20.4g (0.124 mole) of ethyl phenylacetate was added dropwise to the sodium ethoxide over 15 minutes. The solution was refluxed for three hours, poured onto 250g of ice, and extracted with three 80ml portions of ether. The ether was washed with 50mls of ten percent sodium carbonate, the ether discarded, and the aqueous phases combined. The aqueous solution was acidified with 40mls of 18 percent hydrochloric acid to pH of approximately 3, then extracted with four 80ml portions of ether. The ether was combined, washed with 50mls of water, four 50ml portions of ten percent sodium bicarbonate, and 50mls of water. The ether was dried with anhydrous magnesium

sulfate, filtered, and stripped on a rotary evaporator to yield 19.1g of a yellow oil to which was added 50mls of carbon tetrachloride, producing 15.7g (0.059 mole, 59%) of a white powder. This was recrystallized from carbon tetrachloride (25mls per 1.5g of compound) to yield 14.1g (0.053 mole, 53%) of a white powder, melting point 79.0-81.5°C (vacuum sealed capillary). [lit. mpt. 79.0-80.0°C]¹³
 Analysis: M.W. (Mass Spec.) Calcd: 265.31

Found: 265

Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.69; N, 5.28

Found: C, 76.91; H, 5.70; N, 5.31

E. 2-(m-Methoxyphenyl)-4-(phenyl)acetoacetonitrile

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 30mls of absolute ethanol and 2.9g (0.125 atom) of sodium. When all the sodium had reacted, a mixture of 9.2g (0.0625 mole) of m-methoxyphenyl-acetonitrile and 11.4g (0.077 mole) of ethyl phenylacetate was added by a dropping funnel over 15 minutes. The solution was refluxed for three and a half hours, poured over 150g of ice, and extracted with three 50ml portions of ether. The ether was washed with 25mls of ten percent sodium carbonate, the aqueous phases combined, and the ether discarded. The aqueous solution was acidified with 25mls of 18 percent hydrochloric acid to pH of approximately three, then extracted with four 25ml portions of sodium bicarbonate, and finally with 25mls of water. The ethereal solution was then dried with anhydrous magnesium sulfate,

filtered, and stripped on a rotary evaporator to yield 11.6g (0.0437 mole, 70.0%) as clear needles. The needles were recrystallized by dissolution in hot methanol followed by addition of water, to yield 11.5g (69%) of pure product, mpt. 88.0-90.5°C.

Analysis: M.W. (Mass Spec.) Calcd: 265.31

Found: 265

Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.69; N, 5.28

Found: C, 76.72; H, 5.79; N, 5.17

F. 2-(p-Bromophenyl)-4-(p-Methylphenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 30mls of absolute ethanol and 2.9g (0.125 atom) of sodium. When all the sodium had reacted, a mixture of 12.25g (0.0625 mole) of p-bromophenylacetonitrile and 13.72g (0.077 mole) of ethyl p-methoxyphenylacetate was added dropwise over 45 minutes. After addition was complete the solution was refluxed three hours, poured onto 150g of ice, and extracted with three 50ml portions of ether. The ether was washed with 25mls of ten percent sodium bicarbonate, the aqueous phases combined, and the ether discarded. The aqueous solution was acidified with 30mls of ten percent hydrochloric acid to pH of approximately 3, extracted with four 50ml portions of ether, and the ether combined. The ethereal solution was then washed with 25mls of water, four 25ml portions of ten percent sodium bicarbonate, and finally 25mls of water. The ether was dried with anhydrous magnesium sulfate, filtered, and stripped on

a rotary evaporator to yield 17.1g (0.052 mole, 83.3%) of an off-white solid. This was recrystallized from carbon tetrachloride (15mls per 1g of compound) to yield 16.25g (0.049 mole, 79.2%) of product in the form of white crystals, melting point 117.0-118.2°C.

Analysis: M.W. (Mass Spec.) Calcd: 328.2

Found: 328

Calcd. for $C_{17}H_{14}ONBr$: C, 62.21; H, 4.29; N, 4.27;
Br, 24.34

Found: C, 62.13; H, 4.33; N, 4.15
Br, 24.16

G. 2-(p-Methylphenyl)-4-(p-Bromophenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 30mls of absolute ethanol and 2.9g (0.125 atom) of sodium. When all the sodium had reacted, a mixture of 8.2g (0.0625 mole) of p-methylphenylacetonitrile and 18.75g (0.077 mole) of ethyl p-bromophenylacetate was added dropwise over one hour. The solution was then refluxed for four hours, poured onto 150g of ice, and extracted with three 50ml portions of ether. The ether was washed with 50mls of ten percent sodium carbonate, the ether discarded, and the aqueous phases combined. The aqueous solution was acidified with 80mls of ten percent hydrochloric acid to pH of approximately three, extracted with four 100ml portions of ether, and the ether extracts combined. The ethereal

solution was washed with 25mls of water, four 25ml portions of sodium bicarbonate, and finally 25mls of water. Next, it was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield an oil which was dissolved in 30mls of hot carbon tetrachloride. After cooling, this produced 11.0g (0.0335 mole, 53.6%) of white-yellow crystals, melting point 72.0-74.5°C. The crude product was recrystallized by dissolution in hot methanol followed by addition of water to the point of crystallization, giving a final yield of 10.5g (0.0304 mole, 48.7%) of pure product, mpt. 87.0-89.5°C.

Analysis: M.W. (Mass Spec.) Calcd: 328.2

Found: 328

Calcd. for $C_{17}H_{14}ONBr$: C, 62.21; H, 4.29; N, 4.27;

Br, 24.34

Found: C, 62.21; H, 4.38; N, 4.21

Br, 22.99

H. 2-(p-Chlorophenyl)-4-(p-Methoxyphenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 30mls of absolute ethanol and 2.9g (0.125 atom) of sodium. When all the sodium had reacted, a mixture of 9.9g (0.0625 mole) of p-chlorophenylacetonitrile and 14.94 (0.077 mole) of ethyl p-methoxyphenylacetate was added dropwise over one hour. When addition was complete, the solution was refluxed for three hours, poured onto 150g of ice, and

extracted with three 50ml portions of ether. The ether was washed with 50mls of ten percent sodium bicarbonate, the ether discarded, and the aqueous phases combined. The aqueous solution was acidified with 25mls of 18 percent hydrochloric acid to pH of approximately three, extracted with four 50ml portions of ether, and the ether combined. The solution was washed with 25mls of water, four 25ml portions of ten percent sodium bicarbonate, and finally 25mls of water. The ethereal solution was then dried with anhydrous magnesium sulfate, filtered, and stripped to yield 10.27g (0.034 mole, 55%) of an off-white solid which was crystallized from carbon tetrachloride (10mls per 1.5g of compound) to yield 8.8g (0.0294 mole, 47%) of a pale yellow powder, melting point 92.5-93.5°C. [lit. 93.0-94.0°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 299.85

Found: 300

Calcd. for $C_{17}H_{14}O_2NCl$: C, 68.09; H, 4.70; N, 4.70;

Cl, 11.82

Found: C, 68.10; H, 4.69; N, 4.67

Cl, 11.58

I. 2-(p-Methoxyphenyl)-4-(p-Chlorophenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 30mls of absolute ethanol and 2.9g (0.125 atom) of sodium. When all the sodium had reacted, a mixture of 9.25g (0.0625 mole) of p-methoxyphenylacetonitrile and 15.25g (0.077 mole) of ethyl p-chlorophenylacetate was

added slowly through a dropping funnel. After addition was complete, the reaction mixture was refluxed for three hours, poured onto 150g of ice, and extracted with three 50ml portions of ether. The ether was washed with 50mls of ten percent sodium carbonate, the ether discarded, and the aqueous solutions combined. The aqueous phase was acidified with 30mls of 18 percent hydrochloric acid, extracted with four 50ml portions of ether, and the ether combined. The solution was washed with 25mls of water, four 25ml portions of ten percent sodium bicarbonate, and finally 25mls of water. The ethereal solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 13.1g (0.044 mole, 70%) of an off-white solid. This was recrystallized from carbon-tetrachloride (10mls per 1.5g of compound) to yield 11.75g (0.039 mole, 62.3%) of white powder, melting point 69.5-72.0°C. [lit. 74.0-76.0°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 299.85

Found: 300

Calcd. for $C_{17}H_{14}O_2NCl$: C, 68.09; H, 4.70; N, 4.70;

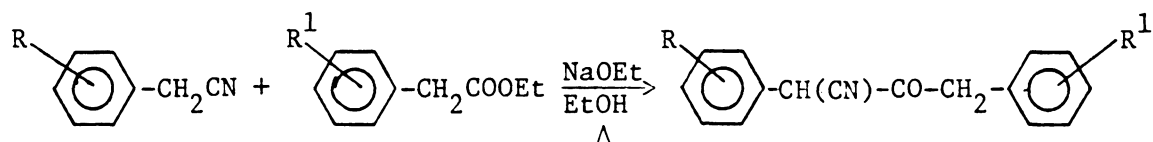
Cl, 11.82

Found: C, 68.17; H, 4.70; N, 4.72

Cl, 11.75

TABLE 5

Preparation of Diphenylacetoacetonitriles



Phenylacetonitrile (R=)	Ester (R ¹ =)	Diphenylaceto- acetonitrile (R=) (R ¹ =)		Yield, %	Mpt., °C
p-Cl	H	p-Cl	H	45.7	127.5-128.5 lit: 131.0-131.2 ⁵⁹
p-Br	H	p-Br	H	64.4	124.0-125.2 lit: 86-87 ⁶⁸
p-Me	H	p-Me	H	65.0	111.0-112.5 lit: 110.5-112.5 ⁶³
p-MeO	H	p-MeO	H	53.0	79.0-81.5 lit: 79.0-80.0 ¹³
m-MeO	H	m-MeO	H	70.0	88.0-90.5
p-Br	p-Me	p-Br	p-Me	79.2	117.0-118.2
p-Me	p-Br	p-Me	p-Br	50.0	87.0-89.5
p-Cl	p-MeO	p-Cl	p-MeO	47.0	92.5-93.5 lit: 93.0-94.0 ⁶³
p-MeO	p-Cl	p-MeO	p-Cl	62.3	69.5-72.0 lit: 74.0-76.0 ⁶³

Preparation of Substituted Diphenyl Propanones

The results of these reactions are summarized in Table 6.

A. 1-(p-Bromophenyl)-3-Phenylpropanone

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 24.4g (0.0776 mole) of 2-(p-bromophenyl)-4-phenylacetoacetonitrile and 150mls of 60 percent (w/w) sulfuric acid. The solution was maintained at 110-120°C until the nitrile absorption in the infrared had disappeared (40-44 hrs.). The orange-red reaction mixture was then poured onto 150g of ice, and extracted with three 150ml portions of ether. The ether was combined, transferred to an Erlenmyer flask, and 150mls of saturated sodium bicarbonate solution was added and stirred overnight. The following morning, the phases were separated, and the aqueous phase extracted with two 50ml portions of ether. The ether solutions were combined with the organic phase, and extracted with one 100ml portion of ten percent sodium hydroxide, two 100ml portions of sodium carbonate, and finally two 50ml portions of water. The ether solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a gold-brown oil. The oil was transferred to a 50ml, single-necked, round-bottom flask surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. This apparatus was connected to a vacuum pump and the product distilled under vacuum (b.p. 185-186°C @ 2.0mm Hg) to yield 17.45g (0.0604 mole, 77.8%) of product in the form

of a yellow liquid which solidified upon cooling.

Analysis: M.W. (Mass Spec.) Calcd: 289.1

Found: 289

B. 1-(p-Chlorophenyl)-3-Phenylpropanone

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 13.8g (0.051 mole) of 2-(p-Chlorophenyl)-4-phenylacetoacetonitrile and 100mls of 60 percent (W/W) sulfuric acid. Heat was applied and the temperature maintained at approximately 125°C until the nitrile absorption in the infrared had disappeared (40-44 hrs.). The fuchsia reaction mixture was poured onto 100g of ice, extracted with three 80ml portions of ether, the ether combined, and transferred to an Erlenmyer flask. Next, 100mls of a saturated sodium bicarbonate solution was added and the mixture stirred overnight. The next morning the phases were separated, the aqueous solution extracted with two 50ml portions of ether, and the ether solutions combined with the organic phase. The ethereal solution was washed with one 75ml portion of ten percent sodium carbonate, and two 50ml portions of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a red-brown oil. The oil was transferred to a 50ml, single-necked, round-bottom flask surmounted by a

Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and water-cooled condenser. The apparatus was connected to a vacuum pump and the product distilled under vacuum (b.p. 155°C @ 0.5mm Hg) to yield 7.9 (0.0322 mole, 63.5%) of a pale yellow liquid. [lit. b.p. 149°C @ 0.4mm Hg]⁵⁹

Analysis: M.W. (Mass Spec.) Calcd: 244.72

Found: 244

C. 1-(p-Methylphenyl)-3-Phenylpropanone

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 17.9g (0.072 mole) of 2-methylphenyl-4-phenylacetoacetonitrile and 130mls of 60 percent (W/W) sulfuric acid. The temperature was maintained at approximately 120°C until the nitrile absorption in the infrared had disappeared (24 hrs.). The reaction mixture was poured onto 120g of ice and extracted with three 100ml portions of ether. The ether was combined, transferred to an Erlenmyer flask, 100mls of saturated sodium bicarbonate solution added, and the mixture stirred overnight. The next morning the phases were separated, the aqueous solution extracted with two 50ml portions of ether, and the ether solutions combined with the organic phase. The ethereal solution was washed with one 75ml portions of ten percent sodium hydroxide, two 75ml portions of ten percent sodium carbonate, and two 50ml portions of water. The organic

solution was dried with anhydrous magnesium sulfate, filtered, and stripped to yield a red-brown oil. The oil was transferred to a 50ml, single-necked, round-bottom flask surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and condenser. The apparatus was connected to a vacuum pump and the product distilled under vacuum (b.p. 152-154 @ 1.2mm Hg; lit b.p. 143°C @ 0.4mm Hg)⁶⁰ to yield 12.9g (0.05744 mole, 80.0%) of product as a yellow liquid.

Analysis: M.W. (Mass Spec.) Calcd: 224.3

Found: 224

D. 1-(p-Methoxyphenyl)-3-Phenylpropanone

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 12.75g (0.0481 mole) of 2-(p-methoxyphenyl)-4-phenylacetoacetonitrile and 140mls of a 1:1 (v/v) solution of hydrochloric acid/glacialacetic acid. The solution was maintained at 110-115°C until the nitrile absorption in the infrared had disappeared (approximately 24 hrs.). The pink solution was then poured onto 100g of ice and extracted with three 80ml portions, the ether combined, and transferred to an Erlenmyer flask. To this was added 100mls of saturated sodium bicarbonate solution and the mixture stirred overnight. The following morning, the phases were separated, and the aqueous phase extracted with two

50ml portions of ether. The ether solutions were combined with the organic phase, and extracted with 75mls of ten percent sodium hydroxide, two 75ml portions of ten percent sodium carbonate, and finally two 50ml portions of water. The ether solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a gold-brown oil. The oil was transferred to a 50ml, single-necked, round-bottom flask surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and condenser. This apparatus was connected to a vacuum pump and the product distilled under vacuum (b.p. 182-184°C @ 1.8mm Hg; lit. b.p. 152-154°C @ 0.4mm Hg)⁶⁰ to yield 8.8g (0.0366 mole, 76.2%) of a clear liquid.

Analysis: M.W. (Mass Spec.) Calcd: 240.3

Found: 240

E. 1-(m-Methoxyphenyl)-3-Phenylpropanone

I. Via Hydrolysis and Decarboxylation of 2-(m-Methoxyphenyl)-4-(Phenyl)acetoacetonitrile

Into a 250ml, single-necked, round-bottom flask was placed 10.0g (0.0376 mole) of 2-(m-methoxyphenyl)-4-(phenyl)acetoacetonitrile and 200mls of a 1:1 (v/v) solution of hydrochloric acid/glacial acetic acid. The yellow solution was maintained at 110-115°C until the nitrile absorption in the infrared had disappeared (approximately 24

hrs.). The reaction mixture was then poured onto 100g of ice and extracted with three 100ml portions of ether, the ether portions were combined, then transferred to an Erlenmyer flask. To this was added 100mls of saturated sodium carbonate solution and the mixture stirred overnight. The following morning, the phases were separated, and the aqueous phase extracted with 50mls of ether. The ether solutions were combined, and extracted with 50mls of ten percent sodium hydroxide, two 25ml portions of ten percent sodium carbonate, and two 25ml portions of water. The ether solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator. The resulting oil was transferred to a 50ml, single-necked, round-bottom flask surmounted by a Claisen adapter, fractionating column (15cm, crimped, with evacuated jacket), and condenser. This apparatus was connected to a vacuum pump and the product distilled under vacuum (b.p. 148-150°C @ 0.15mm Hg; lit.mpt. 150 °C @ 0.6mm Hg)⁶⁰ to yield 4.9g (0.0204 mole, 54.3%) of a pale yellow liquid.

Analysis: M.W. (Mass Spec.) Calcd: 240.3

Found: 240

F. 1-(p-Bromophenyl)-3-(p-Methylphenyl)propanone

I. Via Hydrolysis and Decarboxylation of 2-(p-Methylphenyl)-4-(p-Bromophenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 6.6g (0.0201

mole) of 2-(p-methylphenyl)-4-(p-bromophenyl)acetoacetonitrile and 40mls of 60 percent (w/w) sulfuric acid. The reaction mixture was maintained between 115-125°C until the nitrile absorption in the infrared had disappeared (approximately 24 hrs.). The reaction mixture was then poured onto 100g of ice, extracted with three 50ml portions of ether, and the ether portions combined. The ether was mixed with 50mls of saturated sodium bicarbonate and stirred overnight. The following morning, the phases were separated, the aqueous phase extracted with 50mls of ether, and the ether combined with the organic phase. The organic solution was then washed with 50mls of ten percent sodium hydroxide, two 25ml portions of ten percent sodium carbonate, and two 25ml portions of water. Next, it was dried with anhydrous magnesium sulfate, filtered, and stripped to yield an oil which crystallized upon cooling. This was dissolved in a minimum amount of boiling petroleum ether (b.p. 30-60°C), filtered, and allowed to stand overnight. This afforded 3.08g (0.0107 mole, 53.2%) of pale orange rods and prisms, mpt. 74.0-76.0°C. The filtrate on standing produced an additional 0.7g (0.0023 mole, 6.8%) of pale orange prisms, mpt. 74.0-76.0°C for a combined yield of 62.0%.

Analysis: M.W. (Mass Spec.) Calcd: 303.2

Found: 303

Calcd. for $C_{16}H_{15}OBr$: C, 63.38; H, 4.98; Br, 26.35

Found: C, 62.95; H, 4.95; Br, 27.18

II. Via Hydrolysis and Decarboxylation of 2-(p-Bromophenyl)-4-(p-Methylphenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask was placed 15.2g (0.0463 mole) of 2-(p-bromophenyl)-4-(p-methylphenyl)acetoacetonitrile and 76mls of 60 percent (w/w) sulfuric acid. The flask was equipped with a magnetic stirring bar and reflux condenser. The reaction mixture was maintained at approximately 125°C until an infrared spectrum of an aliquot showed no nitrile peak (40-44 hrs.). The red reaction mixture was then poured onto 100g of ice, extracted with three 75ml portions of ether, the ether layers were combined with 100mls of saturated sodium bicarbonate solution and stirred overnight. The following morning, the phases were separated, and the aqueous phase extracted with 50mls of ether. The ether solutions were combined, then washed with 50mls of ten percent sodium hydroxide, 50mls of ten percent sodium carbonate, and three 50ml portions of water. The ether solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 11.2g (0.0389 mole) of an orange oil which crystallized upon cooling. This was dissolved in 250mls of boiling petroleum ether, filtered, and allowed to stand overnight. This afforded 4.37g (0.015 mole, 32.7%) of orange-yellow rod-like crystals and crystal clusters. The melting point of the first crop was 73.5-74.9°C. Concentration of the filtrate and cooling produced another 2.47g (0.0086 mole, 18.5%) of product, mpt. 74.0-76.0°C. The crops were combined for a total yield of 6.84g (0.0237 mole, 51.2%).

Analysis: M.W. (Mass Spec.) Calcd: 303.2

Found: 303

Calcd. for $C_{16}H_{15}OBr$: C, 66.70; H, 5.24; Br, 27.73

Found: C, 62.95; H, 4.92; Br, 26.96

G. 1-(p-Chlorophenyl)-3-(p-Methoxyphenyl)propanone

I. Via Hydrolysis and Decarboxylation of 2-(p-Methoxyphenyl)-4-p-Chlorophenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask was placed 6.0g (0.020 mole) of 2-(p-methoxyphenyl)-4-(p-chlorophenyl)acetoacetonitrile and 60mls of a 1:1 (v/v) mixture of hydrochloric acid/glacial acetic acid. The reaction mixture was maintained at 110-115°C until the nitrile absorption in the infrared had disappeared (approximately 24 hrs.). The reaction mixture was poured onto 100g of ice, extracted with three 50ml portions of ether, and the ether combined. To the ether was added 100mls of saturated sodium carbonate and the mixture stirred overnight. The following morning, the phases were separated, the aqueous phase extracted with 50mls of ether and the ether combined. To the ether was added 100mls of saturated sodium carbonate and the mixture stirred overnight. The following morning, the phases were separated, the aqueous phase extracted with 50mls of ether and the ether combined with the organic phase. The organic solution was then washed with 50mls of ten percent sodium hydroxide, two 25ml portions of ten percent sodium carbonate, and two 25ml portions of water. Next,

it was dried with anhydrous magnesium sulfate, filtered, and stripped to yield an oil which crystallized upon cooling. Recrystallization from petroleum ether (b.p. 30-60°C) produced 3.3g (0.012 mole, 60%) of pale yellow-tan crystals, mpt. 54.0-54.5°C. [lit. 55-55.5°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 274.75

Found: 274

Calcd. for $C_{16}H_{15}OCl$: C, 69.94; H, 5.50; Cl, 12.90

Found: C, 70.00; H, 5.52

II. Via Hydrolysis and Decarboxylation of 2-(p-Chlorophenyl)-4-(p-Methoxyphenyl)acetoacetonitrile

Into a 100ml, three-necked, round-bottom flask was placed 6.0g (0.02 mole) of 2-(p-chlorophenyl)-4-(p-methoxyphenyl)acetoacetonitrile and 60mls of a 1:1 (v/v) mixture of hydrochloric acid/glacial acetic acid. The reaction mixture was maintained at 110-115°C until the nitrile absorption in the infrared had disappeared (20-24 hrs.). The reaction mixture was poured onto 100g of ice, extracted with three 50ml portions of ether, and the ether portions combined. To the ether was added 100mls of saturated sodium carbonate and the mixture stirred overnight. The following morning, the phases were separated, the aqueous phase extracted with 50mls of ether, and the ether combined with the organic phase. The organic solution was then washed with 50mls of ten percent sodium hydroxide, two 25ml portions of ten percent sodium carbonate, and two 25ml portions of water. Next, it was dried with anhydrous magnesium sulfate, filtered, and stripped to yield

1.20g (0.0044 mole, 22.0%) of a brown oil which was distilled under vacuum to yield 1.04g (0.0038 mole, 19.0%) of a yellow liquid which solidified upon cooling. [b.p. 197-199°C @ 1.3mm Hg]

Analysis: M.W. (Mass Spec.) Calcd: 274.75

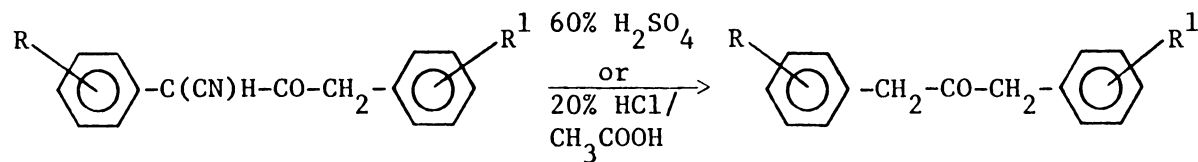
Found: 274

Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.94; H, 5.50; Cl, 12.90

Found: C, 70.00; H, 5.52

TABLE 6

Preparation of Substituted Diphenyl Propanones



Diphenylacetoacetonitrile (R=) (R ¹ =)	Dibenzyl Ketone (R=) (R ¹ =)	Yield (%)	Mpt. (°C)	B.P. (°C)
p-Br H	p-Br H	77.8		185-186 @ 2.0mm Hg
p-Cl H	p-Cl H	63.5		155 @ 0.5mm Hg lit. 149 @ 0.4mm Hg ⁵⁹
p-MeO H	p-MeO H	76.2		182-184 @ 1.8mm Hg lit. 152-154 @ 0.4mm Hg ⁶⁰
p-Me H	p-Me H	80.0		152-154 @ 1.2mm Hg lit. 143 @ 0.4mm Hg ⁶⁰
m-MeO H	m-MeO H	54.3		148-150 @ 0.15mm Hg lit. 150 @ 0.6mm Hg ⁶⁰

TABLE 6 (Cont'd)

Diphenylacetoacetonitrile (R=) (R ¹ =)		Dibenzyl Ketone (R=) (R ¹ =)		Yield (%)	Mpt. (°C)	B.P. (°C)
p-Me	p-Br	p-Me	p-Br	62.0	74.0-76.0	
p-Br	p-Me	p-Me	p-Br	51.3	74.0-76.0	
p-MeO	p-Cl	p-MeO	p-Cl	60.0	54.0-54.5 lit. 55-55.5 ⁶³	
p-Cl	p-MeO	p-MeO	p-Cl	19.0		197-199 @ 1.3mm Hg

Preparation of Tetracyclones

The results of these reactions are summarized in Table 7.

A. 2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-one

Into a one liter, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was placed 42.0g (0.2 mole) of benzil, 42.0g (0.2 mole) of 1,3-diphenyl-2-propanone, and 300mls of 95 percent ethanol. The solution was brought to reflux, and 6.0g (0.107 mole) of solid potassium hydroxide dissolved in 30mls of 95 percent ethanol was added slowly with stirring. Shortly after addition of the potassium hydroxide, purple-black tetracyclone began to precipitate. The reaction mixture was refluxed for 20 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum desiccator. This produced 74.9g (0.195 mole, 97.5%) of black crystals of tetracyclone, mpt. 218-220°C.

[lit. mpt. 218.5-220.0°C]⁶¹

Analysis: M.W. (Mass Spec.) Calcd: 384.5

Found: 384

Calcd. for C₂₉H₂₀O: C, 90.59; H, 5.24

Found: C, 90.58; H, 5.44

B. 2-(p-Bromophenyl)-3,4,5-Triphenyl-2,4-Cyclopentadien-1-one

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 14.5g (0.05 mole) of 1-(p-bromophenyl)-3-phenyl-2-propanone, 10.5g

(0.05 mole) of benzil, and 75mls of 95 percent ethanol. The solution was brought to reflux, and 1.5g (0.027 mole) of solid potassium hydroxide dissolved in 7.5mls of 95 percent ethanol was added slowly with stirring. Shortly after addition of the potassium hydroxide, a voluminous black precipitate was formed. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum dessicator to yield 20.7g (0.0446 mole, 89.4%) of black crystals, mpt. 198-199°C. [lit. 200.4-200.8°C]⁶²

Analysis: M.W. (Mass Spec.) Calcd: 463.4

Found: 463

C. 2-(p-Chlorophenyl)-3,4,5-Triphenyl-2,4-Cyclopentadien-1-one

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was placed 6.12g (0.025 mole) of 1-(p-chlorophenyl)-3-phenyl-2-propanone, 5.25g (0.025 mole) of benzil, and 37.5mls of 95% ethanol. The solution was brought to reflux, and 0.75g (0.0135 mole) of solid potassium hydroxide a dark brown solid precipitated. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 5ml portions of cold 95% ethanol. The product was dried in a vacuum dessicator to yield 9.22g (0.022 mole)

of dark brown crystals, mpt. 187-188°C. [lit. mpt. 188.3-188.8]⁶²

Analysis: M.W. (Mass Spec.) Calcd: 418.9

Found: 419

D. 2-(p-Methylphenyl)-3,4,5-Triphenyl-2,4-Cyclopentadien-1-one

Into a 250ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 11.22g (0.05 mole) of benzil, and 75mls of 95 percent ethanol. The solution was brought to reflux, and 1.5g (0.027 mole) of solid potassium hydroxide dissolved in 7.5mls of 95 percent ethanol was added slowly with stirring. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum dessicator to yield 19.45g (0.0488 mole, 97.6%) of black crystals, mpt. 188-188.5°C. [lit. mpt. 190.7-191.0°C,⁶² 188-188.5°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 398.5

Found: 399

E. 2-(p-Methoxyphenyl)-3,4,5-Triphenyl-2,4-Cyclopentadien-1-one

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 7.21g (0.03 mole) of 1-(p-methoxyphenyl)-3-phenyl-2-propanone, 6.3g

(0.03 mole) of benzil, and 45mls of 95 percent ethanol. The solution was brought to reflux, and 0.90g (0.016 mole) of solid potassium hydroxide dissolved in 4.5mls of 95 percent ethanol was added slowly with stirring. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum dessicator to yield 11.02g (0.0266 mole, 88.6%) of purple crystals, mpt. 186.5-188°C. [lit. mpt. 190-190.5°C,⁶² 188-189°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 414.5

Found: 415

F. 2-(m-Methoxyphenyl)-3,4,5-Triphenyl-2,4-Cyclopentadien-1-one

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 3.42g (0.0145 mole) of 1-(m-methoxyphenyl)-3-phenyl-2-propanone, 2.85g (0.0145 mole) of benzil, and 22mls of 95 percent ethanol. The solution was brought to reflux, and 0.435g (0.0077 mole) of solid potassium hydroxide dissolved in 2.2mls of 95 percent ethanol was added slowly with stirring. The reaction mixture was refluxed for one hour, then stirred overnight at room temperature. The mixture was cooled to 0°C in an ice bath, and the product filtered and washed with three 5ml portions of cold 95 percent ethanol. The product was a brittle crystalline solid which was dried in a vacuum dessicator to yield 3.41g

(0.0082 mole, 56.7%) of black crystals, mpt. 209-211°C.

[lit. mpt. 210-211°C]⁶⁰

Analysis: M.W. (Mass Spec.) Calcd: 414.5

Found: 415

G. 2-(p-Bromophenyl)-5-(p-Methylphenyl)-3,4-Diphenyl-2,4-Cyclopentadien-1-one

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 7.58g (0.025 mole) of 1-(p-bromophenyl)-3-(p-methylphenyl)-2-propanone, 5.25g (0.025 mole) of benzil, and 38mls of 95 percent ethanol. The solution was brought to reflux, and 0.75g (0.0135 mole) of solid potassium hydroxide dissolved in 3.8mls of 95 percent ethanol was added slowly with stirring. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum dessicator to yield 11.91g (0.0249 mole, 99.7%) of black crystals, mpt. 219.0-221.0°C.

Analysis: M.W. (Mass Spec.) Calcd: 477.4

Found: 477

Calcd. for C₃₀H₂₁OBr: C, 75.47; H, 4.43; Br, 16.74

Found: C, 75.52; H, 4.61; Br, 16.82

H. 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-3,4-Diphenyl-2,4-Cyclopentadien-1-one

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and dropping funnel was added 6.86g (0.025 mole) of 1-(p-chlorophenyl)-3-(p-methoxyphenyl)-2-propanone, 5.25g (0.025 mole) of benzil, and 38mls of 95 percent ethanol. The solution was brought to reflux, and 0.75g (0.0135 mole) of solid potassium hydroxide dissolved in 3.8mls of 95 percent ethanol was added slowly with stirring. The reaction mixture was refluxed for 40 minutes, cooled to 0°C in an ice bath, and the product filtered and washed with three 10ml portions of cold 95 percent ethanol. The product was dried in a vacuum dessicator to yield 1.01g (0.0225 mole, 90%) of black crystals, mpt. 206.5-207.5°C. [lit. 207.5-208.5°C]⁶³

Analysis: M.W. (Mass Spec.) Calcd: 448.9

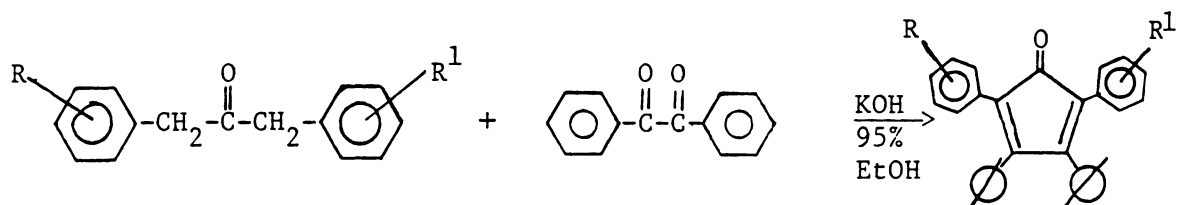
Found: 449

Calcd. for $C_{30}H_{21}O_2Cl$: C, 80.26; H, 4.71; Cl, 7.89

Found: C, 80.03; H, 4.76; Cl, 7.84

TABLE 7

Preparation of Tetracyclones



Dibenzyl Ketone
and
Tetracyclone
(R=) (R¹=)

Yield
(%)

Mpt.
(°C)

H	H	97.5	218-220 lit. 218.5-220.0 ⁶¹
p-Br	H	89.4	198-199 lit. 200.4-200.8 ⁶²
p-Cl	H	88.0	187-188 lit. 188.3-188.8 ⁶²
p-Me	H	97.6	188-188.5 lit. 190.7-191.0 ⁶²
p-MeO	H	88.6	186.5-188 lit. 190-190.5 ⁶²
m-MeO	H	56.7	209-211 lit. 210-211 ⁶⁰
p-Me	p-Br	99.7	219-221
p-MeO	p-Cl	90.0	206.5-207.5 lit. 207.5-208.5 ⁶³

Preparation of 1-(p- or m-Substituted Phenyl)-
2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ols

The results of these reactions are summarized in Table 8.

A. 1,2,3,4,5-Pentaphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 250ml, three-necked, round-bottom flask previously baked and flushed with nitrogen was placed 1.96g (0.08 atom) of magnesium and a few crystals of iodine. The flask was heated until purple iodine vapor filled the flask. At this point a magnetic stirring bar was added and the flask equipped with a reflux condenser and dropping funnel. Bromobenzene (12.55g, 0.08 mole) dissolved in 50mls of anhydrous ether was added dropwise to the activated magnesium under nitrogen gas. After the reaction was complete (approximately 45 minutes), 7.68g (0.08 mole) of tetracyclone in 100ml anhydrous benzene was allowed to drip slowly through the dropping funnel into the refluxing Grignard solution. After addition was complete the solution was refluxed for an additional two hours, cooled in an ice bath, and hydrolyzed with 100ml of ten percent ammonium chloride solution. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 200mls of water and dried over anhydrous magnesium sulfate. The solution was filtered and stripped to a brown oil which was dissolved in approximately 40mls of benzene, and heated to boiling. At this point

100mls of petroleum ether (b.p. 30-60°C) was added and the mixture allowed to stand overnight. This produced 7.9g (0.017 mole, 85%) of a pale yellow powder, melting point 174-176°C. This was recrystallized from 40mls of benzene and 100mls of petroleum ether to yield 7.1g (0.015 mole, 76.9%) of pale yellow powder, mpt. 175-176°C (lit. 175-176°C (lit. 175-176⁶⁴; 176-177°C⁶⁵). As with the other penta-phenylcyclopentadienols, the compound is highly fluorescent.

Analysis: M.W. (Mass Spec.) Calcd: 462.59

Found: 462

Calcd. for $C_{35}H_{26}O$: C, 90.88; H, 5.67

Found: C, 90.71; H, 5.70

II. Via Organolithium Reagent

Into a previously baked and nitrogen flushed 50ml, three-necked, round bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 15mls of anhydrous ether. Lithium wire (0.23g, 0.033 atom) was cut into approximately 30 pieces allowing the pieces to fall directly into the flask as they were cut. At this point a few drops of bromobenzene were added to initiate the reaction. Within 5-8 minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 2.35g, 0.015 mole) in 10mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional hour.

Into a second 100ml, three-necked, round-bottom flask seated in an ice bath was placed 3.84g (0.01 mole) of tetracyclone in 60mls of anhydrous benzene. The flask was equipped with a magnetic stirring bar, a dropping funnel was attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel (plugged with glass wool) and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the final few drops of phenyllithium were added, at which time the solution turned bright yellowish-orange. Stirring was continued for one hour after which the solution was hydrolyzed with 100mls of ten percent ammonium chloride solution. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 100mls of water and dried over anhydrous magnesium sulfate. The solution was filtered, and stripped to a yellow-gold oil which was crystallized from 20mls of benzene and 100mls of petroleum ether. Within ten minutes of dissolution, large crystal clusters began growing in the solution. The following day the solution was filtered to yield 4.05g (0.0087 mole, 87.5%), melting point 175.5-177.0°C (lit. 175-176°C⁶⁴; 176-177°C⁶⁵) of yellow fluorescent crystals.

Analysis: M.W. (Mass Spec.) Calcd: 462.59

Found: 462 .

Calcd. for $C_{35}H_{26}O$: C, 90.88; H, 5.67

Found: C, 90.71; H, 5.70

B. 1-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 250ml, three-necked, round-bottom flask was placed 2.0g (0.081 atom) of magnesium turnings and a few crystals of iodine. The flask was heated until purple vapors of iodine filled the flask. A reflux condenser with drying tube was fitted to the flask and a magnetic stirring bar added. At this point, 13.68g (0.08 mole) of p-bromotoluene dissolved in approximately 50mls of anhydrous ether was added slowly through a dropping funnel. The apparatus was maintained under a nitrogen atmosphere. Gentle heating was applied to maintain refluxing. Refluxing was continued for 45 minutes after addition was complete.

Next, a solution of 7.8g (0.02 mole) of tetracyclone in 150mls of anhydrous benzene was allowed to drip slowly into the Grignard reagent through the dropping funnel. The addition was carried out over approximately 30 minutes, followed by two hours of refluxing.

The mixture was then cooled in an ice bath, hydrolyzed with 200mls of ten percent ammonium chloride solution, and the organic phase separated from the aqueous phase. The aqueous layer was extracted twice with 50mls of benzene, and the benzene layers were combined. This organic solution was then washed with two 50ml portions of water and dried over anhydrous magnesium sulfate. This solution was filtered

and stripped on a rotary evaporator to yield a brown oil which was crystallized from 40mls of carbon tetrachloride. This produced 6.8g (0.014 mole, 71.2%) of yellow fluorescent powder, melting point 186.5-187.5°C (open), melting point 193.0-194.5°C (vacuum sealed capillary). [lit. 188-189°C, 199-200°C,⁶⁶ 192-192.5°C⁶⁷]

Analysis: M.W. (Mass Spec.) Calcd: 476.62

Found: 476

Calcd. for $C_{36}H_{28}O$: C, 90.72; H, 5.92

Found: C, 90.78; H, 6.00

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask was placed 15mls of anhydrous ether. The flask was equipped with a magnetic stirring bar, nitrogen inlet, and reflux condenser topped by a drying tube. Lithium wire (0.055 atom) was cut into approximately 40 pieces, allowing the pieces to fall directly into the flask as they were cut. At this point, a few drops of p-bromotoluene were added to initiate reaction. After 5-8 minutes, lithium bromide began precipitating indicating commencement of reaction. At this point, the remaining halide (4.28g, 0.025 mole total) in 15mls anhydrous ether was added dropwise over 30 minutes through the dropping funnel. Reflux was maintained via heating mantle. When all the halide was added, reflux was continued for another 45 minutes. The solution was cloudy grey. A 100ml, three-necked, round-bottom flask was prepared containing 3.84g (0.01 mole) of tetracyclone in 60mls of anhydrous benzene and

and placed in an ice bath. The flask was equipped with a magnetic stirring bar, nitrogen inlet, drying tube, and dropping funnel. The organolithium reagent was transferred to the dropping funnel and allowed to drip slowly into the tetracyclone solution. The course of reaction was monitored by TLC as follows: An aliquot was withdrawn and hydrolyzed with water, then dried with anhydrous magnesium sulfate and filtered. A silica gel TLC plate was spotted (benzene as eluent), and checked for product ($R_f = 0.7$, fluorescent) and unreacted cyclone ($R_f = 0.75$, visibly purple). After 45 minutes the only spot was that corresponding to product. At this point, the solution was hydrolyzed with 100mls of ten percent ammonium chloride solution and the organic and aqueous layers separated. The aqueous layer was extracted with two 50ml portions of benzene, the benzene combined with the organic layer and washed with two 50ml portions of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped to yield a bright yellow oil. This was crystallized from 15mls of benzene and 100mls of petroleum ether to yield pale yellow star-like crystal clusters. Weight: (0.0092 mole, 92.7%), melting point 189.5–191.0°C (unsealed), 193.0–194.5°C (vacuum sealed capillary). [lit. 188–189, 199–200°C,⁶⁶ 192–192.5°C⁶⁷]

Analysis: M.W. (Mass Spec.) Calcd: 476.62

Found: 476

Calcd. for $C_{36}H_{29}O$: C, 90.72; H, 6.13

Found:

C. 1-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 250ml, three-necked, round-bottom flask was placed 1.22g (0.05 atom) of magnesium turnings and a few crystals of iodine. This was heated until purple vapors of iodine filled the flask. The flask was equipped with a magnetic stirring bar, nitrogen inlet, reflux condenser with drying tube, and dropping funnel. Next, 9.35g (0.05 mole) of p-bromoanisole dissolved in 50mls of anhydrous ether was added dropwise over 30 minutes. Refluxing was maintained via heating mantle for 45 minutes after addition was complete. At this point, 7.7g (0.02 mole) of tetracyclone dissolved in 100mls of anhydrous benzene was added to the dropping funnel and allowed to drip slowly into the refluxing Grignard solution. Refluxing was continued for two hours after addition was complete. The reaction mixture was then hydrolyzed with 200mls of ten percent ammonium chloride solution, the mixture separated, and the aqueous phase extracted with two 100ml portions of benzene. This extract was combined with the organic layer and washed with two 100ml portions of water. The organic phase was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to a brown oil. The oil was crystallized from 40mls of benzene and 100mls of petroleum ether to yield 7.5g (0.0152 mole, 76%) of crude product as a yellow-tan powder. This was recrystallized by dissolving in a minimum amount of n-propanol (approximately 120mls) and allowing to stand overnight. This afforded 6.70g (0.0136 mole, 68%) of 1-(p-methoxyphenyl)-2,3,4,5-tetraphenyl-2,4-

cyclopentadien-1-ol in the form of tan crystals, melting point 199.5-201.5°C. [lit. 203°C,⁶ 201-202°C,⁶⁷ 199-200°C⁶⁸]

Analysis: M.W. (Mass Spec.) Calcd: 492.62

Found: 492

Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.72

Found: C, 87.72; H, 5.67

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask was placed 15mls of anhydrous ether. The flask was equipped with a magnetic stirring bar, nitrogen inlet, reflux condenser and drying tube. Lithium wire (0.45g, 0.065 atom) was cut into approximately 40 pieces directly into the flask. A few drops of *p*-bromoanisole was added to initiate reaction, and after 8-10 minutes lithium bromide began to precipitate. At this point, the remaining halide (5.61g, 0.03 mole total) dissolved in 15mls of anhydrous ether was placed in the dropping funnel and dropwise addition carried out over 30 minutes. Reflux was maintained via heating mantle, and continued for 30 minutes after addition was completed. Another flask (100ml, three-necked, round-bottom) was prepared containing 3.84g (0.01 mole) of tetracyclone dissolved in 60mls anhydrous benzene. The flask was situated in an ice bath and fitted with a dropping funnel and drying tube. The *p*-methoxyphenyllithium was transferred to the dropping funnel and slowly added to the tetracyclone solution. After one hour no cyclone was present (as indicated by TLC) and the solution was then hydrolyzed with 100mls of ten percent

ammonium chloride solution. The aqueous phase was extracted with two 50ml portions of benzene, the organic solutions combined and washed with two 50ml portions of water. The gold organic phase was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a gummy yellow solid which was crystallized by dissolving in 15mls of benzene followed by addition of 50mls of petroleum ether. Within ten minutes yellow crystals of product began to precipitate from the cooling solution. The yield was 3.9g (0.0079 mole, 79%) of yellow crystals, melting point 199.5-201.5°C. [lit. 203°C,⁶ 201-202°C,⁶⁷ 199-200°C⁶⁸]

Analysis: M.W. (Mass Spec.) Calcd: 492.62

Found: 492

Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.72

Found: C, 87.72; H, 5.67

D. 1-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a baked and nitrogen flushed 250ml three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser with drying tube, and nitrogen inlet was placed 0.61g (0.025 atom) of magnesium turnings and a few crystals of iodine. The flask was heated until purple iodine vapors filled the flask. When it had cooled slightly, 5.9g (0.025 mole) of p-dibromobenzene dissolved in 50mls of anhydrous ether was added slowly through the dropping funnel. Refluxing was continued for 60 minutes after all the halide had been added.

Another flask (250ml, three-necked, round-bottom) equipped with magnetic stirring bar, reflux condenser with drying tube, and dropping funnel was prepared and charged with 7.7g (0.02 mole) of tetracyclone dissolved in 100mls of anhydrous benzene. This solution was brought to reflux, and the Grignard reagent transferred to the glass-wool plugged dropping funnel. The Grignard reagent was slowly added to the cyclone solution, and reflux was maintained for two hours after addition was complete. The solution was cooled in an ice bath, hydrolyzed with 200mls of ten percent ammonium chloride solution, and the mixture separated. The aqueous phase was extracted with two 100ml portions of benzene, and the organic phases were combined and washed with two 100ml portions of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow-brown oil. This was dissolved in 40mls of hot benzene, followed by addition of 100mls of petroleum ether which caused immediate precipitation of product in the form of a yellow powder, melting point 228.5-231.0°C. This was recrystallized from 50mls of benzene and 100mls of petroleum ether to yield 8.29g (0.0153 mole, 76.5%) of 1-(p-bromophenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol as a yellow powder, mpt. 234.0-236.0°C (vacuum sealed capillary). [lit. 217-219°C,⁶⁷ 234-236°C⁶⁹]

Analysis: M.W. (Mass Spec.) Calcd: 541.5

Found: 541

Calcd. for $C_{35}H_{25}OBr$: C, 77.63; H, 4.65; Br, 14.76

Found:

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser with drying tube, and nitrogen inlet was placed 15mls of anhydrous ether. Next, 0.38g (0.055 atom) of lithium wire was cut into 30-32 pieces, and allowed to drop directly into the ether as they were cut. At this point, a few drops of p-dibromobenzene were added to initiate reaction. After approximately 15 minutes the remaining halide (0.025 mole, 5.9g total) dissolved in 20mls of anhydrous ether was placed in a dropping funnel and attached to the flask. Dropwise addition was begun, and reflux was maintained for one hour after addition was complete. At this point, the lithium pieces remained unconsumed and no lithium bromide pieces had precipitated. An aliquot of the solution was removed and treated with water--no reaction occurred. As a final test, one drop of a tetracyclone/benzene solution was added to the halide solution and did not decolorize. The conclusion is that no reaction occurred between the lithium and the p-dibromobenzene, a conclusion also reached by Gilman.⁷⁰

E. 1-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser with drying tube, and nitrogen

inlet was placed 1.96g (0.08 atom) of magnesium. The magnesium was activated by heating with iodine. Next, 15.3g (0.08 mole) of p-chlorobromobenzene in 50mls of anhydrous ether was added slowly. Reflux was maintained via heating mantle for 45 minutes after addition was complete. In another 250ml, three-necked, round-bottom flask was placed 7.68g (0.02 mole) of tetracyclone in 100mls of anhydrous benzene. The flask was equipped with a reflux condenser, nitrogen inlet, and dropping funnel. The tetracyclone solution was brought to reflux and the Grignard reagent added slowly through the glass-wool plugged dropping funnel. After addition was complete, the solution was refluxed for two hours, cooled in an ice bath, and hydrolyzed with 200mls of ten percent ammonium chloride solution. The mixture was separated, the aqueous layer extracted twice with 100mls of benzene, and the benzene extract combined with the organic layer. The benzene solution was washed twice with 100mls of water, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow-brown oil. This was crystallized from 40mls of benzene and 100mls of petroleum ether to yield 8.64g (0.0173 mole, 87.0%) of a yellow powder, mpt. 219-222°C. This was recrystallized from 40mls of hot benzene followed by 100mls of petroleum ether to yield 7.95g (0.0159 mole, 79.9%) of a yellow powder, mpt. 223.0-224.5°C (vacuum sealed capillary). [lit. 211-212°C,⁶⁷ 223.0-224.5°C⁶⁹]

Analysis: M.W. (Mass Spec.) Calcd: 497.0

Found: 497

Calcd. for $C_{35}H_{25}OCl$: C, 84.58; H, 5.07; Cl, 7.13

Found: C, 84.59; H, 5.00

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask equipped with magnetic stirring bar, reflux condenser with drying tube, and nitrogen inlet was placed 15mls of anhydrous ether. Next, 0.38g (0.055 atom) of lithium wire was cut into 30-32 pieces, allowing the pieces to fall directly into the flask as they were cut. At this point, a few drops of p-bromochlorobenzene were added to initiate reaction. After approximately 15 minutes, the remaining halide (0.025 mole, 4.78g total) dissolved in 20mls of anhydrous ether was placed in a dropping funnel and attached to the flask. Dropwise addition was begun, and reflux was maintained for one hour after addition was complete. At this point, the lithium pieces remained unconsumed and no lithium bromide had precipitated. An aliquot of the reaction mixture was removed and treated with water, giving no reaction. As a final test, one drop of a tetracyclone/benzene solution was added to the halide solution which became purple (the color of tetracyclone) and did not decolorize. The conclusion is that no reaction occurred between the lithium and the p-bromochlorobenzene.

F. 1-(m-Methoxyphenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a baked and nitrogen flushed apparatus consisting of a 100ml, three-necked, round-bottom flask, condenser with drying tube, addition funnel, and stirring bar was placed 0.40g (0.016 atom) of magnesium turnings and a few crystals of iodine. Heat was applied via mantle to vaporize the iodine. Next, 15mls of anhydrous ether was added to the magnesium under nitrogen gas. A few drops of m-methoxybromobenzene were added to initiate reaction. When reaction had commenced, the remaining halide (2.34g, 0.0125 mole total) in 15mls of anhydrous ether was added dropwise over 15 minutes. The cloudy, pale yellow solution was refluxed for 45 minutes after addition was complete. At this point, 1.92g (0.005 mole) of tetracyclone in 30mls of anhydrous benzene was added to the dropping funnel (and allowed to drip slowly into the refluxing Grignard solution (approximately 15 minutes). The purple color of the cyclone solution was completely dissipated upon addition to the Grignard reagent, the resulting solution being bright yellow. An aliquot was withdrawn after 90 minutes, hydrolyzed, and given a single, fluorescent spot on a silica TLC plate (R_f of approximately 0.48, benzene eluent). The reaction mixture was cooled in an ice bath, and hydrolyzed with 50mls of ten percent ammonium chloride solution. The phases were separated, the aqueous layer extracted with two 25ml portions of benzene, and the benzene extracts combined with the organic layer. This was washed with two 50ml portions of water, dried with anhydrous magnesium sulfate, filtered, and stripped to yield

a brown oil. The oil was crystallized from 15mls benzene and 80mls of petroleum ether, which produced a pale yellow powder and red-brown supernatant. The melting point of the powder was 188.0-191.5°C. This was recrystallized from 15mls of benzene and 100mls of petroleum ether to yield 2.075g (0.042 mole, 84.3%) of pale yellow crystals, mpt. 193.5-194.5°C (vacuum sealed capillary).

Analysis: M.W. (Mass Spec.) Calcd: 492.62

Found: 493

Calcd. for $C_{36}H_{28}O_2$: C, 87.78; H, 5.73

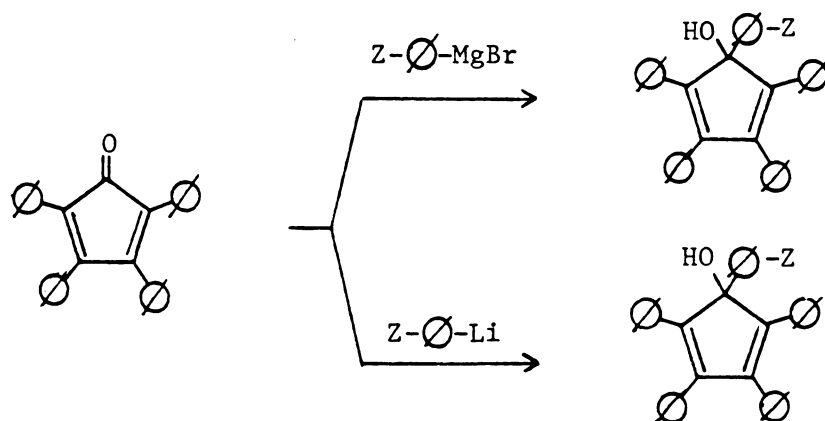
Found: C, 87.81; H, 5.82

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask equipped with reflux condenser with drying tube, magnetic stirring bar, and nitrogen inlet was placed 10mls of anhydrous ether. Lithium wire (0.19g 0.027 atom) was cut directly into the flask (approximately 30 pieces). Next, a few drops of m-bromoanisole were added to initiate reaction. After 10 minutes the remaining halide (2.34g, 0.0125 mole total) in 10mls of anhydrous ether was added dropwise through a dropping funnel over 30 minutes. The solution was refluxed for an additional 60 minutes after addition was complete. At this point, the lithium appeared unconsumed, and an aliquot was tested with water giving no reaction. A few drops of a tetracyclone/benzene solution were added and did not decolorize. The conclusion was that no reaction occurred between the lithium and the m-bromoanisole.

TABLE 8

Preparation of 1-(p- or m-Substituted Phenyl)-
2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ols



Cyclopentadienol (Z=)	Grignard Reaction		Organolithium Reaction	
	Yield (%)	Mpt. (°C)	Yield (%)	Mpt. (°C)
H	76.9	175.0-176.0 ⁶⁴ lit. 175-176 ⁶⁵ 176-177	87.5	175.5-177.0 ⁶⁴ lit. 175-176 ⁶⁵ 176-177
p-Me	71.2	186.5-187.5 193.0-194.5* ⁶⁶ lit. 188-189 ⁶⁶ 199-200 ⁶⁶	92.7	193.0-194.5* ⁶⁶ lit. 188-189 ⁶⁶ 199-200 ⁶⁶ 192-192.5 ⁶⁷
p-MeO	68.0	199.5-201.5 lit. 203 ⁶ 199-200 ⁶⁸	79.0	199.5-201.5 lit. 203 ⁶ 199-200 ⁶⁸
p-Br	76.5	234.0-236.0* ⁶⁷ lit. 217-219 ⁶⁹ 234-236	no reaction	
p-Cl	79.9	223.0-224.5* ⁶⁷ lit. 211-212 ⁶⁷ 223.0-224.5 ⁶⁹	no reaction	
m-MeO	84.3	193.5-194.5*	no reaction	

*vacuum sealed capillary

Preparation of 2- and/or 5-(p- or m-Substituted
Phenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ols

The results of these reactions are summarized in Table 9.

A. 2-(p-Bromophenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 500ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 6.5g (0.014 mole) of 2-(p-bromophenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one and 70mls of anhydrous benzene. Into a 500ml, three-necked Grignard flask attached to the cyclone flask was placed 1.37g (0.056 mole) of magnesium turnings and a few crystals of iodine. The flask was heated to activate the magnesium, and 8.78g (0.056 mole) of bromobenzene in 45mls anhydrous ether was added slowly to the magnesium under nitrogen. When reaction was complete, the Grignard reagent was added dropwise to the refluxing cyclone solution. After addition was complete, the solution was refluxed for two hours, cooled in an ice bath, and hydrolyzed with 70mls of ten percent ammonium chloride solution. The organic layer was separated from the aqueous layer, the aqueous layer was extracted with two 75ml portions of benzene, and the benzene portions combined with the organic layer. The benzene solution was washed twice with 100mls of water and dried over anhydrous magnesium sulfate. The solution was filtered and stripped to a brown oil which was dissolved in 35mls of benzene, and heated to boiling. At this point 90mls of petroleum ether (b.p. 30-60°C) was added and the

solution allowed to cool to room temperature. After three days yellow-brown star-like clusters of crystals had formed and were filtered yielding a first crop of 3.54g (0.0065 mole, 46.7%), mpt. 160.0-161.5°C. The volume of the filtrate was brought up to 200mls with petroleum ether and after one day produced an additional 0.95g (0.0175 mole, 12.5%), mpt. 160.0-161.5, for a total yield of 4.46g (0.0082 mole, 59.4%). [lit. mpt. 160.0-161.5°C]⁶⁸

Analysis: M.W. (Mass Spec.) Calcd: 541.5

Found: 541

II. Via Organolithium Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 45mls of anhydrous ether. Lithium wire (0.70g, 0.10 atom) was cut into approximately 90 pieces allowing the pieces to fall directly into the flask as they were cut. At this point a few drops (10-15 of bromobenzene were added to initiate the reaction. Within 8-10 minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 7.05g, 0.045 mole) in 45mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional 45 minutes. Into a 500ml, three-necked, round-bottom flask seated in an ice bath was placed 13.9g (0.03 mole) of 2-(p-bromophenyl)-3,4,5-

triphenyl-2,4-cyclopentadien-1-one dissolved in 180mls of anhydrous benzene. The flask was equipped with a magnetic stirring bar, a dropping funnel attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the final few drops of phenyllithium were added, at which time the solution turned orange. Stirring was continued for one hour, then the solution was hydrolyzed with 200mls of ten percent ammonium chloride solution. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 100mls of water and dried over anhydrous magnesium sulfate. The solution was filtered, stripped to a brown oil on a rotary evaporator, and crystallized from 25mls of benzene and 130mls of petroleum ether (b.p. 30-60°C). This afforded 13.4g (0.0247 mole, 82.4%) of product in the form of bright yellow crystals, mpt. 160.0-161.5°C. [lit. mpt. 160-161.5°C]⁶⁸

Analysis: M.W. (Mass Spec.) Calcd: 541.5

Found: 541

B. 2-(p-Chlorophenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 500ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 4.54g (0.0108 mole) of 2-(p-chlorophenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one and 70mls of anhydrous benzene. Into a 250ml, three-necked Grignard flask attached to the cyclone flask was placed 1.05g (0.0434 mole) of magnesium turnings that had been activated by heating in the presence of iodine. Bromobenzene (6.814g, 0.0434 mole) dissolved in 35mls of anhydrous ether was added slowly to the magnesium through a dropping funnel. Heat was applied to maintain reflux, under a slow stream of nitrogen. When reaction was complete, the Grignard reagent was added dropwise to the refluxing cyclone solution. After addition was complete, the solution was refluxed for two hours, cooled in an ice bath, and hydrolyzed with 75mls of ten percent ammonium chloride solution. The organic layer was separated, and the aqueous layer extracted twice with 75mls of benzene. The benzene extracts were combined with the organic layer, washed with two 100ml portions of water, dried with anhydrous magnesium sulfate, and filtered. The solution was stripped on a rotary evaporator to yield a brown oil. This oil was crystallized from 20mls of benzene and 50mls of petroleum ether to yield 4.34g (0.0087 mole, 81%) of a bright yellow powder, mpt. 147-151°C. This was recrystallized from benzene/petroleum ether to yield 3.91g (0.0078 mole, 72.9%) of bright yellow powder, mpt. 149-152°C.

Analysis: M.W. (Mass Spec.) Calcd: 497.0

Found: 497.0

Calcd. for $C_{35}H_{25}OCl$: C, 84.58; H, 5.07; Cl, 7.13

Found: C, 84.57; H, 5.10; Cl, 7.80

II. Via Organolithium Reagent

Into a 100ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 23mls of anhydrous ether. Lithium wire (0.35g (0.05 atom)) was cut into approximately 40 pieces allowing the pieces to fall directly into the flask as they were cut. At this point a few drops (8-10) of bromobenzene were added to initiate the reaction. Within ten minutes a grey precipitate of lithium bromide began to form, and the remaining bromobenzene (total of 3.53g, 0.0225 mole) dissolved in 23mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional 45 minutes. Into a 250ml, three-necked, round-bottom flask seated in an ice bath was placed 6.28g (0.015 mole) of 2-(p-chlorophenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one dissolved in 90mls of anhydrous benzene. The flask was equipped with a magnetic stirring bar, a dropping funnel was attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the final drops of phenyllithium were added, at which time the solution turned

brown. Stirring was continued for 1.5 hours, then the solution was hydrolyzed with 100mls of ten percent ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with two 25ml portions of benzene. The benzene extracts were combined with the organic layer, then washed twice with 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a brown oil which was crystallized from 15mls of benzene and 100mls of petroleum ether (b.p. 30-60°C) to yield 5.5g (0.01106 mole, 73.8%) of yellow crystals, mpt. 151-153°C.

Analysis: M.W. (Mass Spec.) Calcd: 497.0

Found: 497.0

Calcd. for $C_{35}H_{25}OCl$: C, 84.58; H, 5.07; Cl, 7.13

Found: C, 84.57; H, 5.10; Cl, 7.80

C. 2-(p-Methoxyphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar and reflux condenser was placed 1.1g (0.045 mole) of magnesium turnings and a few crystals of iodine. Heat was applied to vaporize the iodine and activate the magnesium. Bromobenzene (6.9g, 0.044 mole) dissolved in 50mls of anhydrous ether was added slowly to the magnesium through a dropping funnel, under nitrogen gas. After addition was complete, the solution was refluxed for 45 minutes. At this point, 4.5g (0.11 mole) of 2-(p-methoxyphenyl)-3,4,5-triphenyl-

2,4-cyclopentadien-1-one dissolved in 50mls of anhydrous benzene was placed in the dropping funnel and added slowly to the refluxing Grignard reagent. After addition was complete, the reaction mixture was refluxed for 2.5 hours, then cooled in an ice bath. The mixture was hydrolyzed with 100mls of ten percent ammonium chloride solution, the layers separated, and the aqueous layer extracted with two 75ml portions of benzene. The benzene extracts were combined with the organic layer and washed with two 100ml portions of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a brown oil. This oil was crystallized by dissolution in 25mls of hot benzene followed by addition of 100mls of petroleum ether. This procedure produced 4.60g (0.0093 mole, 84.8%) of yellow-brown crystal clusters, mpt. 160-163°C. This was recrystallized from 25mls of benzene and 100mls of petroleum ether to yield 4.25g (0.0086 mole, 78.4%) of a bright yellow powder, mpt. 163.5-164.0. [lit. mpt. 164.8-165.8°C]⁷¹

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 492

Calcd. for $C_{36}H_{28}O_2$: C, 87.78; H, 5.73

Found: C, 87.76; H, 5.74

II. Via Organolithium Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 23mls of anhydrous ether. Lithium wire, (0.35g,

0.05 atom) was cut into approximately 40 pieces, allowing the pieces to fall directly into the reaction flask. At this point, a few drops (8-10) of bromobenzene were added to initiate the reaction. Within 8-10 minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 3.53g, 0.0225 mole) in 23mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for 30 minutes then cooled in an ice bath. At this point, 6.22g (0.015 mole) of 2-(p-methoxyphenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one dissolved in 90mls of anhydrous benzene was added slowly to the organolithium reagent through a dropping funnel. After addition was complete, the solution was stirred for one hour, then hydrolyzed with 100mls of ten percent ammonium chloride. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a gold-brown oil which was crystallized from 30mls of benzene and 100mls of petroleum ether to yield 6.5g (0.0132 mole, 87.9%) of yellow-brown crystal globules, initial mpt. 158-159°C. As the temperature rose above this point, the compound resolidified and had a second melting point at 163.5-164.5°C. [lit. mpt. 164.8-165.8°C]⁷¹

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 492

Calcd. for $C_{36}H_{28}O_2$: C, 87.78; H, 5.73

Found: C, 87.76; H, 5.74

D. 2-(p-Methylphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 100ml, three-necked, round-bottom flask equipped with a magnetic stirring bar and reflux condenser was placed 1.0g (0.04 mole) of magnesium turnings and a few crystals of iodine. Heat was applied to vaporize the iodine and activate the magnesium. After the flask had cooled slightly, 6.27g (0.04 mole) of bromobenzene in 30mls of anhydrous ether was added slowly to the magnesium through a dropping funnel. When addition was complete, the solution was refluxed for 45 minutes. In another flask (250ml, three-necked, round-bottom) equipped with a magnetic stirring bar and reflux condenser was placed 4.57g (0.0115 mole) of 2-(p-methylphenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one dissolved in 60mls of anhydrous benzene. The cyclone solution was heated to reflux, and a dropping funnel was attached into which the Grignard reagent was transferred. The reagent was added slowly to the refluxing cyclone solution, and reflux was continued for two additional hours after addition was complete. Next, the reaction mixture was cooled to 0°C in an ice bath, then hydrolyzed with 50mls of ten percent ammonium chloride solution. The aqueous layer was separated, and extracted with two 50ml portions of benzene

and the benzene layers combined with the organic layer. The organic solution was washed with two 100ml portions of water, dried over anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a brown oil. The oil was crystallized from 10mls of benzene and 40mls of petroleum ether (b.p. 30-60°C) to yield a yellow-brown powder which was recrystallized to produce 4.16g (0.00874 mole, 76%) of a yellow powder, mpt. 148.2-150.5°C. [lit. mpt. 153-154°C]⁹

Analysis: M.W. (Mass Spec.) Calcd: 476.6

Found: 476

Calcd. for $C_{36}H_{28}O$: C, 90.72; H, 5.92

Found: C, 90.69; H, 5.95

II. Via Organolithium Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 45mls of anhydrous ether. Lithium wire (0.70g, 0.10 atom) was cut into approximately 90 pieces, allowing them to fall directly into the reaction flask as cut. At this point a few drops (10-12) of bromobenzene were added to initiate the reaction. Within 8-10 minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 7.06g, 0.045 mole) in 45mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional 30 minutes. Into a 500ml, three-necked, round-bottom flask seated in an ice bath, 11.95g (0.03 mole) of 2-(p-methylphenyl)-3,4,5-triphenyl-

2,4-cyclopentadien-1-one dissolved in 180mls of benzene was placed. The flask was equipped with a magnetic stirring bar, a dropping funnel attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the final few drops of phenyllithium were added, at which time the solution turned orange. Stirring was continued for one hour, then the solution was hydrolyzed with 200mls of ten percent ammonium chloride solution. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 50mls of water, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow oil. The oil was crystallized from 40mls of benzene and 120mls of petroleum ether (b.p. 30-60°C) to yield 11.62g (0.0244 mole, 81.3%) of a pale yellow powder, mpt. 149.0-151.2°C. [lit. mpt. 153-154°C]⁹

Analysis: M.W. (Mass Spec.) Calcd: 476.6

Found: 476

Calcd. for $C_{36}H_{28}O$: C, 90.72; H, 5.92

Found: C, 90.65; H, 5.98

E. 2-(m-Methoxyphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 50ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet was placed 0.24g (0.01 atom) of magnesium turnings and a few crystals of iodine. The flask was heated to activate the magnesium then allowed to cool slightly. At this point, 1.52g (0.0096 mole) of bromobenzene dissolved in 25mls of anhydrous ether was added dropwise under nitrogen to the magnesium. When addition was complete, the reaction mixture was refluxed for one hour. In another flask (100ml, three-necked, round-bottom) equipped with a magnetic stirring bar and reflux condenser was placed 1.0g (0.0024 mole) of 2-(m-methoxyphenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one dissolved in 25mls of anhydrous benzene. The cyclone solution was heated to reflux, and a dropping funnel was attached into which the Grignard reagent was transferred. The reagent was added slowly to the refluxing cyclone solution, and reflux was continued for 2.5 additional hours. Next, the reaction mixture was cooled to 0°C in an ice bath and hydrolyzed with 25mls of ten percent ammonium chloride solution. The aqueous layer was separated, and extracted with two 20ml portions of benzene, and the benzene combined with the organic layer. The organic phase was then washed with five 25ml portions of water, dried over anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a brown oil. The oil (3.36g, 0.00478 mole, 99.8%) resisted crystallization, and spectroscopic methods indicated a mixture of products present, the major infrared bands were

3540cm^{-1} (OH stretch of the product alcohol), 1720cm^{-1} (C=O stretch of conjugated ketone, and 1700cm^{-1} (unreacted cyclone). The oil was not analyzed further.

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 10mls of anhydrous ether. Lithium wire (0.147g, 0.021 atom) was cut into approximately 20 pieces, falling directly into the reaction flask as cut. At this point, a few drops of bromobenzene (total of 1.52g, 0.0096 mole) in 10mls of anhydrous ether was added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional 30 minutes. In a 100ml, three-necked, round-bottom flask seated in an ice bath was placed 2.0g (0.004 mole) of 2-(m-methoxyphenyl)-3,4,5-triphenyl-2,4-cyclopentadien-1-one dissolved in 30mls of anhydrous benzene. The flask was equipped with a magnetic stirring bar, a dropping funnel was attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the last drops of phenyllithium were added, at which point it became purple-brown. Stirring was continued for four hours during which time the solution gradually became yellow. The reaction mixture was hydrolyzed with 100mls of ten percent ammonium chloride solution, the aqueous phase separated and extracted

with two 50ml portions of benzene. The benzene extracts were combined with the organic layer, and the solution washed with two 25ml portions of water. Next, the organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped to yield a yellow oil. The oil (3.36g, 0.00478 mole, 99.8%) resisted crystallization, but spectroscopic and analysis confirm its identity as 2-(m-methoxyphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol. Infrared: OH stretch, 3540cm^{-1} . No bands in the carbonyl region.

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 492

Calcd. for $\text{C}_{36}\text{H}_{28}\text{O}_2$: C, 87.78; H, 5.73

Found: C, 87.80; H, 5.86

F. 2-(p-Bromophenyl)-5-(p-Methylphenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 50ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet was placed 0.365g (0.015 atom) of magnesium turnings and a few crystals of iodine. The flask was heated to activate the magnesium. At this point, 2.35g (0.015 mole) of bromobenzene dissolved in 30mls of anhydrous ether was slowly added to the magnesium. When addition was complete, the reaction mixture was refluxed for an additional hour. In another flask (100ml, three-necked, round-bottom) equipped with a magnetic stirring bar and

reflux condenser was placed 2.38g (0.005 mole) of 2-(p-bromophenyl)-5-(p-methylphenyl)-3,4-diphenyl-2,4-cyclopentadien-1-one dissolved in 30mls of anhydrous benzene. The cyclone solution was heated to reflux, and a dropping funnel was attached into which the Grignard reagent was transferred. The reagent was added slowly to the refluxing cyclone solution, and reflux was continued for two additional hours. Next, the reaction mixture was cooled in an ice bath and hydrolyzed with 25mls of ten percent ammonium chloride solution. The aqueous layer was separated, and extracted with two 25ml portions of benzene, and the benzene combined with the organic layer. The organic phase was then washed with three 25ml portions of water, dried over anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 2.2g (0.0039 mole, 79.4%) of a brown oil. The oil was crystallized from 5mls of benzene and 40mls of petroleum ether to yield 2.0g (0.0036 mole, 72.0%) of yellow crystals, mpt. 178.0-179.2°C.

Analysis: M.W. (Mass Spec.) Calcd: 555.5

Found: 555

Calcd. for $C_{36}H_{27}OBr$: C, 77.83; H, 4.89; Br, 14.38

Found: C, 77.91; H, 5.17; Br, 14.22

II. Via Organolithium Reagent

Into a 250ml, three-necked, round-bottom flask equipped with magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 23mls of anhydrous ether. Lithium wire (0.35g, 0.05

atom) was cut into approximately 40 pieces, allowing the pieces to fall directly into the reaction flask as cut. At this point, a few drops of bromobenzene were added to initiate reaction. Within 5-8 minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 3.53g, 0.0225 mole) in 23mls of anhydrous benzene was added slowly through a dropping funnel. When addition was complete, the solution was refluxed for another 30 minutes, then cooled in an ice bath. At this point, 7.16g (0.015 mole) of 2-(p-methylphenyl)-5-(p-bromophenyl)-3,4-diphenyl-2,4-cyclopentadien-1-one dissolved in 90mls of anhydrous benzene was added slowly to the organolithium reagent through a dropping funnel. After addition was complete, the solution was stirred for one hour, then hydrolyzed with 100mls of ten percent ammonium chloride. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 25mls of benzene, and the benzene combined with the organic layer. The benzene solution was washed twice with 25mls of water, dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow-brown oil. The oil was crystallized from 15mls of benzene and 90mls of petroleum ether (b.p. 30-60°C) to yield a first crop of yellow crystals, 7.5g (0.0135 mole, 90%) mpt. 175-179°C. Recrystallization from 10mls of benzene and 100mls of petroleum ether gave 6.9g (0.0124 mole, 82.8%) of yellow-tan crystals, mpt. 178.0-179.2°C.

Analysis: M.W. (Mass Spec.) Calcd: 555.5

Found: 555

Calcd. for $C_{36}H_{27}OBr$: C, 77.83; H, 4.89; Br, 14.38

Found: C, 77.93; H, 5.17; Br, 14.36

G. 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol

I. Via Grignard Reagent

Into a 25ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, reflux condenser, and nitrogen inlet was placed 0.184g (0.00756 atom) of magnesium turnings and a few crystals of iodine. The flask was heated to activate the magnesium, then allowed to cool slightly. At this point, 1.18g (0.00756 mole) of bromobenzene dissolved in 15mls of anhydrous ether was added slowly to the magnesium through a dropping funnel. When addition was complete, the reaction mixture was refluxed for an additional 50 minutes. In another flask (50ml, three-necked, round-bottom) equipped with a magnetic stirring bar and reflux condenser was placed 1.0g (0.00189 mole) of 2-(p-chlorophenyl)-5-(p-methoxyphenyl)-3,4-diphenyl-2,4-cyclopentadien-1-one dissolved in 15mls of anhydrous benzene. The cyclone solution was heated to reflux, and a dropping funnel was attached into which the Grignard reagent was transferred. The reagent was added slowly to the refluxing cyclone solution which changed color from deep purple to bright yellow within 15 minutes. The solution was allowed to reflux for another 45 minutes, then cooled in an ice bath and hydrolyzed with

25mls of ten percent ammonium chloride solution. The aqueous layer was separated and extracted with two 25ml portions of benzene, and the benzene portions combined with the organic layer. The organic phase was then washed with three 25ml portions of water, dried over anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 1.07g (0.00222 mole, 117 %) of a brown oil which resisted crystallization. Crystallization was accomplished by dissolution in benzene/petroleum ether followed by seeding with crystals from the lithium reaction. Yield: 0.846g (0.0016 mole, 85%) yellow crystals, mpt. 191-193°C.

Analysis: M.W. (Mass Spec.) Calcd: 527.0

Found: 527

Calcd. for $C_{36}H_{27}O_2Cl$: C, 82.04; H, 5.16; Cl, 6.73

Found: C, 81.98; H, 5.32; Cl, 6.58

II. Via Organolithium Reagent

Into a 50ml, three-necked, round-bottom flask equipped with a magnetic stirring bar, nitrogen inlet, and reflux condenser with drying tube was placed 10mls of anhydrous ether. Lithium wire (0.125g, 0.0166 atom) was cut into approximately 20 pieces, falling directly into the reaction flask as cut. At this point, a few drops of bromobenzene were added to initiate reaction. Within ten minutes a grey precipitate of lithium bromide began to form and the remaining bromobenzene (total of 1.57g, 0.010 mole) in 10mls of anhydrous ether was

added dropwise through a dropping funnel. When addition was complete, the solution was refluxed for an additional 30 minutes. In a 100ml, three-necked, round-bottom flask seated in an ice bath was placed 2.25g (0.005 mole) of 2-(p-methoxyphenyl)-5-(p-chlorophenyl)-3,4-diphenyl-2,4-cyclopentadien-1-one dissolved in 30mls of anhydrous benzene. The flask was equipped with a magnetic stirring bar, a dropping funnel was attached to the center neck, and a drying tube fitted to one side-neck. The phenyllithium was transferred to the dropping funnel and allowed to drip slowly into the cyclone solution. The cyclone solution remained purple until the last drops of phenyllithium were added, at which point it became bright yellow. Stirring was continued for one hour, then the solution was hydrolyzed with 50mls of ten percent ammonium chloride solution, and the phases separated. The aqueous phase was extracted with two 25ml portions of benzene, the benzene extracts combined with the organic layer, and the organic layer washed twice with 25mls of water. Next, the organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield a yellow oil. The oil was crystallized from 10mls of benzene and 100mls of petroleum ether (b.p. 30-60°C) to yield 2.24g (0.00426 mole, 85.2%) of yellow crystals, mpt. 191-193°C.

Analysis: M.W. (Mass Spec.) Calcd: 527.0

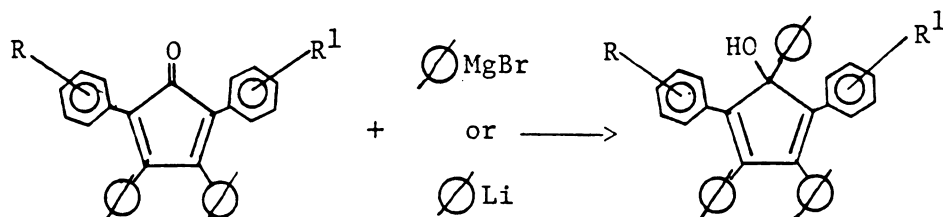
Found: 527

Calcd. for $C_{36}H_{27}O_2Cl$: C, 82.04; H, 5.16; Cl, 6.73

Found: C, 81.98; H, 5.32; Cl, 6.58

TABLE 9

Preparation of 2- and/or 5-(p- or m-Substituted Phenyl)-
1,3,4-Triphenyl-2,4-Cyclopentadien-1-ols



Tetracyclone and

Cyclopentadienol (R=)	(R¹=)	Grignard		Organolithium	
		Yield (%)	Mpt. (°C)	Yield (%)	Mpt. (°C)
<u>p</u> -Br	H	59.4	160.0-161.5 lit. 160-161.5 ⁶⁸	82.4	160.161.5 lit. 160-161.5 ⁶⁸
<u>p</u> -Cl	H	72.9	149.5-152.0	73.8	151-153
<u>p</u> -MeO	H	78.4	163.5-164.0 lit. 164.8-165.8 ⁷¹	87.9	163.5-164.5 lit. 164.8-165.8 ⁷¹
<u>p</u> -Me	H	76.0	148.2-150.5 lit. 153-154 ⁹	81.3	149.0-151.2 lit. 153-154 ⁹
<u>m</u> -MeO	H	*		99.8	oil
<u>p</u> -Br	<u>p</u> -Me	72.0	178.0-179.2	79.4	178.0-179.2
<u>p</u> -Cl	<u>p</u> -MeO	85	191-193	85.2	191-193

*This reaction produced an uncrystallizable oil consisting of a mixture of products. See discussion.

Thermal Isomerization of 1-(p- or m-Substituted
Phenyl) Cyclopentadienols: Preparation of Cyclopentenones

The results of these reactions are summarized in Table 10.

A. 2,2,3,4,5-Pentaphenyl-3-Cyclopenten-1-one via Thermal Isomerization
of 1,2,3,4,5-Pentaphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.0108 mole) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol and 70mls of decane. All glassware had been washed with hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($\text{OH } 3600\text{cm}^{-1}$) and formation of ketone ($\text{C=O stretch, } 1760\text{cm}^{-1}$). When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A white solid precipitated, weighing 2.7g, and was filtered. The filtrate was stripped on a rotary evaporator to yield 2.25g of white tar. The tar and powder were combined and chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 275mls of solvent, leaving the conjugated ketone by-product adsorbed on the column. The recovery from chromatography was 4.5g (0.0097 mole, 90.1%). This was crystallized from benzene/petroleum ether (5mls benzene and 11mls petroleum ether

per 1.0g of compound) to yield 4.05g (0.0087 mole, 81.2%) of pure product in the form of white crystals, mpt. 195-196°C. [lit: 194-195°C]⁷²

Analysis: M.W. (Mass Spec.) Calcd: 462.59

Found: 462

Calcd. for $C_{35}H_{26}O$: C, 90.88; H, 5.67

Found: C, 90.98; H, 5.67

B. 2-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one Via Thermal Isomerization of 1-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.0092 mole) of 1-(p-bromophenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 80mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was pre-purified grade, and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$, 3600cm^{-1}) and formation of ketone ($C=O$ stretch, 1760cm^{-1}). When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A pale yellow solid precipitated weighing 2.8g and was filtered. The filtrate was stripped on a rotary evaporator to yield 2.15g of a pale yellow tar.

The tar and powder were combined and chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 300mls of solvent, leaving the conjugated ketone by-product adsorbed on the column. The recovery from chromatography was 4.48g (0.0082 mole, 90.0%). This was crystallized from benzene/petroleum ether (5mls benzene and 11mls petroleum ether per 1.0g of compound) to yield 4.1g (0.0076 mole, 82.9%) of pure product in the form of white crystals, mpt. 166.5-171.5°C (menis), 173°C (clear). [lit. mpt. 157-168°C]⁶⁸

Analysis: M.W. (Mass Spec.) Calcd: 541.5

Found: 541

Calcd. for $C_{35}H_{25}OBr$: C, 77.63; H, 4.65; Br, 14.76

Found: C, 77.89; H, 4.74; Br, 15.23

C. 2-(m-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one Via Thermal Isomerization of 1-m-Methoxyphenyl-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.0102 mole) of 1-(m-methoxyphenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 70mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was

heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol (-OH , 3600cm^{-1}) and formation of ketone (C=O stretch, 1760cm^{-1}). When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A pale gold solid precipitated, and the precipitate and supernatant were combined and stripped on a rotary evaporator to yield 4.9g of a gold-brown tar. The tar was chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 290mls of solvent, leaving the majority of the conjugated ketone by-product adsorbed on the column. The recovery from chromatography was 3.89g (0.0079 mole, 79.5%). This was crystallized from benzene/petroleum ether (5mls benzene and 11mls petroleum ether per 1.0g of compound) to yield 3.72g (0.00755 mole, 75.5%) of pure product in the form of an electrostatic white powder mpt. $114.0\text{-}116.0^\circ\text{C}$ (menis), 119°C (clear).

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 493

Calcd. for $\text{C}_{36}\text{H}_{28}\text{O}_2$: C, 87.77; H, 5.73

Found: C, 87.66; H, 5.90

D. 2-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one via Thermal Isomerization of 1-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.0105 mole) of 1-(p-methylphenyl)-2,3,4,5-tetraphenyl-2,4-cyclopenta-

dien-1-ol and 70mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($\text{-OH stretch, } 3600\text{cm}^{-1}$) and formation of ketone. When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A pale yellow solid weighing 2.74g precipitated and was filtered. The filtrate was stripped on a rotary evaporator to yield 2.21g of a pale yellow tar. The tar and powder were combined and chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 300mls of solvent, leaving the conjugated ketone by-product adsorbed on the column. The recovery from chromatography was 4.25g (0.0090 mole, 85.8%). This was recrystallized from benzene/petroleum ether (4mls of benzene and 11mls of petroleum ether per 1.0g of compound) to yield 3.98g (0.00837 mole, 79.8%) of pure product in the form of white crystals, mpt. $163\text{--}166^{\circ}\text{C}$ (menis), 171°C (clear).

Analysis: M.W. (Mass Spec.) Calcd: 476.6

Found: 477

Calcd. for $\text{C}_{36}\text{H}_{28}\text{O}$: C, 90.72; H, 5.92

Found: C, 90.49; H, 5.82

E. 2-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one Via Thermal Isomerization of 1-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.0101 mole) of 1-(p-chlorophenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 70mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($\text{-OH stretch, } 3600\text{cm}^{-1}$) and formation of ketone ($\text{C=O stretch, } 1760\text{cm}^{-1}$). When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A yellow solid precipitated, and the precipitate and supernatant were stripped on a rotary evaporator to yield 4.9g of a yellow tar. The tar was chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 300mls of solvent, leaving the conjugated ketone by-product adsorbed on the column. The recovery from chromatography was 3.9g (0.0078 mole, 77.7%). This was crystallized from benzene/petroleum ether (3-4mls benzene and 11mls petroleum ether per 1.0g of compound) to yield 3.61g (0.00726 mole, 72.3%) of pure product in the form of white crystals, mpt. 164-166°C (menis), 171°C (clear).

Analysis: M.W. (Mass Spec.) Calcd: 497.0

Found: 497

Calcd. for $C_{35}H_{25}OCl$: C, 84.57; H, 5.07; Cl, 7.13

Found: C, 84.73; H, 5.12; Cl, 7.59

F. 2-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one Via Thermal Isomerization of 1-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 100ml, three-necked, round-bottom flask was placed 5.0g (0.102 mole) of 1-(p-methoxyphenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 70mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was pre-purified grade, and on-line between the tank and flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$ stretch, 3600cm^{-1}) and formation of ketone ($C=O$ stretch, 1760cm^{-1}). When no more carbinol was present (12-20 hours) the solution was cooled to room temperature. A pale yellow-green solid precipitated, and the precipitate and supernatant were stripped on a rotary evaporator to yield 4.9g of a yellow-green tar. The tar was chromatographed on a 2.5cm x 25.0cm silica gel column using carbon tetrachloride as eluent. The unconjugated ketone eluted in the first 300mls of solvent, leaving the conjugated ketone by-product

adsorbed on the column. The recovery from chromatography was 3.86g (0.00785 mole, 77%). This was crystallized from benzene/petroleum ether (3mls benzene and 11mls petroleum ether per 1.0g of compound) to yield 3.4g (0.0069 mole, 68%) of pure product in the form of pale yellow-white crystals, mpt. 164.5-169°C (menis), 171°C (clear).

[lit. mpt. 130-145°C]⁶⁸

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 493

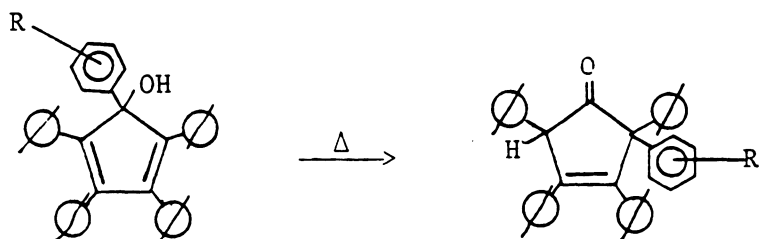
Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73

Found: C, 87.78; H, 5.83

TABLE 10

Preparation of Cyclopentenones via Thermal

Isomerization of 1-(p- or m-Substituted Phenyl)Cyclopentadienols



Cyclopentadienol and Cyclopentenone (R=)	Crude Yield (%)	Purified Yield (%)	Mpt. (°C)
H	99.0	81.2	195-196 lit. 194-195 ⁷²
p-Br	99.0	82.9	166.5-171.5; 173* lit. 157-168 ⁶⁸
m-MeO	98.0	75.5	114.0-116.0; 119*
p-MeO	99.0	68.0	164.5-169; 171* lit. 130-145 ⁶⁸
p-Me	98.0	79.8	163-166; 171*
p-Cl	98.0	72.3	164-166; 171*

*First range is from sintering to collapse to form meniscus; upper reading indicates liquid changing from translucent to clear.

Thermal Isomerization of 2- and/or 5-(p- or m-Substituted
Phenyl)cyclopentadienols: Preparation and
Characterization of the Resultant Cyclopentenones

The results of these reactions are summarized in Table 11.

A. 2-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and/or
2-(p-Bromophenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Bromophenyl)-1,3,4,5-Tetraphenyl-
 2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.00185 mole) of 2-(p-bromophenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol (-OH stretch, 3600 cm^{-1}) and formation of ketone (C=O stretch, 1760 cm^{-1}). When no more carbinol was present (approximately nine hours) the solution was transferred to a 50ml single-neck flask and stripped on a rotary evaporator to yield 0.98g (0.00181 mole, 98%) of a yellow foam.

Analysis: M.W. (Mass Spec.) Calcd: 541.5

Found: 541

Calcd. for $C_{35}H_{25}OBr$: C, 77.63; H, 4.65; Br, 14.76

Found: C, 77.91; H, 4.75; Br, 13.04

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.00046 mole) of the product mixture from the isomerization of 2-(p-bromophenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser, and the solution was brought to 65-70°C with a heating mantle. At this point, 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at 70-80°C for 45 minutes. The solution was then poured onto 50g of ice and 50mls of benzene, then extracted with four 50ml portions of benzene. The extracts were combined, then extracted with four 50ml portions of saturated sodium carbonate solution followed by 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped to yield 0.246g of a brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography, using a 6' x 1/8" stainless steel column packed with five percent OV-275 on Chromosorb W, column temperature 215°C, injector temperature 210°C, detector temperature 240°C. Three peaks were present, identified

by retention times and spiking with pure samples as benzophenone ($t_r=1.95$ min.), bromobenzophenone and benzil ($t_r=4.8$ min.), and bromobenzil ($t_r=9.98$ min.). See Appendix B for comparison of gas chromatogram of the oxidation mixture with a control mixture composed of equimolar amounts of the four products.

B. 2-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-3- Cyclopenten-1-one and/or
2-(p-Chlorophenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Chlorophenyl)-1,3,4,5-Tetra-
 phenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.0020 mole) of 2-(p-chlorophenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$ stretch, 3600cm^{-1}) and formation of ketone ($C=O$ stretch, 1760cm^{-1}). When no more carbinol was present (approximately 9 hours) the solution was transferred to a 50ml, single-neck flask and stripped on a rotary evaporator to yield 0.964g (0.00194 mole, 97%) of a yellow foam.

Analysis: M.W. (Mass Spec.) Calcd: 497.0

Found: 497

Calcd. for $C_{35}H_{25}OCl$: C, 84.58; H, 5.07; Cl, 7.13

Found: C, 84.53; H, 5.11; Cl, 7.97

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.0005 mole) of the product mixture resulting from the thermal isomerization of 2-(p-chlorophenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser, and the solution was brought to 65-70°C with a heating mantle. At this point, 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at 70-80°C for 45 minutes. The solution was then poured onto 50g of ice and 50mls of benzene, then extracted with four 50ml portions of saturated sodium carbonate solution followed by 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.30g of a brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography, using a 6' x 1/8" stainless steel column packed with five percent OV-275 on Chromosorb W, column temperature 215°C, injector temperature 210°C, detector temperature 240°C. Four peaks were present, identified by

retention times and spiking with pure samples as benzophenone ($t_R=1.95$ min.), chlorobenzophenone ($t_R=3.08$ min.), chlorobenzil ($t_R=6.6$ min.), and benzil ($t_R=4.72$ min.). See Appendix B for a comparison of the gas chromatogram of the oxidation mixture with that of a control mixture composed of equimolar amounts of the four products.

C. 2-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and/or 2-(p-Methoxyphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Methoxyphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.0020 mole) of 2-(p-methoxyphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$ stretch, 3600cm^{-1}) and formation of ketone ($C=O$ stretch, 1760cm^{-1}). When no more carbinol was present (approximately 9 hours) the solution was transferred to a 50ml, single-neck flask and stripped on a rotary evaporator to yield 0.965g (0.00196 mole, 98%) of a yellow tar.

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 493

Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73

Found: C, 87.37; H, 5.79

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.00050 mole) of the product mixture resulting from the thermal isomerization of 2-(p-methoxyphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser, and the solution was brought to 65-70°C with a heating mantle. At this point 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was then poured onto 50g of ice and 50mls of benzene, then extracted with four 50ml portions of saturated sodium carbonate followed by 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.260g of a brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography, using a 6' x 1/8" stainless steel column packed with five percent OV-275 on Chromosorb W, column temperature programmed 215°C to 240°C @ 2° per minute, injector temperature 210°C, detector temperature 240°C. Four peaks were present, identified by retention times and spiking with pure samples as benzophenone (t_r =1.87 min.),

benzil ($t_r=4.2$ min.), methoxybenzophenone ($t_r=6.0$ min.), and methoxybenzil ($t_r=12.15$ min.). A comparison with a control mixture comprised of equimolar amounts of the above compounds can be found in Appendix B.

D. 2-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and/or
2-(p-Methylphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Methylphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.0021 mole) of 2-(p-methylphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$ stretch, 3600cm^{-1}) and formation of ketone ($C=O$ stretch, 1760cm^{-1}). When no more carbinol was present (approximately 9 hours) the solution was transferred to a 50ml, single-neck flask and stripped on a rotary evaporator to yield 0.97g (0.0020 mole, 97%) of a yellow tar.

Analysis: M.W. (Mass Spec.) Calcd: 476.6

Found: 477

Calcd. for $C_{36}H_{28}O$: C, 90.72; H, 5.92

Found: C, 90.54; H, 6.04

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.00052 mole) of the product mixture resulting from the thermal isomerization of 2-(p-methylphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. At this point, 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at room temperature for 45 minutes followed by 15 minutes at approximately 50°C. The solution was then poured onto a mixture of 50mls of benzene and 50g of ice, and the aqueous phase separated from the organic phase. The aqueous phase was extracted once with 50mls of benzene and the benzene combined with the organic layer. The organic phase was then extracted with five 50ml portions of saturated sodium carbonate followed by 50mls of water. The organic solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.24g of a brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography, using a 6' x 1/8" stainless

steel column packed with five percent OV-275 on Chromosorb W, column temperature 215°C, injector temperature 210°C, detector temperature 240°C. Four peaks were present, identified by retention times and spiking with pure samples as benzophenone ($t_r=1.95m$), methylbenzophenone ($t_r=2.55m$), methylbenzil ($t_r=6.45m$), and benzil ($t_r=4.8m$). A comparison with a control mixture comprised of equimolar amounts of the above compounds can be found in Appendix B.

E. 2-(m-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and/or 2-(m-Methoxyphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(m-Methoxyphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.0021 mole) of 2-(m-methoxyphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($-OH$ stretch, $3600cm^{-1}$) and formation of ketone ($C=O$ stretch, $1760cm^{-1}$). When no more carbinol was present (approximately 9 hours) the solution was transferred to a 50ml, single-neck flask and stripped on a rotary evaporator to yield 0.98g (0.00198

mole, 98%) of a brown tar.

Analysis: M.W. (Mass Spec.) Calcd: 492.6

Found: 493

Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73

Found: C, 87.70; H, 5.81

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.0005 mole) of the product mixture resulting from the thermal isomerization of 2-(m-methoxyphenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. The solution was brought to 60-65°C and 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at 70-80°C for 45 minutes. The reaction mixture was then poured onto 50g of ice and 50mls of benzene, the layers separated, and the aqueous layer extracted with 50mls of benzene which was combined with the organic layer. The organic layer was extracted with four 50ml portions of saturated sodium carbonate followed by 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.248g of a brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography using a 6' x 1/8" stainless steel column pack with five percent OV-275 on

Chromosorb W. Column temperature was 215°C, injector 210°C, and detector 240°C. Four peaks were present identified by retention times and spiking as m-methoxybenzophenone (t_r =0.6 min.), benzophenone (t_r =2.475 min.), benzil (t_r =5.25 min.), and m-methoxybenzil (t_r =9.38 min.). A comparison with a control mixture comprised of benzil and benzophenone can be found in Appendix B.

F. 2-(p-Bromophenyl)-5-(p-Methylphenyl)-3,4,5-Triphenyl-3-Cyclopenten-1-one and/or 2-(p-Bromophenyl)-5-(p-Methylphenyl)-2,3,4-Triphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Bromophenyl)-5-(p-Methylphenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.00180 mole) of 2-(p-bromophenyl)-5-(p-methylphenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($\text{-OH stretch, } 3600\text{cm}^{-1}$) and formation of ketone ($\text{C=O stretch, } 1760\text{cm}^{-1}$). When no more carbinol was present (approximately 9 hours) the solution was transferred to a 50ml single-neck flask and stripped on a rotary evaporator to yield

0.97g (0.0017 mole, 97%) of a yellow foam.

Analysis: M.W. (Mass Spec.) Calcd: 555.5

Found: 555

Calcd. for $C_{36}H_{27}OBr$: C, 77.83; H, 4.89; Br, 14.38

Found: C, 77.89; H, 5.15; Br, 14.49

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (0.00045 mole) of the product mixture resulting from the thermal isomerization of 2-(p-bromophenyl)-5-(p-methylphenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser. At this point, 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at room temperature for 45 minutes followed by 15 minutes at approximately 50°C. The solution was then poured onto a mixture of 50mls of benzene and 50g of ice, and the aqueous phase separated from the organic phase. The aqueous phase was extracted once with 50mls of benzene and the benzene combined with the organic layer. The organic phase was then extracted with five 50ml portions of saturated sodium carbonate followed by 50mls of water. The organic solution was then dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.258g of a green-brown oil. The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform.

The mixture was analyzed by gas chromatography using a 6' x 1/8" stainless steel column packed with 5% OV-275 on Chromosorb W. Column temperature, 215°C, injector temperature 210°C, detector temperature 240°C. Four peaks were present, identified by retention time and spiking with pure samples as methylbenzophenone (t_r =2.48 min.), bromobenzophenone (t_r = 4.65 min.), methylbenzil (t_r =6.45 min.), and bromobenzil (t_r =10.05 min.). A comparison with a control mixture comprised of equimolar amounts of the above compounds can be found in Appendix B.

G. 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-3,4,5-Triphenyl-3-Cyclopenten-1-one and/or 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-2,3,4-Triphenyl-3-Cyclopenten-1-one

I. Thermal Isomerization of 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol in Decane at 174°C

Into a 25ml, three-necked, round-bottom flask was placed 1.0g (0.00189 mole) of 2-(p-chlorophenyl)-5-(p-methoxyphenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ol and 15mls of decane. All glassware had been washed with ten percent hydrochloric acid, rinsed with acetone, and baked overnight. The flask was equipped with a magnetic stirring bar, reflux condenser with drierite drying tube, and nitrogen inlet. The nitrogen was prepurified grade, and on-line between the tank and the flask was a drierite drying tube and silicone oil bubbler. The solution was heated to reflux under nitrogen and monitored by infrared spectroscopy for disappearance of alcohol ($\text{-OH stretch, } 3600\text{cm}^{-1}$) and

formation of ketone ($\text{C}=\text{O}$ stretch, 1760cm^{-1}). When no more carbinol was present (approximately nine hours) the solution was transferred to a 50ml single-neck flask and stripped on a rotary evaporator to yield 0.97g (0.00184 mole, 97%) of a yellow foam.

Analysis: M.W. (Mass Spec.) Calcd: 527.0

Found: 527

Calcd. for $\text{C}_{36}\text{H}_{27}\text{O}_2\text{Cl}$: C, 82.04; H, 5.16; Cl, 6.73

Found: C, 82.01; H, 5.19; Cl, 6.46

II. Characterization of the Isomerization Products by Oxidative Degradation

Into a 50ml, three-necked, round-bottom flask was placed 0.25g (.00047 mole) of the product mixture resulting from the thermal isomerization of 2-(p-chlorophenyl)-5-(p-methoxyphenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ol and 25mls of acetic anhydride. The flask was equipped with a magnetic stirring bar and reflux condenser and the solution was brought to $65-70^\circ\text{C}$ with a heating mantle. At this point, 0.3g (0.003 mole) of chromium trioxide was added all at once. Stirring was continued and the reaction mixture maintained at $70-80^\circ\text{C}$ for 45 minutes. The solution was then poured onto 50g of ice and 50mls of benzene, then extracted with four 50ml portions of saturated sodium carbonate followed by 50mls of water. The organic solution was dried with anhydrous magnesium sulfate, filtered, and stripped on a rotary evaporator to yield 0.22g of a yellow-brown oil.

The oil was transferred to a 10ml volumetric flask and brought up to volume with chloroform. The mixture was analyzed by gas chromatography using a 6' x 1/8" stainless steel column packed with 5% OV-275 on Chromosorb W. Injector temperature 210°C, column temperature programmed 215-240°C @ 2°C/min., detector temperature 240°C. Four peaks were present, identified by retention times and spiking with pure samples as chlorobenzophenone (t_r =2.85 min.), chlorobenzil (t_r =5.55 min.), methoxybenzophenone (t_r =6.0 min.), and methoxybenzil (t_r =11.85 min.). A comparison with a control mixture comprised of equimolar amounts of the above compounds can be found in Appendix B.

TABLE 11
Thermal Isomerization of 2-(p- or m-Substituted
Phenyl)Cyclopentadienols

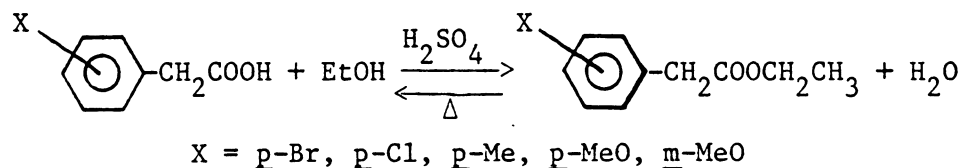
Cyclopentadienol (X=) (Y=)		Pathway 1 Product (%)*	Pathway 2 Product (%)*
H	<u>p</u> -Br	51.8	48.2
H	<u>p</u> -Cl	59.8	40.2
H	<u>p</u> -MeO	56.0	44.0
H	<u>p</u> -Me	49.6	50.4
H	<u>m</u> -MeO	52.2	47.8
<u>p</u> -Me	<u>p</u> -Br	57.0	43.0
<u>p</u> -MeO	<u>p</u> -Cl	42.7	57.3

*Analysis by 200 MHz Proton NMR

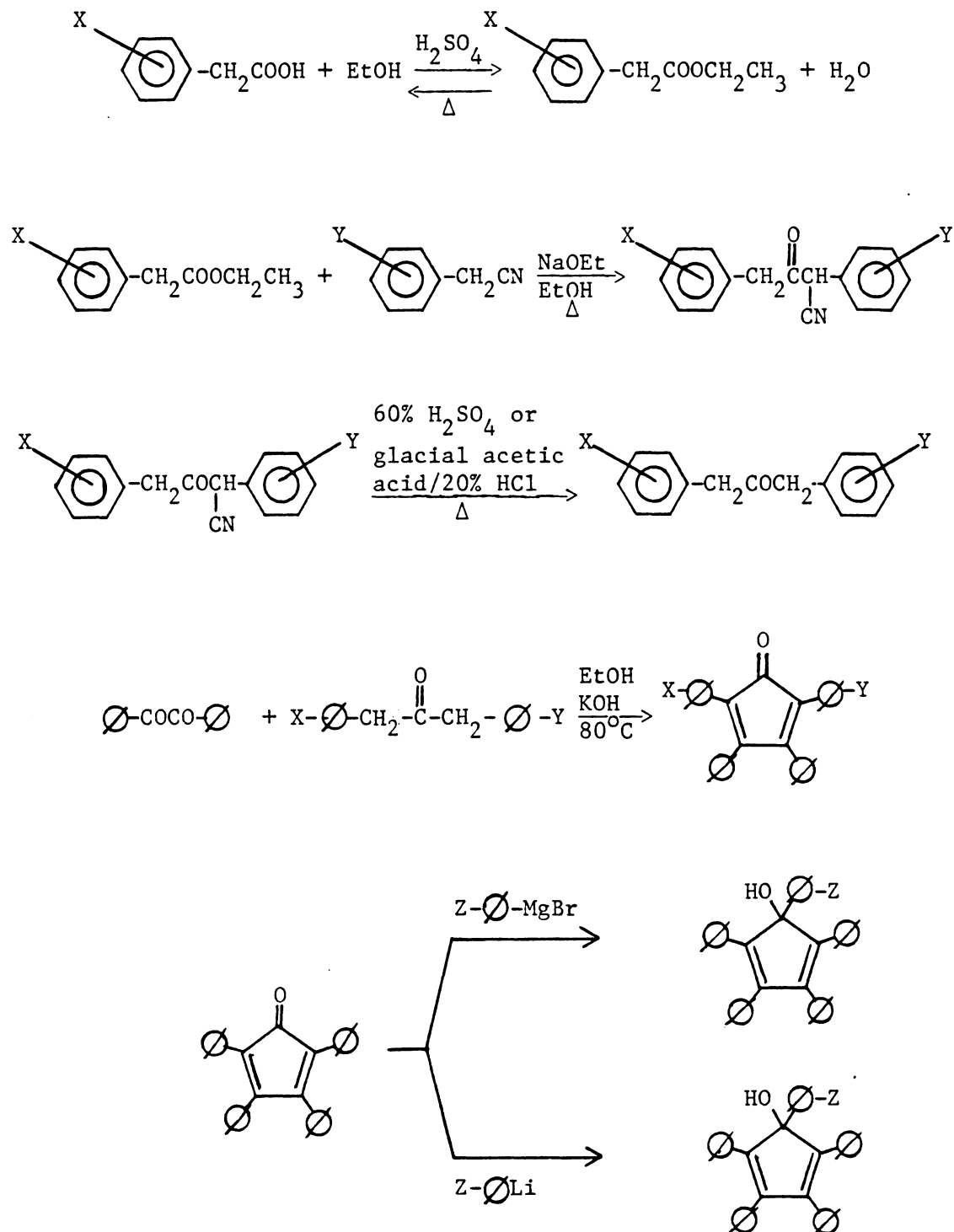
SECTION B. RESULTS AND DISCUSSION

Part 1. Syntheses

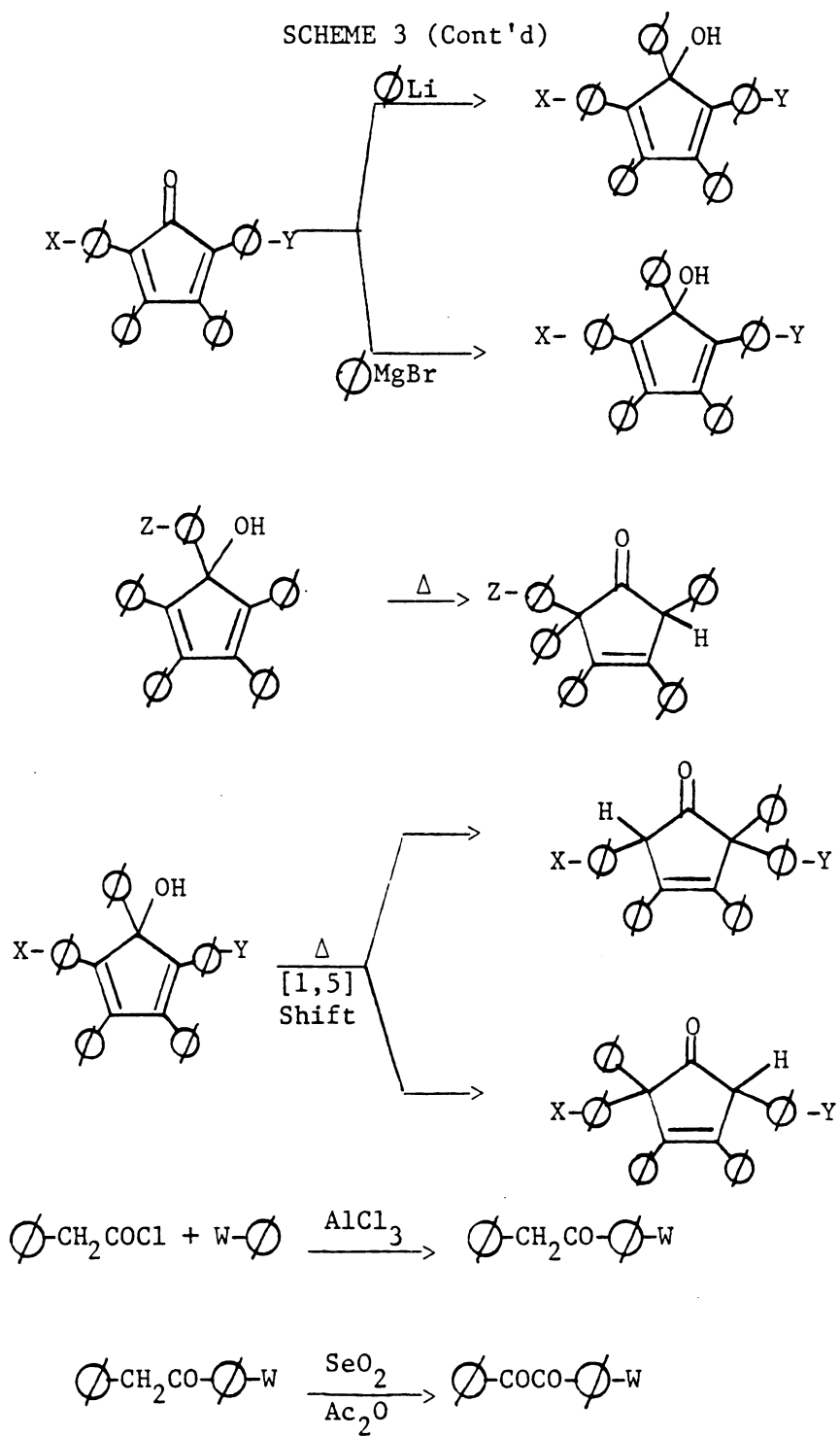
The synthetic pathway leading to the substituted polyaryl carbinols required for the study of electronic effects in the thermal rearrangement of 2- and/or 5-(p- or m-substituted phenyl) cyclopentadienols involved six steps and is illustrated in Scheme 3. In many instances, the compounds were made not only by the usual routes, but also by improved and/or new routes which provide an interesting comparison.

A. Ethyl Phenylacetates

The ethyl (p- or m-substituted phenyl) acetates were prepared by esterification of the appropriate acid using the procedure of Coan and Becker,⁵⁹ in which a large excess of absolute ethanol is used in order to achieve a good yield of ester, requiring on the order of 170mls of absolute ethanol for production of 0.1 mole of ester. The yields for the five substituted esters synthesized ranged from 69.0-81.0 percent (Table 4, see experimental) by this method, after purification. The esters were also prepared by a modification of this procedure whereby the reaction was performed as an azeotropic esterification. This procedure required far less absolute ethanol, on the order of 50mls

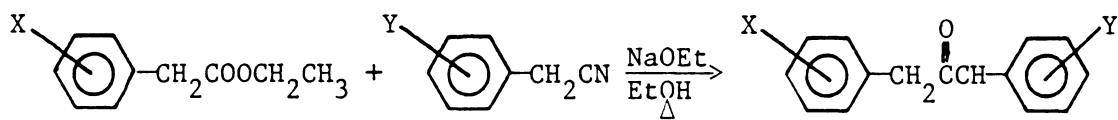


SCHEME 3 (Cont'd)



for production of 0.1 mole of ester. In the azeotropic procedure, high yields were achieved not by forcing equilibrium to the right by flooding with one reactant (ethanol), but rather by constant removal of one of the products, water. This procedure was inherently more efficient since in effect quantitative yields were achieved by complete removal of the water produced, and also this procedure consumed considerably less absolute ethanol. The yields for the five substituted esters when prepared by this method ranged from 86.0-92.0 percent after purification, the average yield being 14 percent higher than by the former method. Purification of the crude products was accomplished by vacuum distillation. See Figure 7 for a representative infrared spectrum.

B. Diphenylacetoacetonitriles



X = p-Br, p-Cl, p-Me, p-MeO, m-MeO, H

Y = p-Br, p-Cl, p-Me, p-MeO, m-MeO, H

The substituted diphenylacetoacetonitriles that were synthesized are summarized in Table 5 (see experimental). The method of preparation is that of Coan and Becker,⁵⁹ involving the base-catalyzed condensation of substituted ethyl phenylacetates with substituted phenylacetonitriles. Since these compounds are hydrolyzed and decarboxylated to produce the next series of compounds, the substituted diphenyl

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>Fig 7</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE _____
PHASE _____		RESOLUTION ☐		<u>ne ester</u>
REMARKS _____	OPERATOR _____	DATE _____		ORIGIN _____

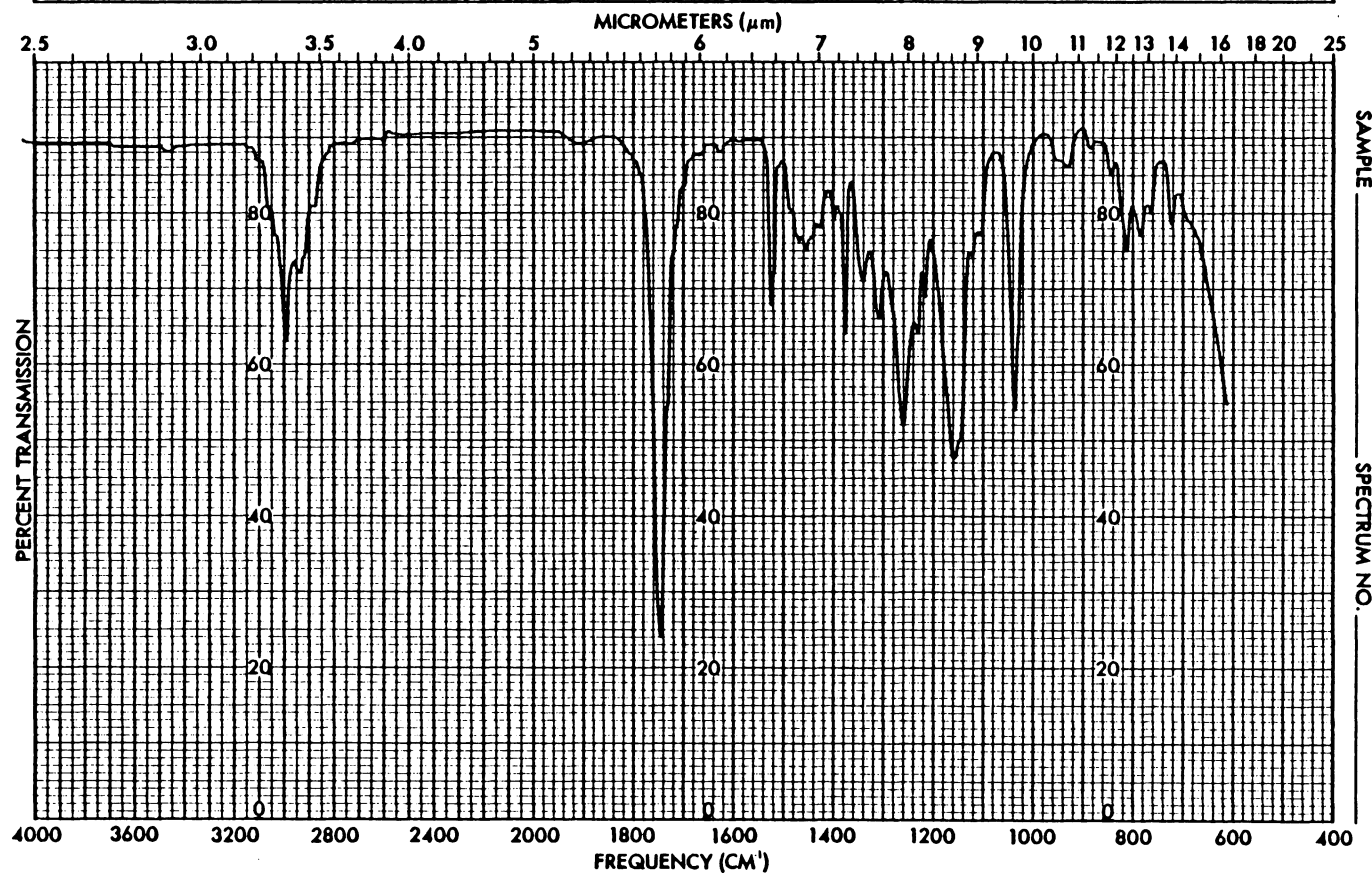


FIGURE 7. Infrared Spectrum of a Representative Ester

propanones, two routes could be used to produce two different keto-nitriles, which when decarboxylated would yield the same diphenyl propanone. For example, 1-(p-bromophenyl)-3-(phenyl)-2-propanone could be prepared from either 2-phenyl-4-(p-bromophenyl)acetoacetonitrile or 2-(p-bromophenyl)-4-(phenyl)acetoacetonitrile. The yields obtained for the substituted diphenylacetoacetonitriles were moderately good, ranging from 50-83 percent before recrystallization. The variations in yield appear randomly dispersed. There is no correlation, for example, of the Hammett value for a particular substituent with yield. By way of example, in the case of the two disubstituted p-chlorophenyl-p-methoxyphenyl keto-nitriles the higher yield was obtained when the electron-donating substituent originated from the substituted phenylacetonitrile, and the electron-withdrawing substituent originated from the substituted ethyl phenylacetate. The reverse was true for the two disubstituted p-bromophenyl-p-methylphenyl ketonitriles. In this case the higher yield was obtained when the electron-donating p-methyl substituent originated from the substituted ethyl phenylacetate, and the electron-withdrawing p-chloro substituent originated from the substituted phenylacetonitrile.

Since the yields for the coupling reaction were good from either route and the subsequent step of decarboxylation afforded good yields within a narrow range (with the exception of the decarboxylation of 2-(p-chlorophenyl)-4-(p-methoxyphenyl)acetoacetonitrile), there was no reason to prefer one of the two routes over the other. Purification in each case was achieved by recrystallization from carbon tetrachloride. See Figure 8 for a representative infrared spectrum.

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>KH Me B-2</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE _____
PHASE _____		RESOLUTION ☐		
REMARKS _____	OPERATOR _____	DATE _____		ORIGIN _____

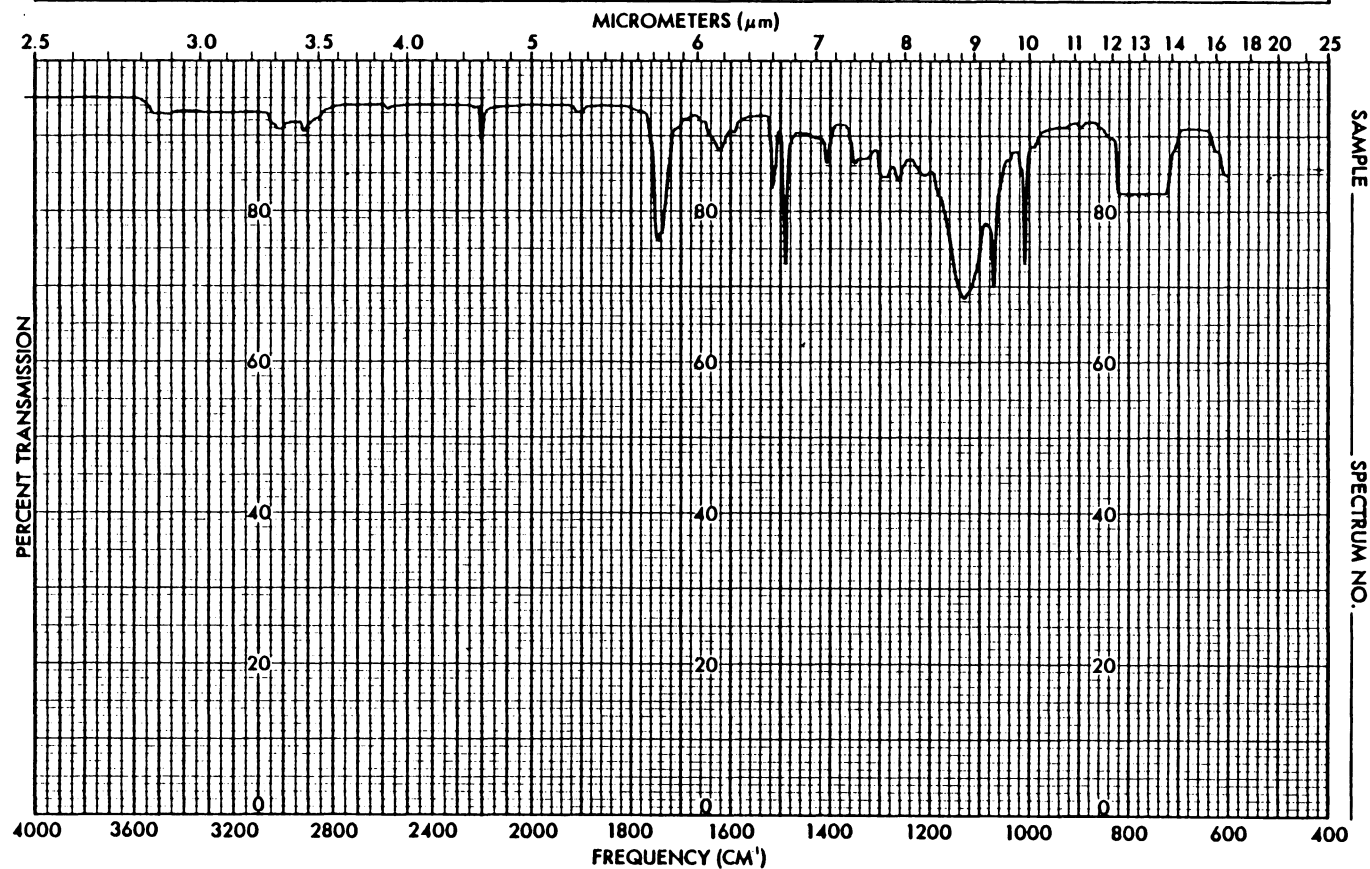
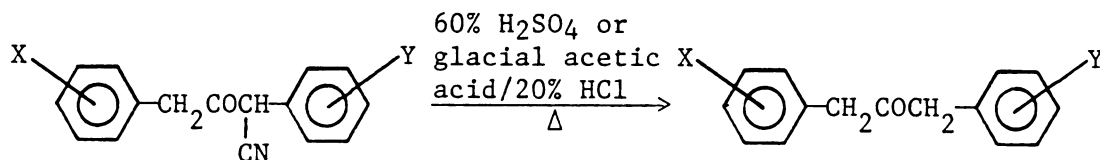


FIGURE 8. Infrared Spectrum of a Representative Keto-nitrile

C. Diphenyl Propanones

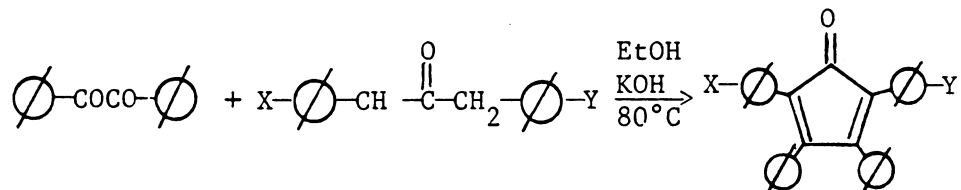
X = p-Br, p-Cl, p-Me, p-MeO, m-MeO, H

Y = p-Br, p-Cl, p-Me, p-MeO, m-MeO, H

The substituted diphenyl propanones were prepared by hydrolysis and decarboxylation of the corresponding substituted ketonitriles.⁵⁹ The reactions were performed using 60% (v/v) sulfuric acid, except in the cases where a methoxy substituent was present, where a 1:1 (v/v) mixture of hydrochloric acid/glacial acetic acid was used. The reasons for the change of medium in the case of the methoxy substituted compounds are the poor solubility and the propensity toward decomposition of the methoxy compounds in the sulfuric acid solution.⁵⁹ Each diphenyl propanone could be prepared from either of two precursor ketonitriles bearing the appropriate substituents. The yields varied within the range of 51.3-80.0 percent, with the exception of the 1-(p-chlorophenyl)-3-(p-methoxyphenyl)propanone (19.0%) when prepared from 2-(p-chlorophenyl)-4-(p-methoxyphenyl)acetoacetonitrile. Coan and Becker⁵⁹ found an analogous exception in the low yield of 1-(p-methoxyphenyl)-3-(phenyl)propanone when prepared from 2-(phenyl)-4-(p-methoxyphenyl)acetoacetonitrile. Their explanation, which can be applied to both cases, is based on work done by Zaugg⁷⁴ and proposes that after hydrolysis of the nitrile

cyclization occurs to yield the corresponding 2-aryl-1,3-naphthohydroquinones. With the above described exception, the yields from decarboxylation fell within a fairly narrow, relatively good range. Thus, there was no reason to prefer either combination of reactants for the two-reaction sequence leading from substituted ethyl phenyl acetates and substituted phenylacetonitriles to substituted propanones. All of the substituted diphenyl propanones synthesized in this project were purified by vacuum distillation, with the exception of 1-(p-bromophenyl)-3-(p-methylphenyl)propanone which crystallized readily from petroleum ether (b.p. 30-60°C). See Figure 9 for a representative infrared spectrum.

D. Tetracyclones



X = p-Cl, p-Br, p-Me, p-MeO, m-MeO, H

Y = H, p-Me, p-MeO

The 2- and/or 5-(p- or m-substituted phenyl)-3,4-diphenyl-2,4-cyclopentadien-1-ones were synthesized by the base-catalyzed condensation of the appropriately substituted diphenyl propanone with benzil. The procedure,⁶¹ originally used for the synthesis of tetraphenylcyclopentadienone (tetracyclone), in most cases affords a nearly quantitative yield. Of the eight cyclones synthesized, only 2-(m-methoxyphenyl)-

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>Fig 9</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE _____
PHASE _____		RESOLUTION ☐		ORIGIN _____
REMARKS _____	OPERATOR _____	DATE _____		

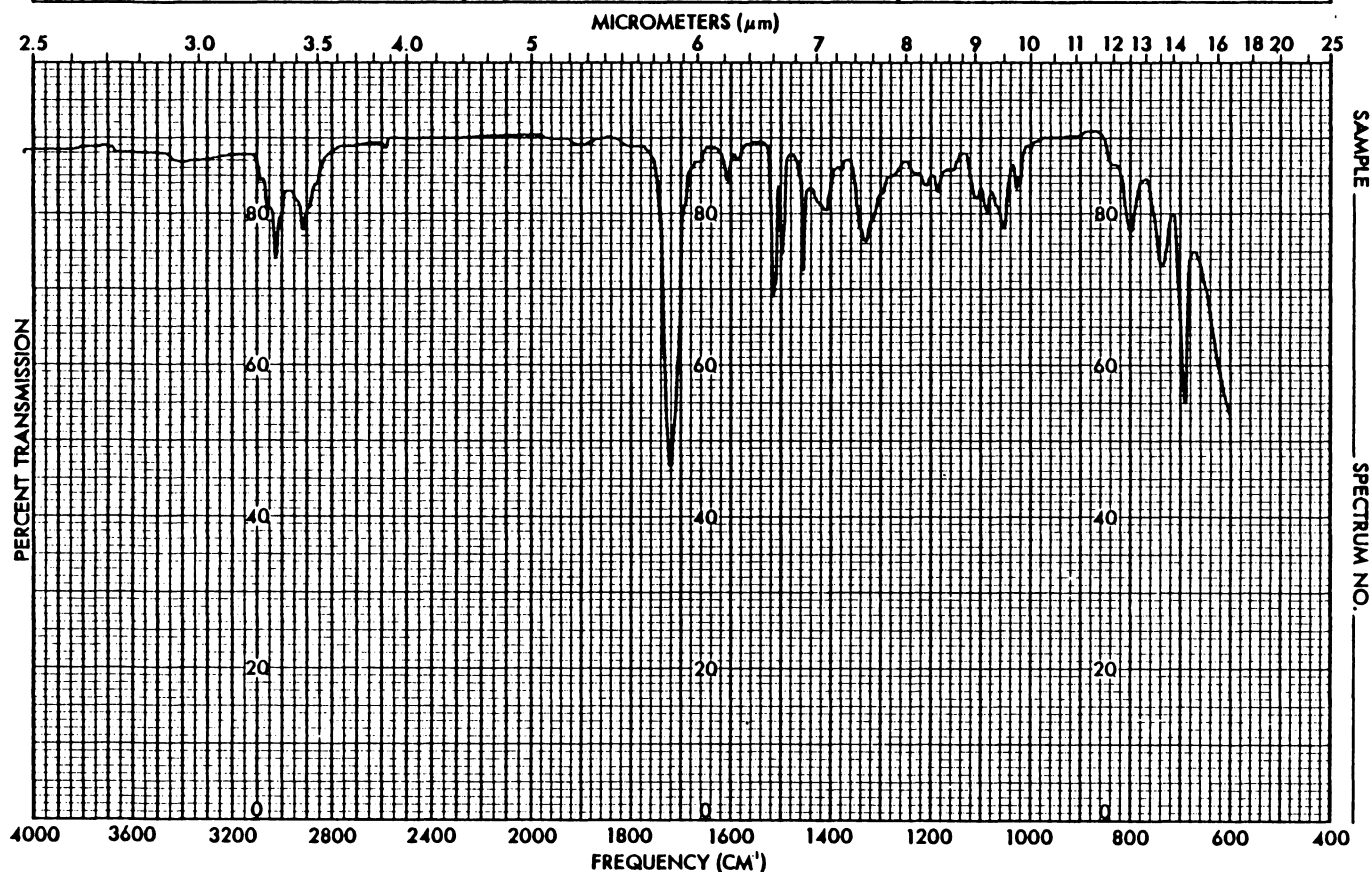
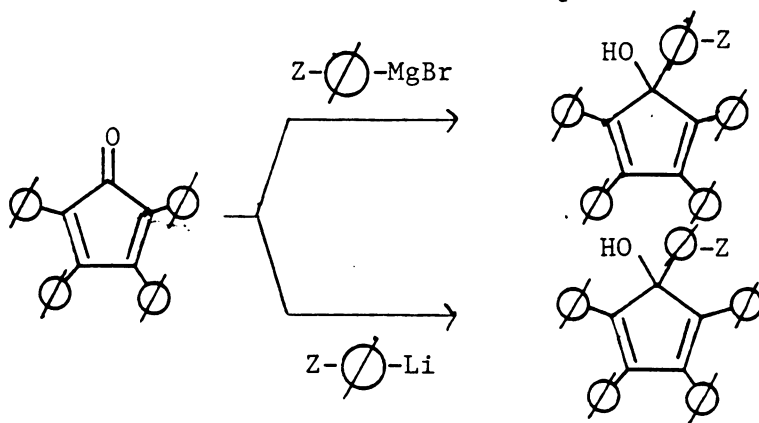


FIGURE 9. Infrared Spectrum of a Representative Diphenyl-3-Propanone

3,4,5-triphenyl-2,4-cyclopentadien-1-one afforded a yield (56.7%) below the range of 88.0-99.7 percent. Presumably, this is a steric effect; the *p*-methoxyphenyl cyclone formed in high yield in contrast to the *m*-methoxyphenyl case. It has been reported that this problem can be overcome, even in the case of ortho-substituents by the use of benzyltrimethylammonium hydroxide as the base.^{75,76,77} Since the yield in this case was still acceptable, although markedly lower than the others, no attempt was made by this author to use benzyltrimethylammonium hydroxide. The cyclones exhibit a narrow range of color variation, from black [2-(*p*-bromophenyl)] to brown [2-(*p*-chlorophenyl)] to purple [2-(*p*-methoxyphenyl)]. The products can be recrystallized from benzene/ethanol solution, but with only rare exception, are sufficiently pure following precipitation from the reaction mixture to be used in subsequent reactions. See Figure 10 for a representative infrared spectrum.

E. 1-(*p*- or *m*-Substituted Phenyl)cyclopentadienols



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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. _____
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>2-(p Br p)-5(p-Me p) cyclohex</u>
PHASE _____		RESOLUTION ☐		
REMARKS _____	OPERATOR _____	DATE <u>7-19-82</u>		ORIGIN _____

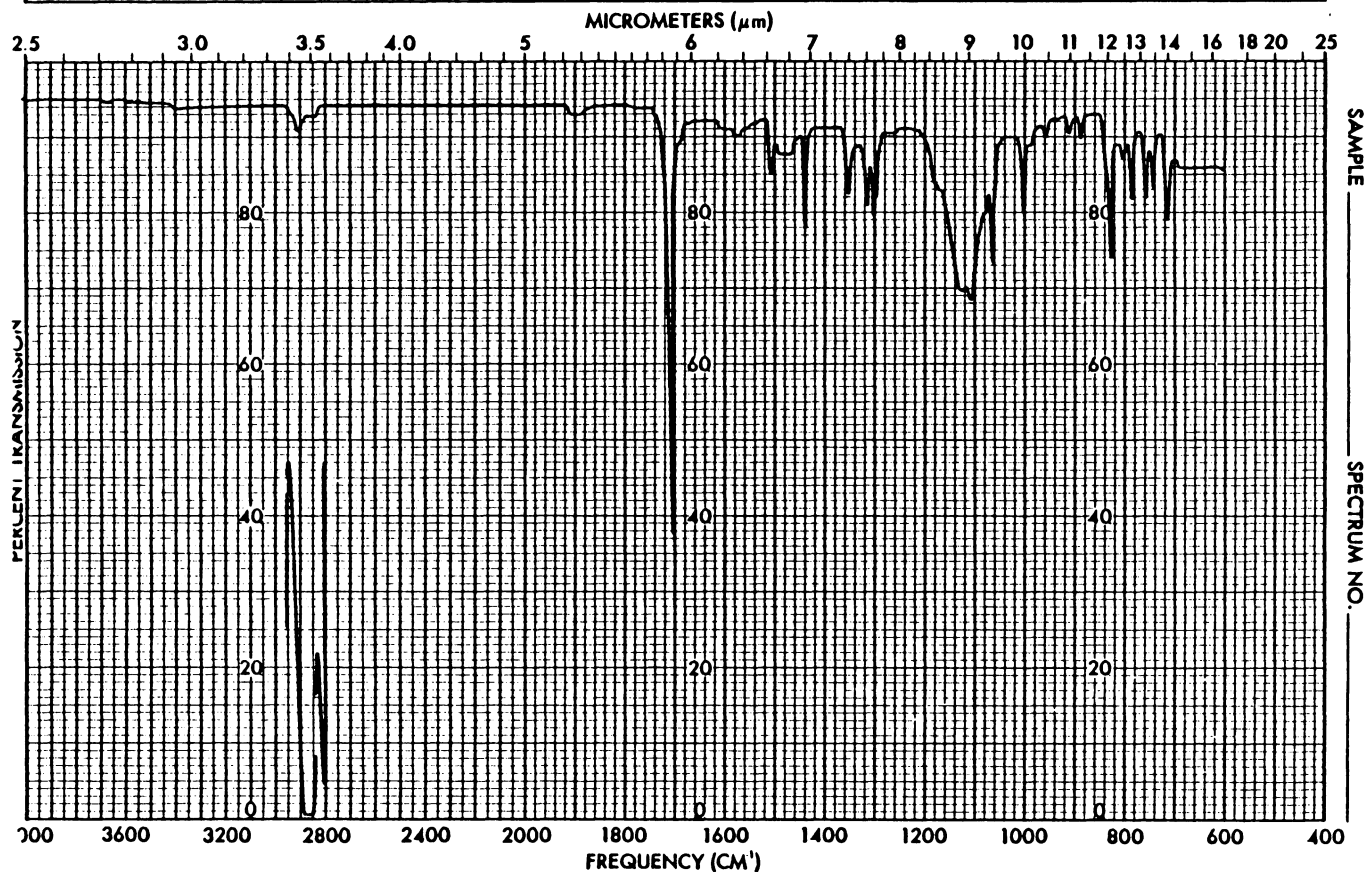


FIGURE 10. Infrared Spectrum of a Representative Tetracyclone

For the purposes of this study, thirteen cyclopentadienols were synthesized which can be divided into two series. One series is the 1-(p- or m-substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols, which were synthesized for the purpose of ultimately thermally isomerizing them to produce a pure sample of one of the two possible products resulting from the thermal isomerization of the 2- and/or 5-(p- or m-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ols. There were two approaches to the synthesis of the alcohols. The most common route was via Grignard reagent.² Alternatively, the use of the appropriate organolithium reagent^{65,66} was attempted for each case. The use of phenyllithium in the synthesis of unsubstituted pentaphenylcyclopentadienol⁷⁸ and 2-(p-methylphenyl)-1,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol⁶⁶ has been reported, but has not been used in the other cases. In the course of this study a number of interesting contrasts between the two reagents surfaced. First, in the case of the 1-(p-substituted phenyl) alcohols, the yields were higher (79.0-92.7%) when synthesized by the organolithium reagent as opposed to 68.0-84.3 percent when the Grignard reagent was used. There are two probable causes for this difference, one being that only a 1.5-2.5 to 1.0 ratio of halide to cyclone was required for the organolithium route as opposed to a 3.0-4.0 to 1.0 ratio when using the Grignard. This resulted in less unreacted halide being present during purification and crystallization. Generally, the products from the lithium reactions crystallized readily and were analytically pure after

one crystallization, whereas the products from the Grignard reactions usually required two crystallizations and afforded amorphous powders. The second cause may be that the organolithium reagent is inherently more efficient by virtue of being a more reactive reagent. The higher reactivity of the organolithium reagent posed a problem in that the resulting unhydrolyzed adduct is so reactive that isomerization to ketone appeared (see Figures 11 and 12 to compare infrared spectra) to be occurring as low as 80°C (refluxing benzene). The thermal energy required to effect isomerization of the alcohols is typically $>140^{\circ}\text{C}$. Even at room temperature, a mixture of alcohol and isomerized product (ketone) were produced using the organolithium reagent. The problem was solved by running these reactions in an ice bath. Further evidence of the highly energetic nature of the organolithium reagents as compared to the Grignards is that the addition to the cyclones occurred within approximately 15-30 minutes at 0°C with the former, while requiring two hours in refluxing benzene with the latter. Unfortunately, there were cases where the preferred organolithiums could not be used, due to the fact that the organolithium reagent itself would not form. These cases included the attempts to form organolithiums from *p*-dibromobenzene, *p*-bromochlorobenzene, and *m*-bromoanisole. Gilman⁷⁰ also has reported the failure of the dihalobenzenes to yield organolithium compounds. Interestingly, Gilman reports high yield formation from both *p*-bromoanisole (as was found in this work) and from *o*-bromoanisole, but does not report any results using *m*-bromoanisole.

The cases which fail to form organolithium compounds all possess, in addition to the halogen which is displaced, an electron-withdrawing group in the benzene ring, i.e., dibromobenzene (p-Br), chlorobromobenzene (p-Cl), and m-bromoanisole (m-OCH₃). The fact that the o- and p- isomers of bromoanisole form organolithium compounds⁷⁰ while the m- isomer does not eliminates the possibility that lack of formation is sterically derived. The effect is therefore due to the presence of a second electron-withdrawing substituent in the molecule.

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. _____
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>Reaction Mixture</u>
PHASE _____		RESOLUTION ☐		
REMARKS _____	OPERATOR _____	DATE _____		ORIGIN _____

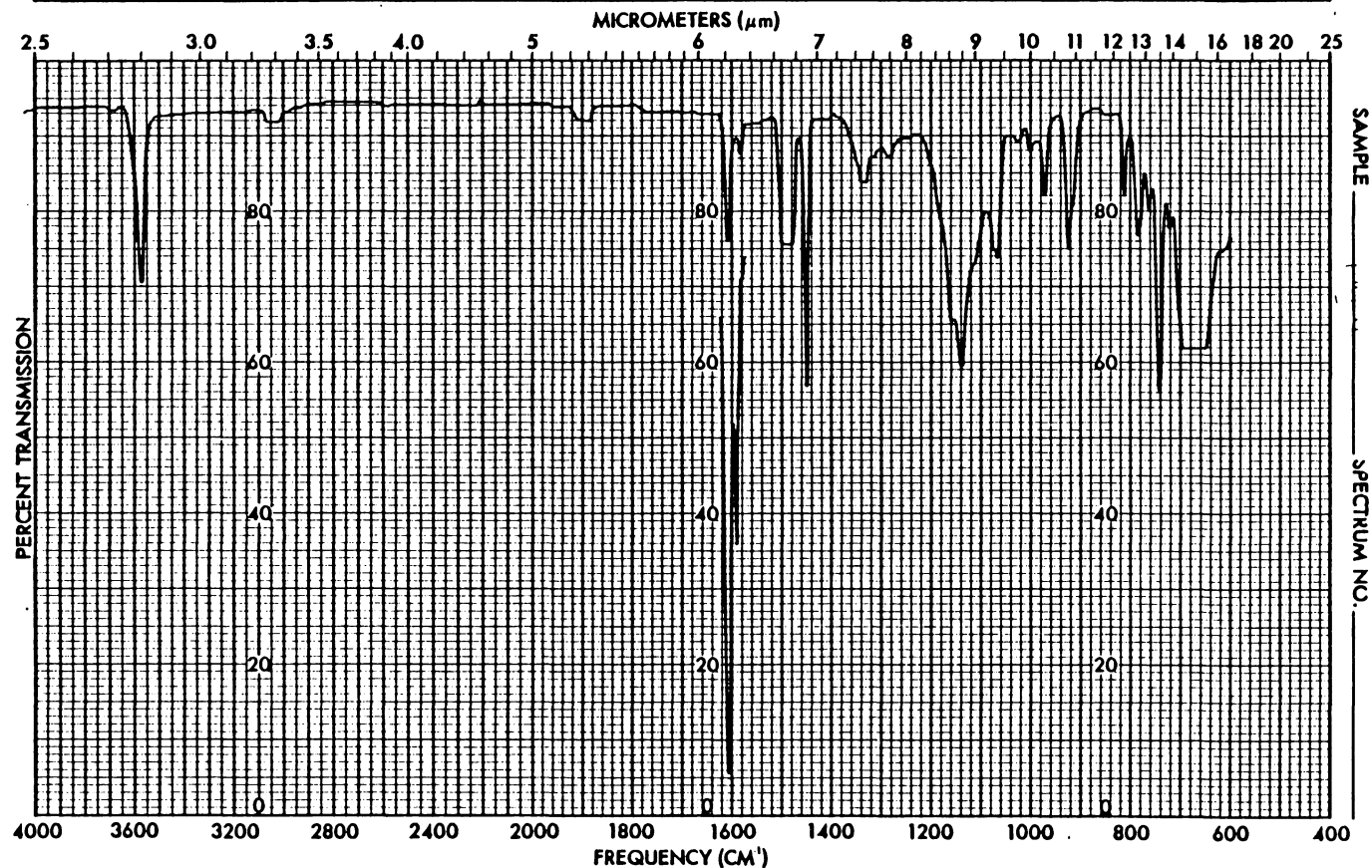


FIGURE 11. Infrared Spectrum of Reaction Mixture from Reaction of a Grignard Reagent with Tetracyclone at 80°C

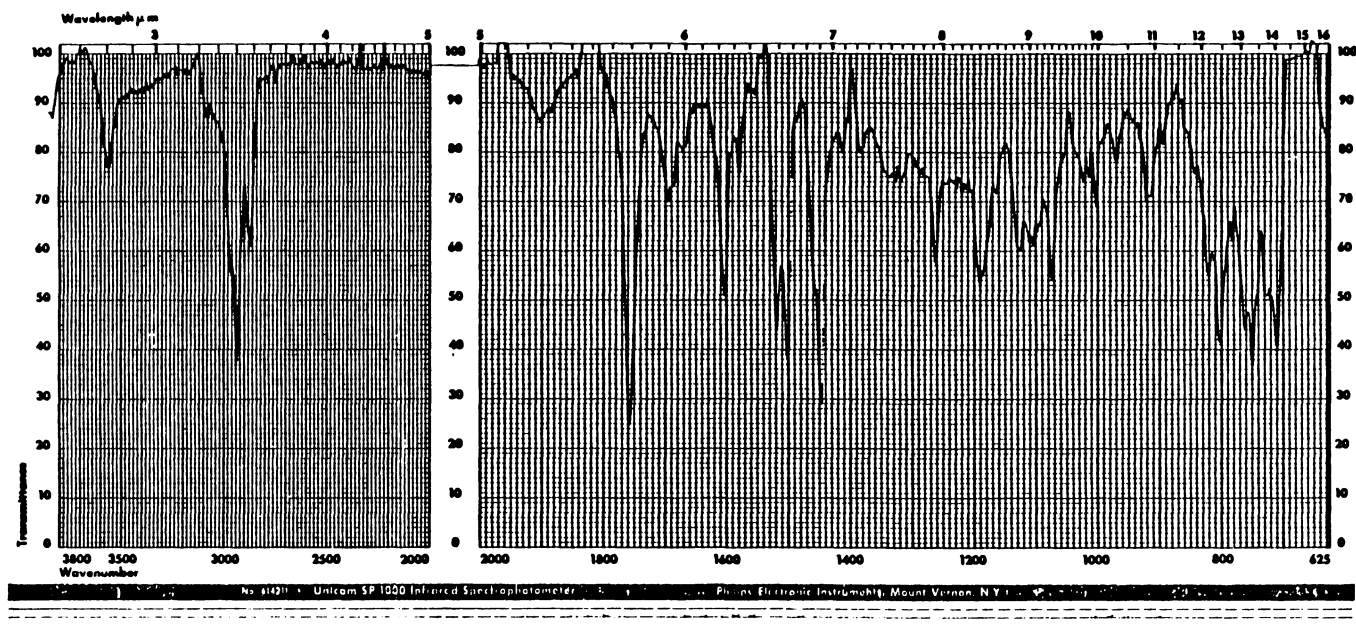
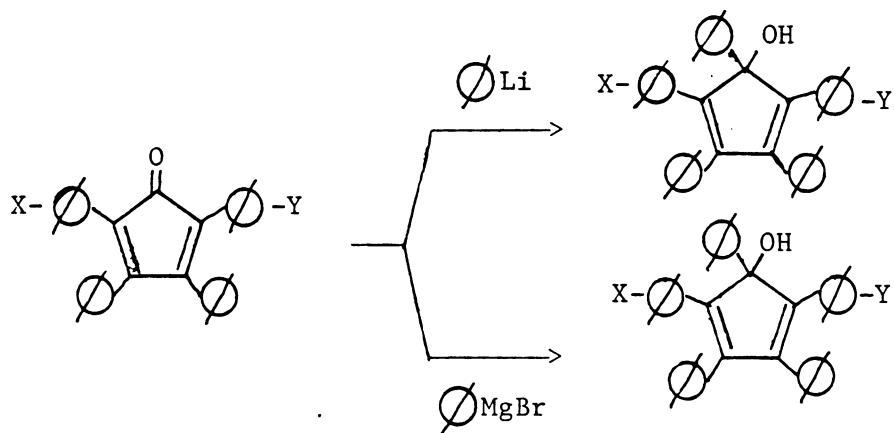


FIGURE 12. Infrared Spectrum of Reaction Mixture from Reaction of an Organolithium Reagent with Tetracyclone at 80°C

F. 2- and/or 5-(p- or m-Substituted Phenyl)cyclopentadienols

X = p-Br, p-Cl, H

Y = p-Me, p-MeO, m-MeO, p-Cl, p-Br, H

In the case of the 2- and/or 5-(p- or m-substituted phenyl) alcohols, again both the Grignard and organolithium reagents were used. The Grignards were of lower yield (60.0-78.4% recrystallized) than the organolithium reactions (73.8-87.9% recrystallized). The bimodal distribution can be attributed to the reasons outlined above for the 1-(p- or m-substituted phenyl) alcohols. This series of alcohols also demonstrated the apparent 1,2- vs. 1,4- addition competition (temperature dependent) when using the organolithium syntheses (see Scheme 4). At low temperature (0-5°C) the reaction is very rapid and clearly gives the 1,2- addition product. At room temperature, 1,2- and 1,4- addition compete as indicated by infrared spectroscopy. In addition to the alcohol (3550-3650cm⁻¹), varying amounts of conjugated ketone (1690-1710cm⁻¹) were produced (see Figure 13). This is not unreacted cyclone,

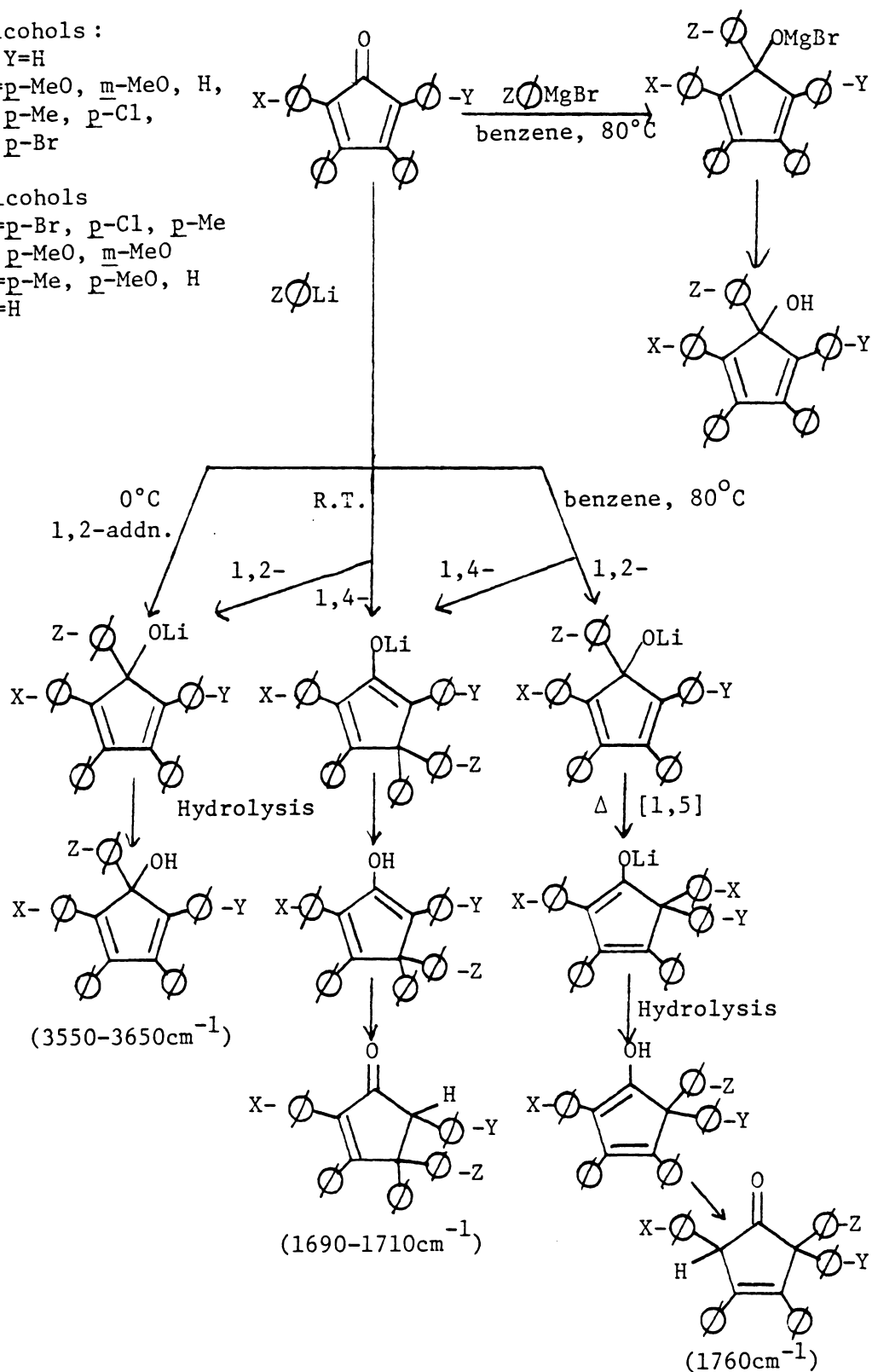
SCHEME 4

1-Alcohols :

X,Y=H

Z=p-MeO, m-MeO, H,
p-Me, p-Cl,
p-Br

2-Alcohols

X=p-Br, p-Cl, p-Me
p-MeO, m-MeO
Y=p-Me, p-MeO, H
Z=H

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>1</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>2,4,6-trinitrophenol</u>
PHASE <u>CCl₄ Benzene</u>		RESOLUTION ☐		
REMARKS _____	OPERATOR _____	DATE <u>7-1-5</u>		ORIGIN _____

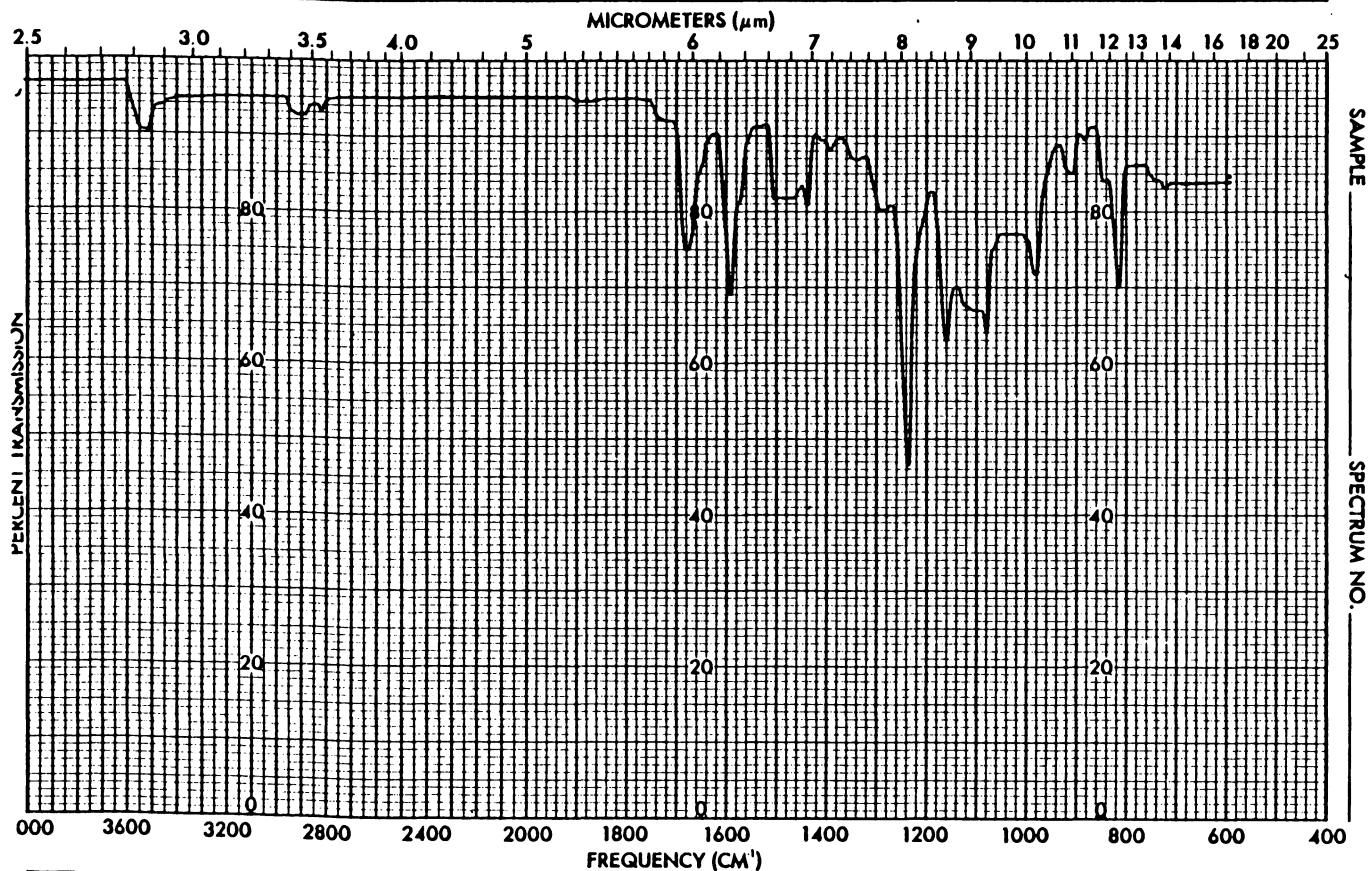


FIGURE 13. Infrared Spectrum of Reaction Mixture from Reaction of an Organolithium Reagent with a Substituted Tetracyclone at Room Temperature

which would be apparent visually by its deep purple color and has a C=O frequency of $1715\text{--}1720\text{cm}^{-1}$. In refluxing benzene (approximately 80°C), 1,2- and 1,4-additions compete once again. In this case, however, 1,2-addition leads not only to alcohol (upon hydrolysis) but also to unconjugated ketone (1760cm^{-1}) via thermal isomerization of the lithium salt of the alcohol. Youssef and Ogliaruso¹ in their initial studies on the parent pentaphenylcyclopentadienol system proved that the magnesium bromide salt of the alcohol will thermally rearrange in refluxing isoamyl ether (173°C). This author is the first to report the thermally induced sigmatropic rearrangement of a lithium alcohol salt.

Of all the alcohols synthesized (both series), only one was unique in its behavior. The 2-(m-methoxyphenyl) alcohol produced uncrystallizable oils as products from both the Grignard and organolithium reactions. At low temperature the organolithium reagent gave clean reaction to produce the desired alcohol, as indicated by IR, NMR and mass spectrometry. From the Grignard, however, a mixture of products was obtained, identified by IR as the alcohol, unreacted cyclone, and a third band in the carbonyl region at 1740cm^{-1} .

See Figure 14.

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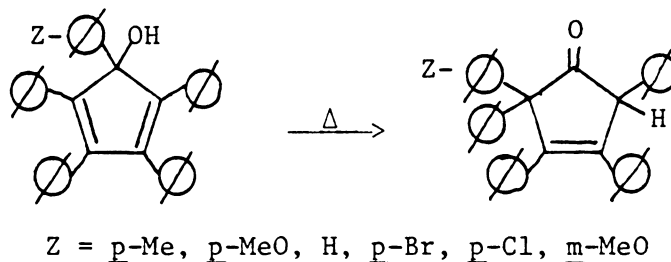
PERKIN-ELMER

CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>1</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>2-(m-Methoxyphenyl) Alc</u>
PHASE <u>Benzene</u>	<u>8 min</u>	RESOLUTION ☐		<u>Synthesis</u>
REMARKS <u>Polystyrene</u>	OPERATOR _____	DATE <u>9-19-82</u>	ORIGIN <u>Crignard</u>	

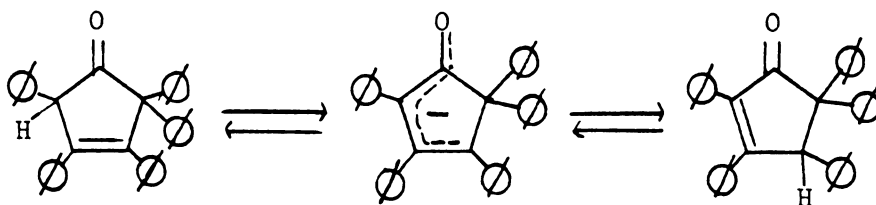


FIGURE 14. Infrared Spectrum of Product from Reaction of 2-(m-Methoxyphenyl)cyclone with Phenylmagnesium Bromide at 80°C

G. Thermal Isomerization of 1-(p- or m-Substituted Phenyl)cyclopentadionols



The 2-(p- or m-substituted phenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-ones were prepared by the thermally induced [1,5]-sigmatropic phenyl rearrangement of the corresponding 1-(p- or m-substituted phenyl)cyclopentadienol.² The primary reason for synthesis of this series of ketones was for use in the analysis of the two-product mixtures resulting from thermal isomerization of the 2- and/or 5- (p- or m-substituted phenyl)cyclopentadionols, since in each case they represent one of the two possible products. The conversion is quantitative, taking from 12-24 hours for completion. Unfortunately, the reaction is highly sensitive to base or peroxides,⁴ the result being conversion of the desired 2-(p- or m-substituted phenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one (hereafter referred to as "unconjugated ketones") to the 2-(p- or m-substituted phenyl)-2,3,4,5-tetraphenyl-2-cyclopenten-1-one (hereafter referred to as "conjugated ketones").



Thus great caution must be observed in excluding these contaminants from glassware, alcohol, and the decane used as solvent. Cutshaw⁶⁸ observed that even when care was taken, approximately five percent of the product from isomerization was conjugated ketone. This situation was also observed by this author in the cases where the alcohol used had been produced via the Grignard synthesis. Surprisingly, if the alcohol used was produced via the organolithium reaction, conjugated ketone by-product was virtually undetectable (see Figures 15 and 16 to compare infrared spectra). Comparison of the alcohols from both reagents spectroscopically and by analysis indicated they were identical. The most plausible explanation is that the greater strength of the oxygen-magnesium bond as compared to the oxygen-lithium bond allows a sufficient amount of the magnesium salt of the alcohol to carry through hydrolysis, work-up and crystallization, decomposing at high temperature and compromising the results of the isomerization. For this reason, alcohols prepared from the organolithium synthesis were preferred for studies of the isomerization. If conjugated ketone was present, it could be removed by chromatography on silica gel. Using carbon tetrachloride as eluent, small percentages of conjugated

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CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>Fig 15</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>2-(pBaϕ)-5-(pMeϕ) Alcho</u> <u>JS₆₄</u>
PHASE <u>CCl₄</u>	<u>8 min</u>	RESOLUTION ☐		<u>8.5 hrs</u>
REMARKS <u>1602, 1583 μ off by 20 μm</u>	OPERATOR _____	DATE <u>9-23-82</u>	ORIGIN <u>(Li)</u>	

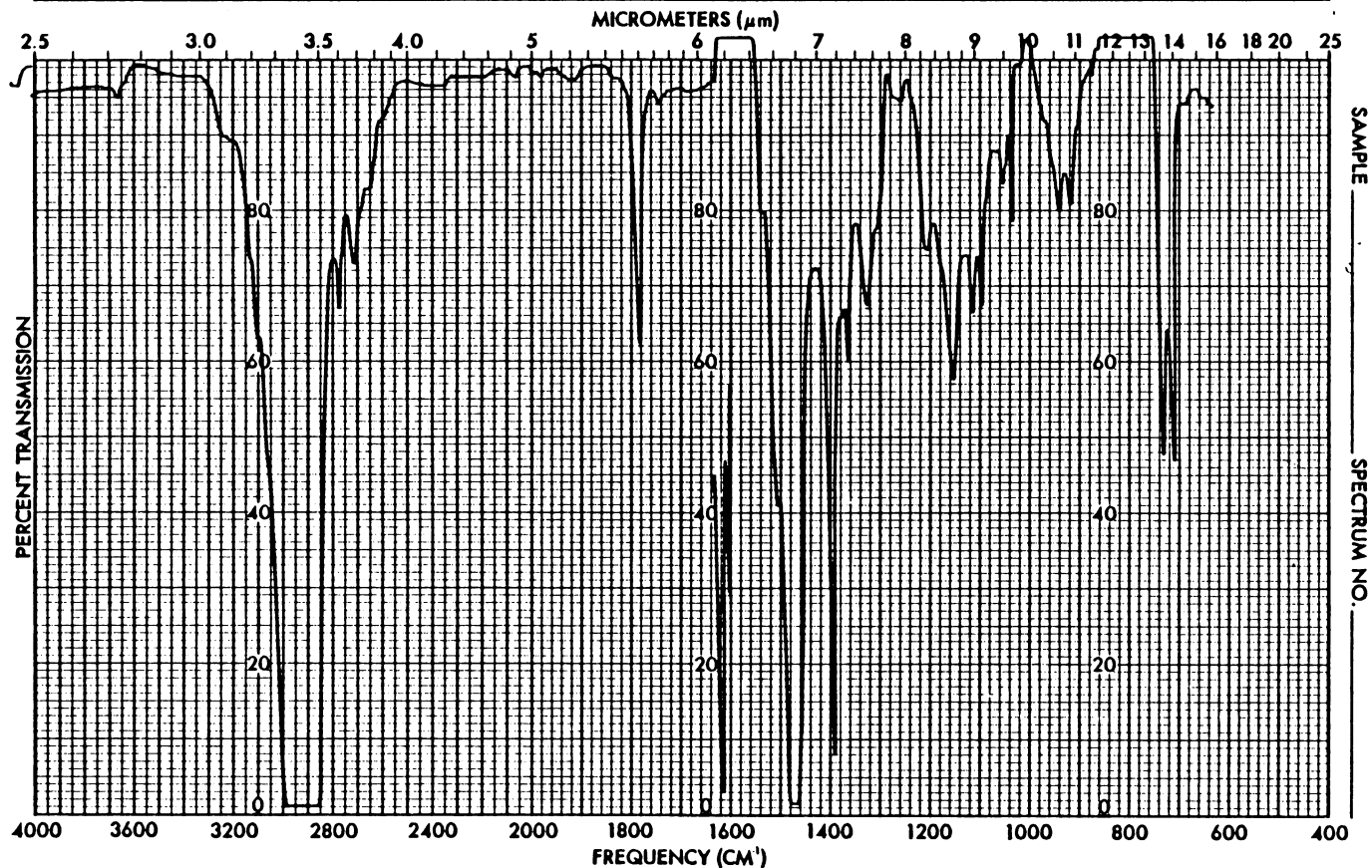


FIGURE 15. Infrared Spectrum of Isomerization Product from an Organolithium-Produced Alcohol

NO. 007-1493

PERKIN-ELMER

CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>3</u> <u>Fig 16</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE <u>2 (Br) 5 (he) Isoin</u>
PHASE <u>CCl₄</u>		RESOLUTION ☐		<u>16 hours</u>
REMARKS <u>1602, 1583</u>	OPERATOR <u>8mm</u>	DATE <u>92382</u>	ORIGIN <u>Magnesium</u>	

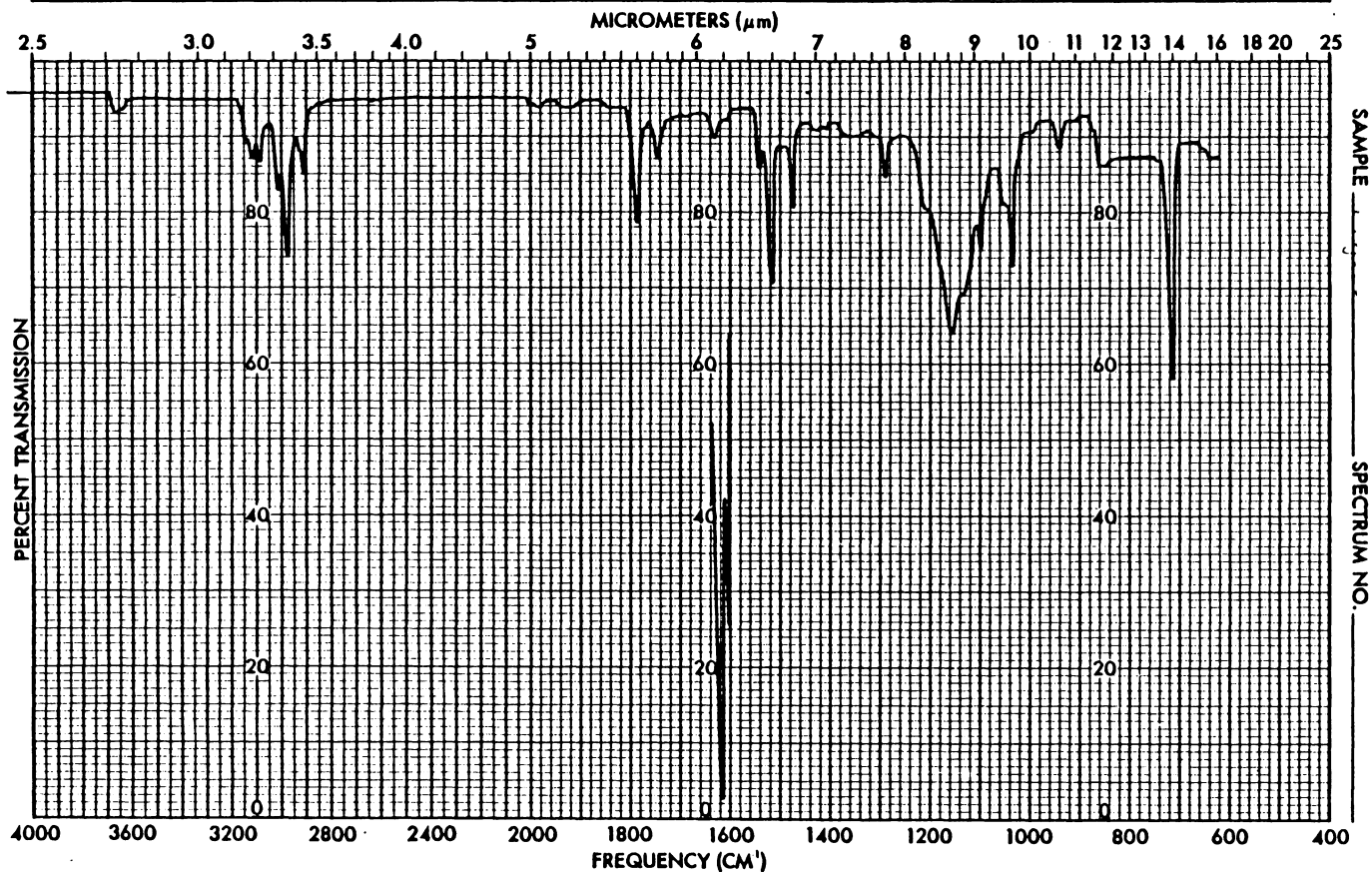
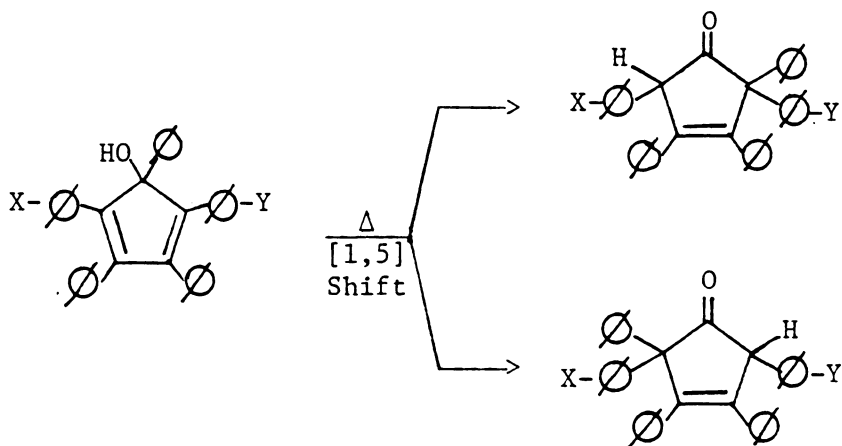


FIGURE 16. Infrared Spectrum of Isomerization Product from a Grignard Reagent-Produced Alcohol

ketone remain adsorbed on the column allowing pure unconjugated product to be obtained. This was followed by crystallization from benzene/petroleum ether to produce tiny, well-formed white crystalline granules. Chromatography followed by crystallization produced ketones of a superior quality to those obtained from crystallization alone. Cutshaw⁶⁸ using crystallization alone reported obtaining 2-(p-bromophenyl)-2,3,4,5-tetraphenyl-3-cyclopenten-1-one as a powder, mpt. 157-170°C whereas using the procedure outlined above this author obtained the same compound as white granules, mpt. 166.5-168.0°C.

H. Thermal Isomerization of 2- and/or 5-(p- or m-Substituted Phenyl)-cyclopentadienols



X = p-Br, p-Cl, H

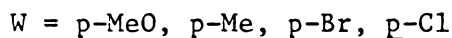
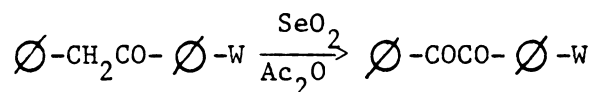
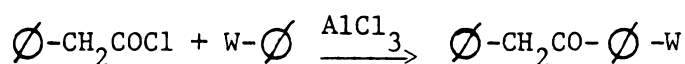
y = p-Me, p-MeO, m-MeO, p-Br, p-Cl

The crux of this dissertation was characterization of the transition state of the [1,5]-sigmatropic phenyl rearrangement known to occur in the cyclopentadienol system. Toward this end, a Hammett series of

2- and/or 5-(p- or m-substituted phenyl)cyclopentadienols were synthesized and thermally rearranged. The rearrangements were performed in refluxing decane (173°C) and required from eight to ten hours to reach completion. It is interesting to note the bimodal distribution of reaction lengths when comparing this series to the 1-(p-substituted phenyl)alcohol series, the latter requiring 12 to 24 hours to reach completion. No explanation is offered as to why the activation energy of one series should differ markedly from the other. The alcohols were prepared from the organolithium reaction, since these produced virtually 100 percent conversion to unconjugated ketone. The Grignard produced alcohols were inferior (although acceptable) for isomerization in that small quantities (approximately five percent) of the conjugated ketone isomer were produced. Two products could be formed by isomerization of each 2- and/or 5-(p- or m-substituted phenyl)alcohol, resulting from migration of phenyl toward carbon two or carbon five of the five-membered ring. Since examination of the product mixture was the crucial point of this dissertation, the cleaner (as regards conversion to unconjugated ketone) organolithium-derived alcohols were used for isomerization. Furthermore, since the only compounds present after isomerization are the products of interest and perhaps less than five percent starting alcohol and conjugated ketones, the reaction mixture was not altered in any manner other than stripping the solvent. The resulting tar or oil was perfectly acceptable for the NMR study and oxidation study. Furthermore, chromatography or crystallization would seriously compromise the results in this case,

since there would be no way to determine whether each of the two possible products were equally recoverable. If, for example, a small percentage of one was irreversibly adsorbed on a column, the ratio of the two would be altered and the results worthless. Conversion is quantitative, as was the case for the 1-(p- or m-substituted phenyl)-alcohol conversions. The products were identified by NMR, mass spectrometry, infrared spectroscopy, and CHN analysis. Furthermore, the product mixtures were identified qualitatively by gas chromatographic analysis of their oxidative degradation products. See the NMR results and oxidation results discussion for the details of these aspects. See Figure 15 for a representative infrared spectrum.

I. 4-Substituted Benzils



The expected products of the oxidative degradation of the two-product mixture resulting from the isomerization of the 2- and/or 5-(p- or m-substituted phenyl)alcohols are a series of substituted benzils and benzophenones. The 4-substituted benzophenones were readily available but the 4-substituted benzils had to be synthesized. The procedure used was adapted from that of Allen and Barker⁸³ and involved

Friedel-Crafts acylation of substituted phenyl with phenylacetyl chloride using aluminum chloride as catalyst. The crude substituted desoxybenzil was in general not purified but oxidized directly to the desired benzil. The overall yields for the two-step sequence ranged from 36.0 to 74.0 percent. The low yield step for every case was the Friedel-Crafts reaction; the selenium dioxide oxidation afforded yields of 93.8-97.4 percent. The only difficulty was removal of selenium metal from the product. In some cases hot filtration through a fine pore büchner funnel was sufficient while other runs required vacuum distillation of the benzil to separate it from the finely divided metal. Crystallization was achieved by dissolution in hot aqueous ethanol with the exception of 4-methylbenzil, which was purified by vacuum distillation to give a liquid product. See Figure 17 for a representative infrared spectrum.

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PERKIN-ELMER

CONCENTRATION _____	SCAN MODE	ACCY. ☐	SURVEY ☐	SPECTRUM NO. <u>3001</u>
THICKNESS _____		HI ENERGY ☐	CAL. ☐	SAMPLE _____
PHASE _____		RESOLUTION ☐		_____
REMARKS _____	OPERATOR _____	DATE _____		ORIGIN _____

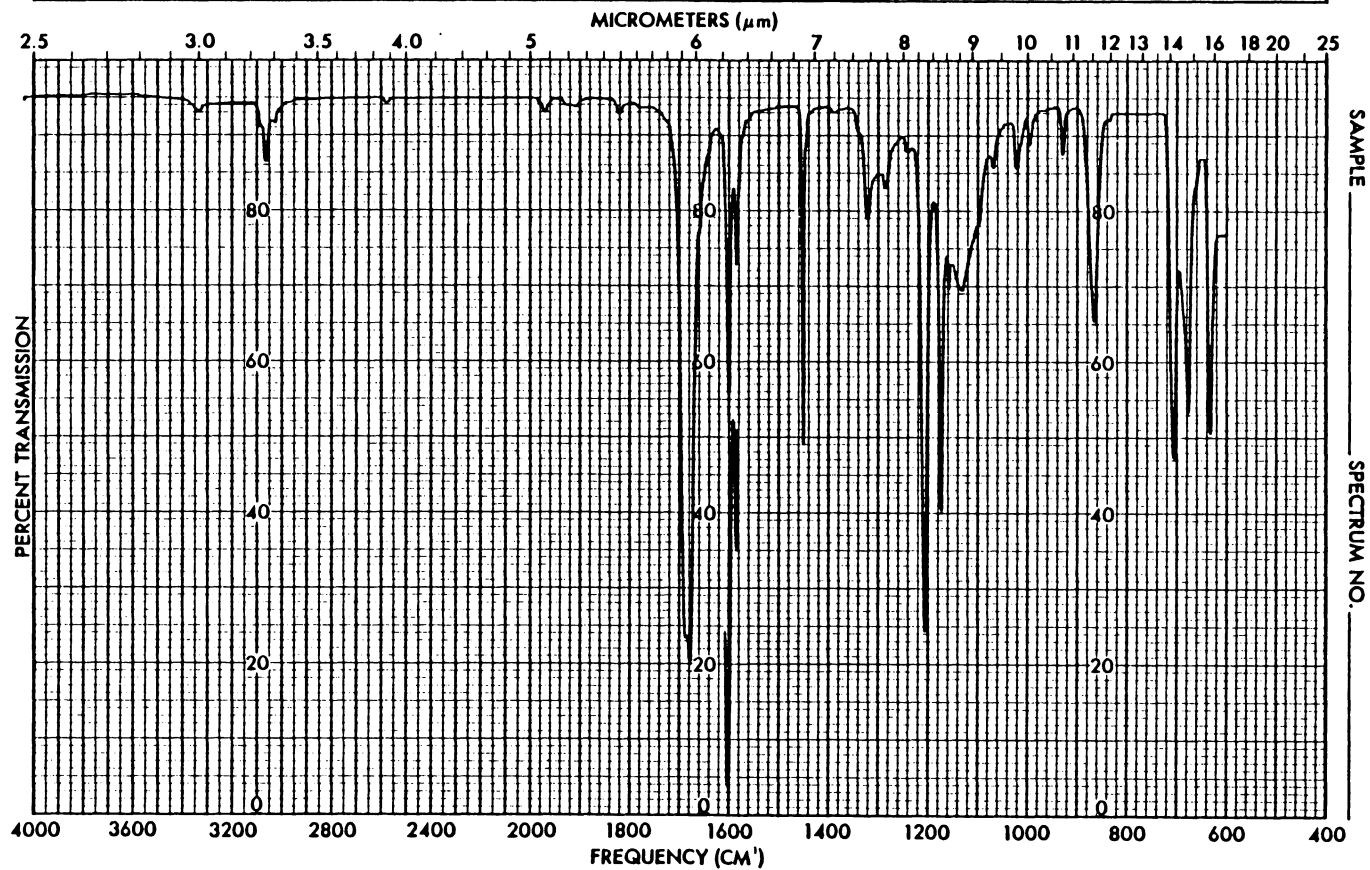
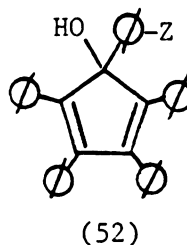
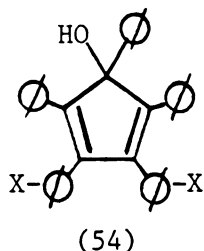


FIGURE 17. Infrared Spectrum of a Representative Benzil

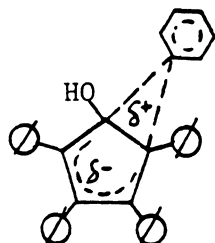
SECTION B. RESULTS AND DISCUSSION

Part 2. NMR and GC Analysis of the Thermal Rearrangements

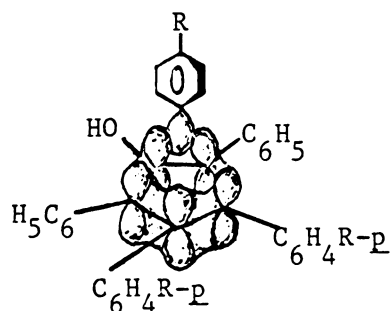
The goal of this project has been the characterization of the nature of electronic effects in the thermal [1,5]-sigmatropic phenyl rearrangement known to occur in the pentaphenylcyclopentadienol system.¹ Earlier studies examined the effect of phenyl substituents upon the π -backbone (54),² and phenyl substituents in the migrating group (52).² These kinetic studies indicated that while differences



in rates were observed, the effects were minimal and linear free energy relationships were not observed. The conclusion was that the rearrangement proceeds via a strictly neutral concerted mechanism, with no contribution from the originally proposed partially charge separate transition state. As a final step in the characterization of the rearrangement, the subject of this dissertation was undertaken. A series of 2- and/or 5-(p- or m-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ols were synthesized and thermally rearranged to investigate the effect, if any, of electron donating and releasing substituents located at the migration terminus.

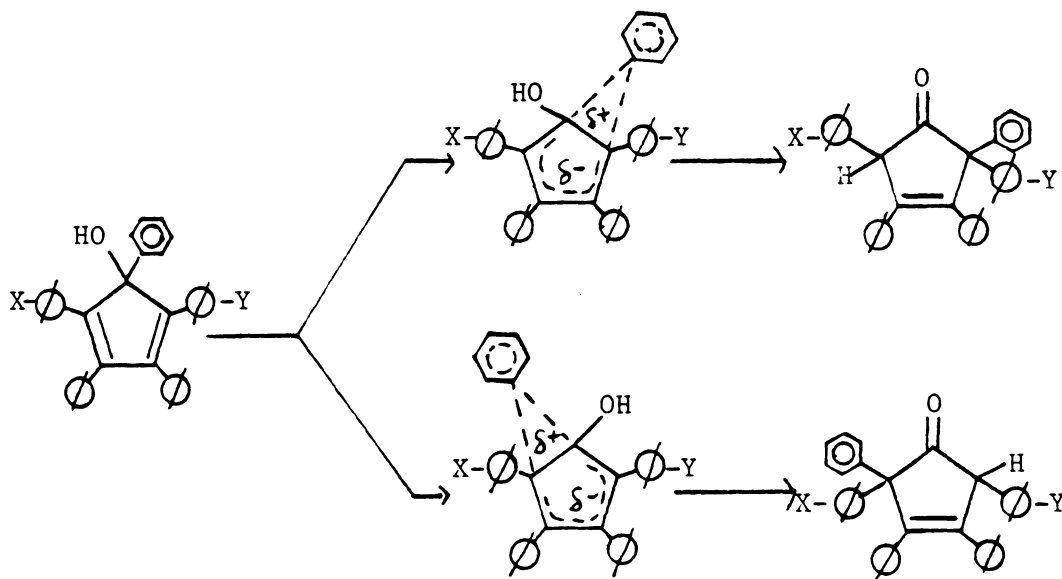


Partially Charge Separated
t-State



Transition State Devoid of
Charge Separation

In a system such as this, with more than one migration pathway available, substituents should interact with the transition state in a manner which would influence the direction of migration. Considering the initially hypothesized transition state when Y is electron-

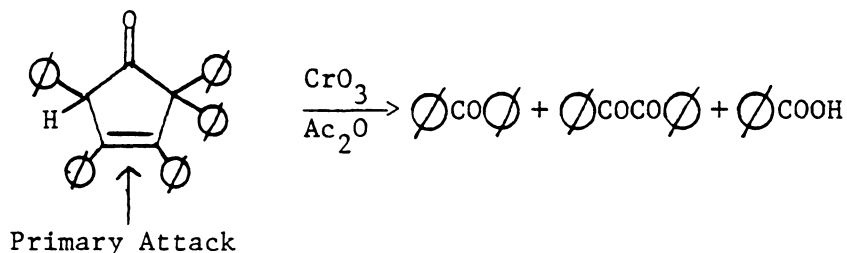


donating (p-Me, p-MeO) and X=H, pathway one leading to form (60) should be preferred since the Y-substituent is stabilizing the δ^+ in the transition state relative to unsubstituted phenyl. If the migrating phenyl group migrates toward the side where X=H, the electron-donating effect of the Y-substituent is forced to interact with a δ^- charge (Path 2), destabilizing the transition state. When Y is electron-withdrawing (p-Br, p-Cl, m-MeO) and X=H, path 2 is preferred since path 1 would produce a transition state in which the electron-withdrawing substituents would exacerbate a δ^+ charge. These effects should be even more pronounced for the cases where X=Br, Y=Me and X=Cl, Y=p-MeO since path 1 allows the electron-donating Y-substituent to stabilize a δ^+ in the transition state, while simultaneously the electron-withdrawing X-substituent is stabilizing a δ^- charge. An attempt by phenyl to migrate by path 2 in this case would require a transition state in which both the δ^+ and δ^- charges are exacerbated by the electron effects of the substituents. The rearrangement in this system is not considered to be reversible. Therefore parallel path first order kinetics leading from reactant to the two products are observed, and therefore the product distribution ratio at $t=\infty$ is a measure also of the ratio of the relative rates of path 1 and path 2. It is this product distribution and its correlation (or lack thereof) to the Hammett values of the substituents that forms the basis of this dissertation.

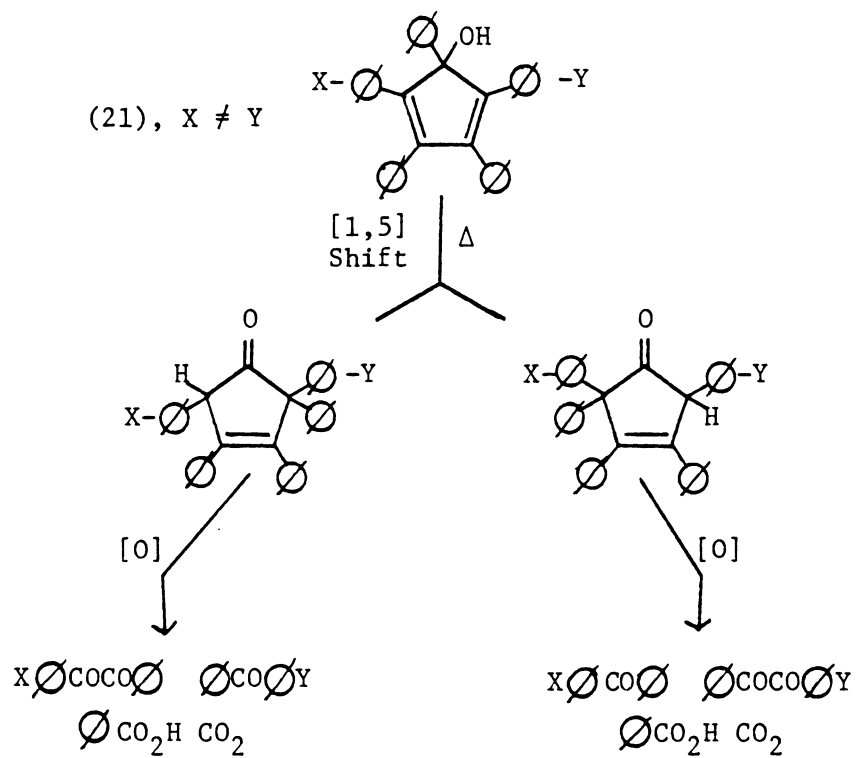
If the product distribution correlated with the nature of the substituents as described above, support would be given to the

δ -charge separated transition state hypothesis. If no preference is shown, i.e., the product ratio is approximately 50/50, then the strictly neutral concerted rearrangement concluded by Perfetti and Oldaker² is favored.

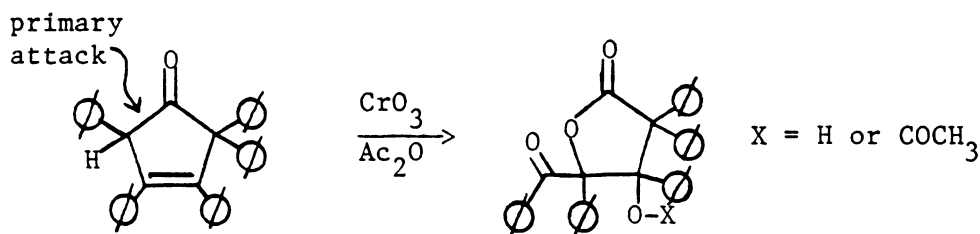
The initial approach, as outlined in earlier sections of this dissertation, was to develop a method for the oxidative degradation of the cyclopentenone ring. Such a method was developed by this author. The intent, as shown schematically in Scheme 1, was to degrade the expected two-product mixture of the thermal rearrangement, and from the ratio of the secondary (oxidation) products, generate the ratio of the primary (isomerization) products to each other. It was found that chromium trioxide in acetic anhydride would cleave the cyclopentenone ring to give substituted benzils, substituted benzo-phenones, and benzoic acid in a yield of 40 to 42 percent, presumably from primary attack at the double bond. The alternate route, primary attack at the enolic site appears to compete with the former route, producing a lactonic product which resists further degradation.



SCHEME 1



X and/or Y = *p*-MeO, *p*-Me, *m*-MeO, H, *p*-Cl, *p*-Br



The fact that a 40 to 42 percent yield of the degradation products is routinely obtained allows this oxidative method (when applied to the substituted cases) to be used to determine whether one, the other, or both of the expected isomerization products were formed from a particular rearrangement. The products of each thermal rearrangement were (in addition to other analyses) oxidized as described and the products identified by comparison with the retention times of the pure compounds, and by spiking with the pure compounds. In each case the four expected products were observed. Thus, the method was used qualitatively to corroborate other analyses. Also, the fact that the four expected products (benzils and benzophenones) were observed in the seven substituted cases serves to support the cleavage pattern proposed in section A of this dissertation. Unfortunately, since the identity of the other 58 to 60 percent of the oxidation products were not clearly identified, this author hesitates to use the method as a means of quantitating the product ratio. In addition, the multiple extractions involved in the work-up of the oxidations would compromise

quantitation by this method, since the solubilities of the products may differ dependent upon the substituents and the ratios thus could be altered.

The second approach to the analysis of the thermal rearrangement products was by NMR spectroscopy. This method was successful and was used to determine the product ratios (see Table 11). Peak assignments and quantitation will be discussed individually for each case before being summarized.

For the mono-substituted cases, one of the two products was readily available. Rearrangement of a 1-(p- or m-substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol produces the same product

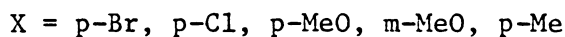
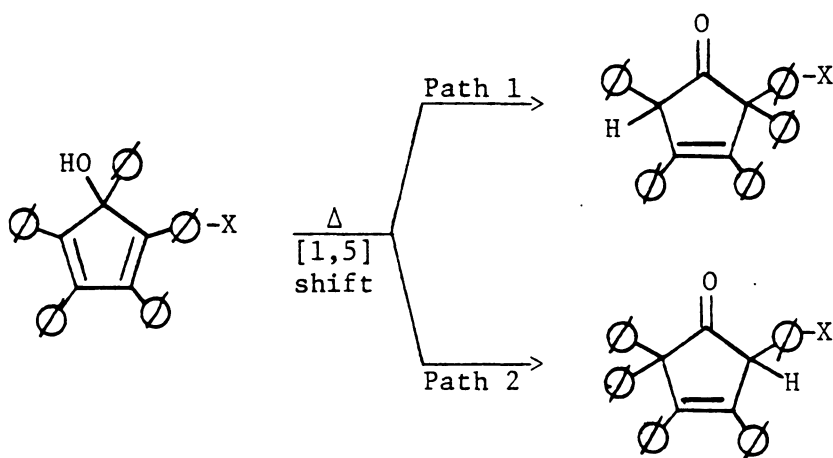
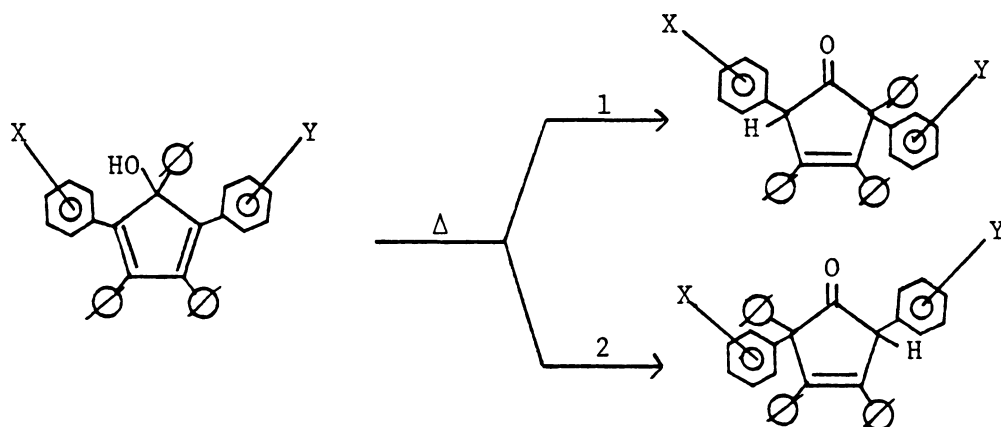


TABLE 11

Thermal Isomerization of 2-(p- or m-Substituted
Phenyl)Cyclopentadienols

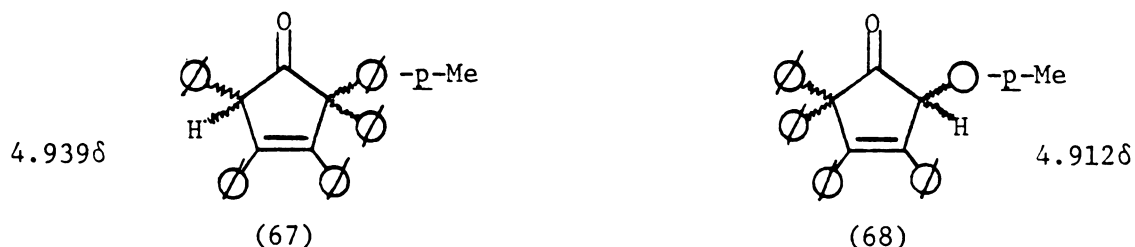


Cyclopentadienol (X=) (Y=)		Pathway 1 Product (%)*	Pathway 2 Product (%)*
H	<u>p</u> -Br	51.8	48.2
H	<u>p</u> -Cl	59.8	40.2
H	<u>p</u> -MeO	56.0	44.0
H	<u>p</u> -Me	49.6	50.4
H	<u>m</u> -MeO	52.2	47.8
<u>p</u> -Me	<u>p</u> -Br	57.0	43.0
<u>p</u> -MeO	<u>p</u> -Cl	42.7	57.3

*Analysis by 200MHz Proton NMR

as that of path 1, with phenyl and substituted phenyl on the same side. These pure samples were synthesized, the NMR spectrum assigned, and then used to spike the product mixture of the rearrangement of the 2-(p- or m-substituted phenyl) alcohols in order to confirm assignments.

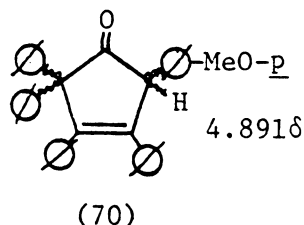
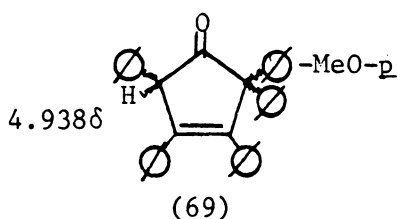
The rearrangement of the 2-(p-methylphenyl) alcohol produced two peaks in the region of interest, at 4.912 δ and at 4.939 δ . The pure sample of (67) indicated a single peak in this region at 4.939 δ , thus assigning the peaks. At 200MHz, the 5.36 Hz separation of these peaks



was excellent (see Appendix C) and integration produced a product ratio of 50.4 percent structure (68) and 49.6 percent structure (67). Following integration of the product mixture, the same NMR tube was spiked with a pure sample of (67). The higher frequency peak increased in area, confirming the assignment. The proton in (68) is at lower frequency than in (67), possibly due to shielding provided by p-methylphenyl as opposed to phenyl attached to the same carbon.

The rearrangement of the 2-(p-methoxyphenyl) alcohol produced two peaks in the region of interest, located at 4.891 δ and 4.938 δ . The

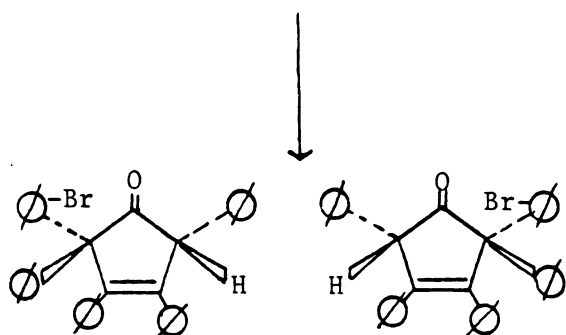
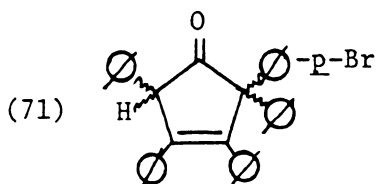
pure sample of (69) indicated a single peak at 4.938δ , thus assigning the peaks. Separation of the signals in this case was exceptional



(9.27 Hz), and again integration was a simple matter. The product ratios were 56.0 percent structure (69) and 44.0 percent structure (70). The sample was spiked with pure (69), increasing the intensity of the peak at 4.938δ and confirming the assignment. In this case, as with *p*-methyl, the proton in (70) appeared at higher field relative to (69), as expected due to the slightly greater shielding by *p*-methoxyphenyl as opposed to phenyl attached to the same carbon.

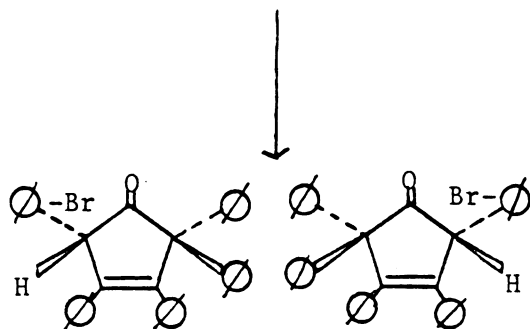
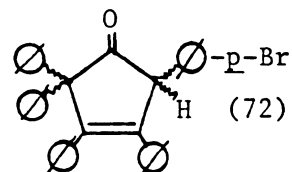
The rearrangement of the 2-(*p*-bromophenyl) alcohol produced two peaks in the region of interest, one at 4.947δ and one at 4.931δ . However, in this case the pure sample of (71) also produced two peaks, at 4.947δ and 4.931δ , whose intensities were 50/50. Examination of the stereochemistry of these compounds readily explains the observed NMR spectra. The compound (71) exists as two pairs of enantiomers, diastereomerically related to each other. This is always the case for the product in which phenyl has migrated toward the side bearing substituted phenyl. The diastereomeric relationship is the cause of

Migration of Phenyl
Toward Substituted Phenyl

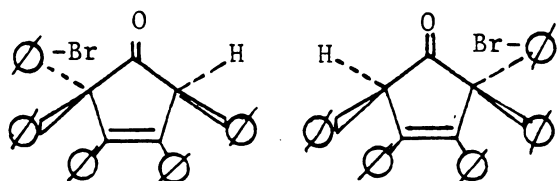


Two Pair of Enantiomers

Migration of Phenyl
Toward Unsubstituted Phenyl



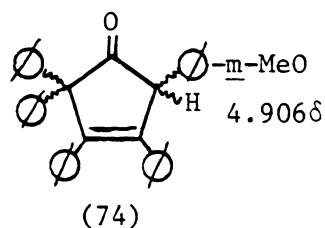
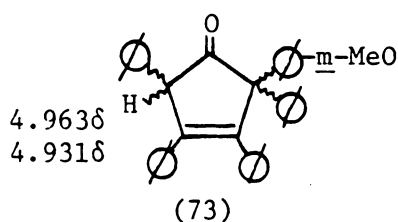
One Pair of Enantiomers



the two proton signals seen for this structurally pure compound. In regard to the first two cases, *p*-methyl and *p*-methoxy, these pairs of diastereomers appeared as a single peak, clearly a case of accidental equivalence. Unequivocal assignments were still able to be made for

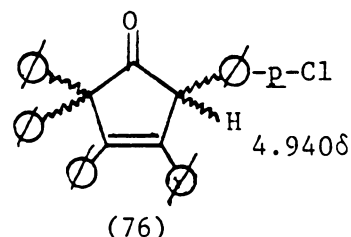
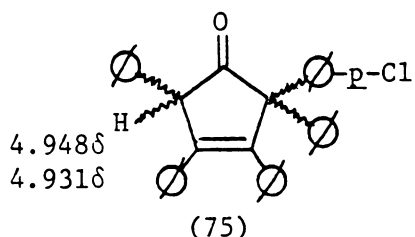
the p-Br case. Since the mixture of diastereomers of (71) produces two peaks of equal intensity, then the more intense peak of the two observed for the product mixture contains (72). Thus the assignments are (71), 4.947 δ and 4.931 δ , and (72), 4.931 δ . Integration was accomplished by algebraically removing the peak area for (71) from the peak area containing (71) and (72). The ratios determined were 48.2 percent for structure (72) and 51.8 percent for structure (71).

The rearrangement of the 2-(m-methoxyphenyl) alcohol produced three peaks, at 4.963 δ , 4.931 δ , and 4.906 δ . In this case, all three peaks corresponding to the two pair of enantiomers of structure (73) and the pair of enantiomers of structure (74) were resolved. A pure sample of (73) revealed two peaks, at 4.963 δ and 4.931 δ . Thus the peaks were assigned, and following integration the tube was spiked



with (73), increasing the area of the two higher frequency peaks and confirming the assignment. Integration gave a product ratio of 52.2 percent of structure (73) and 47.8 percent of structure (74).

The rearrangement products from the isomerization of the 2-(p-chlorophenyl) alcohol indicated three peaks, at 4.948 δ , 4.931 δ , and

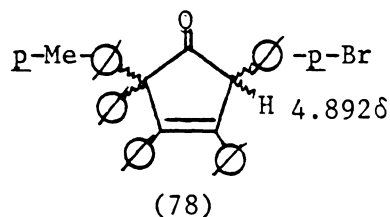
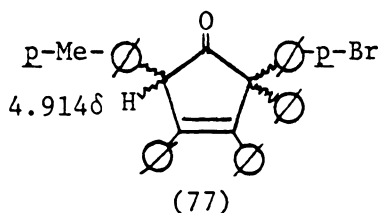


4.940 δ . A pure sample of (75) contained only the peaks at 4.948 δ and 4.931 δ , thus making the assignments shown above. Following integration the sample was spiked with a pure sample of (75) and the assignments thus confirmed. The ratio, to a best approximation, is 59.8 percent of structure (75) and 40.2 percent of structure (76). The integration in this case is not as reliable as in the other four mono-substituted cases, since the peaks involved here overlap to a degree.

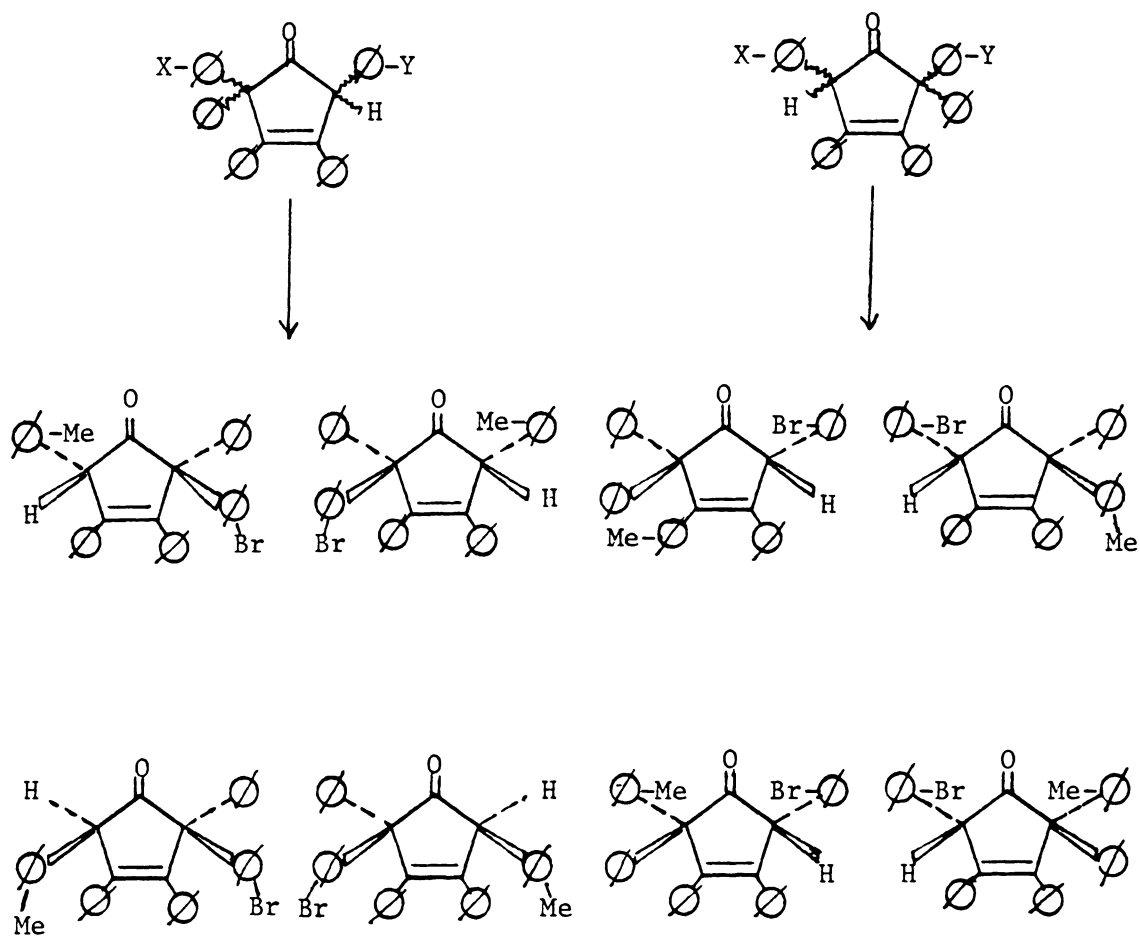
For the two di-substituted cases, no pure sample of either of the two possible products were available, since they could not be produced by simple isomerization of a 1-(p- or m-substituted phenyl) alcohol. Therefore peak assignments were made using the data acquired from the five mono-substituted cases, and confirmed by the oxidation products.

The rearrangement products from the isomerization of the 2-(p-bromophenyl)-5-(p-methylphenyl) alcohol contained two major peaks in the region of interest, at 4.914 δ and 4.892 δ . Assignments were made based on gas chromatographic analysis of the oxidation products, which

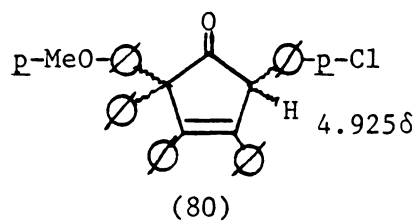
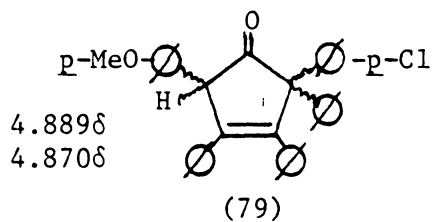
indicated bromobenzophenone to be the dominant peak. Thus, structure (77) was assigned 4.914 δ and structure (78) was assigned 4.892 δ .



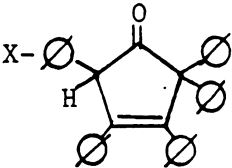
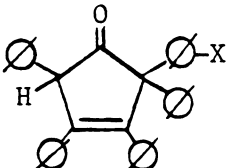
If shielding or deshielding were considered only in terms of whether the proton were adjacent to *p*-methylphenyl (77) or *p*-bromophenyl (78), one may have made the opposite assignment. However, it has been shown⁷⁹ that simple Hammett substituent parameters are not always able to be correlated to NMR shifts. In addition, the gas chromatographic analysis clearly indicated (77) to be the dominant structure. Expansion for integration revealed a small peak at higher frequency (4.932 δ), which could be assigned to either (77) or (78). If assigned to (77) the product ratio is 70 percent for (77) and 30 percent for (78). If assigned to (78), however, the ratio becomes 57 percent (77) and 43 percent (78). The latter assignment is consistent with the findings in the mono-substituted cases. In the disubstituted cases, both migration pathways produce two pairs of enantiomers, as shown below. Only three peaks were observed on the di-substituted compounds, however. This may be attributable to accidental equivalence as observed in the *p*-MeO and *p*-Me mono-cases.



The rearrangement products from the 2-(p-chlorophenyl)-5-(p-methoxyphenyl) alcohol had three well-resolved peaks in the region of interest, at 4.925 δ , 4.889 δ , and 4.870 δ .



From the data compiled for the mono-cases, the following table was devised.

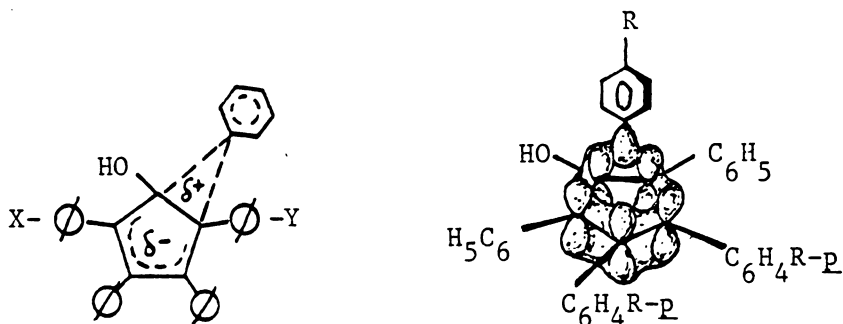
	<u>p-Cl</u>	<u>p-MeO</u>
	4.940 δ	4.890 δ
	4.946 δ 4.931 δ	4.937 δ

In the mono-cases, when the proton was adjacent to p-chlorophenyl, the chemical shift was 4.940 δ ; when adjoined to carbon bearing p-methoxyphenyl, it appeared at 4.890 δ . Thus, tentatively the lowfield peak was assigned to structure (80), and the peaks at 4.889 δ and 4.870 δ to structure (79). Also, in the mono-chloro case, when p-chlorophenyl was on the opposite side of the five-membered ring from the proton, the diastereomers had a separation of 3.17 Hz. In the above assignment of (79) and (80), the two lower frequency peaks have a separation of 3.9 Hz, a comparable value. This assignment was corroborated by the gas chromatographic analysis of the oxidation products, which indicated methoxybenzophenone to be predominant over chlorobenzophenone. The ratios from this assignment are 57.3% of structure (80) and 42.7% of structure (79).

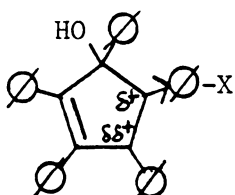
In summary, of the assignments made for the structured isomers, the mono-substituted cases are unequivocal. A pure sample of one of the two products was available for this purpose. Also, the integrations of all of the mono-substituted cases were clear-cut, with the exception of mono-chloro in which the peaks overlapped to a degree. In this context, it should be noted that the mono-chloro integration showed the widest deviation (40.2/59.8) from 50/50 of all the mono-cases, which may be attributable to the lesser reliability of its integration. The disubstituted cases could not be unequivocally assigned, and based upon the chemical shifts of the mono-cases or the gas chromatographic analysis of the oxidation products, a case could be made for either of two possible assignments. Either assignment however, in both the disubstituted cases led to a ratio of approximately 57/43 or approximately 43/57. The assignments were corroborated by the gas chromatographic analysis of the oxidation products.

The NMR data compiled for the seven cases examined is summarized in Table 11.

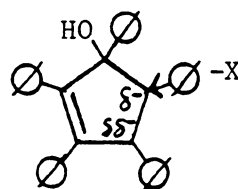
In terms of the initially proposed transition states, the following conclusions may be made. If the transition state was partially



charge separated as shown above, it would be expected that the product distributions would be skewed toward path 1 when Y=p-Me, p-MeO and toward path 2 when Y=m-MeO, p-Br, p-Cl in the mono-substituted cases, in accordance with their Hammett σ_p values. The experimental facts clearly show no such trend, with the mono-cases all falling within the range of 56 to 44 percent for the product ratios, or 59.8 to 40.2 percent if the less accurate mono-chloro integration is included. Along this line, the disubstituted cases where X=electron donating and Y=electron withdrawing should have shown roughly double the skewing of the mono-cases. Clearly, both disubstituted compounds integrated to a ratio range of approximately 57-43 percent. On the basis of these findings, it must be concluded that electronic effects due to variation of the substituents at the migration terminus (either C₂ or C₅) are not a factor in the observed sigmatropic phenyl rearrangement. The possibility exists, that due to the steric constraints of this system, any resonance interaction between the substituents on phenyl and the transition state is precluded. This does not rule out contributions due to inductive effects, and if any slight kind can be visualized it is that direction of migration was toward the more δ^+ carbon (in the ground state molecule). For example, p-Br, p-Cl, p-MeO, and m-MeO are inductively electron withdrawing, and the migrations in these cases ranged from 51.8-59.8 percent toward the + carbon and 48.2-40.2 percent toward the opposite side. The polarization of bonds in the reactant alcohol due to the inductive effect of the substituents is depicted below. The only case where



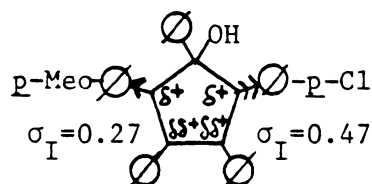
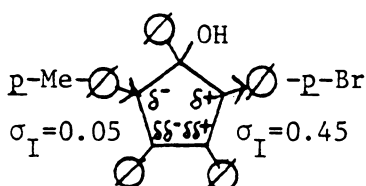
X = m-MeO, p-MeO, p-Br, p-Cl



X = p-Me

migration away from the substituent was greater (50.4% vs. 49.6%) was p-methyl. As indicated, the alcohol in this case would have bonds partially polarized in a manner opposite to that of the other four substituents.

For the disubstituted cases, the molecules would be polarized as below:



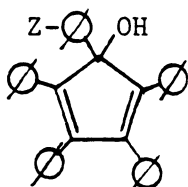
For the mono-methyl case, migration away from p-methyl was slightly favored (50.4% away, 49.6% toward); for mono-bromo migration toward p-bromo was favored slightly (51.8% toward, 48.2% away). These two preferences complement each other in the disubstituted methyl-bromo alcohol, and the product distribution is enhanced (57% toward p-bromo, 43% toward p-methyl). The five mono-cases and the

methyl-bromo alcohol follow this slight correlation to the inductive effect of the substituent. Based on this one would predict that in the methoxy-chloro alcohol, where both substituents are inductively withdrawing, that the substituents would give a fairly even distribution of the two products, with the skewing, if any, toward migration of the phenyl toward $p\text{-Cl}$ ($\sigma_I=0.47$) rather than toward $p\text{-MeO}$ ($\sigma_I=0.27$). The result was just the opposite--a slight preference for migration toward $p\text{-MeO-phenyl}$ (57% vs. 43%). The distribution in this case is the one exception.

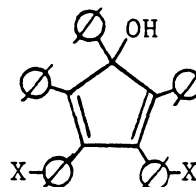
The effects are at best, marginal; at worst, imaginary. The product distributions are so close as to be virtually equivalent. In addition, the small differences do not correspond to the differences in the σ_I values of the substituents. If a true inductive effect is being felt, then $p\text{-Br}$ ($\sigma_I=0.45$)⁸⁰ should have shown a greater distribution than either $p\text{-MeO}$ ($\sigma_I=0.23$) or $p\text{-Me}$ ($\sigma_I=-0.05$). This was not the case. Thus, it appears that any slight differences in the product ratios for the seven cases are random, and not attributable to either resonance or inductive effects due to the substituents at C_2 and C_5 .

These results confirm those of Oldaker and Perfetti,² who studied the effects of phenyl substituents in the migrating group (52) and the π -backbone (54) respectively. In both of these cases, random, small variations were observed in the kinetics of the thermal rearrangements which could not be correlated to any of the usual

parameters, i.e., σ_p , σ_p^+ , σ_p^0 , σ_p^- , σ_n , and σ_m^+ . Oldaker and Perfetti's work led them to the conclusion that the [1,5]-sigmatropic



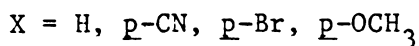
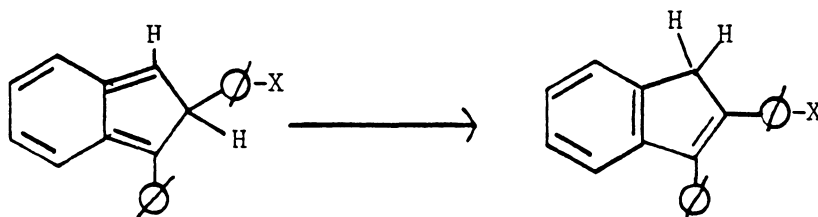
(52)



(54)

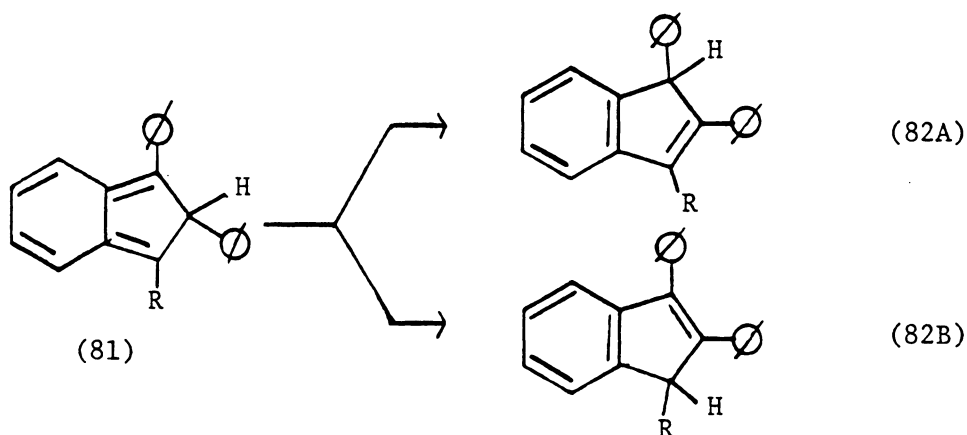
phenyl rearrangement in this system is strictly neutral with no contribution by any of the charge-separated transition states which have been proposed in other systems.^{45,46,47,48}

No neutral phenyl sigmatropic rearrangement has yet afforded a linear free energy relationship. In only one case of a neutral non-phenyl sigmatropic rearrangement has a linear free energy relationship been observed. McCullough^{53, 81} obtained a value of $\rho = -0.6$ for a plot of $\log k$ vs. σ_n for the [1,5] thermal hydrogen migration in the isoindene system.



The small negative slope of the line indicates that the transition state for the [1,5]-shift is electron deficient at the migration origin and that the migrating hydrogen has a slight "hydride" character.

A study by Pettit and Wilson⁸² on the thermal 1,5 -sigmatropic hydrogen shift in another isoindene system is perhaps an even better analogy to the system studied in this dissertation. In this system,



<u>R=</u>	<u>(82A)%</u>	<u>(82B)%</u>
H	25	75
CH ₃	11	79
CO ₂ CH ₃	100	--
COCH ₃	85	15
CN	100	--

hydrogen (in a manner analogous to the subject of this dissertation) could migrate toward either side, i.e. toward phenyl or toward the R-substituent. The results are striking. In all cases a distinct preference was shown, and was correlated by the authors to the relative π -donor or π -acceptor ability of substituent-R vs. phenyl. The

product distribution indicated a distinct propensity for hydrogen to migrate toward the site bearing the stronger σ -donor. The author was also able to correlate the direction of migration with the substituent dependent symmetry of the highest occupied molecular orbital of a model for the transition state. The fact that a distinct product distribution was seen in this case serves to corroborate the conclusion that in the pentaphenyl cyclopentadienol system, the substituents do not interact to a significant degree with the transition state, due to the inability to adopt a conformation amenable to transmission of electronic effects through resonance, and the distance involved between the *p*- or *m*-substituent and the migration terminus precludes inductive interaction.

In conclusion, only one sigmatropic rearrangement has yielded a linear free energy relationship, and while electronic effects have been observed by a number of investigators,^{45,47,72,81,82} a unifying, comprehensive theory has yet to be put forth. It is the conclusion of this author that the pentaphenylcyclopentadienol system represents one end of a spectrum of reactivity, a strictly neutral concerted sigmatropic rearrangement in which electronic effects play little or no role.

SUMMARY

In conclusion, four major points should be emphasized.

First, the original oxidation of 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one with diacetyl chromate by Allen and VanAllan⁶ has been corrected by this author. While Allen and VanAllan reported benzoic acid (no yield given) and benzophenone (60 percent) as the only products, the results within this dissertation clearly demonstrate an equimolar production of benzophenone, benzil, and benzoic acid in a 39 to 42 percent overall yield.

Secondly, the reaction of 13 tetracyclones with substituted and unsubstituted phenyllithium was compared to the reaction of the same tetracyclones with the corresponding Grignard reagents. The lithium reagents were found to be superior in the following aspects:

1. Faster reaction time.
2. Higher yield.
3. The alcohols produced were more readily crystallized.
4. Subsequent isomerization of the lithium-produced alcohols afforded only the desired "unconjugated" ketones.

The third point, and a major discovery, was the demonstration of the first reported thermal sigmatropic rearrangement of a lithium alcohol salt. It was found that at temperatures as low as 80°C, the 1,2-addition of phenyllithium or substituted phenyllithium to the tetracyclones afforded, upon hydrolysis, not the alcohol but rather the unconjugated ketone which results from the [1,5]-sigmatropic phenyl shift known to occur in this system.

Finally, the main goal of this effort was realized, that of determination of the ratios of the two-product mixtures produced by thermal isomerization of the 2- and/or 5- (p- or m-substituted phenyl)-1,3,4-triphenyl-2,4-cyclopentadien-1-ols. From this data the transition state of the [1,5]-sigmatropic phenyl migration known to occur in this system has been characterized as strictly neutral and concerted in accordance with earlier studies.² The electronic effects of various substituents at the migration terminus were found to have no discernible or predictable effects upon direction of phenyl migration.

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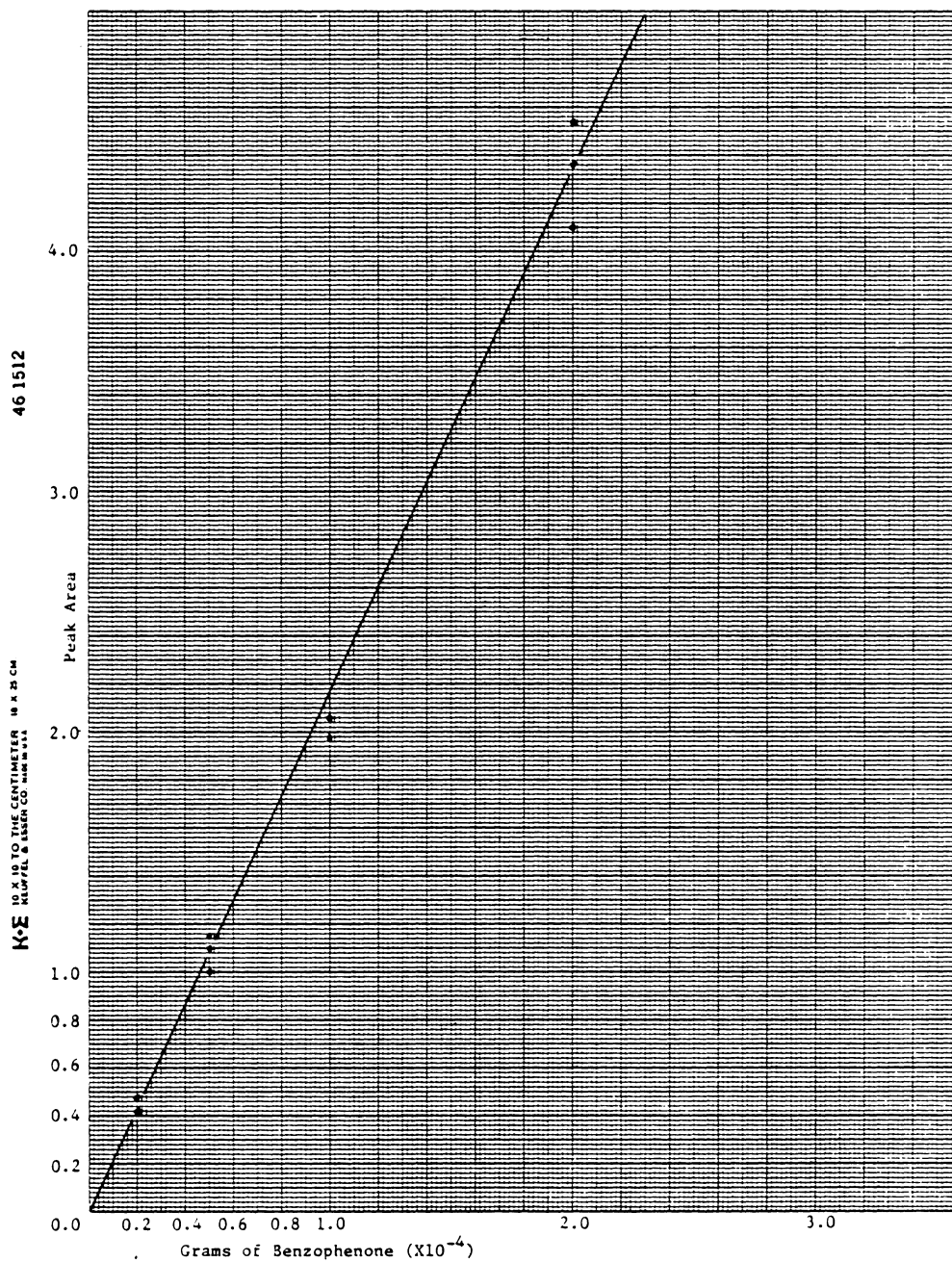
APPENDIX A

Calibration Curves

I. Benzophenone

<u>2ul Injections</u> <u>(%)</u>	<u># grams</u> <u>(X10⁻⁴)</u>	<u>Peak Height</u> <u>(cm)</u>	<u>Peak Width</u> <u>at 1/2 Height</u> <u>(cm)</u>	<u>Area</u> <u>(cm²)</u>
1.0	0.2	1.60	0.30	0.48
1.0	0.2	1.35	0.31	0.42
1.0	0.2	1.60	0.30	0.48
2.5	0.5	4.4	0.23	1.01
2.5	0.5	4.6	0.24	1.10
2.5	0.5	5.0	0.23	1.15
5.0	1.0	8.6	0.23	1.98
5.0	1.0	9.8	0.21	2.06
5.0	1.0	9.4	0.22	2.06
10.0	2.0	14.1	0.29	4.09
10.0	2.0	15.6	0.28	4.37
10.0	2.0	15.1	0.30	4.53

Conditions: 6' x 1/8" stainless steel column. Packing, 5% OV-275 on Chromosorb W. Injector temp., 205°C; Column temp., 230°C; Detector temp., 250°C. FID detector.

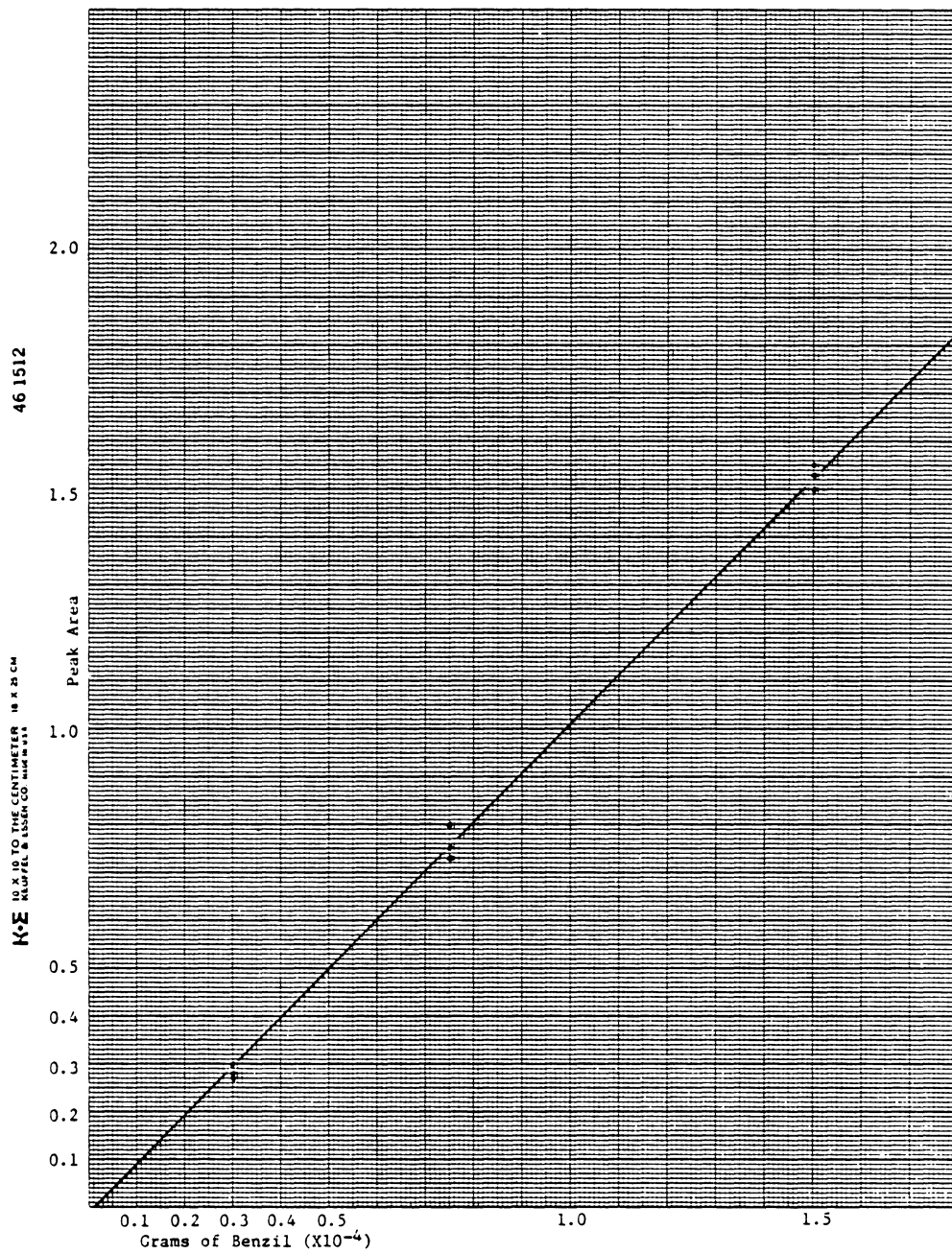


APPENDIX A (Cont'd)

II. Benzil

<u>2ul Injections</u> <u>(%)</u>	<u># grams</u> <u>(X10⁻⁴)</u>	<u>Peak Height</u> <u>(cm)</u>	<u>Peak Width</u> <u>at 1/2 Height</u> <u>(cm)</u>	<u>Area</u> <u>(cm²)</u>
1.0	0.3	1.5	0.18	0.28
1.0	0.3	1.5	0.20	0.30
1.0	0.3	1.5	0.18	0.27
2.5	0.75	3.4	0.22	0.75
2.5	0.75	3.48	0.22	0.80
2.5	0.75	3.4	0.21	0.73
5.0	1.5	5.1	0.30	1.53
5.0	1.5	5.1	0.304	1.55
5.0	1.5	5.0	0.30	1.50

Conditions: 6' x 1/8" stainless steel column. Packing, 5% OV-275 on Chromosorb W. Injector temp., 240°C; Detector temp., 250°C; Column, 220°C. FID detector.



APPENDIX B

- 1a. Equimolar Control Mixture of Benzophenone, Bromobenzophenone, Benzil, and Bromobenzil. See experimental for conditions.
- 1b. Products from Oxidative Cleavage of the Rearrangement Product from the Thermal Rearrangement of 2-(p-Bromophenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol.
- 2a. Equimolar Control Mixture of Benzophenone, Chlorobenzophenone, Benzil, and Chlorobenzil. See experimental for conditions.
- 2b. Products from Oxidative Cleavage of the Rearrangement Products from the Thermal Rearrangement of 2-(p-Chlorophenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol.
- 3a. Equimolar Control Mixture of Benzophenone, Methylbenzophenone, Benzil, and Methylbenzil. See experimental for conditions.
- 3b. Products from Oxidative Cleavage of the Rearrangement Products from the Thermal Rearrangement of 2-(p-Methylphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol.
- 4a. Equimolar Control Mixture of Benzophenone, Benzil, p-Methoxybenzophenone, and p-Methoxybenzil. See experimental for conditions.
- 4b. Products from Oxidative Cleavage of the Rearrangement Products from the Thermal Rearrangement of 2-(p-Methoxyphenyl)-1,3,4,5-Tetraphenyl-2,4-Cyclopentadien-1-ol.
- 5a. Equimolar Control Mixture of Benzil and Benzophenone.
- 5b. Products from Oxidative Cleavage of the Rearrangement Products from the Thermal Rearrangement of 2-(m-Methoxyphenyl)-1,3,4,5-Tetraphenyl-

2,4-Cyclopentadien-1-ol.

6a. Equimolar Control Mixture of Methylbenzophenone, Bromobenzophenone, Methylbenzil, and Bromobenzil.

6b. Products from Oxidative Cleavage of the Rearrangement Products from Thermal Rearrangement of 2-(p-Methylphenyl)-5-(p-Bromophenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol.

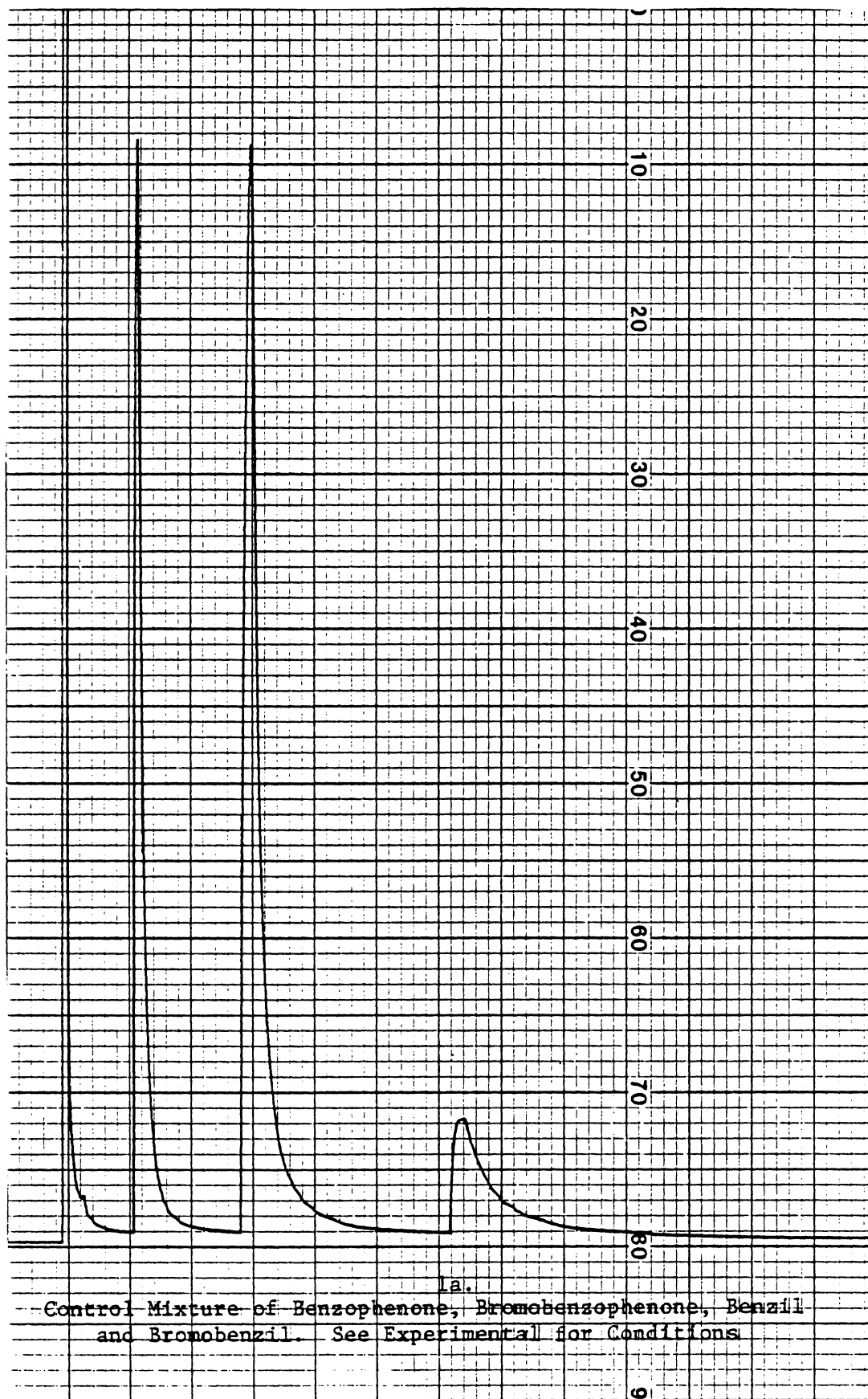
7a. Equimolar Control Mixture of Chlorobenzophenone, Chlorobenzil, Methoxybenzophenone, and Methoxybenzil.

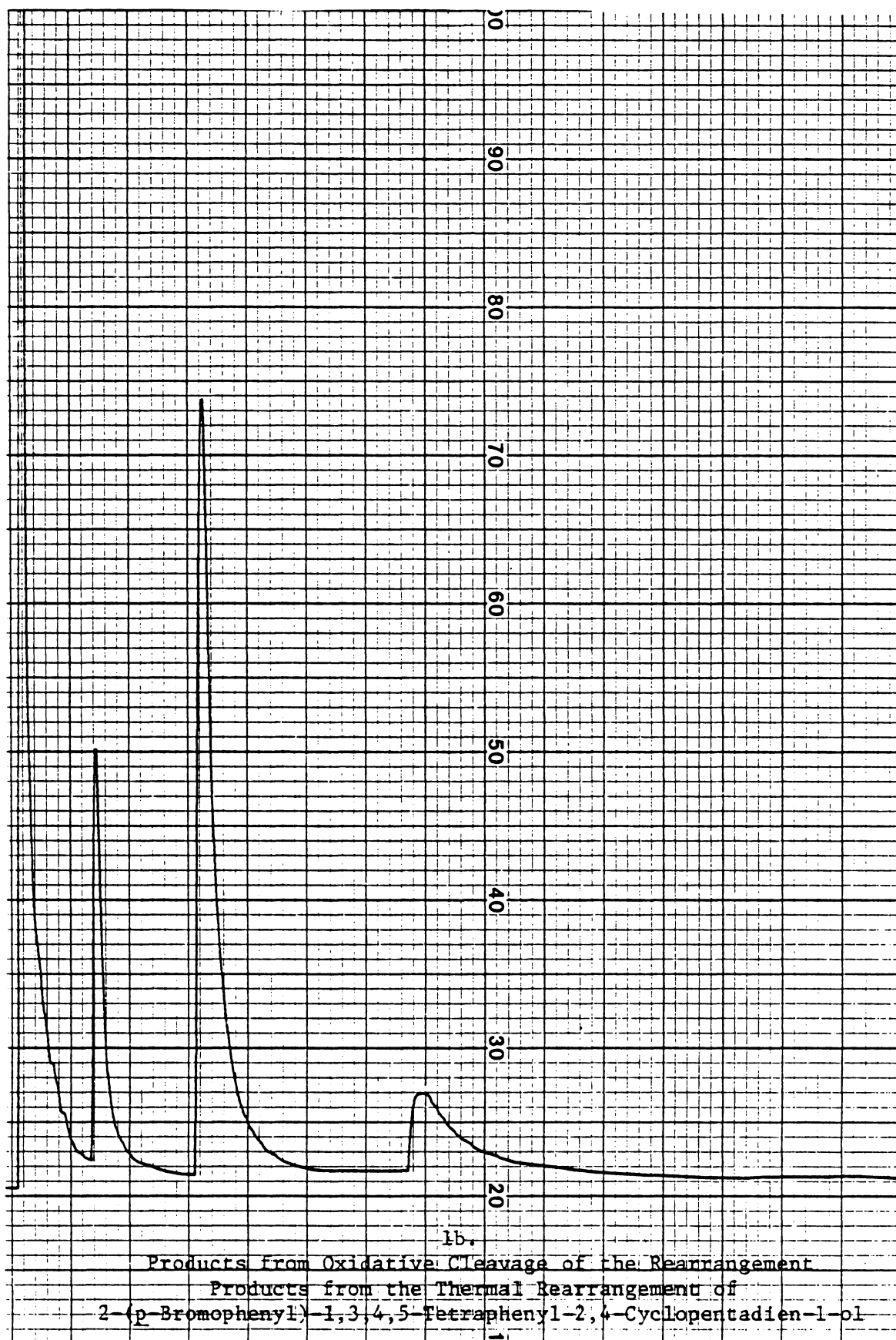
7b. Products from Oxidative Cleavage of the Rearrangement Products from Thermal Rearrangement of 2-(p-Methoxyphenyl)-5-(p-Chlorophenyl)-1,3,4-Triphenyl-2,4-Cyclopentadien-1-ol.

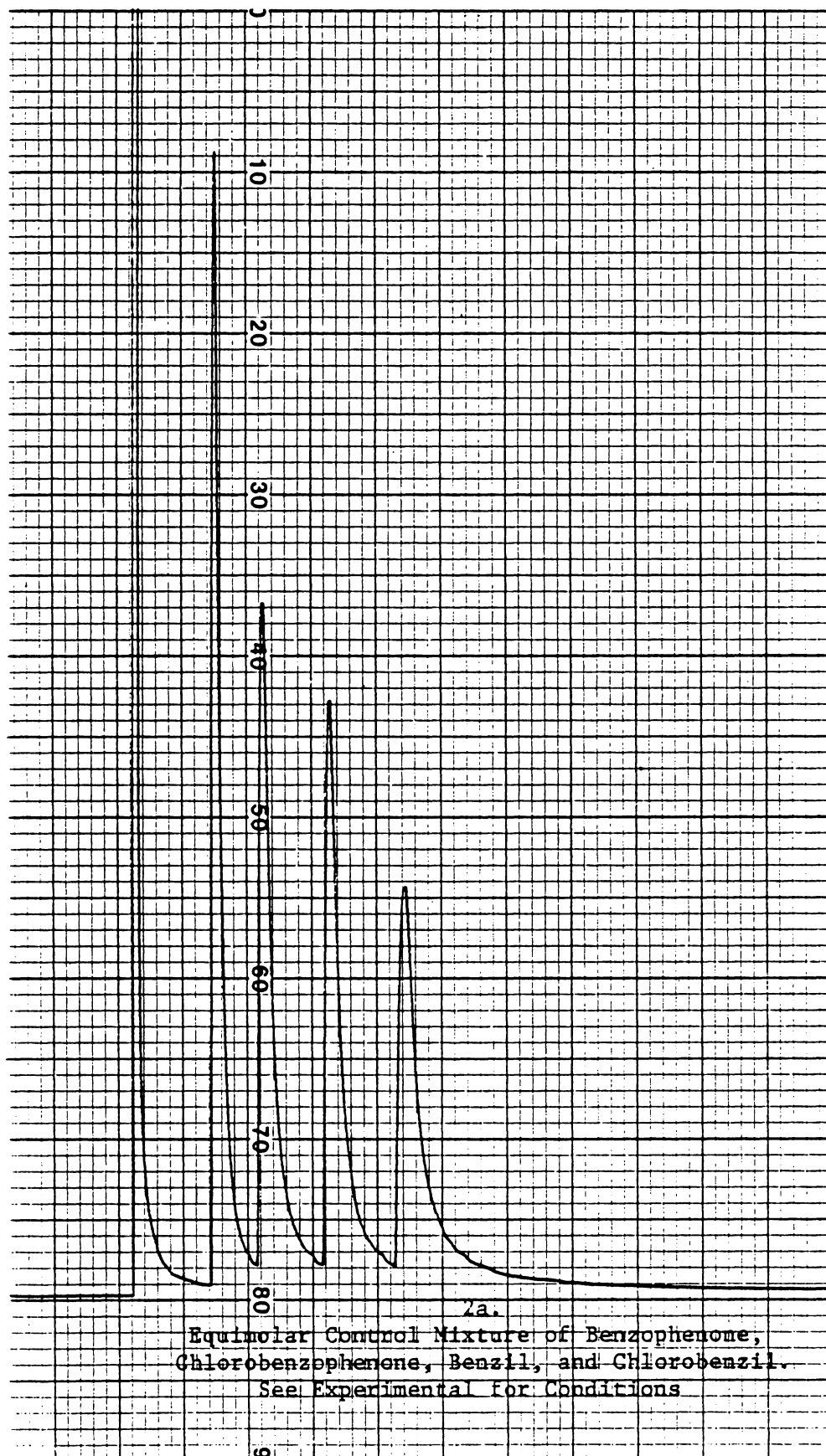
Retention Times

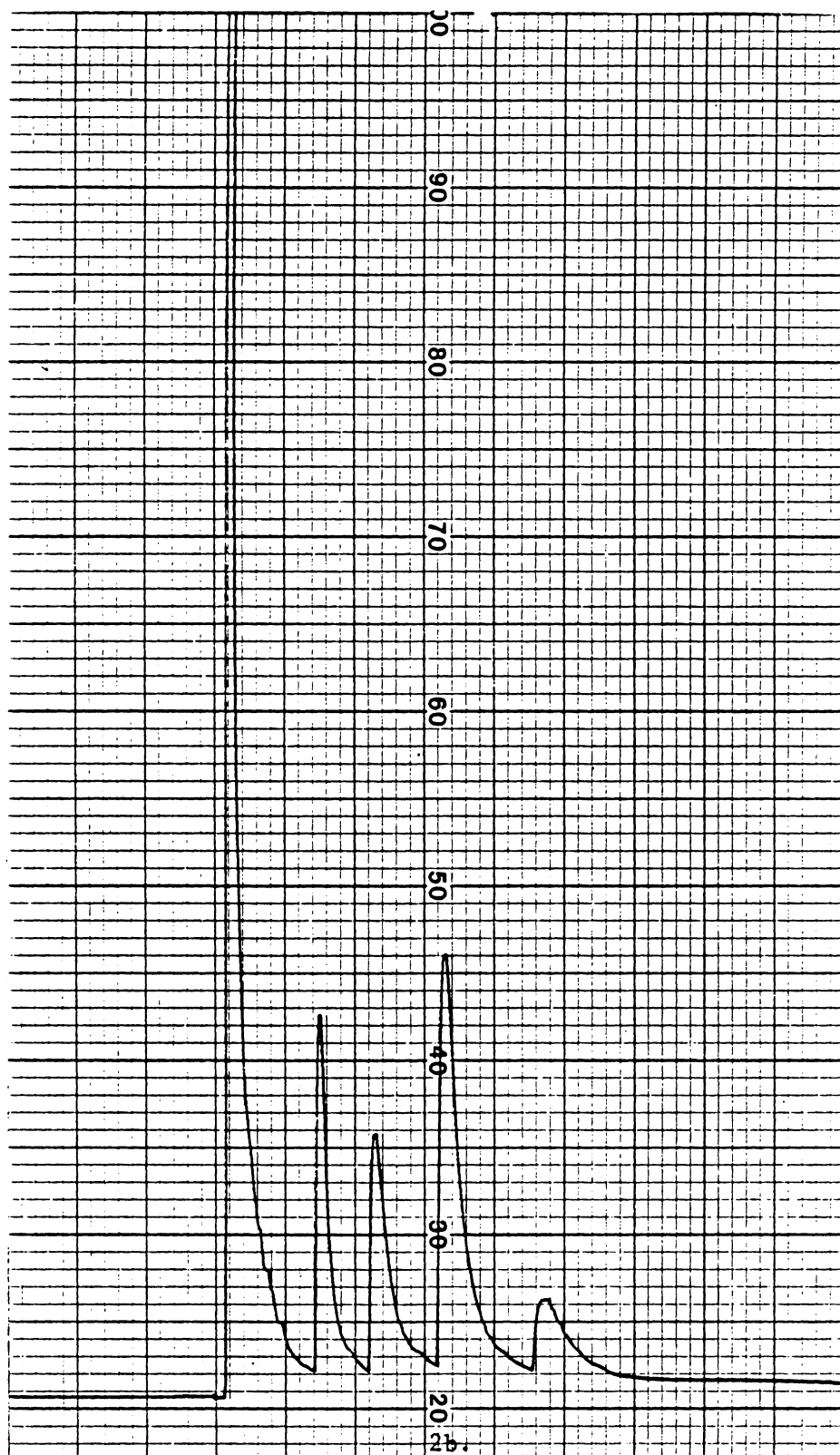
<u>Compound</u>	Column Temperature	
	<u>Isothermal</u> 215°C	<u>Programmed</u> 215-235, 2°/min.
Benzophenone	1.95	----
Methylbenzophenone	2.51	----
Chlorobenzophenone	3.08	2.85
Bromobenzophenone	4.65, 4.8	----
Benzil	4.72, 4.8	----
Methylbenzil	6.45	----
Chlorobenzil	6.6	6.0
Bromobenzil	9.98, 10.05	----
<u>p</u> -Methoxybenzophenone	----	5.55
<u>p</u> -Methoxybenzil	----	11.85, 12.15
<u>m</u> -methoxybenzophenone	----	0.6*
<u>m</u> -Methoxybenzil	----	9.38*

*Programmed 200-235 @ 4°/min.

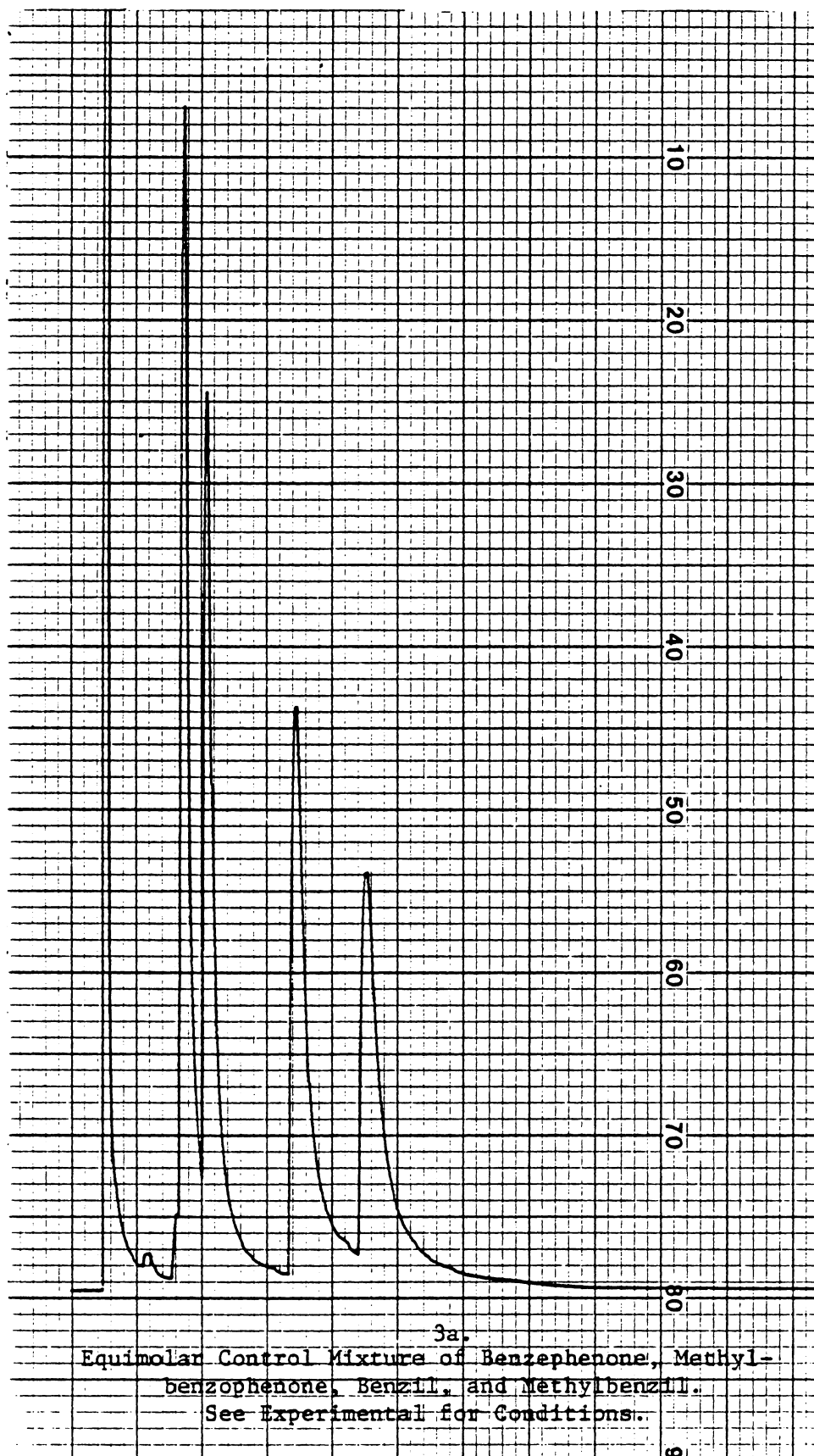


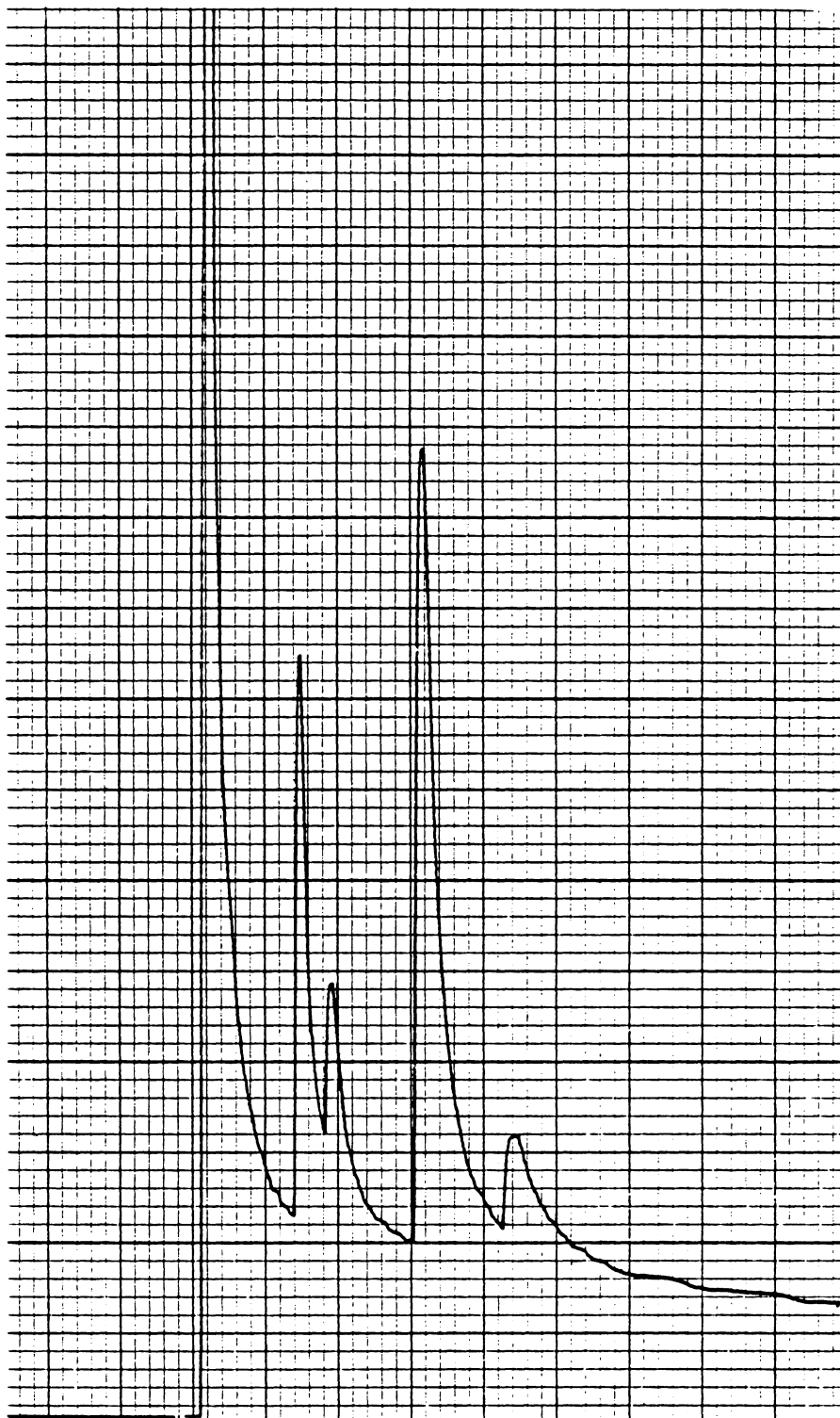






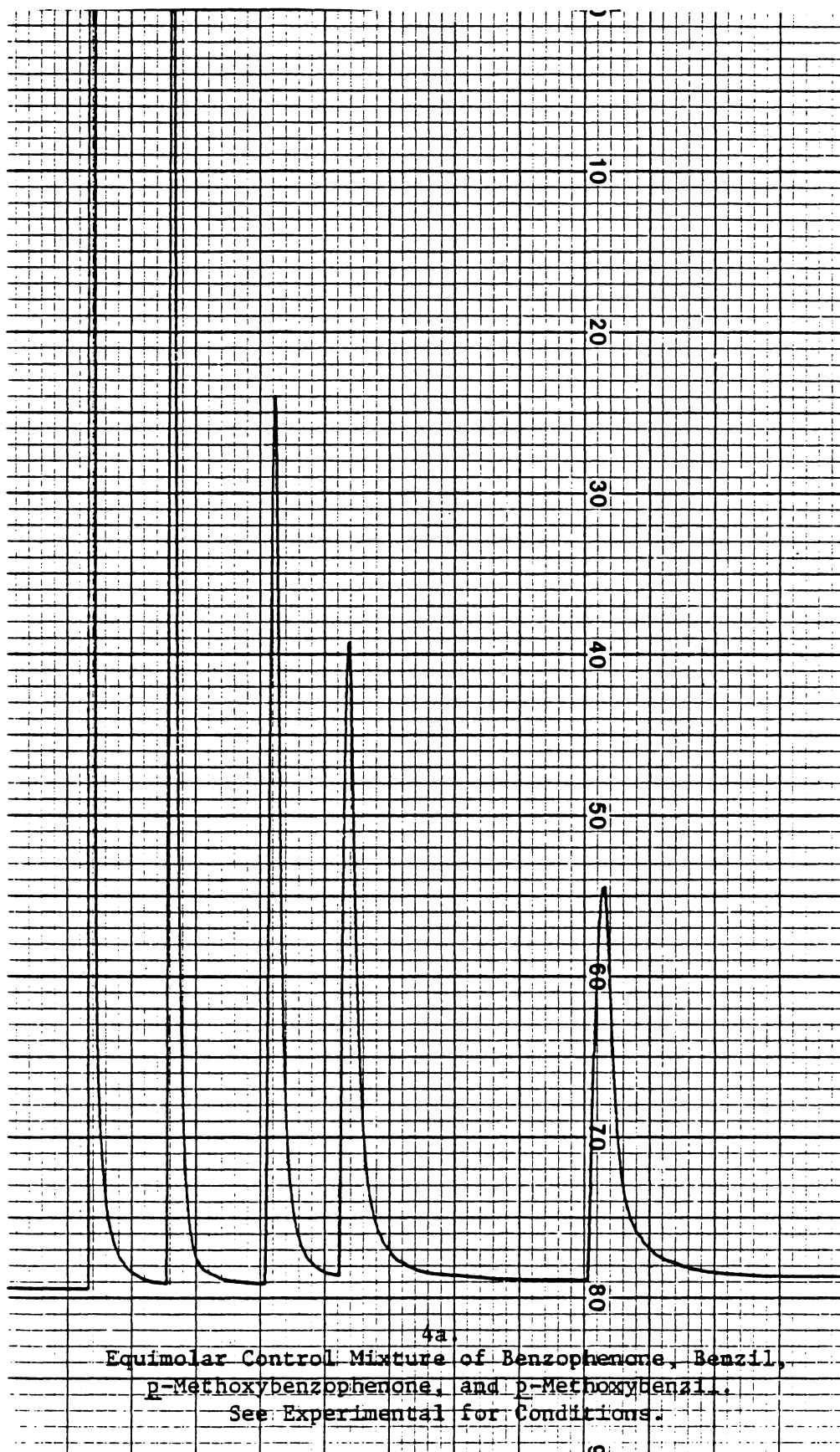
2b.
Products from Oxidative Cleavage of the Rearrange-
ment Products from the Thermal Rearrangement
of 2-(p-Chlorophenyl)-1,3,4,5-
Tetraphenyl-2,4-Cyclopentadien-1-ol

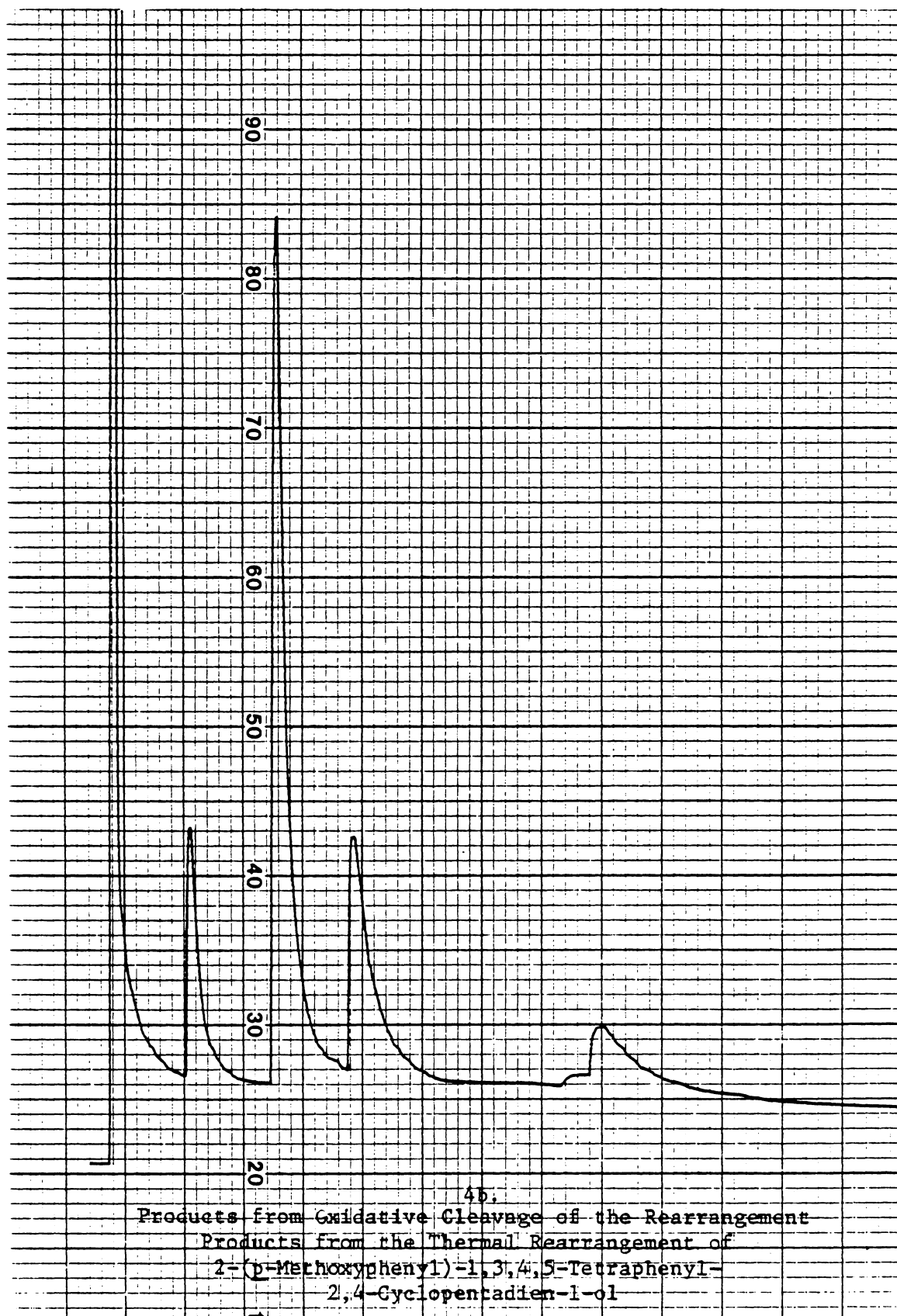


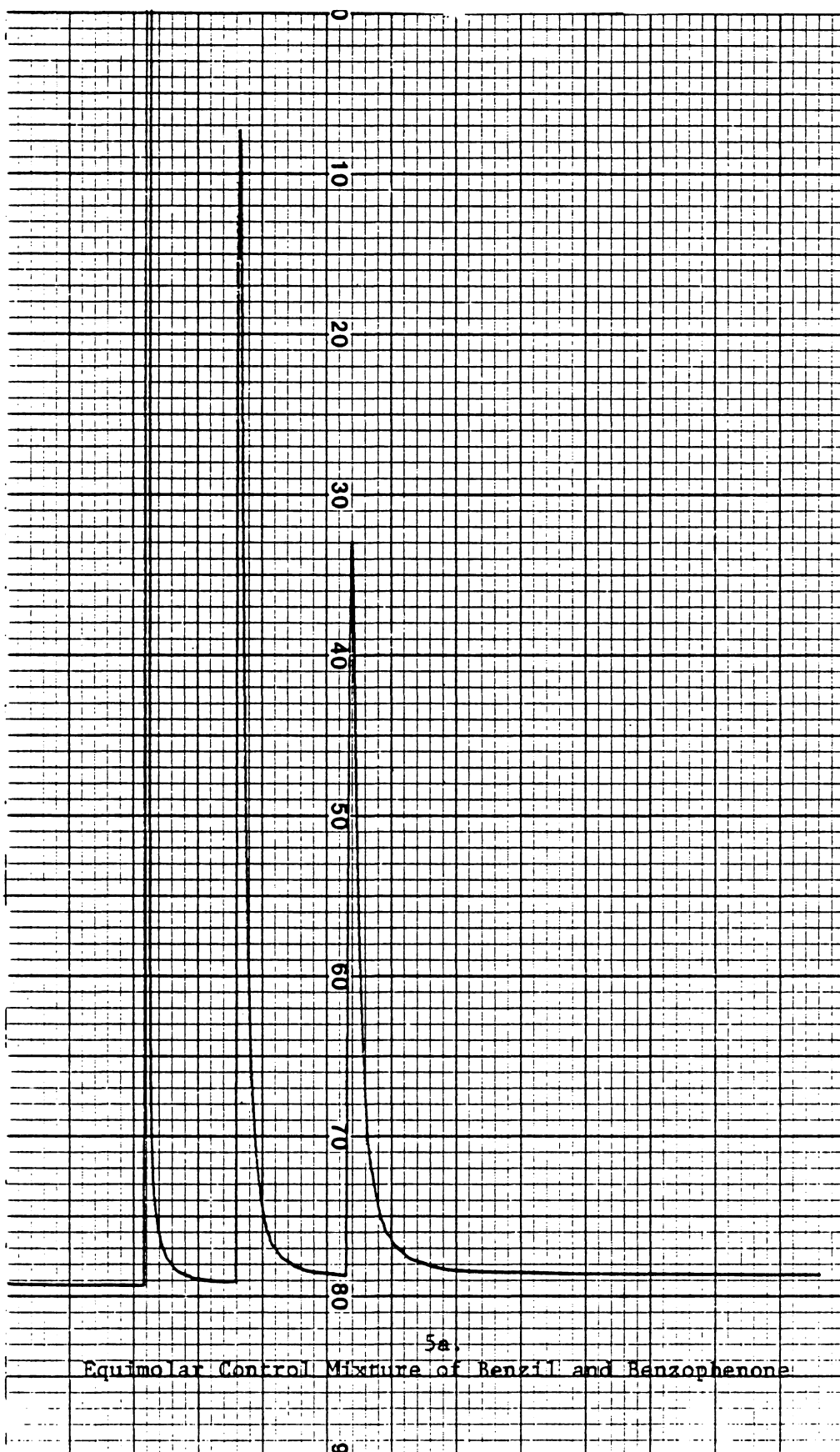


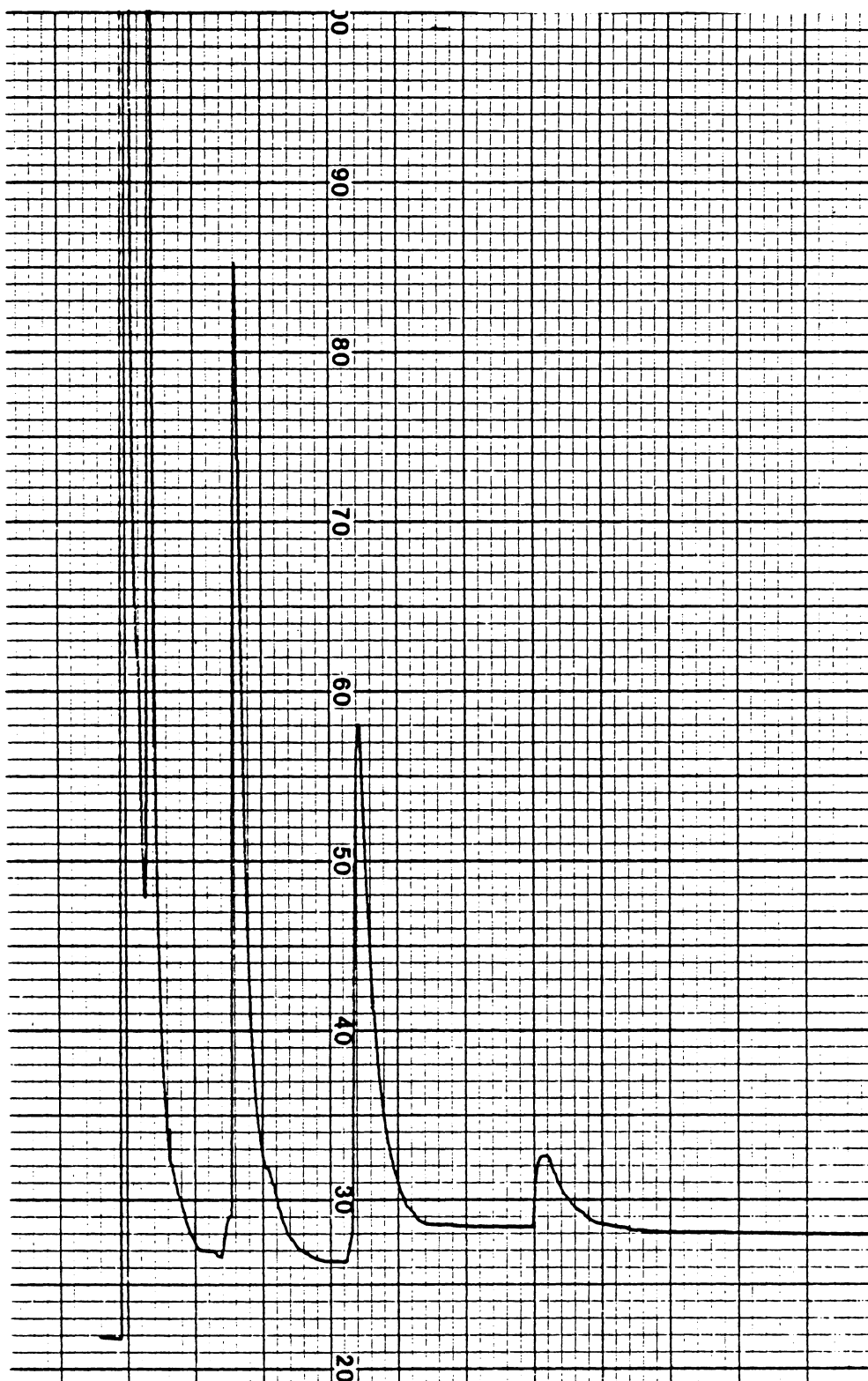
3b.

Products from Oxidative Cleavage of the
Rearrangement Products from the Thermal
Rearrangement of 2-(p-Methylphenyl)-1,3,4,5-
Tetraphenyl-2,4-Cyclopentadien-1-ol



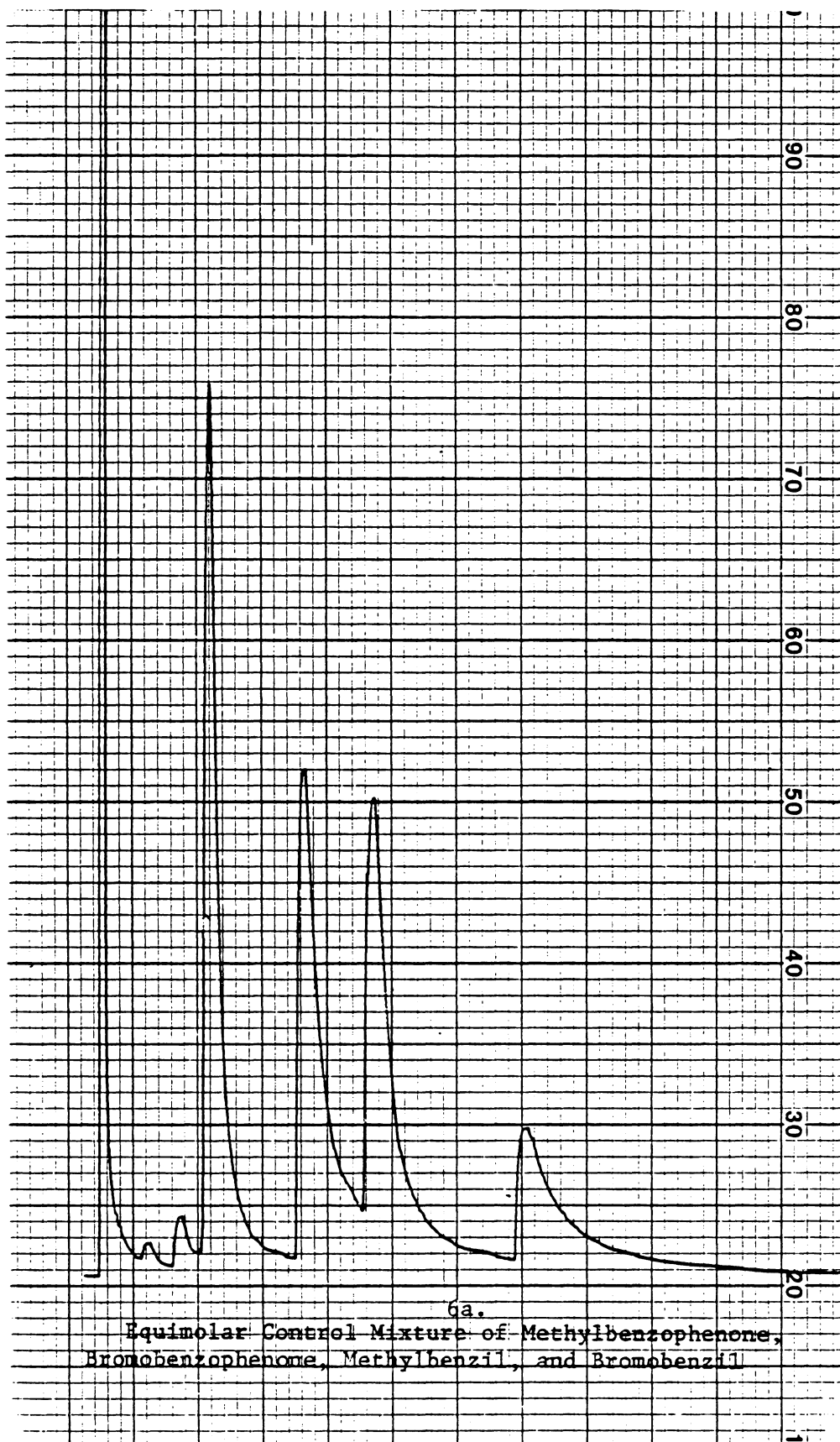


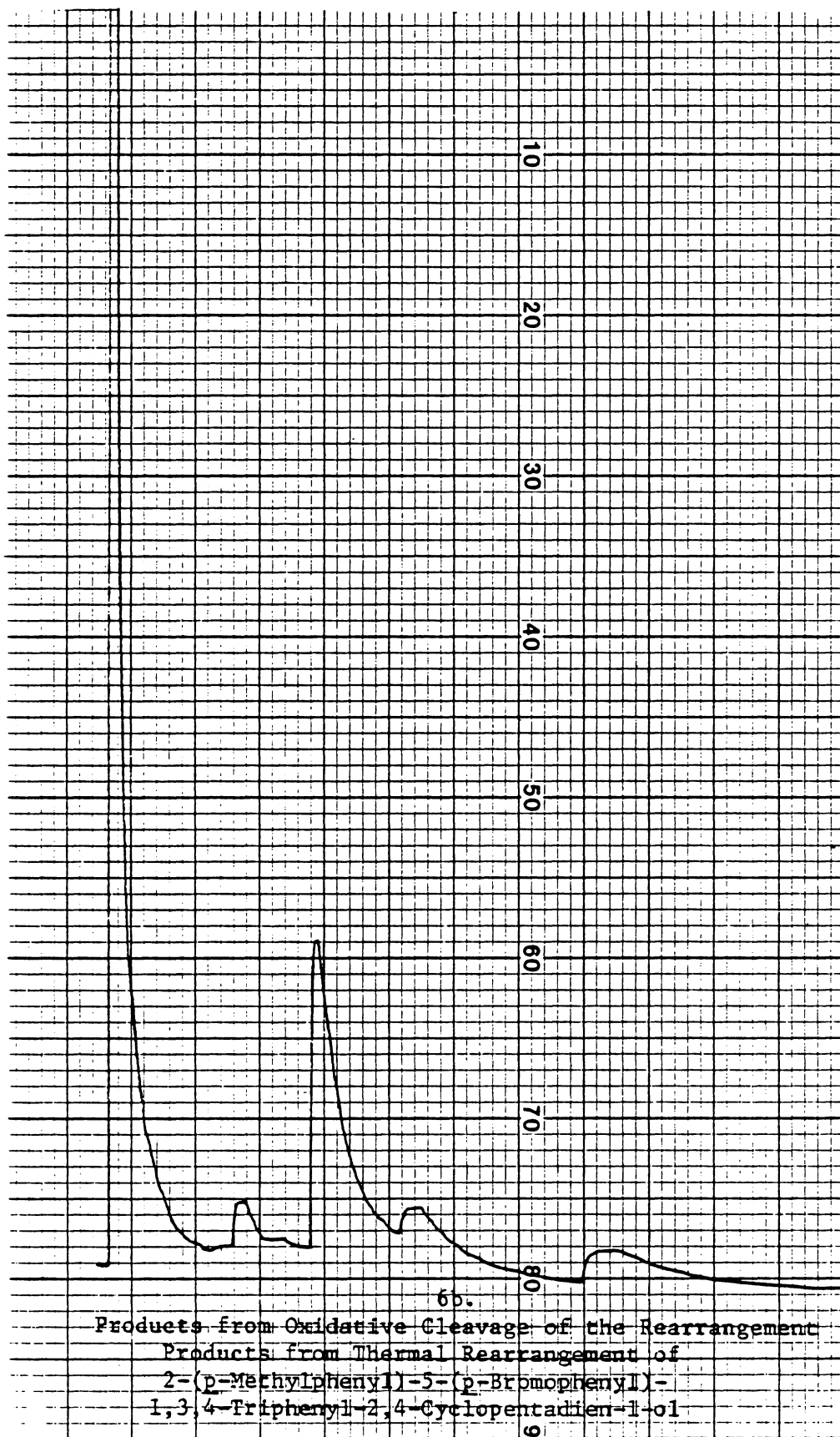


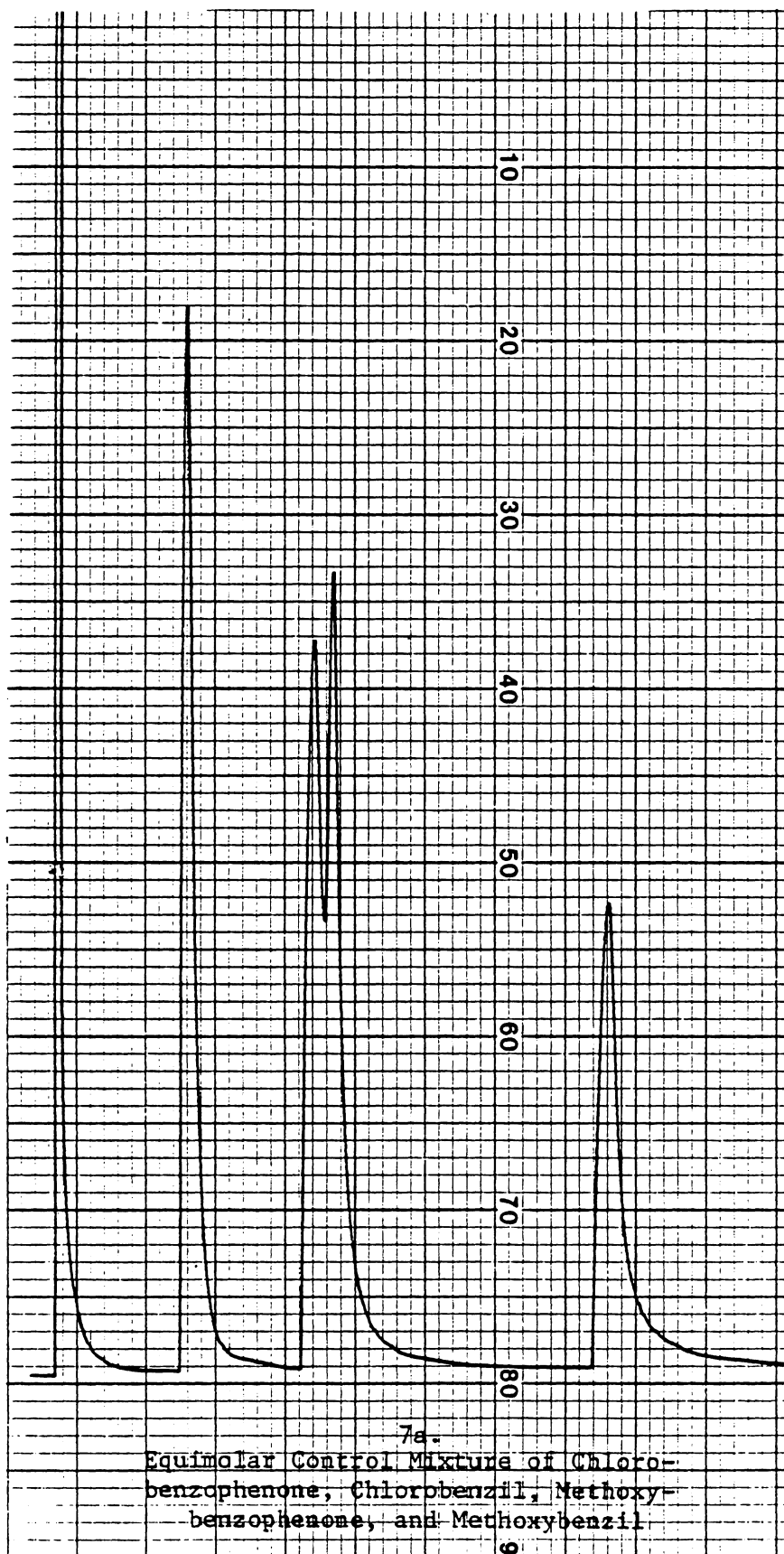


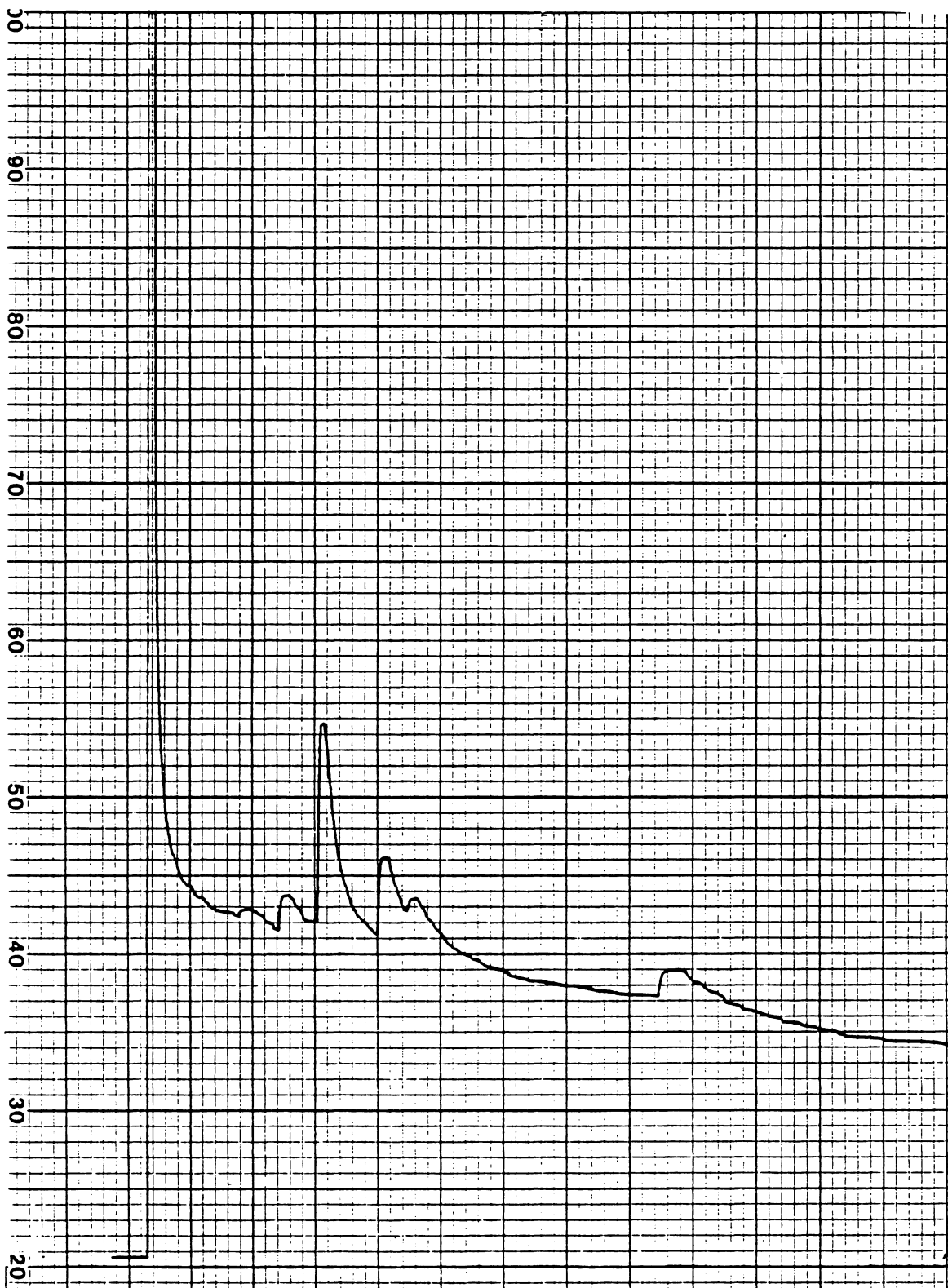
5b.

Products from Oxidative Cleavage of the Rearrangement
 Products from the Thermal Rearrangement of
 2-(*m*-Methoxyphenyl)-1,3,4,5-Tetraphenyl
 2,4-Cyclopentadien-1-ol









7b.

Products from Oxidative Cleavage of the Rearrangement
 Products from Thermal Rearrangement of
 2-(p-Methoxyphenyl)-5-(p-Chlorophenyl)-1,3,4-
 Triphenyl-2,4-Cyclopentadien-1-ol

APPENDIX C

200 MHz NMR Spectral Data

p-Br,

- A. 2-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one
- B. Expansion
- C. Thermal Rearrangement Products: Combination of 2-(p-Bromophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and 2-(p-Bromophenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one
- D. Expansion
- E. "C" Spiked with Sample of "A"
- F. Expansion

p-Cl,

- A. 2-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one
- B. Expansion
- C. Thermal Rearrangement Products: Combination of 2-(p-Chlorophenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and 2-(p-Chlorophenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one
- D. Expansion
- E. "C" Spiked with Sample of "A"
- F. Expansion

p-Me,

- A. 2-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one
- B. Expansion
- C. Thermal Rearrangement Products: Combination of 2-(p-Methylphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and 2-(p-Methylphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one

p-Me, (Cont'd)

- D. Expansion
- E. "C" Spiked with Sample of "A"
- F. Expansion

p-MeO,

- A. 2-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one
- B. Expansion
- C. Thermal Rearrangement Products: Combination of 2-(p-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and 2-(p-Methoxyphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-one
- D. Expansion
- E. "C" Spiked with "A"
- F. Expansion

m-MeO,

- A. 2-(m-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one
- B. Expansion
- C. Thermal Rearrangement Products Combination of 2-(m-Methoxyphenyl)-2,3,4,5-Tetraphenyl-3-Cyclopenten-1-one and 2-(m-Methoxyphenyl)-3,4,5,5-Tetraphenyl-3-Cyclopenten-1-One
- D. Expansion
- E. "C" Spiked with "A"
- F. Expansion

Cl-MeO,

- A. Thermal Rearrangement Products: Combination of 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-3,4,5-Triphenyl-3-Cyclopenten-1-one and 2-(p-Chlorophenyl)-5-(p-Methoxyphenyl)-2,3,4-Triphenyl-3-Cyclopenten-1-one

Cl-MeO, (Cont'd)

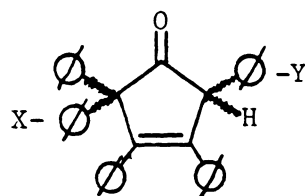
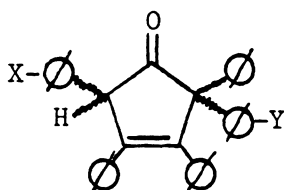
B. Expansion

Br-Me,

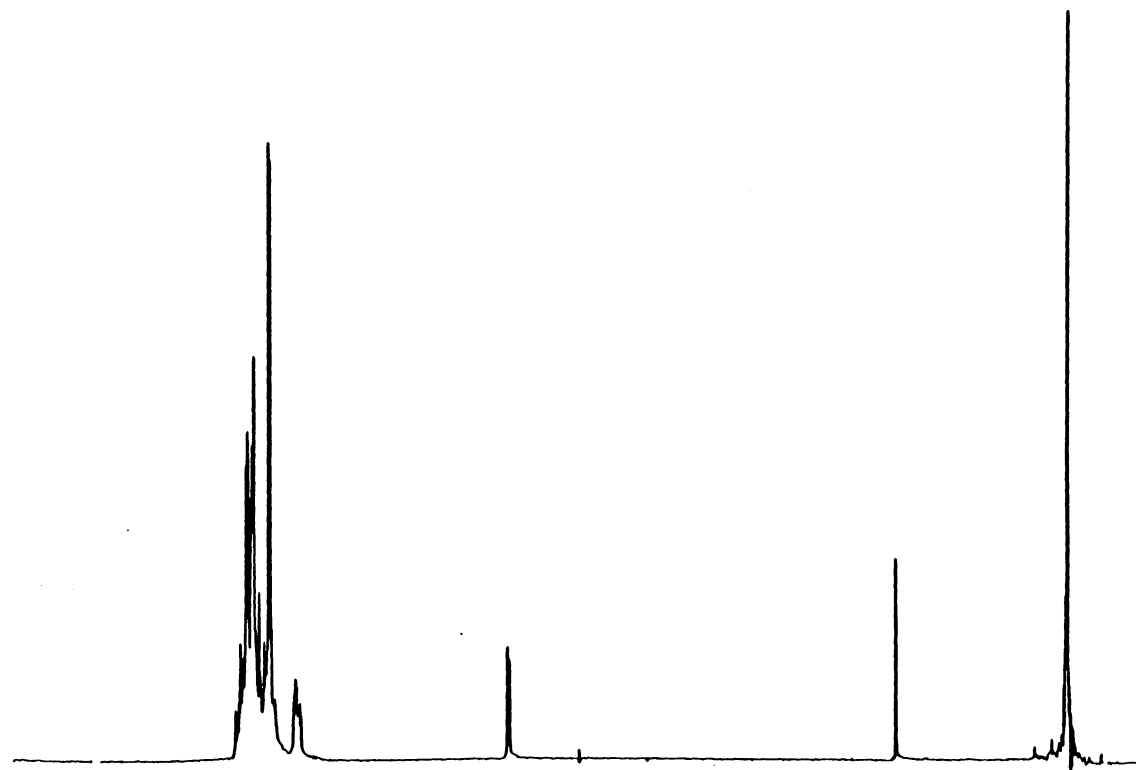
A. Thermal Rearrangement Products: 2-(p-Bromophenyl)-5-(p-Methylphenyl)-3,4,5-Triphenyl-3-Cyclopenten-1-one and 2-(p-Bromophenyl)-5-(p-Methylphenyl)-2,3,4-Triphenyl-3-Cyclopentene-1-one

B. Expansion

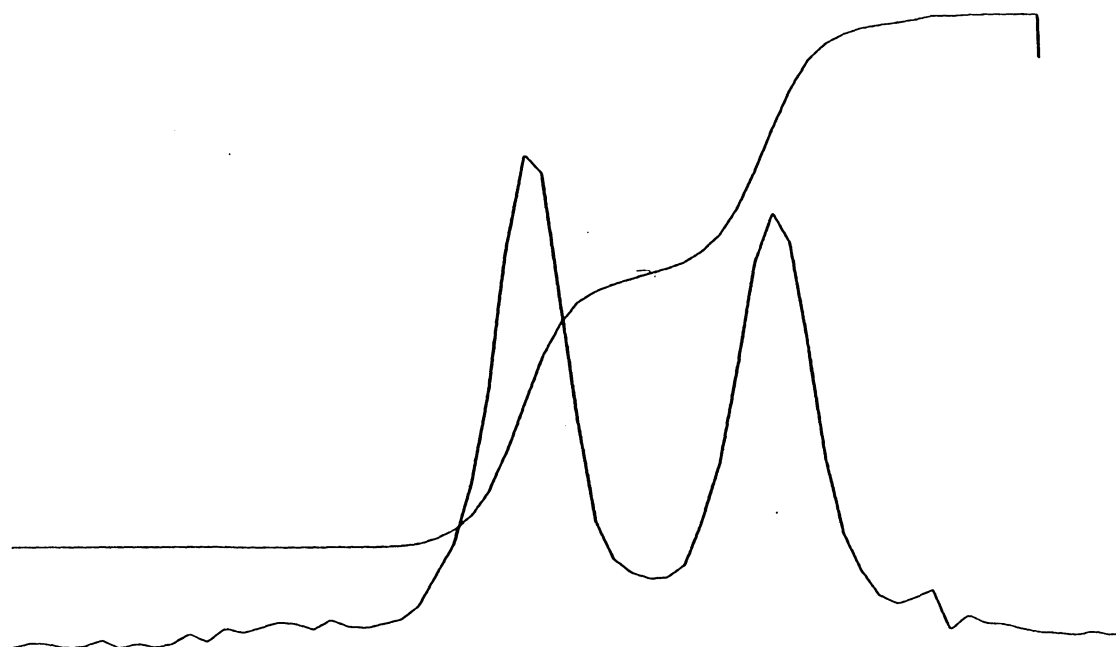
Chemical Shift Assignments



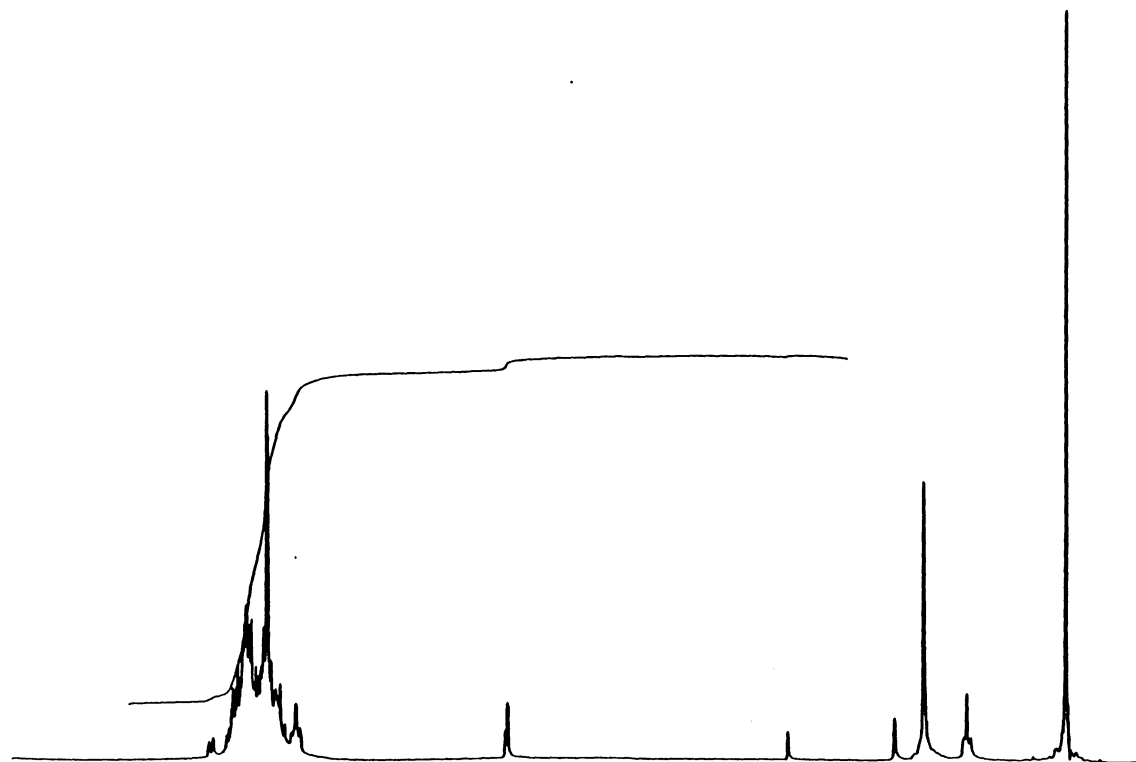
Cyclopentenone (X=) (Y=)		Chemical Shift of Methine Hydrogen (δ =)	Chemical Shift of Methine Hydrogen (δ =)
H	p-Br	4.947 4.931	4.931
H	p-Cl	4.948 4.931	4.940
H	p-Me	4.939	4.912
H	p-MeO	4.938	4.891
H	m-MeO	4.963 4.931	4.906
p-Me	p-Br	4.914	4.892
p-MeO	p-Cl	4.889 4.870	4.925



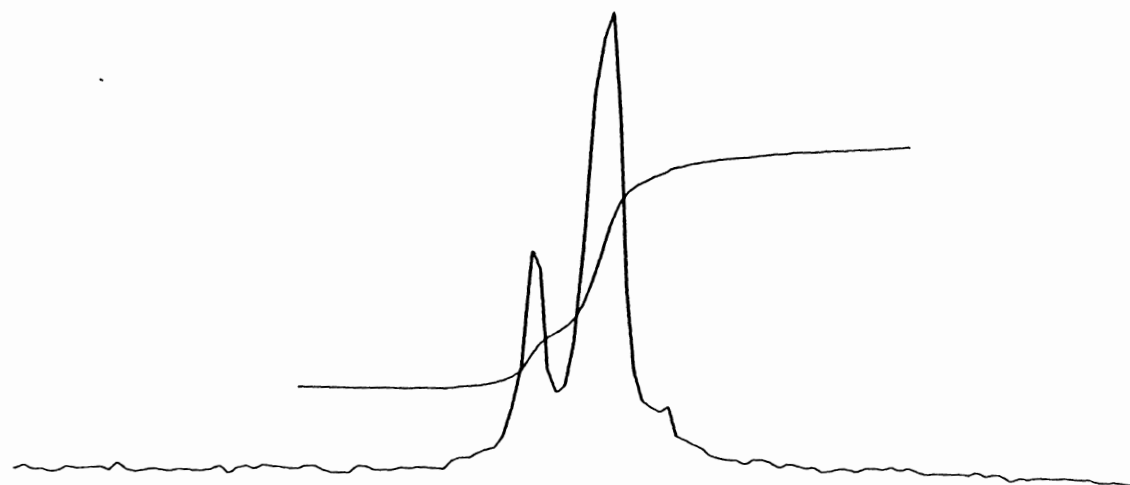
SPECTRUM p-Br "A"



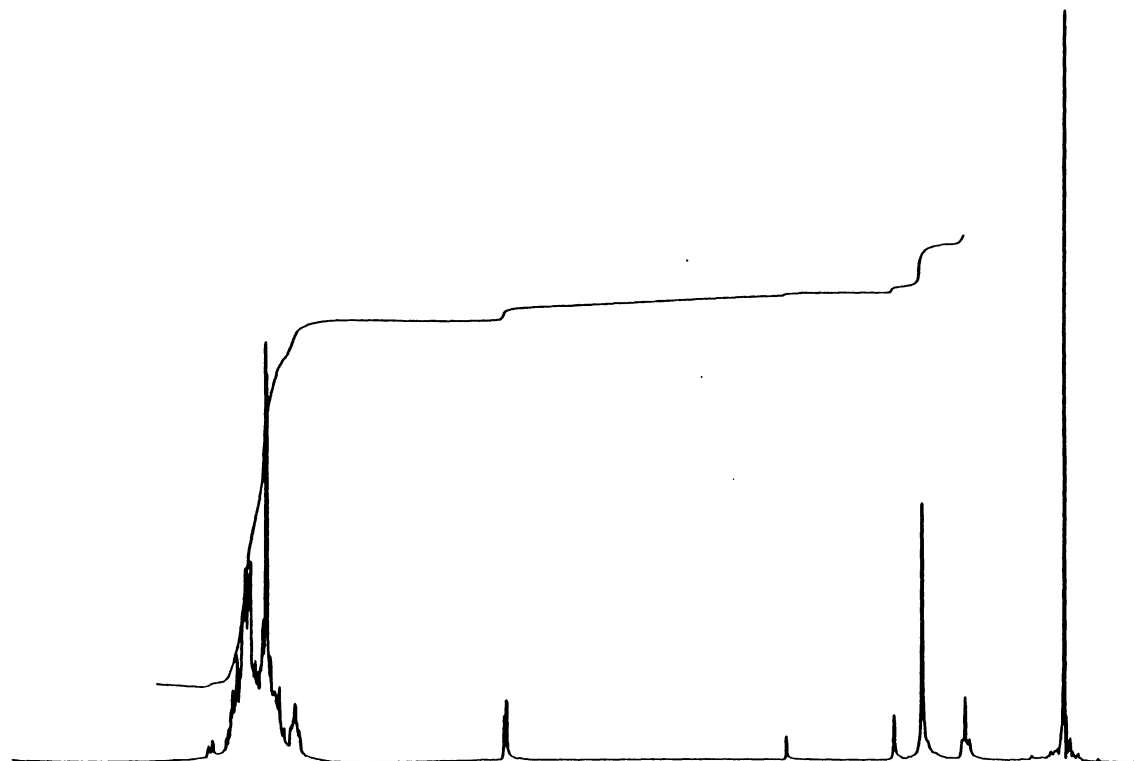
SPECTRUM p-Br "B"



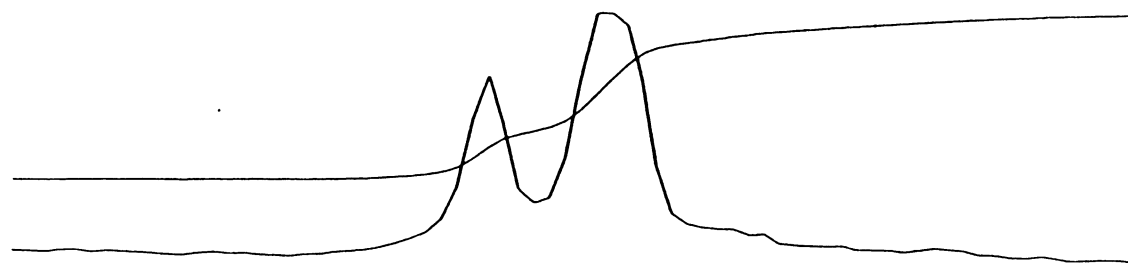
SPECTRUM p-Br "C"



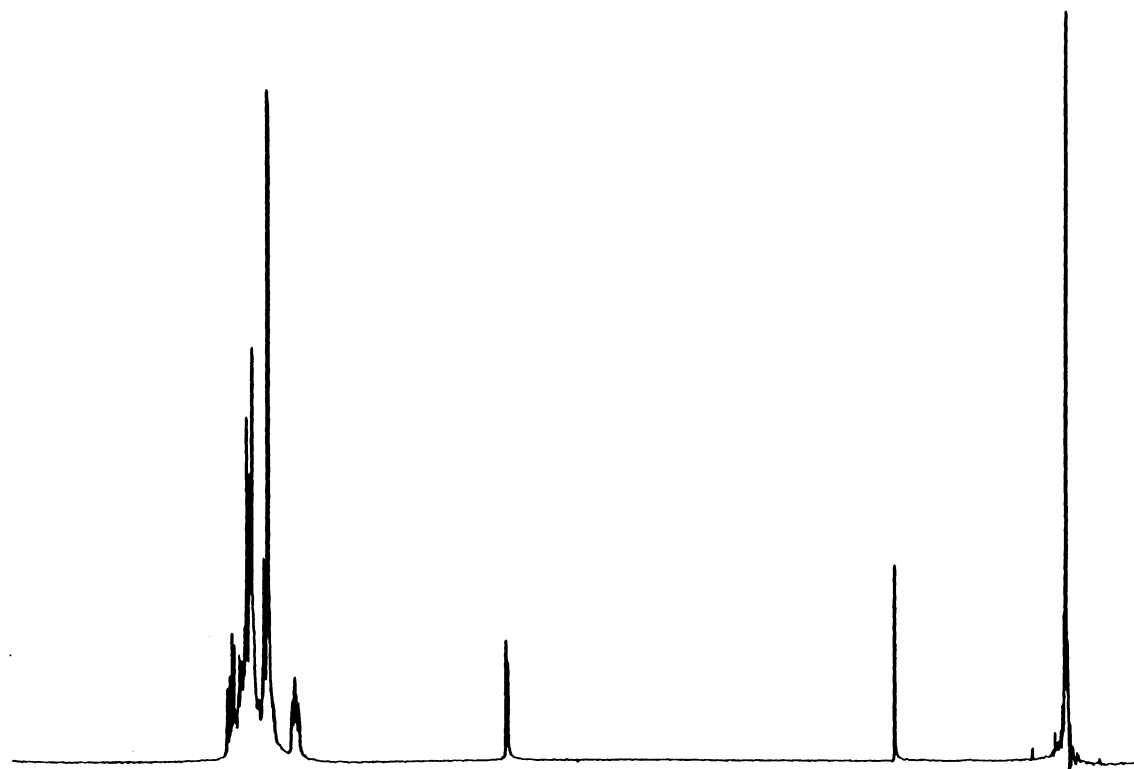
SPECTRUM p-Br "D"



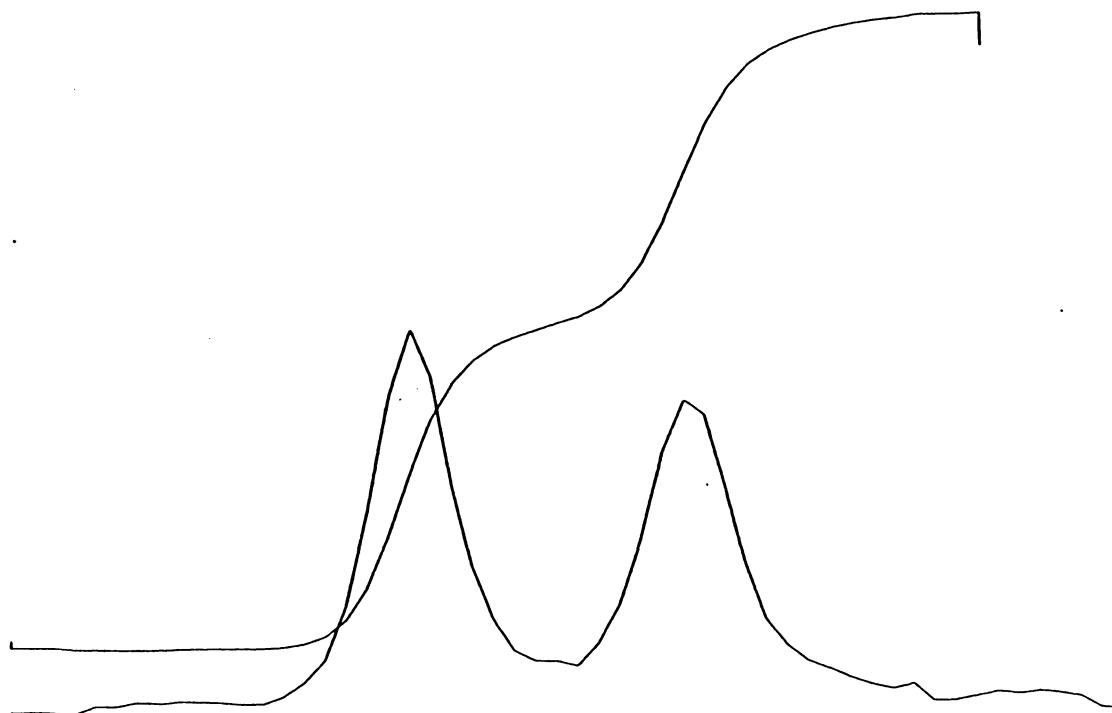
SPECTRUM p-Br "E"



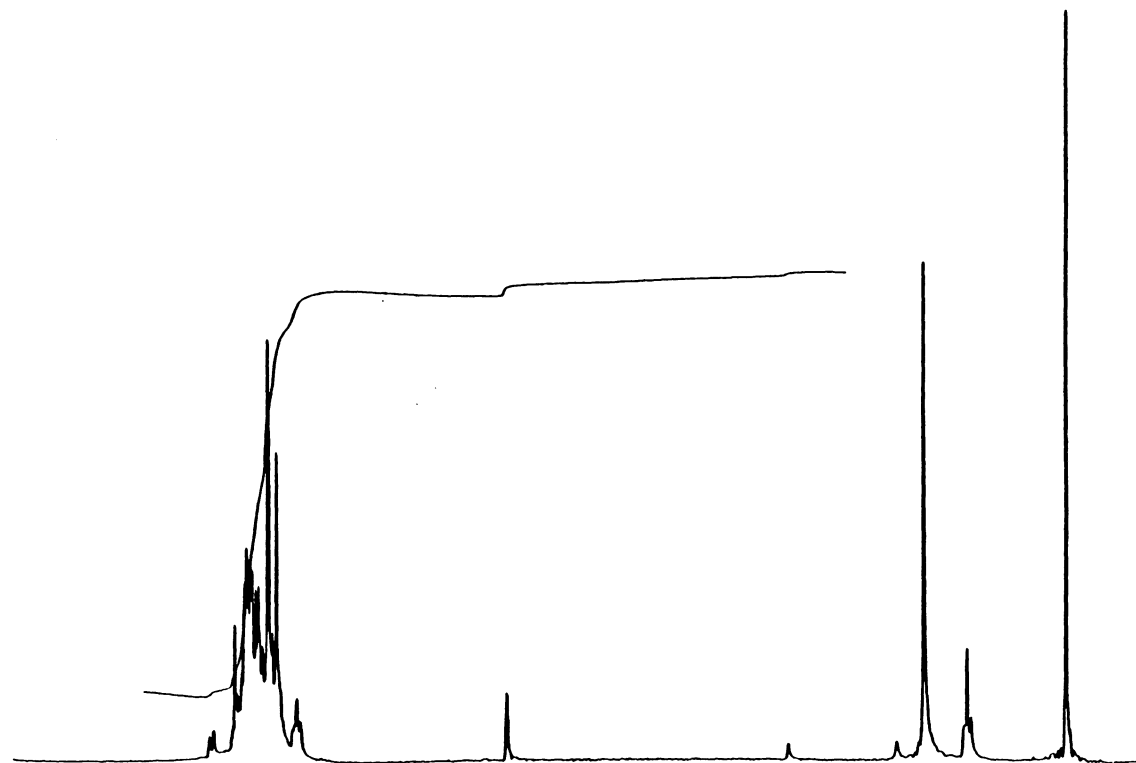
SPECTRUM p-Br "F"



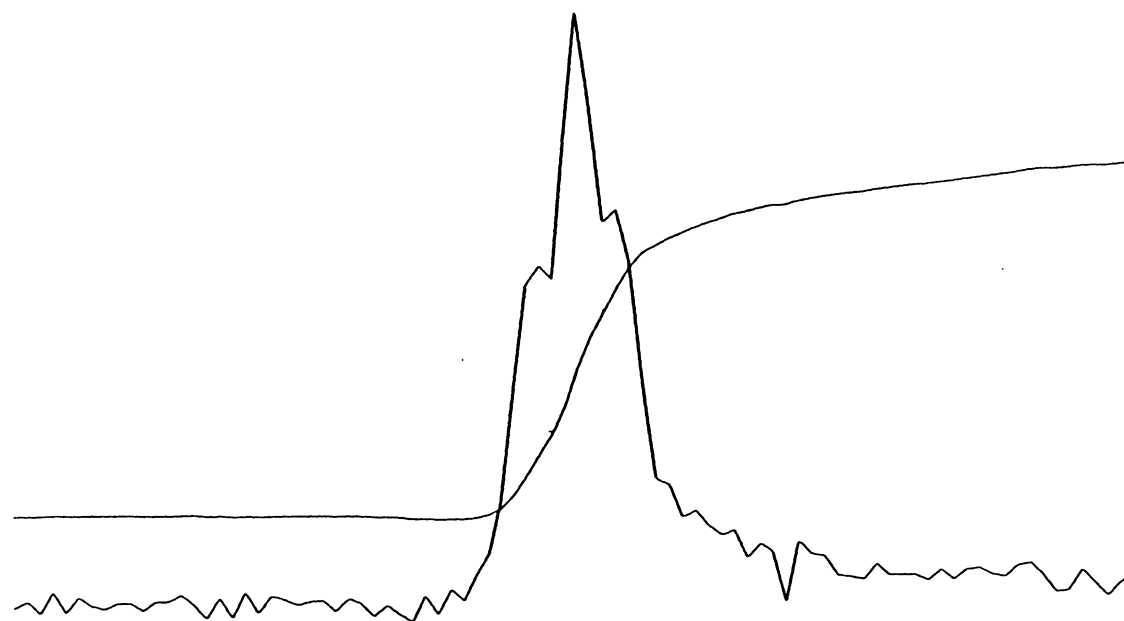
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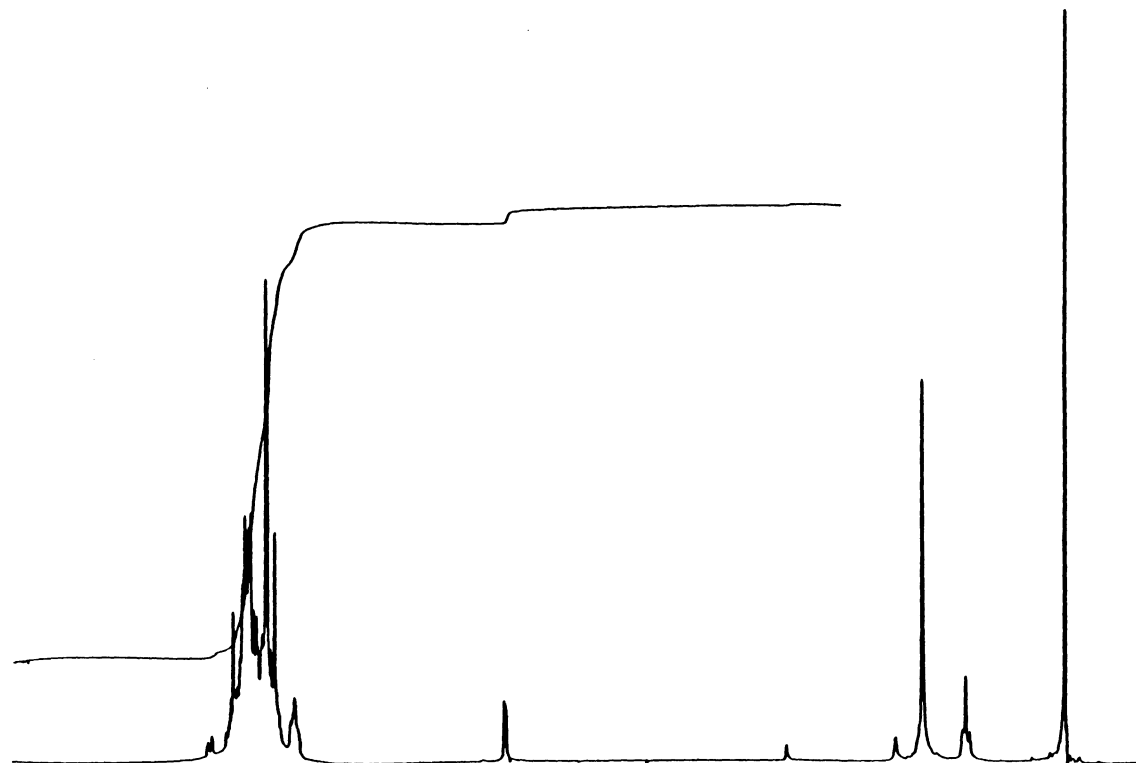
SPECTRUM p-C1 "B"



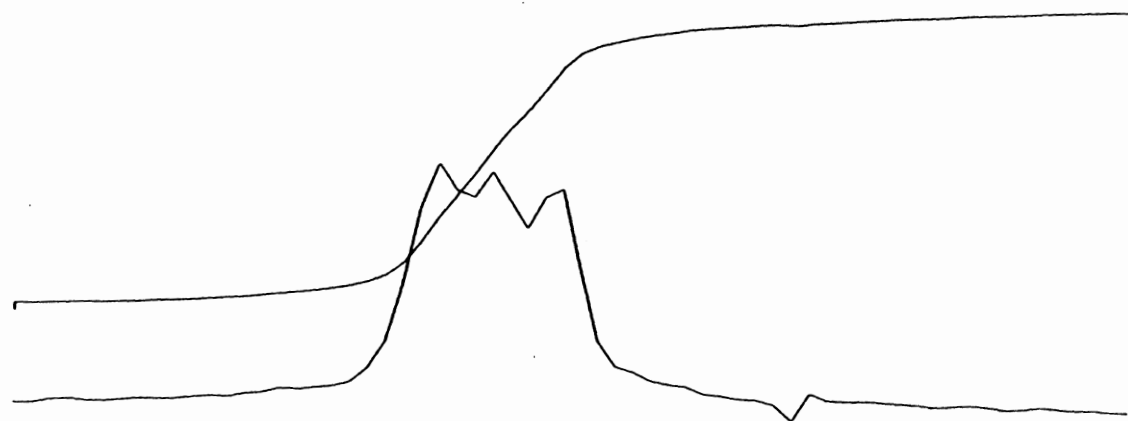
SPECTRUM p-Cl "C"



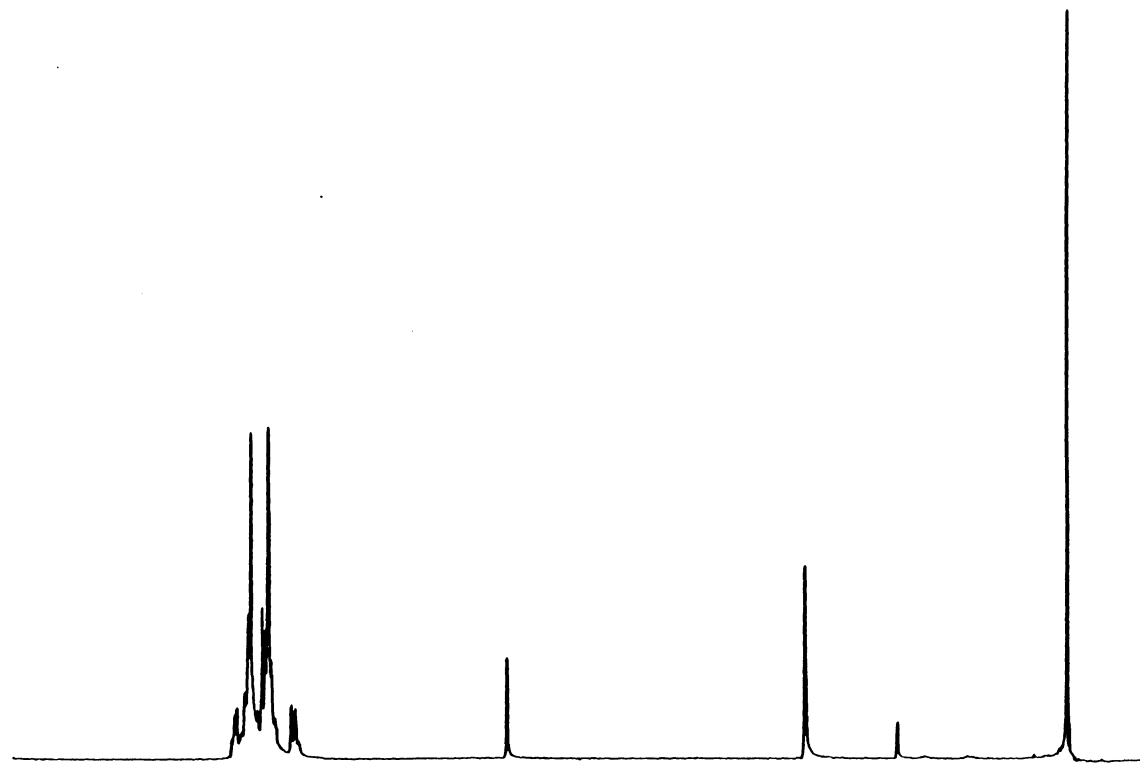
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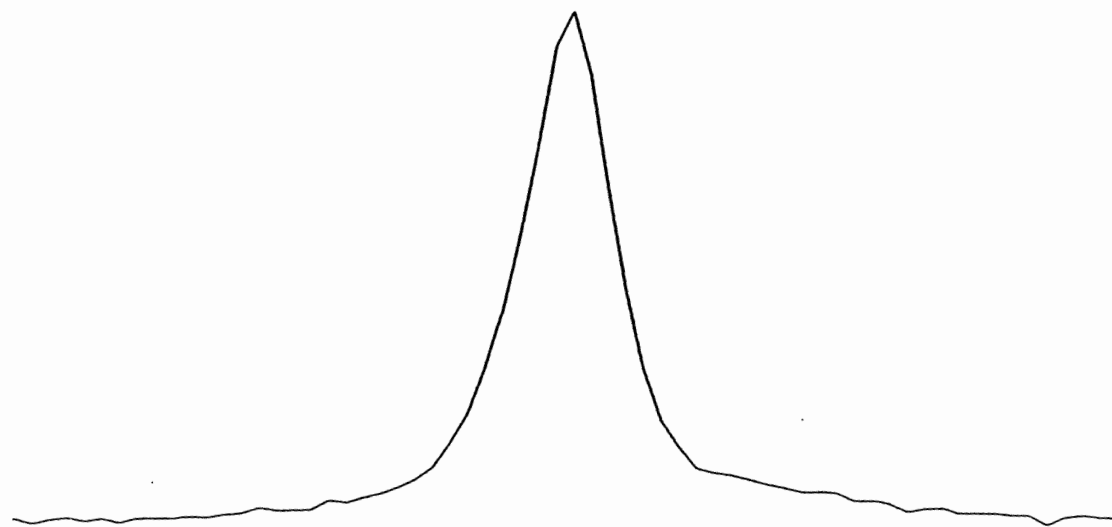
SPECTRUM p-Cl "E"



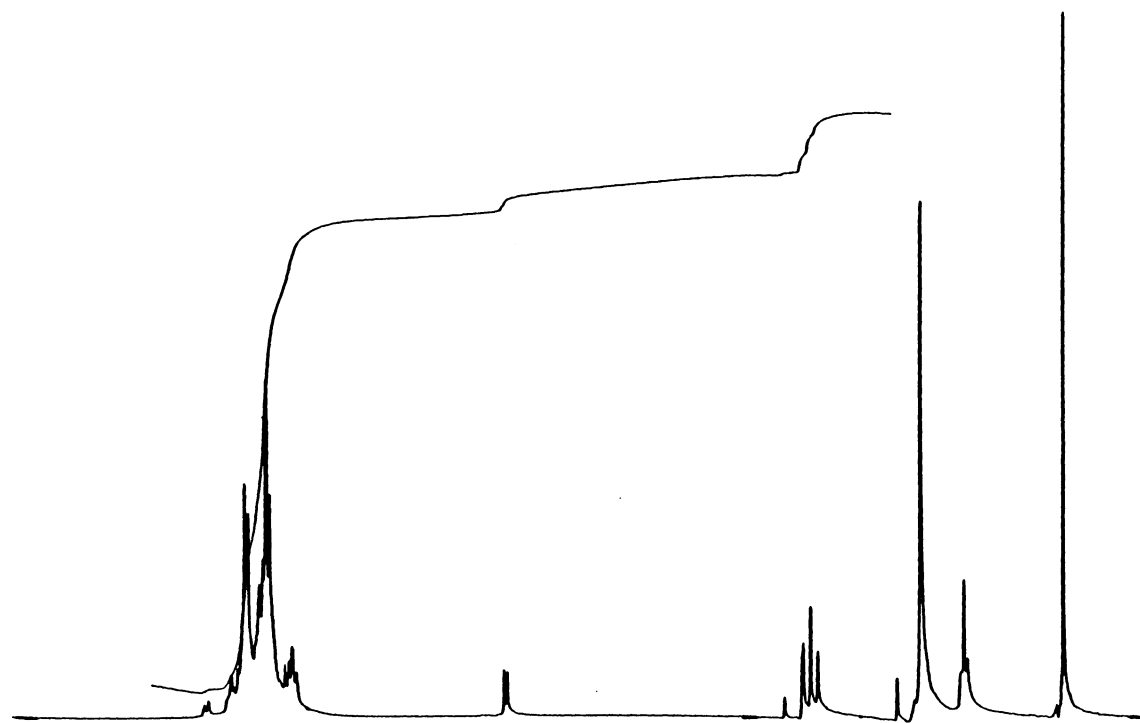
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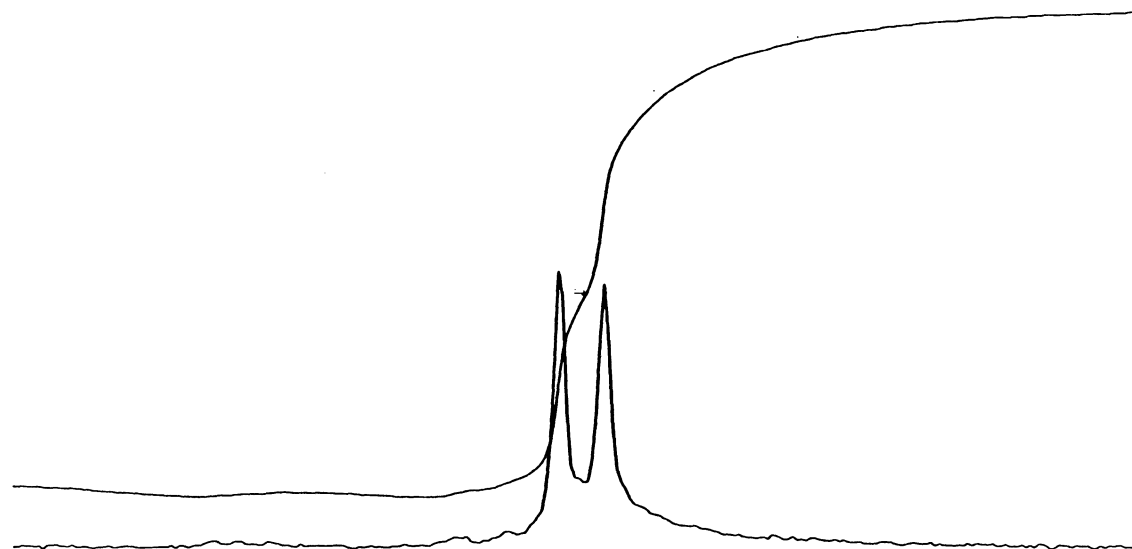
SPECTRUM p-Me "A"



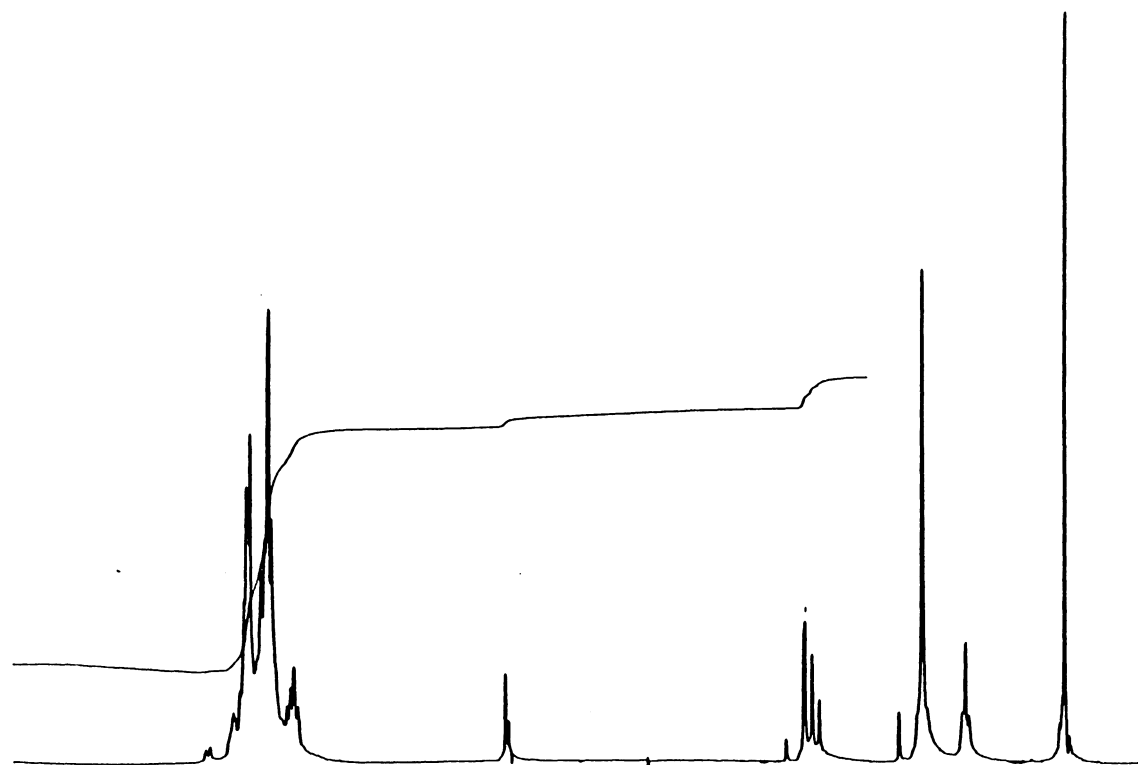
SPECTRUM p-Me "B"



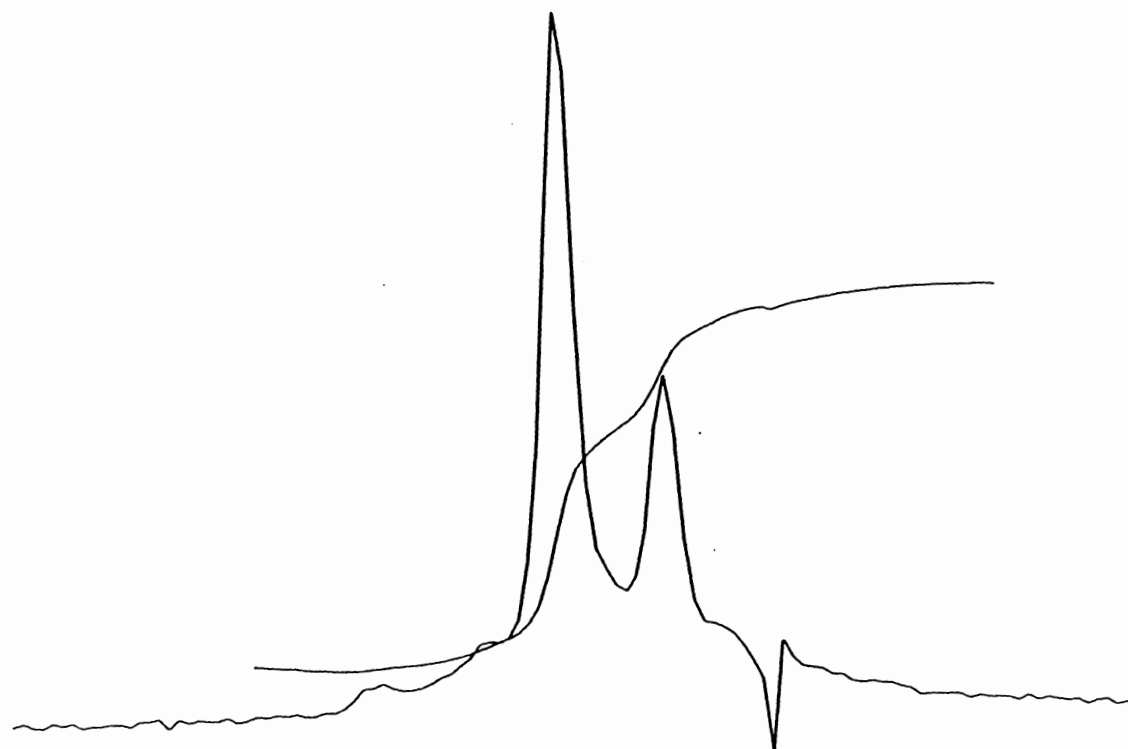
SPECTRUM p-Me "C"



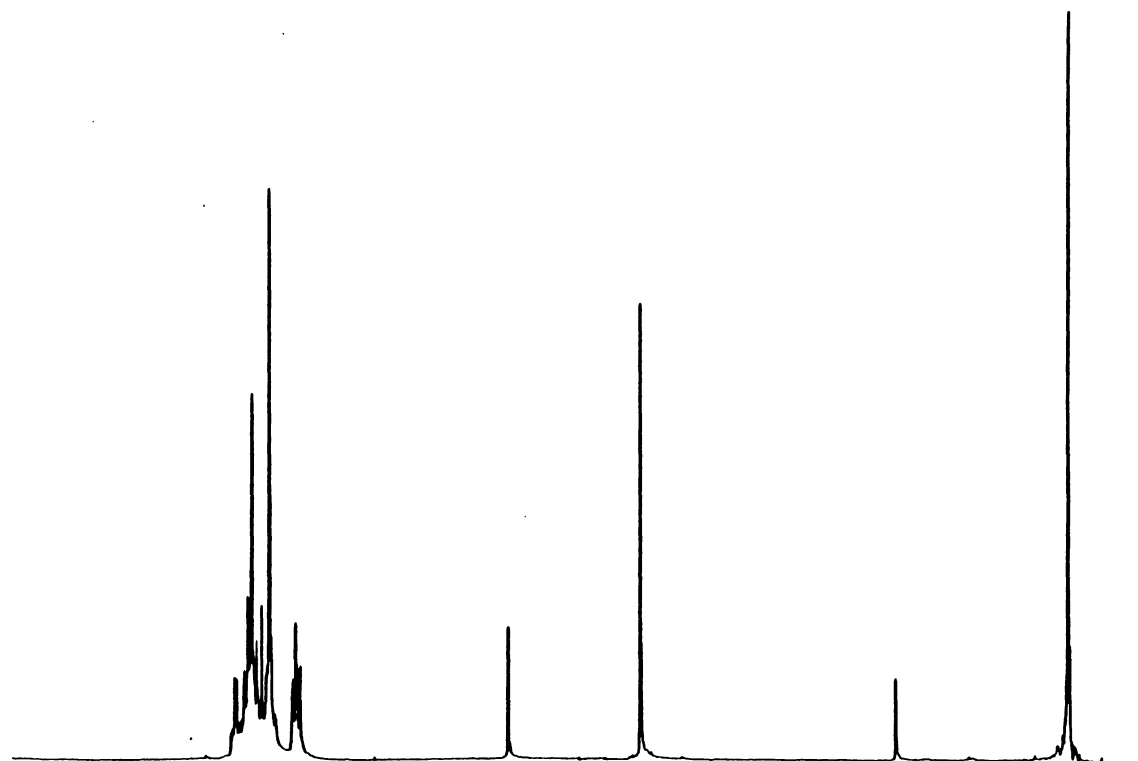
SPECTRUM p-Me "D"



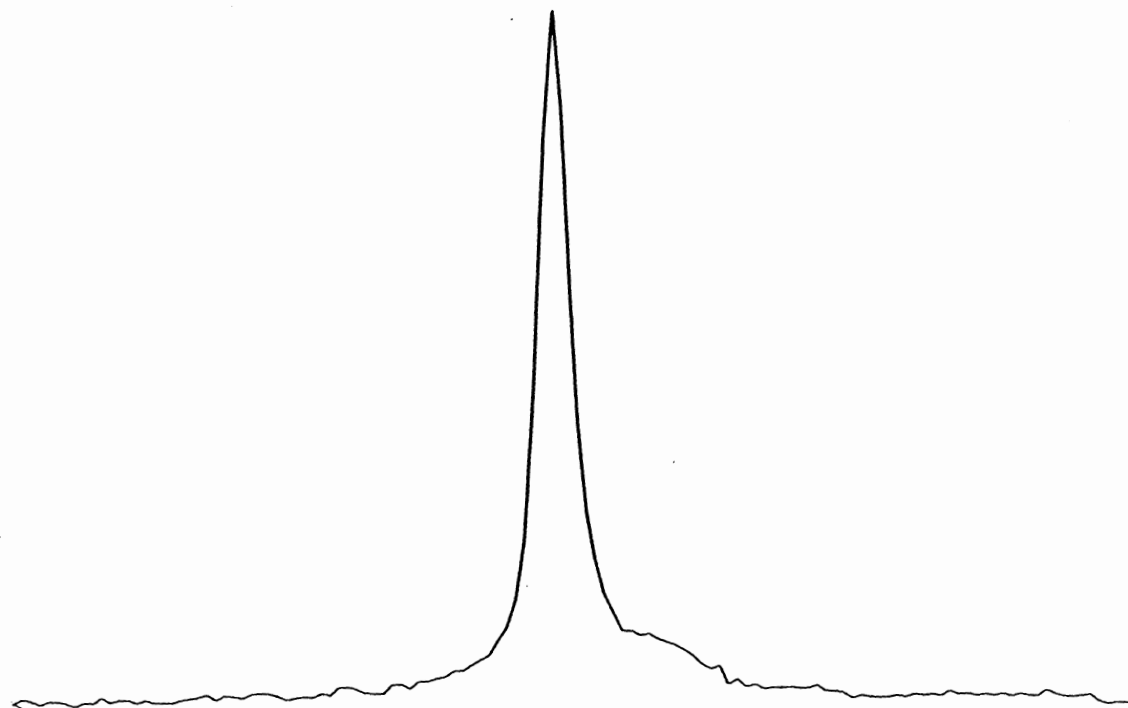
SPECTRUM p-Me "E"



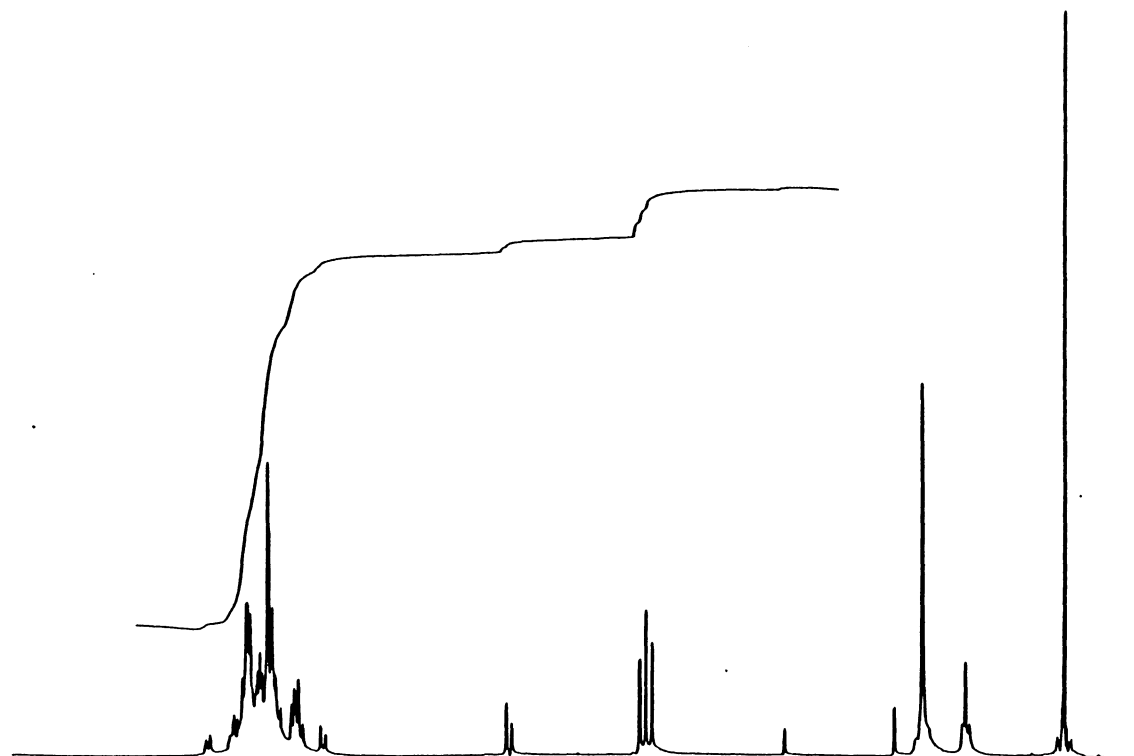
SPECTRUM p-Me "F"



SPECTRUM p-MeO "A"



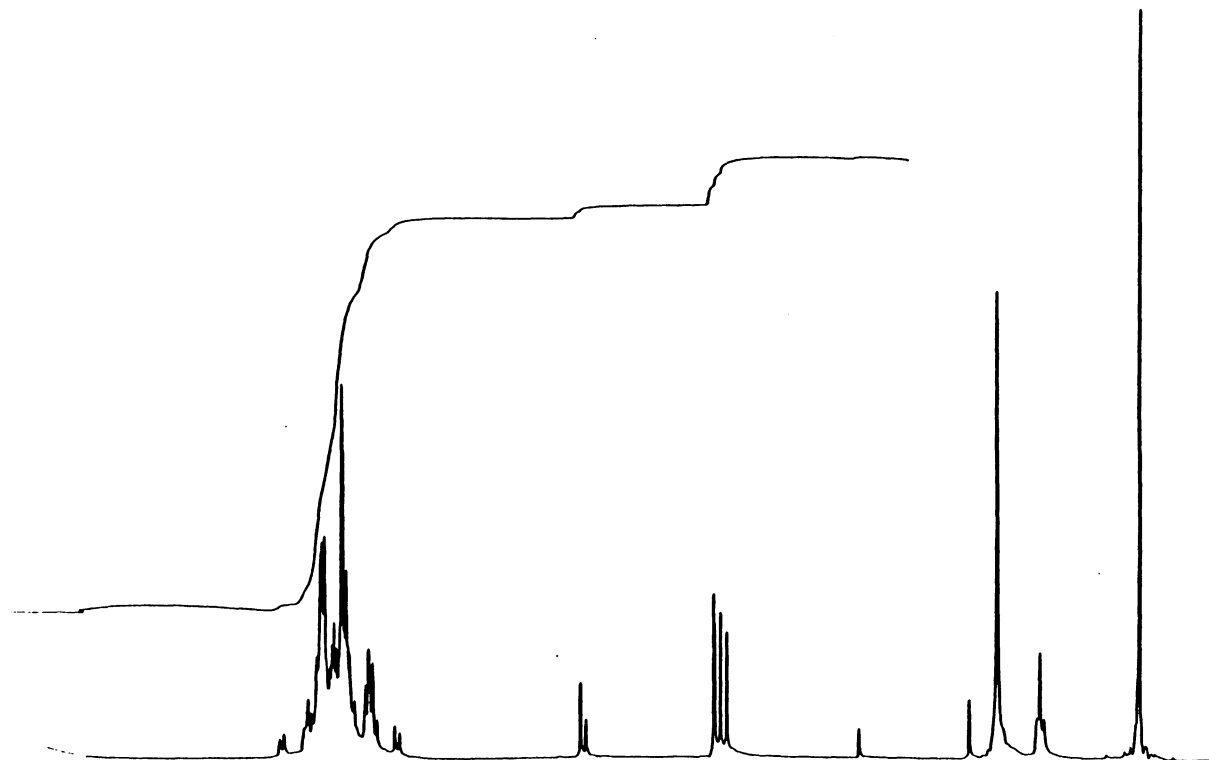
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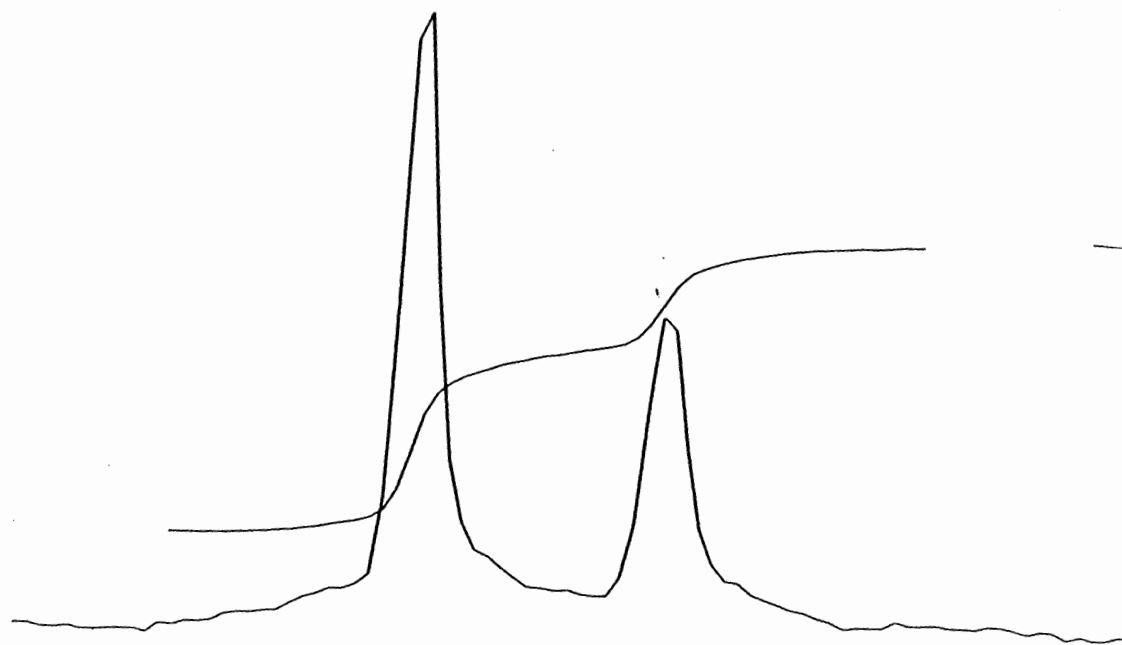
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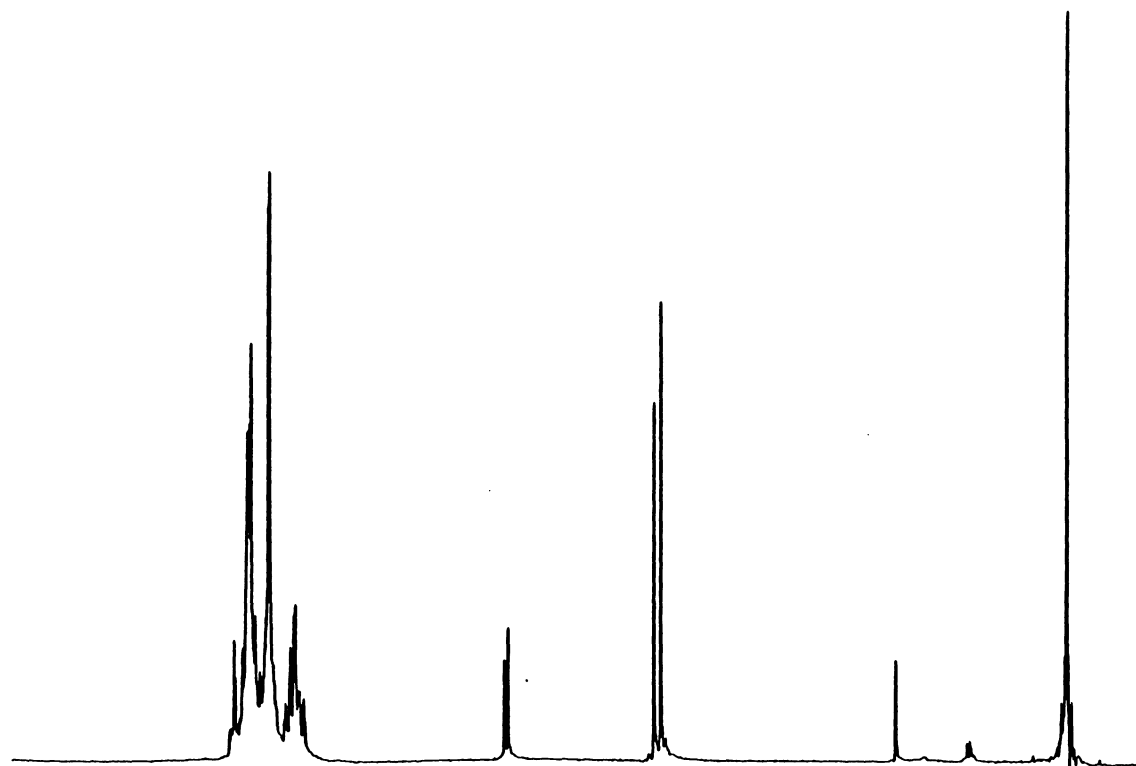
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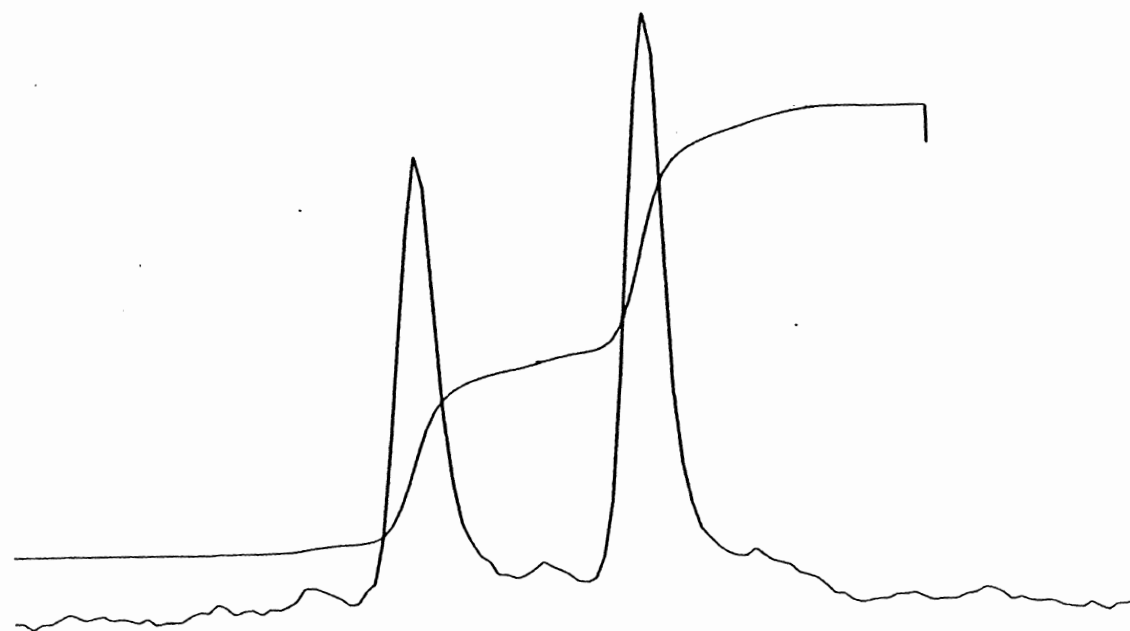
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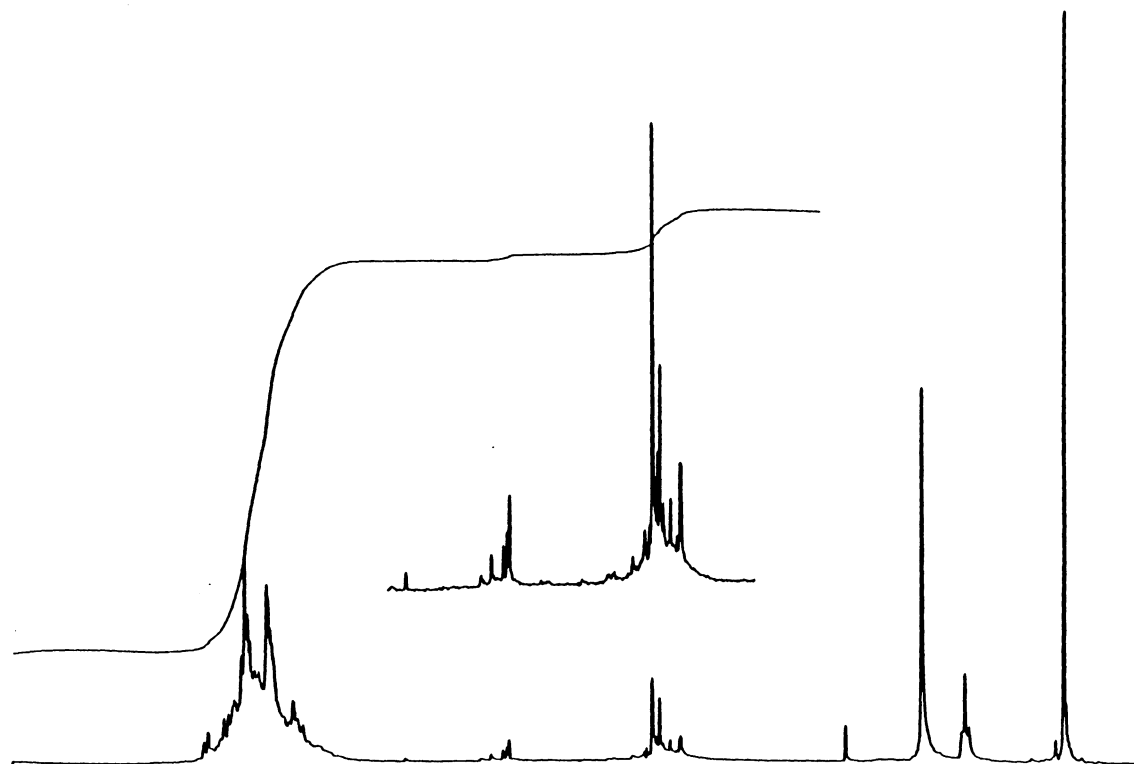
SPECTRUM p-MeO "F"



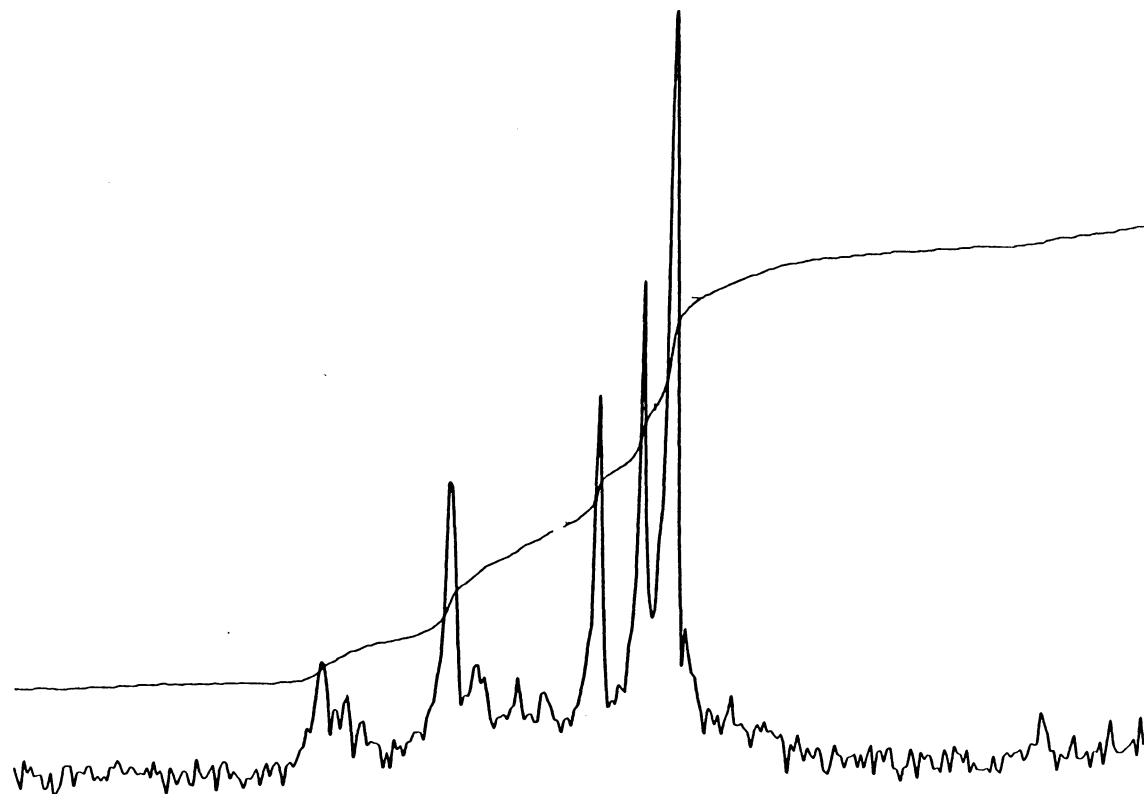
SPECTRUM m-MeO "A"



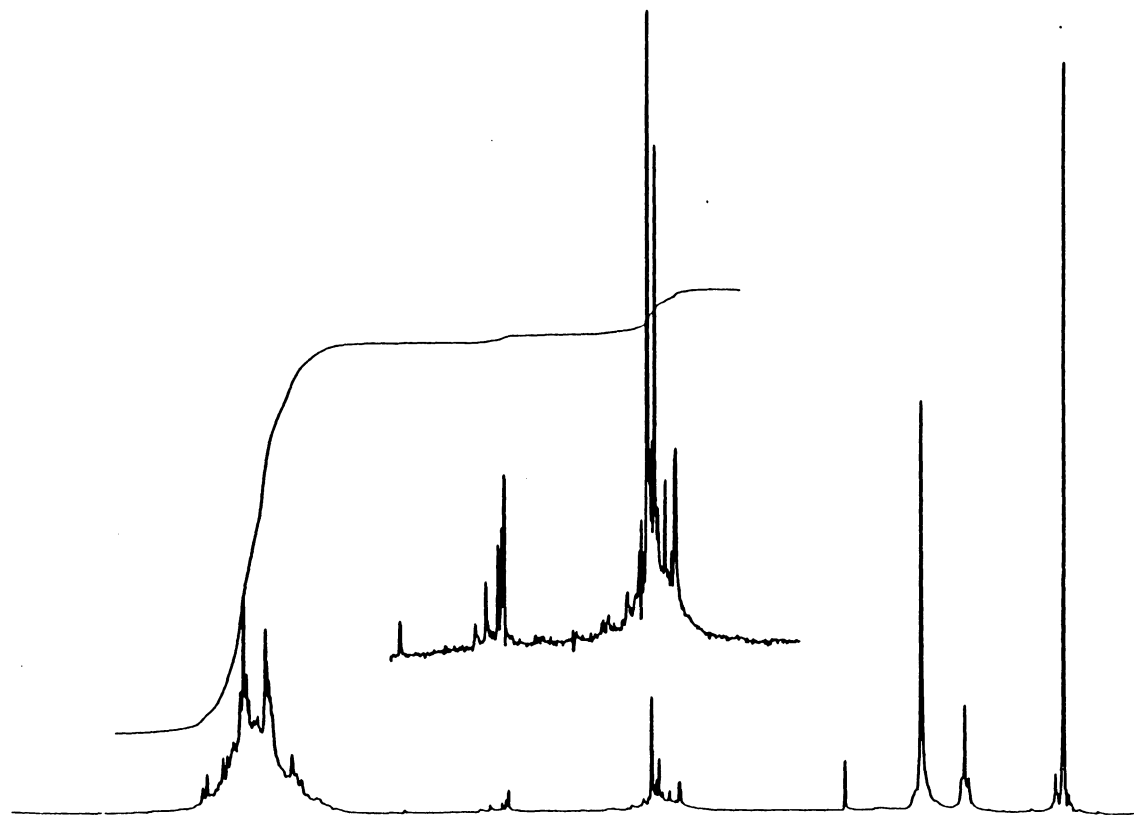
SPECTRUM m-MeO "B"



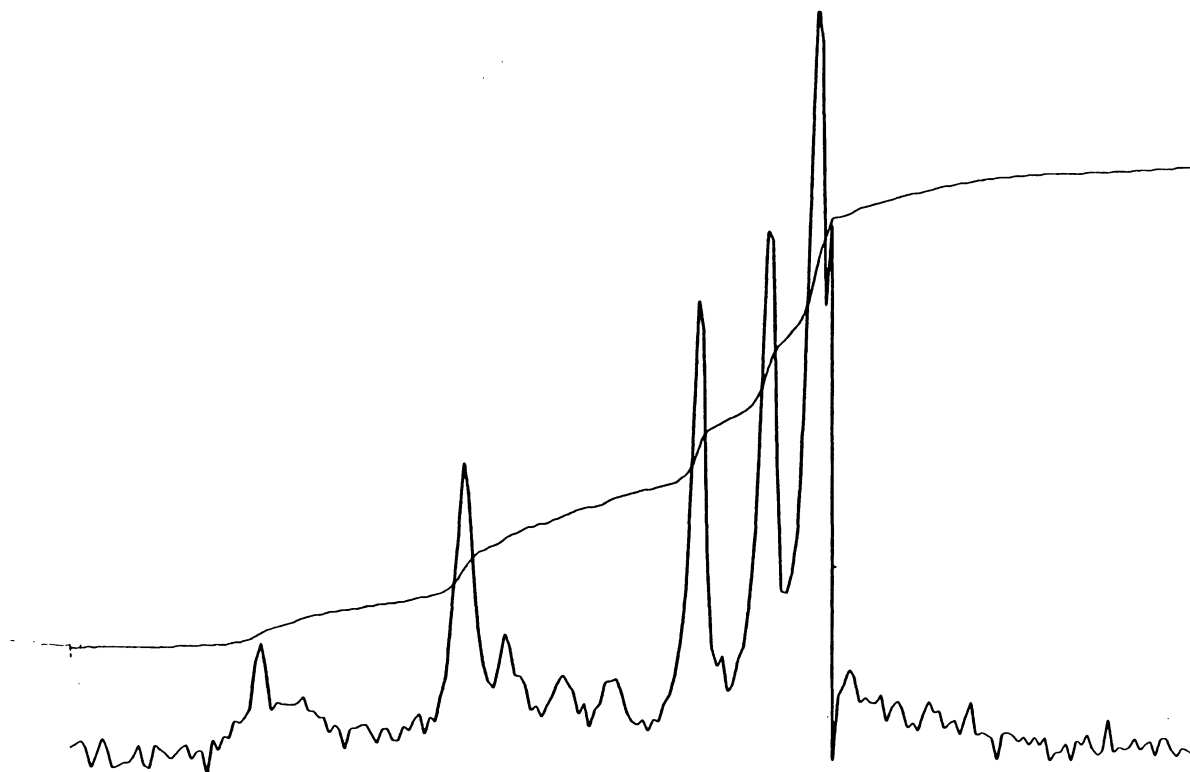
SPECTRUM m-MeO "C"



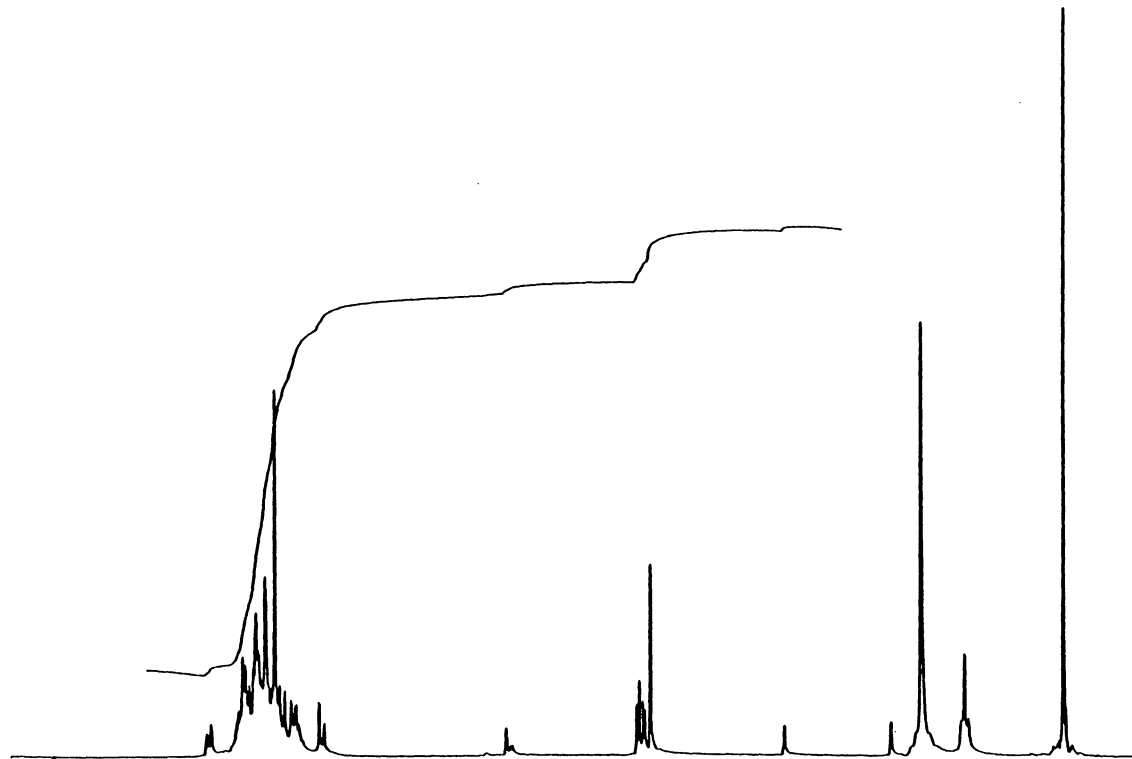
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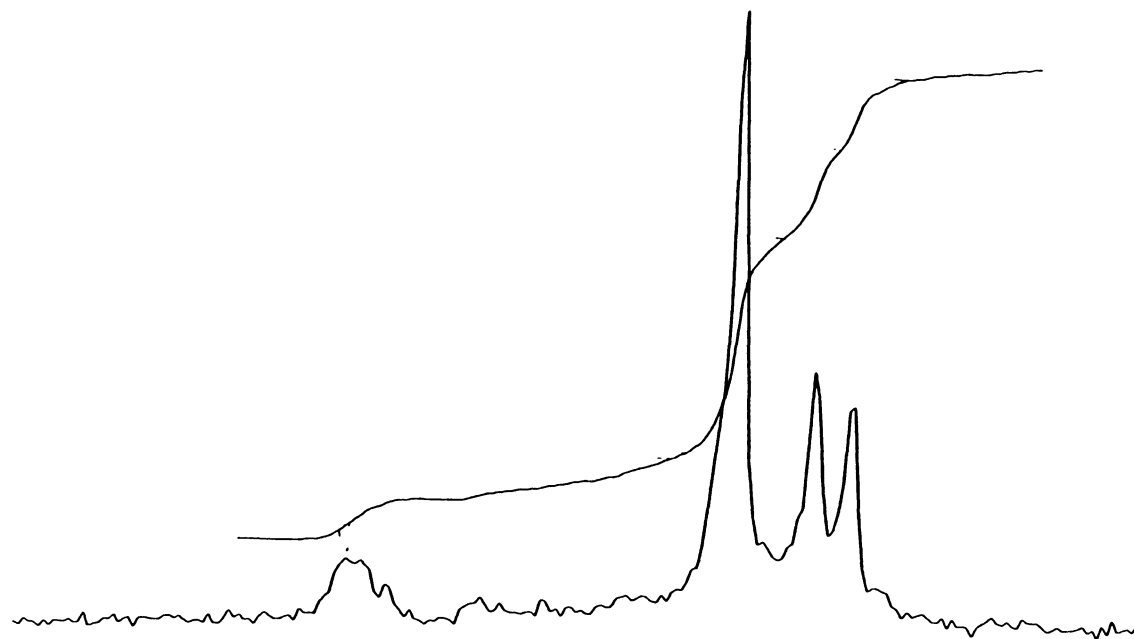
SPECTRUM m-MeO "E"



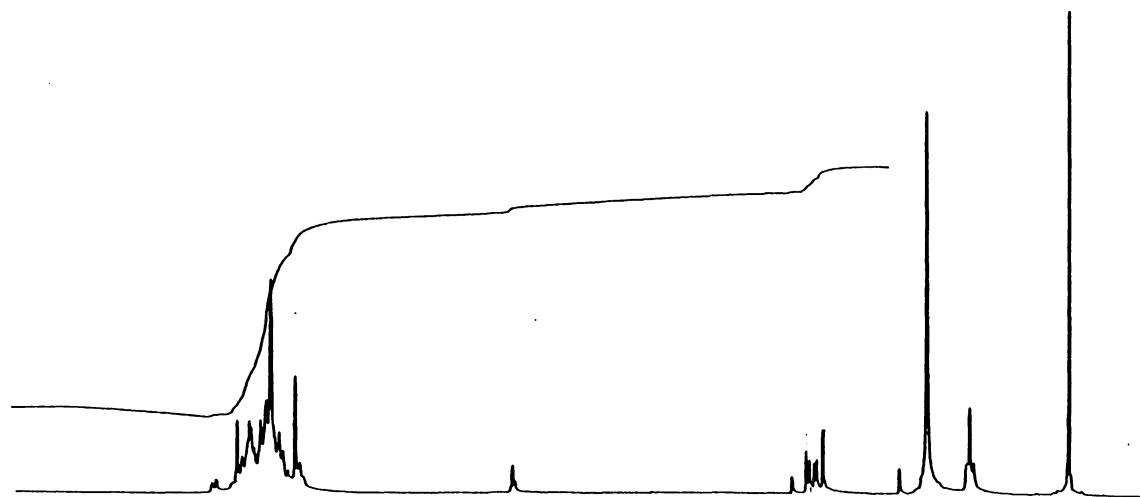
SPECTRUM m-MeO "F"



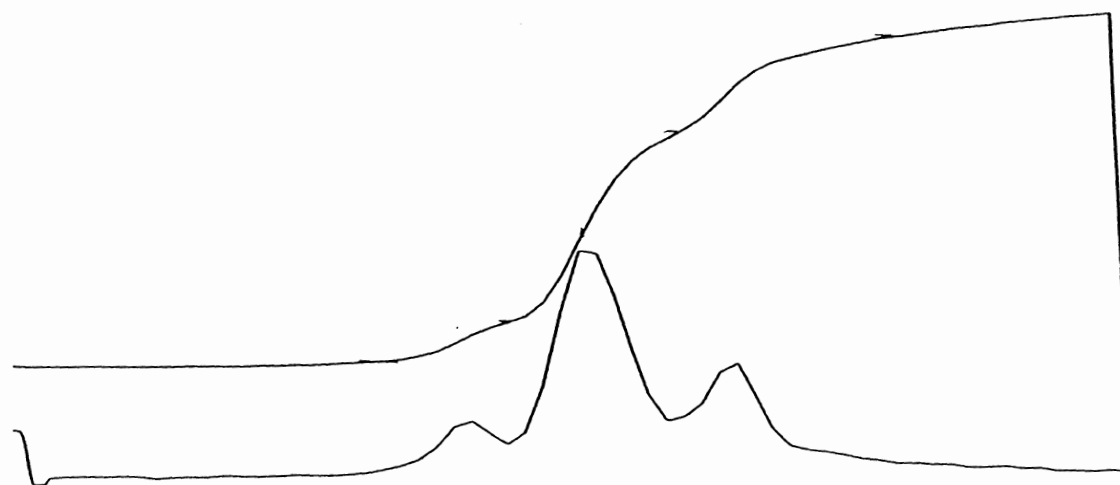
SPECTRUM p-Cl/p-MeO "A"



SPECTRUM p-Cl/p-MeO "B"



SPECTRUM p-Br/p-Me "A"



SPECTRUM p-Br/p-Me "B"

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the scanned document**