


STUDY OF THE KINETICS OF THE [1,5]-SIGMATROPIC
PHENYL REARRANGEMENT IN 3,4-BIS(para-SUBSTITUTED PHENYL)-
1,2,5-TRIPHENYL-2,4-CYCLOPENTADIEN-1-OLS

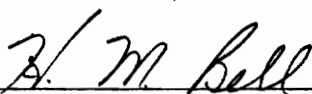
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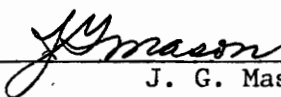
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in
Chemistry

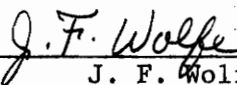
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DEDICATION

To Patricia Ann in appreciation for her patience and support in making this work possible and sharing the dark days, as well as the bright days, during my graduate study for this degree.

And to my Father and Mother who have encouraged and helped me for as long as I can remember.

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I also wish to thank Mrs. Brenda Mills and her family and Guy Brooklyn Oldaker, III, without whose help this dissertation would not have been presented in the excellent format that it is at present.

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INTRODUCTION

A considerable amount of work has been published by Youssef and Ogliaruso dealing with the reactions of polyarylated carbinols, specifically the carbinol 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.¹⁻⁴ Their work laid the foundation for this study concerned with a deeper understanding of the electronic effects associated with the superficial [1,5]-sigmatropic rearrangement that this family of polyarylated carbinols has been observed to undergo. To this end it was important to investigate the kinetics of this rearrangement, in a series of para-substituted carbinols, to see if the results of this investigation would lend support to a transition state that was consistent with the observed sigmatropic reactions. Work was started dealing with two series of substituted carbinols, the 1-para-substituted phenyl derivatives and the 3- and 4-para-substituted phenyl derivatives. This study deals with the results obtained from the kinetic investigation of the 3- and 4-para-substituted phenyl carbinols.

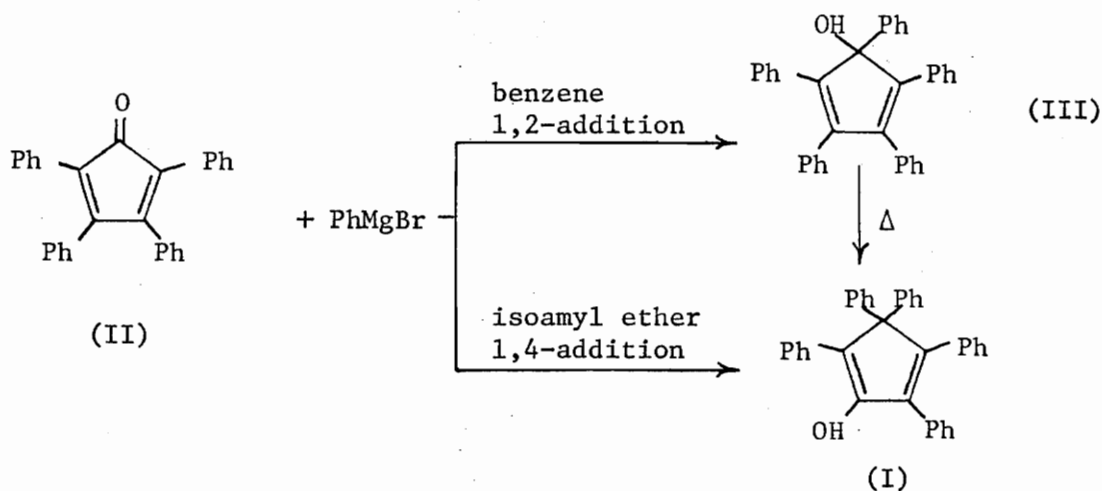
Nine 3- and 4-para-substituted phenyl derivatives were prepared and studied, namely the N,N-dimethyl-, t-butyl-, methoxy-, methyl-, thiomethyl-, fluoro-, chloro-, bromo- and iodo-. The corresponding rearranged ketones, and 3- and 4-para-substituted phenyl-2,2,5-triphenyl-3-cyclopenten-1-ones were also synthesized.

A cursory study of the mass spectral fragmentation of the 1-para-phenyl and 3- and 4-para-phenyl substituted alcohols was also

investigated. The results of the latter study are also included in this dissertation.

HISTORICAL

In 1943, Allen and Van Allan⁵ reported that 2,3,3,4,5-pentaphenyl-1,4-cyclopentadien-1-ol (I) could be prepared by either direct 1,4-Grignard addition of phenylmagnesium bromide in isoamyl ether to tetraphenylcyclopentadienone (II) or by thermal isomerization of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (III) formed by the 1,2-addition of phenylmagnesium bromide in benzene to tetraphenylcyclopentadienone (II).



In 1961, Dufraisse et al.,⁶ reinvestigated the thermal isomerization of III in the absence of solvent, and found that, in addition to two other minor products which were formed, the correct structure of the major product produced was not I but 2,2,3,4,5-pentaphenyl-3-cyclopentien-1-one (IV).⁷ They explained the formation of IV via a pinacol rearrangement of III.

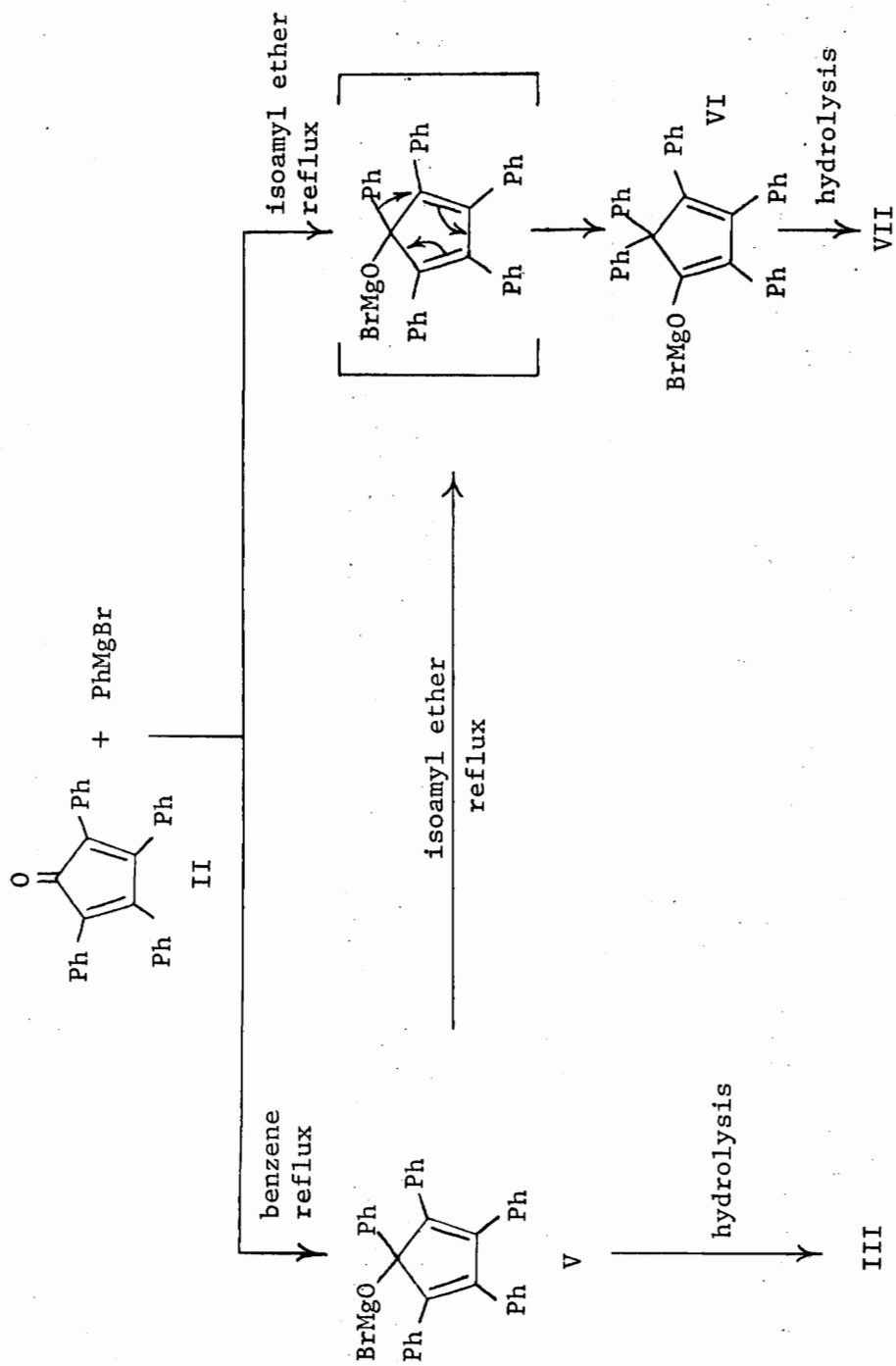
Youssef and Ogliaruso, in 1972,¹ reinvestigated both the 1,4-Grignard addition of phenylmagnesium bromide to II and the thermal isomerization of III. They established that both reactions produce IV

not via a pinacol rearrangement as previously reported but via a symmetry-allowed suprafacial [1,5]-sigmatropic phenyl shift. In addition they repeated all the reactions which involved interconversions of the pentaphenylated cyclopentadienol system originally reported by Allen and Van Allan and corrected the structures of all the products subsequently produced.

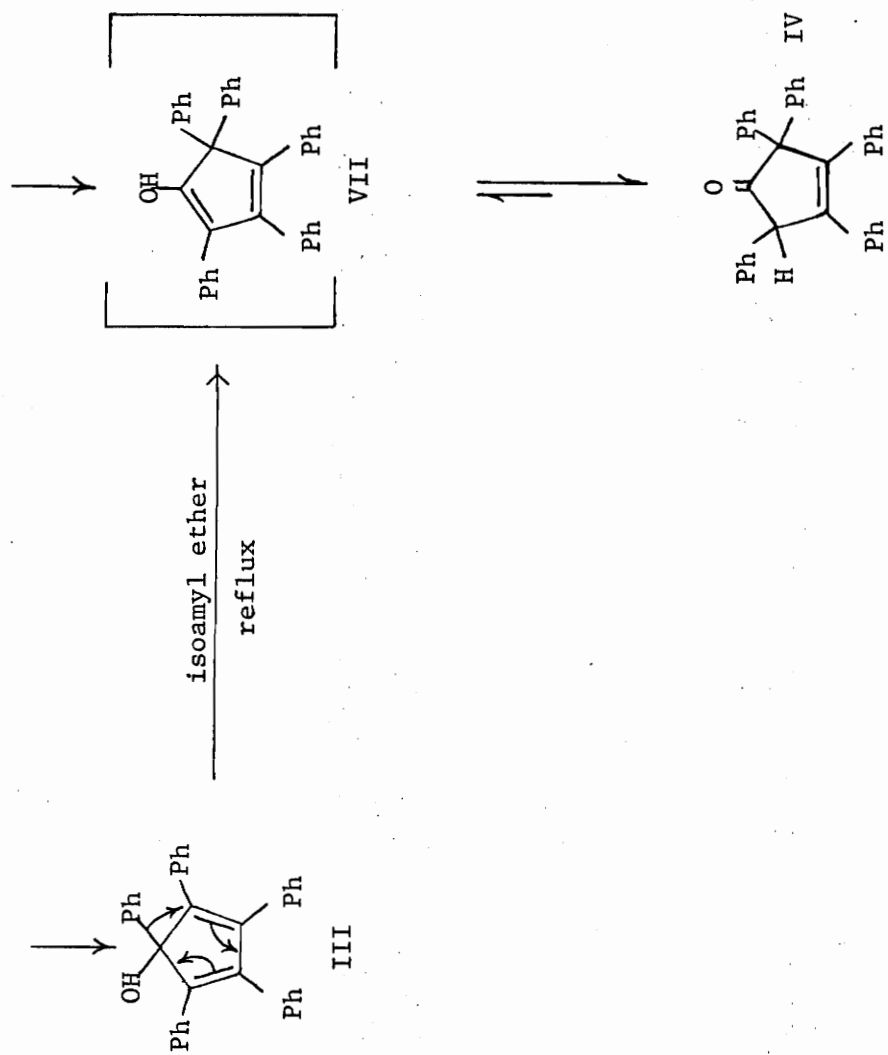
Addition of phenylmagnesium bromide in refluxing isoamyl ether to II, followed by hydrolysis, afforded a 65% yield of IV. The structural assignment of the product was aided by the spectral properties of a sample of IV independently synthesized⁷ and by a mixture melting point comparison which showed no depression. To establish that IV is formed by the thermal isomerization of the magnesium bromide salt V formed by 1,2-addition of phenylmagnesium bromide to II, V was prepared and its reaction upon heating was investigated. Grignard addition of phenylmagnesium bromide to II in benzene afforded the desired magnesium bromide salt V, since quenching afforded the dienol III. Replacing the solvent of V by isoamyl ether and allowing the solution to reflux for 8 hours before hydrolysis and work-up afforded 65% of enone IV. The reactions noted above are outlined in Scheme I.

These results indicated that a direct 1,6-addition of the phenyl magnesium bromide to II did not occur, but that the 1,2-addition product V initially formed when phenylmagnesium bromide is added to II thermally rearranged to VI. This rearrangement was believed to occur through a phenyl migration by a symmetry-allowed suprafacial [1,5]-sigmatropic shift. This was the first such rearrangement reported for

SCHEME I



SCHEME I (continued)



magnesium salts obtained from Grignard reactions. It was striking that such a rearrangement was so facile and afforded such good yields of rearranged products. Hydrolysis of the magnesium bromide salt VI afforded only IV, probably through the dienol VII, which would indicate a keto-enol tautomerization in which form IV is highly favored.

To establish such a sigmatropic shift is possible in the cyclopentadienol system, III was prepared^{5,7,9} and isolated in 90% yield and was then placed under reflux for 6 hr in isoamyl ether. This procedure afforded a 90% conversion of III to IV, probably through the dienol VII. The ease with which the dienol III was isomerized to the enone IV was striking and took place much more clearly and in higher yield in the presence of solvent than in the absence^{5,6} of solvent.

The initial studies² of the mechanism of this phenyl shift were performed to establish that the rearrangement was indeed sigmatropic and that it proceeded without any ionic or radical character. Compound III was allowed to reflux in isoamyl ether for 6 hours with a strong stream of oxygen bubbling through the refluxing solution continuously. The yield of enone was 90%. These results were exactly the same as those obtained when the reaction was run without oxygen. This indicated that the observed phenyl shift is not radical in nature, since the presence of a radical inhibitor did not affect the yield of IV obtained. To eliminate the possibility of the rearrangement proceeding through some type of ionic mechanism, the reaction was run again using DMSO, a solvent having a considerably higher dielectric constant compared to

isoamyl ether: isoamyl ether, ϵ 2.82;¹⁰ DMSO, ϵ 46.6.¹¹ The rate of the reaction in both solvents was monitored by chromatography and was found to be the same. These results indicated that it was unlikely that any ionic character was associated with the phenyl migration. Having eliminated the possibility of any ionic or radical character to the observed rearrangement, it was left to be characterized as a [1,5]-sigmatropic phenyl shift, which had to be suprafacial if it was thermally induced and it was to obey the Woodward-Hoffmann rules.

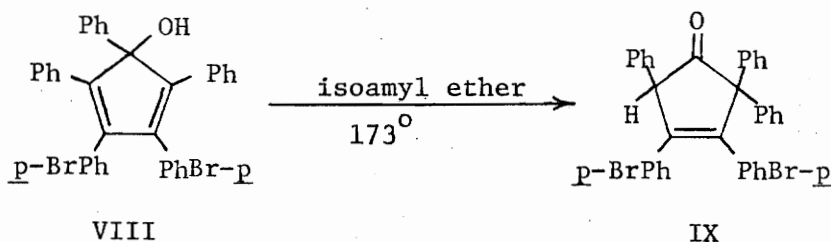
In 1973 Youssef and Ogliaruso² published the second in a series of papers dealing with the reactions of polyarylated carbinols. This paper dealt with the kinetic study of the suprafacial [1,5]-sigmatropic rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one.

The kinetic study of the suprafacial [1,5]-sigmatropic rearrangement investigated by Youssef and Ogliaruso² was performed at 173° in isoamyl ether and at 173°, 180°, 190° and 200° in diphenyl ether. The rearrangement was observed to be first order throughout the temperature range investigated; the rates observed were monitored by glpc, and the rate constants (k) at the temperatures used were found to be 0.28, 0.40, 1.09, and $2.7 \times 10^{-2} \text{ hr}^{-1}$, respectively. Calculations of the activation energy of this phenyl [1,5]-sigmatropic shift from the Arrhenius equation gave $36.1 \pm 3.6 \text{ Kcal/mol}$, while ΔS^\ddagger for this phenyl migration was -7 eu.

It was concluded that the [1,5]-sigmatropic phenyl migration was not solvent dependent considering their initial results in DMSO and also considering the results obtained here in isoamyl ether and diphenyl ether. In both cases there was no

change in the observed rate. In addition, since previously reported results¹ indicated that this rearrangement proceeds without any ionic or radical character, it appeared that the transition state for this phenyl shift is similar to the proposed transition state for sigma-tropic hydrogen migrations,^{12,25} and that the phenyl rearranges via a true sigmatropic mechanism in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.

During this continuing study^{3,4,26} of the [1,5]-sigmatropic phenyl rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (III) to give 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one (IV) it became necessary to investigate the rearrangement of the 3- and 4-para-substituted phenyl derivatives of III. This investigation began by using the para-bromo substituted derivative (VIII) and proceeded as previously described.^{1,5} However, attempts to analyze the kinetics of



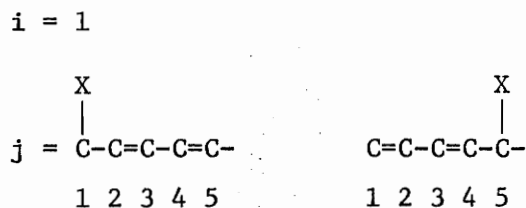
this rearrangement by gas liquid chromatographic analysis of samples proved fruitless. Although a separation of the alcohol VIII and the ketone IX was observed, it was also observed that thermal rearrangement of VIII to IX occurred on the column under these conditions. In 1975 Berg, Ogliaruso and McNair²⁷ obtained a reliable quantitative

separation of the alcohol VIII and ketone IX by a high pressure liquid chromatographic technique. This technique forms the basis of the kinetic study used in this dissertation.

Sigmatropic Rearrangements

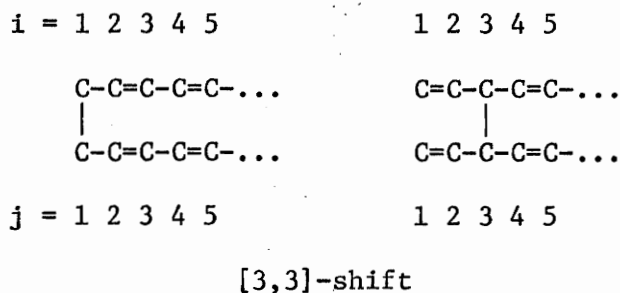
Sigmatropic reactions are uncatalyzed unimolecular one-step processes whereby a sigma bond migrates to a new position if it is flanked by one or more π -electron systems, e.g. 1,5 H-transfers in the Claisen and Cope rearrangements.^{29,30} Sigmatropic rearrangements can also be defined as the reorganization of a molecular skeleton upon heating or photolysis, where the σ - and π -bonds shift in a concerted fashion with conservation of orbital symmetry. The net effects of this rearrangement is the formation of a σ -bond at the opposite end of the π -system with a concerted shift of the π -bonds.³¹ There are no special requirements that the molecular backbone atoms be carbon atoms.

The general nomenclature for sigmatropic rearrangements is classified by 2 numbers, i and j , set in brackets $[i,j]$. The numbers refer to the number of the atoms to which each end of the migrating σ -bond interacts, with the numbering beginning from the original two atoms forming the initial σ -bond. For example:



[1,5]-shift.

The Claisen and Cope rearrangements are classified as sigmatropic rearrangements of the order [3,3]:



There are two distinct ways of effecting a sigmatropic migration for a [1,5]-shift of a hydrogen atom, a suprafacial process or an antarafacial process (Page 14).

In the suprafacial process the transferred hydrogen atom is associated at all times with the same face of the π -system; in other words, the migrating σ -bond moves across the same face of the π -electron system. The suprafacial process is the most common sigmatropic rearrangement.

In the [1,5]-antarafacial shift the migrating hydrogen atom is passed from the top face of one carbon terminus to the bottom face of the other carbon terminus.

The selection rules for neutral [i,j] thermal sigmatropic rearrangements, are shown below.³²

HOMO Selection Rules for [i,j]

Sigmatropic Migrations

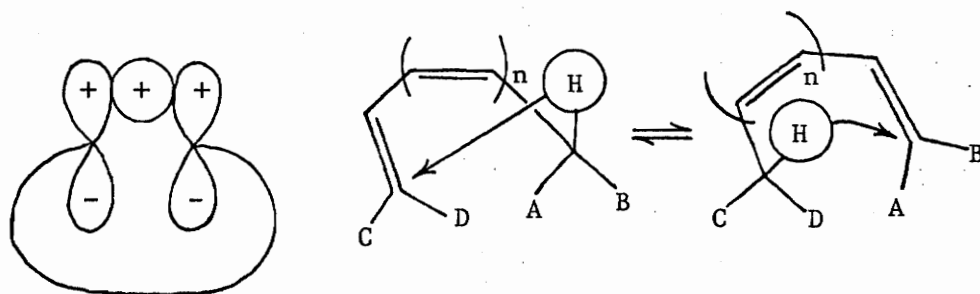
<u>i</u>	<u>Allowed</u>	<u>Forbidden</u>
3	antara-retention supra-inversion	antara-inversion supra-retention
5	antara-inversion supra-retention	antara-retention supra-inversion
7	antara-retention supra-inversion	antara-inversion supra-retention

The greatest amount of research in the area of [i,j]-sigmatropic rearrangements has been done, where $j = 5$, because of the ease in which the [1,5] shifts take place in contrast to the [1,3] or the [1,7] shifts and because of the lack of availability of model systems where the [1,3] or the [1,7] shifts could take place; although, equally important model systems such as the 1,3-cyclohexadiene and 1,3,5-cycloheptatriene have been used by Schiess and Fünfschilling^{33,34} and Kloosterziel,³⁵⁻⁴¹ respectively.

During the last 10 years an enormous number of excellent reviews^{29,30,32,45-59} have been written describing the results of a small legion of workers laboring to demonstrate the wide applicability of orbital symmetry rules (or lack thereof) in sigmatropic processes in a wide range of systems. The area of interest for this dissertation however, is the effect of substitution at several points in the system upon the overall migrating rate. It is important to

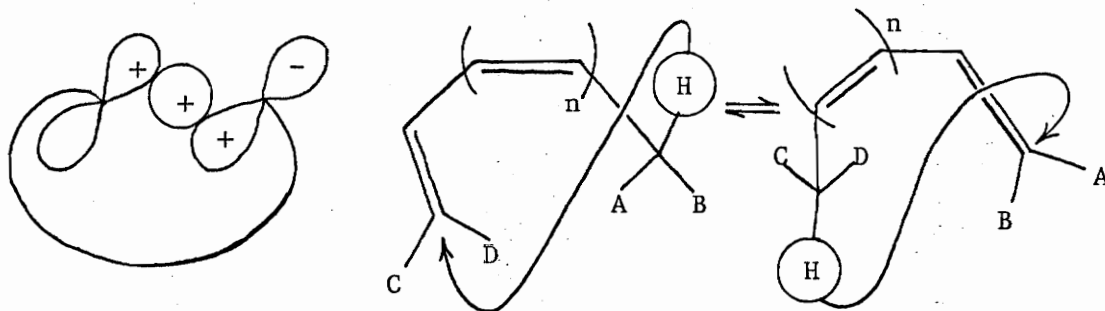
Concerted Sigmatropic Suprafacial Process

($n = 1, 3, \dots$)



Concerted Antarafacial Process

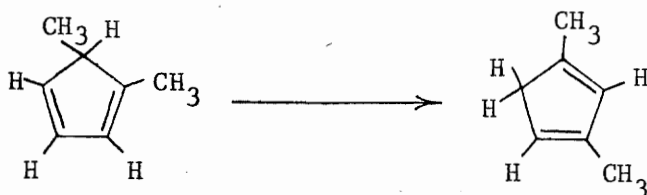
($n = 0, 2, 4, \dots$)



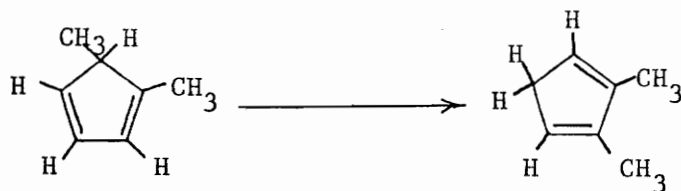
note here that in construction of the Woodward-Hoffmann rules electronic effects were not considered important in directing the rate of sigmatropic reactions.⁵⁹ It has been shown, however, that substituents effects do exhibit dramatic electronic effects in directing the course of thermal sigmatropic reactions, in a wide variety of systems. Below are reviewed some of the published work associated with electronic effects in sigmatropic rearrangements.

A. Rearrangements in 5-Membered Rings:

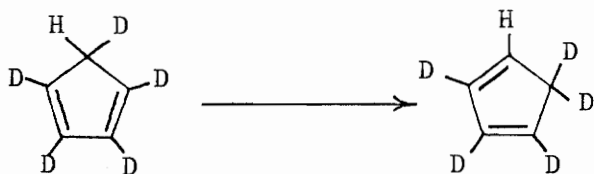
Since the initial work of Mironov¹³ on methyl-substituted cyclopentadienes and on 5-deuteriocyclopentadiene, several thermal sigmatropic reactions of cyclopentadiene systems have been discovered. McLean and Haynes¹⁴ studied the [1,5]-hydrogen rearrangement of 1-methylcyclopentadiene to 5-methylcyclopentadiene and 1,2-dimethyl-



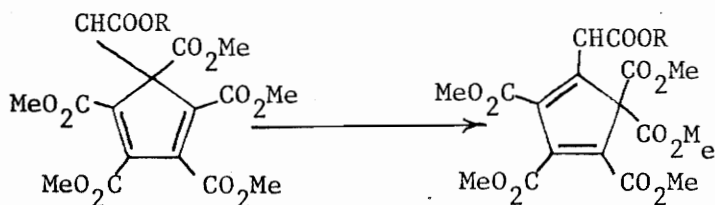
cyclopentadiene to 2,3-dimethylcyclopentadiene and both have investi-



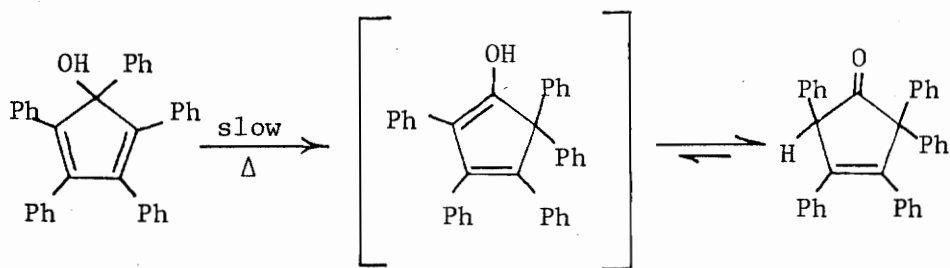
gated the rearrangement of isotopically labeled 5-H-perdeuteriocyclopentadiene, while Backes^{16,17,63} has reported on [1,5]-ester



migrations in cyclopentadiene systems and Ogliaruso has investigated [1,5]-phenyl migration in 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol



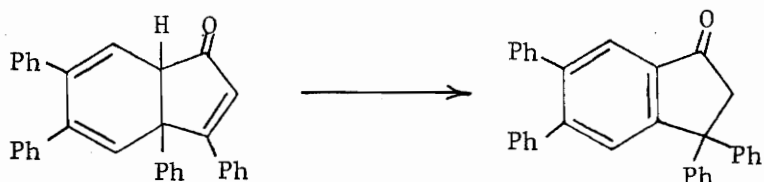
to 2,2,3,4,5-pentaphenyl-3-cyclopenten-1-one.¹ Work on the unsub-



stituted indene system has been performed by Roth,¹⁵ Alder,¹⁹ Berson²⁰ and Isaacs,²¹ while Koelsch and Johnson²² and more recently Miller²³ have reported studies on substituted indene systems.



More recently Wawzonek²⁴ has reported on the thermal sigmatropic rearrangement of 3a, 7a-dihydro-3,3a,5,6-tetrahydrophenylinden-1-one to 3,3,5,6-tetraphenylindan-1-one.



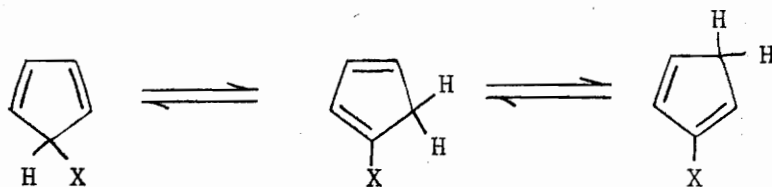
The preceding paragraphs have presented a brief look at the number and kinds of systems that have exhibited thermal sigmatropic rearrangements. Each of these systems lend themselves nicely to substitution with various groups that should also undergo thermal sigmatropic rearrangement in which their rates of migration could be measured. It is with this purpose in mind that the following discussion of these known systems which have been reported to undergo thermal sigmatropic rearrangements and which show substituent effects, was written. It should be noted that the number of systems that have appeared in the literature which have shown substituent effects are few, but that these systems are representative of the systems that have shown sigmatropic rearrangements in general.³² The following

discussion centers on the representative families of compounds which have shown substituent effects. This discussion will be followed by a tabular representation of the literature data and an analysis of the existing data in light of certain basic unifying elements which effect the transition state in such rearrangements.

B. Sigmatropic Rearrangements in Cyclopentadiene Systems Which Have Shown Electronic Affects:

The simplest system that has shown electronic affects in a sigma-tropic rearrangement has been the cyclopentadiene system.

Breslow and coworkers⁶⁰ have studied the effect of halogen substitution on [1,5]-hydrogen migration in cyclopentadiene. Compared to the parent hydrocarbon (i.e., X = H), halogen substitution slows the rate of hydrogen migration considerably. A considerable rate differential exists between the different members of the halogen



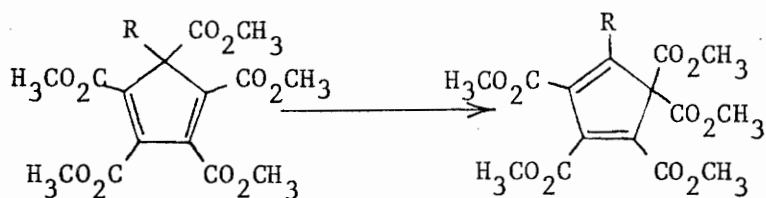
Relative Rate of Rearrangement

cyclopentadiene	1.00 [b]
1-Cl-cyclopentadiene	0.67
1-Br-cyclopentadiene	0.64
1-I-cyclopentadiene	0.17

[b]-Cyclopentadiene being used as the
standard

family. Breslow has rationalized this behavior as indicating that a localized positive charge on carbon must be involved in the [1,5]-transition state. The fact remains that the halogens are the only substituents which are known that retard sigmatropic hydrogen migrations in simple systems, though no other electron withdrawing groups have been tried.

The second study in a cyclopentadiene system was by Hoffmann and coworkers⁶³ dealing with the influence of substituents on the rate of [1,5]-methylcarboxylate ester migration in a pentamethylcyclopentadienepentacarboxylate system.



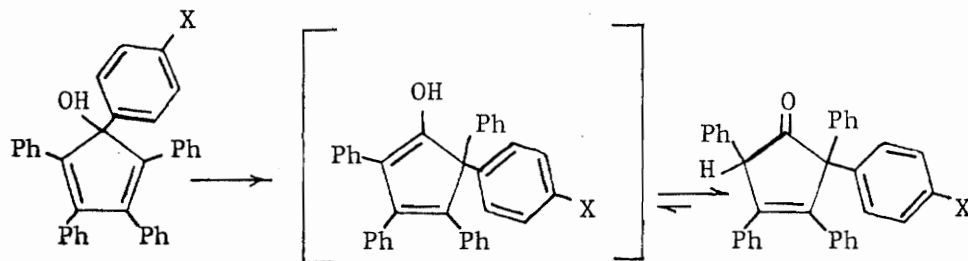
R = CH₃S, Cl, CH₃, C₆H₅, CH₃OCOCH₂, CH₃O, NC, C₆H₅NH, (CH₃)₂N

Relative Rates of Rearrangement at 400°K

<u>R</u>	<u>R_{rel} [s⁻¹]</u>
CH ₃ S	0.28
Cl	0.33
CH ₃	1.0 [a]
C ₆ H ₅	1.9
CH ₃ OCOCH ₂	2.1
CH ₃ O	12.0
CN	15.5
C ₆ H ₅ NH	125
(CH ₃) ₂ N	260

[a] Corresponds to $k = 2.26 \times 10^{-4} \text{ sec}^{-1}$
 at 400°K; $\Delta H^\ddagger = 26.9 \pm 2.1 \text{ kcal mol}^{-1}$;
 $\Delta S^\ddagger = -8.6 \pm 2.8 \text{ cal K}^{-1} \text{ mol}^{-1}$

Finally Youssef⁷⁴ has found distinct electronic effects on a [1,5]-thermal sigmatropic phenyl rearrangement using (1-para substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol derivatives.

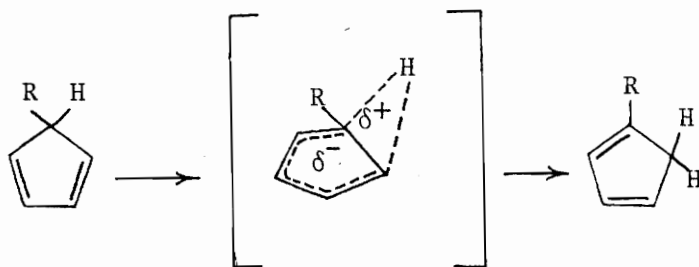


$X = \text{C}(\text{CH}_3)_3 > \text{OCH}_3 > \text{CH}_3 > \text{H} > \text{Cl} > \text{Br}$

It is evident from the results shown above that substituent effects do play a role in directing the rate of these reactions.

It becomes clear at this point that if substituents can effect the rate of a reaction, then some basic unifying element should be operative in each of these examples. It thus appears that the transition state for each of these examples directs the action of the substituents which lie along the π -backbone of the system involved in the sigmatropic rearrangement. A transition state is set up by the rearrangement of the electron density through the length of the π -backbone.⁴⁴ Changes in electron density set up areas of high (δ^-) and low (δ^+) electron density.⁴² The substituents either help to relieve these areas of charge destabilization and increase the rate of reaction or hinder them and decrease the overall rate of reaction.

The transition state for the H-migration in 1-substituted-cyclopentadiene is illustrated below with supporting evidence



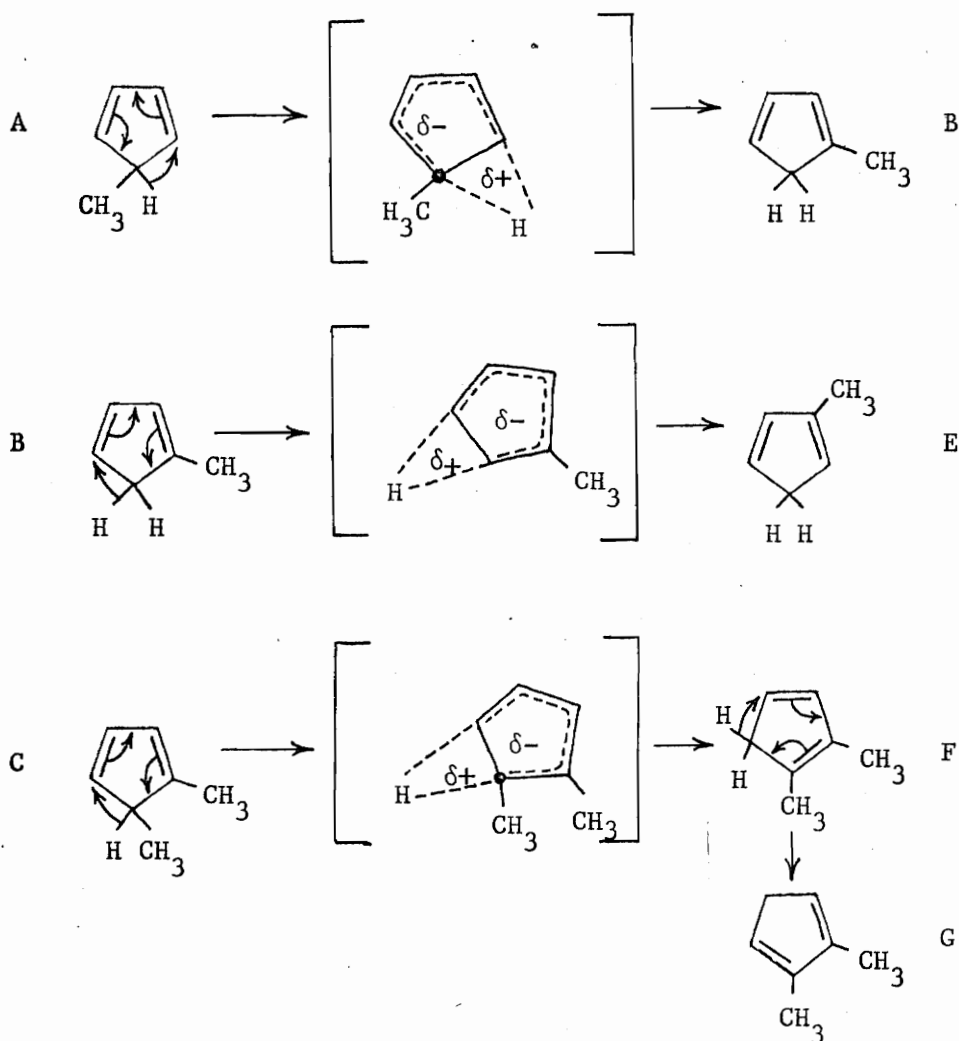
for this picture coming from several sources; in 1974 Shchembelov and Ustynyuk⁴⁴ performed a series of calculations showing that the transition state has an area of electron charge destabilization, namely an area of low electron density (δ^+) on the migrating hydrogen

(cf. 0.86) and conversely an area of high charge density (δ^-) on the cyclopentadienyl portion of the transition state. It was also shown that with optimization of the geometry, in the cyclopentadiene system, the calculated value of the enthalpy of activation for the hydrogen shift was close to the experimental value.

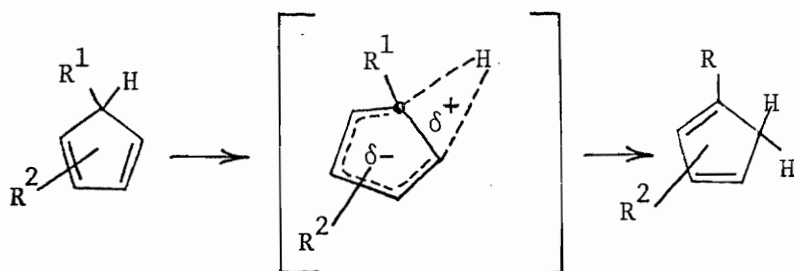
Activation Enthalpies

	$\Delta H_{\text{exp}}^{\ddagger}$ (kcal·mol ⁻¹)	$\Delta H_{\text{calc}}^{\ddagger}$ (kcal·mole ⁻¹)
cyclopentadiene-d ₅	24 ¹⁵	17

This transition state also seems to explain certain experimental results. McLean and Haynes⁷⁰ noted "hydrogen migrates most rapidly from a carbon also carrying a methyl substituents", in methyl-substituted cyclopentadiene systems. They also recognized that lower rates of isomerization appeared with an increased number of methyl substituents. These observations can be satisfactorily rationalized by looking at the transition state in general, its development and decomposition, and the substituent's inherent ability to enter into conjugation and/or its ability to act as an electron donor or withdrawer. The examples that McLean and Haynes⁷⁰ put forth are outlined below: A rearranged to B faster than B rearranged to E, and similarly, C rearranged to F and then G faster than B rearranged to E. To justify these observations one must consider the transition states shown, and



it appears that these transition states are set up rapidly. Justification for this comes from the observation of Breslow⁶⁰ that, when

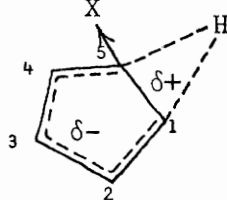
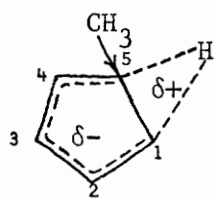


$R_1 = \text{halogen}$ and $R_2 = \text{H}$ the observed rate of the reaction is slower than when $R_1 = \text{methyl}$ and $R_2 = \text{H}$. He states that since carbon-5 must rehybridize from sp^3 to the more electronegative sp^2 , a methyl substituent would facilitate this (through hyperconjugation) to a greater extent than a halogen. Thus, the energy barrier for the rearrangement when R_1 is halogen is much higher than the barrier for the rearrangement when R_1 is methyl.

The observation by McLean and Haynes⁷⁰ that the more substituents present the slower the observed rate can also be explained by this transition state. If $R_1 = \text{methyl}$ and $R_2 = \text{methyl}$ two effects are taking place. First, R_1 may enter into conjugation with the π -backbone through hyperconjugation and lower the energy barrier to activation, and secondly, R_2 being electron donating destabilizes the partial negative charge (δ^-) in the cyclopentadienyl backbone and increases the energy barrier.

Using this view of the transition state the rates of rearrangement observed by McLean and Haynes⁷⁰ may be easily justified: A should rearrange faster than C, and B should rearrange the slowest.

Breslow's⁶⁰ observation when $R_1 = \text{halogen}$ is also explained by the preceding arguments dealing with the electronegativity and the partial charge delocalization in the transition state. In this case it is important to realize that the electronegativity argument could be extended since halogens are weak π -donors by resonance and are withdrawing by induction. Thus, McLean's report⁷⁰ that methyl substitution on C-5 accelerates the rate is consistent with Breslow's finding

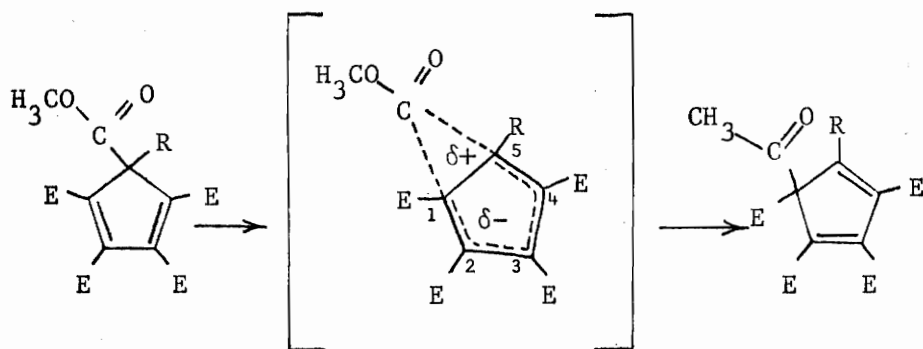


X = Cl, Br, I

that halogen in C_5 decelerates the rate, since the methyl (R_1) favors and the halogen disfavors the rehybridization of C-5 to (more electro-negative) sp^2 and that this effect is overbalanced by the newly-developed conjugation. In other words, the electron withdrawing ability of the halogens far outweighs their ability to enter into conjugation as π -donors and thus the observed rate is decreased.

The final two examples in the cyclopentadiene family that have shown sigmatropic migrations involve carbon migrations.

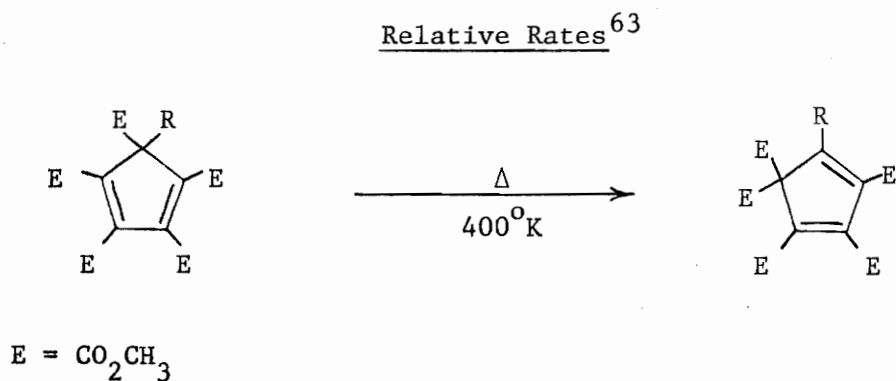
Hoffman and coworkers¹⁶ have looked at substituent effects on [1,5]-sigmatropic ester shifts as mentioned previously and the transition state involved is illustrated below. As seen previously, the



E = CO_2CH_3

R substituent at the C-5 position plays a role similar to the methyl group in the 5-methylcyclopentadiene case illustrated previously.

The relative rates of rearrangement at 400°K (reported below) can be explained in the light of the previously outlined hypothesis.

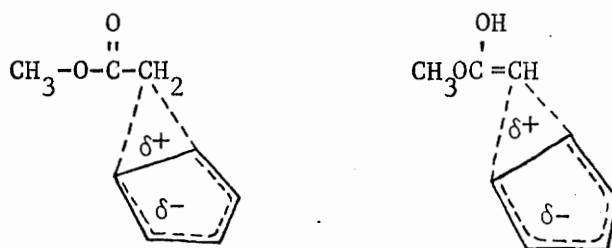


<u>R</u>	<u>k_{rel}s⁻¹</u>
CH ₃ S	0.28
Cl	0.33
CH ₃	1.0
C ₆ H ₅	1.9
C ₆ H ₅ "NH	125
(CH ₃) ₂ "N	260
CH ₃ O	12.0
CN	15.5
CH ₃ OCOCH ₂	2.1

The table shows two things; first, electron donating species increase the rate of reaction and secondly, those substituents that can π-donate or enter into conjugation increase the rate even though

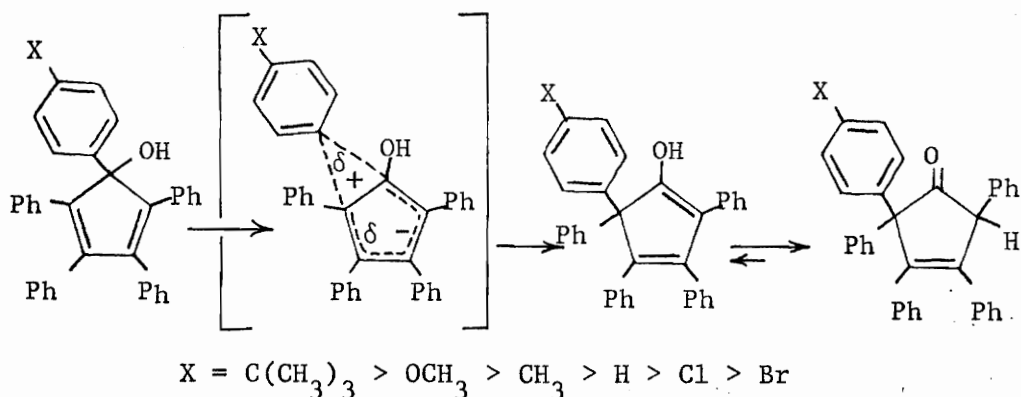
they might be strongly electron withdrawing by induction. Thus, we see that NC and C_6H_5 increase the rate to a greater extent than CH_3 , and that Cl retards the rearrangement less than SCH_3 , allowing for the fact that Cl being a stronger electron withdrawer is also a stronger π -donor compared to SCH_3 . The remaining substituents exhibited the observed rates as follows:

CH_3OCOCH_2 migrated faster than C_6H_5 since, as illustrated below, the enol would increase the conjugation to a further extent. Finally,



the lone pair on the nitrogen of $C_6H_5\ddot{N}H$ and $(CH_3)_2\ddot{N}$ would certainly increase their ability to π -donate better than any of the substituents listed above.

No studies have yet been published to establish the substituent effects in [1,5] phenyl migrating though [1,5] phenyl migrations are known.^{23,76} However, evidence of substituent effects in 4-(para-substituted phenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ol has been observed.⁷⁴ Two things should be noted with regard to this system; first, this work presents the only verified [1,5] phenyl sigmatropic rearrangement³² exhibiting substituent effects, and secondly, this work presented the first clear case of substituent

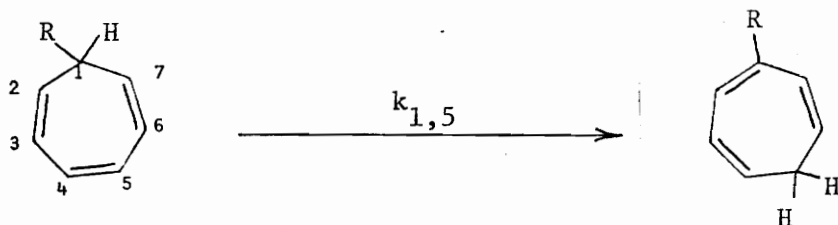


effects in a simple [1,5] phenyl shift. It should be realized that with this system we no longer have to labor under the rationale of gross effects for substituents, since the Hammett¹¹⁵ σ -concept and Hine's¹¹⁶ D_x -parameters are neither adequate nor applicable in the aforementioned cases.⁶³ For this model system Hammett's σ_p values have been shown to work and gave the investigator substantiated values for substituent effects.

C. Electronic Effects Demonstrated in [1,5] Sigmatropic Rearrangements of Seven-Membered Ring Systems:

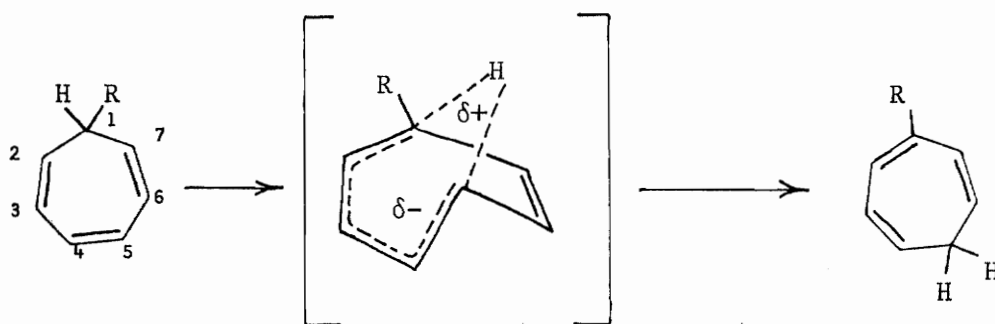
Kloosterziel and coworkers have studied the problem of electronic effects in sigmatropic rearrangements of substituted 1,3,5-cycloheptatrienes by considering the electronic effect of various R groups on $k_{1,5}$ obtained during a sigmatropic [1,5]-proton shift.

Relative Rates of $k_{1,5}$
Obtained During the [1,5]-H Shift in
1,3,5-Cycloheptatriene

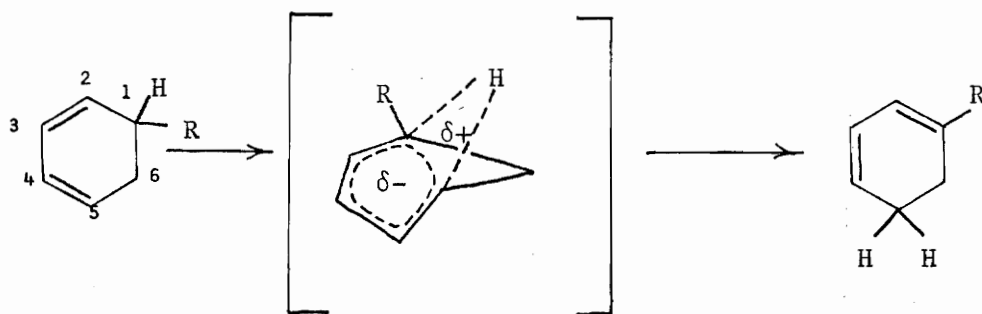


<u>R</u>	<u>$k_{1,5}$</u>
$N(CH_3)_2$	700
$(CH_3)_2NC_6H_4$	150
OCH_3	100
C_6H_5	100
CN	60
SCH_3	40
CH_3	9
D	1
H	1

Although little was known about the geometry of cycloheptatriene in 1963, Kloosterziel and coworkers^{40,41} initially proposed a transition state as illustrated below, to explain the [1,5]-hydrogen sigma-tropic rearrangement in cycloheptatriene.

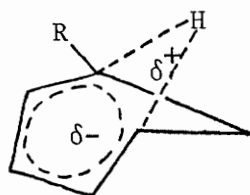


In 1974, de Dobbelaere and coworkers⁴² used INDO calculations to relate activation enthalpies to homoconjugation in the transition state for 1,3-cyclohexadiene and for 1,3,5-cycloheptatriene. The results of their calculations showed an electron density of 0.94 on the moving



hydrogen of cyclohexadiene in the transition state and that homoconjugation existed between carbons 1 and 5. These data imply very strongly that the true transition state has associated with it areas of low electron density (δ^+), and consequently, an area of high electron density (δ^-) most likely be associated with the cyclopentadienyl

portion of the transition state. Therefore, the illustration



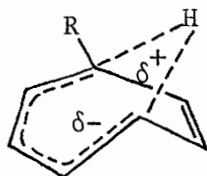
R = H,

R = CH₃, = X

R = C(CH₃)₃, = XI

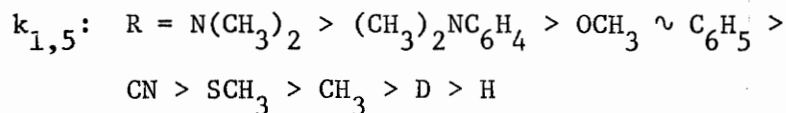
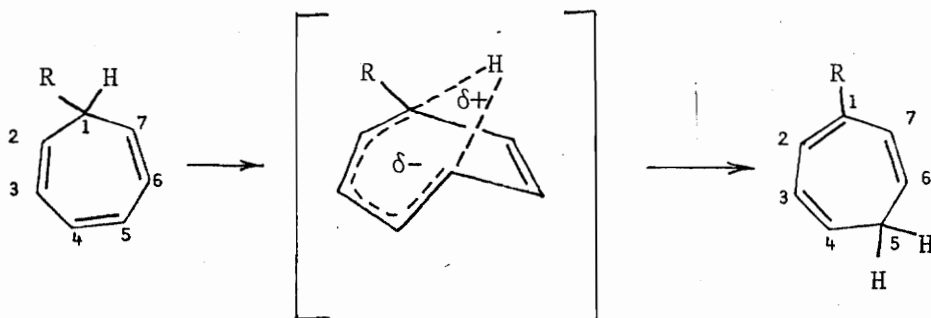
shown above seems to be the most likely representation of the transition state involved in this rearrangement. It is also interesting to note that Spangler⁴³ has reported that XI rearranges faster than X in the range of 300–350°K. This behavior may be ascribed to the fact that although the formation of the transition state with the t-butyl and methyl occurs at about the same rate, the t-butyl substituent is more electron donating than the methyl substituent and therefore the t-butyl assists in the breakdown of the transition state to a greater extent by relieving the charge destabilization and thus increasing the rate of reaction.

Considering the 1,3,5-cycloheptatriene system again, calculations were performed⁴² to investigate the possibility of homoconjugation and changes in the electron density associated with its transition state. The migrating hydrogen carried a value of 0.99 electron density, but no homoconjugation was involved and it was noted that double bond at the 2,3-position is not involved in the transition state. Thus, based



R = H,

upon these calculations the transition state can be illustrated as shown below. de Dobbelaere explained that the value of the electron density of the moving hydrogen and his inability to obtain evidence for the homoconjugation may be attributed to the fact that INDO calculations underestimate the effects of ring strain. Based on the fact that activation enthalpies can be related to homoconjugation in the transition state it seems highly unlikely that such a system would not possess homocyclopentadienyl conjugation and a lower electron density on the moving hydrogen. Evidence which supports de Dobbelaere observations were presented by Kloosterziel and coworkers in a series of papers³⁵⁻⁴¹ dealing with the thermal [1,5]-hydrogen shift in a series of 7-substituted-1,3,5-cycloheptatrienes.



It is of interest to note three important conclusions that can be obtained from the data presented above.

1. The electronic effect of a group is a dominant effect, i.e. strong electron donating substituents ($\text{N}(\text{CH}_3)_2$) increase the rate more than weak electron donating groups (SCH_3).

2. The ability of a substituent to enter into conjugation with the π -backbone increases the rate of reaction. Thus even though CN is an electron withdrawing group, stabilization of the transition state can be achieved through extended conjugation of the transition state.

3. Effects can be transmitted through phenyl rings; $(\text{CH}_3)_2\text{NC}_6\text{H}_5$ exhibits a greater effect than phenyl itself.

From the conclusions presented above, it appears that the effect a substituent displays is determined by two relative effects, the first being the degree to which it can donate or release electron density, and the second, its ability to enter into increased delocalization of the π -system through conjugation. Thus, we are concerned with the inductive and resonance effects of substituents but not those of the classic Hammett type.⁶³ Clearly the latter of these two effects is dominant. Thus, in predicting gross effects two concepts should be evaluated:

1. Gross substituent effects should be evaluated in terms of their ability to enter into conjugation and secondly and perhaps less significantly,

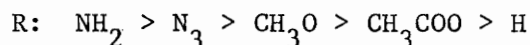
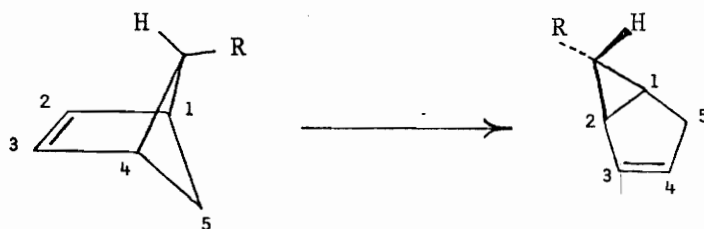
2. The electron donating and/or withdrawing ability of a group plays a minor role in directing the effect of a substituent in the transition state.

It is interesting to note that Exner has noted these same effects in his series of classic papers⁷⁹ concerned with the importance and separation of inductive and mesomeric effects.

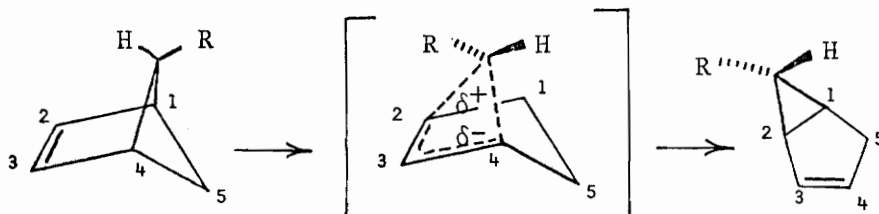
D. Electronic Effects Demonstrated In [1,3] Sigmatropic Rearrangements In Complex Systems:

Bicyclic and heteroaromatic systems have also been known to show electronic effects in sigmatropic rearrangements, specifically in those cases of [1,3] sigmatropic carbon migrations.

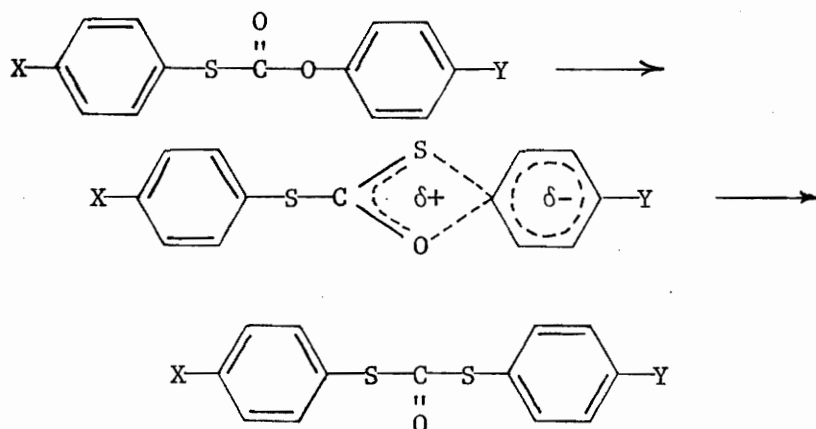
In the conversion of anti-5-substituted bicyclo[2.1.1]hex-2-enes exclusively to syn-substituted bicyclo[3.1.0] hexenes, methoxyl and similar substituents accelerate the conversion compared to the parent compound.



Substituent effects in [1,3] carbon migrations have not been studied in any detail but it can be seen from the transition state proposed below that similar arguments, as used before in the cycloheptatriene case are also applicable here to rationalize the data below.



Araki⁶⁴ has found in an apparent [1,5]-phenyl migration (from S to O), that electron-donating groups retarded, and electron withdrawing groups enhanced the rate of rearrangement. The transition state for this system then may be shown as below. In the sigma bond



migration electron density is pushed onto the S, which shifts the electron density toward O, an equally electronegative species; in turn O shifts this electron density into the phenyl ring which can more easily stabilize the additional electron density. Consequently, the transition state exhibits a partial positive ($\delta+$) charge in the migration area and a partial negative ($\delta-$) charge in the phenyl ring. The transition state illustrated satisfies the experimental data.



Reaction		Migrating Group	T range K ^o medium	E _u	ΔH^\ddagger	ΔS^\ddagger
X	Y			Kcal/mol	Kcal/mol	e.u.
H	OCH ₃	C ₆ H ₅	446-506	39.2	38.1	-6.5
H	H	C ₆ H ₅		38.3	37.2	-5.4
H	NO ₂	C ₆ H ₅		34.7	33.6	-5.3

X = H

Y = NO₂ > CN > COCH₃ > Cl > H > CH₃ > OCH₃; $\rho_{476} = 1.87$

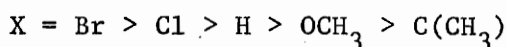
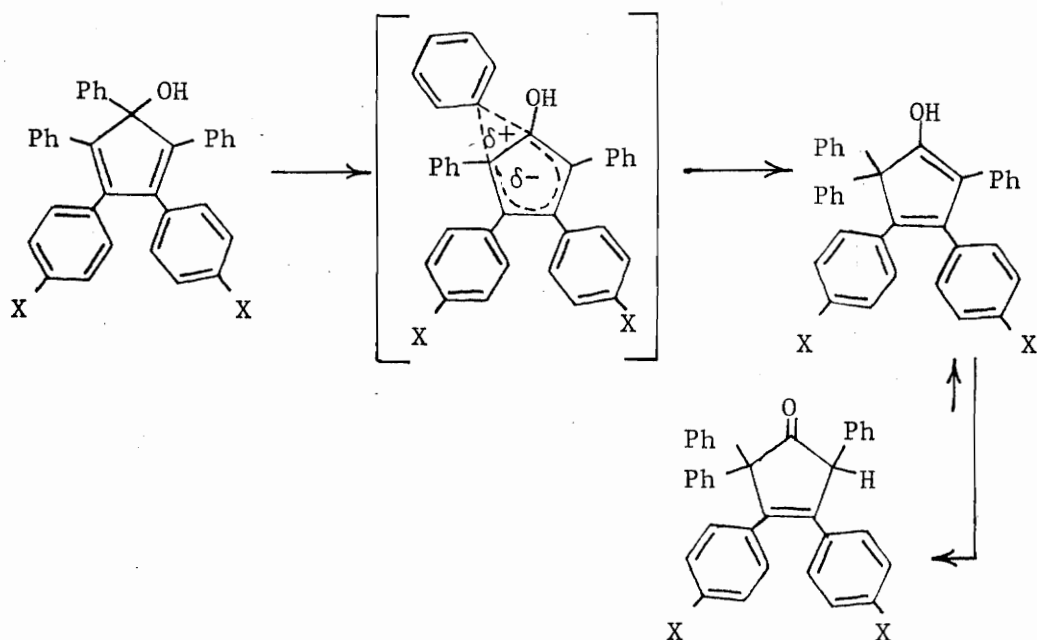
Y = NO₂

X = OCH₃ > CH₃ > H > Cl > NO₂; $\rho_{443} = -0.41$

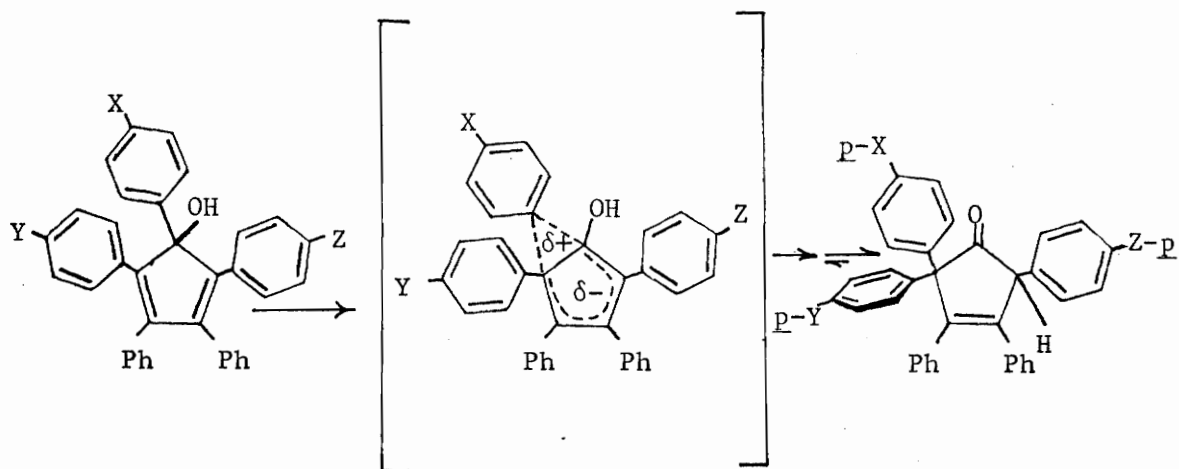
Clearly the data represented above is consistent with the previous arguments. The point of interest, here though, is the opposite effects seen in electron donating and withdrawing groups in reference to the O,S diarylthiocarbonate, depending upon which of the phenyl rings the substituents are being varied. For example, when Y=NO₂ and X = OCH₃, CH₃, Cl or NO₂, it can be seen that the effects of the substituents can be transmitted through a π -system towards the migrating origin to effect the transition state giving the opposite effects in reference to when the varied substituent is Y. Also the ρ (rho) values illustrate this, since when the substituents which direct the formation of the transition state are located at Y (the migration origin) the ρ is greater and positive than when these same substituents are located at X (the migration terminus) where ρ value is smaller and negative.

In summary then, the previously outlined hypothesis has been substantiated by documented evidence of its existence. The concept of a transition state directing the actions of a substituent is old and has been demonstrated here in electronically influenced sigmatropic rearrangements. Its applicability in predicting the relative rates of reaction is the proposition of this dissertation.

The relative rates of reaction for the [1,5]-suprafacial thermal phenyl rearrangement of 3,4-bis[4-substituted phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ol should be, as follows; for a series of substituents the rates should increase $\text{Br} > \text{Cl} > \text{H} > \text{OCH}_3 > \text{C}(\text{CH}_3)_3$, if the hypothesis is correct. The transition state should be the same as the model system,^{1,74} but should show the opposite relative rates of reaction. Transmissional effects of the substituents similar to Araki are involved in this system.



These compounds lend themselves to extensive research in transition state models and in studies of the ability to change the rates of reactions by placing different substituents in different areas of the π -backbone. Additional work⁷⁷ has already been started in directing the action of the transition state in experiments as shown below. The



X = H

Y = electron donating substituent

Z = electron withdrawing substituent

transition state should be set up on the side that will help satisfy the ensuing charge destability and thus help the reaction to go to the final product. Therefore the phenyl where X = H should migrate toward the phenyl where Y is equal to an electron donating substituent. This is the only reasonable choice since in this case both of the substituted phenyls accelerate the rate as they ease the charge destabilization. As these investigations continue a complete picture of the substituent effect in sigmatropic rearrangements should slowly unfold.

EXPERIMENTAL

Preparation of Solvents

Purification of Isoamyl Ether

To 1000 ml of isoamyl ether was added 3 ml of water. Then 50 g of calcium hydride (CaH) was slowly added to the solution and after 3 days of stirring, the bubbling stopped, and the isoamyl ether was distilled. The fraction boiling at a constant 173° was collected and passed through a dry column of alumina (Brockman activity 1, neutral, 80-200 mesh, column; 3.5 x 30 cm) under nitrogen. The isoamyl ether, collected at this point, was dry and peroxide free. The isoamyl ether could be stored under an atmosphere of Argon for approximately two weeks. After this time, catalytic amounts of peroxides began to form which were undesirable if the ether was to be used for thermal rearrangements.

All other solvents used were of reagent or spectral grade and needed no further purification.

Instrumentation

Melting points were determined on a Thomas-Hoover melting point apparatus in open capillary tubes and are not corrected.

Elementary analyses were performed on a departmental Perkin-Elmer Model 240, C, H, and N analyzer.

Infrared spectra of samples were taken on a Beckman IR-5A, Beckman IR-5 and/or Perkin-Elmer IR 621 grating infrared spectrophotometer using the polystyrene peaks as standards.

Nuclear magnetic resonance spectra were obtained on a JEOL PS-100 spectrometer using TMS as external standard.

Mass spectra were obtained on an Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer and a Varian MAT 112 double focusing mass spectrometer connected to a SpectroSystem 101 MS Varian Mat (620/L-100) computer system equipped with a Tektronix storage oscilloscope to provide hard copies of spectra at 75 eV, with an ionizing current of 80 μ A. Carbinols were introduced into the ionization chamber using a direct inlet probe. The ionization chamber was maintained at (nominal) 175^o and the inlet systems were adjusted between 100-150^o as to maintain an analyzer tube pressure between 1.0 and 3.0 x 10⁻⁶ Torr. Low voltage spectra were recorded with a filament current of 2.0 to 2.4 μ A and a reduced repeller voltage of 0.5 V. Mass assignments were based upon high boiling perfluorokerosene as an internal standard.

High performance liquid chromatography was conducted on a MS1-B500 chromatograph with a constant pressure pneumatic amplifier pump operated at 380 psi. The U.V. detector (254 nm) was set at 0.64 absorbance full scale for sample sizes of 2 μ l and at 0.32 absorbance for sample sizes of 1 μ l. The mobile phase was MeOH/n-C₆H₁₄ (0.01%/99.99%) flowing at 1.4 ml/min. The column was 2 ft x 2.1 mm i.d. stainless steel tubing, dry packed with Vydac Absorbant. Peaks were recorded on a 10 mV recorder and their area was obtained by triangulation.²⁸

Preparation of Benzils4,4'-Di(t-Butyl)Benzil:

A. p-(t-Butyl)Bromobenzene. -- This preparation was based on the work of Marvel et al.⁸⁰ A solution of 80 g (0.5 mol) of bromine in 67 g (0.5 mol) of t-butylbenzene was placed in a 250 ml round bottom one-necked flask fitted with an efficient reflux condenser. A dry ice-acetone condenser was then placed atop the reflux condenser since the initial reaction is extremely vigorous. Irradiation was performed in a Rayonet Photochemical Reactor using irradiation lamps of a broad wavelength for 8 hrs. When the reaction ceased to evolve hydrogen bromide (HBr) (12 hrs), the mixture was washed with 100 ml of 10% sodium bisulfate (NaHSO_4), 100 mls of water, 100 ml of 10% sodium carbonate (Na_2CO_3) and again with 100 ml of water. The organic layer was separated, dried and distilled at atmospheric pressure through a 14 in fractionation column. A small amount of unreacted t-butylbenzene was obtained, but the bulk of the distillate was collected at 230° [Lit.⁸⁰ $231-2^\circ$ (760 mm), 103° (10 mm)]. The yield was 85 g (0.4 mol, 80%).

B. t-Butylbenzaldehyde. -- The procedure was essentially that reported by Tchitchibabine et al.⁸¹ Into a 250 ml Grignard flask equipped with a reflux condenser, a drying tube, a nitrogen inlet and an addition funnel was placed 3 g of powdered magnesium and a few crystals of iodine. This flask was then flamed to activate the

magnesium, and as the hot flask cooled a solution of 21.3 g (0.10 mol) of p-(t-butyl)bromobenzene diluted with 60 ml of dry ether was placed in the addition funnel and added slowly to the hot activated magnesium in the Grignard flask over a period of 30 min. The flask was heated occasionally during the preparation of the reagent by means of a heating tape and when the reaction had terminated (approximately 2.5 hrs) the reagent was refluxed one additional hr.

The Grignard reagent was filtered through a plug of glass wool at the bottom of the Grignard flask and was added dropwise over a 1 hr period to a warm stirring solution of triethyl orthoformate contained in a 250 ml 3-necked, round bottom flask equipped with a reflux condenser and a nitrogen inlet. Rapid stirring and good reflux were found to facilitate a complete reaction. After all the Grignard reagent was added to the triethyl orthoformate the heating was continued for 1.5 hrs. After this time, the flask was cooled, the mixture decomposed by acidification with approximately 200 ml of glacial acetic acid, washed with 500 ml of water, dried over anhydrous sodium sulfate (Na_2SO_4) and distilled on a water bath to remove the ether.

The oily residue was stirred for 0.5 hr with 20 ml of warm 10% hydrochloric acid (HCl), separated and treated with 20 ml of fresh 10% hydrochloric acid (HCl). This procedure was repeated three times.

At this point the oily residue could either be dissolved in 50 ml of ether and dried with anhydrous sodium sulfate (Na_2SO_4) or the bisulfite adduct could be made using a saturated solution of sodium

bisulfate (NaHSO_4), separated, decomposed with 100 ml of saturated sodium carbonate (Na_2CO_3), dried and distilled.

If the former method was used two fractions were obtained, an early forerun boiling at 110° to 190° principally containing unreacted *p*-(*t*-butyl)-bromobenzene and a later major fraction boiling at 238 - 240° containing the *p*-(*t*-butyl)benzaldehyde. If the latter procedure was applied the entire distillate boils at 238 - 240° and contains *p*-(*t*-butyl)benzaldehyde. The yield of the aldehyde obtained by either method was 30-40% of the theoretical based upon the amount of *p*-(*t*-butyl)-bromobenzene used. Redistillation of the aldehyde afforded a colorless liquid boiling at 245 - 246° [Lit.⁸¹ 245 - 246°] which is insoluble in water and has a characteristic heavy odor.

C. 4,4'-Di-(*t*-Butyl)Benzoin. -- Into a 250 ml, 3-necked round bottom fitted with a Fredericks condenser and a magnetic stirrer was placed 4.25 g (0.05 mol) of potassium cyanide (KCN) and 20 ml of water. The mixture was stirred until it became a homogeneous solution. At this point 27.25 g (0.168 mol) of *p*-(*t*-butyl)benzaldehyde dissolved in 50 ml of 95% ethanol was added.

The resulting mixture was refluxed for 3 hr, but after approximately 1.5 hrs the benzoin starts to precipitate. At the end of the 3 hr period the mixture is cooled, filtered, washed with 10 ml of cold 95% ethanol, and pressed dry. The product obtained was a white powder mp 163.5 - 164° , which after three recrystallizations from 20 ml 95% ethanol afforded 10.9 g (0.034 mol, 40%) of pure benzoin mp 163.5 - 164° [Lit.⁸² 163.5 - 164°].

D. 4,4'-Di-(t-Butyl)Benzil. -- The 4,4'-di-(t-butyl)benzoin prepared above was oxidized to the corresponding benzil according to procedure of Weiss and Appel.⁸³ Into a 1ℓ three-necked, round bottom flask equipped with a stirrer and two Fredericks condensers was placed 44 g (0.136 mol) of the benzoin, 32.8 g (0.420 mol) of ammonium nitrate (NH_4NO_3), 0.655 g (32.8 mmol) of cupric acetate monohydrate, ($[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$), and 230 ml of 80% acetic acid. The solution was refluxed for 3 hr and allowed to stand overnight. It was refluxed for one additional hour, cooled, filtered, and the precipitate washed with 20 ml of 50% acetic acid and 100 ml of water and dried. Thus was obtained 38.5 g (0.12 mol, 88%) of light yellow-green microcrystals which, after two recrystallizations from 70 ml of 95% ethanol, had a mp of 104-104.5° [Lit.⁸² 104-104.5°].

4,4'-Bis(dimethylamino)Benzil. -- This preparation was based on that of Tuzun, Ogliaruso, and Becker.⁸⁴ In a 3 ℓ, 3-necked flask equipped with an efficient mechanical stirrer of high torque, reflux condenser with a calcium chloride drying tube, thermometer and a dropping funnel was placed 133 g (1.00 mol) of anhydrous aluminum chloride (AlCl_3) and 200 ml of dry carbon disulfide. The mixture was cooled in an ice bath and stirred while 182 g (1.5 mol) of N,N-dimethylaniline was slowly added through the dropping funnel during a 15 min period. The dropping funnel was then washed with 20 ml of dry carbon disulfide, which was added to the reaction mixture. Any aluminum chloride (AlCl_3) sticking to the walls of the flask was then scraped into the mixture which was

an easily stirred slurry of a white solid in a light green liquid.

The reaction mixture was cooled to $5-10^{\circ}$ in an ice salt bath and with continued stirring a solution of 31.7 g (21.3 ml, 0.250 mol) of oxalyl chloride in 200 mls of carbon disulfide was added through the dropping funnel over a course of 2 hr. The temperature should never go above 5° , for best yield. After the addition was complete the thick black reaction mixture was allowed to warm to room temperature, refluxed for 1 hr, and then cooled to $0-5^{\circ}$ in an ice bath. One hundred grams of chipped ice was added with stirring followed by 400 ml of cold water. Steam was then passed into the flask until the carbon disulfide and unreacted dimethylaniline were removed, and the green black complex was decomposed to a mixture of a green solid and a blue solid; this requires 1-2 hr.

One liter of water was added making the volume 2 l and after the solution had been cooled to room temperature, it was extracted with 1 l of chloroform and then 150 ml of chloroform (no more than this amount!). The combined dark blue extracts were washed with 550 ml of 8.5% hydrochloric acid (HCl), then with 200 ml of water and dried over anhydrous sodium sulfate (Na_2SO_4). The chloroform solution was distilled or flash evaporated until the volume was 250 ml and then it was passed through an 8.5 x 25 cm column (300 g) of Alcoa F-20 alumina. The adsorbate was eluted with 1 l of chloroform. The elutant was evaporated to 250 ml, washed with 500 ml of 10% sodium hydroxide (NaOH) and then with 100 ml of water and distilled to dryness. The residue, a crude yellow-green semisolid was

stirred and brought to boil with 250 ml of ethyl acetate and then cooled to room temperature while stirring. Filtration afforded 39-40g (0.134 mol, 52-55%) of the benzil. Recrystallization of the benzil in 150 ml of benzene gave 39 g of bright yellow crystals of mp 202-203° [Lit.⁸⁴ 199-200°].

4,4'-Dimethoxybenzil. -- The oxidation procedure of Weiss and Appel⁸³ was used to oxidize commercial p-anisoin. Into a 500 ml, one-necked round-bottom flask equipped with a mechanical stirrer was placed 100 g (0.368 mol) of p-anisoin, 34.9 g (0.436 mol) of ammonium nitrate (NH_4NO_3), 0.872 g (0.0044 mol) of cupric acetate monohydrate ($[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$), 303 ml of 80% acetic acid, and the resulting solution was refluxed for 2 hr. At this point the solution was cooled, the solid filtered, washed with cold 80% acetic acid and then water. This afforded 85 g (0.313 mol, 85%) of yellow 4,4'-dimethoxybenzil, mp 130-131°. Recrystallization from 1400 ml of 95% ethanol afforded 81.2 g (0.300 mol, 95.5% recovery) of pure product, mp 131.4-132.4° [Lit. 132°⁸³ 133°⁸⁵].

4,4'-Dimethylbenzil:

A. 4,4'-Dimethylbenzoin. -- Into a 1 l, three-necked round-bottom flask equipped with a reflux condenser and a mechanical stirrer was placed 30 g (0.46 mol) of potassium cyanide (KCN), 150 ml of water, and the solid dissolved with stirring. When solution

was effected, 178 g (1.5 mol) of p-tolualdehyde and 300 ml of 95% ethanol were added. The solution was refluxed for 3 hr and cooled with stirring to yield an oil which descended to the bottom of the flask. Continued stirring at room temperature afforded crystallization of the oil. The crystals were filtered, washed with cold 95% ethanol, and pressed dry to yield 151 g (0.675 mol, 90%) of white crystalline 4,4'-dimethylbenzoin, mp 87.5-88.5°, [Lit.⁸⁶ 88-89°].

B. 4,4'-Dimethylbenzil. -- This is essentially the oxidation procedure of Weiss and Appel.⁸³ Into a 1 l three-necked round-bottom flask fitted with a magnetic stirrer and two Fredericks condensers were placed the 151 g (0.675 mol) of 4,4'-dimethylbenzoin produced above, 72.3 g (0.93 mol) of ammonium nitrate (NH_4NO_3), 1.5 g (0.007 mol) of cupric acetate monohydrate [$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$], and 520 ml of 80% acetic acid, and the resulting solution was washed with cold 80% acetic acid, affording 142.8 g (0.56 mol, 88%) of yellow crystals, mp 101-103°. Recrystallization from 350 ml of 95% ethanol afforded 96% recovery of pure yellow 4,4'-dimethylbenzil, mp 102.6-103.2°, [Lit.⁸⁶ 104-105°].

4,4'-Dimethylthiobenzil:

A. p-Methylmercaptobenzaldehyde. -- Into a 3 l, three-necked round-bottom flask equipped with a stirrer, thermometer, reflux condenser with a drying tube, and a gas inlet tube were placed 346 g (3.10 mol) of zinc cyanide ($\text{Zn}(\text{CN})_2$), 242 g (1.95 mol) of thioanisol

(Aldrich Chemical Co.) and 700 ml of dry benzene. The flask was then cooled in an ice bath to 5°, and a swift stream of dry hydrogen chloride gas passed into the solution for 0.75 hr, during which time the temperature rose to 15°. With continuous stirring and cooling, 343 g (2.57 mol) of anhydrous aluminum chloride was added over a period of 10 min. The reaction was then allowed to stir for 8.5 hrs while the temperature rose to room temperature. During this time the solution turned dark green. One liter of 18% hydrochloric acid was then added with stirring, and the mixture allowed to stand overnight. The mixture was then refluxed for 4 hrs and steam distilled until clear (ca. 25 l). The distillate was extracted twice with ether and the ether dried over anhydrous sodium sulfate. The ether was then removed on the rotary evaporator and the oil distilled to yield 122.7 g (0.806 mol, 41.4%) of p-methylmercaptobenzaldehyde, bp 118-120°/4 mm, [Lit. 153°/17 mm,⁸⁷ 273°^{88,89}].

B. 4,4'-Dimethylthiobenzoin. -- Into a 1 l flask equipped with a reflux condenser was placed 100 g (0.656 mol) of p-methylmercaptobenzaldehyde, 30 g (0.461 mol) of potassium cyanide (KCN) dissolved in 150 ml of water, and 350 ml of 95% ethanol. The solution was refluxed for 2 hrs and allowed to cool slowly to room temperature, during which time a red oil deposited which later turned to a light yellow solid. The reaction was cooled in ice, filtered, and the precipitate was washed repeatedly with cold 95% ethanol, and then dried in air. The crude product was used as obtained in the next reaction, and the yield was not recorded at this point.

C. 4,4'-Dimethylthiobenzil. -- The 4,4'-dimethylthiobenzoin produced above was oxidized to the corresponding benzil according to the procedure of Weiss and Appel.⁸³ Into a 1ℓ, three-necked round-bottom flask equipped with a stirrer and two Fredericks condensers was placed the crude 4,4'-dimethylthiobenzoin, 32.8 g (0.420 mol) of ammonium nitrate (NH_4NO_3), 0.655 g (32.8 mol) of cupric acetate monohydrate ($[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$), and 230 ml of 80% acetic acid. The solution was refluxed for 3 hrs and allowed to stand overnight. It was refluxed for an additional hour, cooled, filtered, and the precipitate washed with 50% acetic acid, then water, and dried. There was obtained 61.9 g (0.205 mol, 62.4%) of crude 4,4'-bismethylmercaptobenzil, mp 140-145°. Recrystallization from 95% ethanol afforded yellow needles [Lit.⁹⁰ 161-162°].

4,4'-Difluorobenzil:

A. 4,4'-Difluorobenzoin. -- Into a 1 ℓ flask equipped with a reflux condenser was placed 160 ml of 95% ethanol, 80 ml of water, 15.4 g (0.237 mol) of potassium cyanide (KCN) (0.237 mol) and 95.8 g (0.772 mol) of p-fluorobenzaldehyde (Pierce Chemical Co.). The solution was refluxed for 2 hr, cooled and the ethanol removed on a rotary evaporator over a steam bath. The residue was taken upon 800 ml of ether and washed with two 100 ml portions of water, then 100 ml each of 10% sodium carbonate (Na_2CO_3) solution and water. It was then extracted with a saturated sodium hydrogen sulfite (NaHSO_3) solution until neutralization with base showed the absence of aldehyde,

eight 100 ml portions being required. After washing the ethereal solution with two 100 ml portions of water, and drying over anhydrous sodium sulfite (Na_2SO_3) the ether was distilled to give 73.3 g (0.296 mol, 76.6%) of a red-orange oil. The crude 4,4'-difluorobenzoin was then catalytically oxidized using ammonium nitrate (NH_4NO_3).

B. 4,4'-Difluorobenzil. -- This procedure was essentially that of Weiss and Appel.⁸³ Into a 3 l, 3-necked, round bottom flask equipped with a stirrer and two reflux condensers was placed 73.3 g (0.296 mol) of crude 4,4'-difluorobenzoin, 29.6 g (0.370 mol) of ammonium nitrate (NH_4NO_3), 0.591 g (2.96 m mol) of cupric acetate [$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$] and 210 ml of 80% acetic acid. The reaction mixture was heated to reflux cooled until evolution of nitrogen began and then refluxed for 1.75 hr. The solution was cooled slowly, filtered, diluted with an equal volume of water, the resulting precipitate collection, and the combined precipitates washed with 100 ml of water. Recrystallization from 800 ml of 95% ethanol gave 39.0 g (0.159 mol, 53.8%) of 4,4'-difluorobenzil, mp 117.8-118.4° [Lit. 121.5-122.5°, ⁹¹ 123-123.5°⁹²].

4,4'-Dichlorobenzil:

A. 4,4'-Dichlorobenzoin. -- This is essentially the procedure of Lutz and Murphy.⁹³ For best results, the p-chlorobenzaldehyde should be purified before use, and all unreacted p-chlorobenzaldehyde had to be removed from the initial reaction product before final oxi-

dation to the benzil. The purification procedure was as follows:

500 g (3.35 mol) of commercial p-chlorobenzaldehyde (Eastman Chemical Co.) was dissolved in 800 ml of ether and extracted three times with a total of 800 ml of 10% sodium carbonate solution. The resulting ether solution was washed with 200 ml of water, dried over sodium sulfate, and the ether removed by distillation. Vacuum distillation of the resulting oil (78^o/5 mm) afforded 92% recovery of pure p-chlorobenzaldehyde.

Into a 500 ml one-necked round-bottom flask was placed 300 g (2.15 mol) of purified p-chlorobenzaldehyde, 300 ml of methanol, 5 g of a saturated aqueous solution of potassium cyanide (KCN), and the solution heated to reflux. When the solution had turned a dark red (about 20 min) the flask was placed on a rotary evaporator and the methanol removed under vacuum. The resultant red paste was taken up in 250 ml of benzene and extracted three times with 100 ml portions of 20% aqueous sodium bisulfite (Na₂SO₃) solution. This treatment turned the red benzene solution yellow-green. The third sodium bisulfite wash solution was tested by adding aqueous sodium hydroxide (NaOH) solution (a clouding of the solution indicates the presence of p-chlorobenzaldehyde). When all p-chlorobenzaldehyde had been removed, the benzene solution was washed twice with 100 ml portions of water, dried over anhydrous magnesium sulfate MgSO₄, and the benzene removed on the rotary evaporator. The thick orange oil resulting from this treatment was taken up in 1 l of pentane, heated, filtered, and allowed to stand overnight in the refrigerator. This afforded 80 g

(0.285 mol, 26.5%) of white 4,4'-dichlorobenzoin, mp 87-88°, [Lit.⁹⁴ 87-88°].

B. 4,4'-Dichlorobenzil. -- This procedure is essentially that of Weiss and Appel.⁸³ Into a 1 l one-necked round-bottom flask equipped with a magnetic stirrer were placed 80 g (0.285 mol) of 4,4'-dichlorobenzoin, 30 g (0.375 mol) of ammonium nitrate (NH_4NO_3), 0.655 g (32.8 mol) of cupric acetate monohydrate ($[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$), and 350 ml of 80% acetic acid, and the mixture was allowed to reflux with stirring for 1.5 hr. At this point, the hot solution was transferred to a beaker where it solidified. It was then filtered, washed with cold 80% acetic acid, and finally with water. This treatment afforded 73.8 g (0.26 mol, 92%) of bright yellow crystals, mp 194-195°, [Lit. 195-196°,^{95,96} 200°⁹⁷]. Recrystallization from 2.5 l of ethanol afforded a 96% recovery of pure yellow crystals of 4,4'-dichlorobenzil, mp 197-198.5°.

4,4'-Dibromobenzil:

A. 4,5-Diphenylglyoxalone. -- This procedure was that of Corson and Freeborn.⁹⁶ A mixture of 212 g (1 mol) of benzoin, 110 g (1.8 mol) of urea and 800 ml of glacial acetic acid in a 2 l round-bottom flask was heated under a reflux condenser for 7 hr (color begins reddish orange but later changed to dark yellow). The hot solution was quickly poured into a 2 l beaker and allowed to stand at least 3 hr. The cold mixture was then transferred by means of a large wooden spoon or spatula to a 30 cm Büchner funnel and sucked as dry as

possible with the help of a rubber dam. The crystals were pressed down during the suction filtration. The filtrate was discarded. The crystals were returned to the beaker, stirred mechanically with 500 ml of ether for 30 min, filtered again by suction (unreacted benzoic acid is removed by the ether, in which diphenylglyoxalone was only sparingly soluble), and spread out to dry at least overnight (the product was difficult to dry completely). The product was dissolved by heating with 1 l of glacial acetic acid in a 2 l round-bottom flask attached to a reflux condenser (use at least 500 ml of glacial acetic acid), and the clear solution was poured, with mechanical stirring, into 2.5 l of water in a 4 l (1 gal) crock. Stirring was continued for 30 min. (The water removed the unreacted urea.) The mixture was filtered on a 30 cm Büchner funnel and pressed and sucked as dry as possible. The crystals were transferred to the 2 l beaker and stirred mechanically for 10 min with 1 l of water. After filtration, the washing with water was repeated. The product was then returned to the beaker, stirred with 750 ml of ether and filtered again. The material was then air-dried. The yield of white fluffy crystals of diphenylglyoxalone. mp 334-335^o was 220-230 g (93-97%), [Lit.⁹⁷ 324^o].

B. 4,4'-Dibromobenzil. -- This procedure was essentially that used by Biltz.⁹⁹ A solution of 125g (0.525 mol) of 4,5-diphenylglyoxalone and 500 g (3.125 mol) of bromine dissolved in 3125 ml of glacial acetic acid was refluxed in a 5 l, 5-necked round bottom flask equipped with a magnetic stirrer and 15 ft of highly efficient

condenser on which gas traps were connected. The solution was refluxed for 3.5 hrs with the evolution of copious quantities of hydrogen bromide (HBr) gas. At the end of this 3.5 hr period the reaction was quenched with 300 ml of water, whereupon a substantial precipitate of yellow crystalline needles began to form. After refluxing for another 0.5 hr the solution was cooled, the crystals were filtered by suction and recrystallized from 2000 ml of benzene. This afforded 189 g (0.514 mol, 97.8%) of the benzil having a mp of 228-229° [Lit. 223-224°, ^{99a}228-229°^{99b}], which was in the form of long flat yellow needles.

4,4'-Diodobenzil:

A. p-Iodobenzaldehyde. -- This procedure was that used by Bowen and Wilkinson.¹⁰⁰

Into a 1000 ml 3-necked, round bottom flask was placed 100 g (0.527 mol) of stannous chloride (anhydrous, SnCl₂) and 475 ml of dry ether. By means of a fritted disc dispersion tube dry hydrogen chloride (HCl) gas was passed through the solution for 0.75 hrs at a rapid rate. At this point approximately 1/2 of the stannous chloride had dissolved and the rest was finely crushed by means of a magnetic stirrer (pH < 1). Then 25 g of p-iodobenzonitrile (0.109 mol) was added to the flask, the stirring discontinued and the flask sealed. The flask was allowed to stand for 3 days with occasional stirring. During this time the tin chloride adduct of the aldehyde precipitated onto the sides of the flask. After 3 days the flask was unsealed,

100 ml of water was added to the reaction mixture, the ether was decanted and the light green semi-solid was steam distilled. Steam distillation was continued until no more crystals were found precipitating on the sides of the condenser (approximately 2 l). After the distillate was cooled, the aldehyde (a white solid) precipitated in the water. The aldehyde was filtered and the water filtrate was extracted 3 times with 50 mls of ether. The ether extracts were pooled and used to dissolve the filtered aldehyde. This ether solution was then dried, filtered and the ether was then removed on a rotovap. After all the ether had been distilled a white powder remained which could be easily transferred to a watchglass and air dried. The aldehyde prepared in this manner had a melting point of 77-78° [Lit.¹⁰⁰ 78°]. Yield was 85% of the theoretical, 21.5 g (0.0927 mol).

B. 4,4'-Diodobenzoin. -- Into a 250 ml, 3-necked, round bottom flask equipped with a magnetic stirrer was added 41 g (0.177 mol) of pure p-iodobenzaldehyde in 82 ml of methanol. Then 0.1 g of potassium cyanide (KCN as a saturated solution in 0.5 ml of water) was added to the refluxing solution of the aldehyde. The solution turned yellow-orange as it was refluxed for 3.5 hrs. After this period of time the methanol was flash evaporated under reduced pressure and the residual red to yellow pasty mass was taken up in 250 ml of benzene. The benzene solution was extracted with 100 ml portions of 20% aqueous sodium bisulfite (NaHSO_3) solution until the aqueous extract indicated the absence of aldehyde when neutralized with base. The benzene solution was then washed with four 100 ml portions of water. The benzene

layer was then dried over anhydrous magnesium sulfate (MgSO_4) and the benzene flash evaporated. A thick yellow oil resulted which was taken up in 200 ml of hexane and allowed to stand for 3 days at which time the oil solidified as the hexane slowly evaporated. The benzoin is a white compound and may be isolated as such having a melting point of $121-122^\circ$. The product after being exhaustively recrystallized from methanol had a mp of $121-122^\circ$ [Lit.¹⁰¹ $121-122^\circ$]. The product from the hexane evaporation was a yellow powder, mp $119.5-121^\circ$. The surface of the benzoin was coated with the yellow benzil. Yield was 28.4 g, (0.0612 mol) 69.2% of the theoretical.

C. 4,4'-Diiodobenzil. -- Using the procedure of Weiss and Appel,⁸³ 28g (0.060 mol) of the benzoin, 10 g (0.128 mol) of ammonium nitrate (NH_4NO_3), 0.2 g (0.9 mmol) of cupric acetate monohydrate ($[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$) and 120 ml of 80% acetic acid were refluxed for 4 hrs. At the end of this time the benzil had been produced quantitatively and had precipitated from the hot solution. The solution was cooled, filtered and washed with 20 ml of water. The mother liquor was also filtered and additional crystals which had precipitated from the water were also collected. The entire lot of crystals were continually washed with 100 ml portions of water until all odor of the acetic acid was gone. The crystals were dried. The melting point of these yellow microcrystals were $257-8$ [Lit. 225^{101}]. The yield was quantitative. Recrystallization from boiling p-xylene afforded long yellow needles having a mp of $257-8^\circ$.

Synthesis of Tetracyclones3,4-Bis-(4-(t-butyl)phenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one. --

This compound was prepared by Fieser's method¹⁰² from 4,4-di-(t-butyl)-benzil and 1,3-diphenyl-2-propanone. In a 250 ml round bottom flask, 10.5 g (0.0326 mol) of the benzil and 6.85 g (0.0326 mol) of 1,3-diphenyl-2-propanone was dissolved in 50 ml of hot absolute ethanol. The flask was fitted with a reflux condenser and magnetic stirrer and placed in a heating mantle. The temperature of the solution was raised nearly to the boiling point and a solution of 1 g of potassium hydroxide (KOH) in 5 ml of absolute ethanol was added slowly in two portions through the condenser. When the frothing had subsided, the mixture was refluxed for 5 min and then cooled to 0°. The dark crystalline product was filtered with suction and washed with three 10 ml portions of cold 95% ethanol. The product melted at 251-2° and weighed 13.1 g (26.4 mmol), a 72.9% yield.

Analysis:

Calculated for $C_{37}H_{36}O$: C, 89.52; H, 7.29.

Found: C, 89.72; H, 7.37.

Mass spectral mol. wt.: Calc., 496; Found, 496

3,4-Bis(4-dimethylaminophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one.^{104,105} --

This compound was prepared by the procedure of Ogliaruso.¹⁰³ In a 5 ml, round-bottom flask was placed 0.1 g (0.30 mmol) of 4,4'-bis(dimethylamino)benzil, 0.28 g (1.3 mmol) of dibenzyl

ketone and 1 ml of a 25% potassium hydroxide (KOH) solution in 95% ethanol. The flask was stoppered, sealed with paraffin and stirred magnetically for 150 hrs. The reaction mixture was then diluted with 50 ml of H₂O, whereupon the solution turned a dark brown. Extracting with a mixture of benzene and cyclohexane (9:1) gave a dark solution which was chromatographed directly on Alcoa activated alumina, and was developed with benzene. Evaporating the benzene to essential dryness and adding a few drops of ethanol afforded 0.105 g (0.22 mmol, 68%) of very dark red needles, mp 270-271. Recrystallization from 200 ml of a mixture of benzene and methyl alcohol (1:1) afforded pure material, mp 272-3° [Lit.¹⁰³ mp 272-273°].

3,4-Bis(4-anisole)-2,4-diphenyl-2,4-cyclopentadien-1-one.¹⁰⁶⁻¹⁰⁸ --

Into a 500 ml round bottom flask equipped with a reflux condenser and mechanical stirrer was placed 5.25 g (0.025 mol) of dibenzylketone, 6.4 g (0.025 mol) of 4,4'-dimethoxybenzil and 160 ml of 95% ethanol. The solution was heated to reflux then 0.75 g of potassium hydroxide (KOH) dissolved in 4 ml of 95% ethanol was added. After refluxing for 20 min the mixture was cooled in ice, filtered, the precipitate washed with 15 ml of cold 95% ethanol, and dried to give 6.95 g (15.65 mmol, 62.6%) of product mp 222-223° [Lit. 225-6°¹⁰⁷; 222-3°¹⁰⁸].

3,4-Bis(4-tolyl)-2,4-diphenyl-2,4-cyclopentadien-1-one.¹⁰⁶⁻¹⁰⁸ --

Into a 500 ml round bottom flask equipped with a reflux condenser was placed 10.5 g (0.05 mol) of dibenzylketone, 12.0 g (0.05 mol) of

4,4'-dimethylbenzil and 75 ml of 95% ethanol. The solution was heated to reflux, then 1.5 g of potassium hydroxide (KOH) in 8 ml of 95% ethanol was added. After refluxing for 15 min the mixture was cooled in ice, filtered, the precipitate washed with 10 ml of cold 95% ethanol and dried to give 19.8 g (48.06 mmol, 95%) of product. Recrystallization from 200 ml of a mixture of benzene-ethanol (1:1) afforded pure material mp 218-219^o. [Lit. 222.5-223^o108 218-219^o107]

3,4-Bis(4-methylmercaptophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-

one.¹¹² -- Into a 125 ml flask equipped with a reflux condenser was placed 6.04 g (20.0 mmol) of 4,4'-bis(methylmercapto)benzil, 4.20 g (20.0 mmol) of dibenzyl ketone and 35 ml of 95% ethanol. The solution was heated to reflux then 3 ml of 95% ethanol containing 0.6 g of potassium hydroxide (KOH) was added. After refluxing for 15 min., the mixture was cooled in ice, filtered, the precipitate washed with cold 95% ethanol, and dried to give 9.05 g (19.0 mmol, 95.1%) of product, mp 203.0-204.0^o. Recrystallization from 50 ml of 50% benzene-ethanol affords pure material, mp 204.0-204.5^o.

Analysis:

Calculated for: C₃₁H₂₄OS₂: C, 78.11; H, 5.08; S, 13.45.

Found: C, 78.23; H, 5.29; S, 13.43.

3,4-Bis(4-fluorophenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one.^{111,112} --

Into a 125 ml flask equipped with a reflux condenser was placed 7.38 g (30.0 mmol) of 4,4'-difluorobenzil, 6.30 g (30.0 mmol) of dibenzyl

ketone and 45 ml of 95% ethanol. The reaction mixture was heated to reflux, then 4.5 ml of 95% ethanol containing 0.9 g of potassium hydroxide (KOH) was added. After refluxing 15 min., the mixture was cooled in ice, filtered, the precipitate washed with cold 95% ethanol and dried to yield 10.73 g (25.6 mmol, 85.3%) of product, mp 212.0-214.0°. Recrystallization from 70 ml of 50% benzene-ethanol solution afforded pure material, mp 213.0-214.0°.

Analysis:

Calculated for $C_{29}H_{18}F_2O$: C, 82.84; H, 4.32; F, 9.04.

Found: C, 82.84; H, 4.30; F, 9.06.

3,4-Bis(4-chlorophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one. -- Into a 1000 ml round bottom flask 42 g (0.151 mol) of 4,4'-dichlorobenzil and 32 g (0.152 mol) of 1,3-diphenyl-2-propanone were dissolved in 300 ml of hot ethanol. The flask was fitted with a reflux condenser, the temperature of the solution was raised nearly to the boiling point and a solution of 6 g of potassium hydroxide (KOH) in 30 ml of absolute ethanol was added. When the frothing had subsided the mixture was refluxed for 20 min and then cooled to 0°. The cyclone was then filtered off and washed with 10 ml of 95% ethanol and air dried. Recrystallization from 300 ml of a 50% benzene-95% ethanol solution afforded (3.8 g, 0.084 mol, 55%) pure material mp 252-3° [Lit. 253-4°, 109 252-3°¹¹⁰].

3,4-Bis(4-Bromophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one.^{106,107}

111 -- Into a 500 ml round-bottom flask 36.8 g (0.1 mol) of 4,4'-dibromobenzil and 21 g (0.1 mol) of dibenzyl ketone were dissolved in 150 ml of hot absolute ethanol. The flask was equipped with a reflux condenser and magnetic stirrer. The reaction mixture was heated to near reflux then 3 g of potassium hydroxide (KOH) dissolved in 15 ml of 95% ethanol was added. After refluxing 15 min, the mixture was cooled in ice, filtered, the precipitate washed with 10 ml of cold 95% ethanol and dried to yield 54.2 g (0.1 mol, 100%) of product, mp 251-2°. Recrystallization from 300 ml of a solution of 50% benzene-95% ethanol yielded pure material, mp 251.5-252° [Lit. 251-252°¹⁰⁷].

3,4-Bis(4-iodophenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one.¹¹² --

Into a 250 ml flask was placed 13.86 g (30.0 mmol) of 4,4'-diiodobenzil, 6.30 g (30.0 mmol) of dibenzyl ketone and 120 ml of triethylene glycol. The reaction mixture was heated to 200° at which point a homogenous solution resulted. It was allowed to cool slowly, and at 180° a heavy crystallization of 4,4'-diiodobenzil took place. At 118°, 6 ml of 40% benzyltrimethylammonium hydroxide in methanol was added with stirring, and the solution allowed to cool slowly with stirring. At 114°, a precipitate formed, and at 80° it was cooled rapidly in ice water and then 120 ml of methanol was added. The reaction was filtered, the precipitate washed thoroughly with methanol and dried to give 12.86 g (20.2 mmol, 67.4%), mp 219.0-221.0° of product. Recrystallization from 150 ml of a solution of 50% benzene-95% ethanol afforded pure material, mp 221.0-222.0°.

Analysis:

Calculated for $C_{29}H_{18}I_2O$: C, 54.74; H, 2.85; I, 39.89

Found: C, 55.02; H, 2.90; I, 39.55

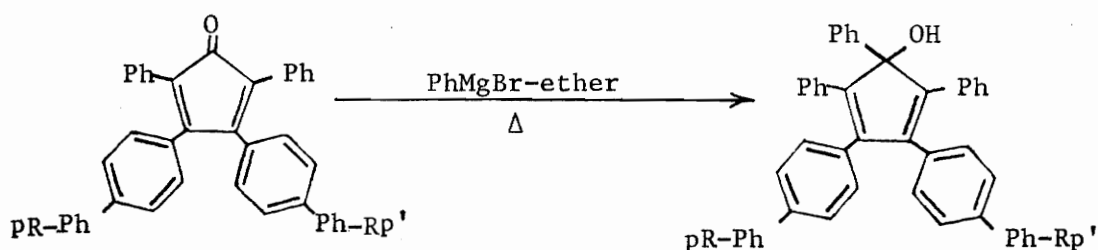
Preparation of Carbinols

3,4-Bis[4-(substituted phenyl)]-1,2,5-triphenyl-2,4-cyclopentadien-1-ol. -- Presented here is the general procedure used for the preparation of all the carbinols from the 3,4-Bis[4-(substituted phenyl)]-1,2,5-triphenyl-2,4-cyclopentadien-1-ones using inverse phenylmagnesium bromide addition.

Into a 500 ml 3-necked round bottom flask equipped with a magnetic stirrer and a reflux condenser was placed 0.02 mol (see table for specific number of grams for each cyclone) of the tetracyclone dissolved in 100 mls of anhydrous benzene. To this solution, an ether solution of phenylmagnesium bromide was added, prepared from 1.96 g (0.08 mol) of magnesium, 13.4 g (0.08 mol) of bromobenzene and 50 ml of anhydrous ether. After the addition of sufficient Grignard solution to decolorize the purple cyclone to a light pink color, the mixture was refluxed for 2 hr, cooled in an ice bath, hydrolyzed with 100 ml of 10% ammonium chloride solution and the organic layer separated, washed twice and 200 ml of water and dried over anhydrous magnesium sulfate. The organic solution was filtered and concentrated to about 30 ml and was added to 200 ml of petroleum ether (bp 30-60^o). This afforded the crude alcohol. Three recrystallizations from 1500 ml of petroleum ether (30-60^oC) to which a saturated solution of the alcohol in benzene was added afforded a near quantitative yield of pure alcohol. The table below gives grams of each cyclone used, mp (^oC) for each alcohol, literature references and analysis for each carbinol.

TABLE I

Preparation of Carbinols



<u>Cyclone</u>	<u>Cyclone</u>	<u>Yield %</u>	<u>MP °C and Lit. Ref. or Analysis</u>
<u>R and</u>	<u>g Used</u>		<u>Carbinol</u>
<u>Molecular</u>	<u>(0.02 Mol)</u>		
<u>Weight</u>			
-C(CH ₃) ₃ (Mol. Wt. 496)	9.92	99	218-219; Calcd. for C ₄₃ H ₄₂ O: C, 89.85; H, 7.36. Found: C, 89.56; H, 7.22 M.S. m/e - 574.
-N(CH ₃) ₂ (Mol. Wt. 470)	9.40	50	225-226 (lit. 270-271, ¹¹⁷ 252, ¹⁰⁵ 225-226 ¹⁰³). M.S. m/e - 548.
-OCH ₃ (Mol. Wt. 444)	8.88	99	195-196; Calcd. for C ₃₇ H ₃₀ O ₃ : C, 85.03; H, 5.76. Found: C, 84.82; H, 5.98. M.S.: m/e - 522.

TABLE I (continued)

<u>Cyclone</u> R and Molecular Weight	<u>Cyclone</u> g Used (0.02 Mol)	<u>Yield %</u>	MP °C and Lit. Ref. or Analysis for Carbinol
SCH ₃ (Mol. Wt. 476)	9.52	99	195-195.5; Calcd. for C ₃₇ H ₃₀ O ₁ S ₂ : C, 80.14; H, 5.42; S, 11.55. Found: C, 79.89; H, 5.49; S, 11.55. M.S.; m/e - 554.
CH ₃ (Mol. Wt. 412)	8.24	99	207-208; Calcd. for C ₃₇ H ₃₀ O: C, 90.58; H, 6.16. Found: C, 90.27; H, 6.32. M.S.; m/e - 490.
F (Mol. Wt. 420)	8.40	99	163-164; Calcd. for C ₃₅ H ₂₄ OF ₂ : C, 84.32; H, 4.85; F, 7.62. Found: C, 84.19; H, 5.12; F, 7.55. M.S.; m/e - 498.
Cl (Mol. Wt. 452)	9.04	85	159-160; Calcd. for C ₃₅ H ₂₄ OCl ₂ : C, 79.10; H, 4.55; Cl, 13.34. Found: C, 79.08; H, 4.58; Cl, 13.55. M.S.; m/e - 528/532, mw - 530.

TABLE I (continued)

<u>Cyclone</u> R and Molecular Weight	<u>Cyclone</u> g Used (0.02 Mol)	<u>Yield %</u>	MP °C and Lit. Ref. or Analysis for Carbinol
Br (Mol. Wt. 542)	10.84	99	190-191 (Lit. ¹¹⁰ 195) M.S.; m/e - 618/622; m.w. - 620.
I (Mol. Wt. 636)	12.72	99	224-225; Calcd. for C ₃₅ H ₂₄ OI ₂ : C, 58.82; H, 3.36. Found: C, 58.67; H, 3.28. M.S.; m/e - 714.

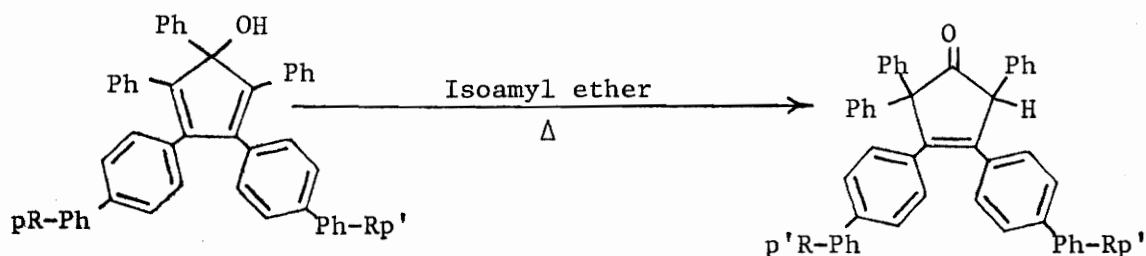
Preparation of Ketones3,4-Bis[4-(substituted phenyl)]-2,2,5-triphenyl-3-cyclopenten-1-ones. --

A general procedure for the preparation of all the ketones will be outlined below.

Into a 100 ml three-necked, round bottom flask equipped with a reflux condenser, drying tube, nitrogen inlet and magnetic stirrer was placed 50 ml of peroxide free isoamyl ether and brought to reflux (173°, bp of isoamyl ether). At this point 3.0 g of the alcohol was added as a solid all at once. The resulting mixture was refluxed 44 hrs, and then cooled to room temperature. The solvent was removed under vacuum to afford a viscous yellow oil, which crystallized from a mixture of 150 ml of 1:50 benzene-petroleum ether (bp 30-60°) to give a quantitative yield of each ketone. The infrared, mass spectra and elemental analysis of each ketone as well as the molar quantities of each alcohol is given in the table below.

The preparation of the N,N-dimethyl and thiomethyl substituted ketone were attempted. Both of these substituted alcohols decomposed at the temperature used for the rearrangement and are not included in the following table. The fluoro-substituted alcohol was also not prepared since this alcohol was not used in the kinetic experiments to follow.

TABLE II
Preparation of Ketones



R and Molecular Weight	Mmoles of Alcohol	M.P. °C and Analysis for Ketones
-C(CH ₃) ₃ (Mol. Wt. 574)	5.23	196.5-197°; Calcd. for C ₄₃ H ₄₃ O ₁ : C, 89.85; H, 7.37. Found: C, 89.89; H, 7.34. M.S.; m/e - 574; IR: 1755 cm ⁻¹ .
-OCH ₃ (Mol. Wt. 522)	5.47	174-174.5; Calcd. for C ₃₇ H ₃₀ O ₃ : C, 85.03; H, 5.76. Found: C, 85.30; H, 5.82. M.S.; m/e - 522; IR: 1775 cm ⁻¹ .
-CH ₃ (Mol. Wt. 490)	6.12	167.5-168°; Calcd. for C ₃₇ H ₃₀ O ₁ : C, 90.57; H, 6.19. Found: C, 90.30; H, 6.33. M.S.; m/e - 490; IR: 1755 cm ⁻¹ .

TABLE II (continued)

R and Molecular Weight	Mmoles of Alcohol	M.P. °C and analysis for Ketones
-Cl (Mol. Wt. 530)	5.66	153.5-154 ^o ; Calcd. for C ₃₅ H ₂₄ OCl ₂ : C, 79.10; H, 4.55. Found: C, 79.07; H, 4.76. M.S.; m/e - 530; IR: 1740 cm ⁻¹ .
-Br (Mol. Wt. 620)	4.84	166-167 ^o ; Calcd. for C ₃₅ H ₂₄ OBr ₂ : C, 67.76; H, 3.91. Found: C, 67.60; H, 4.21. M.S.; m/e - 618/622; IR: 1755 cm ⁻¹ .
-I (Mol. Wt. 714)	4.20	184-185 ^o ; Calcd. for C ₃₅ H ₂₄ OI ₂ : C, 58.82; H, 3.36. Found: C, 58.92; H, 3.64. M.S.; m/e - 714; IR: 1755 cm ⁻¹ .

KINETIC STUDIES

Kinetic Studies of the Sigmatropic Rearrangements of 3,4-Bis(4-substituted phenyl)- 1,2,5-triphenyl-2,4-cyclopentadien-1-ols

The kinetic studies of the sigmatropic rearrangement of the polyarylated alcohols were performed as follows: Tetraethylene glycol (20 ml) was heated to $180 \pm 0.2^{\circ}$ by means of a Thermowatch lab controller and at this temperature 200 mg of alcohol was added as a solid all at once. During this period of heating, approximately 1/2 ml samples were taken at different times without otherwise disturbing the reaction. The samples were cooled immediately by means of a cold water bath, then injected separately into the high performance liquid chromatograph.* The peak areas of the two peaks which appeared from each injection were determined, the percentage concentration corresponding to the peak area of the alcohol was calculated and then the logarithm of the concentration was determined. These data are recorded (Table III). Also plots of the logarithm of the concentration of each starting alcohol versus time were made (Figures 1-5).

The above experiment was repeated under the same conditions given above except that the temperature was changed to $190^{\circ} \pm 0.2^{\circ}$, to allow the kinetics to be investigated at a higher temperature.

*The high pressure liquid chromatography conditions are given in the general experimental section.

TABLE III

The Isomerization of 3,4-Bis(4-t-butyl phenyl)
1,2,5-triphenyl-2,4-cyclopentadien-1-ol

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>180° ± 0.2°</u>		
1	0	2.000
2	10800	1.920
3	12600	1.861
4	16400	1.693
5	18000	1.664
6	21600	1.541

slope: 3.498×10^{-5}

intercept: 2.029

rate: 8.057×10^{-5}

$r = 0.974$

<u>190° ± 0.2°</u>		
1	0	2.000
2	5400	1.829
3	6300	1.681
4	7200	1.653
5	9000	1.415
6	10800	1.279
7	12650	1.146
8	14400	1.000
9	18000	0.602

slope: 9.305×10^{-5}

intercept: 2.029

rate: 2.143×10^{-4}

$r = 0.997$

TABLE III (continued)

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>$200^{\circ} \pm 0.2^{\circ}$</u>		
1	0	2.000
2	900	1.802
3	1800	1.672
4	2700	1.633
5	4500	1.301
6	5400	1.255
7	6300	1.130
8	7800	0.903
9	10800	0.602
10	13500	0.176

slope: 1.272×10^{-4}

intercept: 1.923

rate: 2.930×10^{-4}

$r = 1.012$

$210^{\circ} \pm 0.2^{\circ}$

1	0	2.000
2	900	1.720
3	1800	1.583
4	2400	1.371
5	3600	1.041
6	4500	0.698
7	5400	0.477
8	6300	0.301

slope: 2.803×10^{-4}

intercept: 2.024

rate: 6.456×10^{-4}

$r = 0.996$

TABLE III (continued)

The Isomerization of 3,4-Bis-(4-tolyl)-
1,2,5-triphenyl-2,4-cyclopentadien-1-ol

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>180° ± 0.2°C</u>		
1	0	2.000
2	3600	1.886
3	10800	1.662
4	25200	1.146
5	32400	0.977
6	39600	0.653

slope: 3.344×10^{-5}

intercept: 2.009

rate: 7.700×10^{-5}

r = 0.999

190° ± 0.2°C

1	0	2.000
2	3600	1.756
3	5800	1.607
4	7200	1.544
5	10800	1.217
6	14580	0.778
7	18000	0.477

slope: 9.163×10^{-5}

intercept: 2.046

rate: 2.110×10^{-4}

r = 0.995

TABLE III (continued)

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>200° ± 0.2°C</u>		
1	0	2.000
2	900	1.826
3	1900	1.707
4	2700	1.653
5	3600	1.491
6	6800	1.041
7	7300	0.903
8	9000	0.602
9	10900	0.398

slope: 1.491×10^{-4}

intercept: 2.006

rate: 5.434×10^{-4}

$r = 0.997$

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>210° ± 0.2°C</u>		
1	0	2.000
2	600	1.799
3	1200	1.740
4	1800	1.574
5	2400	1.332
6	3800	0.954
7	4200	0.845
8	5400	0.477

slope: 2.858×10^{-4}

intercept: 2.038

rate: 6.581×10^{-4}

$r = 0.997$

TABLE III (continued)

The Isomerization Reaction of 1,2,3,4,5-
Pentaphenyl-2,4-cyclopentadien-1-ol

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>180° ± 0.2°</u>		
1	0	2.000
2	7210	1.641
3	10820	1.513
4	14400	1.310
5	18010	1.154
6	25200	0.931
7	32400	0.740
8	39600	0.391

slope: 3.895×10^{-5}
intercept: 1.927
rate: 8.969×10^{-5}
 $r = 0.995$

<u>190° ± 0.2°</u>		
1	0	2.000
2	1800	1.819
3	3600	1.607
4	5400	1.439
5	7200	1.278
6	9000	1.110
7	10800	0.977
8	14400	0.602

slope: 9.403×10^{-5}
intercept: 1.963
rate: 2.166×10^{-4}
 $r = 0.999$

TABLE III (continued)

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>200° + 0.2°C</u>		
1	0	2.000
2	900	1.875
3	1800	1.724
4	3600	1.406
5	4500	1.243
6	5400	1.079
7	7200	0.845
8	10800	0.301

slope: 1.597×10^{-4}

intercept: 1.992

rate: 3.678×10^{-4}

$r = 0.999$

210° + 0.2°C

1	0	2.000
2	900	1.838
3	2700	1.491
4	3900	1.11
5	4500	0.698
6	5400	0.602

slope: 2.800×10^{-4}

intercept: 1.994

rate: 6.447×10^{-4}

$r = 0.9880117737$

TABLE III (continued)

The Isomerization Reaction of 3,4-Bis(4-chlorophenyl)-

1,2,5-triphenyl-2,4-cyclopentadien-1-ol

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>180° ± 0.2°C</u>		
1	0	2.000
2	900	1.954
3	3600	1.748
4	6500	1.525
5	10800	1.301
6	14400	1.06
7	21600	0.653
8	25900	0.301

slope: 6.380×10^{-5}

intercept: 1.983

rate: 1.469×10^{-4}

r = 0.999

190° ± 0.2°C

1	0	2.000
2	1800	1.789
3	3600	1.590
4	5600	1.267
5	7300	1.060
6	9300	.813
7	10800	.602
8	14400	.172

slope: 6.380×10^{-5}

intercept: 1.983

rate: 1.469×10^{-4}

r = 0.999

TABLE III (continued)

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>200° ± 0.2°C</u>		
1	0	2.000
2	950	1.752
3	1800	1.525
4	2700	1.301
5	4000	.954
6	4500	.875
7	5400	.477
8	7300	.176

slope: 2.561×10^{-4}

intercept: 1.985

rate: 5.897×10^{-4}

$r = 0.994$

210° ± 0.2°C

1	0	2.000
2	700	1.643
3	1200	1.414
4	1800	1.130
5	2400	.845
6	3000	.544
7	3600	.243

slope: 4.829×10^{-4}

intercept: 1.992

rate: 1.112×10^{-3}

$r = 1.000$

TABLE III (continued)

The Isomerization of 3,4-Bis(4-bromophenyl)-
1,2,5-triphenyl-2,4-cyclopentadien-1-ol

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>180° ± 0.2°</u>		
1	0	2.000
2	3600	1.872
3	4500	1.756
4	5400	1.735
5	6300	1.708
6	8100	1.512
7	10080	1.333
8	12672	1.114
9	17388	0.699

slope: 8.490×10^{-5}

intercept: 2.188

rate: 1.955×10^{-4}

$r = 0.997$

190° ± 0.2°

1	0	2.000
2	900	1.854
3	1800	1.803
4	2700	1.699
5	3600	1.607
6	4500	1.431
7	5400	1.230
8	6300	1.146
9	7200	1.0

slope: 1.396×10^{-4}

intercept: 2.033

rate: 3.215×10^{-4}

$r = 0.992$

TABLE III (continued)

<u>Sample Number</u>	<u>Time sec</u>	<u>Log % Conc</u>
<u>200° ± 0.2°</u>		
1	0	2.000
2	600	1.851
3	1200	1.732
4	1800	1.577
5	2400	1.389
6	3000	1.176
7	3600	1.021
8	4500	0.778
9	5500	0.602
10	6300	0.301
slope: 2.699×10^{-4}		
intercept: 2.023		
rate: 6.215×10^{-4}		
r = 0.998		
<u>210° ± 0.2°</u>		
1	0	2.000
2	600	1.851
3	1200	1.544
4	1800	1.161
5	2400	0.903
6	3000	0.477
slope: 5.648×10^{-4}		
intercept: 2.020		
rate: 1.301×10^{-3}		
r = 0.998		

Figure 1

Variation with time of the logarithm of the concentration of 3,4-Bis-(4-t-butyl phenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol at 210, 200, 190 and $180^{\circ} \pm 0.2^{\circ}$.

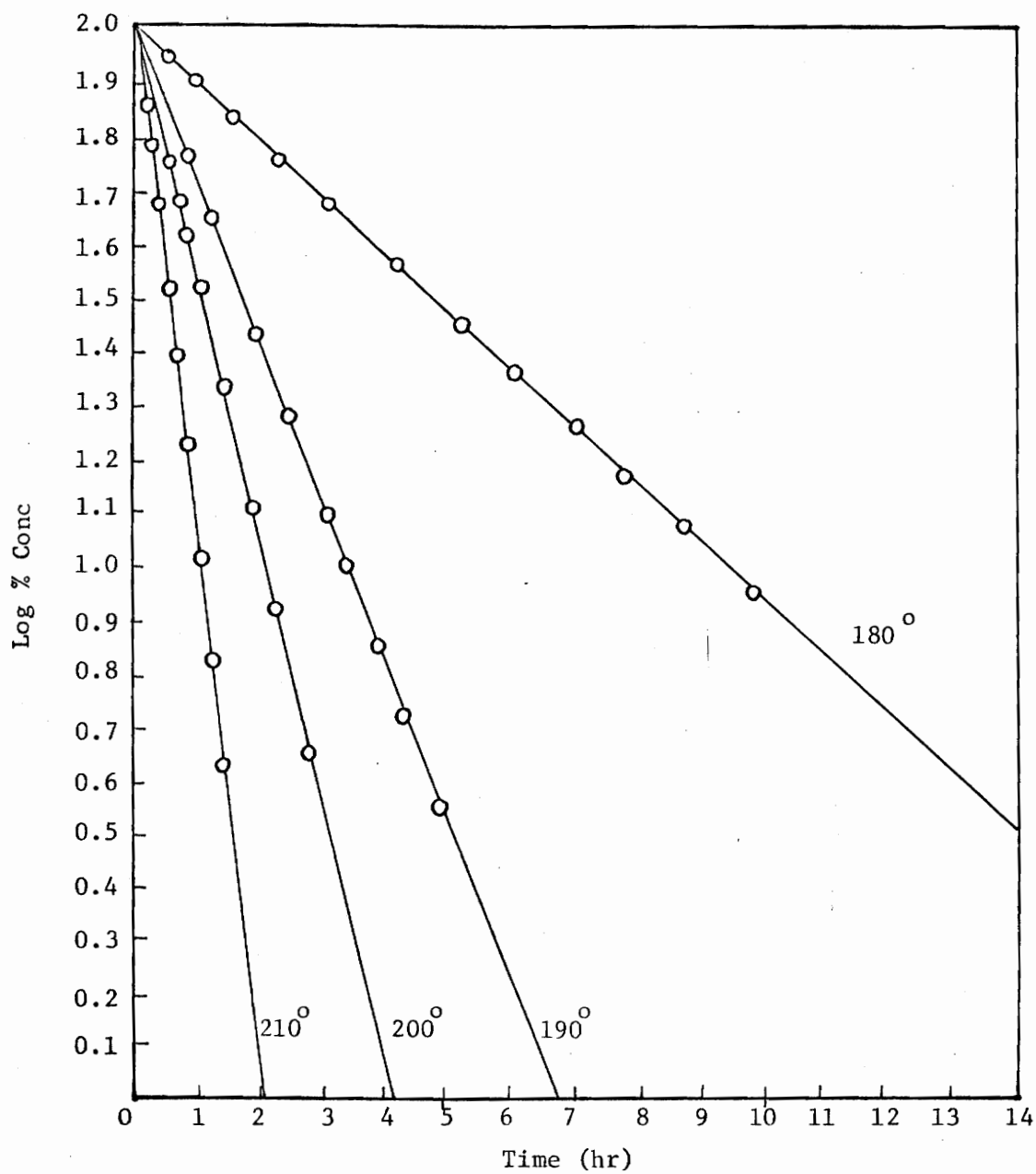


Figure 2

Variation with time of the logarithm of the concentration of 3,4-Bis-(4-tolyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol at 210, 200, 190, and $180 \pm 0.2^\circ$.

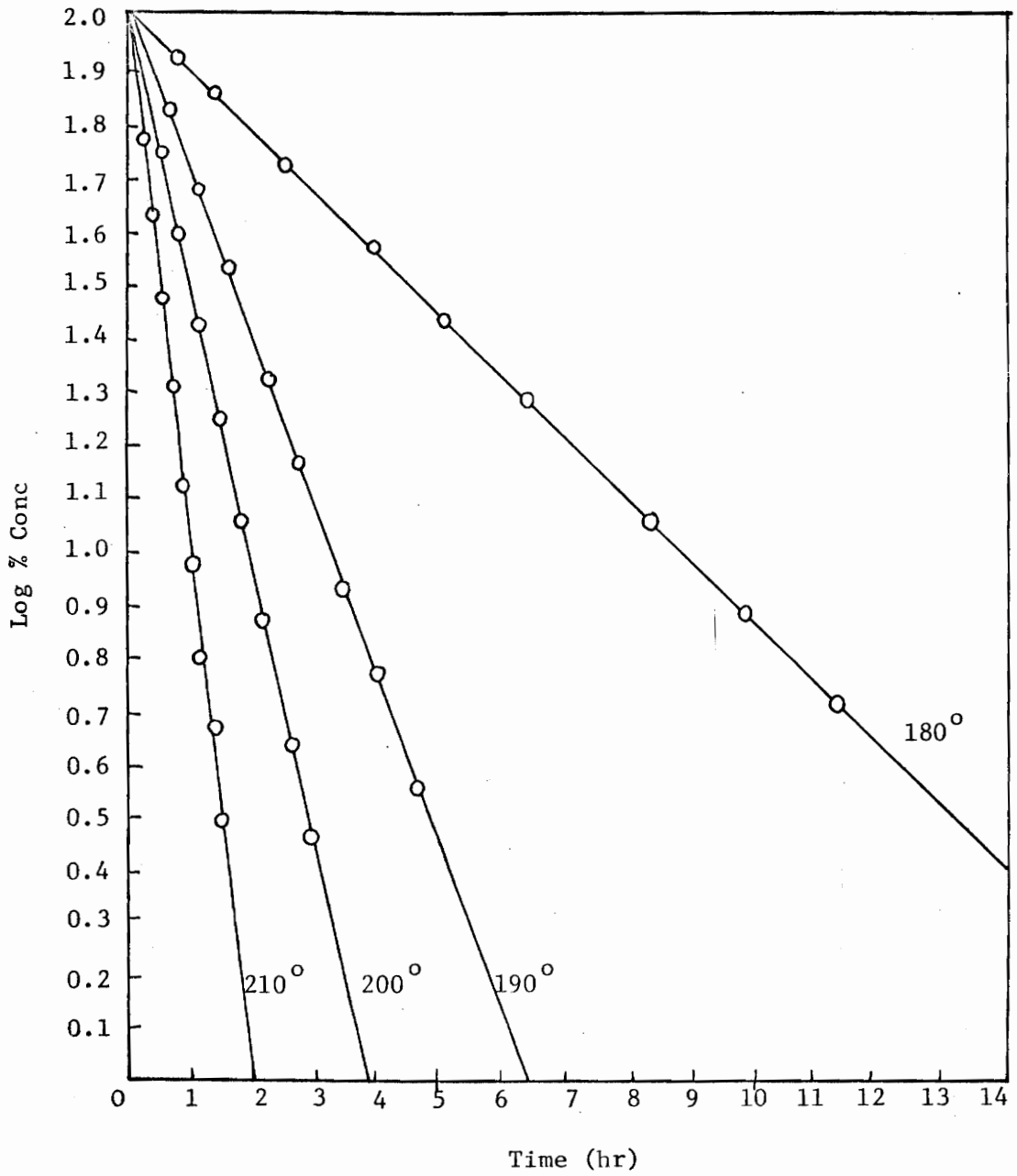


Figure 3

Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 210, 200, 190 and $180 \pm 0.2^{\circ}$.

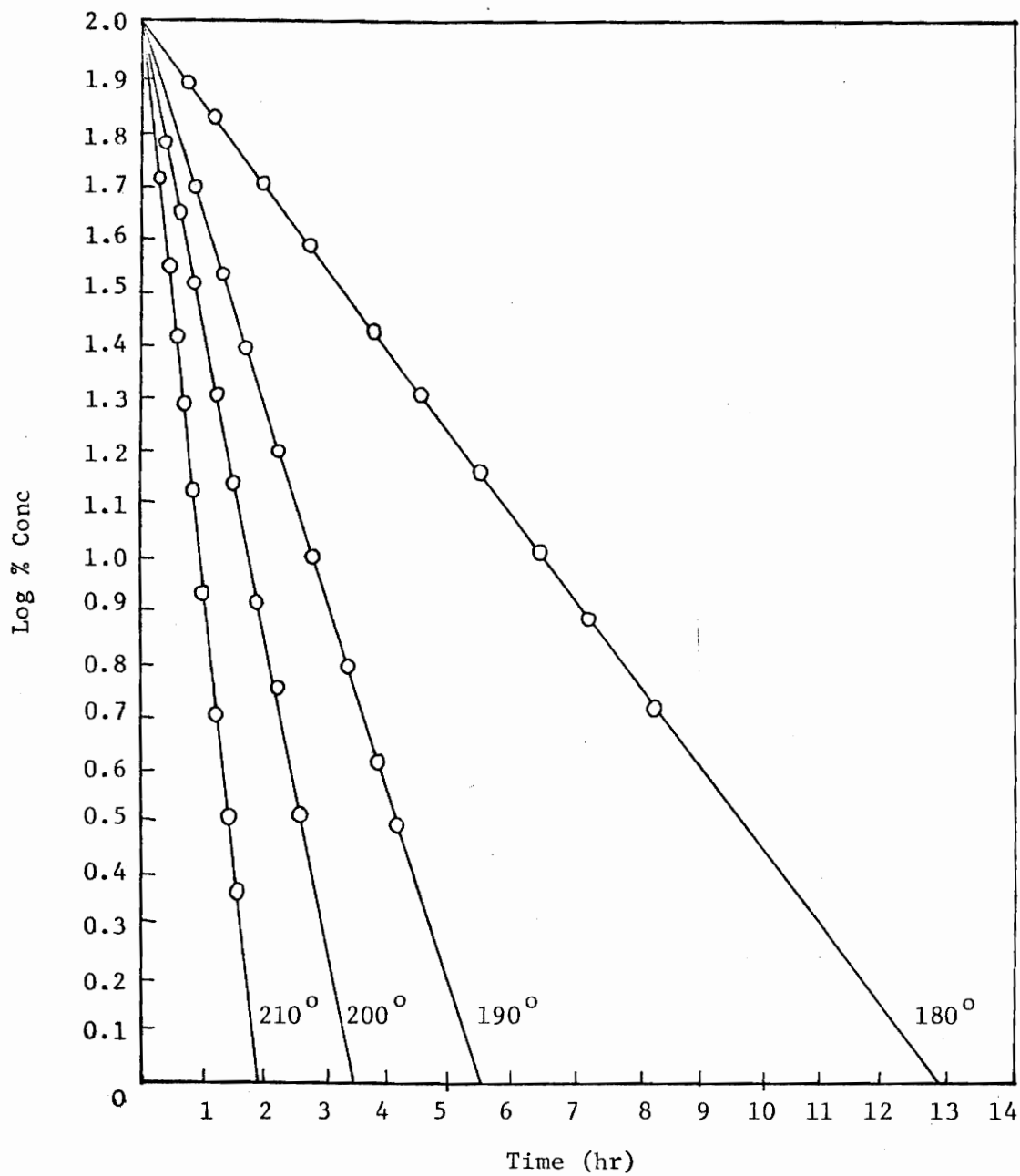


Figure 4

Variation with time of the logarithm of the concentration of 3,4-Bis-(4-chlorophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol at 210, 200, 190 and $180 \pm 0.2^\circ$.

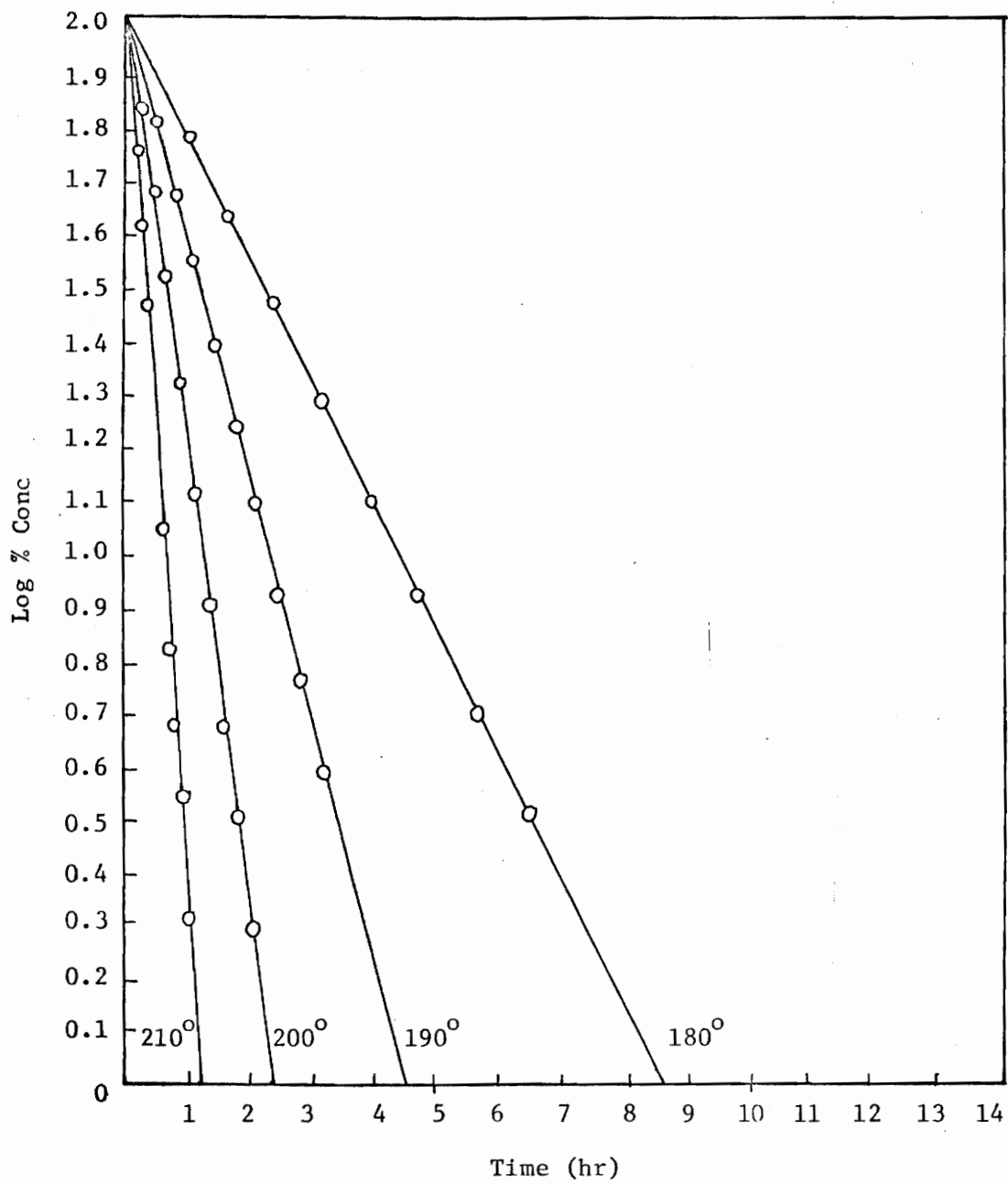
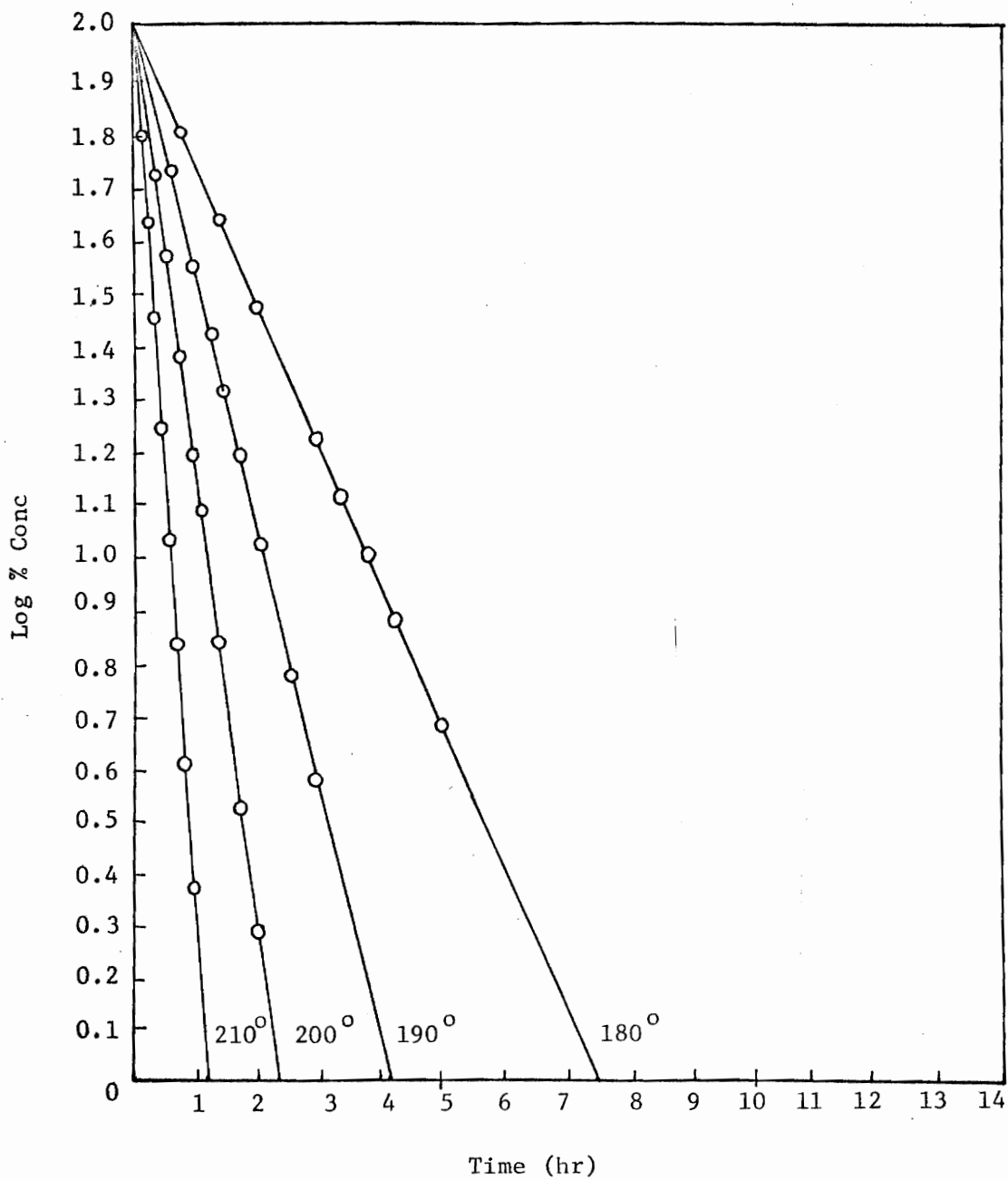


Figure 5

Variation with time of the logarithm of the concentration of 3,4-Bis-(4-bromophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol at 210, 200, 190, $180 \pm 0.2^\circ$.



The sampling technique was the same as recorded above. The time at which the samples were taken and percent logarithm of the concentrations of the starting material are recorded in Table III. Plots of the logarithm of the concentration of starting materials versus time are shown as before in Figures 1-5 for each corresponding alcohol.

Again the above experiment was repeated under the same conditions given above except the temperature of the mixture was raised to $200 \pm 0.2^{\circ}$. The sampling technique was the same as described above. Table III again shows the time at which the samples were taken and the percentage concentration the percent logarithm of the concentration at each time. Figures 1-5 show the plots of the logarithm of the concentration of the starting alcohol versus time.

The last run was carried out under the same conditions given above except the temperature was again raised, this time to $210^{\circ} \pm 0.2^{\circ}$. The sampling technique used was as described above. Figures 1-5 show plots of the logarithm of the concentration of the starting material versus time for each of the corresponding alcohols.

Plotting the logarithm of the concentration of the starting materials at different temperatures versus time afforded the curves illustrated in Figures 6-9. This shows that the slopes increase as the temperature is increased, which is in accord with increases in the rate of the reaction with increases in the temperature. It can be seen from any of these plots, (Figures 6-9) that at 210° , the reaction goes to completion in less time than at 180° . This is an indication that the reaction is temperature dependent. The fact that this sigma-

Figure 6

Variation with time of the logarithm of the concentration of several substituted polyarylated alcohols at $180 \pm 0.2^{\circ}$.

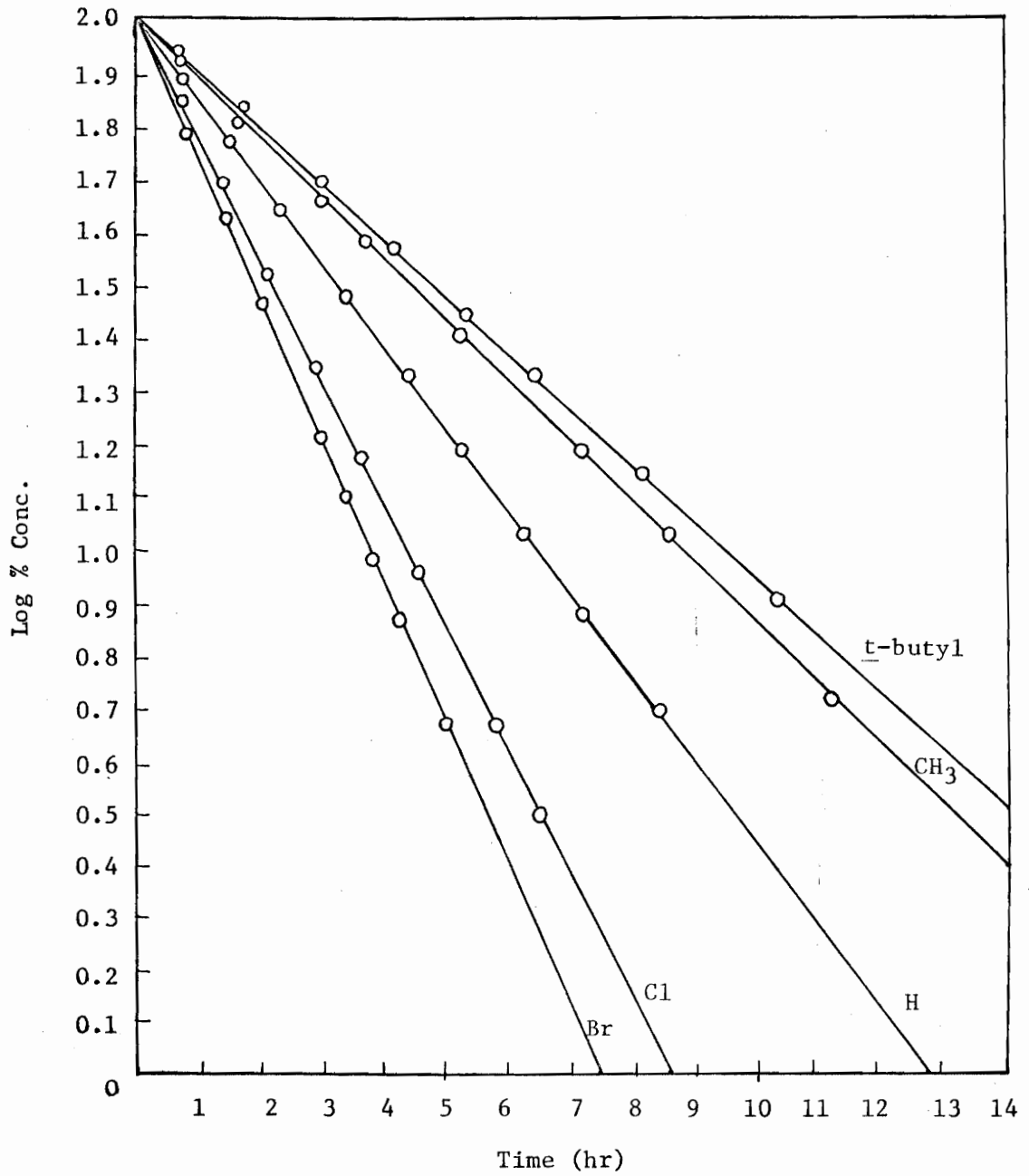


Figure 7

Variation with time of the logarithm of the concentration of several substituted polyarylated alcohols at $190 \pm 0.2^{\circ}$.

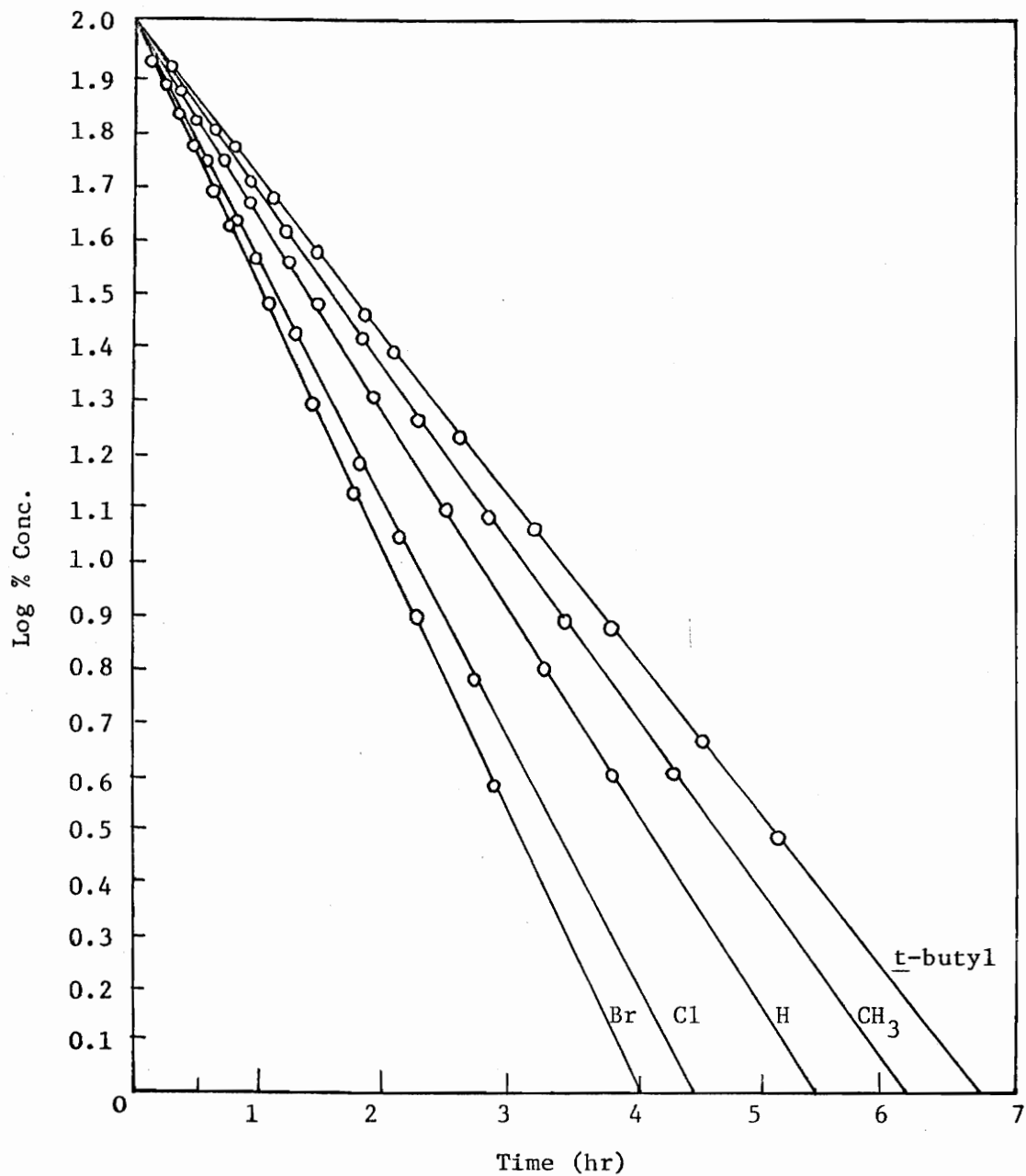


Figure 8

Variation with time of the logarithm of the concentration of several substituted polyarylated alcohols at $200 \pm 0.2^{\circ}$.

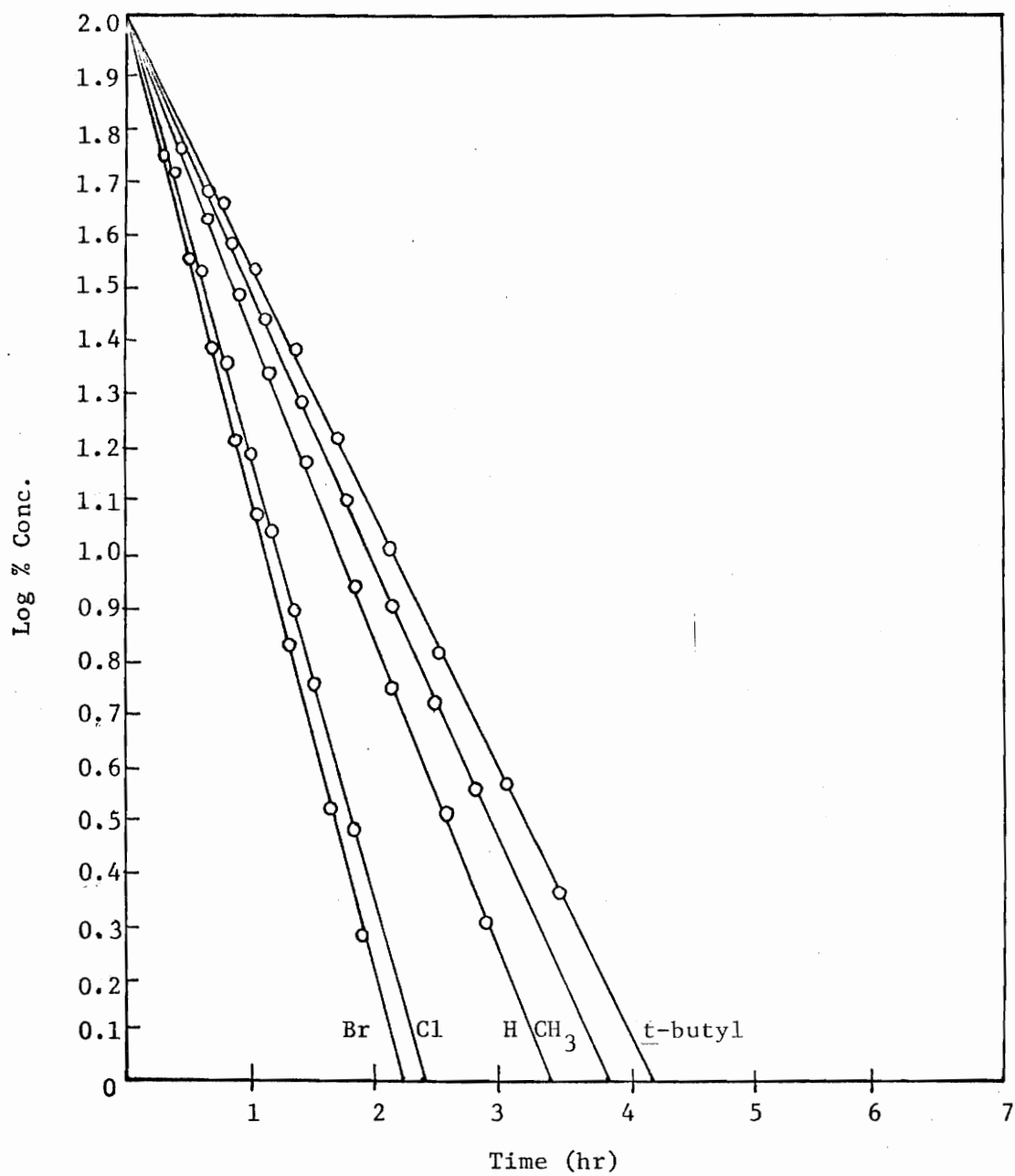
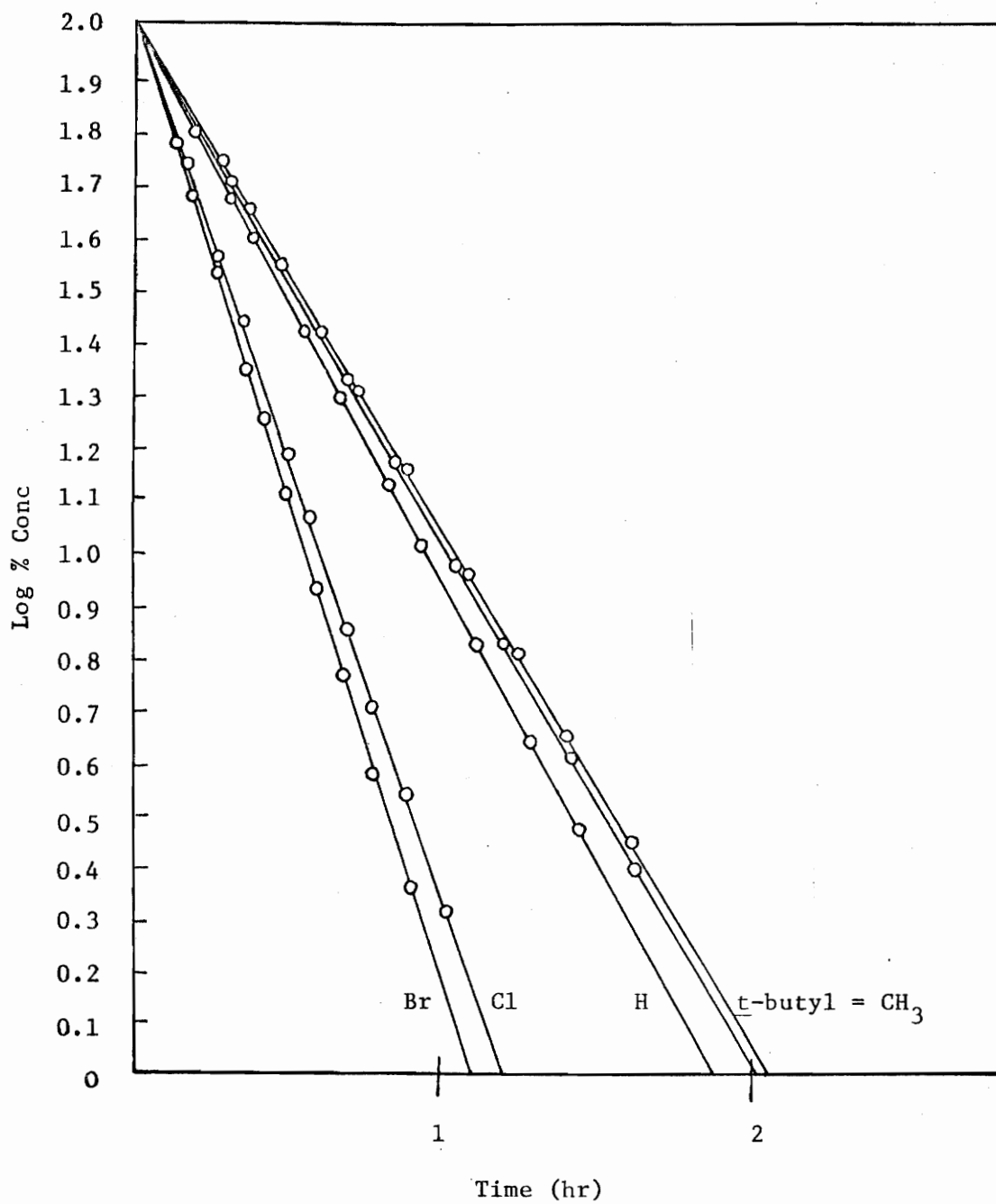


Figure 9

Variation with time of the logarithm of the concentration of several substituted polyarylated alcohols at $210 \pm 0.2^\circ$.



tropic rearrangement of these alcohols is a first order reaction, was confirmed from plots of the logarithm of the concentration of the starting materials versus time, since a straight line was obtained which is a characteristic of first order reactions. Using a least square program to calculate the slopes of the curves shown in Figures 1-5, it was possible to calculate the rate constants for each individual kinetic run, where the rate constant k could be evaluated from the slope using the equation:

$$k = -(\text{slope}) \times 2.303 \quad (1)$$

Using this expression, the rate constant k for each of the four kinetic runs were calculated per alcohol. In Appendix II are summarized the values of the slopes and the rate constants obtained for each of the four kinetic runs on each alcohol. The activation energies of these sigmatropic rearrangements were calculated as follows:

Plotting logarithm k versus $1/T(^{\circ}\text{K})$, which is the Arrhenius plot afforded the curves shown in Figures 10-14. Again the least square program was used to calculate the slopes of these plots (Table IV). The activation energy was then calculated from the Arrhenius equation shown below:

$$\frac{d \ln k}{dt} = \frac{E}{RT^2} \quad (2)$$

$$\ln k = -\frac{E}{RT} + \text{constant} \quad (3)$$

$$-\frac{E}{R} = \frac{\ln k}{T} + \text{intercept} \quad (4)$$

$$\text{or } E = -(\text{slope}) \times R \quad (5)$$

Figure 10

Variation of Log k versus $1/T$ over the temperature range of
 $180-210 \pm 0.2^\circ$ for the evaluation of E_a of
3,4-Bis(4-t-butylphenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

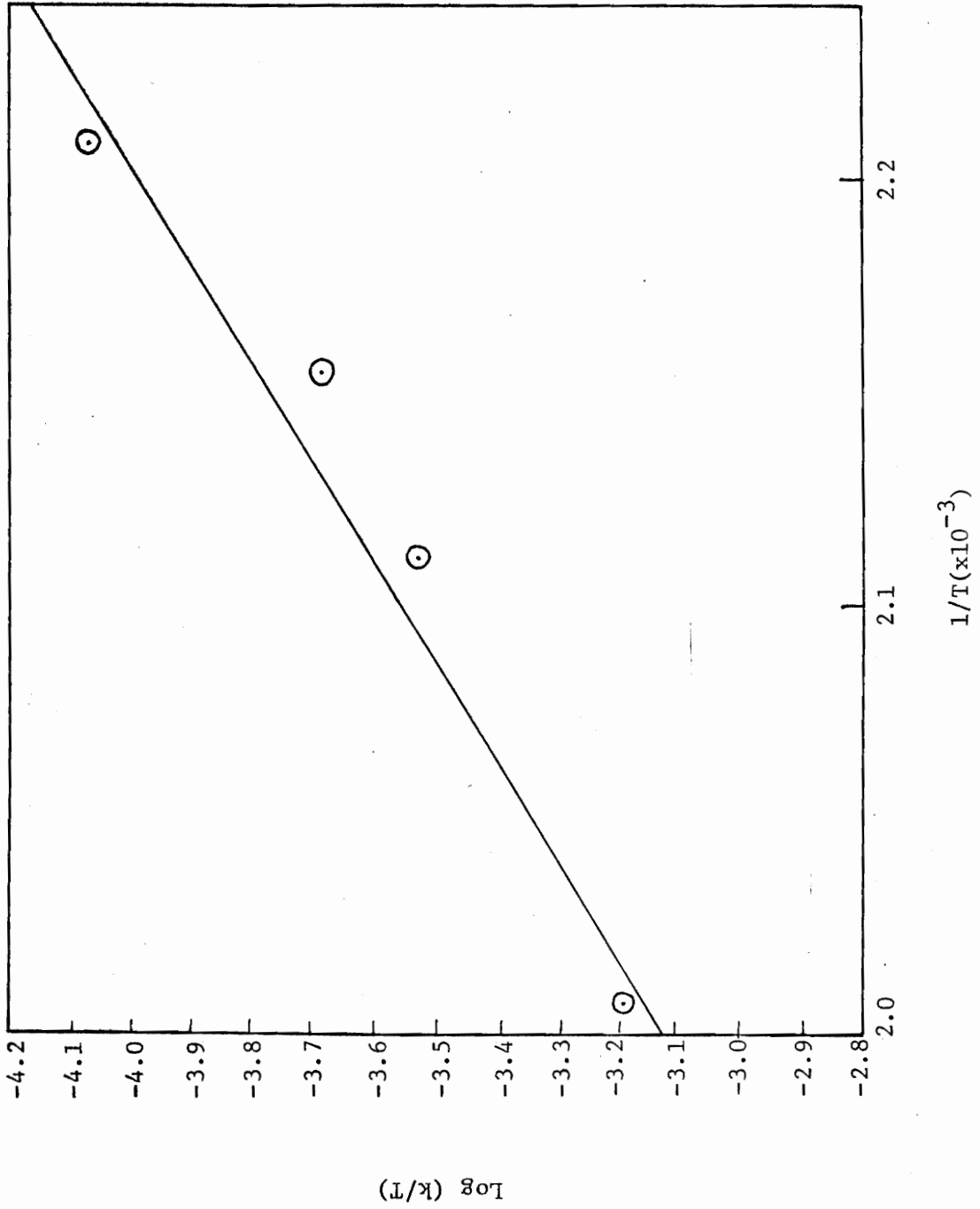


Figure 11

Variation of Log k versus $1/T$ over the temperature range of
 $180-210 \pm 0.2^\circ$ for the evaluation of E_a of
3,4-Bis(4-tolyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

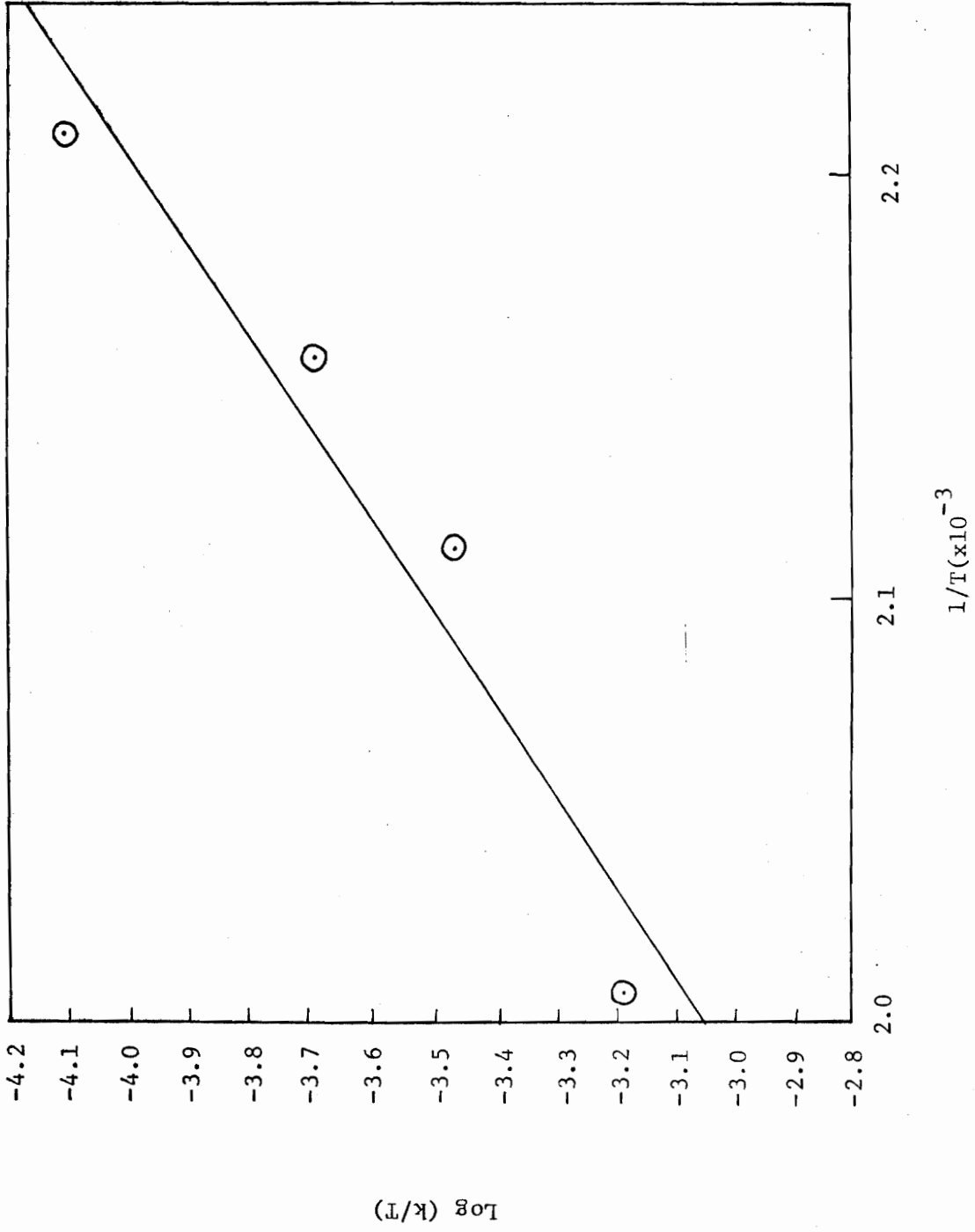


Figure 12

Variation of Log k versus $1/T$ over the temperature range of $180-210 \pm 0.2^\circ$ for the evaluation of E_a of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.

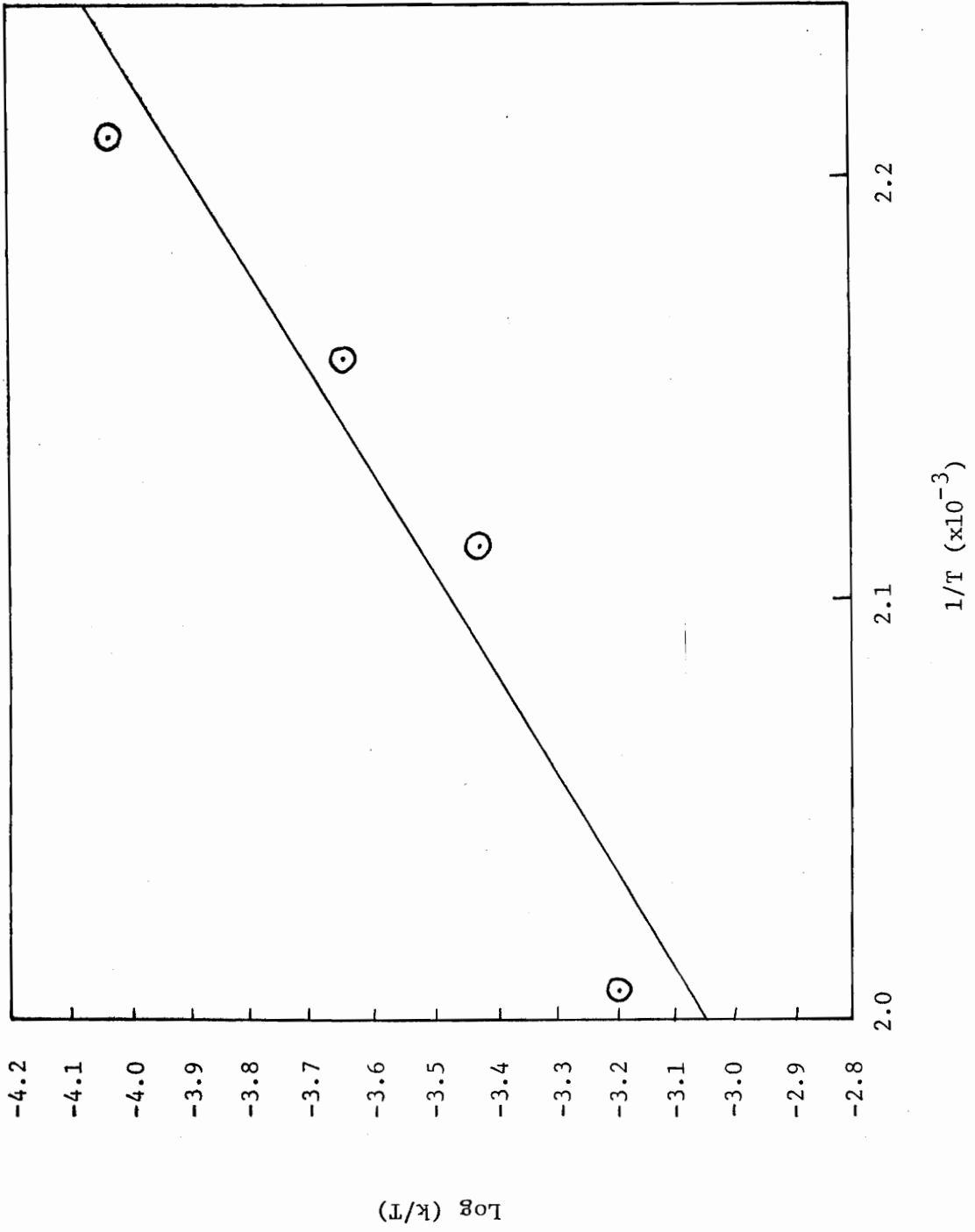


Figure 13

Variation of Log k versus $1/T$ over the temperature range of
 $180-210 \pm 0.2^\circ$ for the evaluation of E_a of
3,4-Bis(4-chlorophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

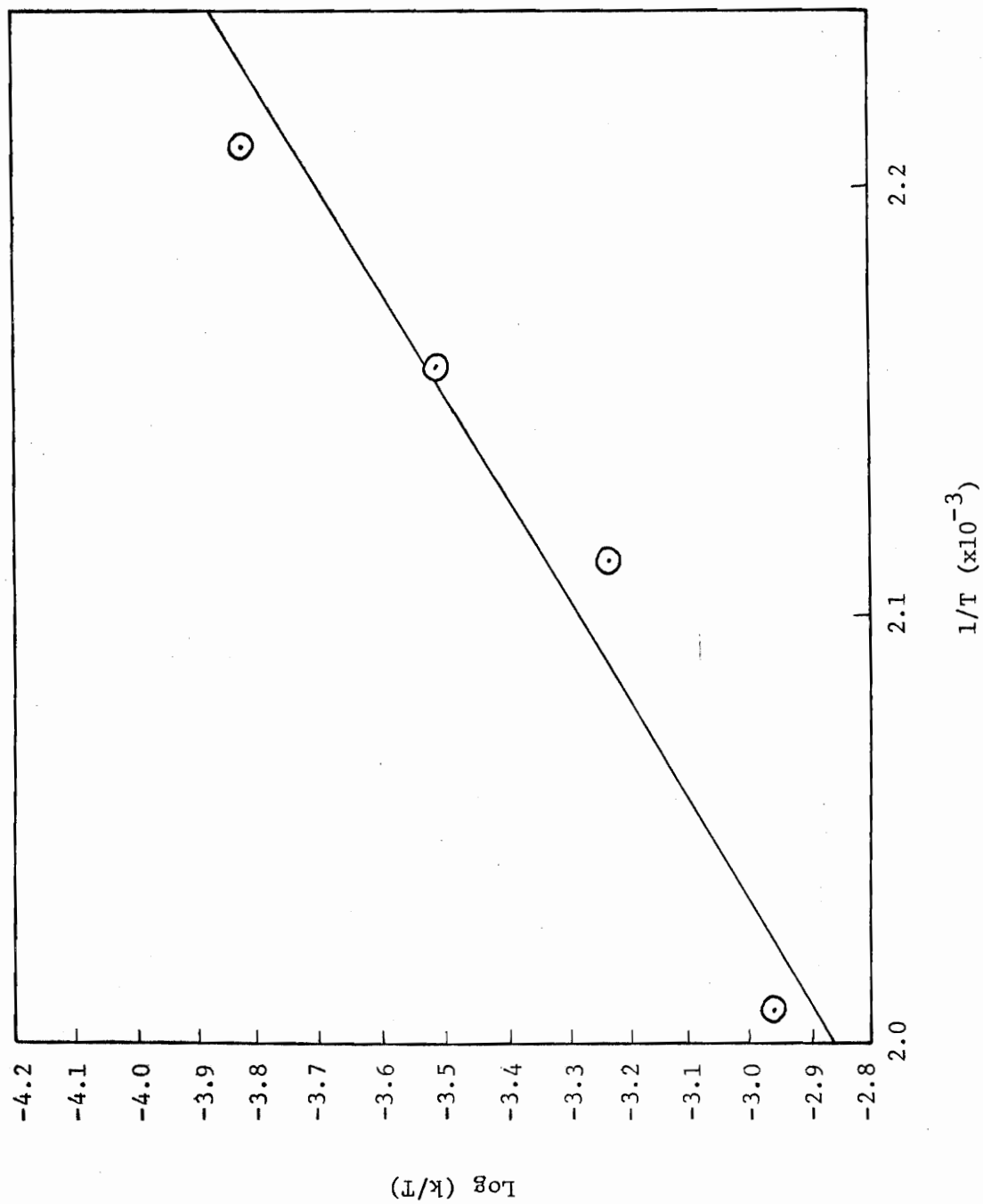


Figure 14

Variation of Log k versus $1/T$ over the temperature range of
 $180-210 \pm 0.2^\circ$ for the evaluation of E_a of
3,4-Bis(4-bromophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

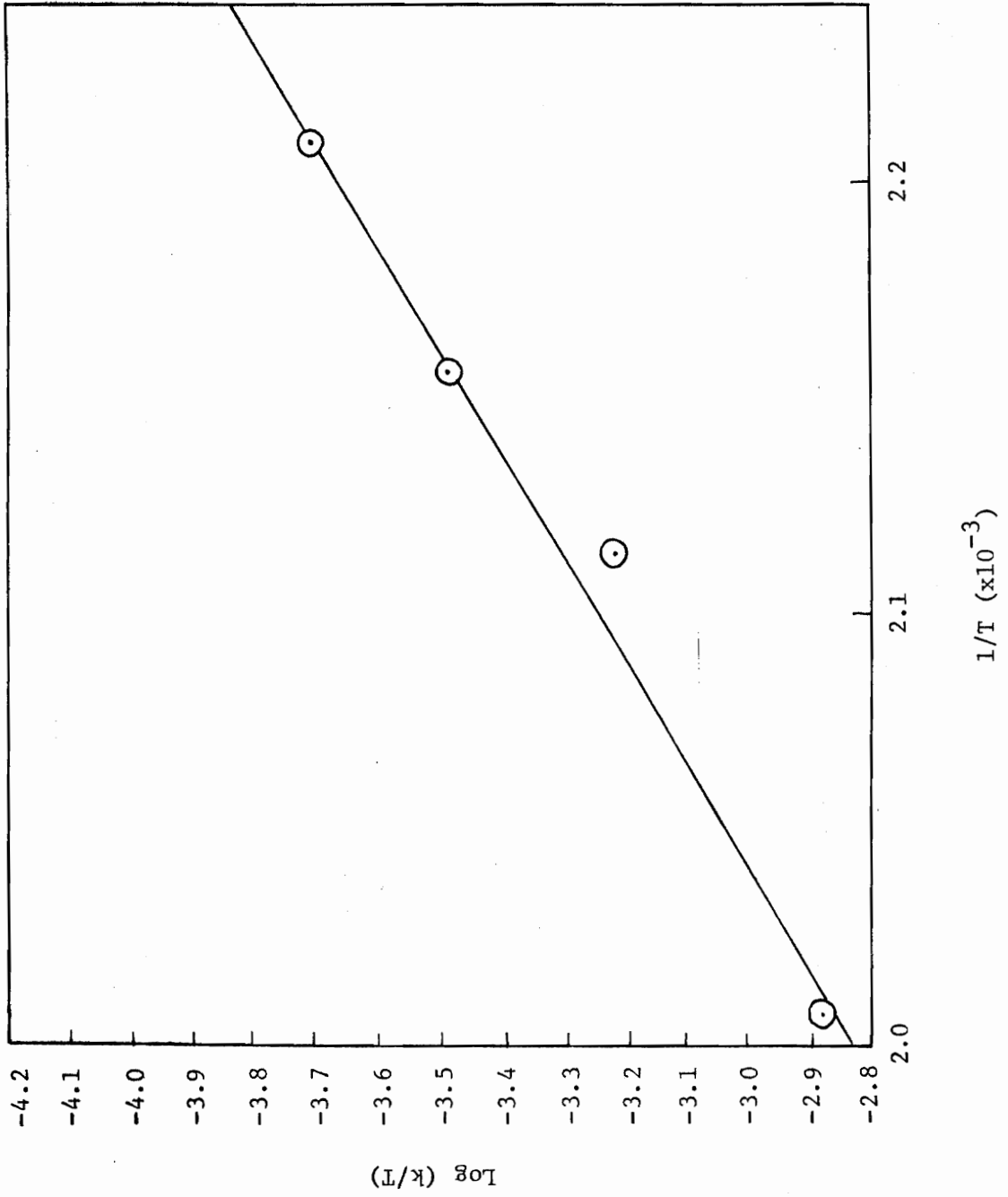


TABLE IV

Calculated Values of Activation Energies (E_a), Enthalpies of Activation (ΔH^\ddagger), and Entropies of Activation (ΔS^\ddagger) for Thermal [1,5]-Sigmatropic Phenyl Rearrangements in 3,4-Bis(4-substituted phenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ols

Substituent	E_a (Kcal/mol)	ΔH^\ddagger (Kcal/mol)	ΔS^\ddagger (eu)*
t-butyl	28.7 \pm 3.0	27.7 \pm 3.0	-16.6 \pm 2.3 [†]
methyl	30.3 \pm 2.2	29.3 \pm 2.3	-13.1 \pm 1.2
H	28.8 \pm 1.5	27.9 \pm 1.4	-16.1 \pm 1.6
chloro	29.3 \pm 0.7	28.4 \pm 0.6	-14.0 \pm 0.4
bromo	27.4 \pm 2.5	26.5 \pm 2.5	-17.8 \pm 2.1


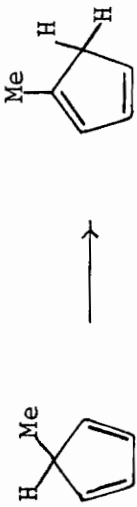
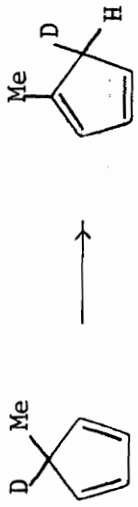
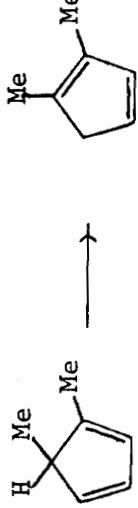
*These ΔS^\ddagger values are average values of the individual ΔS^\ddagger at 180, 190, 200 and 210° which are recorded in Appendix II.

[†]Error analysis of ΔS^\ddagger was obtained from calculations of ΔS^\ddagger from the error analyses of Log A values from the Arrhenius Plots where:

$$\Delta S^\ddagger = 4.575 \log A - 60.53.$$

TABLE V

Known Thermal Sigmatropic Rearrangements

Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger , kcal/ mol*	ΔS^\ddagger , eu	Ref
	D	318-338 (CCl ₄)	12.11	23.6	- 3.3	15
	H	279-298 (CCl ₄)	10.87	19.3	-10.8	71
	D	292-313 (CCl ₄)	11.88	21.7	- 6.2	71
	H	303-227 (neat)		22.5	- 4	70

[1,5] Hydrogen Shifts in Cyclic Dienes and Trienes

TABLE V (continued)

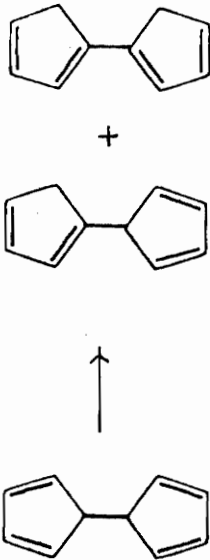
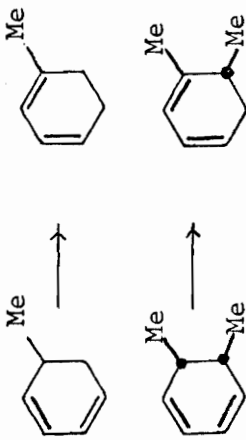
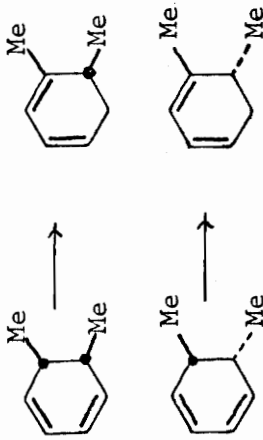
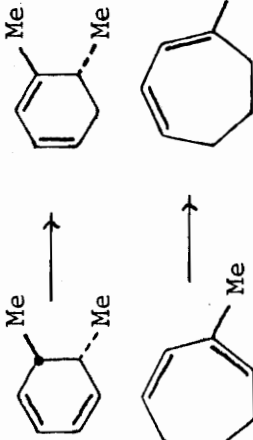
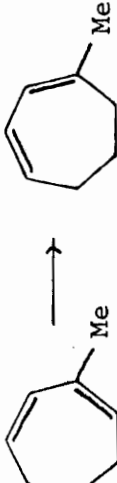
Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger , kcal/mol*	ΔS^\ddagger , eu	Ref
	H	(heptane)		18.6	-16	118
	H	573-634	11.2	34.0	-10.7	119
	H	455-473 (hexane)		32.1	-7	120
	H	455-473 (hexane)		35.1	-3	120
	H	413-433		29.5	-7.4	121 122

TABLE V (continued)

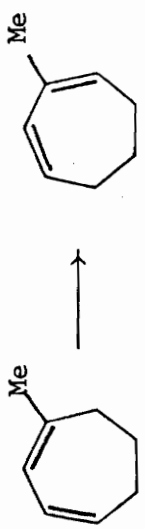


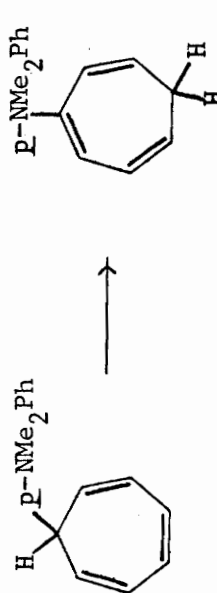

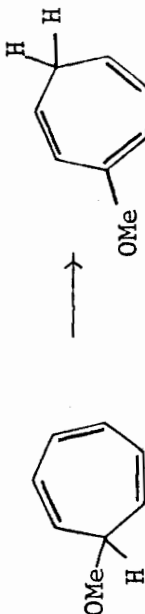


Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/mol*	ΔS^\ddagger , eu	Ref
	H	413-433		28.6	-9.9	121 122
	H	371-413 (neat)	11.1	30.2	-11.5	40
	H	353-393 (decane)	10.8	26.9	-11.7	41
	H	373-413 (neat)	11.3	27.6	-9.3	37

TABLE V (continued)

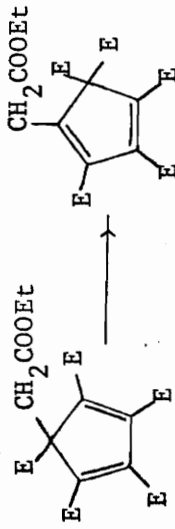
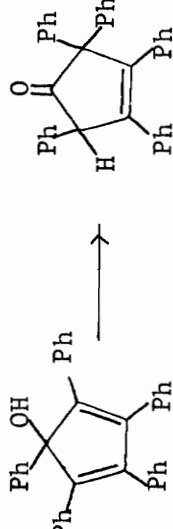
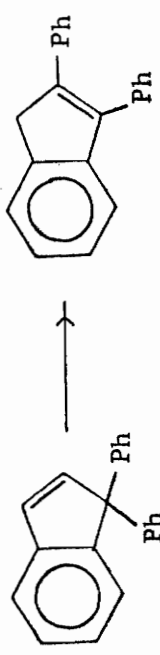
Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/mol*	ΔS^\ddagger , eu	Ref
	H	402-499	12.6	32.3	- 4.9	25
	H	353-413 (neat)	10.0	25.7	-15.0	26
	Me	625-660	13.9	44.2	+ 6	123
	Me	625-660	14.4	44.4	+ 3	123

[1,5] sp³-Hybridized Carbon Shifts

TABLE V (continued)

Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/mol*	ΔS^\ddagger , eu	Ref
	Me	625-660	14.6	40.3	- 1	123
	Me	608-702	13.7	43.8	+ 1	124
	Me	473-530	13.9	42.3	+ 3	130
[1,5] Migrations of Carbon Functional Groups						
	E = COOMe	386-423 (PhCl)		25.3	- 9.7	4
	COOMe	386-423 (PhCl)		25.1	-10.4	16

TABLE V (continued)

Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/mol*	ΔS^\ddagger , Ref eu
 Reverse	COOMe	370-407 (PhMe)		25.3	-10.9 16
	C ₆ H ₅	446-473 (PhOPh)		35.3	-7.5 2
	C ₆ H ₅	523-553 (PhOPh)		27.2	-27.2 5

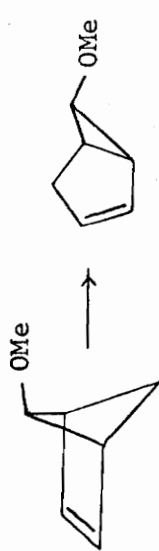
[1,5] Migration of Phenyl Groups

TABLE V (continued)

Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/mol*	ΔS^\ddagger , eu	Ref
	C ₆ H ₅	493-509 (PhOPh)		26.7	-25.1	75
	-CH ₂ - bridge	422-463	13.95	34.29	- 5.5	72 13
	-CH ₂ - bridge	358-378 (n-dodecane)		27.5	- 2	61

[1,5] sp³-Hybridized Carbon Shifts

TABLE V (continued)

Reaction	Migrating group	T range, °K (medium)	Log A (sec ⁻¹)	ΔH^\ddagger kcal/ mol*	ΔS^\ddagger eu	Ref
	-CH ₂ ⁻ bridge	310-323 (CCl ₄)		24.5	- 0.5	62

*The Arrhenius activation energy (E_a) has been converted to ΔH^\ddagger by the relationship $\Delta H^\ddagger = E_a - RT_m$ where T_m is the mean absolute temperature, so as to make direct data comparison easier.

where the slope was calculated from the Arrhenius plot.

The activation energies compare favorably with the activation energy calculated for other [1,5]-sigmatropic shifts (see Table V, Known Thermal Sigmatropic Rearrangements) but not with that previously reported for the unsubstituted phenyl in the parent alcohol.

As can be seen in this table, the previous report² of the Arrhenius activation energy associated with the phenyl migration in 1,2,3,4,5-pentaphenylcyclopentadienol had a value of 36.1 kcal/mol. As explained in the introduction, of this dissertation, these results were obtained by analysis of the rearranged mixture using gas chromatography at a high column temperature. Further rearrangement of the mixture may have taken place at this high temperature (retention time, 39 min) to account for this discrepancy in the activation energy observed.

Enthalpies of activation, ΔH^\ddagger , and entropies of activation, ΔS^\ddagger , were then obtained from plots of $\log (k/T)$ with $1/T$ (K^0) (Figures 15-19).

$$\frac{\Delta H^\ddagger}{RT} = \frac{\ln k}{T} \quad (6)$$

The slope equals $-\Delta H^\ddagger/2.303R$ and the intercept is approximately equal to $(\Delta S^\ddagger/2.303R) + 10.32$. Because of the error already associated with the above approximation ΔS^\ddagger was calculated using the equation shown below: ¹¹⁵

$$\Delta S^\ddagger = 4.575 (\log k - \log T - 10.32) + \Delta H^\ddagger/T \quad (7)$$

Although the potential error in this calculation may be large when a single experimental point or closely related set of points are employed in the evaluation of data, linear least square analysis of the data produced a correlation coefficient of 0.988 or better indicating that our assurance limits are quite good (See Appendix II).

Finally a Hammett plot of $\log k/\log k_o$ versus σ_p was attempted, but as can be seen from Appendix III this was not an effective representation of the results obtained. Thus, Hammett plot of $\log k$ versus σ_p was made, where ρ values of -0.813, -0.400 (-0.73 extrapolated value), -0.690 and -0.657 for rate data at 180, 190, 200 and $210 \pm 0.2^\circ$ were obtained using the following equations, respectively (Figure 20).

$$\log \frac{k_x}{k_o} = \rho\sigma \quad (8)$$

$$\log k_x = \rho\sigma + \log k_o \quad (9)$$

where $\log k_x$ = rate constant of the substituted alcohol

$\log k_o$ = rate of the parent alcohol

$\sigma = \sigma_p$ [see Table VI]

ρ = rho value or degree of sensitivity of the reaction at hand toward the substituent

Several important conclusions can be made at this point concerning the hypothesis set forward in the preceding section on Sigma-tropic Rearrangements; concerning electronic effects associated with the rearrangement, the transition state, and temperature effects associated with the rho values obtained.

Figure 15

Variation of $\log (k/T)$ versus $1/T$ over the temperature range of $180-210 \pm 0.2^\circ$ for the evaluation of ΔH^\ddagger of 3,4-Bis(4-t-butylphenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

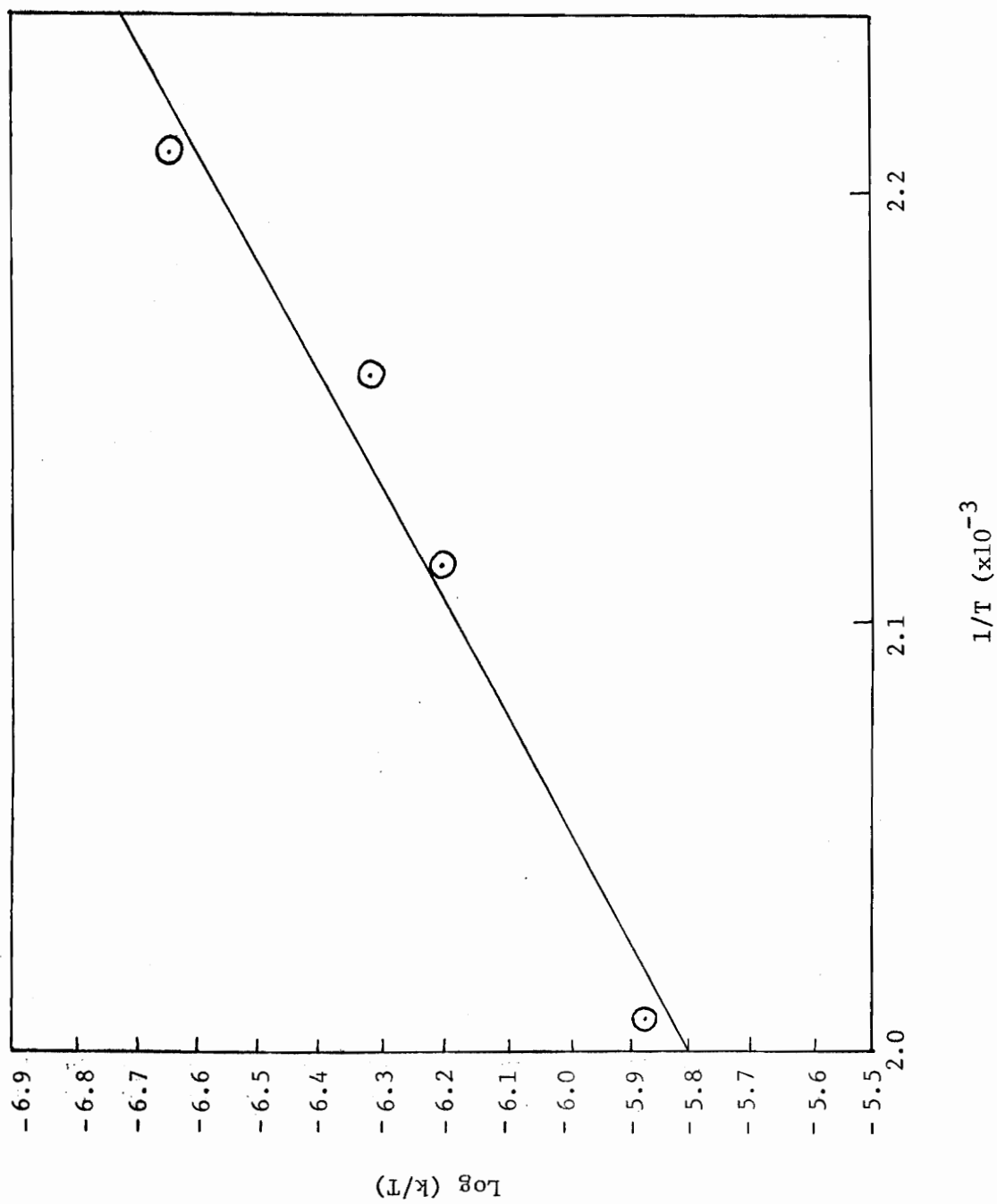


Figure 16

Variation of $\log (k/T)$ versus $1/T$ over the temperature range of
180-210 \pm 0.2° for the evaluation of ΔH^\ddagger of
3,4-Bis(4-tolyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

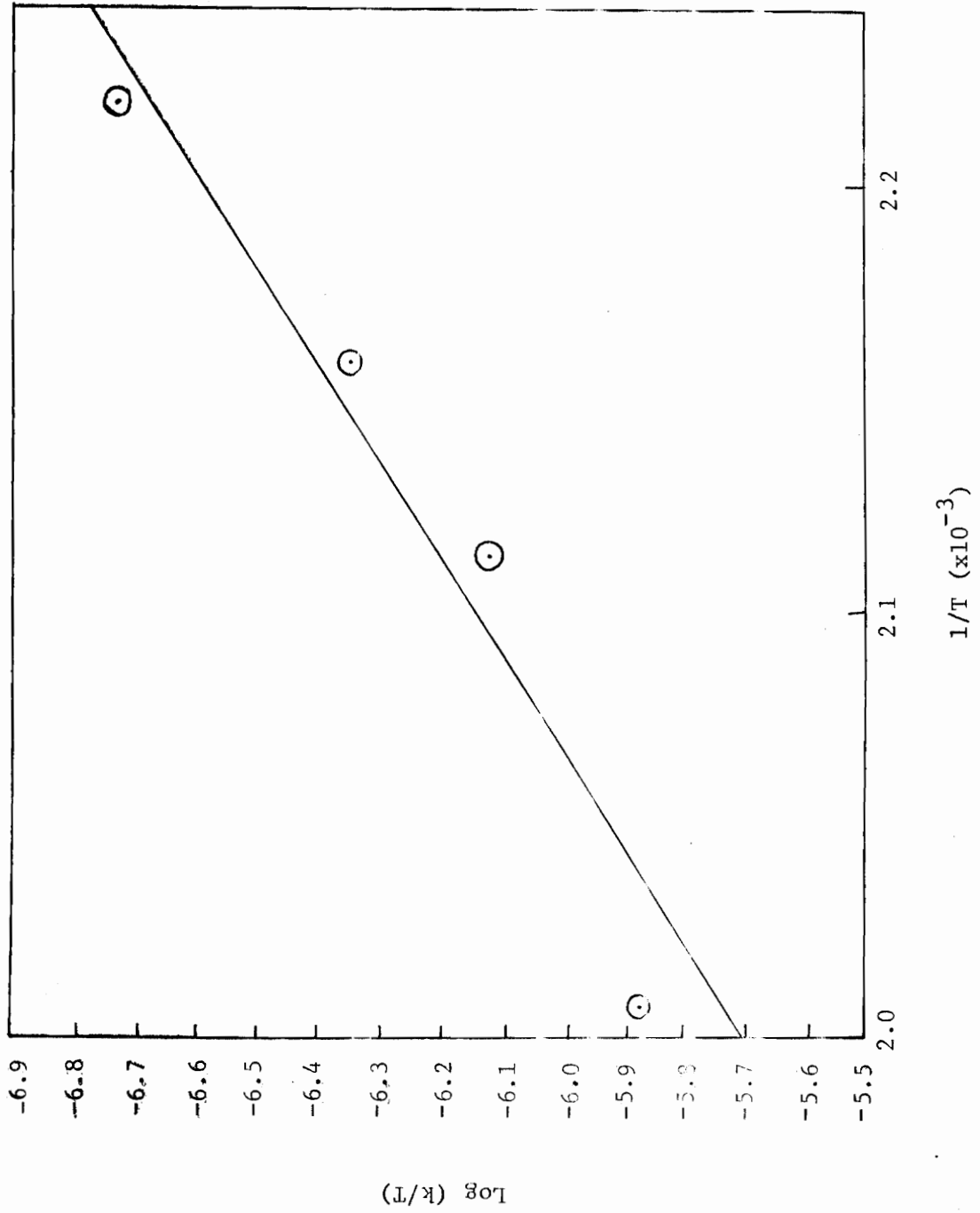


Figure 17

Variation of $\log (k/T)$ versus $1/T$ over the temperature range of $180-210 \pm 0.2^\circ$ for the evaluation of ΔH^\ddagger of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol.

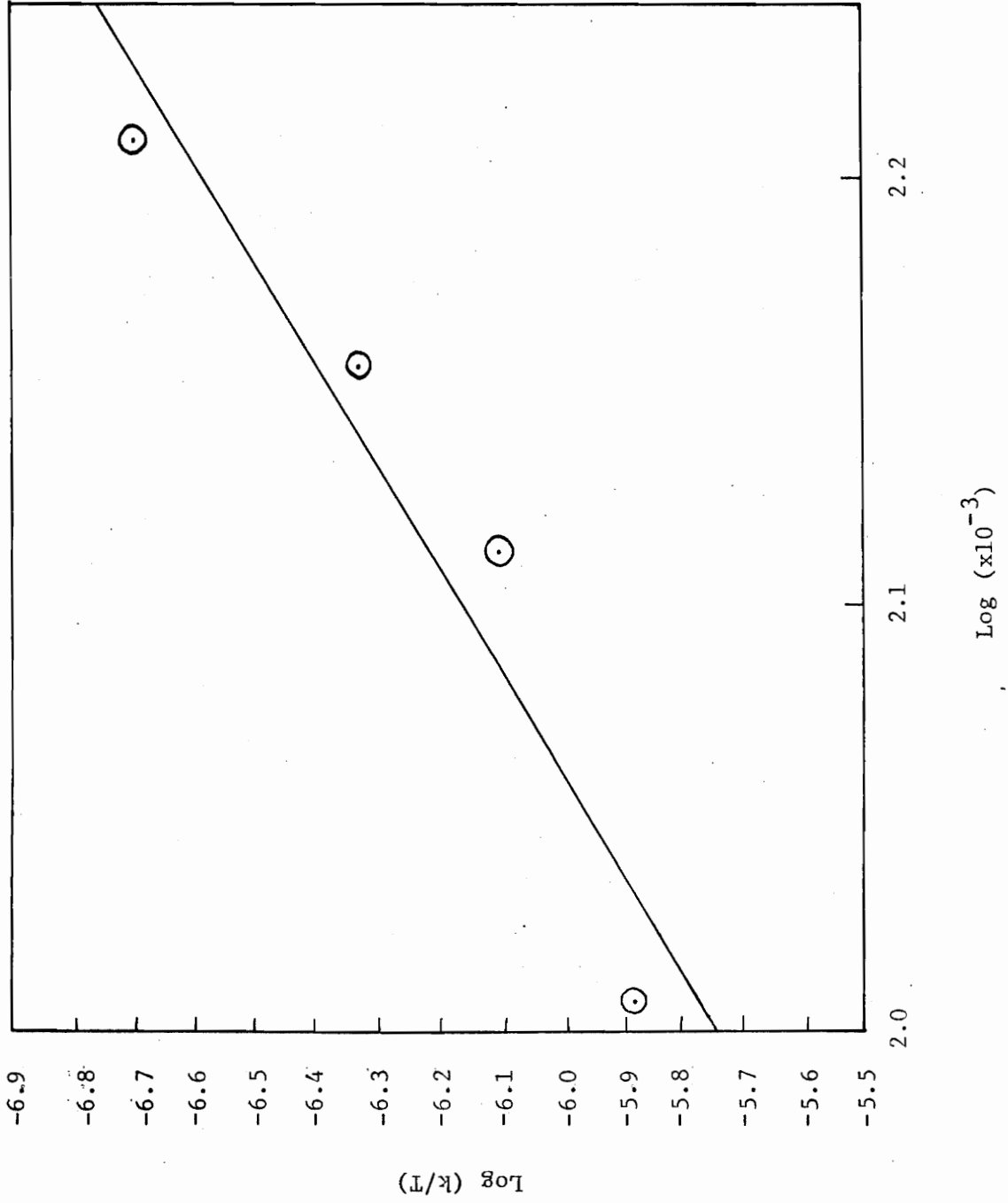


Figure 18

Variation of $\log (k/T)$ versus $1/T$ over the temperature range of $180-210 \pm 0.2^\circ$ for the evaluation of ΔH^\ddagger of 3,4-Bis(4-chlorophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

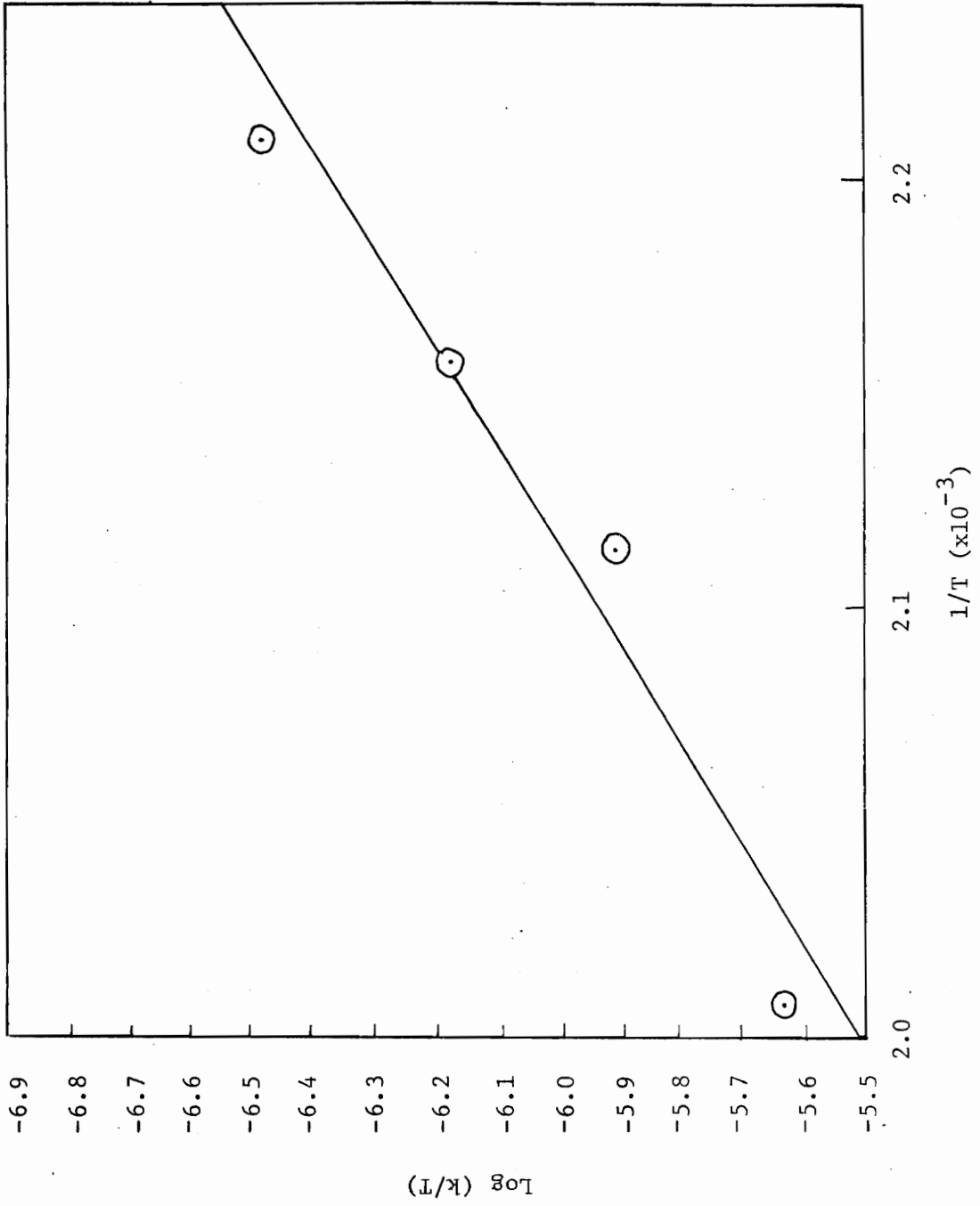


Figure 19

Variation of $\log (k/T)$ versus $1/T$ over the temperature range of $180-210 \pm 0.2^\circ$ for the evaluation of ΔH^\ddagger of 3,4-Bis(4-bromophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

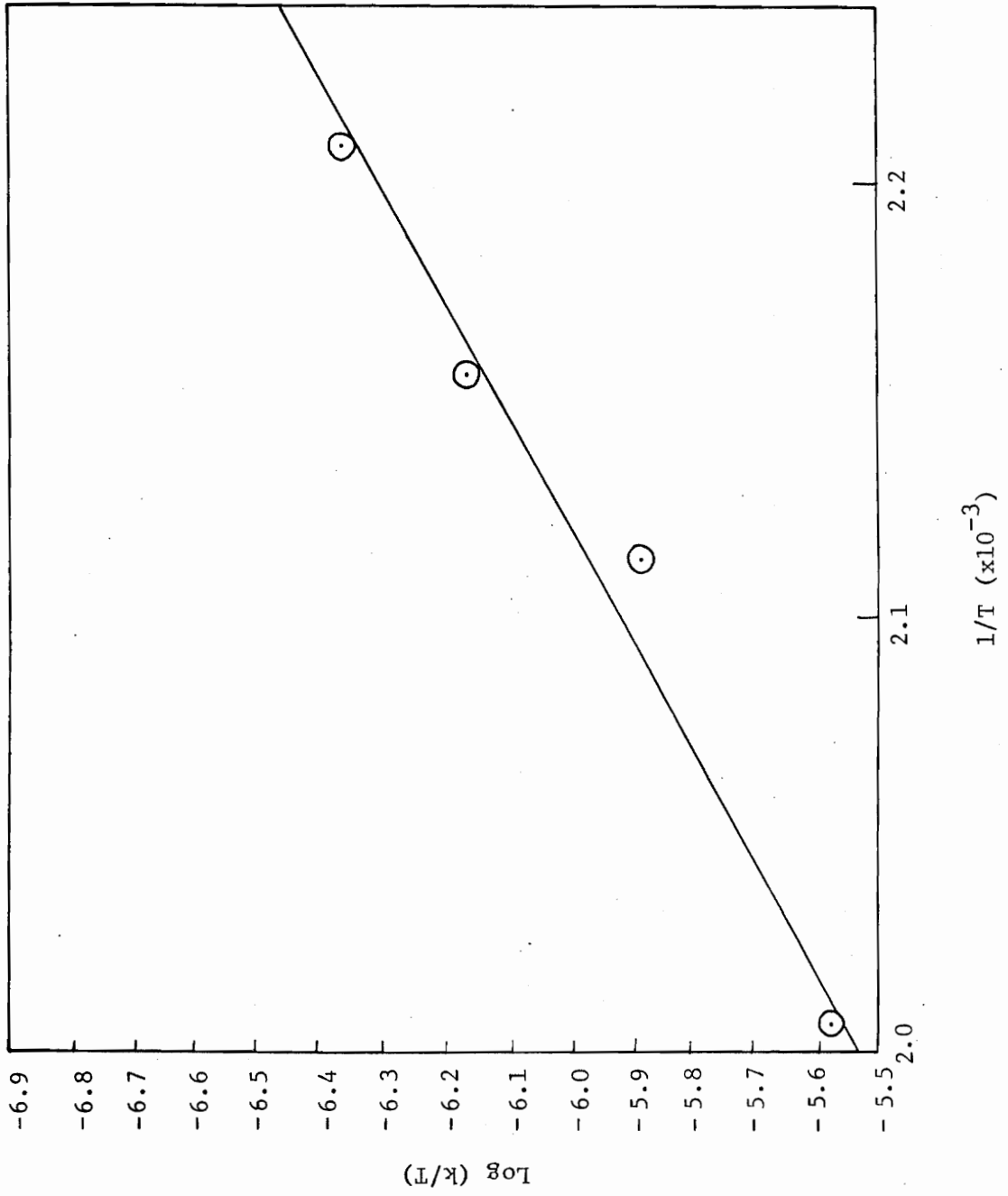


Figure 20

Hammett Plot of Variation of Temperature versus Rho (ρ)

▲ = Temperature at $210 \pm 0.2^\circ$

X = Temperature at $200 \pm 0.2^\circ$

O = Temperature at $190 \pm 0.2^\circ$

● = Temperature at $180 \pm 0.2^\circ$

--- = Calculated line from extrapolated ρ value; see plot of ρ versus $1/T$

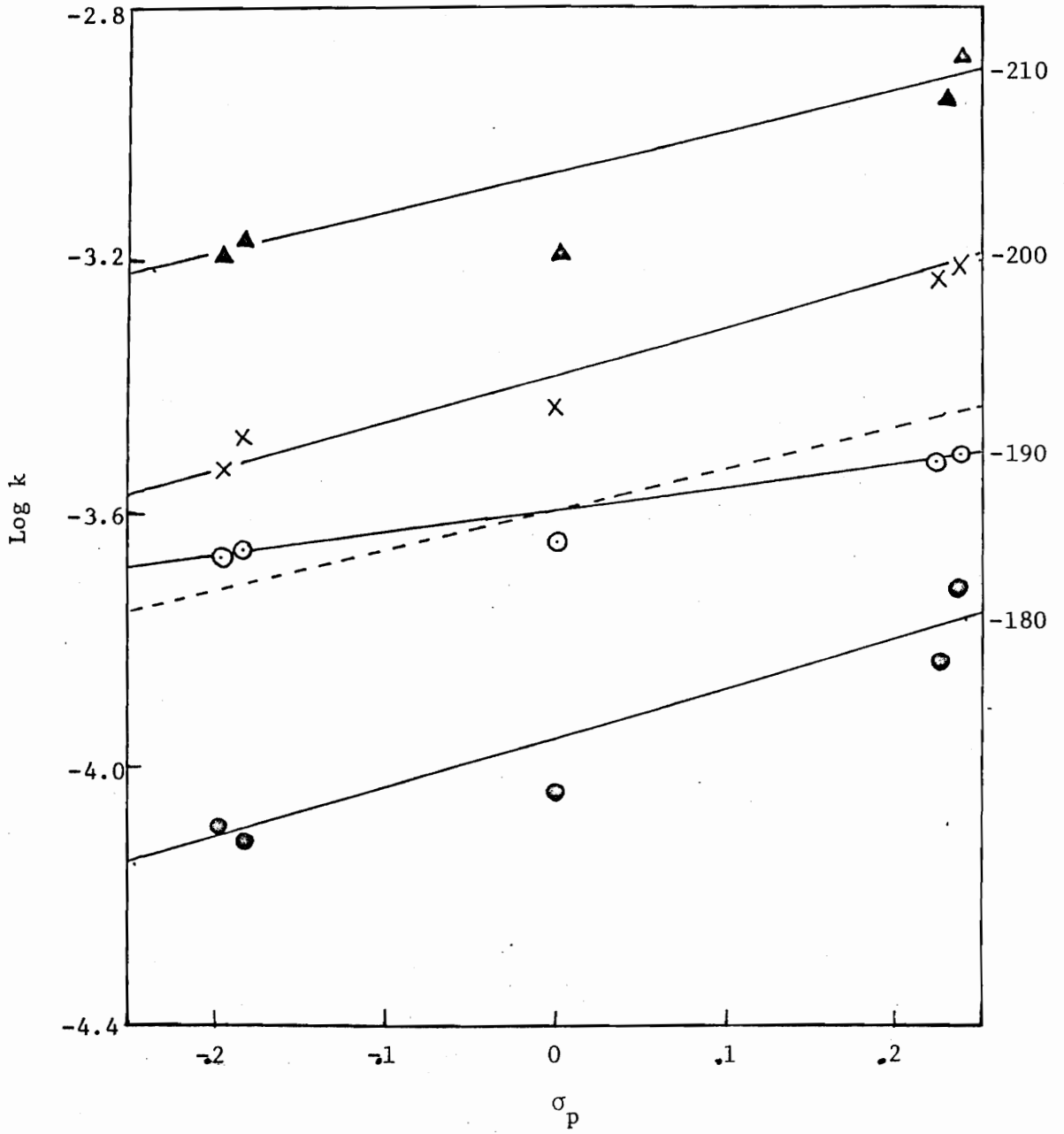


TABLE VI

Equations Obtained in Hammett Plots

For the Determination of Rho (ρ)

$$\log k_{\text{temp}} = \rho\sigma + \log k_{\text{H}}$$

T °C	Equation	r [†]
180 ± 0.2	$\log k_{180} = -0.813 \sigma^* - 3.97$	0.94
190 ± 0.2	$\log k_{190} = -0.400 \sigma - 3.61$	0.96
200 ± 0.2	$\log k_{200} = -0.690 \sigma - 3.39$	0.97
210 ± 0.2	$\log k_{210} = -0.658 \sigma - 3.09$	0.92

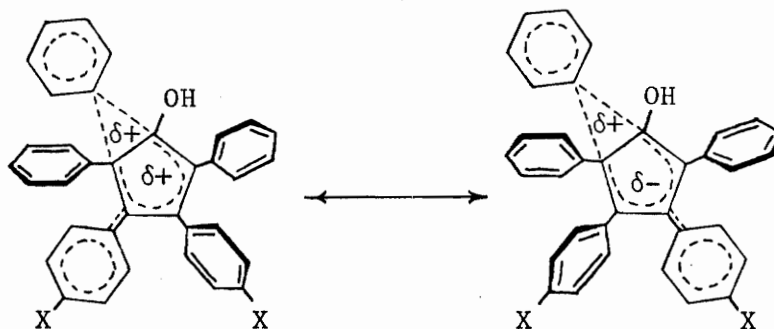
* σ varies with substituent; the values for σ used were:

Substituent	σ_p^{115}
t-butyl	-0.197
methyl	-0.170
H	0
chloro	+0.227
bromo	+0.232

† r = correlation coefficient

Electron donating groups accelerate the reaction as can be seen in the previous data and tables. Electron withdrawing group conversely decrease the rate of reaction. These are the hypothesized conclusions made in the aforementioned sections.

The transition state illustrated below is that which would be expected in justifying the observed rates. The 3 and 4 para-substituted



phenyl substituents are positioned on the π backbone and their effects can thus be felt at the migrating origin, since the mesomeric interactions should be strong in such a highly conjugated system. In this vein if we look at the values of the Arrhenius activation parameters, greater insight can be gained about the transition state. The average E_a , with a mean temperature of 453-483^oK, is 28.9 ± 2.0 kcal/mol. The average value of ΔH^\ddagger is 27.9 ± 2.0 kcal/mol; this is in good agreement with the fundamental equation below, illustrating that we were looking at

$$E_a = \Delta H^\ddagger - RT \quad (10)$$

an approximate 1.5 kcal/mol error in this particular temperature range. The average ΔS^\ddagger for a mean temperature of 453-483°K is -15.6 eu. This implies a greater degree of order in the transition state than in the starting material. Indeed this should be expected since either the 3- or 4-para-substituted phenyl rings should be in a position for π overlap with the cyclopentadiene ring, considering the transition state pictured above. If this is the case, electronic effects can be effectively transmitted through this extended π system; but it must be emphasized that, because of steric limitations, only one of the substituted phenyl rings can be coplanar with the cyclopentadiene ring at any one time.

The observed electronic effects were demonstrated by a Hammett plot of $\log k$ versus σ_p^{64} showing ρ values of -0.813, -0.400 (-0.73 extrapolated value), -0.690 and -0.658 at 180, 190, 200 and 210°C. The rather small effects (ρ being a sensitivity factor relating the substituent to the rate) are to be expected since the substituents are farthest removed from the migration origin. The variable value of ρ and the results obtained demonstrate that electron donating groups increase the rate of reaction. This supports the transition state which shows an increase in electron density in the π backbone.

Since several ρ values were determined it is interesting to note that the ρ values showed the theoretically predicted inverse relationship to temperature, with the exception of the data obtained at 190° which may have resulted from experimental difficulties with the temperature monitoring system.

$$\rho = k(1-\beta/T) \quad (11)$$

Also we were able to determine that the value for the isokinetic temperature should be in the range of 320° by a plot of ΔH^\ddagger versus ΔS^\ddagger (Figure 21) and a plot of ρ versus $1/T$ (Figure 22). The slope

$$\Delta\Delta H^\ddagger = \beta \Delta\Delta S^\ddagger \quad (12)$$

$$\rho = k(1 - \beta/T) \quad (13)$$

in the former case was $\beta = T$ and in the latter case the intercept was equal to $-k$ while the slope was βk and therefore $-(\beta k/-k) = \beta = T_{iso}$. As can be seen from the plot of ρ versus $1/T$ that the calculated isokinetic temperature was 388°C. This value has more error associated with it since the value of ρ at 190° was used for the determination. From the above information it was determined that the data was not influenced by the isokinetic effect.

In conclusion then, it has been demonstrated that electronic effects do play a significant role in determining the rate of sigma-tropic migrations, in general. It also appears that there is convincing evidence for the establishment of a transition state (page 135) that passes areas of partial increases and decreases in electron density. As stated before it is the establishment of these areas of partial charge density which direct the actions of the substituents through the π -backbone as demonstrated by the observed reaction rates.

Figure 21

Plot of ΔH^\ddagger versus ΔS^\ddagger for

Determination of Isokinetic Temperature

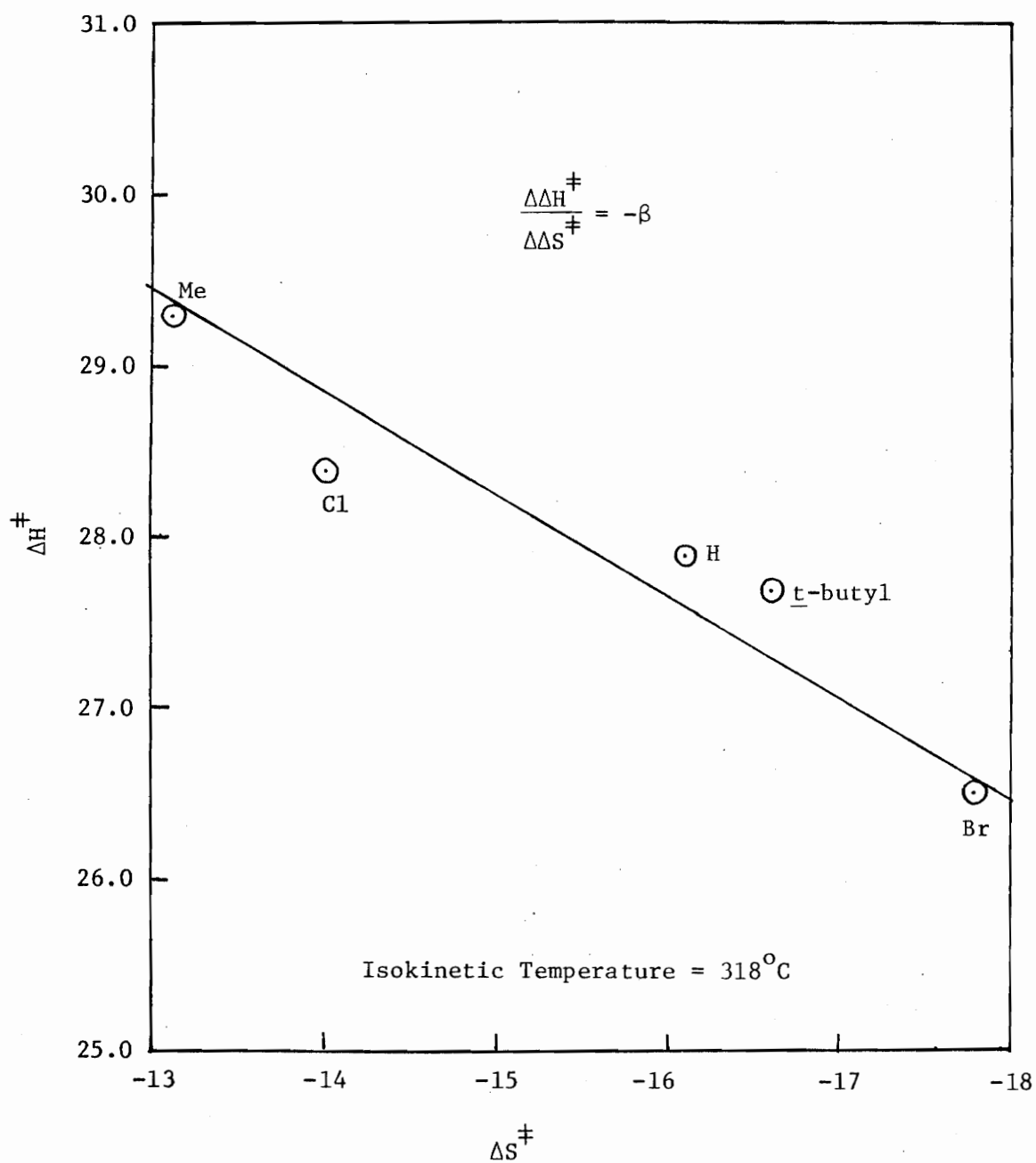
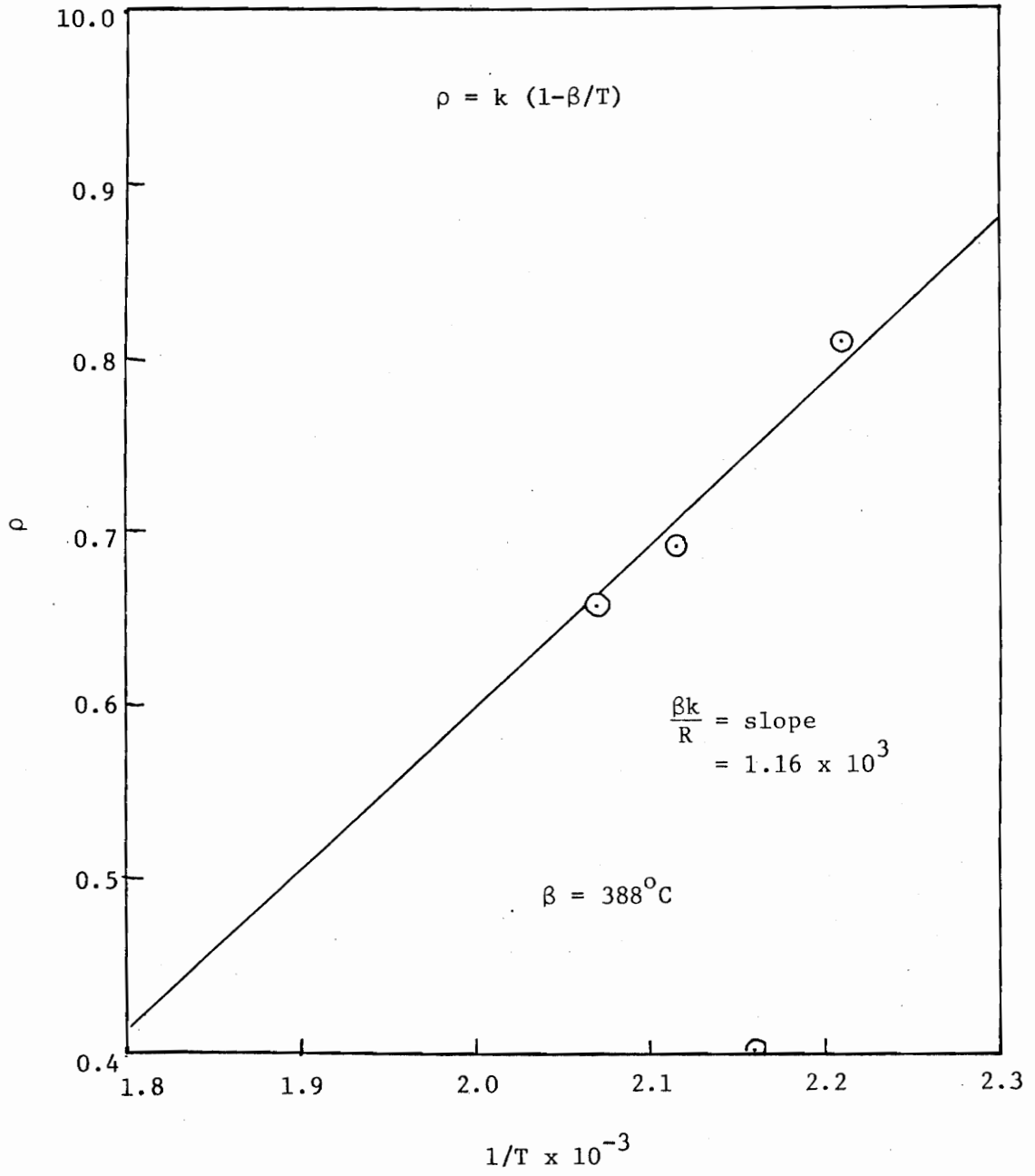


Figure 22

Variation of ρ (Rho) with $1/T$ for
Determination of Isokinetic Temperature



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APPENDIX I

The Mass Spectral Fragmentation of Substituted Pentaphenylcyclopentadienols

Abstract

The mass spectral decomposition pathway for a series of pentaphenylcyclopentadienols substituted in the para position of the 1- or 3- and 4-phenyl rings has been observed to consist of a continuum of two superimposed pathways with the choice of the major decomposition mode being determined by the electron donating or withdrawing ability of the substituent. Attempts to establish a linear free energy relationship for the mass spectral decomposition of the 1-p-substituted phenyl carbinols were unsuccessful, whereas similar attempts with the 3- and 4-p-substituted phenyl carbinols were successful.

General Theory

Attempts to correlate the mass spectral behavior of organic molecules with their structures have been made using two basic approaches, one theoretical and one empirical. The theoretical approach, known as the quasi-equilibrium theory (QET), was initially postulated by Eyring's group at Utah in the early 1950's.^{1,2} Proceeding from the generally accepted assumption that the ionization process by electron impact is a vertical transition, and in accordance with the Franck-Condon principle, they postulated that the excited parent-molecule ion does not

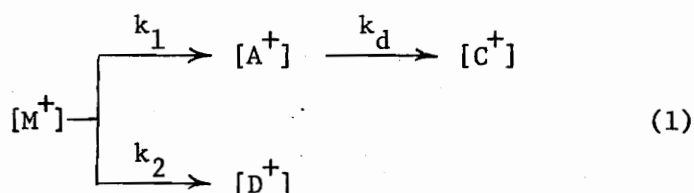
immediately decompose into various fragments but that the parent-molecule ion may undergo several vibrations prior to decomposition. During these vibrations, there is a high probability of radiationless transitions which result in a distribution of the excitational energy in a completely random fashion. The parent-molecule ion decomposes only when it reaches a certain "activated complex" configuration with sufficient energy in particular degrees of freedom. The result is a "quasi-equilibrium" between parent-molecule ion, activated complex, and fragment ions and molecules. Predictions can then be made of the relative populations of the parent-molecule ions and the principal fragments based on an analysis of the rate constants for each fragmentation in terms of a system of harmonic oscillators. Subsequent researchers^{3,4} have placed the postulate on a sound theoretical base and demonstrated its applicability to a large number of systems. No attempt has been made herein to calculate relative populations of ions based on the QET, but the basic postulates are encountered in every attempt to analyze the processes occurring within the spectrometer.

The empirical approach uses general concepts of physical organic chemistry - inductive and resonance effects and stereochemistry - to make qualitative predictions concerning the likely fragmentation patterns of organic molecules.^{5,6} Quantitative correlations of fragmentation patterns with the Hammett substituent constants (σ)¹⁶ obtained in solution indicated that both ionic abundances and appearance potentials might be valid both theoretically^{10,11} and in practice.^{12,13}

The substituent may alter the population of a particular ion as a result of one or more of the following effects:^{14,15}

- a) change in internal energy distribution of the parent-molecule ion or a precursor fragment,
- b) change in the rate of formation of a specific fragment, and
- c) change in the rate of fragmentation into smaller or different ions via rearrangement.

Chin and Harrison¹⁰ have used the above, in conjunction with several of the postulates of the QET, to derive an expression correlating the rates of decomposition with ionic concentration. The parent-molecule ion, $[M^+]$, formed by electron impact, will decompose if it has sufficient internal energy (excitation), and the product distribution will depend upon the factors listed above. In Equation 1, the concentration of the particular fragment of interest, $[A^+]$, will be determined by Equation 2, where k_t is the sum of all rate constants resulting in decomposition of the molecular ion.



$$[A_0^+] = \frac{k_1}{k_t} [[M_0]^+ - [M]^+] \quad (2)$$

and $[M]^+ = f[M_0]^+$ where $[M_0]^+$ is the total number of parent molecule ions formed by the initial electron impact process, and $[M]^+$ is the

concentration observed at any one time. The quantity f represents the fraction of the total ionization appearing as $[M]^+$. If the observed concentration $[A]^+$ is determined from Equation 3

$$[A]^+ = f' [A_0]^+ \quad (3)$$

where f' is the fraction of $[A_0]^+$ ions incapable of further fragmentation, then the ratio of daughter to parent-molecule ion is determined by Equation 4, which can be greatly simplified when $f' \rightarrow 1$ and $k_t \rightarrow k_1$.

$$\frac{[A]^+}{[M]^+} = \frac{f' [A_0]^+}{f [M_0]^+} = f' \frac{k_1}{k_t} [(1/f)-1] \quad (4)$$

As can be seen from the assumptions, this treatment is valid only when decomposition of the daughter ion is negligible and when the stabilities of the parent-molecule ion and daughter ion are approximately equal, i.e. when the ratio observed at the detector is not significantly different from the ratio at the source.

A kinetic approach to mass spectrometry has been used in interpreting the spectra of a number of substituted benzophenones and acetophenones.⁷ If a molecular ion M decomposes to a fragment ion A , the rate of change of concentration of A in the ion source is given by equation 5, where the second term on the right includes terms for real or apparent loss of A because of instrumental parameters.

$$\frac{d[A]}{dt} = k_1[M] - \Sigma k_2[A] - \Sigma k_{inst}[A] \quad (5)$$

Applying the steady-state approximation ($d[A]/dt = 0$), we obtain equation 6.

$$\frac{[A]}{[M]} = \frac{k_1}{\Sigma k_2 + \Sigma k_{inst}} \quad (6)$$

Hence mass spectra in which the common fragment ion A may be formed from different molecular ions can be related, for if A is formed with the same energy distribution from each molecular ion, the denominator of the term on the right equation 6 is not dependent on the mode of formation of A. Therefore, if we define $Z = [A]/[M]$, and $Z_o = [A]_o/[M]_o$, where A is now formed from the molecular ion M_o of a standard substance, equation 7 follows.

$$\frac{Z}{Z_o} = \frac{[A]/[M]}{[A]_o/[M]_o} = \frac{k_1}{k_1^o} \quad (7)$$

Since the ratio of the concentration of the fragment ion A to the concentration of the molecular ion is given by the relative peak heights corresponding to the two species, the effect of molecular structure on the rate of formation of A from two different molecular ions can be evaluated.

Moreover, if there is a linear free energy relationship in the effect of a substituent Y on the rate of formation of A from M, and of some other A' from some other M', then equation 8 holds, and using

7 and 8, the expression 9 may be derived.

$$\log \frac{k_1^y}{k_1^o} = C \log \frac{k_1'^y}{k_1'^o} \quad (8)$$

$$\log \frac{Z}{Z_o} = C \log \frac{Z'}{Z'_o} = \sigma \rho \quad (9)$$

This relationship has been tested in a variety of systems^{7,10,12,13,16,17,18)} and good linear correlations were found.

The definition of metastable peaks should be included here since it will lead to less confusion in the following sections.

Metastable peaks are ions which are formed by fragmentation of an ion somewhere along its path of flight from the source into the analyzer tube.¹⁹ It is presumed that these fragments are produced by the same processes as those occurring in the ion source before acceleration. The result is an ion which is accelerated as though it had one mass, but is focused at a lower mass, and explains the characteristic features of metastable peaks in spectra. The peaks are of relatively low intensity, generally 1% or less of the base peak. They are likely to occur at non-integral masses, and they tend to be broad and "out of focus." Because metastable peaks are dependent for their abundance upon the abundance of the precursor ion, metastable peaks for the decomposition of low intensity ions are often not detectable. Metastable peaks appear at, or around, an m/e described by Equation 10,¹⁹

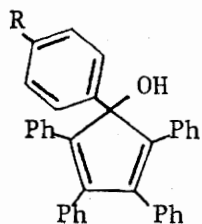
$$m^* = m^2/m_0 \quad (10)$$

where m^* is the m/e of the observed metastable, m is the mass of the daughter ion, and m_0 is the mass of the precursor ion. Metastable peaks are, therefore, more likely to appear at non-integral masses¹⁹ and avoid being lost in the integral mass peaks, but half-masses and high intensity ions often do obscure low intensity metastables. Finally, metastable ion peaks are broad, from 0.25 m/e to several mass units, because the instrument is focused for a different velocity to charge ratio, because the decomposition may occur over a greater distance than the "normal" decomposition, and because the kinetic energy lost almost always will affect the focus of the ion. While the positioning of the focusing slits has some effect on both the intensity and shape of the metastable peak, the ions can usually be characterized according to peak shapes, "Gaussian" (approximately rounded and symmetrical), or "flat-topped" (which may or may not be symmetrical). Flat-topped metastables are almost always broader than the Gaussian metastables in the same spectrum, and the shape is characteristic of a greater number of energy states in the precursor from which energy is converted into kinetic energy upon the formation of the daughter.

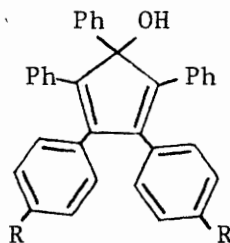
Historical

The mass spectral fragmentations of tetracyclone, tetraaryl-quinones and tetraphenylthiophene dioxides have been extensively studied by Bursey, et al.,²⁰⁻²⁴ who has also published extensively on the use of fluorine as a "dead label" in the decomposition of pentaphenylcyclopentadienols.^{20,22,24} The most interesting aspect of their work is the mass spectral production and decomposition of the parent and fluorosubstituted tetraphenyltetrahedrane radical cations from the decomposition of 1,2,3,4,5-pentaphenylcyclopentadien-2,4-ol-1 (1, R = H) and its *p*-fluoro derivatives.²⁴

Since a large number of mono- and disubstituted pentaphenylcyclopentadienols have been prepared in our laboratories for a kinetic study of the electronic effects involved in a [1,5]-sigmatropic phenyl shift in such systems,^{25,26,27} it became of interest to study the mass spectral fragmentations of the complete family of 1-(*p*-substituted phenyl)-2,3,4,5-tetraphenylcyclopentadien-2,4-ols-1 (1), and bis-3- and 4-(*p*-substituted phenyl)-2,5-diphenylcyclopentadien-2,4-ols-1 (2) shown below. Of the substituted carbinols shown only two have been



1



2

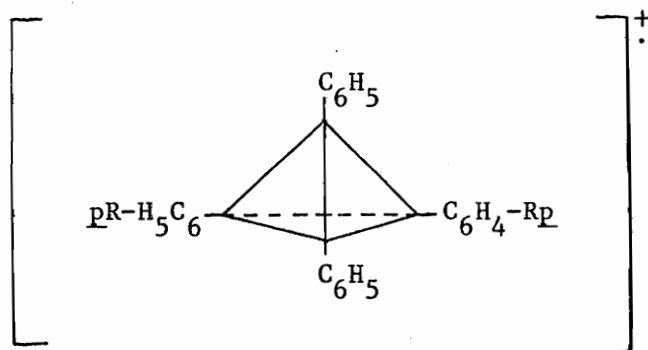
R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$, $-\text{CH}_3$,

$-\text{H}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{CF}_3$

R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_3$, $-\text{OCH}_3$,

$-\text{CH}_3$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$

studied previously by Bursey et al.,²⁴ 1, R = -H and -F, and in our hands both showed the identical metastables reported²⁴ for the breakdown of the tetraphenyltetrahedrane radical cation (3). However, this



3

R = H or F

observation is incidental to our major interest which is concerned with a study of the substituent effects in the initial decomposition of the substituted pentaphenylcyclopentadienol molecular ions.

Result and Discussion

The substituent effect we have observed for the initial decomposition of 1 causes a continuum of two superimposed decomposition paths. At one extreme of the continuum is the decomposition pathway observed for 1 (R = -C(CH₃)₃). This alcohol decomposes in the manner "normally" expected for the pentaphenylcyclopentadienols, i.e., breakdown of the substituents at C-1 of the five membered ring.

Figure 1A

Decomposition of 1 ($R = -C(CH_3)_3$) Containing A
Strongly Electron Donating Substituent

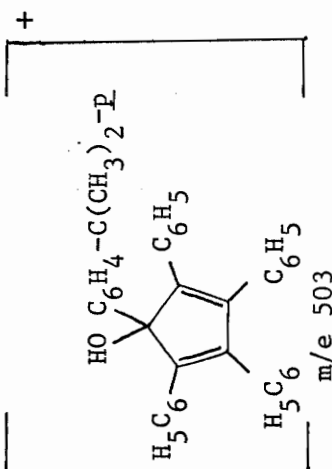
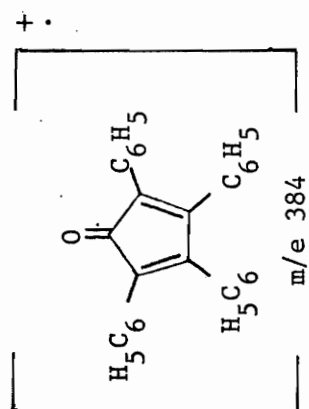
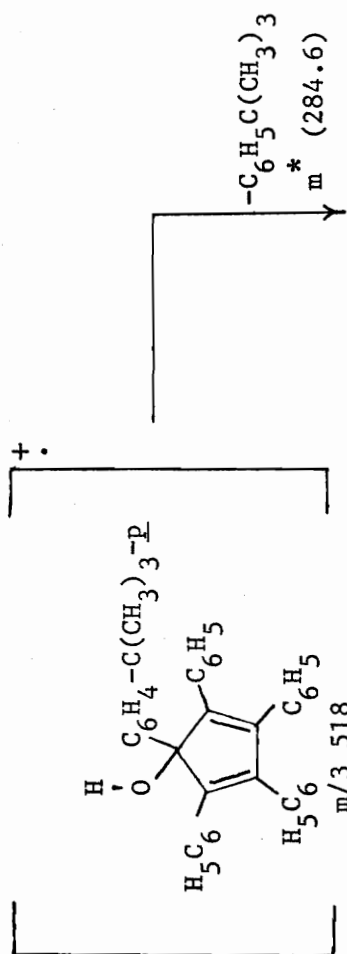
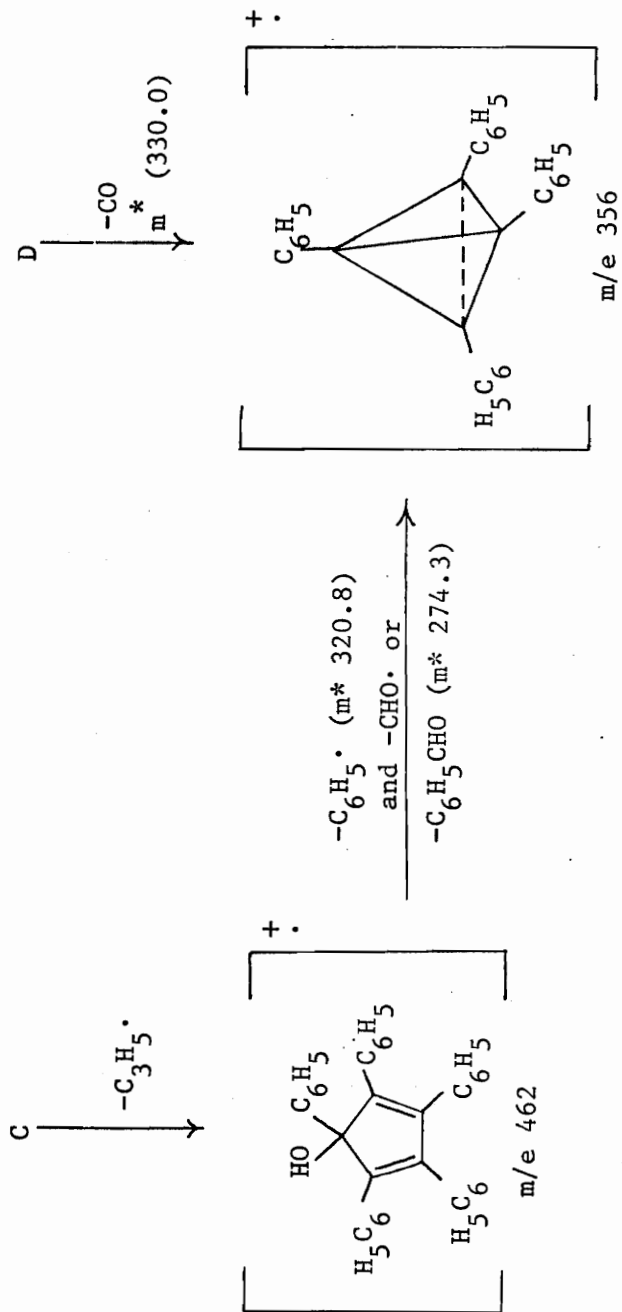
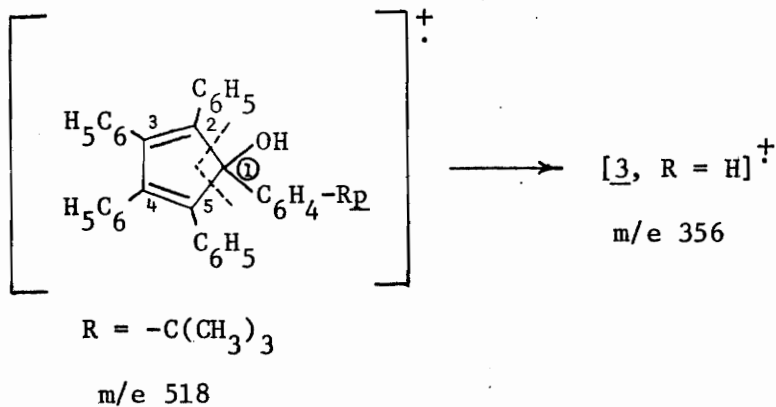


Figure 1B

Decomposition of 1 (R = $-\text{C}(\text{CH}_3)_3$) Containing A
Strongly Electron Donating Substituent





By critical investigation of the peak intensities and prominent metastable peaks it was established that the breakdown consisted of loss of $\text{CH}_3\cdot$ and a $\text{C}_3\text{H}_5\cdot$ moiety, followed by loss of $\text{C}_6\text{H}_5\cdot$ (metastable 320.8) and $\text{CHO}\cdot$, or the loss of $\text{C}_6\text{H}_5\text{CHO}$ (metastable 274.3), with prominent metastables at 284.6, for the loss of $-\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_3$ and at 330.0 for the loss of a CO moiety (Fig. 1). This is the breakdown to be expected for a t-butyl group, or, if the C-1 fragment remains intact which seems unlikely, for a t-butylphenylcarbinol.

Investigation of 1 ($\text{R} = -\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ or $-\text{CH}_3$) was expected to show a similar decomposition pathway consisting of the sequential loss of $\text{C}_6\text{H}_5\text{R}$ followed by the loss of CO. This was indeed observed as the major decomposition pathway, however, a minor decomposition pathway was also observed. This pathway consisted of the loss of $\text{C}_6\text{H}_5\cdot$ followed by formation of a proposed epoxide intermediate with subsequent loss of $\text{CHO}\cdot$ (if $\text{R} = -\text{N}(\text{CH}_3)_2$ or $-\text{CH}_3$) to produce the monosubstituted tetraphenyltetrahedrane cation radical. In the dimethylamino substituted case [1, $\text{R} = -\text{N}(\text{CH}_3)_2$], the decomposition continues with the loss of

Figure 2A

Decomposition of 1 (R = $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ and $-\text{CH}_3$)
Containing Weak Electron Donating Substituents

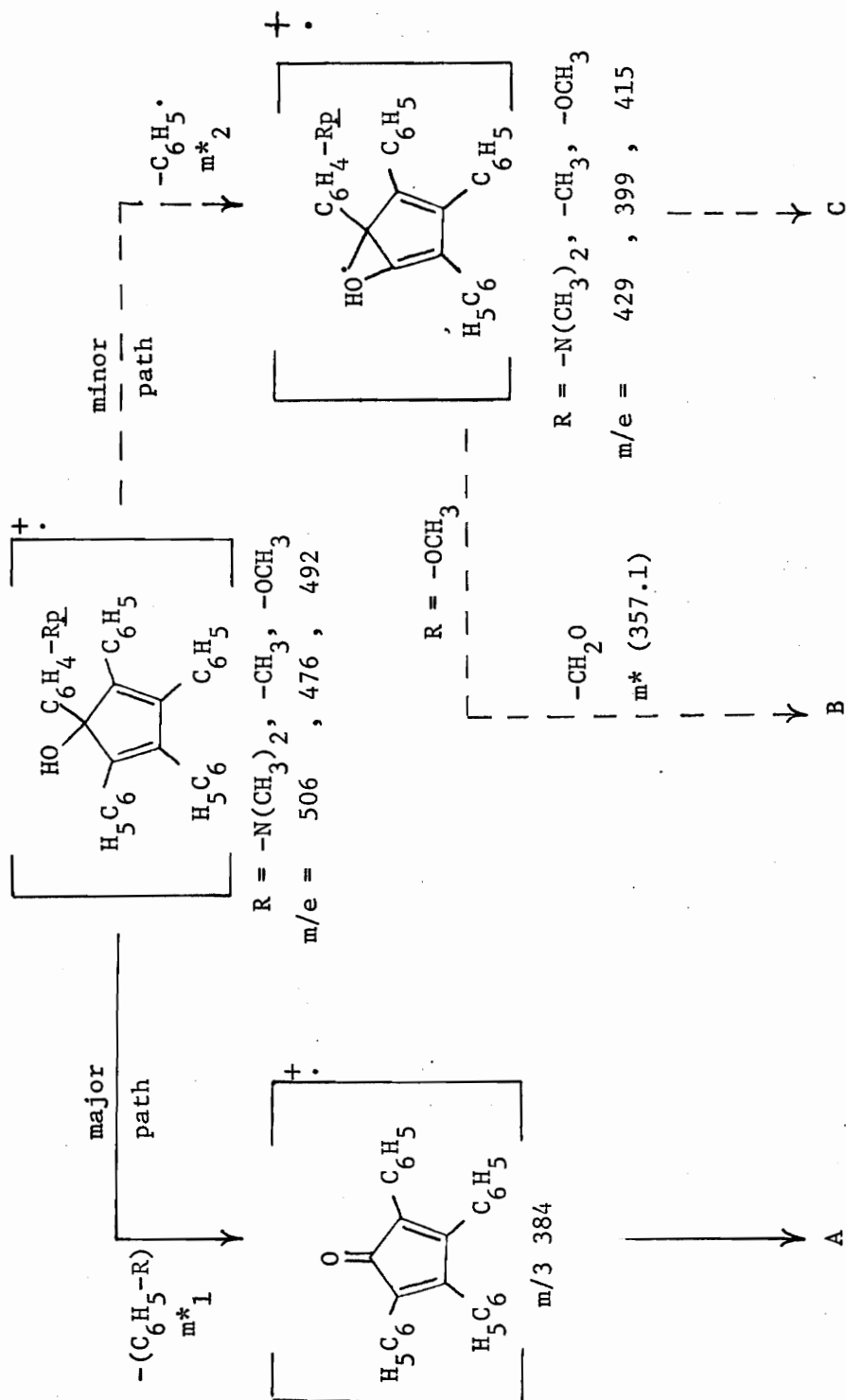


Figure 2B

Decomposition of 1 (R = $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ and $-\text{CH}_3$)

Containing Weak Electron Donating Substituents

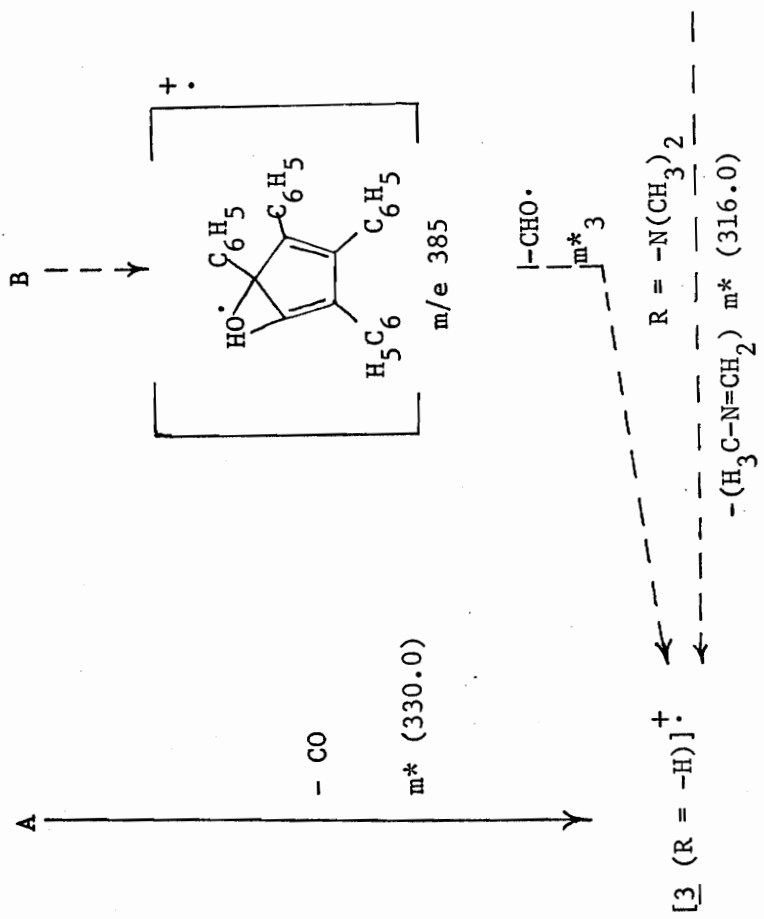
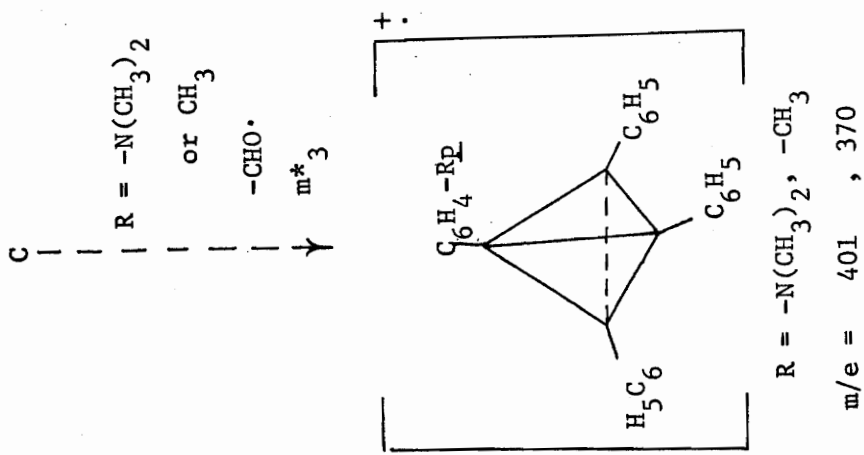


Figure 2

cont'd.

$R = -N(CH_3)_2, -CH_3, -OCH_3$
 $m^*_1 = 291.1, 309.7, 299.6$
 $m^*_2 = 363.7, 334.4, 350.0$
 $m^*_3 = \text{obscured by intense normal peaks}$

$\text{H}_3\text{C-N=CH}_2$ to produce 3 ($\text{R} = \text{H}$). The overall decomposition observed in the methoxy substituted carbinol (1, $\text{R} = -\text{OCH}_3$) was loss of CH_2O followed by loss of CHO (Fig. 2).

Two interesting observations about the minor decomposition pathway of the carbinols 1 containing weakly electron donating substituents are: first, the formation of an odd-electron species (m/e 356) from an even-electron species (m/e 429), an observation which has been previously reported,²⁴ and, second, the more unusual loss of a neutral CH_2O fragment from an even-electron species (m/e 415) followed by the loss of CHO to produce an odd electron species (m/e 356).

The minor decomposition pathway discussed above is observed to become the major decomposition pathway as the substituents were changed from strongly electron donating to weakly electron donating to weakly electron withdrawing to strongly electron withdrawing. Thus, observation of the mass spectral decomposition of 1 ($\text{R} = -\text{F}$, $-\text{Cl}$ or $-\text{CF}_3$) shows the major decomposition pathway to consist of loss of C_6H_5 followed by the loss of CHO with the corresponding metastables produced recorded in Fig. 3. With the aid of metastables it can be seen, that with these substituents, the minor pathway appears to be decomposition in the "normal" manner, i.e., loss of RC_6H_4 followed by loss of CHO to produce 3 ($\text{R} = -\text{H}$) (Fig. 3). In the case of 1 ($\text{R} = -\text{Br}$) however, although the minor decomposition pathway is exactly as described above, and approximately 25% of the parent molecular ion decomposes via the major pathway already discussed for the other electron withdrawing substituents, the majority (~75%) of the parent ion decomposes via a dif-

Figure 3A

Decomposition of 1 (R = -F, -Br, -Cl and -CF₃)
Containing Electron Withdrawing Substituents

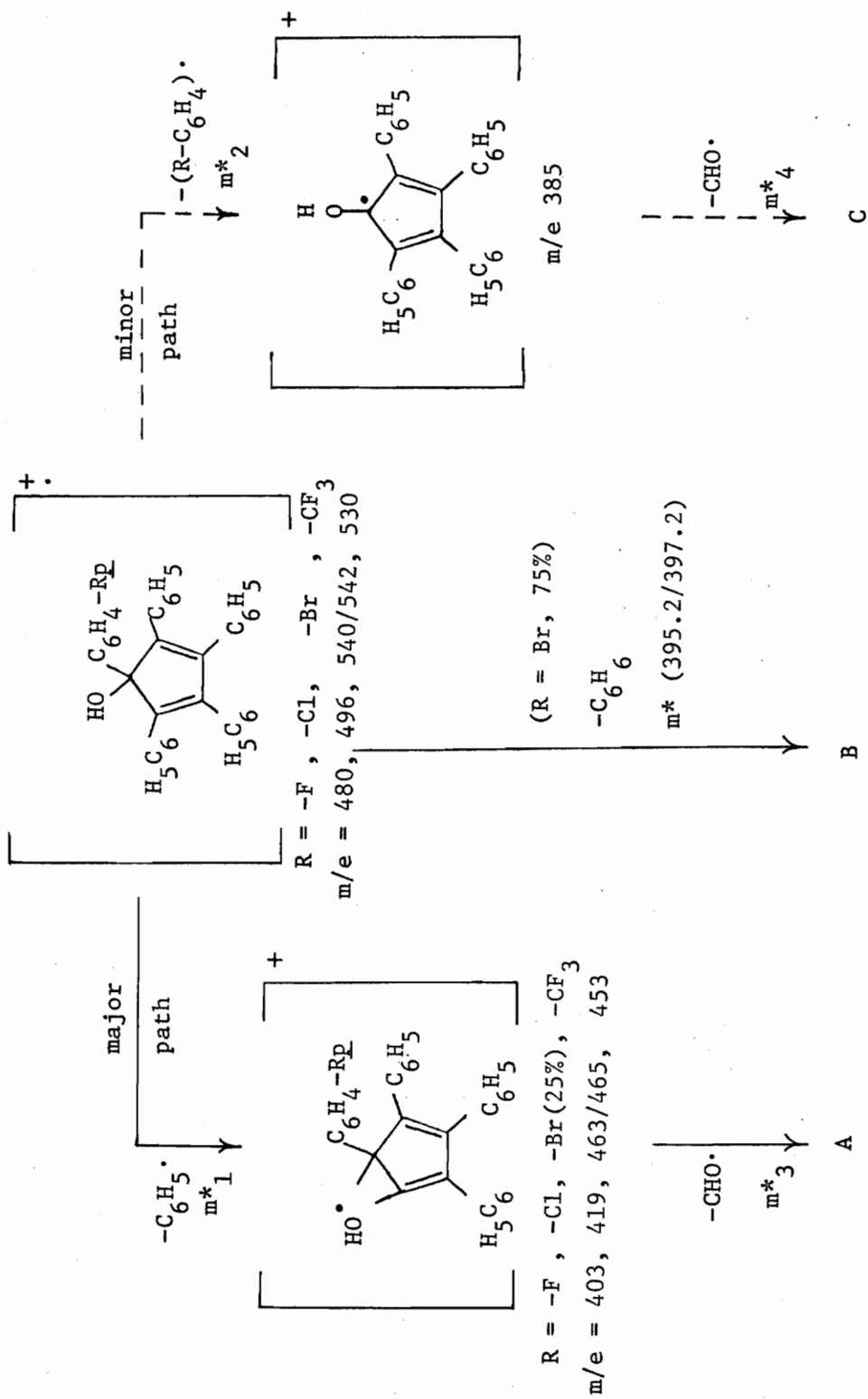


Figure 3B

Decomposition of 1 (R = -F, -Br, -Cl and -CF₃)
Containing Electron Withdrawing Substituents

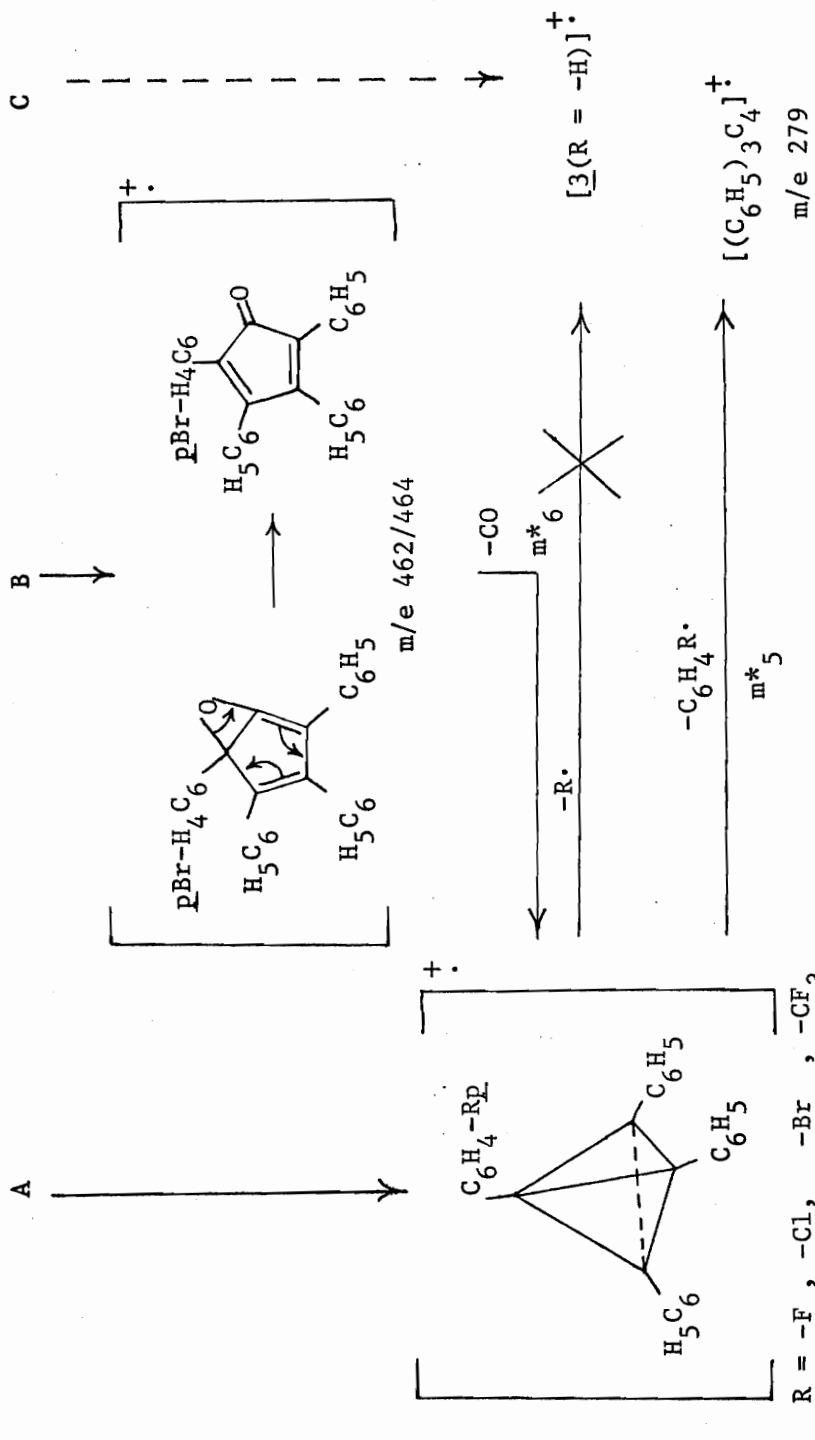


Figure 3

cont'd.

R =	-F	,	-Cl	,	-Br	,	-CF ₃
m* ₁	=	338.3,	353.9,	396.9/398.9,	387.1		
m* ₂	=	308.8,	298.8,	274.4/273.5,		^a	
m* ₃	=	347.0,	363.2,	406.8/408.8,	396.8		
m* ₄	=	329.1,	329.1,	234.6/233.8,		^b	^a
m* ₅	=	208.1,	199.5,	179.3/178.5,	183.6		
m* ₆	=	-	,	-	,	^c	,

^aMolecular ion very weak, approaching background intensity.

^bMetastables for loss of p-BrC₆H₄CHO.

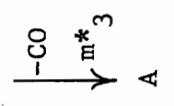
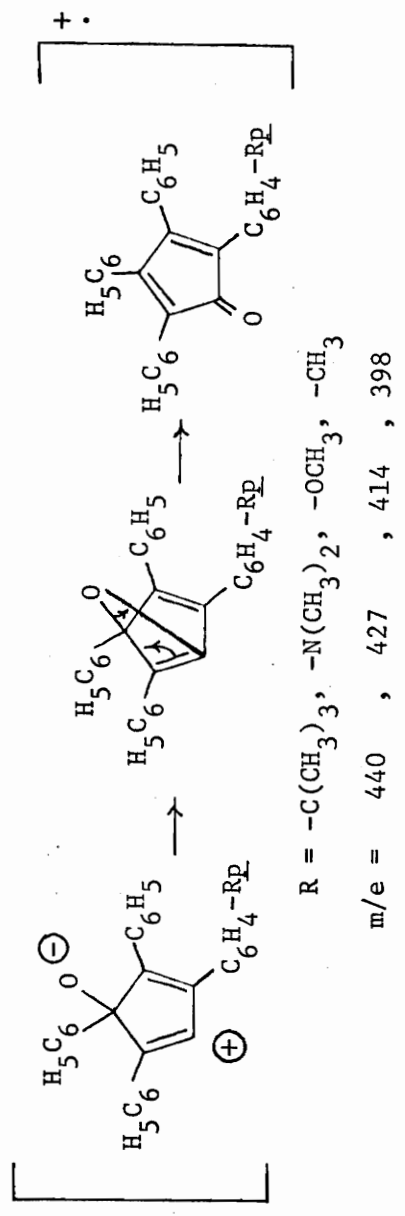
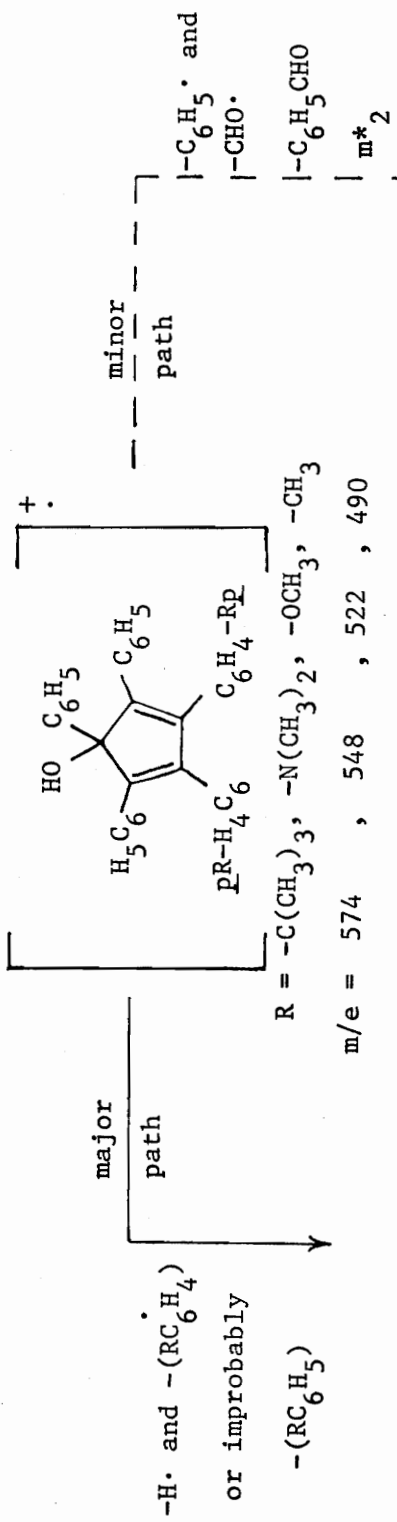
^cObscured by intense normal peaks.

ferent major decomposition pathway. In this case the same monosubstituted tetraphenyltetrahedrane cation radical which is obtained in the cases where $R = -F, -Cl, -CF_3$ and $-Br$ (to an extent of 25%) is again obtained, and the overall atoms lost are the same totally, however, these atoms are lost in different units with the loss of C_6H_6 occurring first followed by the loss of CO . To establish if this new major decomposition pathway was unique for 1 ($R = -Br$) alone, the *p*-iodo analogue (1, $R = -I$) was investigated and, although it is not illustrated on Fig. 3, this carbinol also decomposed via the two major pathways reported for 1 ($R = -Br$) but in a 10% to 90% ratio, respectively. Possibly the differences in electronegativity between $-F, -Cl, -Br$ and $-I$ can account for this difference in the ratio of the major decomposition pathways.

The decomposition of the carbinol 1 ($R = -Br$) also involves an interesting rearrangement through a proposed epoxide intermediate. A similar rearrangement has been found to play a significant role in the decomposition of the disubstituted carbinols 2. Observation of the mass spectral decomposition of 2 again shows that the substituents do play a significant role in the choice of which route in the decomposition continuum the molecule will follow. With electron donating substituents, the major decomposition pathway is observed to be loss of one $p-RC_6H_4$ group, most likely via a stepwise loss of $H\cdot$ and $RC_6H_4\cdot$ instead of a concerted loss of $p-RC_6H_5\cdot$. This loss is followed by formation and rearrangement of a bicyclic ether and elimination of CO (Fig. 4). The metastables observed (Fig. 4) lend proof for this

Figure 4

Decomposition of 2 (R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ and $-\text{CH}_3$)
Containing Electron Donating Substituents

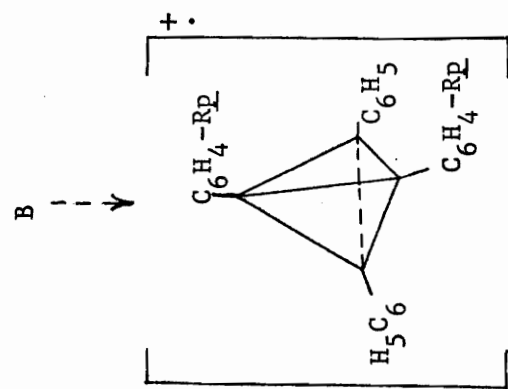


B

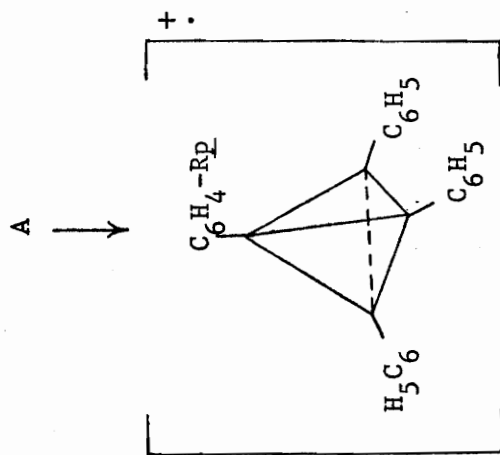
Figure 4B

Decomposition of 2 (R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ and $-\text{CH}_3$)

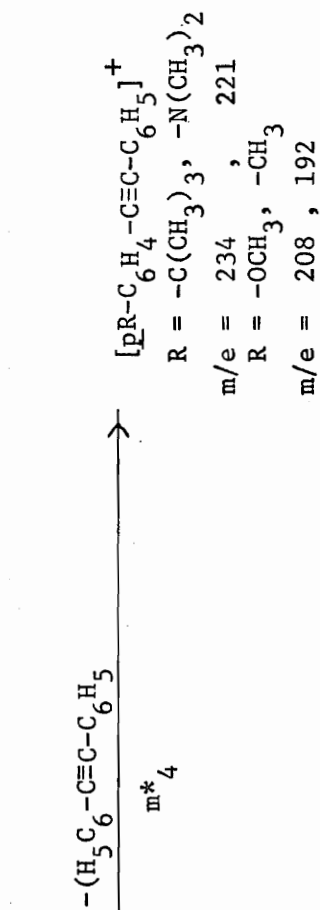
Containing Electron Donating Substituents



R = $-\text{C}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$, $-\text{CH}_3$
 m/e = 468, 442, 416, 384



R = $-\text{C}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$, $-\text{CH}_3$
 m/e = 412, 399, 386, 370



$[\text{pR}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{C}_6\text{H}_5]^+$
 R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_2$
 m/e = 234, 221
 R = $-\text{OCH}_3$, $-\text{CH}_3$
 m/e = 208, 192

Figure 4

cont'd.

	R = -C(CH ₃) ₃ , -N(CH ₃) ₂ , -OCH ₃ , -CH ₃			
m* ₁	= 337.6	, 333.3	, 328.7,	323.7
m* ₂	= 381.5	, ^a	, 331.5,	300.9
m* ₃	= 385.5	, 372.8	, 359.7,	343.9
m* ₄	= 132.8	, 122.4	, 112.0,	99.6

^aObscured by intense normal peaks.

this unusual pathway for decomposition of 2 containing electron donating substituents.

The minor decomposition pathway observed for these compounds (2, R = $-\text{C}(\text{CH}_3)_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$ and $-\text{CH}_3$) again consisted of loss of the units $\text{C}_6\text{H}_5\cdot$ and $\text{CHO}\cdot$ sequentially or loss of the entire $\text{C}_6\text{H}_5\text{CHO}$ unit, to produce the monosubstituted tetraphenyltetrahedrane cation radical.

Represented in Fig. 5 are the major and minor decomposition pathways for the carbinols 2 (R = $-\text{Br}$, $-\text{Cl}$ and $-\text{F}$) containing electron-withdrawing substituents. It can be seen that in these cases the major and minor decomposition pathways observed for 2 containing electron donating substituents have now become reversed.

Aside from the unique bicyclic ether formation and decomposition proposed during the decomposition of these carbinols, it is also interesting to note that in varying degrees and with all substituents, loss of one of the monosubstituted phenyl units is observed even though this unit is structurally removed from the carbinol center in the molecule.

Although Bursey et al.,²⁴ have described the major decomposition pattern of the *p*-fluoro substituted carbinols they studied as a "stepwise loss of the elements aryl and $\text{CHO}\cdot$ " and we have also observed this stepwise loss with the *p*-halo carbinols 2, it does not appear that this sequence represents the major decomposition pathway for either the fluoro, bromo or chloro substituted carbinols 2 (R = $-\text{F}$, $-\text{Br}$, or $-\text{Cl}$) because of the greater intensities observed for both the ions

Figure 5A

Decomposition of 2 (R = -Br, -Cl and -F)
Containing Electron Withdrawing Substituents

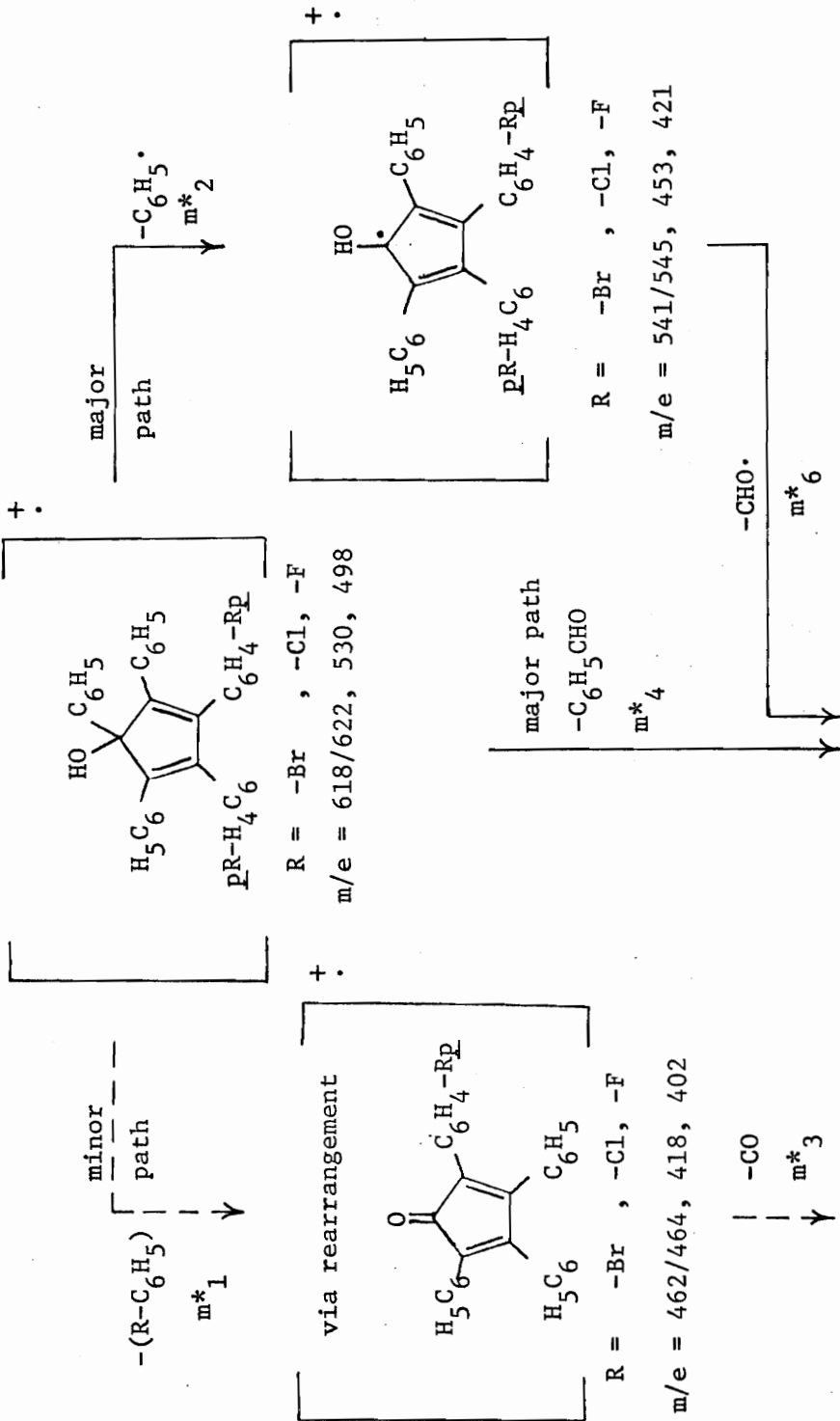


Figure 5B

Decomposition of 2 (R = -Br, -Cl and -F)
Containing Electron Withdrawing Substituents

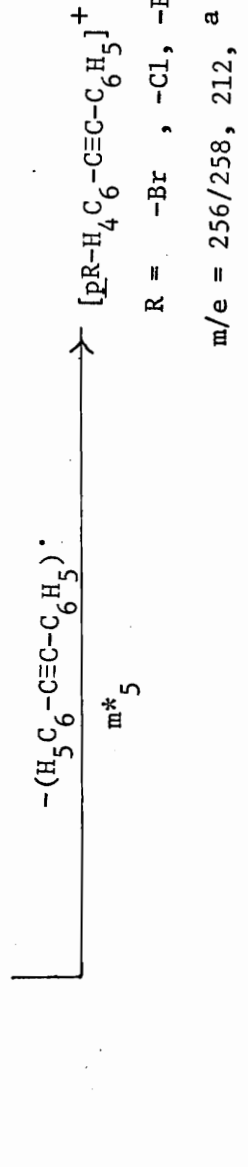
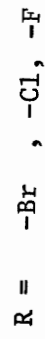
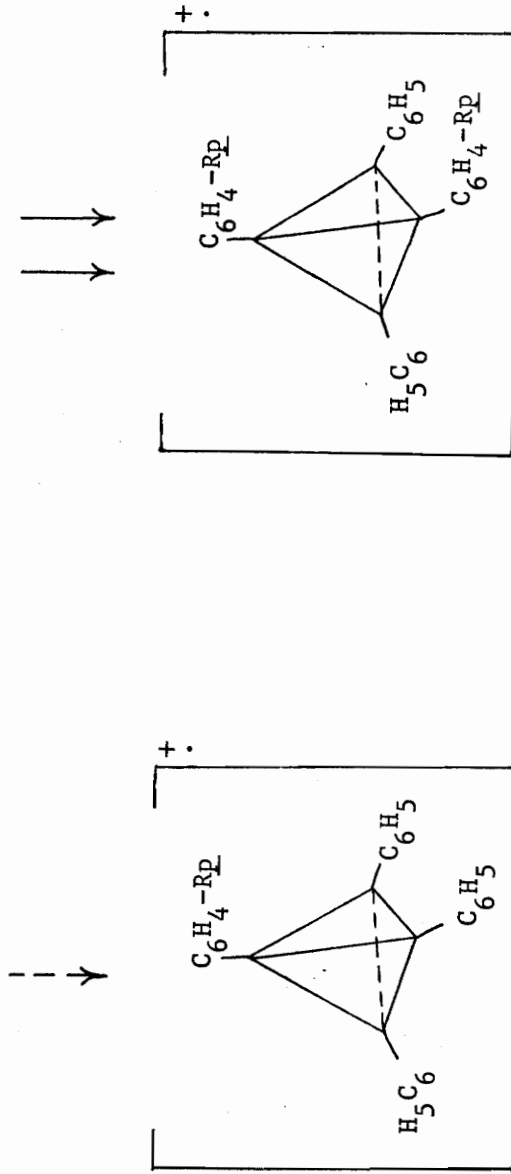


Figure 5

cont'd.

R =	-Br	,	-Cl	,	-F
m* ₁	= 345.3/346.1,	329.6,	324.5		
m* ₂	= 473.5/477.5,	387.1,	355.9		
m* ₃	=	a	,	a	, 347.9
m* ₄	=	a	,	339.2,	308.5
m* ₅	= 151.0/152.6,	115.2,	102.7		
m* ₆	=	a	,	a	, 364.9

^aObscured by intense normal peaks.

corresponding to $P-C_6H_4X$ and the metastables at 324.5, 345.7 or 329.6, respectively, which are consistent with the loss of C_6H_4X from the parent ions of 2 ($R = -F, -Br$ or $-Cl$). It also appears that this loss of C_6H_4F from the parent ion of 2 ($R = -F$) may have occurred in the *p*-fluoro substituted carbinols studied by Bursey et al.,²⁴ and may be the reason that they were unable to unequivocally establish T_d symmetry for 3 ($R = -F$).

In view of the results obtained with both classes of carbinols 1 and 2, it appears that in every case the major fragmentation pathway involves the loss of the most electron donating aromatic group, either as $Ar\cdot$, or as $Ar\cdot$ and $H\cdot$, or possibly as ArH . Thus, given a choice between the loss of RC_6H_4 ($R = -C(CH_3)_3, -N(CH_3)_2, -OCH_3$ or $-CH_3$) or $C_6H_5\cdot$, carbinols 1 and 2 fragment by loss of RC_6H_4 (Figures 2 and 4), but given a choice between the loss of RC_6H_4 ($R = -F, -Cl, -Br$ or $-CF_3$) or $C_6H_5\cdot$, the same carbinols fragment by loss of $C_6H_5\cdot$ preferentially (Figures 3 and 5).

In addition to the partial hydrogen and phenyl scrambling observed to occur in the respective molecular ions of all of the mono- and disubstituted carbinols 1 and 2 studied before fragmentation, it was also observed that the intensity ratios of the normal peaks for these carbinols were independent of both the ionization voltage used (down to values very near the appearance potentials) and the temperature of the probe (80-240°). The most startling observation about the mass spectral fragmentation of these carbinols was made with the aid of high-resolution mass spectrometry²⁸ which shows that oxygen is

lost (M-16)⁺ from the parent ions of all the carbinols studied.

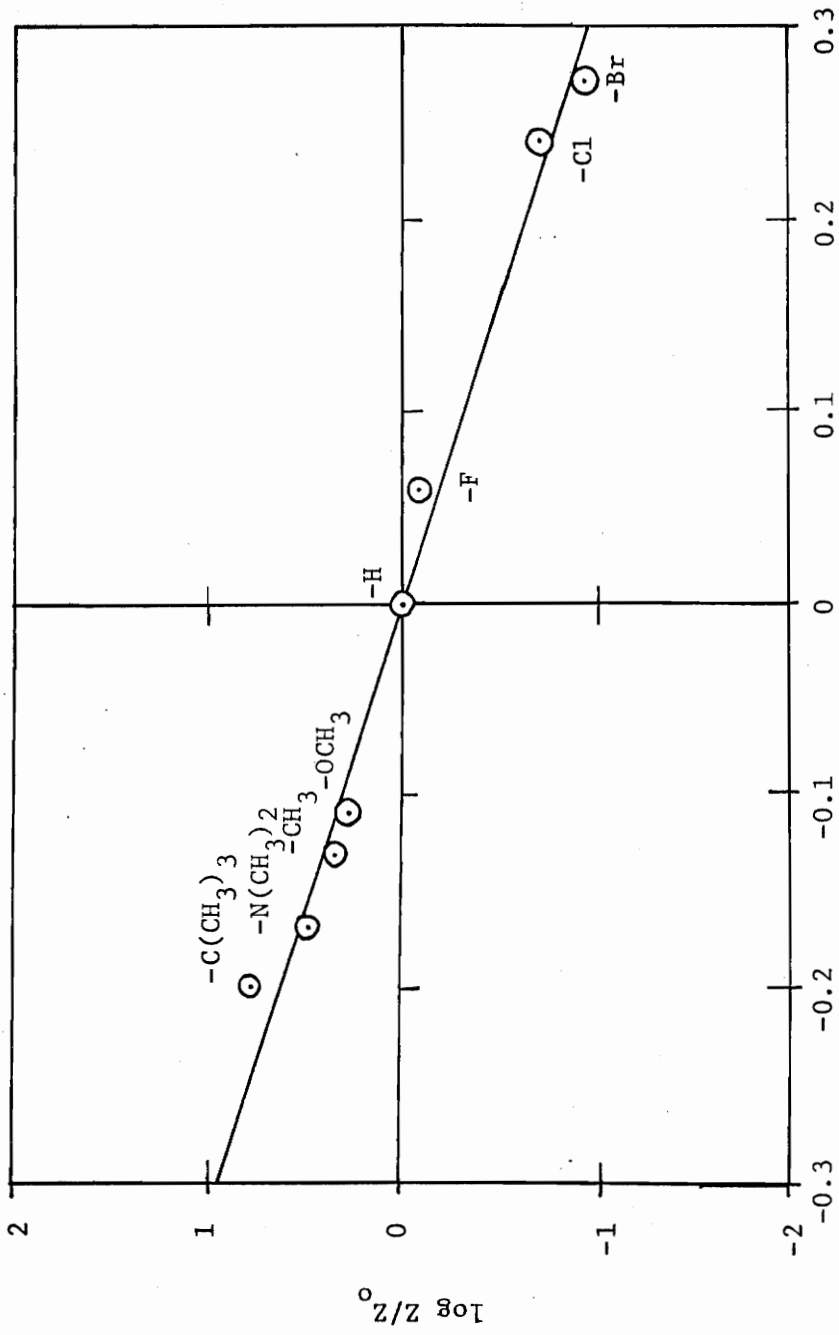
Although attempts to establish a linear free energy relationship^{29-31,13} and a Hammett plot for the carbinols 1 proved unsuccessful using any of the common fragmentation routes in the initial portion of the decomposition of these alcohols, attempts to establish such a relationship with the carbinols 2 was successful. Thus, using the relationship shown below, a plot of $\log Z/Z_0$ versus σ_p ³² for the carbinols 2 afforded a straight line relationship with ρ calculated to be -2.84 using a linear least square program (Fig 6). The negative ρ

$$Z = \frac{[(P-RC_6H_4)(C_6H_5)_3C_5O]^+}{[(P-RC_6H_4)_2(C_6H_5)_3C_5OH]^+}$$

obtained indicates that the mass spectral decomposition of these carbinols is assisted by electron donation at the reaction site, and 3- and 4-position of the cyclopentadiene ring, and as the substituent R becomes less electron donating this decomposition pathway decreases in importance. This approach holds for the carbinols 2 where R = -N(CH₃)₂, -OCH₃, -Br, -Cl and -F, but not where R = -C(CH₃)₃ or -CH₃, since with these substituents there is considerable loss of -CH₃. However, if a plot of $\log Z/Z_0$ versus σ_p is made for 2 when R = -CH₃ and where Z₀ is the parent molecular ion minus a CH₃ (m/e 475), and Z equals the parent minus C₆H₅CH₃, a point on the existing straight line is obtained. Application of this approach to 2 where R = -C(CH₃)₃ and where Z₀ = P-CH₃ and Z = P-[C₆H₅C(CH₃)₃] affords similar results.

Figure 6

Hammett Plot of $\log Z/Z_o$ vs. σ_p For Carbinols 2



EXPERIMENTAL SECTION

General. -- See this section in the main body of this thesis

Preparation of Carbinols 1. -- These carbinols were prepared in the normal manner^{33,34} by Grignard addition of the appropriately *p*-substituted phenylmagnesium bromide to tetracyclone.

<u>R</u>	<u>mp (°C) and lit ref or analysis</u>
H	175-176 ³⁵
-C(CH ₃) ₃	103-104; Calcd for C ₃₉ H ₃₄ O: C, 90.31; H, 6.61. Found: C, 90.13; H, 6.72.
-N(CH ₃) ₂	229-230 (lit ³⁶ 248-249).
-OCH ₃	201-202 (lit ^{37,38} 203).
-CH ₃	192-192.5 (lit ³⁹ 188-189, 199-200).
-F	183.5-184.5 (lit ²⁴ 180-182).
-Cl	211-212; Calcd for C ₃₅ H ₂₅ OCl: C, 84.58; H, 5.07; Cl, 7.13. Found: C, 84.64; H, 5.01; Cl, 7.10.
-Br	217-219; Calcd for C ₃₅ H ₂₅ OBr: C, 77.64; H, 4.65; Br, 14.75. Found: C, 77.62; H, 4.57; Br, 14.73
-CF ₃	210-211; Calcd for C ₃₆ H ₂₅ OF ₃ : C, 81.49; H, 4.75; F, 10.74. Found: C, 81.40; H, 4.77; F, 10.69.

Preparation of Carbinols 2. -- These carbinols were prepared by Grignard addition of phenylmagnesium bromide to the appropriate 3,4-Bis-[(p-substituted phenyl)]-2,5-diphenyl-2,4-cyclopentadien-1-ones.

<u>R</u>	<u>Ref to substituted cyclone starting material</u>	<u>mp (^oC) and lit ref or analysis for carbinols 2</u>
-C(CH ₃) ₃	a	218-219; Calcd for C ₄₃ H ₄₂ O: C, 89.85; H, 7.36. Found: C, 89.56; H, 7.22.
-N(CH ₃) ₂	34,36,40	225-226 (lit 270-271, ²⁴ 252, ³⁶ 225-226 ⁴⁰).
-OCH ₃	41,42,43	195-196; Calcd for C ₃₇ H ₃₀ O ₃ : C, 85.03; H, 5.79. Found: C, 84.82; H, 5.98.
-CH ₃	41,42,43	207-208; Calcd for C ₃₇ H ₃₀ O: C, 90.58; H, 6.16. Found: C, 90.27; H, 6.32.
-F	20	163-164; Calcd for C ₃₅ H ₂₄ OF ₂ : C, 84.32; H, 4.85; F, 7.62. Found: C, 84.19; H, 5.12; F, 7.55.
-Cl	43,44	159-160; Calcd for C ₃₅ H ₂₄ OC1 ₂ : C, 79.10; H, 4.55; Cl, 13.34. Found: C, 79.08; H, 4.58; Cl, 13.55.
-Br	33,41,42	190-191 (lit ³³ 195).

^aNew compound, preparation of benzil, cyclone and carbinol given in main body of dissertation.

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APPENDIX II

Calculation of E_a^\ddagger , ΔH^\ddagger and ΔS^\ddagger
for Substituted Alcohols

A. 3,4-Bis(para-t-butylphenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol

C ^o	Temp K ^o (<u>+0.2^o</u>)	k (sec ⁻¹)	1/T (K ^o) x 10 ⁻³	log k	log (k/T)
180	= 453	8.057 x 10 ⁻⁵	2.208	-4.064	-6.749
190	= 463	2.143 x 10 ⁻⁴	2.156	-3.669	-6.334
200	= 473	2.930 x 10 ⁻⁴	2.114	-3.553	-6.207
210	= 483	6.456 x 10 ⁻⁴	2.070	-3.190	-5.873

$$E_a: \log k = \frac{-E_a}{RT}$$

Linear Least Square Calculation:

$$\begin{aligned} \text{slope} &= 6.274 \times 10^{-3} \\ \text{intercept} &= -9.787 \\ E_a &= 28.71 \text{ kcal}\cdot\text{mol}^{-1} \\ r &= 0.989 \end{aligned}$$

$$\Delta H^\ddagger: \log\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT}$$

Linear Least Square Calculation:

$$\begin{aligned} \text{slope} &= 6.072 \times 10^{-3} \\ \text{intercept} &= -6.684 \\ \Delta H^\ddagger &= 27.78 \text{ kcal}\cdot\text{mol}^{-1} \\ r &= 0.988 \end{aligned}$$

$$\Delta S^\ddagger: \Delta S^\ddagger = 2.303 R (\log k - \log T - 10.32) + \Delta H^\ddagger/T$$

	ΔS^\ddagger (eu)	T(C° ± 0.2°)
	13.3	180
	12.7	190
	13.1	200
	13.2	210
$\Delta S^\ddagger_{\text{ave}}$	13.1	

B. 3,4-Bis(para-tolyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol.

C°	Temp K° (±0.2°)	k (sec ⁻¹)	1/T (K°) x 10 ⁻³	log k	log (k/T)
180	= 453	7.700 x 10 ⁻⁵	2.208	-4.113	-6.769
190	= 463	2.110 x 10 ⁻⁴	2.156	-3.675	-6.341
200	= 473	3.434 x 10 ⁻⁴	2.114	-3.464	-6.139
210	= 483	6.581 x 10 ⁻⁴	2.070	-3.181	-5.865

$$E_a: \log k = \frac{-E_a}{RT}$$

Linear Least Square Calculation: slope = 6.625 x 10⁻³
intercept = -10.55
 $E_a = 30.31 \text{ kcal}\cdot\text{mol}^{-1}$
r = 0.995

$$\Delta H^\ddagger: \log\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT}$$

Linear Least Square Calculation: slope = 6.423 x 10⁻³
intercept = -7.447
 $\Delta H^\ddagger = 29.39 \text{ kcal}\cdot\text{mol}^{-1}$
r = 0.994

$$\Delta S^\ddagger: \Delta S^\ddagger = 2.303 R (\log k - T - 10.32) + \Delta H^\ddagger/T$$

	ΔS^\ddagger (eu)	T (C° ± 0.2)
	16.8	180
	16.2	190
	16.9	200
	16.6	210
$\Delta S^\ddagger_{\text{ave}}$	16.6	

C. 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol

C°	Temp K° (±0.2°)	k (sec ⁻¹)	1/T (K°) x 10 ⁻³	log k	log (k/T)
180	= 453	9.094 x 10 ⁻⁵	2.208	-6.697	-4.041
190	= 463	2.166 x 10 ⁻⁴	2.156	-6.330	-3.664
200	= 473	3.678 x 10 ⁻⁴	2.114	-6.1092	-3.434
210	= 483	6.448 x 10 ⁻⁴	2.070	-5.8745	-3.190

$$E_a: \log k = \frac{-E_a}{RT}$$

Linear Least Square Calculation:

$$\begin{aligned} \text{slope} &= 6.122 \times 10^{-3} \\ \text{intercept} &= -9.500 \\ E_a &= 28.01 \text{ kcal} \cdot \text{mol}^{-1} \\ r &= 0.997 \end{aligned}$$

$$\Delta H^\ddagger: \log\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT}$$

Linear Least Square Calculation:

$$\begin{aligned} \text{slope} &= 6.104 \times 10^{-3} \\ \text{intercept} &= -6.703 \\ \Delta H^\ddagger &= 27.93 \text{ kcal} \cdot \text{mol}^{-1} \\ r &= 0.993 \end{aligned}$$

$$\Delta S^\ddagger: \Delta S^\ddagger = 2.303 R (\log k - \log T - 10.32) + \Delta H^\ddagger/T$$

ΔS^\ddagger (eu)	T(C° ± 0.2)
-16.2	180
-15.8	190
-16.1	200
-16.2	210
$\Delta S^\ddagger_{\text{ave}}$ -16.1	

D. 3,4-Bis(para-chlorophenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ol

Temp C°	K° (±0.2°)	k (sec ⁻¹)	1/T (K°) x 10 ⁻³	log k	log (k/T)
180	= 453	1.469 x 10 ⁻⁴	2.208	-3.832	-6.489
190	= 463	2.992 x 10 ⁻⁴	2.156	-3.523	-6.189
200	= 473	5.989 x 10 ⁻⁴	2.114	-3.229	-5.904
210	= 483	1.112 x 10 ⁻³	2.070	-2.953	-5.637

$$E_a = \log k = \frac{-E_a}{RT}$$

Linear Least Square Calculation:

$$\text{slope} = 6.421 \times 10^3$$

$$\text{intercept} = -10.33$$

$$E_a = 29.38 \text{ kcal}\cdot\text{mol}^{-1}$$

$$r = 0.999$$

$$\Delta H^\ddagger: \log\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT}$$

Linear Least Square Calculation:

$$\text{slope} = 6.218 \times 10^3$$

$$\text{intercept} = -7.233$$

$$\Delta H^\ddagger = 28.45 \text{ kcal}\cdot\text{mol}^{-1}$$

$$r = 0.995$$

$$\Delta S^\ddagger: \Delta S^\ddagger = 2.303 R (\log k - \log T - 10.32) + \Delta H^\ddagger/T$$

	$\Delta S^\ddagger(\text{eu})$	$T(\text{C}^\circ \pm 0.2^\circ)$
	-14.0	180
	-14.0	190
	-14.0	200
	-14.0	210
$\Delta S^\ddagger_{\text{ave}}$	-14.0	

E. 3,4-Bis(para-bromophenyl)-2,4-cyclopentadien-1-ol.

C°	Temp K° ($\pm 0.2^\circ$)	k (sec^{-1})	1/T (K°) $\times 10^{-3}$	log k	log (k/T)
180	= 453	1.955×10^{-4}	2.208	-3.708	-6.364
190	= 463	3.215×10^{-4}	2.156	-3.492	-6.158
200	= 473	6.215×10^{-4}	2.114	-3.206	-5.881
210	= 483	1.301×10^{-3}	2.070	-2.885	-5.569

$$E_a: \log k = \frac{-E_a}{RT}$$

Linear Least Square Calculation: slope = 6.007×10^3
intercept = -9.515
 $E_a = 27.49 \text{ kcal}\cdot\text{mol}^{-1}$
 $r = 0.992$

$$\Delta H^\ddagger: \log\left(\frac{k}{T}\right) = -\frac{\Delta H^\ddagger}{RT}$$

Linear Least Square Calculation: slope = 5.804×10^3
intercept = -6.409
 $\Delta H^\ddagger = 26.56 \text{ kcal}\cdot\text{mol}^{-1}$
 $r = 0.992$

$$\Delta S^\ddagger: \Delta S^\ddagger = 2.303 R (\log k - \log T - 10.32) + \Delta H^\ddagger/T$$

	ΔS^\ddagger (eu)	T(C ^o ± 0.2 ^o)
	-17.7	180
	-18.0	190
	-17.9	200
	-17.8	210
$\Delta S^\ddagger_{\text{ave}}$	-17.8	

APPENDIX III

Values of Log k/ko for Hammett Plot of

Log k/ko versus σ_p

<u>Substituent</u>	<u>σ_p</u>	Log k/ko	Log k/ko	Log k/ko	Log k/ko
		<u>180°</u>	<u>190°</u>	<u>200°</u>	<u>210°</u>
<u>t-butyl</u>	-0.197	-0.053	-0.005	-0.099	0
<u>methyl</u>	-0.170	-0.72	-0.011	-0.03	+0.009
<u>H</u>	0	0	0	0	0
<u>chloro</u>	+0.227	+0.21	+0.141	+0.205	+0.237
<u>bromo</u>	+0.233	+0.33	0.172	0.228	0.305

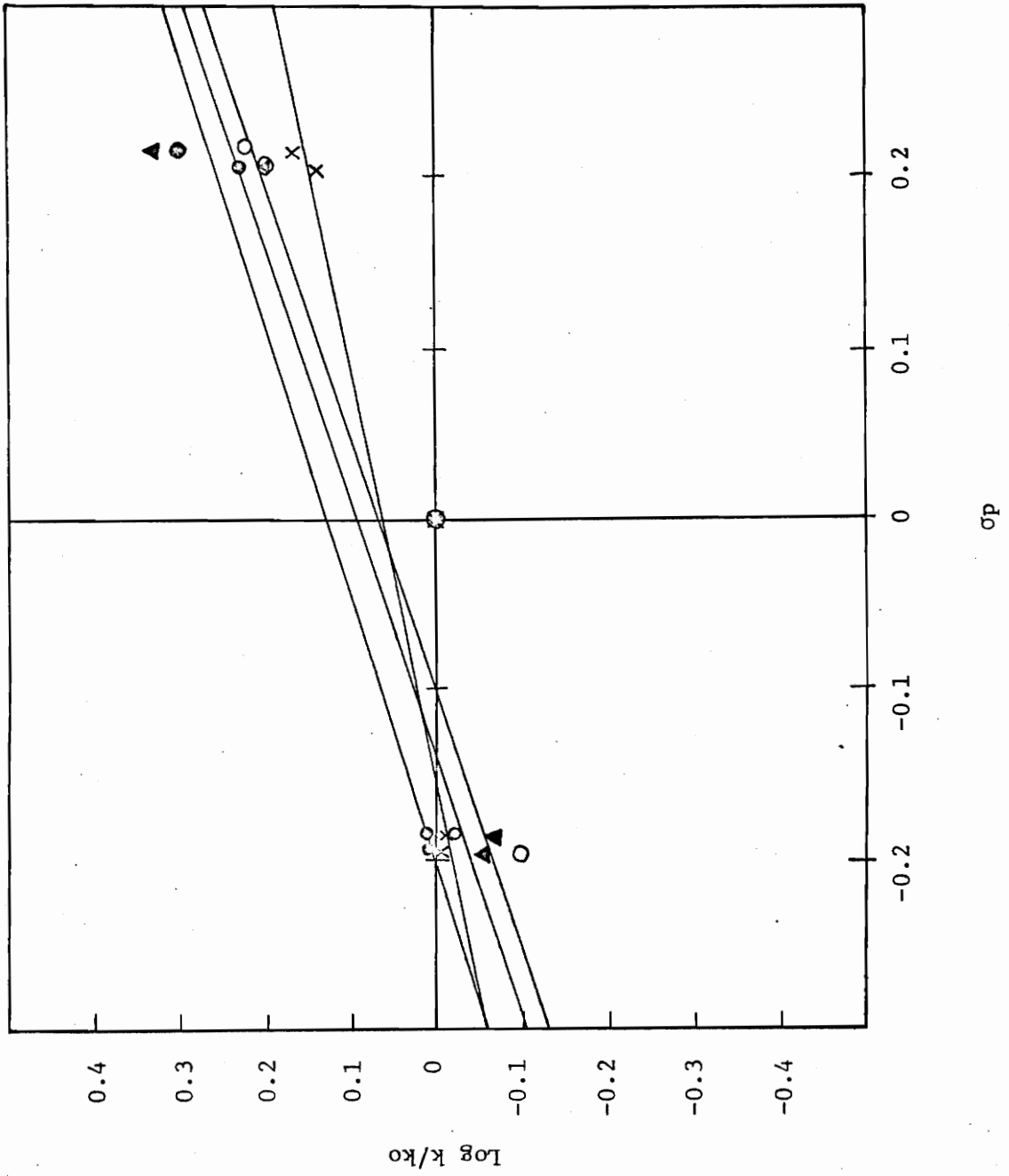
Classical Hammett Plot of $\text{Log } k/k_o$ versus σ_p

● = Temperature at $210 \pm 0.2^\circ$

▲ = Temperature at $200 \pm 0.2^\circ$

X = Temperature at $190 \pm 0.2^\circ$

○ = Temperature at $180 \pm 0.2^\circ$



VITA

Thomas A. Perfetti was born March 22, 1952 in Jeannette, Pennsylvania. He received the Bachelor of Science degree in Chemistry from Indiana University of Pennsylvania in 1974, where he worked 2 years in the field of Biochemistry, and the Doctor of Philosophy in Chemistry from Virginia Polytechnic Institute and State University in 1977, where he specialized in Organic synthesis and Organic-Analytical techniques.

The author is a member and past president of the Alpha Theta Chapter of Phi Lambda Upsilon, 1976-1977, a member of Phi Beta Chi, member of Sigma Xi, and member of the American Chemical Society and past president of its Student Affiliate at Indiana University of Pennsylvania (1974). He has received fellowships from the Petroleum Research Fund (1974), N.A.S.A. (1976), and also a scholarship from the State of Virginia in 1976. In addition he received teaching and research fellowships from Virginia Polytechnic Institute and State University during the entire 3 years of his stay here.

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He has accepted employment with R. J. Reynolds Industries, Winston-Salem, North Carolina and will be working as a Senior Research Chemist and Chemical Consultant.

Thomas A. Perfetti married Patricia Ann Finley on August 16, 1975 in Belle Vernon, Pennsylvania and they are at present living happily in Blacksburg, Virginia.

Thomas A. Perfetti

A STUDY OF THE KINETICS OF THE [1,5]-SIGMATROPIC
PHENYL REARRANGEMENT IN 3,4-BIS(para-SUBSTITUTED
PHENYL)-1,2,5-TRIPHENYL-2,4-CYCLOPENTADIEN-1-OLS

by

Thomas A. Perfetti

(ABSTRACT)

A kinetic study of the suprafacial [1,5]-sigmatropic phenyl rearrangements of 3,4-bis-(para-substituted)-1,2,5-triphenyl-2,4-cyclopentadien-1-ols to 3,4-bis-(para-substituted)-2,2,5-triphenyl-3-cyclopenten-1-ones, where the substituent were, t-butyl, methyl, hydrogen, chloro and bromo, has been performed at 180, 190, 200 and $210 \pm 0.2^\circ$ in tetraethylene glycol. The rearrangement was observed to be first order throughout the temperature range investigated, and the rate constants (k) at the temperatures used were found to be 8.057, 2.143, 2.930 and $6.456 \times 10^{-4} \text{ sec}^{-1}$ for the t-butyl substituent; 7.700, 2.110, 3.434, and $6.581 \times 10^{-4} \text{ sec}^{-1}$ for the methyl substituent; 0.909, 2.166, 3.678 and $6.448 \times 10^{-4} \text{ sec}^{-1}$ for the unsubstituted alcohol; 1.469, 2.992, 5.989 and $11.12 \times 10^{-4} \text{ sec}^{-1}$ for the chloro substituent; and 1.955, 3.215, 6.215 and $13.01 \times 10^{-4} \text{ sec}^{-1}$ for the bromo substituent, respectively. Calculations of the activation energy of this phenyl [1,5]-sigmatropic shift from the Arrhenius equation give values of 28.71, 30.31, 28.01, 29.38 and 27.49 $\text{kcal} \cdot \text{mol}^{-1}$ for the above substit-

uents respectively, while ΔH^\ddagger for these phenyl migrations were 27.78, 29.39, 27.93, 28.45 and 26.56 kcal·mol⁻¹, respectively. ΔS^\ddagger values were also calculated to be -16.6, -13.1, -16.1, -14.0 and -17.8 eu, respectively for a mean temperature range of 453-483 \pm 0.2°K. The isokinetic temperature was calculated to be 320°. Calculated rho (ρ) values for the sigmatropic migrations were -0.813, -0.400, -0.690 and -0.658 at 180, 190, 200 and 210 \pm 0.2°C. These results are used to discuss both the mechanism of this rearrangement and the transition state for rearrangements in the pentaphenylcyclopentadienol system. In a much broader sense these results and the results of previously documented sigmatropic rearrangements exhibiting electronic influences were used to formulate a general scheme to predict the outcome of those sigmatropic rearrangements that entail an electronic effect as seen in the rates of the above reactions. This scheme used as its basis the transition state approach invoking inductive and mesomeric arguments to rationalize the observed rates of the sigmatropic rearrangements of this dissertation, those of previously documented sigmatropic rearrangements and finally to predict a relative rate of rearrangements in general.

Finally a mass spectral investigation of the fragmentation patterns of 1-para-phenylsubstituted 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols and 3,4-bis(para-substituted phenyl)-1,2,5-triphenyl-2,4-cyclopentadien-1-ols was undertaken. A continuum of two superimposable pathways with the choice of the major decomposition mode being determined by the electron donating or withdrawing ability of the substit-

uent was established. Linear free energy relationships for mass spectral decomposition were presented as well as a justification for this behavior.