

A STUDY OF THE CYCLODEHYDROHALOGENATION OF
12-(2-CHLORO-5-METHYLPHENYL)BENZ[A]ANTHRACENE

by

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TO MY PARENTS

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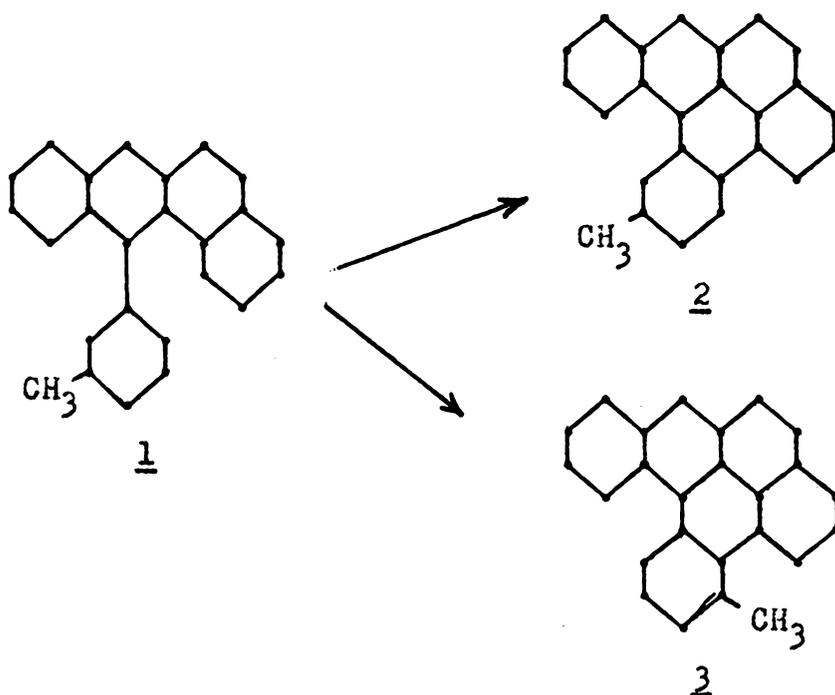
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INTRODUCTION

INTRODUCTION^a

In the study of the cyclodehydrogenation of 12-(3-methylphenyl)benz[a]anthracene (1), Zajac (1) pointed out that the hydrocarbon might undergo ring closure at either of the ortho positions of the phenyl ring. These positions are not equivalent with respect to the methyl group and ring closure might yield either 2-methyldibenzo[a,1]pyrene (2) or 4-methyldibenzo[a,1]pyrene (3) or a mixture of both isomers.



^aIn this thesis all rings are aromatic unless otherwise indicated.

When compound 1 was dehydrogenated only one isomer was isolated. This conclusion is supported by gas chromatographic analysis; the chromatogram shows the presence of only one component. Further evidence was obtained from elemental analysis. The isomer which was isolated could be either compound 2 or compound 3. Thus, the purpose of this investigation was to determine which isomer, 2 or 3, was actually isolated. It was decided to synthesize 2 through an unequivocal synthesis. If the physical constants of compound 2, synthesized unequivocally, are the same as those of the compound isolated from the dehydrogenation of 1 it can be concluded that Zajac isolated 2. On the other hand if the physical constants are different, it can be concluded that he isolated 3.

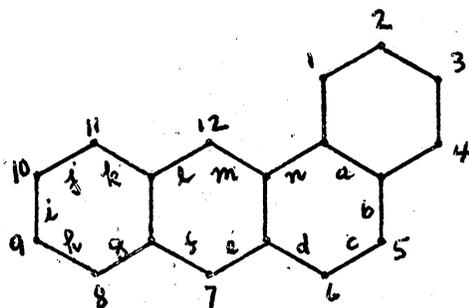
It was decided to synthesize a compound in which one of the ortho positions, para to the methyl group, of the phenyl ring of 1 was substituted with a halogen. This new compound could then be cyclodehydrohalogenated to compound 2. The proposed compound 12-(2-chloro-5-methylphenyl)benz[a]anthracene (21) was synthesized as shown in Chart II. However, the cyclodehydrohalogenation could not be accomplished.

NOMENCLATURE

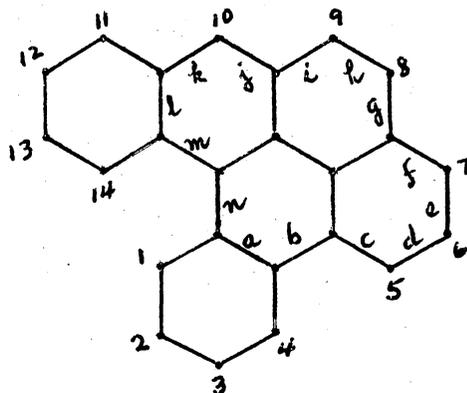
NOMENCLATURE

The nomenclature used throughout this thesis is in accordance with the recommendations presented in the Journal of the American Chemical Society, 82, 5545, (1960).

For example:



Benz[a]anthracene



Dibenzo[a,1]pyrene

HISTORICAL

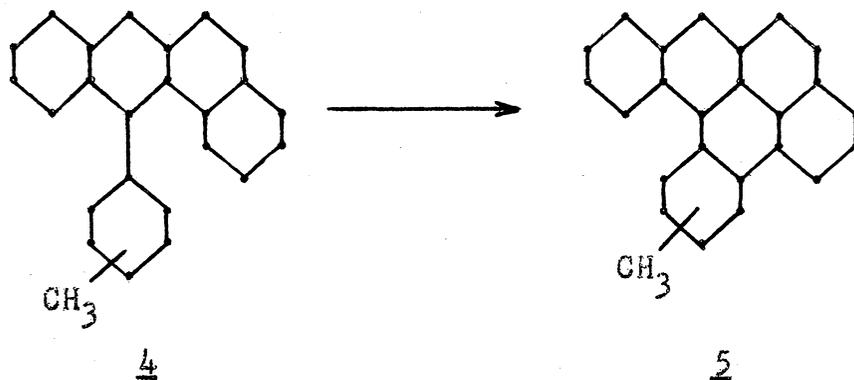
HISTORICAL

Since the discovery of naphthalene in 1820, over 215 individual compounds have been isolated from coal tar. Because some of these hydrocarbons have been found to have carcinogenic activity, a number of aromatic polynuclear hydrocarbons have been synthesized in connection with intensive cancer research that is being done at the present time.

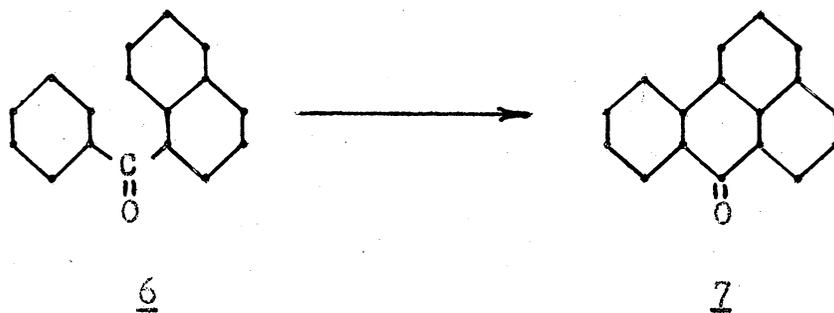
A number of methods have been used to synthesize the aromatic hydrocarbons. Some of the useful methods are the Elbs reaction (2), succinic anhydride synthesis (3), Bradsher's aromatic cyclodehydration (4), aromatic cyclodehydrogenation (5), and cyclodehydrohalogenation (6).

Cyclodehydrogenation implies ring formation by the removal of hydrogen from at least two points in a molecule or between two or more molecules.

Cyclodehydrogenation reactions, usually catalyzed by anhydrous aluminum chloride, have been known for years and have been used profitably to synthesize hydrocarbons (1) in the following manner:



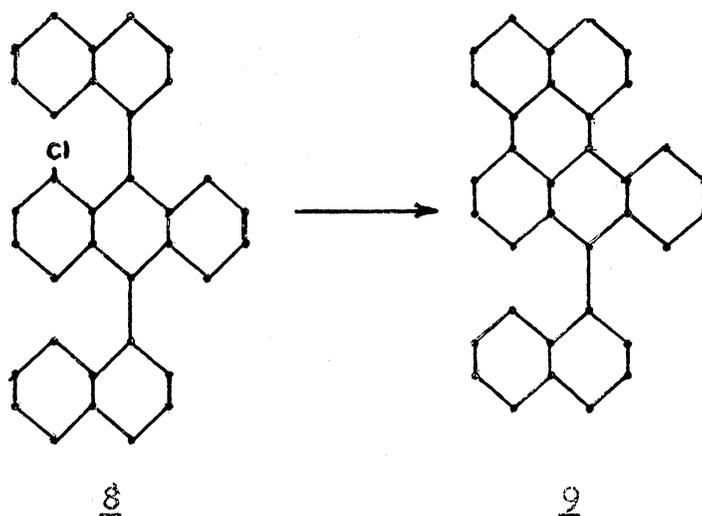
or as used by Scholl (7) to synthesize 1,9-benzanthrone (7) in 76% yield from phenyl 1-naphthyl ketone (6).



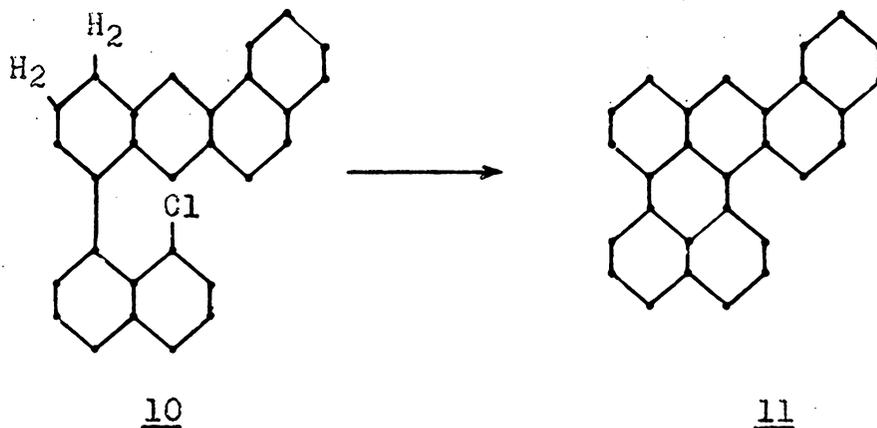
Although the cyclodehydrogenation reaction has been very useful in the synthesis of a wide variety of compounds, it sometimes leads to the synthesis of several isomers as has been discussed in the Introduction.

In order to avoid ambiguities cyclodehydrohalogenation reactions (5,8) have been used to synthesize

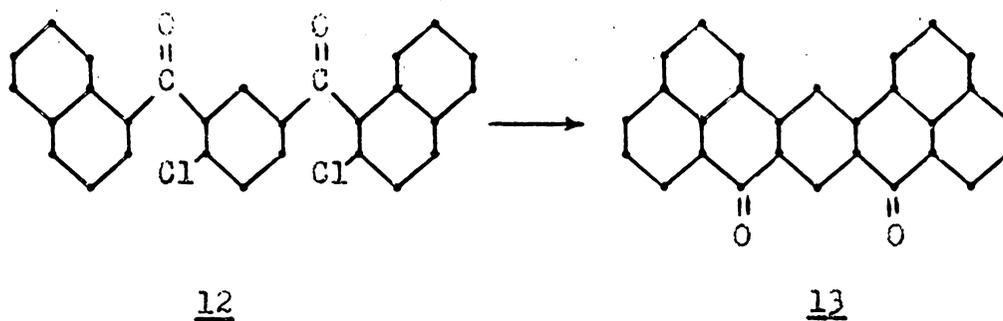
compounds unequivocally. Clar (5) has used potassium hydroxide and quinoline to synthesize 9 from 8.



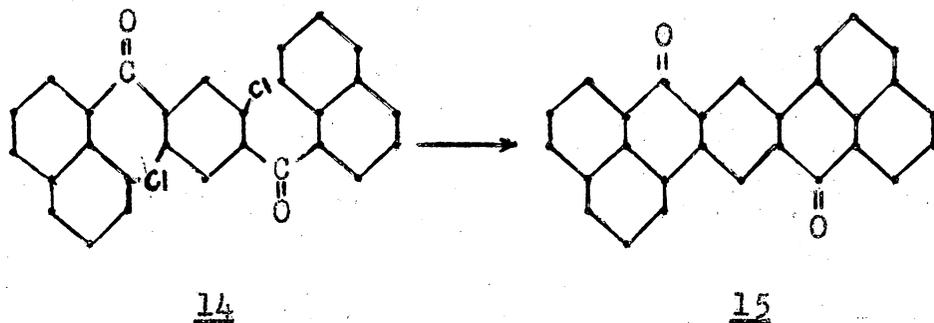
In the synthesis of 9 from 8 Clar fails to mention the yield. It is assumed that he did not isolate 9 in good yields. In This Laboratory Mahone (8) has used potassium hydroxide and quinoline to synthesize naphtho[2,1-a]perylene (11) from 8-[1-(8-chloro-naphthyl)]-10,11-dihydrobenz[a]anthracene (10).



It is interesting to notice that the action of potassium hydroxide and quinoline upon compound 10 yielded compound 11 by cyclodehydrohalogenation and aromatization. In the synthesis of 1,14,11,12-di-benzopentacene-5,7-quinone (13) (9) from 1,3-dichloro-4,6-di-(α -naphthoyl)benzene (12) using potassium hydroxide and quinoline the compound was probably isolated in poor yields because no yields are given.



The synthesis of 13 using potassium hydroxide and ethanol gave poorer results. Clar does, however, mention that in the synthesis of heptazethrene-7,15-quinone (6) (15) from 1,4-dichloro-2,5-(α -naphthoyl)-benzene (14) using potassium hydroxide and quinoline compound 15 was isolated in yields no better than 10%.



He isolated 15 after boiling the tars with water several times and finally with dilute ammonia. Trituration of the tars with ether produced 15 which was then recrystallized from nitrobenzene.

DISCUSSION OF RESULTS

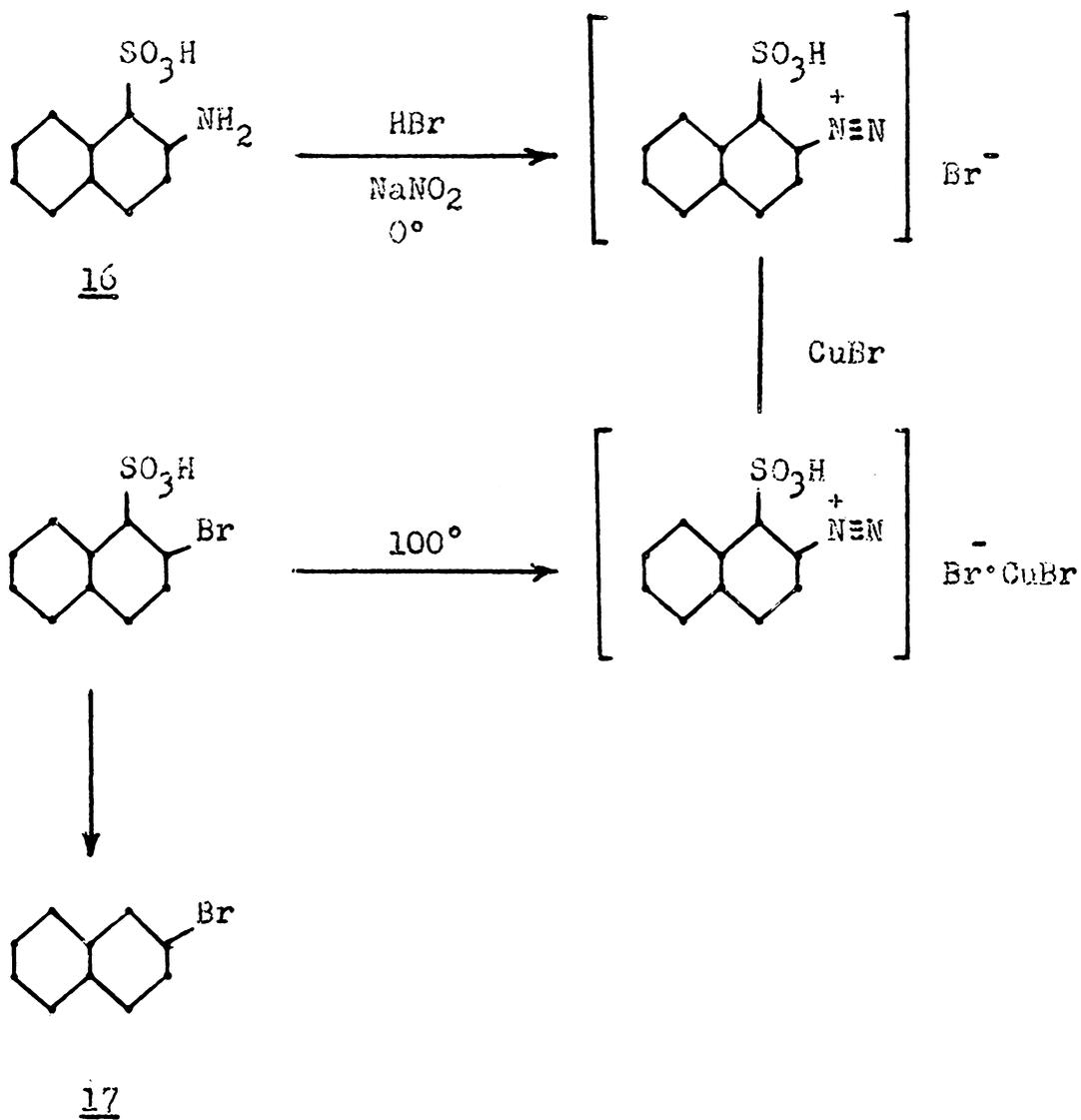
DISCUSSION OF RESULTS

Preparation of 2-Bromonaphthalene (17).

The utilization of the Grignard reagent of 2-bromonaphthalene is perhaps the most practical route to obtain 2-(2-naphthylmethyl)substituted benzophenones as shown in Chart II. Since 2-bromonaphthalene is so useful it is desirable to synthesize this compound by the route which provides the best yield.

2-Bromonaphthalene can be prepared by the Newman and Wise (10) method in good yield, but the method suffers the disadvantage of using the carcinogen 2-naphthylamine. Thus, it was decided to use the method of Wolfe and Doukas (11) as improved by Polss (12). 2-Bromonaphthalene is prepared as shown in Chart I, by diazotizing 2-naphthylamine-1-sulfonic acid and then treating the stable diazonium salt with cuprous bromide and hydrobromic acid to obtain 2-bromonaphthalene-1-sulfonic acid. The sulfonic acid group was then removed by sulfuric acid hydrolysis and 2-bromonaphthalene was isolated in 59% yield. The 2-bromonaphthalene which had been

CHART I

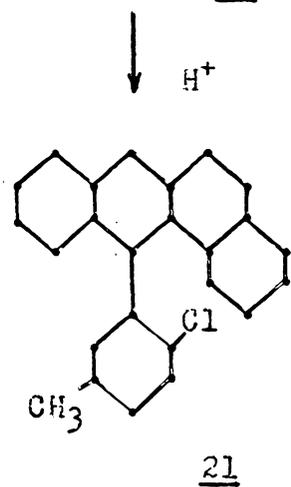
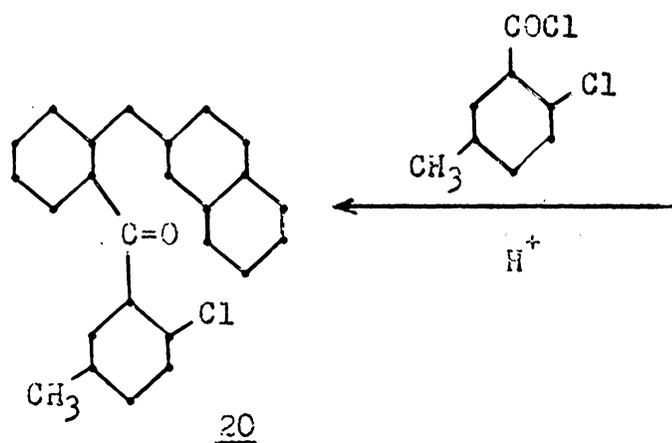
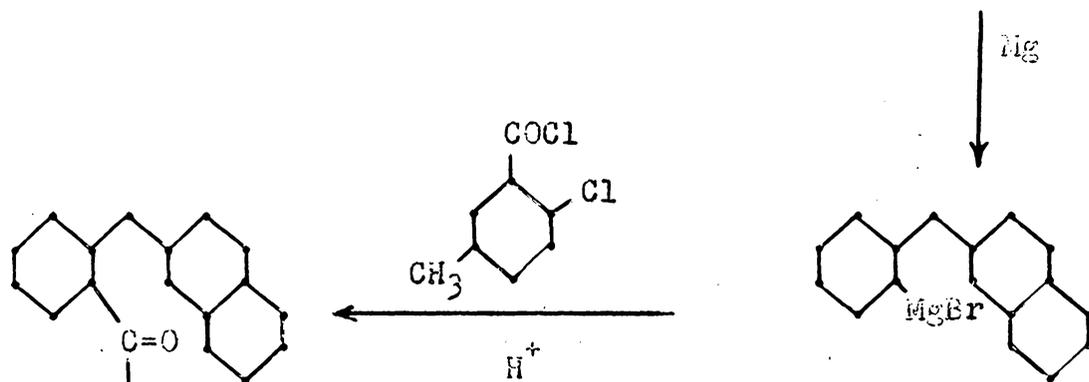
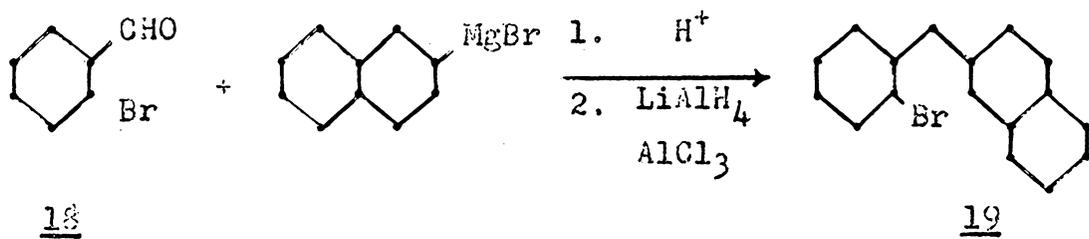


purified by passing through an alumina column formed Grignard reagent in 85% yield.

Preparation of 2-(2-Naphthylmethyl)-2'-chloro-5'-methylbenzophenone (21).

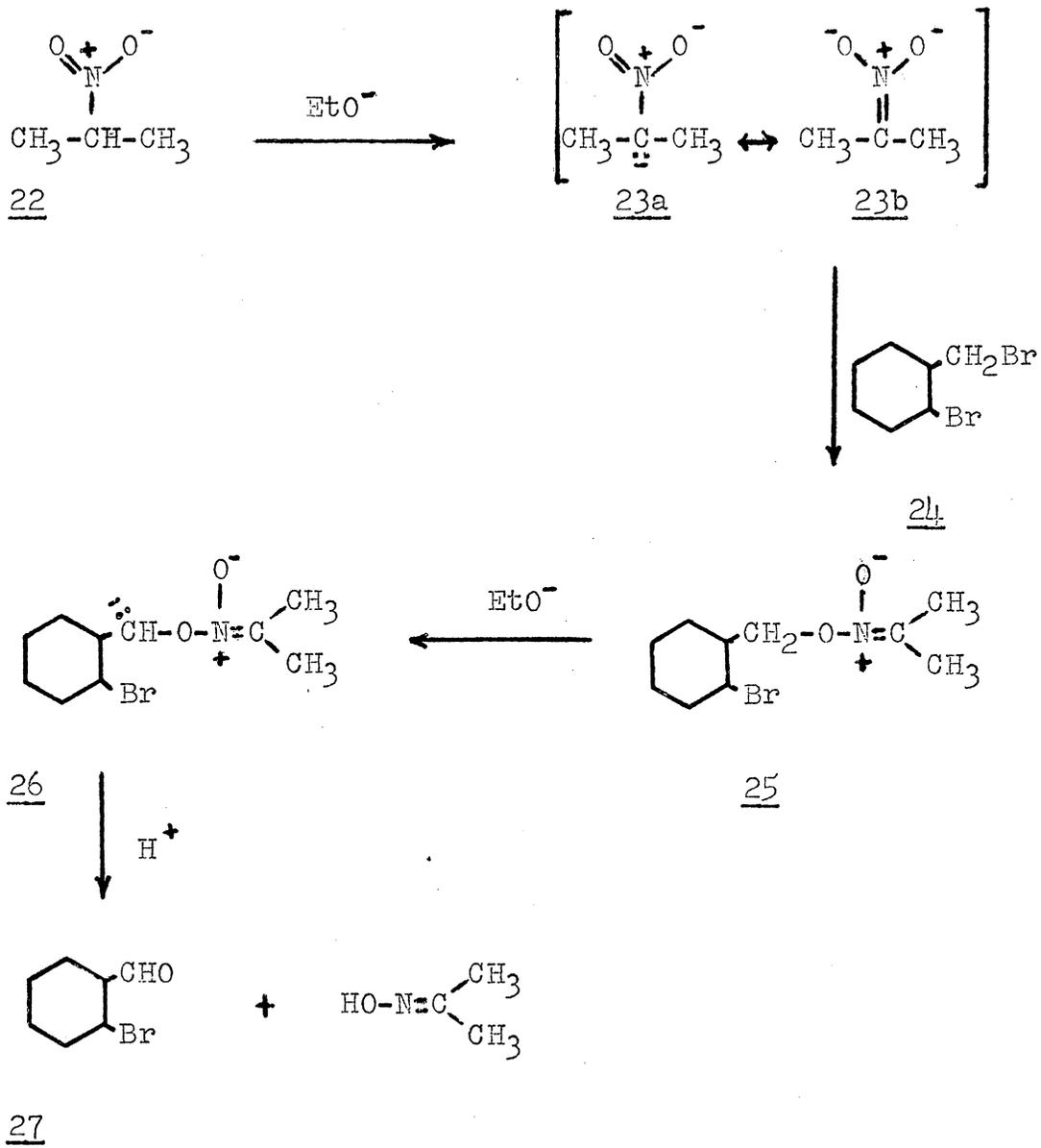
2-(2-Naphthylmethyl)-2'-chloro-5'-methylbenzophenone was synthesized as shown in Chart II. Of the several ways of preparing 2-bromobenzaldehyde the most direct route is the oxidation of 2-bromotoluene using chromic acid (13). However, the reported yields are only about 40%. The more tedious method involves the side-chain bromination of 2-bromotoluene to 2-bromobenzal bromide followed by hydrolysis to the aldehyde (14). The yields by this method are about 70%, but this method suffers the disadvantage of taking several days to isolate the product and of giving a product which can only be purified with difficulty. A new method for the preparation of 2-bromobenzaldehyde, shown in Chart III, involves the conversion of 2-bromotoluene to 2-bromobenzyl bromide (15) which can then be converted to the corresponding aldehyde 18 (16).

CHART II



The 2-bromobenzyl bromide (24) was prepared by treating 2-bromotoluene with N-bromosuccinimide and benzoyl peroxide. The 2-bromobenzyl bromide can be converted to the corresponding aldehyde by treating the compound with 2-nitropropane in the presence of sodium ethoxide in absolute ethanol. The nitro-paraffin salt formed 23 can react as an ambident nucleophile; it can either form a new carbon-carbon bond or a new carbon-oxygen bond. The formation of a new carbon-oxygen bond yields an unstable nitronic ester 25 which can be converted to an aldehyde under the influence of base. According to Gould (17) it appears that the ambident nucleophile will attack with its most electronegative atom as the conditions for S_N1 substitution become more favorable, but if the reaction acquires more of the character of a bimolecular substitution, the incoming group attacks with the less electronegative atom. It is obvious that the conditions for the conversion of 2-bromobenzyl bromide to 2-bromobenzaldehyde are favorable for S_N1 substitution which will favor attack by the more electronegative atom of the 2-nitropropane ion. This method has the advantage of giving reasonable

CHART III

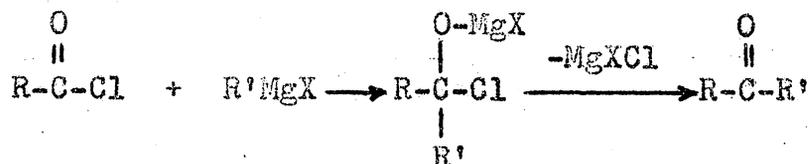


yields (69%) of the desired aldehyde and also has the advantage of requiring a short time to isolate the desired product.

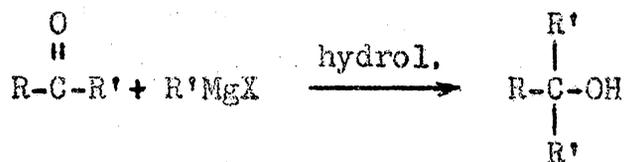
The reaction involving the Grignard reagent of 2-bromonaphthalene (17) and 2-bromobenzaldehyde (18) was first performed by Light (18). The normal product from the reaction of Grignard reagent with an aldehyde is a secondary alcohol, but investigators in This Laboratory have observed abnormal products; they have observed 2-naphthyl 2-bromophenyl ketone and 2-(2-naphthylmethyl)bromobenzene. At present this abnormal reaction is being investigated to try to explain the formation of the abnormal products. Since the desired product was 2-(2-naphthylmethyl)-bromobenzene (19) the crude product of the reaction of the Grignard reagent of 17 and 18 was reduced by allowing it to react with a mixture of aluminum chloride and lithium aluminum hydride.

The Grignard reagent of 2-(2-naphthylmethyl)-bromobenzene was allowed to react with 2-chloro-5-methylbenzoyl chloride, as shown in Chart II, to yield (57%) the desired 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone (20). It is known that the

reaction of a Grignard reagent with an acid chloride yields first a ketone:



The ketone can, of course, react with more Grignard reagent to give a tertiary alcohol:



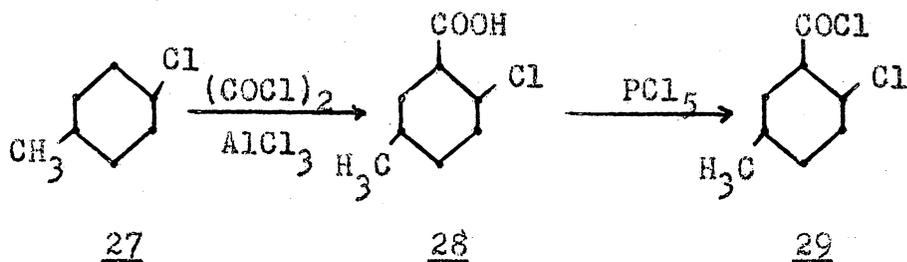
In order to avoid the formation of the tertiary alcohol the Grignard reagent is added dropwise to the acid chloride solution so that the Grignard reagent is never present in excess. Thus, the reaction can be stopped at the ketone stage. Consequently, this technique was employed for the synthesis of 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone. The structure of 20 was established by elemental analysis and infrared absorption spectra^a. The

^aThroughout this thesis the infrared absorption spectra were obtained by using an IR-5 Beckman Spectrophotometer.

carbonyl group of 20 exhibits the characteristic infrared absorption band at 1664 cm^{-1} . (Fig. 1). The purity of 20 was established by gas chromatographic analysis before an analytical sample was prepared.

Anal. Calcd. for $\text{C}_{25}\text{H}_{19}\text{OCl}$: C, 80.96; H, 5.16; Cl, 9.56. Found: C, 80.50; H, 5.38; Cl, 9.50.

2-Chloro-5-methylbenzoyl chloride (29) was synthesized from 2-chloro-5-methylbenzoic acid (28) by treatment with phosphorous pentachloride (19). The acid 28 was prepared by allowing p-chlorotoluene to react with oxalyl chloride in the presence of anhydrous aluminum chloride (20).

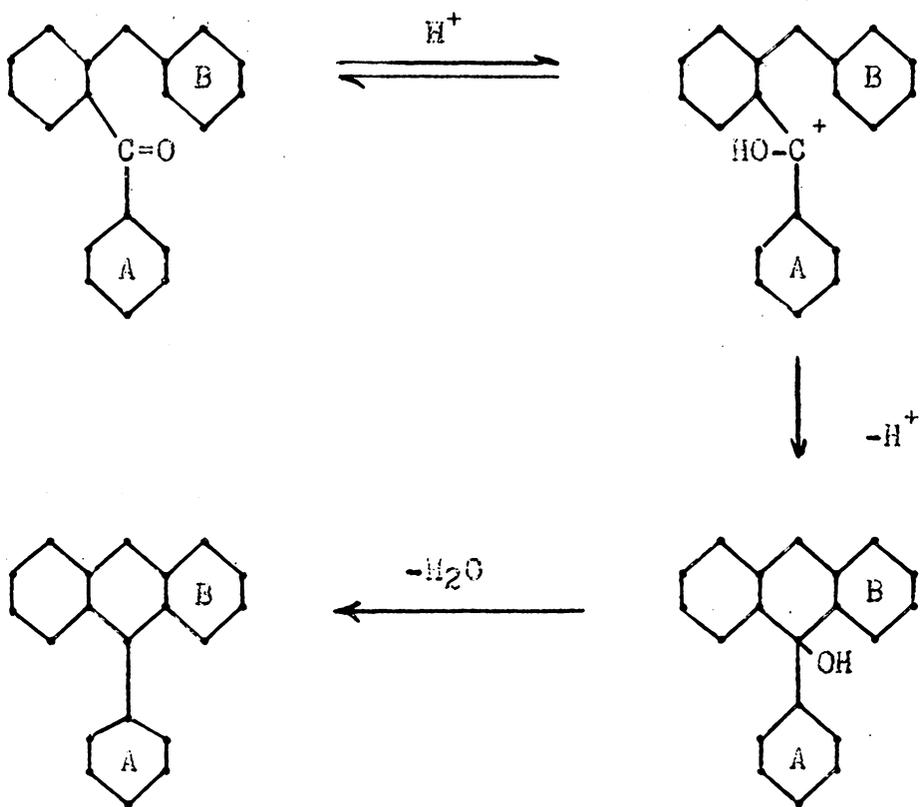


Cyclodehydration of 2-(2-Naphthylmethyl)-2'-chloro-5'-methylbenzophenone (20).

Bradsher and Vingiello (21) and Vingiello and Van Oot (22,23) have established the mechanism of

the aromatic cyclodehydration of ketones as shown in Chart IV. The reaction involves the following steps: (a) the reversible addition of a proton to the carbonyl oxygen, (b) an electrophilic attack of the positively charged carbon atom upon the ortho position of ring B, (c) the elimination of a proton and (d) transannular elimination of water. It has been observed that one of the most important factors, on which the rate of cyclization depends, appears to be the nature and position of substituents on ring A. The cyclodehydration is usually carried out in a 2:1 glacial acetic acid and 48% hydrobromic acid mixture. It was observed (19,24) that 2'-halo substituted ketones could not be cyclodehydrated by heating under reflux in the standard acid mixture. When more drastic conditions were used, heating in a Carius tube to 150°, more satisfactory results were obtained (25). In the present investigation the sealed tube technique was used. 2-(2-Naphthylmethyl)-2'-chloro-5'-methylbenzophenone was dissolved in a 2:1 solution of glacial acetic acid and 45% hydriodic acid. The solution was placed in a Carius tube which was then sealed and heated to

CHART IV



180° for two hours. When the reaction mixture had cooled to room temperature a white solid separated from solution, 12-(2-chloro-5-methylphenyl)-benz[a]anthracene (80%). The solid which had the appearance of a glass was washed with water and then dissolved in 95% ethanol and a number of common solvents to attempt crystallization; all attempts were futile. Since the benz[a]anthracene 21 could not be crystallized it was decided to distil it. A viscous yellow-green oil was collected. The structure of the product was established by ultraviolet spectra^a and elemental analysis. The product had a spectrum characteristic of a benz[a]anthracene (Fig. 2). The elemental analysis was consistent with the structure assigned to 12-(2-chloro-5-methylphenyl)benz[a]anthracene (21).

Anal. Calcd. for C₂₅H₁₇Cl: C, 85.09; H, 4.85; Cl, 10.05. Found: C, 85.44; H, 4.55; Cl, 10.17.

Toward the end of this investigation a gas chromatography instrument became available. The

^aThroughout this thesis ultraviolet absorption spectra were obtained by using a DK-2A Beckman Spectrophotometer.

instrument became a very useful tool as will be pointed out later in this discussion.

Since the preparation of 12-(2-chloro-5-methyl-phenyl)benz[a]anthracene was of prime importance it was decided to prepare the compound in as high yields and short reaction time as possible. As mentioned above the desired compound 21 could be obtained in good yields and in relatively short reaction time. The next logical step was to determine its purity after it had been eluted through an alumina column. To determine its purity gas chromatographic analysis^a was used. The chromatogram showed two peaks which suggested that one impurity was present. In previous work (26,27,28,29) it has been observed that in the syntheses of 7- and 12-substituted benz[a]anthracenes cleavage occurs if the substituents are bulky. In the synthesis of 7-cyclohexylbenz[a]anthracene Delia (26) isolated about 32% of benz[a]anthracene and attributed this observation to steric hindrance involving the 6 and 8 peri hydrogens of the

^aThroughout this thesis a Micro-Tek GC-2500R gas chromatography unit equipped with an ionization detector was used.

benz[a]anthracene moiety and the bulky cyclohexyl substituent. Similar results have been observed (27) in the case of 12-(ortho substituted phenyl)benz[a]anthracene. In this case the steric interaction involves the 12-substituent and the benz group of the benz[a]anthracene moiety. In the case of 12-(2-chloro-5-methylphenyl)benz[a]anthracene the 12-substituent is very bulky and for this reason cleavage should not be totally unexpected. Because of the reasons just stated it was suspected that the first peak in the chromatogram of the product of the cyclodehydration of ketone 20 was benz[a]anthracene. To confirm the suspicion a pure sample of benz[a]anthracene was characterized using identical conditions as those used for the product of the cyclodehydration of ketone 20. The retention time of pure benz[a]anthracene was identical with that of the first peak of the chromatogram of the cyclodehydrated product of ketone 20. Since this method of cyclodehydration offered good yields, short reaction time and the crude product could easily be reisolated pure enough to be used in the next reaction, it was decided to use this method to

prepare enough 12-(2-chloro-5-methylphenyl)benz[a]-anthracene to study the cyclodehydrohalogenation reaction. The ketone 20 could also be cyclodehydrated using the standard glacial acetic acid-hydrobromic acid mixture and the sealed tube technique. This reaction suffered the disadvantage of poorer yields (69%), longer reaction time (10 hours) and a crude product which could only be purified with difficulty. Ketone 20 could also be cyclodehydrated using phenyl acid phosphate; the yields were not very good (63%), although the reaction time was only two hours. The product, a yellow-green glass, isolated from the two latter methods could not be crystallized using a variety of solvents and solvent mixtures. The gas chromatogram of the product of the two latter methods showed identical retention time with that of the chromatogram of the cyclodehydration using the acetic acid-hydriodic acid mixture.

Attempted Cyclodehydrohalogenation of 12-(2-chloro-5-methylphenyl)benz[a]anthracene (21).

Cyclodehydrohalogenation reactions have been used (8,30) to synthesize polynuclear hydrocarbons

unequivocally. Clar et al. (30) have worked on this field with some degree of success. They have used potassium hydroxide and quinoline to bring about cyclodehydrohalogenation (30); in This Laboratory Mahone (8) has had success using this method. With this in mind it was hoped to synthesize 2-methyl-dibenzo[a,1]pyrene unequivocally by cyclodehydrohalogenating 12-(2-chloro-5-methylphenyl)-benz[a]anthracene. The reaction appeared straightforward and success was expected. Using the potassium hydroxide method from very mild to drastic conditions led only to recovery of starting material or complete destruction of starting material. When 12-(2-chloro-5-methylphenyl)benz[a]anthracene was added to potassium hydroxide and quinoline and the mixture allowed to reflux for 30 minutes 80% of starting material was recovered. The rest of the starting material was destroyed. Tar could be observed as a dark brown band at the top of the alumina column used to purify the reaction mixture. When more drastic conditions were used, heating to 300° for five hours in an autoclave, no starting material was recovered; only tars could be

isolated. The cases mentioned are extreme cases. Reactions with conditions intermediate with the ones mentioned only yielded recovery of starting material in varying amounts. Since this method did not yield satisfactory results, attention was turned to alkoxides, such as ethoxide. This type of reaction also led to the recovery of starting material and no formation of the desired product, 2-methyldibenzo[a,1]pyrene. The material isolated from the potassium hydroxide-quinoline and alkoxide reactions was analyzed using the gas chromatographic technique. Since the product from the cyclodehydrogenation of 12-(3-methylphenyl)benz[a]-anthracene, 2-methyldibenzo[a,1] pyrene or 4-methyldibenzo[a,1]pyrene, was characterized gas chromatographically, the retention time of 2 or 3 was known. Under the conditions used the retention time of 2 and 3 should be very close to each other. Therefore, it is not essential to know which isomer was actually isolated in the cyclodehydrogenation of 1. The chromatogram of the semi-crude reaction mixture of the above mentioned reactions did not have any peaks around the time in which the dibenzopyrene

was expected to elute. The results of the experiments suggested that a new approach to the problem be considered.

Since the cyclodehydrohalogenation could not be accomplished using basic conditions, it was hoped that a Lewis acid such as anhydrous aluminum chloride would catalyze the removal of hydrogen chloride. This approach proved to be worse since it led not only to unsatisfactory results, but it also destroyed the starting material in reaction times as short as five minutes. 12-(2-Chloro-5-methylphenyl)benz[a]anthracene dissolved in anhydrous benzene was allowed to react with anhydrous aluminum chloride in reaction times varying from five hours to five minutes. In each case the starting material was destroyed and no evidence of the desired material, 2-methyldibenzo[a,1]pyrene, could be detected. Since aluminum chloride destroyed the starting material, attention was turned to a milder Lewis acid, stannic chloride. Using stannic chloride as a catalyst led to the recovery of starting material (60%) and tar formation. Since aluminum chloride destroyed the starting

material and stannic chloride destroyed only part of the starting material, it was decided to perform an experiment using an aluminum chloride-stannic chloride mixture. The experiment led to the destruction of the starting material. No evidence of 2-methyldibenzo[a,1]pyrene was observed.

Although the right conditions for the cyclodehydrohalogenation of 12-(2-chloro-5-methylphenyl)benz[a]anthracene were not found, the data obtained during the gas chromatographic studies are very valuable since it can be used for other phases of the work being done in This Laboratory.

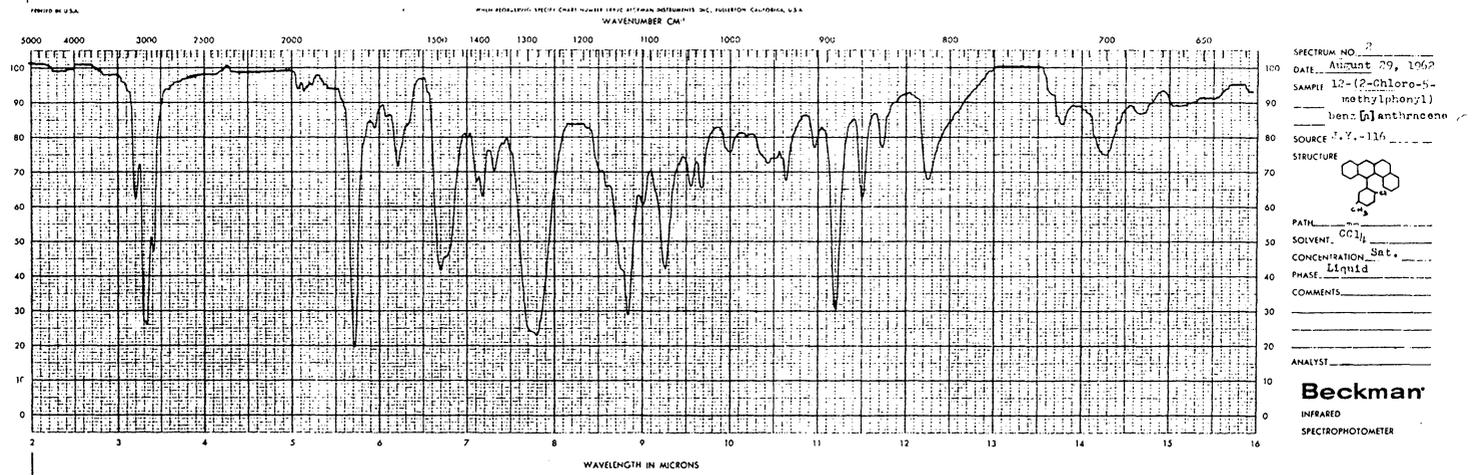
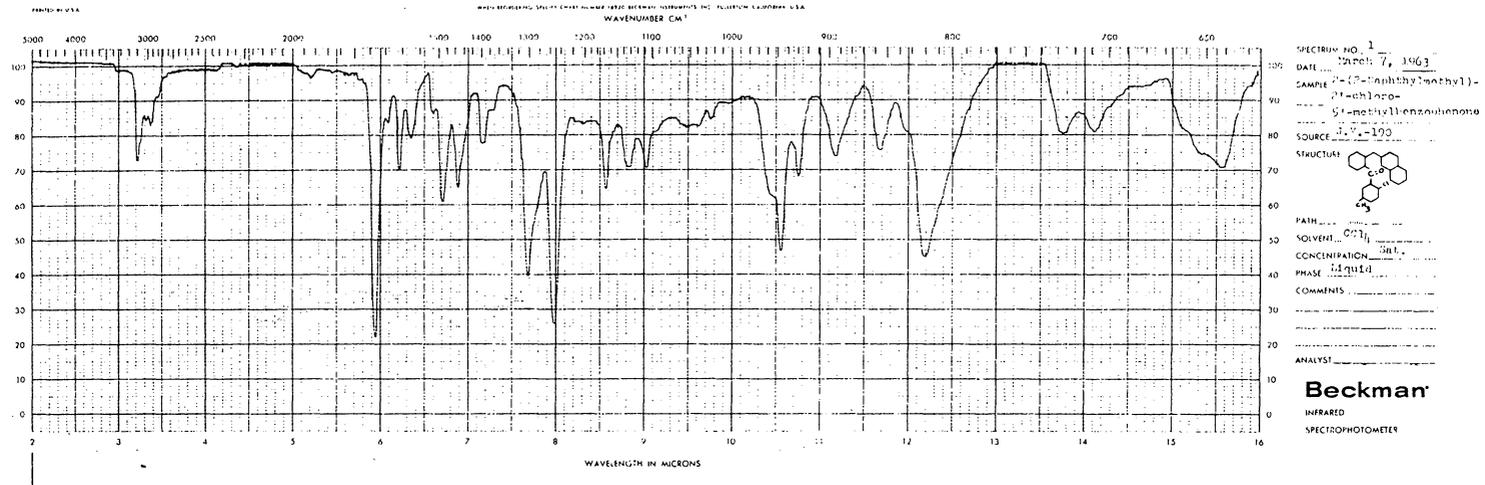


Figure 1

Beckman DK-2 CHART

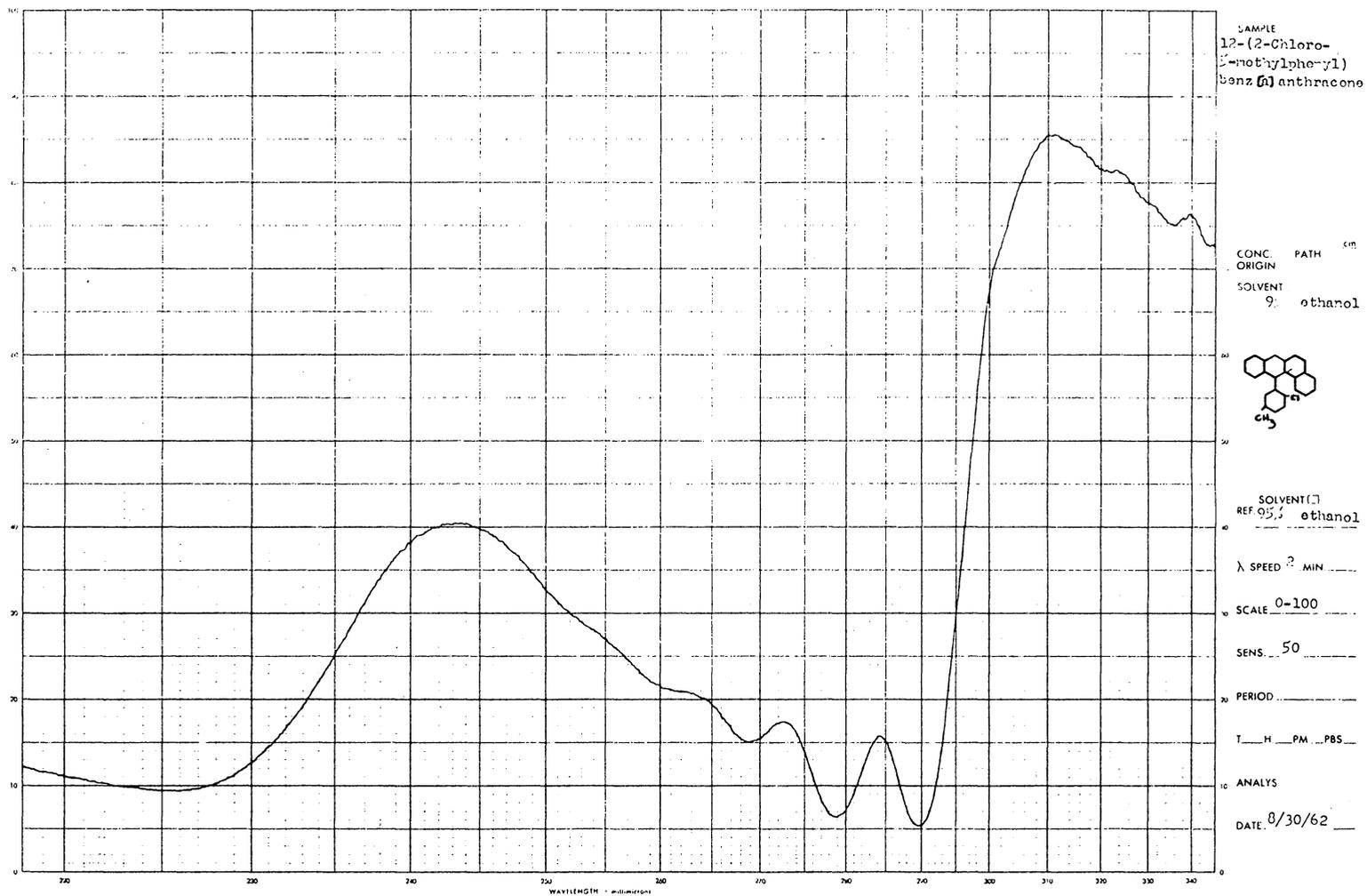


Figure 2

EXPERIMENTAL

EXPERIMENTAL^{a,b,c}

2-Bromonaphthalene (17) (12).

In a two gallon beaker fitted with a mechanical stirrer 446 g. (2 mole) of 2-naphthylamine-1-sulfonic acid was dissolved in 3600 ml. of aqueous sodium hydroxide (2.05 mole). An aqueous solution of 138 g. (2 mole) of sodium nitrite was then added. The resulting solution was filtered and added drop-wise into a five gallon jar, insulated and fitted with a mechanical stirrer, containing 1000 ml. of 37% hydrobromic acid and crushed ice. During the addition the temperature was kept at 0-5° by constantly adding crushed ice. The diazonium salt that forms was collected in a Buchner funnel, washed with a liter of iced water and pressed dry. While the diazotization was in progress, cuprous bromide was prepared. To a solution of 1200 g. (4.8 mole) of

^aAll melting points were taken on a Fisher-Johns melting point block and are corrected.

^bThe elemental analysis of new compounds was done by Galbraith Laboratories, Knoxville, Tennessee.

^cAll temperatures are expressed in degrees Centigrade.

cupric sulfate and 2000 ml. of water 700 g. (6.8 mole) of sodium bromide was added. While stirring, 302 g. (2.4 mole) of sodium sulfite was added over a period of ten minutes. Then an excess of sodium sulfite was added until the blue color disappeared. The mixture was allowed to cool to room temperature. The precipitate, cuprous bromide, was collected in a Buchner funnel and washed with cold water. The cuprous bromide was placed in a five gallon jar, fitted with a stirrer, and a solution of 300 ml. of 48% hydrobromic acid and 800 ml. of water was added. While stirring, the diazonium salt was added portion-wise to the cuprous bromide suspension. When all the diazonium salt had been added the mixture was heated in a steam bath until the evolution of nitrogen had subsided. The resulting hot mixture was filtered through a Buchner funnel while hot. The filtrate was placed in a 4000 ml. beaker which contained 450 g. of potassium bromide; the mixture was stirred until it turned into a paste. The paste was allowed to cool to room temperature; then filtered through a Buchner funnel. The crude 2-bromo-1-naphthalene-sulfonic acid which was collected in the Buchner

funnel was washed with one liter of a 20% aqueous potassium bromide solution and pressed dry. The crude 2-bromo-1-naphthalenesulfonic acid was air dried over-night. The crude 2-bromo-1-naphthalenesulfonic acid was placed in a 3-neck 5-liter round bottom flask, which was equipped with a mechanical stirrer and a reflux condenser. Then 800 g. of crushed ice and 800 ml. of concentrated sulfuric acid were added. The mixture was refluxed 16 hours. The mixture was allowed to cool to room temperature; the precipitated 2-bromonaphthalene was filtered and washed with water to remove the acid. The acid solution was extracted once with benzene. The benzene layer was separated and washed with water until all the acid had been removed. The benzene solution was dried over magnesium sulfate and concentrated. The 2-bromonaphthalene which was obtained upon concentration of the benzene solution was combined with the filtered 2-bromonaphthalene. The crude product was distilled under vacuum, b.p. 120-121° at 5 mm. The yield of 2-bromonaphthalene was 244 g., 59%. The 2-bromonaphthalene which solidified upon cooling had a yellow color. The product was dissolved in

500 ml. of normal-hexane and passed through an acid alumina (activity I, 80-200 mesh) column which was wet-packed with normal-hexane. An additional three liters were used to wash the column. The solution was concentrated to dryness and the resulting white flaky 2-bromonaphthalene (243 g., 59%) melted at 56.5-57°, (Lit. [11] m.p. 56.8-57°).

2-Bromotoluene (31).

A solution of 162 g. (1.5 mole) of commercial o-toluidine in 880 ml. (6 mole) of 40% hydrobromic acid in a three-liter flask was cooled and kept below 10° throughout the experiment. The solution was diazotized with 116 g. (1.7 mole) of sodium nitrite, added about 10 g. at a time. After each addition the flask was stoppered and shaken until all the red fumes were absorbed. When the diazotization was complete, 5 g. of copper powder was added; the flask was attached to a reflux condenser and allowed to stand in the ice bath until the evolution of nitrogen had subsided; the mixture was heated in a steam bath for half-an-hour. Then one liter of water was added and the mixture steam distilled until about three liters of distillate had

been collected. The distillate was made alkaline with 10 g. of powdered sodium hydroxide and the red bottom layer of crude 2-bromotoluene was separated. About 140 g. of the crude 2-bromotoluene was washed with concentrated sulfuric acid, which removed most of the color, and twice with water. The crude 2-bromotoluene was dried over magnesium sulfate and distilled. The yield of the fraction boiling at 176-180° was 101 g. (39%), (Lit. [31] b.p. 178-181°; 110-120 g., 42-47%).

2-Bromobenzyl Bromide (24) (15).

A solution of 171 g. (mole) of 2-bromotoluene and 4.4 g. of benzoyl peroxide in 350 ml. of anhydrous benzene, in a five-liter three-neck flask fitted with a mechanical stirrer and an efficient reflux condenser, was brought to a vigorous boil. A mixture of 178 g. (1 mole) of N-bromosuccinimide and 4.4 g. of benzoyl peroxide was added portion-wise and as fast as the foaming allowed. When all the powder had been added and the foaming had subsided, the reaction mixture was cooled first in a water bath then in an ice bath. The succinimide was filtered and washed with 200 ml. of anhydrous benzene. The benzene was removed using a flash evaporator. The crude product was distilled

under reduced pressure. A colorless product (200 g., 80%) which distilled at 100-110° at 3 mm. was collected (12).

2-Bromobenzaldehyde (18) (16).

A solution of 11.5 g. (0.50 mole) of sodium and 500 ml. of absolute ethanol was added to a one-liter three-neck flask equipped with a reflux condenser and a mechanical stirrer. The solution was allowed to cool to room temperature. Then 46 g. (0.52 mole) of 2-nitropropane followed by 125 g. (0.50 mole) of 2-bromobenzyl bromide was added. The reaction mixture was stirred for 18 hours. The sodium bromide was removed by filtration and the ethanol was removed in a flash evaporator. The residue which contained sodium bromide and product was dissolved in 100 ml. of ethyl ether and 150 ml. of water. The layers were separated; the ether layer was washed with two 50 ml. portions of 10% sodium hydroxide to remove any acetoxime and excess 2-nitropropane. The ether layer was then washed with 50 ml. of water. The ether solution was dried over magnesium sulfate. The ether was removed in a flash evaporator and the resulting oil distilled under reduced

pressure. 2-Bromobenzaldehyde (64 g., 69%) was collected at 117-119° at 12 mm. (Lit. [14] 118-119°, 12 mm.).

2-(2-Naphthylmethyl)bromobenzene (19) (32).

A Grignard reagent was prepared from 24.3 g. (1 mole) of magnesium turnings and 200 g. (0.96 mole) of 2-bromonaphthalene in 500 ml. of anhydrous ether. When the reaction was complete, one milliliter of the Grignard reagent was quenched in standardized sulfuric acid; the excess acid was titrated with standardized sodium hydroxide. The Grignard reagent formed in 85% yield. Then 152 g. (0.864 mole) of 2-bromobenzaldehyde was added drop-wise to the Grignard reagent. The reaction mixture was refluxed for two hours and allowed to stir over-night. The reaction mixture was decomposed with 20% aqueous ammonium chloride. The aqueous layer was removed and the ether layer washed with water and dried over magnesium sulfate. The solution was concentrated and distilled under reduced pressure. An oil (168 g.) boiling at 185-196° at 0.25 mm. was collected. The oil was dissolved in anhydrous ether and added drop-wise to

a mixture of 31.6 g. (0.834 mole) of lithium aluminum hydride and 222 g. (1.665 mole) of aluminum chloride in 500 ml. of anhydrous ether (33). The reaction mixture was refluxed for two hours and the excess lithium aluminum hydride was decomposed with ethyl acetate. The mixture was then poured into 2000 ml. of sulfuric acid solution. The layers were separated; the ether layer was washed with water and dried over magnesium sulfate. 2-(2-Naphthylmethyl)bromobenzene (113 g., 44%) boiled at 188-190° at 0.5 mm. (Lit. [32] b.p. 230-240°, 2 mm.).

2-Chloro-5-methylbenzoic Acid (28) (20).

A mixture of 50 g. (0.395 mole) of p-chlorotoluene and 150 ml. of anhydrous carbon disulfide was placed in a one-liter three-neck round bottom flask equipped with a mechanical stirrer and a reflux condenser connected to a water trap. The mixture was cooled to ice bath temperature then 50 g. (0.395 mole) of oxalyl chloride was added. The solution was allowed to stir for a while then 60 g. (0.43 mole) of aluminum chloride was added in two equal portions. The second portion was added when the vigorous reaction of the first portion had subsided. The mixture was allowed to stir for

24 hours. At the end of 24 hours the reaction mixture was cooled to ice bath temperature again. The cold reaction mixture was slowly poured into a four-liter beaker containing 150 g. of ice, 100 ml. of water and 20 ml. of concentrated hydrochloric acid. The mixture was stirred until all the aluminum compounds had dissolved; then it was extracted with ether. The ether solution was extracted twice with 50 ml. of 10% sodium hydroxide. The solution was made acid to pH 1-2 with concentrated hydrochloric acid. The precipitated acid was filtered and dried (36 g., 54%) in a vacuum desiccator; the acid was recrystallized from 95% ethanol, m.p. 161-162° (Lit. [20] m. p. 162-163°).

2-Chloro-5-methylbenzoyl Chloride (29) (20).

A mixture of 19 g. (0.112) mole of 2-chloro-5-methylbenzoic acid and 20.9 g. (0.112 mole) of phosphorus pentachloride was placed in a 100 ml. round bottom flask fitted with a reflux condenser connected to a water trap. When the initial reaction had subsided the mixture was heated to 100° for five hours. The product, 2-chloro-5-methylbenzoyl chloride (20 g., 95%), was distilled and the fraction boiling at 130-132° at 20 mm. was collected.

2-(2-Naphthylmethyl)-2'-chloro-5'-methylbenzo-
phenone (20) (34).

A Grignard reagent was prepared from 2.9 g. (0.12 mole) of magnesium turnings and 35.8 g. (0.12 mole) of 2-(2-naphthylmethyl)bromobenzene in 250 ml. of anhydrous ether. The reaction mixture was allowed to reflux for five hours. The Grignard reagent was then transferred into a dropping funnel under nitrogen gas pressure and added slowly into a boiling solution of 23.28 g. (0.12 mole) of 2-chloro-5-methylbenzoyl chloride and 500 ml. of anhydrous benzene. The ether was allowed to distil and an additional 150 ml. of anhydrous benzene was added to the reaction mixture. The reaction mixture was allowed to reflux for four hours; it was decomposed by pouring it into a four-liter beaker containing 1000 g. of ice, 600 ml. of water and 120 ml. of concentrated sulfuric acid. The aqueous layer was removed and the organic layer was washed twice with a 10% sodium carbonate solution and twice with water. The organic layer was dried over magnesium sulfate and concentrated. The residue was distilled; yield 26 g. (57%), b.p. 250-253°, at 0.4 mm. The viscous yellow-green oil was crystallized

from 95% ethanol. The resulting crystals were further purified by passing them through a basic alumina column. After concentration a white oil was crystallized from 95% ethanol. An analytical sample was prepared from the resulting crystals, m.p. 104-105°.

Anal. Calcd. for $C_{25}H_{19}OCl$: C, 80.96; H, 5.16; Cl, 9.56. Found: C, 80.50; H, 5.38; Cl, 9.50.

12-(2-Chloro-5-methylphenyl)-7,12-dihydrobenz[a]-anthracene (36).

A solution of 1 g. (0.0026 mole) of 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone and 50 ml. of glacial acetic acid was placed in a Carius tube. To the solution 30 ml. of 45-47% hydriodic acid was added. The Carius tube was sealed and heated in an oven to 180° for eight hours. The tube was allowed to cool to room temperature. The white crystals that had separated were recrystallized from 95% ethanol, m.p. 161-162°; yield 0.6 g. (63%) (35).

12-(2'-Chloro-5-methylphenyl)benz[a]anthracene (21) (35).

A. Hydriodic acid and acetic acid (35).

A solution of 1 g. (0.0026 mole) of 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone and 55 ml. of

glacial acetic acid was placed in a carius tube. To the solution 30 ml. of 45-47% hydriodic acid was added. The Carius tube was sealed and heated in an oven to 180° for two hours. The tube was allowed to cool to room temperature. The white solid which formed was filtered and washed with water to remove excess acid. The product was distilled, b.p. 85-86° (0.3 mm.); yield 0.75 g. (80%).

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 85.09; H, 4.85; Cl, 10.05. Found: C, 85.44; H, 4.55; Cl, 10.17.

B. Hydrobromic acid and acetic acid (25).

A solution of 1 g. (0.0026 mole) of 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone and 50 ml. of glacial acetic acid was placed in a Carius tube. To the solution 30 ml. of 40% hydrobromic acid was added. The Carius tube was sealed and heated in an oven to 180° for ten hours. The tube was allowed to cool to room temperature. The red acid solution was neutralized with 20% sodium hydroxide and extracted with benzene. The black gummy residue at the bottom of the tube was dissolved in benzene. The benzene solutions were combined, washed with water and dried over magnesium sulfate. The product was adsorbed on

alumina; the thimble was placed in a Soxhlet extractor and the product extracted with petroleum ether. Yield 0.65 g. (69%).

C. Phenyl acid phosphate^a (37).

A mixture of 1 g. (0.0026 mole) of 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone and 6 g. of phenyl acid phosphate was heated to 125° for two hours. The mixture was allowed to cool to room temperature then water was added and a black gummy material separated. The gummy material was dissolved in benzene. The benzene solution was washed with water and dried over magnesium sulfate. The product was adsorbed on alumina. The thimble was placed in a Soxhlet extractor and the product extracted with petroleum ether. Yield (63%), 0.55 g.

^aThis substance was used as obtained from the Virginia-Carolina Chemical Company, Richmond, Virginia, without further purification. It is a light tan solid, m.p. 46-48°, and it is described by the manufacturer as a mixture of diphenyldihydrogen phosphate, phenyldihydrogen phosphate and varying amounts of polyphosphates.

Attempted Cyclodehydrohalogenation of 12-(2-Chloro-5-methylphenyl)benz[a]anthracene (21).

A. via Aluminum chloride.

A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 60 ml. of anhydrous benzene in a 100 ml. round bottom flask 6 g. of anhydrous aluminum chloride was added. The mixture was heated to 100° for five hours. The same experiment was repeated using reaction times of two hours and five minutes. In each case, the reaction mixture was allowed to cool to room temperature and decomposed with dilute hydrochloric acid. The layers were separated; the acid layer was extracted once with benzene. The benzene solutions were combined, washed with water and dried over magnesium sulfate. The solution was concentrated to about five ml. and eluted through a basic alumina column using petroleum ether as the eluant. Bands exhibiting blue and yellow fluorescence were formed. Upon concentration of each of the fractions an orange oil was obtained. Neither of the oils could be crystallized. The oils could not be characterized.

B. via Aluminum chloride-stannic chloride.

A mixture of 0.6 g. of anhydrous aluminum chloride, 0.5 g. of stannic chloride and 50 ml. of anhydrous benzene was placed in a 100 ml. round bottom flask. The mixture was allowed to reflux. Then a boiling solution of 0.5 g. (0.0014 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 25 ml. of anhydrous benzene was added to aluminum chloride-stannic chloride mixture. The reaction mixture was allowed to reflux for five minutes. The reaction mixture was allowed to cool to room temperature; then decomposed with dilute hydrochloric acid. The layers were separated; the benzene layer was washed with water and dried over magnesium sulfate. The benzene solution was concentrated to about two ml. and eluted through a basic alumina column using petroleum ether as the eluant. A blue fluorescing fraction and yellow fluorescing fraction were collected. The resulting oils, upon concentration, failed to crystallize. The oils could not be characterized.

C. via Stannic chloride.

To a solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 60 ml. of anhydrous

benzene in a 100 ml. round bottom flask 6 g. of anhydrous stannic chloride was added. The mixture was heated to 100° for five minutes and then allowed to cool to room temperature. The reaction mixture was decomposed with dilute hydrochloric acid; the layers were separated. The benzene layer was washed with water and dried over magnesium sulfate. The solution was concentrated to about five ml. and eluted through an alumina column using petroleum ether as the eluant. A band exhibiting blue fluorescence developed. The blue fluorescing fraction was collected and the solution concentrated; 0.6 g. of 12-(2-chloro-5-methylphenyl)benz[a]anthracene was recovered.

D. via Potassium hydroxide and quinoline (5).

1. To a solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 30 ml. of quinoline was added 20 g. of potassium hydroxide pellets. The mixture was allowed to reflux for half-an-hour. The reaction mixture was allowed to cool to room temperature and then poured into dilute hydrochloric acid solution. The acid solution was extracted with ethyl ether. The organic layer was washed with dilute hydrochloric acid, with water and

dried over magnesium sulfate. To the dry solution about 20 g. of acid alumina was added and then concentrated to dryness. The product was extracted from a Soxhlet extractor using petroleum ether as the eluant. Only a blue fluorescing color was observed. The solution was concentrated until a yellow-green oil remained. The oil could not be crystallized. The oil (0.8 g., 80%) was 12-(2-chloro-5-methylphenyl)-benz[a]anthracene.

2. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 30 ml. of quinoline was placed in an autoclave. To the solution 20 g. of potassium hydroxide pellets was added. The mixture was heated to 300° for five hours. The autoclave was allowed to cool to room temperature and dilute hydrochloric acid was added to the reaction mixture. The acid solution was then extracted with ethyl ether. The organic layer was washed with dilute hydrochloric acid twice, with water twice and dried over magnesium sulfate. To the dry solution acid alumina was added and concentrated to dryness. The product was extracted from a Soxhlet extractor using petroleum ether as the eluant. The resulting solution

was concentrated to about 25 ml. and passed through an acid alumina column using petroleum ether as the eluant. Bands exhibiting blue, green, purple and yellow fluorescence developed. A blue fluorescing fraction was removed using petroleum ether as the eluant. A second blue fraction was removed using a 4:1 mixture of petroleum ether and benzene. No other band could be removed. Upon concentration of the different fractions oils were obtained. The oils proved to be untractable mixtures which could not be identified.

3. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 30 ml. of quinoline was placed in an autoclave which contained 20 g. of potassium hydroxide pellets. The mixture was heated to 220° for three hours. The reaction mixture was worked up as shown above. The oils that were isolated could not be characterized.

4. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 30 ml. of quinoline was placed in an autoclave which contained 20 g. of potassium hydroxide pellets. The mixture was heated to 200° for two hours. The

reaction mixture was worked up as shown above. The oil which was isolated (0.6 g., 60%) was 12-(2-chloro-5-methylphenyl)benz[a]anthracene.

5. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 25 ml. of quinoline was brought to a reflux. To the refluxing solution 1 g. of potassium hydroxide pellets was added. Each pellet was added singly. The reaction mixture was allowed to reflux for eight hours. The reaction mixture was allowed to cool to room temperature and then poured into dilute hydrochloric acid. The acid solution was decanted and the tarry residue which remained in the flask was boiled with water. The water was allowed to cool and decanted off. The tarry residue was then boiled with dilute ammonium hydroxide solution. The ammonium hydroxide solution was decanted off and the tarry residue was air dried; the residue was then ground with acid alumina and chromatographed using petroleum ether as the eluant. Only one band developed, the band exhibiting blue fluorescence. The oil resulting from the concentration of the fraction was 12-(2-chloro-5-methylphenyl)benz[a]anthracene (0.3 g., 30%).

E. via Sodium ethoxide.

1. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 25 ml. of absolute ethanol was added to 75 ml. of absolute ethanol in which 6 g. (0.26 mole) of sodium had been dissolved. The solution was allowed to reflux for 15 hours. The reaction mixture was cooled to room temperature and poured into water and extracted with ethyl ether. The organic layer was washed with water and dried over magnesium sulfate. To the dry solution about 20 g. of acid alumina was added and concentrated to dryness. The product was extracted from a Soxhlet extractor using petroleum ether. The extract was concentrated until a yellow-green oil was obtained. The oil (1 g., 100%) was 12-(2-chloro-5-methylphenyl)benz[a]anthracene.

2. A solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)benz[a]anthracene and 5 ml. of absolute ethanol was poured into a 150 ml. round bottom flask which contained 75 ml. of absolute ethanol in which 5.3 g. (0.23 mole) of sodium had been dissolved. To the solution 25 ml. of glycerin was added. The reaction mixture was allowed to reflux

for three and a half hours. The reaction mixture was worked up as shown above. Upon extraction from the Soxhlet extractor the solution was concentrated to about 25 ml. and chromatographed through an acid alumina column using petroleum ether as the eluant. Only a band exhibiting blue fluorescence developed which upon collection and concentration yielded a yellow-green oil (0.7 g., 75%). The oil was 12-(2-chloro-5-methylphenyl)benz[a]anthracene.

Attempted Cyclodehydrohalogenation of 12-(2-chloro-5-methylphenyl)-7,12-dihydrobenz[a]anthracene (8).

To a solution of 1 g. (0.0028 mole) of 12-(2-chloro-5-methylphenyl)-7,12-dihydrobenz[a]anthracene and 30 ml. of quinoline was added 20 g. of potassium hydroxide pellets; the mixture was allowed to reflux for 30 minutes. The mixture was allowed to cool to room temperature and then poured into dilute hydrochloric acid. The acid solution was extracted with ethyl ether. The organic layer was washed with dilute hydrochloric acid, water and dried over magnesium sulfate. To the dry solution about 20 g. of acid alumina was added and then concentrated to dryness. The product was extracted from a Soxhlet

extractor by refluxing petroleum ether. The extract was then concentrated to about 25 ml. and chromatographed through an acid alumina column using petroleum ether as the eluant. Only a band exhibiting blue fluorescence developed. The fraction was collected and concentrated until an orange oil remained. The oil was dissolved in 95% ethanol and 0.08 g. of starting material was recovered, m.p. 161-162° and 0.81 g. of 12-(2-chloro-5-methylphenyl)benz[a]anthracene.

Gas Chromatographic Conditions

Gas chromatographic analysis was carried out in a Micro-Tek GE-2500R unit equipped with dual columns and an ionization detector. Conditions:

Packing	3.5% SE-30 on Gas-Chrom Z
Column length	4' x 1/4"
Column temperature	260°
Detector temperature	310°
Hydrogen flow rate	45 cc/min. (20 psig)
Helium flow rate	6.2 (rotameter reading), (40 psig)
Air flow rate	1.2 (rotameter reading), (20 psig)
Sensitivity	32 x 10 ²
Sample size	2-4 μ l
Sample concentration	25 μ g μ l ⁻¹

The packing was prepared by dissolving 1.75 g. of SE-30 in 1200 ml. of methylene chloride. The solute was then adsorbed on Gas-Chrom Z (48.25 g.) by slowly concentrating the solution to dryness. The columns were packed to constant weight with the aid of an aspirator and a vibrator. The vibrator was used to insure uniform packing.

SUMMARY

SUMMARY

The new ketone, 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone (20), was cyclodehydrated to the new 12-(2-chloro-5-methylphenyl)benz[a]anthracene (21) in a 2:1 mixture of glacial acetic acid and 45% hydriodic acid and heating in a sealed tube for two hours to 180°.

The purity of ketone 20 was determined by gas chromatographic analysis and its structure determined by elemental analysis and by its infrared absorption spectrum. The elemental analysis and ultraviolet spectral pattern of 21 are in accordance with the structure assigned to 21, 12-(2-chloro-5-methylphenyl)benz[a]anthracene.

Gas chromatographic studies were fruitful because conditions for the analysis of some aromatic polynuclear hydrocarbons have been established. The retention times of benz[a]anthracene, 12-(3-methylphenyl)benz[a]anthracene, 2-(2-naphthylmethyl)-2'-chloro-5'-methylbenzophenone and 12-(2-chloro-5-methylphenyl)benz[a]anthracene have been recorded.

Although the right cyclodehydrohalogenation conditions of 12-(2-chloro-5-methylphenyl)benz[a]-anthracene (21) using potassium hydroxide and quinoline, sodium ethoxide, aluminum chloride, stannic chloride, and aluminum chloride-stannic chloride mixture could not be found, gas chromatographic studies were fruitful.

LITERATURE CITED

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1. F. A. Vingiello and W. W. Zajac, J. Org. Chem., 26, 2228 (1961).
2. L. Fieser, in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 129-254.
3. J. Cook and H. Hewett, J. Chem. Soc., 398 (1933).
4. C. K. Bradsher, Chem. Revs., 38, 447 (1946).
5. E. Clar et al., J. Chem. Soc., 2652 (1956).
6. E. Clar and I. A. Macpherson, Tetrahedron, 18, 1411 (1962).
7. R. Scholl and C. Seer, Ann., 394, 111 (1912).
8. L. G. Mahone, M. S. Thesis, V. P. I. (1961).
9. E. Clar et al., Tetrahedron, 3, 325 (1958).
10. M. S. Newman and P. H. Wise, J. Am. Chem. Soc., 63, 2847 (1941).
11. W. C. Wolfe and H. H. Doukas, J. Chem. Ed., 28, 472 (1951).
12. P. Polss, Ph. D. Thesis, V. P. I. (1963).
13. O. L. Brady and J. K. Lahiri, J. Chem. Soc., 1954 (1934).
14. R. Adams and E. H. Volleweiler, J. Am. Chem. Soc., 40, 1732 (1918).
15. E. Campaign and B. F. Tuller, "Organic Syntheses," 33, 96 (1953).
16. H. B. Hass and M. L. Bender, "Organic Syntheses," 30, 99 (1950).

17. E. S. Gould, "Mechanisms and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 296.
18. R. J. Light, B. S. Thesis, V. P. I. (1957).
19. G. J. Buese, M. S. Thesis, V. P. I. (1951).
20. R. S. Scholl, K. Meyer and A. Keller, *Ann*, 513, 295-304 (1934).
21. C. K. Bradsher and F. A. Vingiello, *J. Am. Chem. Soc.*, 71, 1434 (1949).
22. F. A. Vingiello, J. G. Van Oot and H. H. Hannabas, *ibid.*, 74, 4546 (1952).
23. F. A. Vingiello and J. G. Van Oot, *ibid.*, 73, 5070 (1951).
24. J. E. Bondurant, M. S. Thesis, V. P. I. (1950).
25. F. A. Vingiello, M. O. L. Spangler and J. E. Bondurant, *J. Org. Chem.*, 25, 2091 (1960).
26. F. A. Vingiello and T. J. Delia, *J. Org. Chem.*, 26, 1005 (1961).
27. F. A. Vingiello and A. Borkovec, *J. Am. Chem. Soc.*, 78, 3205 (1956).
28. C. K. Bradsher and D. J. Beavers, *J. Am. Chem. Soc.*, 78, 3193 (1956).
29. G. B. Vaughan, Private Communication.
30. E. Clar *et al.*, *J. Chem. Soc.*, 2655 (1956).
31. L. A. Bigelow, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 9 (1929), pp. 22-24.
32. C. K. Bradsher, *J. Am. Chem. Soc.*, 62, 1077 (1940).

33. J. Blackwell and U. J. Hickinbotton, J. Chem. Soc., 1405 (1961).
34. C. K. Bradsher and F. A. Vingiello, J. Org. Chem., 13, 786 (1948).
35. L. Ojakaar, M. S. Thesis, V. P. I. (1961).
36. F. A. Vingiello and A. Borkovec, J. Am. Chem. Soc., 77, 4823 (1955).
37. M. O. L. Spangler, Ph. D. Thesis, V. P. I. (1959).

VITA

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ABSTRACT

In the study of the cyclodehydrogenation of 12-(3-methylphenyl)benz[a]anthracene, Zajac pointed out that the hydrocarbon might undergo ring closure at either of the ortho positions of the phenyl ring. These positions are not equivalent with respect to the methyl group and ring closure might yield either 2-methyldibenzo[a,1]pyrene or 4-methyldibenzo[a,1]pyrene or a mixture of both isomers.

When the compound, 12-(3-methylphenyl)benz[a]anthracene, was dehydrogenated only one isomer was isolated. The isomer which was isolated could be either of the two possibilities. Therefore, it was decided to synthesize 2-methyldibenzo[a,1]pyrene unequivocally. By comparing the physical properties of the compound synthesized unequivocally with those of the compound from the cyclodehydrogenation of 12-(3-methylphenyl)benz[a]anthracene it can be determined which isomer was isolated by Zajac. Therefore, 12-(2-chloro-5-methylphenyl)benz[a]anthracene was synthesized; this compound could then be cyclodehydrohalogenated to the corresponding 2-methyldibenzo[a,1]pyrene. Using potassium

hydroxide-quinoline and alkoxides led only to the recovery of starting material or to the destruction of it, depending on whether the reaction conditions were mild or drastic. Aluminum chloride destroyed the starting material in reaction time as short as five minutes. Stannic chloride destroyed only part of the starting material. An aluminum chloride-stannic chloride mixture also destroyed the starting material. In none of the experiments mentioned could the presence of 2-methyldibenzo[a,1]pyrene be detected. Although the right conditions for the cyclodehydrohalogenation were not found, the data obtained during the gas chromatographic studies are very valuable because it can be used for the other phases of the work being done in This Laboratory.