

SYNTHESIS OF SOME NEW
SUBSTITUTED DIBENZO(a,e)FLUORANTHENES

by

Abdullatif K. Youssef, B.S.

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APPROVED:

Chairman, Dr. Frank A. Vingiello

Dr. J. F. Wolfe

Dr. J. G. Mason

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TABLE OF CONTENTS

	Page
I. INTRODUCTION.	2
II. NOMENCLATURE.	5
III. HISTORICAL.	7
IV. DISCUSSION OF RESULTS	15
A. Preparation of Starting Materials	15
1. The required ketones	15
2. 7-(Monomethyl and dimethylphenyl)benz(a)- anthracenes	19
3. 7-(Halophenyl)benz(a)anthracenes.	21
B. Rearrangement of 12-Phenylbenz(a)anthracene	24
C. Cyclodehydrogenation Studies.	29
1. 7-(Monomethyl and dimethylphenyl)benz(a)- anthracenes	29
2. 7-(Halophenyl)benz(a)anthracenes.	37
D. Spectral Correlations	41
1. Infrared Spectra.	41
2. Ultraviolet Spectra	41
V. EXPERIMENTAL.	46
A. General	46
B. Preparation of Starting Materials	47
C. Cyclodehydrogenations	51
VI. SUMMARY	82
VII. APPENDIX.	85
VIII. LITERATURE CITED.	106
IX. VITA.	111

This work is gratefully dedicated to

My Parents

since they provided all kinds of
encouragement and all the possibilities
to finish this step in my life.

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SPECTRA IN THE APPENDIX

No.		Page
	Ultraviolet Spectra	
1.	7-(3-Fluorophenyl)benz(a)anthracene.	85
2.	7-(4-Fluorophenyl)benz(a)anthracene.	85
3.	7-Fluorodibenzo(a,e)fluoranthene	86
4.	8-Fluorodibenzo(a,e)fluoranthene	86
5.	7-Chlorodibenzo(a,e)fluoranthene	87
6.	8-Chlorodibenzo(a,e)fluoranthene	87
7.	7-Bromodibenzo(a,e)fluoranthene.	88
8.	Dihydro-7-methyldibenzo(a,e)fluoranthene	88
9.	7-Methyldibenzo(a,e)fluoranthene	89
10.	8-Methyldibenzo(a,e)fluoranthene	89
11.	9-Methyldibenzo(a,e)fluoranthene	90
12.	Dihydrodibenzo(a,e)fluoranthene.	90
13.	Dibenzo(a,e)fluoranthene	91
14.	7,9-Dimethyldibenzo(a,e)fluoranthene	91
15.	8,9-Dimethyldibenzo(a,e)fluoranthene	92
16.	7,8-Dimethyldibenzo(a,e)fluoranthene	92
17.	6,8-Dimethyldibenzo(a,e)fluoranthene	93
	Infrared Spectra	
18.	2-(1-Naphthylmethyl)-3-fluorobenzophenone.	94
19.	2-(1-Naphthylmethyl)-4-fluorobenzophenone.	94
20.	7-Bromodibenzo(a,e)fluoranthene.	95
21.	8-Chlorodibenzo(a,e)fluoranthene	95

No.		Page
22.	7-Chlorodibenzo(a,e)fluoranthene.	96
23.	7-(4-Fluorophenyl)benz(a)anthracene	96
24.	7-(3-Fluorophenyl)benz(a)anthracene	97
25.	8-Fluorodibenzo(a,e)fluoranthene.	97
26.	7-Fluorodibenzo(a,e)fluoranthene.	98
27.	9-Methyldibenzo(a,e)fluoranthene.	98
28.	8-Methyldibenzo(a,e)fluoranthene.	99
29.	7-Methyldibenzo(a,e)fluoranthene.	99
30.	Dihydrodibenzo(a,e)fluoranthene	100
31.	8,9-Dimethyldibenzo(a,e)fluoranthene.	100
32.	7,9-Dimethyldibenzo(a,e)fluoranthene.	101
33.	6,8-Dimethyldibenzo(a,e)fluoranthene.	101
34.	7,8-Dimethyldibenzo(a,c)fluoranthene.	102
35.	Dihydro-7-methyldibenzo(a,e)fluoranthene.	102

Nuclear Magnetic Resonance Spectra

36.	Dihydrodibenzo(a,e)fluoranthene	103
37.	Dihydro-7-methyldibenzo(a,e)fluoranthene.	104

INTRODUCTION

I. INTRODUCTION

Cancer has afflicted mankind from pre-historic times. The first realization that it might be due to external factors and not to the "wrath of God" followed the publication by Sir Percival Pott of "Surgical observations" in 1775, in which he reported high incidence of scrotal cancer in chimney sweeps. This clearly indicated the presence of some carcinogenic factors in soot.

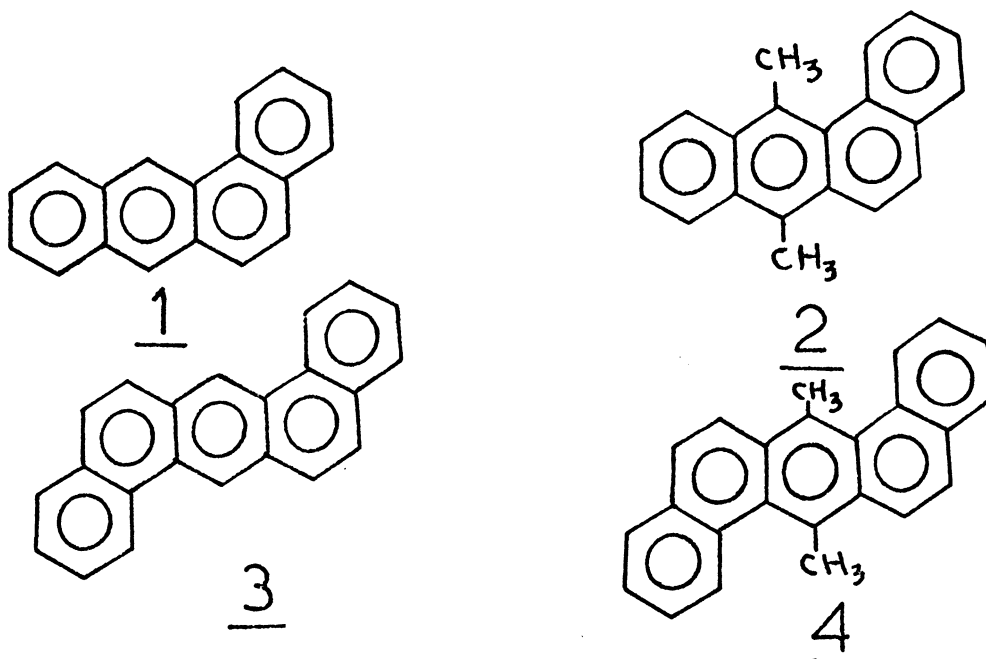
Japanese workers were the first to succeed in inducing skin tumors by repeated applications of tar to the skin of experimental animals. Yamagiwa and Ishikawa¹ used rabbits and Tsutsui² used mice.

After their success, the next logical step was the determination of the active material in coal tar. Recent studies on the environment and health aspects of air pollution have unveiled the fact that the organic fraction of air pollutants contain polycyclic aromatic hydrocarbons³. Some of them are known carcinogens, others unknown compounds.

The discovery of the relationship between polycyclic aromatic hydrocarbons and carcinogenic activity was paramount in stimulating the already increasing research in the field of polycyclic aromatic hydrocarbons.

Great interest has been placed on compounds containing the basic carbon skeleton of benz(a)anthracene, since the structure is common to many polycyclic aromatic hydrocarbons which are carcinogenic. J. W. Cook⁴ demonstrated that benz(a)anthracene itself exhibits very weak carcinogenic properties.

The substitution of certain groups (methyl or phenyl) into the benz(a)anthracene structure produces compounds which are strongly carcinogenic such as 7,12-dimethylbenz(a)anthracene, dibenz(a,h)anthracene, and 7,12-dimethyldibenzo(a,h)anthracene.



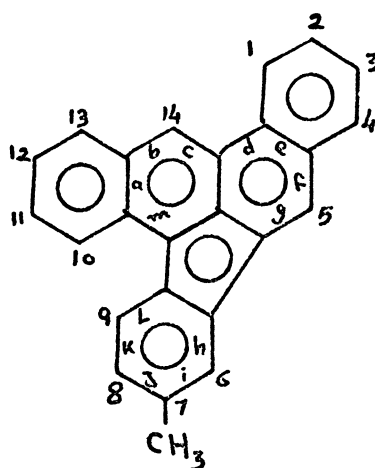
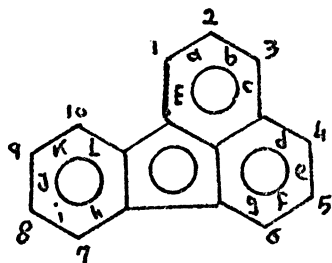
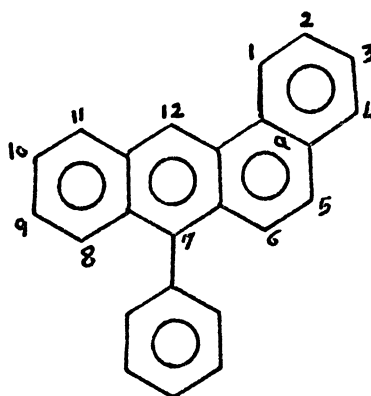
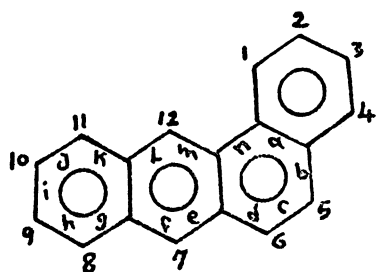
In 1951 Clar⁷ reported the synthesis of dibenzo(a,l)pyrene via 12-phenylbenz(a)anthracene. It proved to be very strongly carcinogenic. The fact that the compound Clar synthesized was a very strong carcinogen led other workers to synthesize derivatives of dibenzo(a,l)pyrene using a method similar to Clar's and to test them for carcinogenic activity.

In a rather startling paper in 1966, D. Lavit-Lamy and N. P. Buu-Hoi⁵ reported that the product previously reported by Clar as dibenzo(a,l)pyrene was in fact dibenzo(a,e)fluoranthene. We have recently supported this report by experimental data⁶ (see Chart V), so the object of this investigation was to synthesize some derivatives of dibenzo(a,e)fluoranthene for obvious reasons.

NOMENCLATURE

II. NOMENCLATURE

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



HISTORICAL

III. HISTORICAL

Since the discovery of naphthalene in the early 19th Century over 200 individual compounds have been isolated from coal tar. Some of these compounds have been found to have carcinogenic activity.

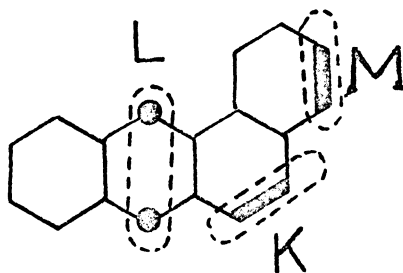
In 1915 the Japanese workers Yamagiwa and Ishikawa¹ succeeded in inducing skin tumours by repeated applications of tar to the skin of rabbits, and Kennaway⁸ was able to produce carcinogenic tars from organic materials such as human tissue, cholesterol, etc. He was the first scientist to produce tumours in mice with a synthetic polycyclic aromatic hydrocarbon, dibenzo(a,h)anthracene (prepared by Clar's method⁹).

Among more than 450 compounds which have been found to be carcinogenic, more than 200 compounds are polycyclic hydrocarbons. Polycyclic aromatic hydrocarbons have several features which distinguish them from many of the more recently discovered carcinogens. They act at the site of application, the effective dose is minute, and they have been found to induce tumours in almost every tissue and animal species in which they have been tested.

The observation by I. Heiger¹⁰ that coal tar which produced cancer most effectively had a characteristic fluorescence spectrum, with bands at 400, 418 and 444 mμ led others to examine a number of polycyclic compounds obtained from tar or by synthesis.

Sung¹¹ attempted to relate carcinogenicity with absorption spectra. Compounds with peaks in the absorption spectra below 354.5 mμ were non-carcinogenic, but 42% of the compounds with peaks in the absorption spectra above 354.5 mμ were carcinogenic. These included benzo(a)pyrene, cholanthrene, 20-methyl cholanthrene, and various benz(a)anthracenes.

Many attempts to correlate carcinogenic potency with the electronic configuration of polycyclic aromatic hydrocarbons originated in 1928 with Otto Schmidt¹² and were extended by Pullman¹³ and his co-workers. They concluded that in carcinogenic molecules, the bond order of the phenanthrenoid bond, called K or Krebs region, was taken as a model for the attachment of cell constituents to the hydrocarbons. In a series of polycyclic hydrocarbons good correlation has been found between the calculated values for the "bond order" of the K region and the rate of addition of osmium tetroxide¹⁴. Badger¹⁴ suggested that the phenanthrenoid 9,10 bond is necessary for carcinogenic activity. But in fact this is not so, because there are compounds which are carcinogenic which do not possess a free phenanthrenoid bond, e.g., 9,10-dimethylantracene.

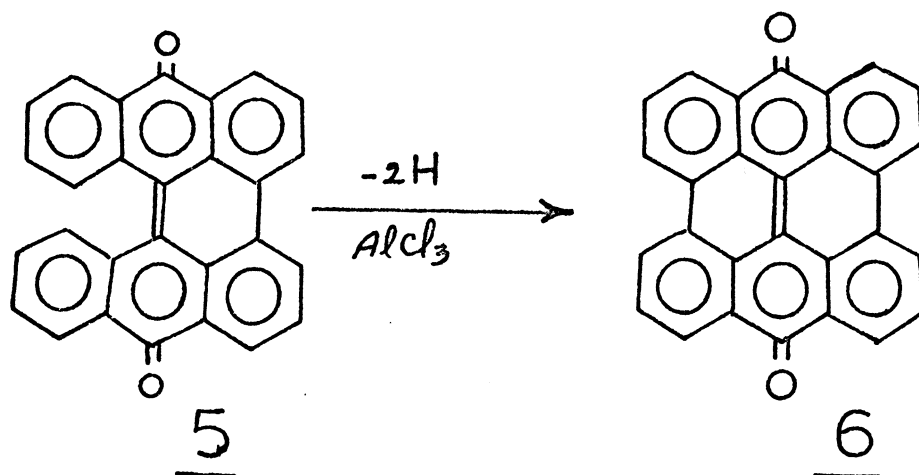


A number of polycyclic aromatic hydrocarbons have been synthesized in connection with intensive cancer research that is being done at the present time. One of the useful methods used in this investigation is "aromatic cyclodehydrogenation"¹⁹.

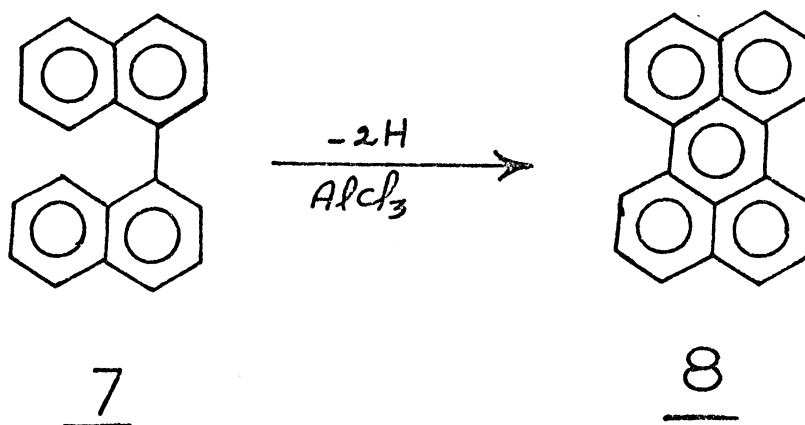
Cyclodehydrogenation reactions, usually catalyzed by anhydrous aluminum chloride, have been known for years and have been used profitably to synthesize hydrocarbons.

The first instance of using a chemical agent as a cyclodehydrogenation agent was reported by Scholl and Mansfield²⁰. They observed that meso-benzodanthrone (5) was converted to meso-dinaphthylanthrone

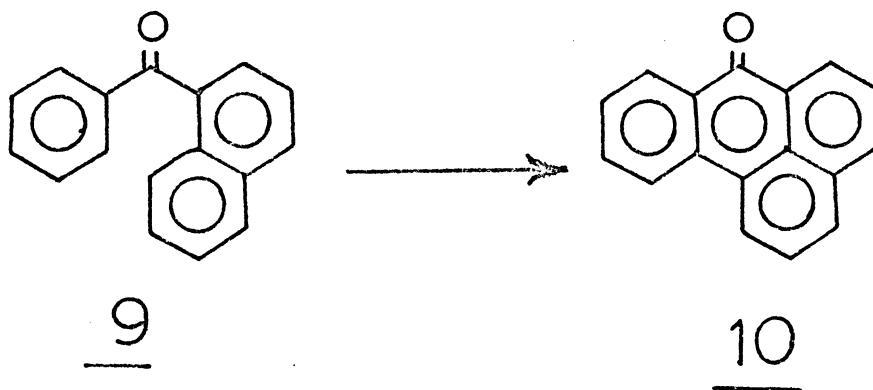
(6) upon treatment with aluminum chloride.



Another early instance of the union of aromatic nuclei by means of aluminum chloride at elevated temperature was the preparation of perylene (8) from 1,1'-dinaphthyl (7)



and benzoanthrone (10) from 1-benzoyl naphthalene (9).

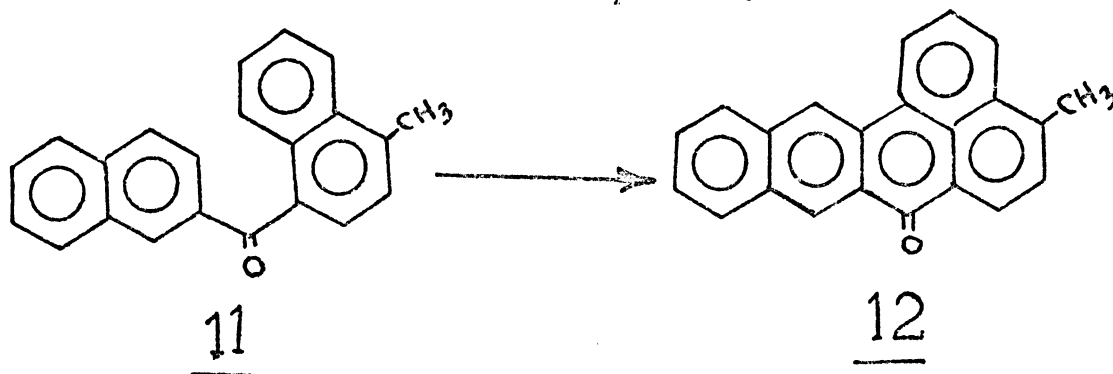


In 1883-5 Friedel and Crafts reported the formation of biphenyl from benzene and aluminum chloride. Homer²¹ also reported the formation of binaphthyl from naphthalene in the presence of aluminum chloride. Scholl examined these reactions more fully and found that by means of anhydrous aluminum chloride at 80-140°, aromatic nuclei can be successfully united with the formation of new rings, particularly in the case of aromatic ketones²² or quinones. The carboxyl group acts as a temporary acceptor for the hydrogen which then is removed by atmospheric oxygen.

Kränzlein²³ considered the Scholl reaction to be the intramolecular dehydrogenation of aromatic nuclei resulting in the formation of a condensed ring system under the influence of Friedel Crafts catalysts as aluminum chloride.

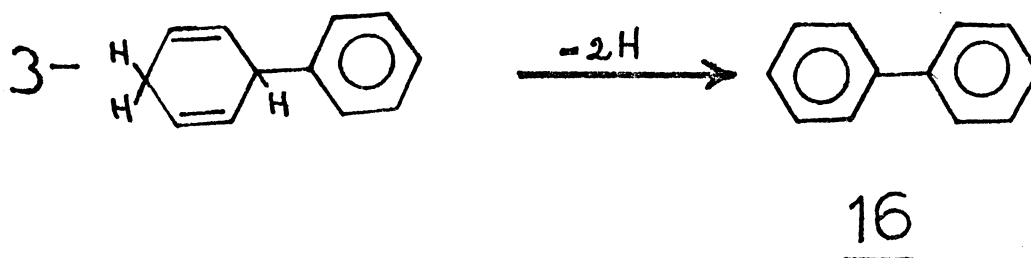
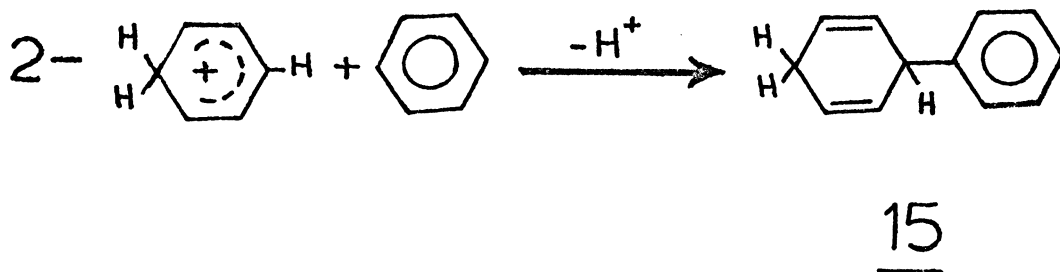
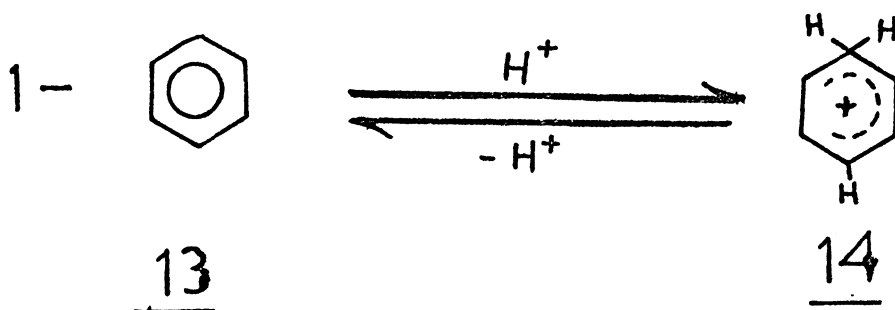
The elimination of two aryl-bond hydrogens accompanied by the formation of an aryl-aryl bond under the influence of Friedel-Crafts catalysts is known as the Scholl reaction²⁴.

An important contribution to the Scholl reaction came from Baddeley²⁵ when he showed that many reactions effected by aluminum chloride and other Friedel-Crafts reagents do not occur in the absence of hydrogen chloride or traces of water. Baddeley demonstrated this fact by studying the conversion of 4-methylnaphthyl 2-naphthyl ketone (11) to 4-methylbenzo(1)-benzanthrone (12) in chlorobenzene with a slight molar excess of aluminum chloride at room temperature.

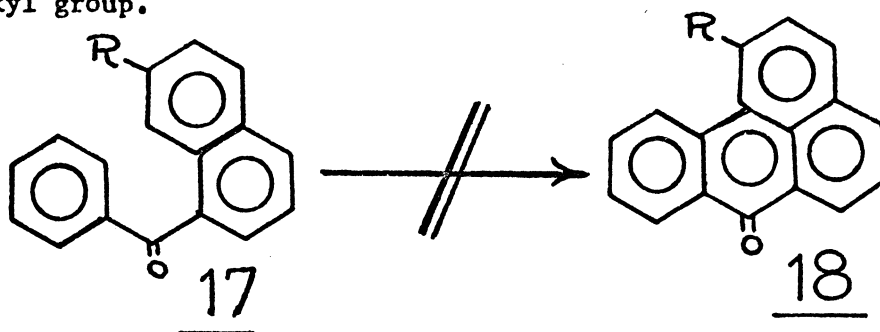


The conversion of 11 to 12 did not take place when a stream of dry nitrogen or oxygen was passed through the solution, but when a stream of hydrogen chloride was passed through the solution the reaction took place readily. The work of Brown, Olah and McCaulay explained the role of the hydrogen chloride in Baddeley's experiment and also supported the suggestion of Nenitzescu and Balaban that Friedel-Crafts acids such as hydrogen chloride - aluminum chloride and water-aluminum chloride protonate the aromatic system.

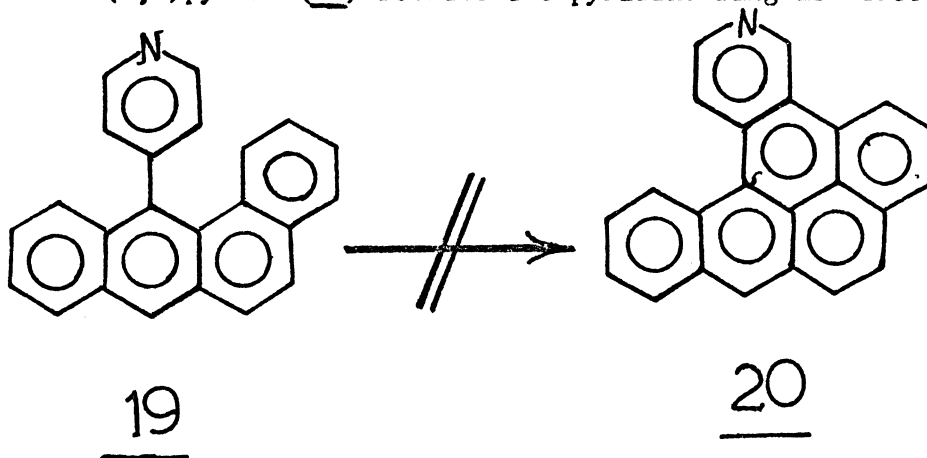
Nenitzescu and Balaban²⁶ proposed a mechanism for the Scholl reaction as follows:



(1)-The first step suggested for this mechanism is the protonation reaction. They suggested that the catalysts in the Scholl reaction are strong Friedel-Craft acids (hydrogen chloride - aluminum chloride or water - aluminum chloride) which are able to protonate the basic aromatic nucleus and form a sigma complex which can then attack an aromatic nucleus. (2)-The second step is the electrophilic substitution. Taking into consideration the steric factors as well as the different reactivities in various positions, 7-alkyl-1-benzoylnaphthalene (17)²⁷ can not be converted to benzanthrone 18 because of the steric hindrance of the alkyl group.

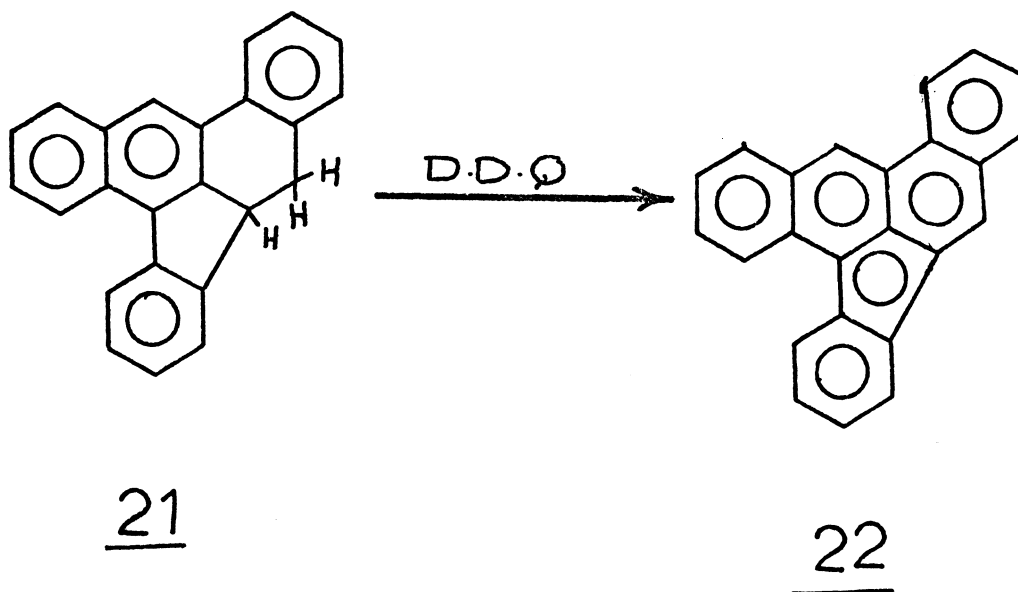


When the electron rich positions are involved, the reaction proceeds in good yield. 12-(4-Pyridyl)benz(a)anthracene (19)²⁹ did not cyclize to 14-azodibenzo(a,h)pyrene (20) because the pyridine ring is deactivated.



(3)-The third step is the dehydrogenation. In most cases it is difficult to separate the intermediate dihydro derivative. Usually the intermediate

dihydro derivative is dehydrogenated under the conditions of the reaction to the final product, as in the case of the preparation of diphenyl from benzene. With aluminum chloride the dihydro compound is not isolated because it is difficult to stop the reaction at this stage. But in some cases it is possible to isolate the dihydro derivative. For example, dihydrodibenzo(a,e)fluoranthene (21) can be isolated and then dehydrogenated to dibenzo(a,e)fluoranthene (22)³¹ using D.D.Q. (2,3-dichloro-5,6-dicyanobenzoquinone).



DISCUSSION OF RESULTS

IV. DISCUSSION OF RESULTS

A. Preparation of Starting Materials

2-(1-Naphthylmethyl)chlorobenzene (25).

The cross condensation reaction of 2-chlorobenzyl chloride and 1-naphthylmagnesium bromide which was applied by Quo³³ was used in the present work offering better yield than the method introduced by Bradsher³².

2-(1-Naphthylmethyl)benzonitrile (26).

The Rosenmund-von Braun reaction³⁴ was used for the preparation of 2-(1-naphthylmethyl)benzonitrile, using N-methyl-2-pyrrolidone as the solvent^{35,36} instead of anhydrous pyridine.

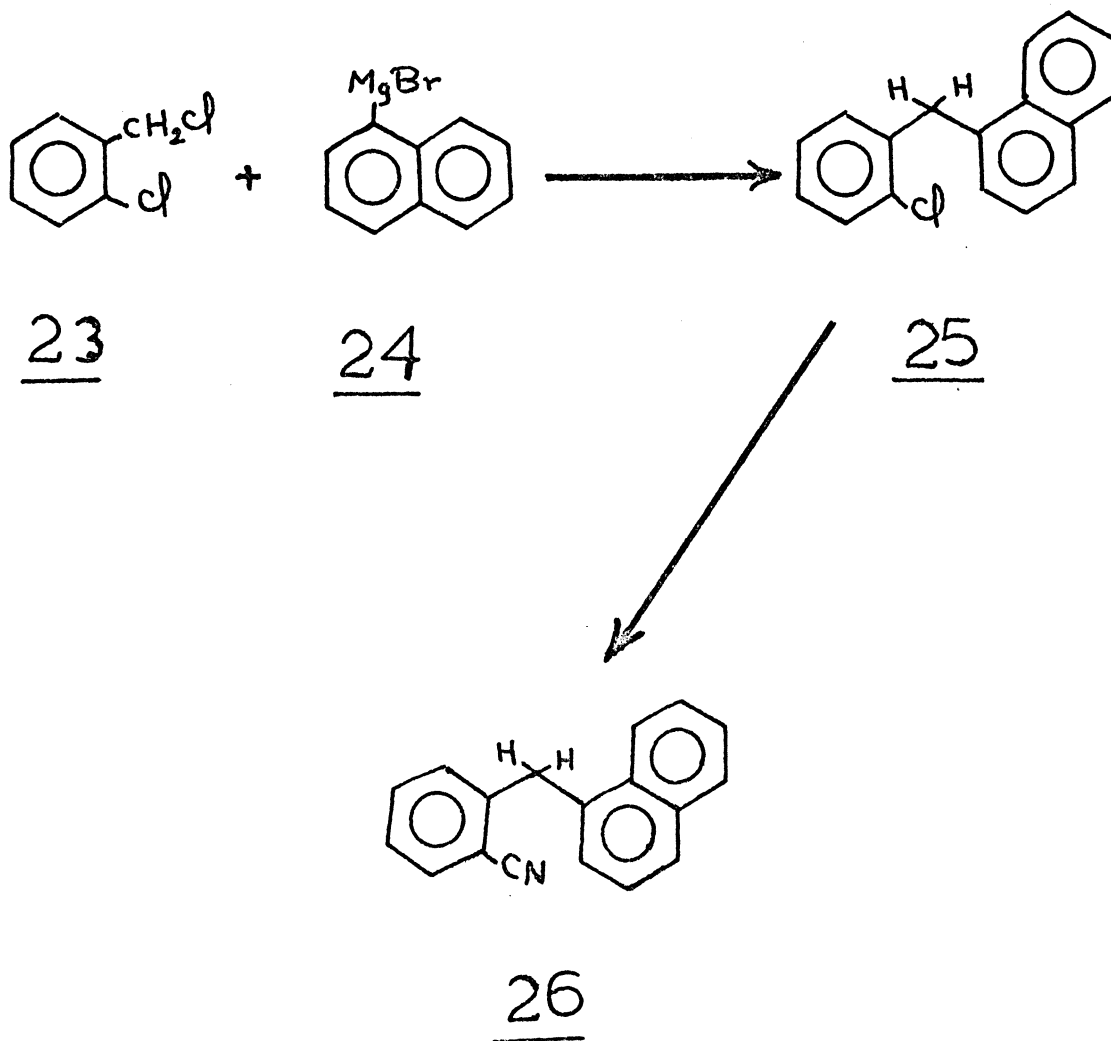
1. The Required Ketones

Preparation of 2-(1-naphthylmethyl)-3-fluorobenzophenone (28).

2-(1-naphthylmethyl)-3-fluorobenzophenone (28) was synthesized as shown in Chart II. The Grignard reagent of 3-fluorobromobenzene was allowed to react with 2-(1-naphthylmethyl)benzonitrile. Then the Grignard reagent complex was decomposed with a solution of 20% ammonium chloride. The ketimine was converted into the corresponding ketone by heating with 25% sulfuric acid for 22 hours. The ketone was then isolated in the usual manner from the organic layer.

The structure of this ketone was established by elemental analysis, and infrared absorption spectrum.

CHART I



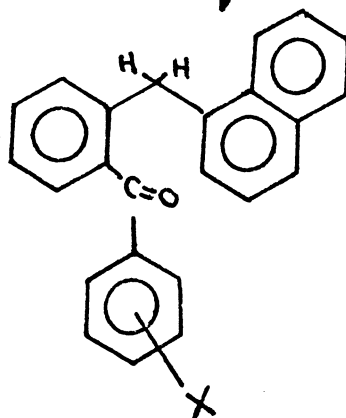
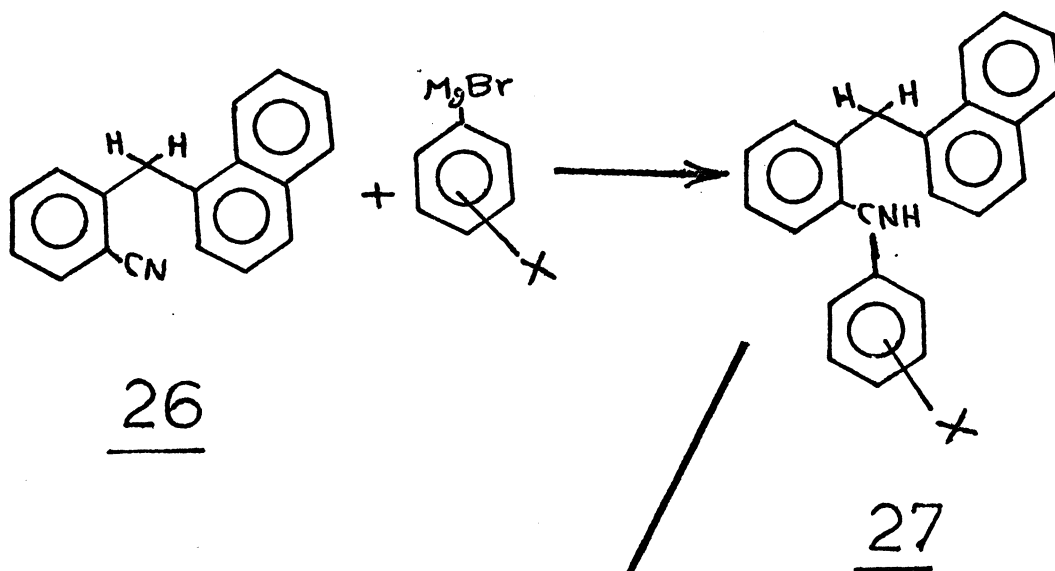
Preparation of 2-(1-naphthylmethyl)-4-fluorobenzophenone (29).

The ketone 2-(1-naphthylmethyl)-4-fluorobenzophenone (29) was prepared in the same way as was the 3-isomer (see Chart II). The Grignard reagent of 4-fluorobromobenzene was allowed to react with 2-(1-naphthylmethyl)benzonitrile. Then the Grignard reagent complex was decomposed with 20% ammonium chloride and the ketimine converted to the corresponding ketone by heating with 25% sulfuric acid for 20 hours. The ketone was then isolated in the usual manner from the organic layer.

Preparation of 2-(1-naphthylmethyl)-2-fluorobenzophenone.

2-(1-naphthylmethyl)-2-fluorobenzophenone was prepared as follows: The 2-bromotoluene was prepared from a commercial o-toluidine³⁹ by treating with 40% hydrobromic acid and sodium nitrite. Then the 2-bromotoluene was brominated to 2-bromobenzyl bromide by N-bromo-succinimide and benzoyl peroxide⁴⁰. The 2-(1-naphthylmethyl)bromobenzene was prepared by allowing the Grignard reagent of 1-bromonaphthalene to react with 2-bromobenzyl bromide in boiling benzene to give a colorless oil yield of 52%⁴¹. After the column chromatography with neutral alumina to remove a blue coloration which developed, the colorless bromo compound was found to form the Grignard reagent readily. The Grignard reagent of 2-(1-naphthylmethyl)bromobenzene was allowed to react with 2-fluorobenzoyl chloride in boiling toluene. Then the Grignard complex was decomposed with 25% sulfuric acid, and the ketone was then isolated in the usual manner from the organic layer⁴².

CHART II



28
29

X = 3-F

X = 4-F

Preparation of 2-(1-naphthylmethyl)-4-chlorobenzophenone.

The Grignard reagent of 4-chlorobromobenzene was allowed to react with 2-(1-naphthylmethyl)benzonitrile in boiling benzene. The Grignard reagent complex was decomposed with 20% ammonium chloride and the ketimine converted into the corresponding ketone by heating with 25% sulfuric acid for twenty hours. Then the ketone was isolated in the usual manner from the organic layer⁴³.

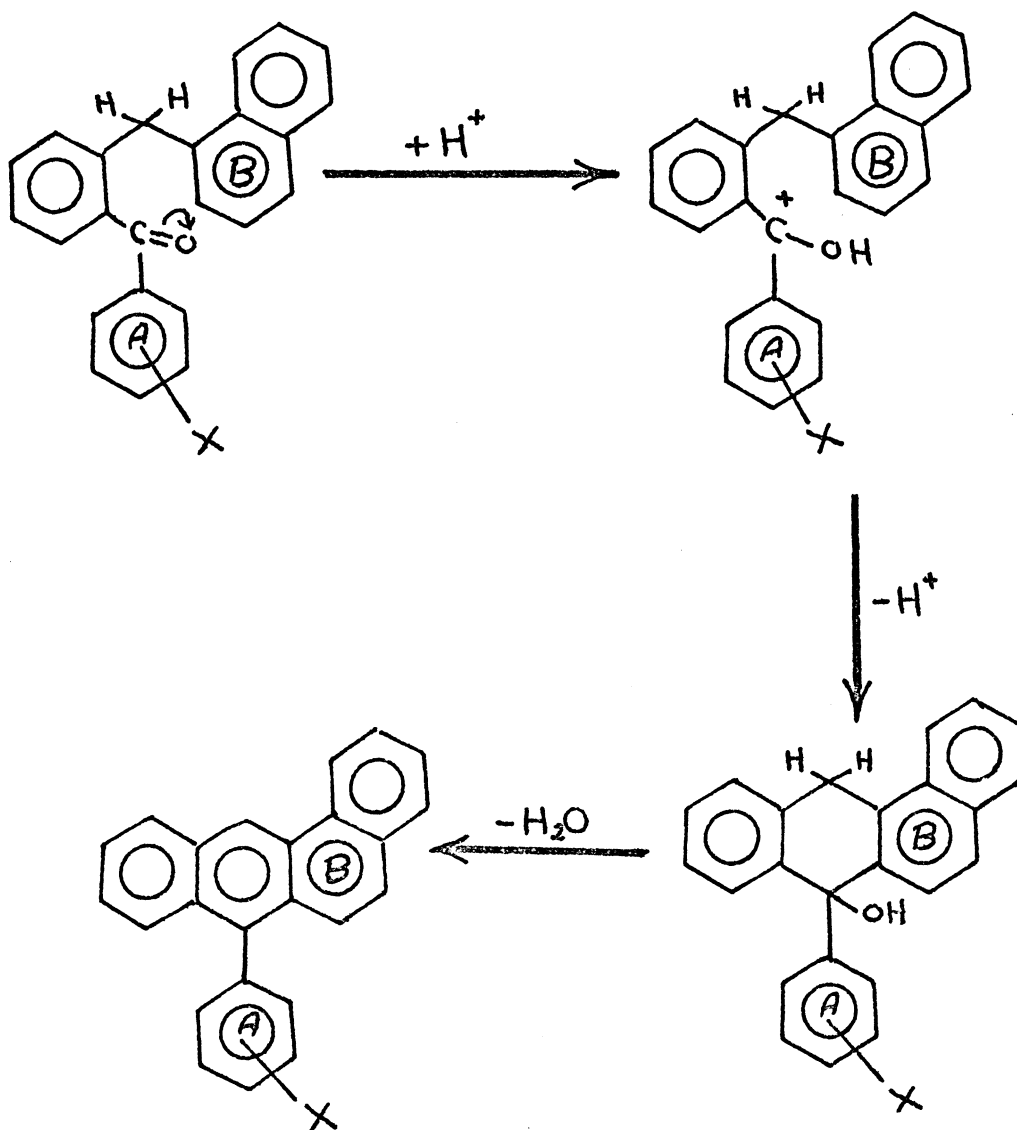
Preparation of 2-(1-naphthylmethyl)-4-methoxybenzophenone.

The Grignard reagent of 4-bromo anisole was allowed to react with 2-(1-naphthylmethyl)benzonitrile in boiling benzene. The Grignard reagent complex was decomposed with 20% ammonium chloride and the ketone converted into the corresponding ketone by heating with 25% sulfuric acid for twenty hours. Stevens⁴⁴ distilled the organic material under reduced pressure at 256°-280° and 3 mm, but in this preparation the crude product was chromatographed through a column packed with neutral alumina. The eluent was benzene. The yellow oil was crystallized as white crystals from petroleum ether (30-60°). Yield 90%.

2. Preparation of 7-(monomethylphenyl and dimethylphenyl)benz(a)anthracenes (35)-(42).

The 7-(phenyl, monomethylphenyl and dimethylphenyl)benz(a)anthracenes were prepared according to the procedure illustrated in Chart IV. The ketones were prepared essentially according to the procedure of Vingiello and Borkovec^{53, 54}. However, a slight modification of their procedure was employed in this investigation. Originally, in these investigations the appropriate Grignard reagent ($R, R' C_6H_5MgBr$) was allowed to react with 2-(1-naphthylmethyl)benzonitrile, the Grignard complex was

CHART III



- | | |
|-----------|------------------------|
| <u>30</u> | X = 2-F |
| <u>31</u> | X = 3-F |
| <u>32</u> | X = 4-F |
| <u>33</u> | X = 4-Cl |
| <u>34</u> | X = 4-OCH ₃ |

hydrolyzed with an ammonium chloride solution, and the resulting ketimine was isolated as the hydrochloride. The ketimine salt was then collected and hydrolyzed with a sulfuric acid solution. It was found advantageous to simply hydrolyze the Grignard complex with about a 5 molar excess of 25% sulfuric acid solution, and heat the resulting suspension under reflux for 18 to 48 hours until the salt hydrolyzed to the ketone which dissolved in the organic layer. This procedure was applied to the preparation of all of the ketones. The ketones were cyclized to the corresponding hydrocarbons by means of a 48% hydrobromic acid and glacial acetic acid mixture, either by heating the mixture under reflux for a couple of hours or by placing the mixture in a Carius tube and heating it. The sealed tube was then heated in a Carius furnace for 18 hours at 180°. The hydrocarbons were isolated in some cases by chromatographic separation of the reaction mixture on an alumina column (Fisher's neutral alumina 80-200 mesh) wet packed with petroleum ether 30°-60°⁵⁵.

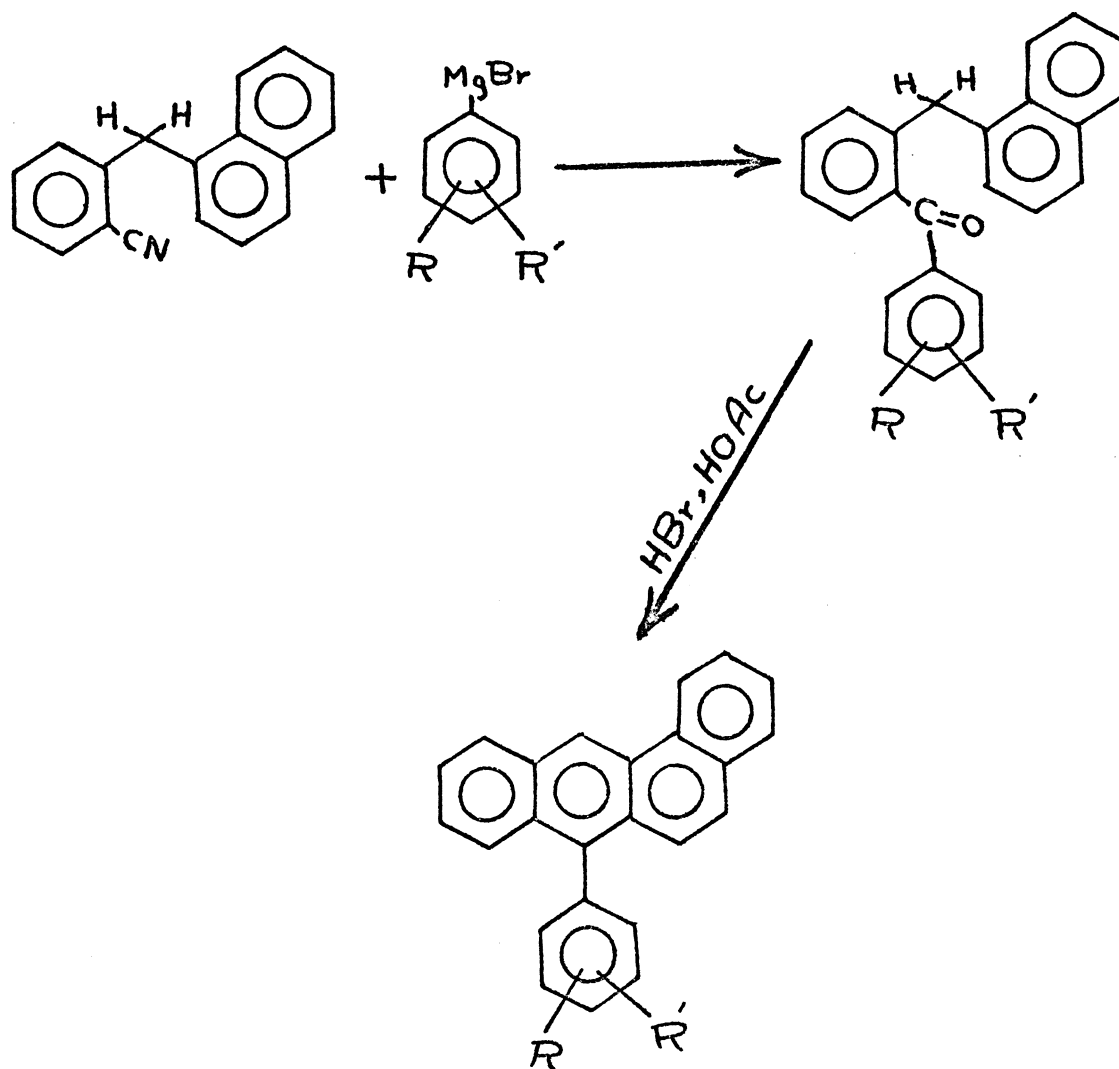
3. 7-(Halophenyl)benz(a)anthracenes

Cyclodehydration of 2-(1-naphthylmethyl)-3-fluorobenzophenone (31).

Bradsher and Vingiello⁴⁵ and Vingiello and van Oot^{46,47} have established the mechanism of the aromatic cyclodehydration of ketones as shown in Chart III. 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
- d - transannular elimination of water.

Chart IV



- | | |
|-----------|---|
| <u>35</u> | (a) $\text{R} = \text{R}' = \text{H}$ |
| <u>36</u> | (b) $\text{R}' = 2 - \text{CH}_3, \text{R} = \text{H}$ |
| <u>37</u> | (c) $\text{R}' = 3 - \text{CH}_3, \text{R} = \text{H}$ |
| <u>38</u> | (d) $\text{R}' = 4 - \text{CH}_3, \text{R} = \text{H}$ |
| <u>39</u> | (e) $\text{R}' = 2 - \text{CH}_3, \text{R} = 3 - \text{CH}_3$ |
| <u>40</u> | (f) $\text{R}' = 2 - \text{CH}_3, \text{R} = 4 - \text{CH}_3$ |
| <u>41</u> | (g) $\text{R}' = 3 - \text{CH}_3, \text{R} = 4 - \text{CH}_3$ |
| <u>42</u> | (h) $\text{R}' = 3 - \text{CH}_3, \text{R} = 5 - \text{CH}_3$ |

It has been observed that one of the most important factors on which the rate of cyclization depends is the nature and position of substituents on ring A. The cyclodehydration was carried out in a 3:1 glacial acetic acid and 48% hydrobromic acid mixture. The corresponding ketone and the acid mixture was heated under reflux for three hours, then cooled to room temperature. During cooling the product was precipitated as dirty white crystals which were recrystallized from 95% ethanol as white crystals, mp 155-156°, yield 85%. The structure of the product was established by the ultraviolet spectrum, infrared spectrum and elemental analysis.

Cyclodehydration of 2-(1-naphthylmethyl)-4-fluorobenzophenone (32).

The cyclodehydration of 2-(1-naphthylmethyl)-4-fluorobenzophenone, which was similar to that of its isomer, the 3-fluoro substituted ketone, was carried out in a 3:1 glacial acetic acid and 48% hydrobromic acid mixture. The mixture was heated under reflux for three hours, then cooled to room temperature. During the cooling the product precipitated as pale yellow crystals, which recrystallized from 95% ethanol as pale yellow crystals, mp 175-176°, yield 75%. The structure of the product was established by the ultraviolet spectrum and elemental analysis.

Cyclodehydration of 2-(1-naphthylmethyl)-2-fluorobenzophenone (30).

The cyclodehydration of 2-(1-naphthylmethyl)-2-fluorobenzophenone was carried out under more drastic conditions^{48,49} by heating in a Carius tube at 180° for seven hours^{50,51}, the product was worked up in the usual way.

Cyclodehydration of 2-(1-naphthylmethyl)-4'-chlorobenzophenone (33).

The cyclodehydration of 2-(1-naphthylmethyl)-4'-chlorobenzophenone was carried out in phenyl acid phosphate⁵² by heating the mixture at 140° for two hours. The chloro substituted aromatic hydrocarbon was then separated and worked up in the usual way.

Cyclodehydration of 2-(1-naphthylmethyl)-4-methoxybenzophenone (34).

The cyclodehydration of 2-(1-naphthylmethyl)-4-methoxybenzophenone was carried out in phenyl acid phosphate⁵² by heating the mixture to 140-145° for three hours. Then the methoxy substituted aromatic hydrocarbon was isolated in the usual manner.

B. Rearrangement of 12-(phenyl)-
benz(a)anthracene (43) to 7-(phenyl)benz(a)anthracene (45)

The Scholl reaction has been used extensively to synthesize highly condensed aromatic polynuclear hydrocarbon⁵⁶. The extensive exploitation of this reaction has led to many successful experiments and, of course, to unsuccessful experiments.

Although the reaction is not very well understood, the study of successful and unsuccessful experiments has given some insight into this reaction when applied to arylbenzanthracenes (see Chart V).

12-Substituted arylbenz(a)anthracenes are readily accessible^{57,58}; therefore a large number of these compounds have been subjected to Scholl reaction conditions. All of these compounds behaved similarly as evidenced by the ultraviolet spectral patterns of the products (specifically 12-phenylbenz(a)anthracene (43))⁵⁹. 12-(Mono and dimethylphenyl)-benz(a)anthracenes⁵⁷ have been subjected to Scholl reaction conditions (treatment with aluminum chloride using benzene as a solvent).

Clar⁵⁹ first performed this reaction by treating a solution of 12-phenylbenz(a)anthracene and benzene with anhydrous aluminum chloride. From this reaction Clar isolated a product to which he assigned the structure of dibenzo(a,l)pyrene (44). Clar based his conclusion on the ultraviolet spectrum, and on the thought that six membered rings form preferentially over five membered rings.

Using Clar's experiment as a model, cyclodehydrogenation of 12-(mono and dimethylphenyl)benz(a)anthracenes were performed⁵⁷. Based on ultraviolet spectral patterns, the results of these experiments were consistent with Clar's experiment, and as a result it was concluded that derivatives of dibenzo(a,l)pyrene had been synthesized. The yields in these experiments were very poor, 10-20%. Clar did not report a yield, presumably because it also was very poor.

In 1966 Lavit-Lamy and Buu Hoi conclusively demonstrated that Clar had synthesized dibenzo(a,e)fluoranthene (46), not dibenzo(a,l)pyrene (44)⁶⁰. Lavit-Lamy and Buu Hoi reached their conclusion by independently synthesizing dibenzo(a,e)fluoranthene (46). The ultraviolet spectrum of dibenzo(a,e)fluoranthene (46) and the ultraviolet spectrum of the product isolated by Clar are identical.

Lavit-Lamy and Buu Hoi explain that dibenzo(a,e)fluoranthene arises from the rearrangement of 12-phenylbenz(a)anthracene (43) to 7-phenylbenz(a)anthracene (45) and subsequent cyclodehydrogenation of the latter. In fact Lavit-Lamy and Buu Hoi did not mention formation of the intermediate dihydro compound, probably because they distilled the product, and the heat favored dehydrogenation to yield the aromatic compound, dibenzo(a,e)fluoranthene. Actually the dihydro compound was sublimed, giving a mixture of the dihydro compound and the aromatic compound. In

this laboratory we were able to study this rearrangement using G.L.C. analysis, using a Micro-Tek Model 1600 gas chromatograph with a hydrogen flame detector and 4 ft. x 1/8 in. column packed with 2.5% SE 52 on Gas-Chrom Z operated at a column temperature of 225°. The helium flow rate was 115cc/min. Taking into consideration two factors in this study:

1 - The retention time

2 - Increase in peak area

a - The retention time of each of the following standard compounds was:

12-phenylbenz(a)anthracene (120 seconds)

7-phenylbenz(a)anthracene (172.5 seconds)

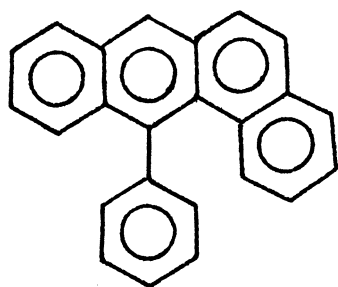
benz(a)anthracene (26 seconds)

b - The retention time of the peaks, which appeared after the injection of the products (of the reaction of 100 mg of 12-phenylbenz(a)anthracene with 300 mg of anhydrous aluminum chloride in dry boiling benzene. This mixture was heated under reflux for ten minutes, cooled, decomposed with dilute hydrochloric acid, separated) in the G.C. are (26, 172.5, 120 seconds).

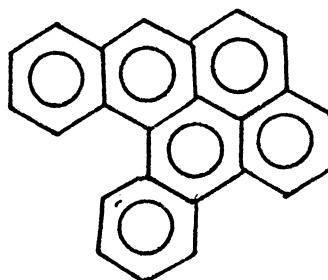
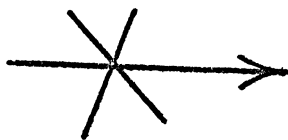
By comparison of the retention time of the standard compounds and the retention time of the peaks which developed after injection of the product, we found that we had the starting material (12-phenylbenz(a)-anthracene) and 7-phenylbenz(a)anthracene (which came from the rearrangement of 12-phenylbenz(a)anthracene) and benz(a)anthracene.

So it was logical to draw our attention to the next step, mixing the product with 12-phenylbenz(a)anthracene, 7-phenylbenz(a)anthracene,

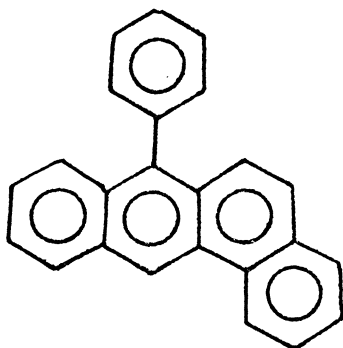
CHART V



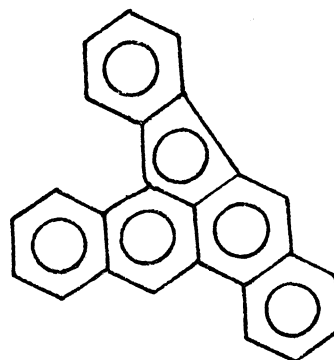
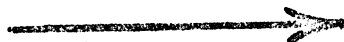
43



44



45



46

Percentage Yield

Refluxing Time Products	10 min	15 min	20 min	30 min
Benz(a)- anthracene	20%	48%	35.5%	23%
7-Phenylbenz- (a)anthracene	30%	35%	29%	37%
12-Phenylbenz- (a)anthracene	50%	0%	0%	0%
Dibenzo(a,e)- fluoranthene	very small amount	very small amount	small amount	small amount
unknown products		17%	35%	40%

and benz(a)anthracene respectively. In each case the corresponding peak was increased and no new peak formed.

Under these conditions the column temperature was not sufficient to detect the corresponding peak of dibenzo(a,e)fluoranthene, so the column temperature was raised to 260°. The following table shows the results at different conditions.

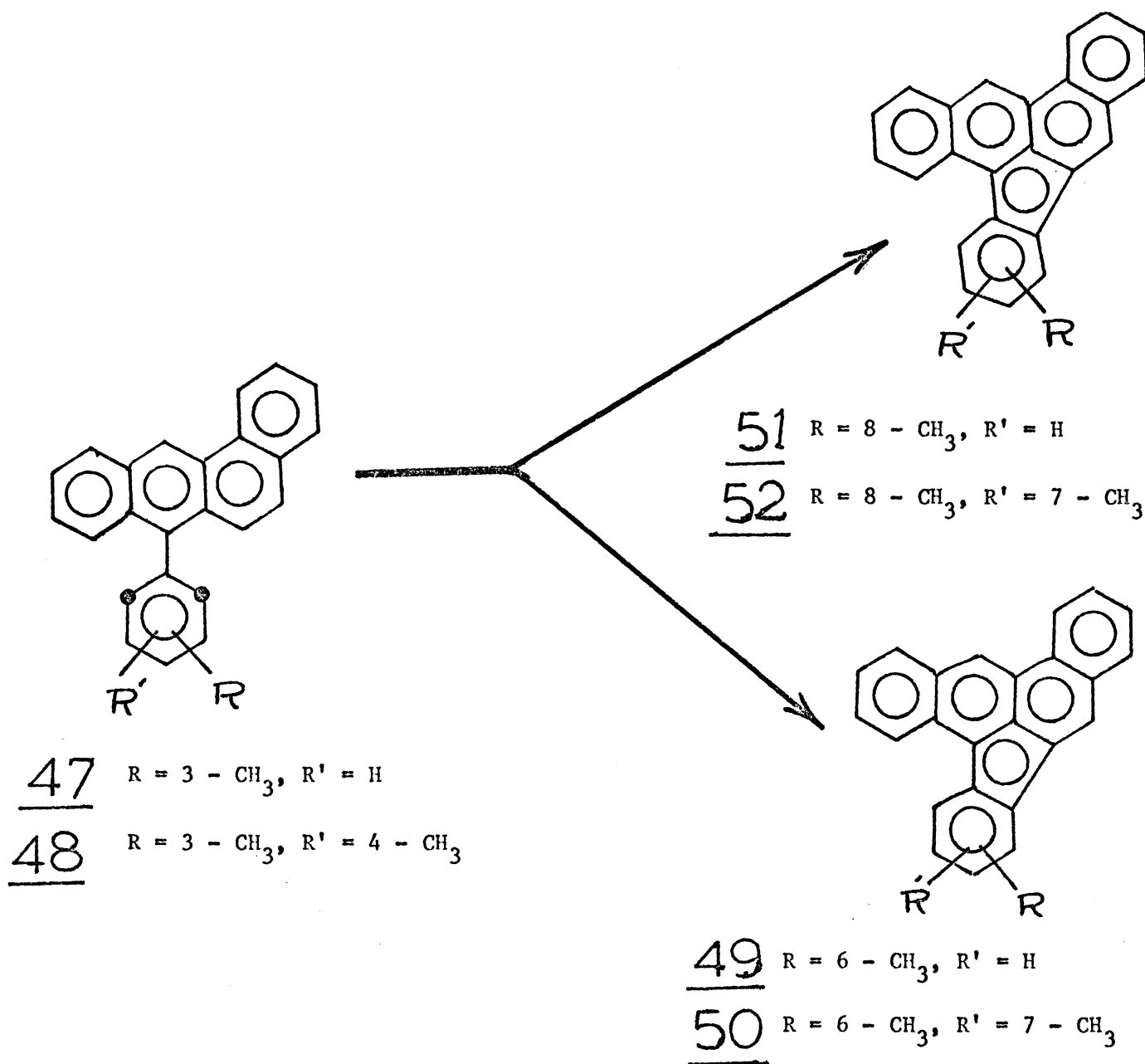
C. Cyclodehydrogenation Studies

1. 7-(Monomethyl and dimethylphenyl)benz(a)anthracenes

Let us consider now the cyclodehydrogenation of 7-(monomethyl and dimethylphenyl)benz(a)anthracene.

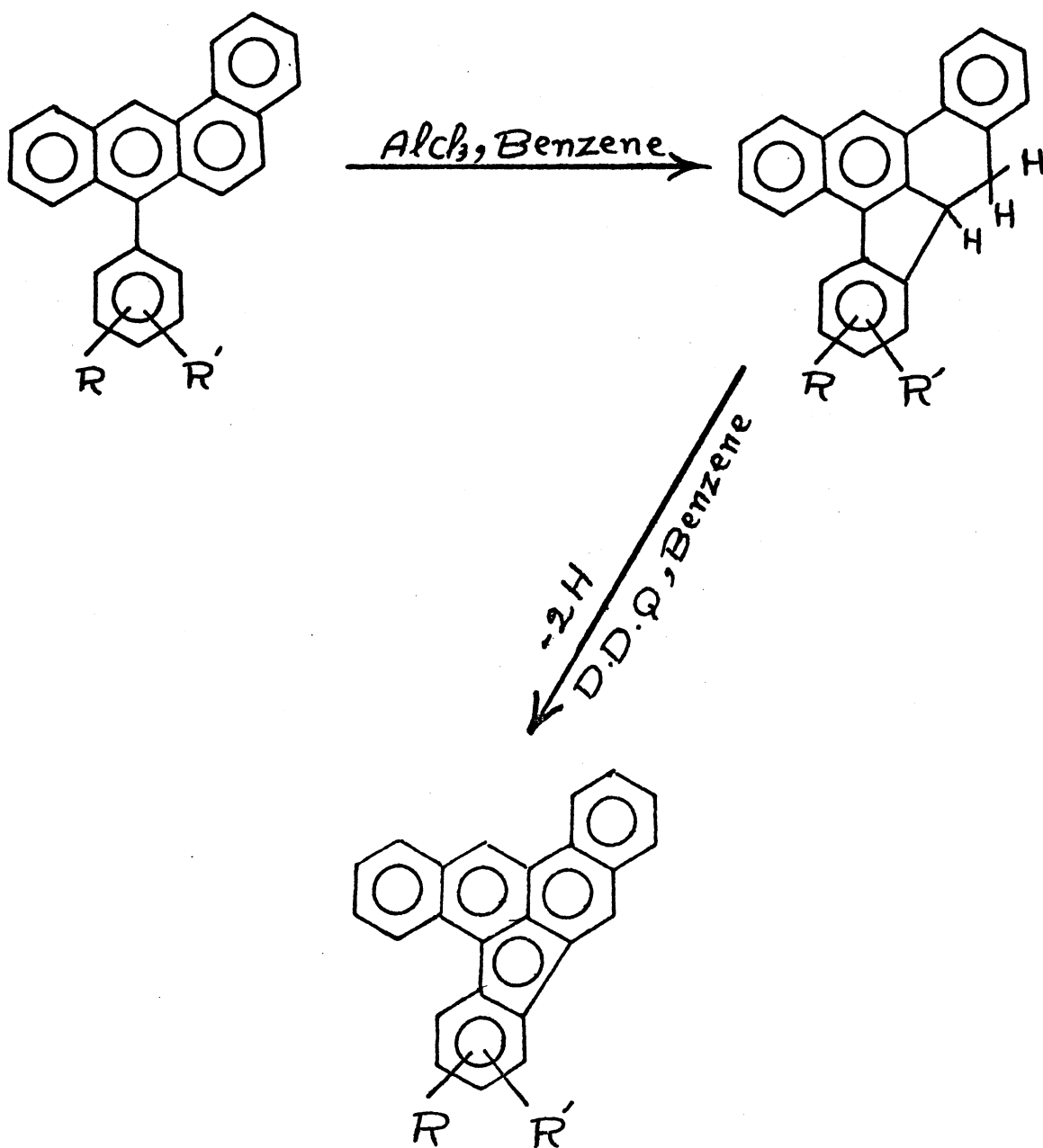
Aluminum chloride catalyzes nuclear dehydrogenation condensations of aromatic hydrocarbons, with the formation of higher ring compounds. This reaction may be intermolecular or intranuclear.

Dehydrogenation condensations of this type have been frequently mentioned in the literature as side reactions observed upon treatment of aromatic hydrocarbons with aluminum chloride. In many cases the cyclodehydrogenation reaction is the only simple route to the desired compounds, but the mechanism of the aluminum chloride-catalyzed cyclodehydrogenation is not well known. Before considering the individual cyclodehydrogenation reaction it might be well to point out that ring closure of 7-(3-methylphenyl or 3,4-dimethylphenyl)benz(a)anthracene might take place at either of two ortho positions of the phenyl ring. These positions are not equivalent with respect to the methyl groups and ring closure might yield either Compound 49 or 51 (Chart VI). Let us consider the aluminum chloride-catalyzed cyclodehydrogenation in some detail.



The corresponding hydrocarbon to be cyclodehydrogenated (one part by weight) was dissolved in anhydrous benzene and added to the powdered anhydrous aluminum chloride (three parts by weight). The resulting mixture immediately turned to a deep, chianti color. The mixture was heated under reflux for about 25 minutes as in the case of 7-phenyl 53, 3-methylphenyl 47, 4-methylphenyl 55, 3,5-dimethylphenyl 56 and 3,4-dimethylphenylbenz(a)anthracene 48. The mixture was then cooled to room

CHART VI



temperature and decomposed with 10% hydrochloric acid solution. The organic layer was separated, washed with water, dried over a suitable drying agent (anhydrous magnesium sulfate or calcium chloride), concentrated to a few ml and chromatographed (Fisher's alumina 80-200 mesh was used as the adsorbent and benzene and petroleum ether 30-60° (2:3) were used to wet pack the column). When the column was developed with the eluent one yellow band appeared on the column and at the top was red material. The yellow band contained the desired products. The solution obtained from the elution of the yellow band was concentrated to a few ml as a yellow oil and was crystallized from 95% ethanol with a few drops of benzene to give tiny yellow crystals. Rechromatographing these tiny yellow crystals gave colorless crystals.

The yields are high in general as shown in Table I. The products were characterized by n.m.r spectra, ultraviolet spectra, elemental analysis, and determination of the molecular weight by mass spectra as dihydro compounds. The purity of these compounds was checked by gas chromatography. In the case of 7-(2-methylphenyl)benz(a)anthracene (54), 2,4-dimethylphenylbenz(a)anthracene (58), and 2,3-dimethylphenylbenz(a)anthracene (57), it was necessary to increase the refluxing time from 25 minutes to twelve hours to obtain the highest yield possible.

The difficulty of the cyclization of 7-(2-methylphenyl) (54) 2,3-dimethylphenyl (57) and 2,4-dimethylphenylbenz(a)anthracene (58) is apparent from their structural formulas. The steric hinderance of methyl group in the ortho position of the phenyl ring probably retarded the cyclization, but it was overcome by long heating. All these dihydro compounds were dehydrogenated (aromatized) by heating them with D.D.Q.

TABLE I

Starting materials 7(R,R' phenyl benz(a)- anthracene	Yield of dihydro compounds
<u>53</u> R = R' = H	70% (a) R = R' = H
<u>54</u> R = H, R' = 2 - CH ₃	50% (b) R = H, R' = 9 - CH ₃
<u>47</u> R = H, R' = 3 - CH ₃	76% (c) R = H, R' = 8 - CH ₃
<u>55</u> R = H, R' = 4 - CH ₃	88% (d) R = H, R' = 7 - CH ₃
<u>48</u> R = 3 - CH ₃ , R' = 4 - CH ₃	55% (e) R = 8 - CH ₃ , R' = 7 - CH ₃
<u>56</u> R = 3 - CH ₃ , R' = 5 - CH ₃	76% (f) R = 6 - CH ₃ , R' = 8 - CH ₃
<u>57</u> R = 2 - CH ₃ , R' = 3 - CH ₃	50% (g) R = 9 - CH ₃ , R' = 8 - CH ₃
<u>58</u> R = 2 - CH ₃ , R' = 4 - CH ₃	30% (h) R = 9 - CH ₃ , R' = 7 - CH ₃

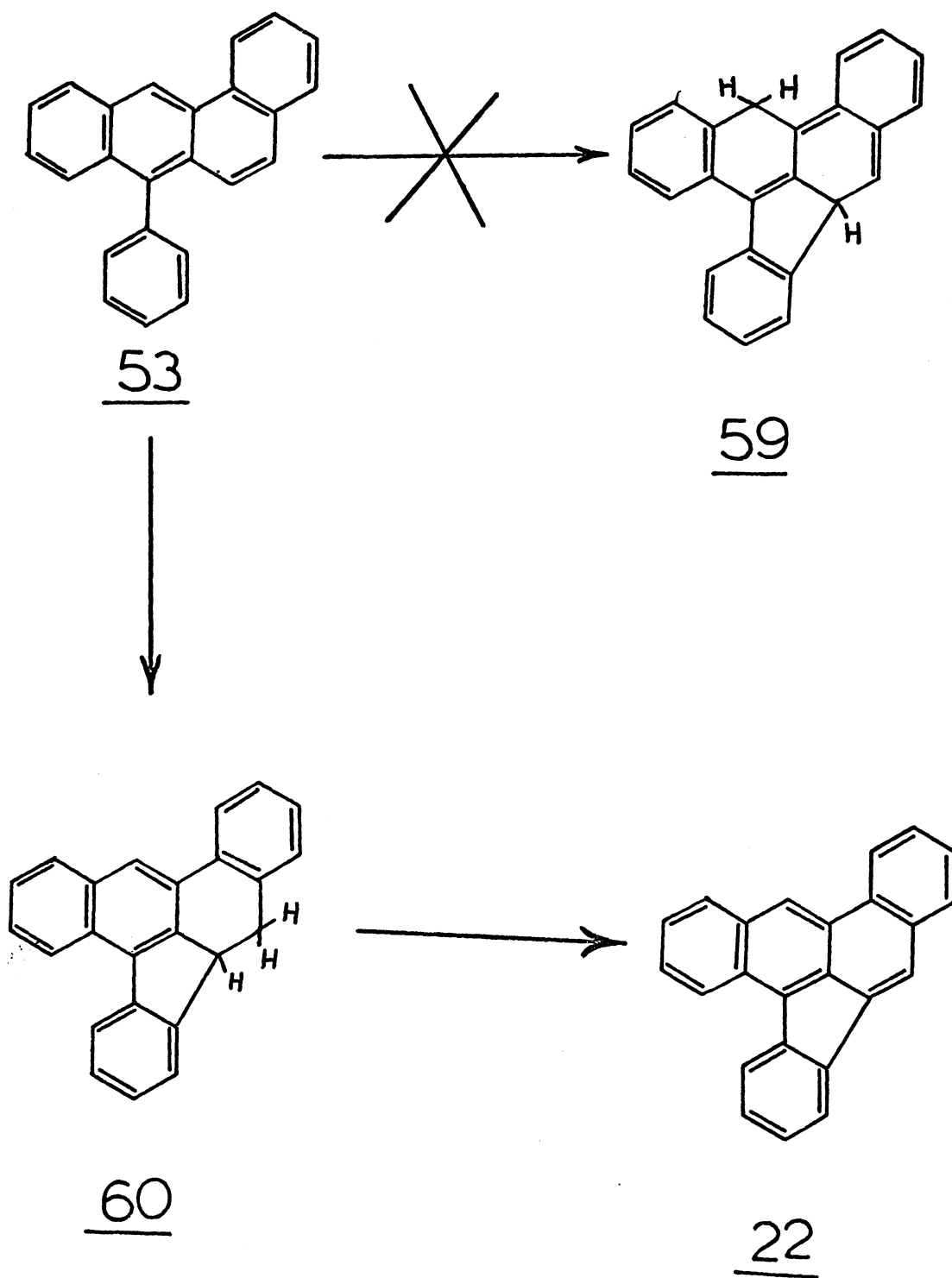
(2,3-dichloro-5,6-dicyanobenzoquinone). One part of the dihydro compound was dissolved in dry benzene and added to one part of D.D.Q. The mixture was heated under reflux for six hours, cooled to room temperature and decomposed with 10% sodium hydroxide solution. When the decomposition was completed, the basic solution turned yellow. The organic layer was separated, washed with water, dried, concentrated, and crystallized as tiny yellow crystals from 95% ethanol and a few ml of benzene. The yield was quantitative.

All of these products (aromatic compounds) were characterized by elemental analysis, infrared absorption spectra, and ultraviolet spectra (see infrared spectra 27, 28, 29, 31, 32, 33, 34 and ultraviolet spectra 9, 10, 11, 13, 14, 15, 16, 17 in the Appendix).

The structure of the dihydro compounds were assigned as structure 60. The choice of structure 60 over the other possible structures was made on the basis of n.m.r. spectrum, which shows clearly that the methylene hydrogen atoms are split. This is consistent with the structure 60 where an aliphatic hydrogen atom is adjacent to the methylene hydrogen atoms. Other plausible structures such as 59 have an isolated methylene group which would appear as a singlet; however, the n.m.r. spectrum did not show a singlet peak corresponding to the isolated methylene group and these are therefore rejected.

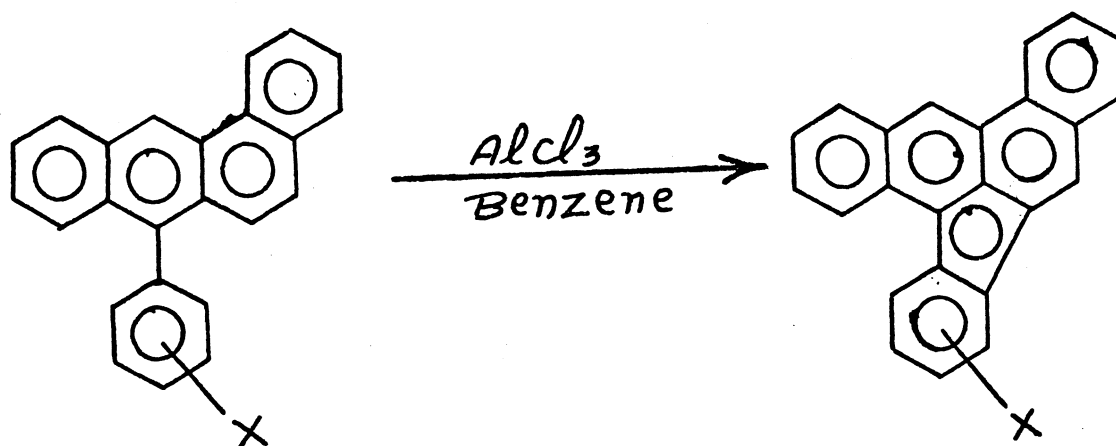
The ultraviolet spectrum shows a 1,3-diarylnaphthalene structure, while the infrared spectrum shows the methynyl hydrogen and the methylene hydrogen atoms. (See Chart VII.) The yields are high in general as shown in Table I. The products were characterized by n.m.r. spectra, ultraviolet spectra, elemental analysis, and determination of the molecular weight by mass spectra as dihydro compounds. The purity of these

CHART VII



compounds was checked by gas chromatography. In the case of 7-(2-methylphenyl)benz(a)anthracene (54), 2,4-(dimethylphenyl)benz(a)anthracene (58), and 2,3-(dimethylphenyl)benz(a)anthracene (57), it was necessary to increase the refluxing time from 25 minutes to twelve hours to obtain the highest yield possible.

In the case of the following halo substituted aromatic hydrocarbons, 7-(3-fluorophenyl)benz(a)anthracene (61), 7-(4-fluorophenyl)benz(a)anthracene (62), 7-(3-chlorophenyl)benz(a)anthracene (63) and 7-(4-chlorophenyl)benz(a)anthracene (64), the corresponding halo-substituted hydrocarbon to be cyclodehydrogenated (one part by weight) was dissolved in anhydrous aluminum chloride (six parts by weight). The resulting mixture immediately turned to a deep chianti color. The mixture was heated under reflux for two and one-half hours because of the presence of the halogen atom, which is unfavorable to the cyclization. The yield of this reaction was only the starting material. However, the reaction was repeated under the same conditions. The desired compound with high yield was obtained when the mixture was heated under reflux for 24 hours, using the usual manner for separation of the product. In this case, we were not able to separate the intermediate dihydro compounds which were dehydrogenated during the refluxing to the haloaromatic compounds (65,66,67,68).



Starting Materials	Yield of Products
<u>61</u> X = 3-F	<u>65</u> 62% X = 8-F
<u>62</u> X = 4-F	<u>66</u> 46% X = 7-F
<u>63</u> X = 3-Cl	<u>67</u> 55.5% X = 8-Cl
<u>64</u> X = 4-Cl	<u>68</u> 50% X = 7-Cl

2. 7-(Halophenyl)benz(a)anthracenes

Let us take the cyclodehydrogenation of halo substituted aromatic hydrocarbon in some details.

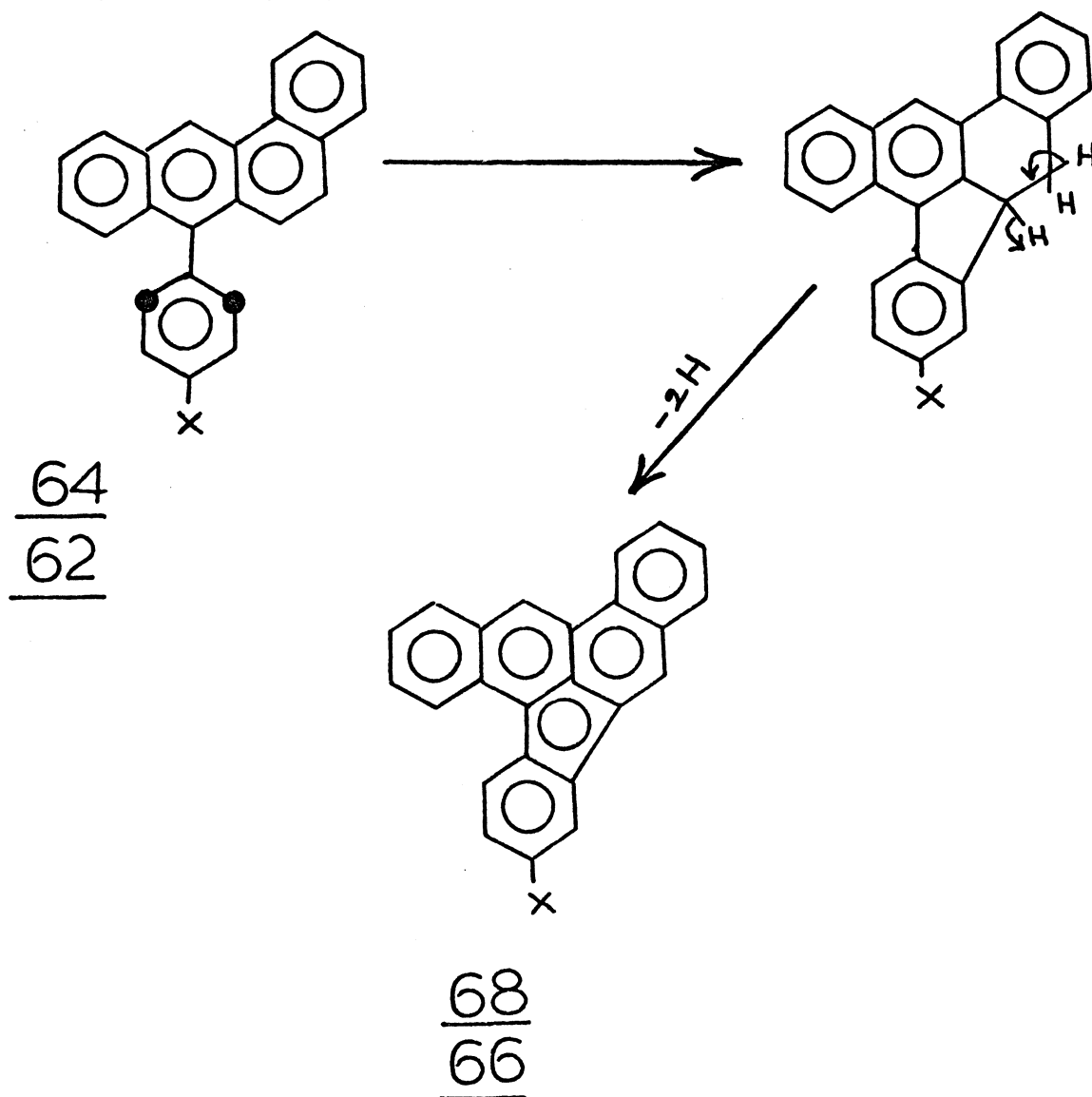
We should take into consideration three factors which have effect on the cyclodehydrogenation of halo substituted aromatic compounds:

1. The excess of aluminum chloride
2. The refluxing time
3. Electronic effect.

In the case of halo substituted aromatic compounds, one part of the halo compound and six parts of aluminum chloride were used. The yield of this reaction was the halo aromatic compound without isolation of the dihydro compound.

In the case of the mono methyl and dimethyl substituted aromatic compounds with ratios of one to three, the yield was the stable dihydro compound as an intermediate. When the latter compounds were treated as in the case of halo compound with the ratio of one to six, the dihydro compound as the intermediate step with good yield was the only product from the reaction with aluminum chloride. It thus appears that aluminum chloride in different ratios does not have an effect on the reaction to give dihydro compounds or aromatic compounds. Its role in this reaction is only to cyclize the ring, and the other two factors have the effect on the reaction in giving two different products.

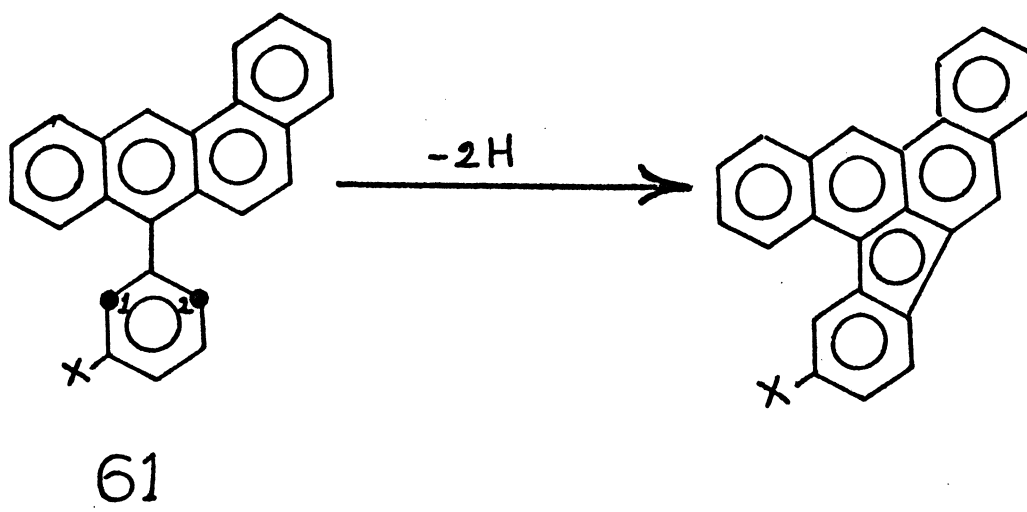
In the case of 7-phenyl-p-halobenz(a)anthracene 62



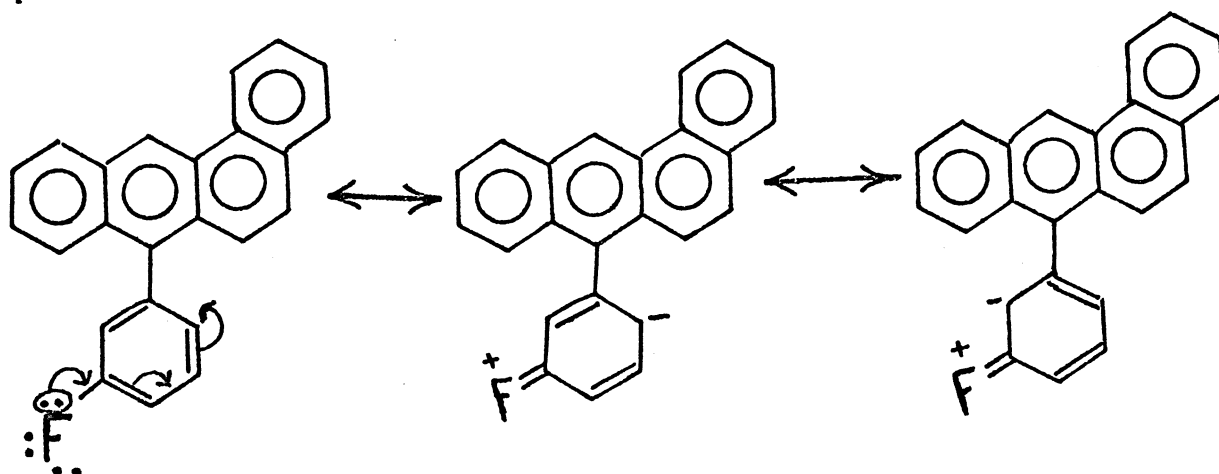
The two ortho positions are less reactive towards an electrophile due to the -I effect of the halogen atom; the +M effect of the halogen atom is not felt at all at these positions so this causes the reaction to take longer to complete.

The dihydro compound presumably was formed first and dehydrogenated to the corresponding halo substituted aromatic compound, which here is more facile than in the case of the corresponding methyl compounds, due to the electron withdrawing effect of the halogen.

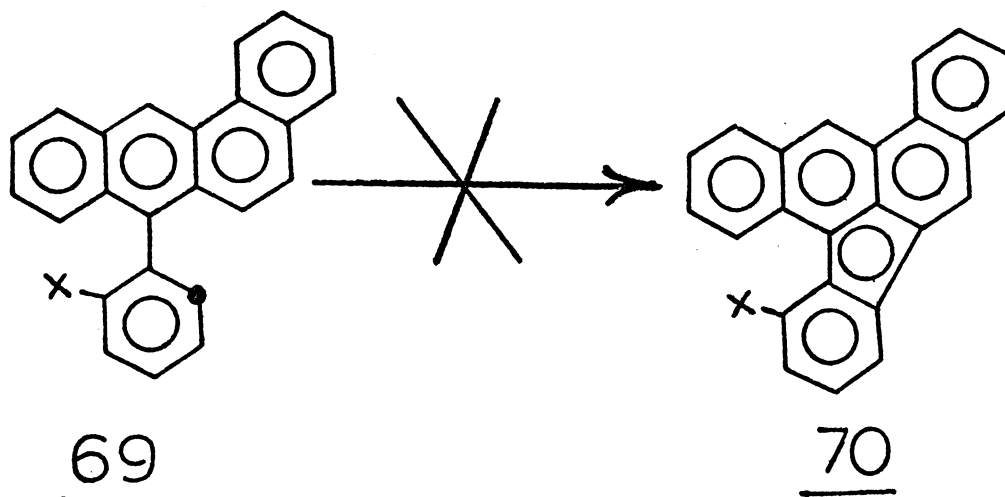
In the case of 7-Phenyl-m-halobenz(a)anthracene 61



In this case the 2 position is more favorable for electrophilic cyclization than the 1 position. Even though the +M effect of the halogen atom is felt strongly at either of these two positions, in position 1 the -I effect of the halogen atom is felt much more than that in position 2.



In the case of 7-phenyl-o-halobenz(a)anthracene 69



The failure to cyclize this compound (7-phenyl-2-fluorobenz(a)anthracene) may be either due to the steric factor or due to the electronic factor or both, but the steric factor is overruled where the 7-(o-methylphenyl)benz(a)anthracene offer much more steric hindrance than 7-phenyl-o-halobenz(a)anthracene. So it is presumed that the electronic factor is the intervening factor to prevent the cyclization of the above compound. Looking at the molecule, only one position is available for electrophilic attack, and this position is not at all favored by the resonance effect of the fluorine atom, being meta oriented. But the -I effect of the fluorine atom is very much felt at this position, meta to the fluorine atom, and so the probability of electrophilic attack is reduced to zero. The product obtained after a 24 hour reflux period as in the case of the other halo compounds was found to be the starting materials. All these products 7-fluoro, 8-fluoro, 7-chloro, 8-chloro and 7-bromo dibenzo(a,e)fluoranthene, were characterized by elemental analysis, infrared absorption spectra and ultraviolet spectra.

D. Spectral Correlations

1. Infrared Spectra

Infrared spectra of polynuclear aromatic hydrocarbons are complex and show a number of sharp and intense absorption bands. The feature of primary importance includes the carbon-hydrogen stretching vibrations near 3000 cm^{-1} . The C=C skeletal in plane vibrations at $1600 - 1450\text{ cm}^{-1}$, and the strong bands in the $900 - 650\text{ cm}^{-1}$ range due to out of plane carbon-hydrogen deformation frequencies.

The later region is known as the finger-print region which may be employed for the identification of specific ring systems. These vibrations have been studied in different types of polynuclear aromatic compounds and it has been found that the presence of one, two, three, or four adjacent hydrogen atoms in one six membered ring gives rise to strong absorptions in the regions $900 - 860$, $860 - 800$, $810 - 750$, and $770 - 735\text{ cm}^{-1}$ respectively.

A study of the infrared spectra of the dibenzo(a,e)fluoranthene derivatives were made and the corresponding out of plane carbon-hydrogen bending absorption frequencies are listed in Table II.

2. Ultraviolet Spectra

The ultraviolet spectra pattern for the dibenzo(a,e)fluoranthene derivatives are correlated with the spectral patterns of other dibenzofluoranthenes were given by Clar⁶⁴. See Table III considering λ_{max} and $(\log \epsilon)$ for:

7-methyldibenzo(a,e)fluoranthene (1), 8-methyldibenzo(a,e)fluoranthene (2), 9-methyldibenzo(a,e)fluoranthene (3), 7,8-dimethyldibenzo(a,e)fluoranthene (4), 7,9-dimethyldibenzo(a,e)fluoranthene (5),

8,9-dimethyldibenzo(a,e)fluoranthene (6), 6,8-dimethyldibenzo(a,e)-
fluoranthene (7).

TABLE II

C-H Out of Plane Bending Vibrations (cm^{-1})

<u>Compound</u>	<u>Adjacent Hydrogens</u>			
	<u>4</u>	<u>3</u>	<u>2</u>	<u>Single</u>
7-Methyldibenzo(a,e)fluoranthene	745	-	815	878
8-Methyldibenzo(a,e)fluoranthene	745	-	820	890
9-Methyldibenzo(a,e)fluoranthene	742	770	-	880
7,8-Dimethyldibenzo(a,e)fluoranthene	742	-	-	880
6,8-Dimethyldibenzo(a,e)fluoranthene	745	-	-	885
7,9-Dimethyldibenzo(a,e)fluoranthene	747	-	-	885
8,4-Dimethyldibenzo(a,e)fluoranthene	745	-	830	878
8-Chlorodibenzo(a,e)fluoranthene	745	-	815	880
7-Chlorodibenzo(a,e)fluoranthene	745	-	812	878
7-Fluorodibenzo(a,e)fluoranthene	745	-	812	885
8-Fluorodibenzo(a,e)fluoranthene	745	-	808	895
Dihydrodibenzo(a,e)fluoranthene	740	-	-	880
Dihydro-7-methyldibenzo(a,e)fluoranthene	738	-	812	880

All these compounds show C-H stretching vibrations between 3020-3050 cm^{-1} .

Methyl C-H stretching vibrations in the compounds containing methyl and dimethyl groups show bands at $\sim 2850 \text{ cm}^{-1}$.

TABLE III

1	2	3	4	5	6	7
400	400	401	401	400	400	400
(4.11)	(4.06)	(4.04)	(4.08)	(4.08)	(4.26)	(4.08)
380	380	380	380	380	378	380
(4.13)	(4.11)	(4.08)	(4.11)	(4.11)	(4.01)	(4.11)
362	362	362	362	362	359	362
(4.21)	(4.24)	(4.17)	(4.24)	(4.23)	(4.09)	(4.23)
332	331	332	334	331	334	331
(3.71)	(3.80)	(3.65)	(3.80)	(3.90)	(3.93)	(3.90)
318	315	317	318	314	305	314
(3.92)	(3.89)	(3.86)	(3.91)	(3.91)	(4.01)	(3.91)
299	304	299	300	298	294	298
289	290	289	290	289	272	289
264	264	264	266	264		264

EXPERIMENTAL

V. EXPERIMENTAL

A. General

- I. The ultraviolet spectra were recorded on a Beckman DK-2A recording spectrophotometer using 95% ethanol as the solvent.
- II. All infrared spectra were obtained using a Beckman IR-5 spectrophotometer either in 1 cm quartz cells using carbon tetrachloride or as a potassium bromide disk. Sample concentrations are noted on the spectra when a disk was used.
- III. All melting points were taken on a Fisher-Johns melting point block and were corrected.
- IV. All analyses were performed in this laboratory on an F & M Scientific Corporation Model 185 C, H and N Analyzer, except for halogen compounds, which were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.
- V. Conditions for gas chromatography:

Gas chromatographic analysis was carried out in a Micro-Tek Model 1600

Conditions:

Packing 2.5% SE-52 on Gas Chrom Z

Column length: 4' x 1/8"

Column temperature: 225°C

Detector temperature: 250°C

Inlet temperature: 240°C

Helium flow rate: 115 cc/min.

Air flow rate: 20 lbs. per sq. in.

Sensitivity: 4

The packing was prepared by dissolving 25 g of SE-52 in 1000 ml of methylene chloride. The solute was then absorbed on Gas Chrom Z (50.0 g) by slowly concentrating the solution to dryness. The column was packed with the aid of a vibrator to insure uniform packing.

The retention times were measured by a line drawn from the solvent peak to a perpendicular bisecting the apex of the product peak. The recorder retention times for a benzene solution of analytical pure samples were:

Compound	Retention time
Benz(a)anthracene	26 sec.
12-Phenyl benz(a)anthracene	120 sec.
7-Phenyl benz(a)anthracene	172.5 sec.
Dibenzo(a,e)fluoranthene	_____

All peak areas were recorded using a model 201B disc integrator equipped with a digital counter.

B. Preparation of Starting Materials

2-Chlorophenyl-1-naphthylcarbinol

A Grignard reagent was prepared from 103.5 g (0.5 mole) of 1-bromonaphthalene and 12.2 g (0.5 g atom) of magnesium turnings in 150 ml of anhydrous ethyl ether in a three-necked, round-bottomed flask equipped with a mechanical stirrer, take-off condenser, and dropping funnel. After the reaction was completed, a solution of 70.5 g (0.5 mole) of 2-chlorobenzaldehyde dissolved in 100 ml of anhydrous ethyl ether was added to the mixture dropwise. After the addition was completed, the resulting mixture was allowed to stand overnight while stirring. Then

the mixture was heated and allowed to reflux for one hour, cooled to room temperature, and the Grignard complex decomposed with 125 ml of 20% ammonium chloride solution. The organic layer was separated. The aqueous layer was extracted twice with ether, and the extracts combined with the other organic layer. The organic material was then washed twice with water, dried over anhydrous magnesium sulfate, concentrated, and distilled under reduced pressure (200-210°, 1.2 mm). Yield 52 g 40% (Lit⁶³ bp 215-216°, 4 mm).

2-(1-Naphthyl methyl)chlorobenzene (25)

In a 2l, three-necked, round-bottomed flask equipped with a mechanical stirrer and take-off condenser was placed 60.00 g (0.22 mole) of 2-(1-naphthyl hydroxide)chlorobenzene, 500 ml of 90% acetic acid, 12 g of red phosphorus, and 12 g of iodine. The resulting mixture was allowed to stand overnight and heated under reflux for 31 hours. The mixture was filtered (caution--lachrymatory material is found in this reaction). The red colored solution was allowed to cool by crushed ice until the temperature reached between 0°-5°. Then sodium hydroxide solution was added by stirring until the solution was basic. After that the organic layer was separated. The aqueous layer was extracted several times and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated, and finally distilled under reduced pressure (195-205°, 2 mm). Yield 23 g 40% (Lit⁵⁵ 203-204°, 3 mm).

2-(1-Naphthylmethyl)chlorobenzene (25)

A Grignard reagent was prepared from 103.5 g (0.5 mole) of 1-bromonaphthalene and 12 g (0.5 g atom) of magnesium turnings in 200 ml of

anhydrous ethyl ether in a 2 l, three-necked, round-bottomed flask equipped with a mechanical stirrer, take-off condenser, and separatory funnel. After the reaction was completed, dry benzene was added (200 ml) and the ethyl ether was removed by means of the take-off condenser until the temperature of the solution reached between 50°-60°. A solution of 49 g (0.3 mole) of 2-chlorobenzyl chloride in 120 ml of dry benzene was added to the Grignard reagent. After the addition was completed, the mixture was heated under reflux for 12 hours and cooled to room temperature. The solution was hydrolyzed with an equivalent amount of 10% hydrochloric acid solution. The organic layer was separated. The aqueous layer was extracted twice with benzene and the extracts combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. The crude product was heated under reduced pressure in a round-bottomed flask equipped with Hopkins Condenser. A by-product which sublimed was collected on the cold finger of the condenser. Finally the oil was distilled under reduced pressure (180-200°, 2 mm). The product was collected as a clear pale yellow oil. Yield 47 g 62% (Lit⁵⁵ 203-204°, 3 mm). Other experiments at the same conditions yielded 64%, 71%.

2-(1-Naphthylmethyl)benzonitrile (26)

The 2-(1-naphthylmethyl)chlorobenzene 25 g (0.1 mole) was dissolved in 80 ml of freshly distilled N-methyl-2-pyrrolidone which was distilled at 194°. The solution, in a 2 l, three-necked, round-bottomed flask, equipped with a mechanical stirrer and condenser, was heated to about 100°, then a fine powder of cuprous cyanide (12.3 g) was added to the

solution slowly. After the solution was completed, it was refluxed for 24 hours at a temperature between 180-190°. Then the solution was cooled to 90°C and a solution of sodium cyanide (76 g in 165 ml of water) was added slowly and left stirring about one hour at the above temperature. It was then cooled to room temperature and 185 ml of benzene was added slowly through a separatory funnel and left overnight to complete separation. The organic layer was separated from the aqueous layer, which was extracted twice with benzene and combined with the other organic layer. The organic material was acidified with 10% hydrochloric acid solution, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Eventually, the product was distilled under reduced pressure (198-202°, 1.5 mm). The product was a viscous yellow oil which solidified upon standing. Yield 15 g 62%.

2-(1-Naphthylmethyl)benzophenone

Phenylmagnesiumbromide was prepared from 11.8 g (0.075 mole) of bromobenzene and 1.8 g (0.075 g atom) of magnesium turnings in 150 ml of anhydrous ethyl ether in a 2 l, three-necked, round-bottomed flask fitted with a mechanical stirrer and an efficient reflux condenser. After the reaction was completed, most of the ethyl ether had been removed, and a solution of 12.2 g (0.05 mole) of 2-(1-naphthylmethyl)-benzonitrile in 100 ml of dry toluene was added to the Grignard reagent dropwise. The resulting mixture was heated under reflux for 12 hours. Then 50 ml of 20% ammonium chloride solution was added to decompose the complex. The toluene layer was decanted and the residue was extracted twice with benzene. The organic material was then placed in the apparatus that was used first and the benzene was distilled until the temperature of the reflux reached 90°C. To the flask was added slowly at room

temperature 80 ml of 25% sulfuric acid solution. After the addition was completed, the solution was allowed to reflux for three hours, then cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Finally it was distilled under reduced pressure (258-260°, 1.5 mm). The product was a very viscous pale yellow oil, which was crystallized as white crystals from 95% ethyl alcohol and a few drops of benzene. mp 103-104°. Yield 13 g 82%. Another experiment under the same conditions yielded 10.5 g 65%. (Lit⁵⁵ bp 248-251°, 1 mm).

7-Phenyl benz(a)anthracene (35)

In a round-bottomed flask equipped with a condenser 0.5 g (0.0015 mole) of 2-(1-naphthylmethyl)benzophenone, 24 ml of glacial acetic acid and 6 ml of 48% hydrobromic acid solution was heated under reflux for two and one-half hours. During the refluxing the product appeared as dirty white crystals. After that, it was cooled to room temperature, the solid material separated by filtration, washed twice with water, and left to dry. Finally it was recrystallized from 95% ethyl alcohol and a few drops of benzene. The resulting hydrocarbon was a white crystalline material, mp 180-181°. Yield 0.44 g 93%. (Lit⁵⁵ 98% mp 183-184°).

C. Cyclodehydrogenations

Dibenzo(a,e)fluoranthene (46)

In a 500 ml, round-bottomed flask equipped with a condenser 3.00 g of anhydrous aluminum chloride in 120 ml of dry benzene was heated gently. To it was added 1 g (0.0033 mole) of 7-phenyl benz(a)anthracene in 60 ml of dry hot benzene (the red brown color developed immediately).

The solution was heated under reflux for twenty minutes, cooled to room temperature, and poured into a beaker containing about 200 ml of 10% hydrochloric acid solution. The organic layer (yellow color) was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to a few ml, and crystallized from 95% ethyl alcohol and a few drops of benzene as yellow tiny crystals, which were chromatographed (the column was packed with neutral alumina, and the eluent was petroleum ether 30-60°). The eluent was concentrated to give white crystals. mp 190-191°. Yield 0.7 g 70%. The product was identified as the dihydro compound.

1. The mass spectra showed the right molecular weight (304).

2. Anal. Calculated for $C_{24}H_{16}$: C, 94.74; H, 5.26.

Found C, 94.74; H, 5.23.

3. U.V. spectrum. Page 90 No: 12

4. I.R. spectrum. Page 100 No: 30

5. N.M.R. spectrum. Page 103 No: 36

This dihydro compound was dehydrogenated (aromatized) with D.D.Q. (2,3-dichloro 5,6-dicyano benzoquinone). The weight of the dihydro compound was equal to the weight of D.D.Q. This mixture was heated under reflux in a round-bottomed flask in dry benzene for six hours, cooled to room temperature, and poured into a beaker containing 10% sodium hydroxide solution until the color of the solution changed to yellow. Then the organic layer was separated. The aqueous solution was extracted with benzene and combined with the organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to a few ml. Then it was crystallized as yellow orange

crystals from 95% ethyl alcohol and a few drops of benzene. The product was chromatographed (the column was packed with neutral alumina and the eluent was petroleum ether 30-60°), which was used first to remove the blue band while the yellow band (the aromatic compound) remained at the top. After the blue band had been removed the benzene was used as an eluent to remove the yellow band which was collected, concentrated, and crystallized as tiny yellow crystals from 95% ethyl alcohol and benzene, mp 227-228° (Lit⁶¹ mp 232°).

2-(1-Naphthylmethyl)-4-methylbenzophenone

A Grignard reagent was prepared from 1.8 g (0.075 g atom) of magnesium turnings and 13.0 g (0.075 mole) of 4-bromotoluene in 150 ml of dry ethyl ether in a 2 l, three-necked, round-bottomed flask equipped with a mechanical stirrer and a take-off condenser. After the reaction was completed, most of the ethyl ether was removed, and a solution of 12 g (0.05 mole) of 2-(1-naphthylmethyl)benzonitrile in 100 ml of dry toluene was added slowly to the Grignard reagent. After the addition was completed, the mixture was heated under reflux for 18 hours, then cooled to room temperature and decomposed with 25% sulfuric acid solution, which was added slowly under stirring while keeping the solution at room temperature. Upon addition of 240 ml of 25% sulfuric acid the yellow crystals were formed. After the addition was completed, it was heated under reflux for 48 hours, at which time all the solid had gone into the solution. The solution was cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Finally it was distilled under reduced pressure (1.2 mm, 245-250°). The product was a very

viscous yellow oil. Yield 11.5 g 70%. The oil was pure enough to be used for the next reaction. (Lit⁵⁵ 84%).

7-(4-Methyl phenyl)benz(a)anthracene (38)

In a round-bottomed flask equipped with a condenser, 1.00 g (0.0028 mole) of 2-(1-naphthylmethyl)4-methylbenzophenone, 50 ml of glacial acetic acid and 15 ml of 48% hydrobromic acid solution was heated under reflux for 4 hours, then cooled to room temperature, extracted with benzene, neutralized with sodium carbonate solution, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Then it was crystallized as yellow crystals from 95% ethanol and a few drops of benzene. Yield 0.66 g 70%. It was necessary to make it very pure for the next reaction, so it was recrystallized two times to finally give light yellow crystals, mp 122-123°. (Lit⁵⁵ 80% mp 121-122°).

7-Methyl dibenzo(a,e)fluoranthene

A. In a 250 ml, round-bottomed flask equipped with a condenser, 1.5 g of anhydrous aluminum chloride in 60 ml of dry benzene was heated gently and to it was added 0.5 g (0.0015 mole) of 7-(4-methylphenyl)benz(a)-anthracene in 30 ml of hot dry benzene (the red brown color developed directly). The solution was heated under reflux for 25 minutes, cooled to room temperature, and poured into a beaker containing around 100 ml of 10% hydrochloric acid solution. The organic layer (yellow color) was separated. The aqueous layer was extracted with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to a few ml, and crystallized from 95% ethyl alcohol and a few drops of

benzene, as yellow tiny crystals, which were chromatographed through a column packed with neutral alumina (mesh 80-200). The eluent was petroleum ether 30-60°. The eluent was concentrated to give white crystals. The analytical sample was chromatographed twice and crystallized four times. mp 203-204°. Yield 0.44 g (88%). The product was identified as the dihydro compound.

1. The mass spectra gave the right molecular weight (318).

2. Anal. Calculated for $C_{25}H_{18}$: C, 94.34; H, 5.66.

Found C, 94.30; H, 5.74.

3. U.V. spectrum. Page 88 No: 8

4. I.R. spectrum. Page 102 No: 35

5. N.M.R. spectrum. Page 104 No: 37

This dihydro compound was dehydrogenated (aromatized) with D.D.Q. in a ratio of 1:1 by weight. This mixture was heated in dry benzene under reflux in a round-bottomed flask equipped with a condenser for around six hours, then cooled to room temperature and poured into a beaker containing 10% sodium hydroxide solution (the aqueous layer changed to yellow). The organic layer was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to a few ml. Then it was crystallized as yellow orange crystals from 95% ethyl alcohol and a few drops of benzene. The product was chromatographed on a column packed with neutral alumina (mesh 80-200). Petroleum ether 30-60° was first used to remove the blue fluorescent band. The eluent was changed to a mixture of petroleum ether and benzene in a ratio of 1:1 to wash the

yellow band down. Finally the second eluent was concentrated to a few ml and crystallized as tiny yellow crystals from 95% ethanol with a few drops of benzene. The yield was quantitative after treatment with D.D.Q. The analytical sample was chromatographed twice and crystallized four times to give a product of tiny bright yellow crystals, mp 224-225°.

1. Anal. Calculated for $C_{25}H_{16}$: C, 94.93; H, 5.07

Found C, 94.94; H, 5.12

2. U.V. spectrum. Page 89 No: 9

3. I.R. spectrum. Page 99 No: 29

B. This experiment was repeated as follows: 0.5 g of 7-(4-methylphenyl)benz(a)anthracene and 3.0 g of anhydrous aluminum chloride. The mixture was heated under reflux for 25 minutes, cooled to room temperature and treated as mentioned before in part A. The yield was 0.415 g 90% and was identified as the dihydro compound. mp 203-204°. A mixed melting point was taken with the products of A and B and no depression in the melting point was noted. The same U.V. spectra was observed.

2-(1-Naphthylmethyl)3-methylbenzophenone

A Grignard reagent was prepared from 1.8 g (0.075 g atom) of magnesium turnings and 13.0 g (0.075 mole) of 3-bromotoluene in 150 ml of dry ethyl ether in a 2 l, three-necked, round-bottomed flask equipped with a mechanical stirrer and take-off condenser. After the reaction was completed, most of the ethyl ether had been removed. A solution of 12.0 g (0.05 mole) of 2-(1-naphthylmethyl)benzonitrile in 100 ml of anhydrous toluene was added slowly to the Grignard reagent. After the addition was completed, the mixture was heated under reflux for 18 hours, then cooled to room temperature and decomposed with 240 ml of

25% sulfuric acid solution, which was added slowly by stirring while keeping the mixture at room temperature. After the addition was completed, the solid material, which was formed during the addition of the acid as yellow crystals, was heated under reflux for 48 hours, at which time all the solid material had gone into solution. The solution was cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Finally it was distilled under reduced pressure (1.5 mm, 247-251°). The product was a viscous yellow oil, crystallized from ethanol as white crystals, mp 116-117°. Yield 20 g 60%. (Lit⁵⁵ 80% mp 114-115°).

7-(3-Methylphenyl)benz(a)anthracene (37)

In a round-bottomed flask equipped with a condenser 1.0 g (0.0028 mole) of 2-(1-naphthylmethyl)4-methylbenzophenone, 50.0 ml of glacial acetic acid and 15 ml of 48% of hydrobromic solution was heated under reflux for 3 hours, then cooled to room temperature, extracted with benzene, neutralized with a concentrated solution of sodium carbonate, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. It was then crystallized as white crystals from 95% ethyl alcohol and some drops of benzene, mp 110-111°. Yield 0.75 g 80%. It was important to have this compound pure for the next reaction. (Lit⁵⁵ 88% mp 110-111°).

8-Methyl dibenzo(a,e)fluoranthene

In a 250 ml round-bottomed flask equipped with a condenser, 1.5 g of anhydrous aluminum chloride in 70 ml of anhydrous benzene was heated

gently. To it was added 0.5 g (0.0015 mole) of 7-(3-methylphenyl)-benz(a)anthracene in 30 ml of hot anhydrous benzene (the red brown color developed immediately). The solution was heated under reflux for 25 minutes, cooled to room temperature, and poured into a beaker containing around 100 ml of 10% hydrochloric acid solution. The organic layer turned to yellow and was separated. The aqueous layer was extracted twice with benzene, and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to a few ml, and crystallized as yellow tiny crystals from 95% ethyl alcohol and a few drops of benzene. This material was chromatographed using the same column used for its isomer (7-methyl dibenzo(a,e)fluoranthene). The eluent was concentrated to give pale yellow crystals. Yield 0.38 g 76%. Another experiment under these conditions gave a yield of 80%. The product was identified as the dihydro compound.

This dihydro compound was dehydrogenated (aromatized) with D.D.Q. in a ratio of 1:1 by weight. This mixture was heated in anhydrous benzene under reflux in a round-bottomed flask equipped with a condenser for six hours, then cooled to room temperature and poured into a beaker containing 10% sodium hydroxide solution (the aqueous layer changed to yellow). The organic layer was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to a few ml. Then it was crystallized as yellow tiny crystals from 95% ethyl alcohol and a few drops of benzene. The product was passed through a column packed with neutral alumina (mesh 80-200). Petroleum ether 30-60° was used to remove the blue band,

then a mixture of petroleum ether 30-60° and benzene in a ratio of 1:1 to wash the yellow band down. Finally the second eluent was concentrated to a few ml and crystallized as tiny yellow crystals from 95% ethanol with some drops of benzene. The yield was quantitative after treatment with D.D.Q. The analytical sample was prepared by chromatographing twice and crystallizing four times to give a product of tiny yellow crystals, mp 166-167°.

1. Anal. Calculated for $C_{25}H_{16}$: C, 94.93; H, 5.07

Found C, 95.09; H, 5.27

2. U.V. spectrum. Page 89 No: 10

3. I.R. spectrum. Page 99 No: 28

2-(1-Naphthylmethyl)2-methyl benzophenone

A Grignard reagent was prepared from 1.8 g (0.075 g atom) of magnesium turnings and 13.0 g (0.075 mole) of 2-bromotoluene in 150 ml of anhydrous ethyl ether in a 2 l, three-necked, round-bottomed flask fitted with a mechanical stirrer and an efficient reflux condenser. After the reaction was completed, most of the ethyl ether was removed. A solution of 12.0 g (0.05 mole) of 2-(1-naphthyl methyl)benzonitrile in 100 ml of dry toluene was added slowly to the Grignard reagent. After the addition was completed, the mixture was heated under reflux for 18 hours, then cooled to room temperature and decomposed with 240 ml of 25% sulfuric acid solution, which was added slowly by stirring and at room temperature. After the addition was completed, the solid material which was formed during the addition of the acid as yellow crystals was heated with reflux for 48 hours, at which time all the solid material had gone into the solution. The solution was cooled to room temperature. The

organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Finally it was distilled under reduced pressure (1.5 mm, 240-245°). The product was a viscous yellow oil. The distilled product was pure enough to be used for the next reaction. (Lit⁵⁵ 81%).

7-(2-Methylphenyl)benz(a)anthracene (36)

1.0 g (0.002 mole) of 2-(1-naphthylmethyl)-2-methylbenzophenone, 40 ml of glacial acetic acid and 15 ml of 48% of hydrobromic acid solution were placed in a Carius tube, sealed, and heated in a Carius furnace at 180° for 18 hours. Then the tube was allowed to cool to room temperature and opened. The organic material was extracted with benzene and neutralized with a concentrated solution of sodium carbonate. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, concentrated, and chromatographed using a column packed with neutral alumina and n-hexane as the eluent. The eluent was concentrated to leave a yellow oil which crystallized as pale yellow crystals from 95% ethyl alcohol. mp 132-132.5°. Yield 0.67 g 70%. (Lit⁵⁵ 74% mp 132.5-133°).

9-Methyl dibenzo(a,e)fluoranthene

In a 250 ml, round-bottomed flask equipped with a condenser, 1.5 g of anhydrous aluminum chloride in 70 ml of anhydrous benzene was heated gently, and to it was added 0.5 g (0.0015 mole) of 7-(2-methylphenyl)-benz(a)anthracene in 30 ml of hot anhydrous benzene (the red brown color developed immediately). The solution was heated under reflux for 12 hours, cooled to room temperature, and poured into a beaker containing

about 100 ml of 10% hydrochloric acid solution. The organic layer was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to about 5 ml and crystallized from 95% ethyl alcohol and some drops of benzene to give reddish crystals. The product was chromatographed using the same column that was used for its isomer (7-methyl dibenzo(a,e)-fluoranthene), recognizing that the red material was held at the top of the column. The eluent was concentrated to give pale yellow crystals. Yield 0.25 g 50%. The product was identified as the dihydro compound.

The dihydro compound was dehydrogenated (aromatized) with D.D.Q. in a ratio of 1:1 by weight. This mixture was heated under reflux in dry benzene for six hours in a round-bottomed flask equipped with a condenser, then cooled to room temperature and poured into a beaker containing 10% sodium hydroxide solution (the aqueous layer changed to yellow). The organic layer was separated. The aqueous layer was extracted with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to a few ml. Then it was crystallized as yellow tiny crystals from 95% ethyl alcohol and a few drops of benzene. The product was chromatographed through a column packed with neutral alumina (mesh 80-200). Petroleum ether 30-60° was first used to wash down the blue band. After all the blue band had been removed, a mixture of petroleum ether 30-60° and benzene in a ratio of 1:1 was used to wash down the desired band (yellow fluorescence). Then this eluent was concentrated to about 5 ml and crystallized as tiny yellow crystals from 95% ethyl alcohol and a few drops of benzene. The yield

was quantitative. The analytical sample was prepared by rechromatography and crystallization four times to give tiny yellow crystals, mp 216-216°.

1. Anal. Calculated for $C_{25}H_{16}$: C, 94.93; H, 5.07

Found C, 94.90; H, 5.08

2. U.V. spectrum. Page 90 No: 11

3. I.R. spectrum. Page 98 No: 27

2-(1-Naphthylmethyl)3,5-dimethylbenzophenone

A Grignard reagent was prepared from 2.2 g (0.09 g atom) of magnesium and 18.5 g (0.1 mole) of 1-bromo 3,5-dimethylbenzene in 125 ml of dry ethyl ether in a 2 l, three-necked, round-bottomed flask equipped with a mechanical stirrer and a take-off condenser. After the reaction was completed, most of the ether was removed, and a solution of 12.2 g (0.05 mole) of 2-(1-naphthylmethyl)benzonitrile in 200 ml of dry toluene was added dropwise (during the addition the flask was heated gently). When the addition was completed, the mixture (milky yellow) was heated under reflux for 18 hours, then cooled to room temperature and decomposed with 25 ml of a 20% ammonium chloride solution. The organic red layer was separated and the residue in the flask washed twice with water. The combined extracts were washed with water and placed back in the apparatus. 80 ml of 25% sulfuric acid was added slowly. After the addition was completed, the mixture was heated under reflux for three hours, then cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. The oily product was chromatographed (neutral alumina and benzene). The yellow oil was crystallized from ethanol. Yield 11 g 80%,

mp 91-92.5°. (Lit⁶² yield 87% from the Ketimine mp 93-94°).

7-(3,5-Dimethyl)benz(a)anthracene (42)

A mixture of 1.00 g of 2-(1-naphthylmethyl)-3,5-dimethylbenzo-phenone, 30 ml of glacial acetic acid and 15 ml of 48% hydrobromic acid was sealed in a glass tube and heated at 250° for five hours. The tube was allowed to cool to room temperature. The organic material was extracted with benzene, separated, washed with water, dried over anhydrous magnesium sulfate, and concentrated. The product was chromatographed (neutral alumina and benzene). This product was obtained as a yellow oil after evaporation of the eluent crystallized from ethanol as pale yellow crystals melted at 116-117°. Yield 0.77 g 80%. (Lit⁶² yield from ketimine 96%, mp 118-120°).

6,8-Dimethyl dibenzo(a,e)fluoranthene

In a round-bottomed flask (250 ml) equipped with a condenser, 3 g of anhydrous aluminum chloride in 100 ml of dry benzene was heated gently, and to it was added 1.00 g of 7-(3,5-dimethyl phenyl)benz(a)-anthracene in 50 ml of hot dry benzene (the red brown color developed directly). The mixture was heated under reflux for 25 minutes, cooled to room temperature and dropped into a beaker containing about 100 ml of 10% hydrochloric acid (the solution turned to yellow). The organic material was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed with water, dried over anhydrous magnesium sulfate, concentrated to a few ml and crystallized from 95% ethyl alcohol with a few drops of benzene to give yellow tiny crystals which were chromatographed

on a column packed with neutral alumina (mesh 80-200). The eluent was petroleum ether 30-60°. The eluent was evaporated to give pale yellow crystals. Yield 0.76 g 76%. The product was identified as the dihydro compound.

The dihydro compound was dehydrogenated (aromatized) with D.D.Q. in a ratio of 1:1 by weight. The dihydro compound was dissolved in dry hot benzene, and to it was added the D.D.Q. In a round-bottomed flask equipped with a condenser the mixture was heated under reflux for six hours, cooled to room temperature and poured into a flask containing around 100 ml of 10% sodium hydroxide solution. The organic layer was separated. The aqueous layer was extracted with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to a few ml. Then it was crystallized as tiny yellow crystals from 95% ethanol and a few drops of benzene, which was chromatographed on a column (neutral alumina). Petroleum ether 30-60° was first used to remove the blue fluorescent band which came first. The eluent was changed to a mixture of petroleum ether and benzene in a ratio of 1:1 to wash down the yellow fluorescent band. Finally the second eluent was concentrated to a few ml and crystallized as tiny bright yellow crystals from 95% ethanol with a few drops of benzene. The yield was quantitative. The analytical sample was chromatographed twice and crystallized four times to give crystals melted at 191-192°.

1. Anal. Calculated for $C_{26}H_{18}$: C, 94.54; H, 5.46

Found C, 94.25; H, 5.48

2. U.V. spectrum. Page 93 No: 17

3. I.R. spectrum. Page 101 No: 33

7,8-Dimethyl dibenzo(a,e)fluoranthene

In a round-bottomed flask (250 ml) equipped with a condenser, 3 g of anhydrous aluminum chloride in 100 ml of dry benzene was heated gently, and to it was added one g of 7-(3,4-dimethylphenyl)benz(a)-anthracene in 50 ml of hot dry benzene (the red brown color developed immediately). The mixture was heated under reflux for 30 minutes, cooled to room temperature, and treated as in the case of the 6,8-isomer. Yield 0.55 g 55%. The product was identified as the dihydro compound.

The dihydro compound was dehydrogenated with D.D.Q. in a ratio of 1:1. The dihydro compound was dissolved in dry hot benzene, and to it was added the D.D.Q. In a round-bottomed flask equipped with a condenser, the mixture was heated under reflux for six hours, cooled to room temperature, and treated as in the case of the 6,8-isomer. The yield was quantitative. The analytical sample was prepared by chromatographing the yellow crystals twice and recrystallizing them four times. The product was collected as tiny bright yellow crystals, mp 187-188°.

1. Anal. Calculated for $C_{26}H_{18}$: C, 94.54; H, 5.46

Found C, 94.52; H, 5.50

2. U.V. spectrum. Page 92 No: 16

3. I.R. spectrum. Page 102 No: 34

7,9-Dimethyldibenzo(a,e)fluoranthene

In a round-bottomed flask equipped with a condenser, 600 mg of anhydrous aluminum chloride in 25 ml of dry benzene was heated gently, and to it was added 200 mg of 7-(2,4-dimethylphenyl)benz(a)anthracene in 25 ml of hot dry benzene (the red brown color developed immediately).

The mixture was heated under reflux for 12 hours, cooled to room temperature, and treated as in the case of the 6,8-isomer. Yield 60 mg 30%. The product was identified as a dihydro compound.

The dihydro compound was dehydrogenated with D.D.Q. in a ratio of 1:1. The dihydro compound was dissolved first, and to it was added the D.D.Q. In a round-bottomed flask equipped with a condenser, the mixture was heated under reflux for six hours, cooled to room temperature, and treated as in the case of the 6,8-isomer. The yield was quantitative, and the analytical sample was obtained by chromatographing the yellow crystals twice and recrystallizing them four times. The product was collected as tiny bright yellow crystals, mp 164-165°.

1. Anal. Calculated for $C_{26}H_{18}$: C, 94.54; H, 5.46

Found C, 94.62; H, 5.57

2. U.V. spectrum. Page 91 No: 14

3. I.R. spectrum. Page 101 No: 32

8,9-Dimethyldibenzo(a,e)fluoranthene

In a round-bottomed flask equipped with a condenser, 600 mg of anhydrous aluminum chloride in 25 ml of dry benzene was heated gently, and to it was added 200 mg of 7-(2,3-dimethylphenyl)benz(a)anthracene in 25 ml of hot dry benzene (the red brown color developed immediately). The mixture was heated under reflux for 12 hours, cooled to room temperature, and treated as in the case of the 6,8-isomer. Yield 100 mg 50%. The product was identified as the dihydro compound.

The dihydro compound was dehydrogenated with D.D.Q. in a ratio of 1:1. The dihydro compound was dissolved, and to it was added the D.D.Q. In a round-bottomed flask equipped with a condenser, the mixture was

heated under reflux for six hours, cooled to room temperature, and treated as in the case of the 6,8-isomer. The yield was quantitative. The analytical sample was obtained by chromatographing the yellow crystals twice and recrystallizing them four times. The product was collected as tiny bright yellow crystals, mp 192-193°.

1. Anal. Calculated for $C_{26}H_{18}$: C, 94.54; H, 5.46

Found C, 94.36; H, 5.51

2. U.V. spectrum. Page 92 No: 15

3. I.R. spectrum. Page 100 No: 31

2-(1-Naphthylmethyl)-4-fluorobenzophenone (29)

A Grignard reagent was prepared from 3.6 g (0.15 g atom) of magnesium turnings and 26 g (0.15 mole) of 4-fluorobromobenzene in 300 ml of anhydrous ethyl ether in a 2 l, three-necked, round-bottomed flask fitted with a mechanical stirrer and an efficient reflux condenser. After the reaction was completed, most of the ethyl ether was removed. A solution of 24 g (0.10 mole) of 2-(1-naphthylmethyl)benzonitrile in 300 ml of dry toluene was added slowly to the Grignard reagent. After the addition was completed, the mixture was heated under reflux for 18 hours, then cooled to room temperature and decomposed with a solution of 20% ammonium chloride (about 200 ml). After that the organic layer was separated, washed twice with water, combined with 200 ml of a solution of 25% sulfuric acid and heated under reflux for 20 hours, then cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, and concentrated. Finally it was distilled under reduced pressure (1.2 mm, 225-230°). The product was a viscous yellow oil. Yield 20 g, 60%. The

IR spectra (No. 19 Page 94) showed the absorption of the ketone group. This new intermediate compound was not identified by elemental analysis.

7-(4-Fluorophenyl)benz(a)anthracene (32)

In a round-bottomed flask equipped with a condenser 1.00 g (0.002 mole) of 2-(1-naphthylmethyl)-4-fluorobenzophenone, 50 ml of glacial acetic acid and 15 ml of 48% hydrobromic acid solution were heated under reflux for 3 hours. During the refluxing, the product appeared as pale yellow crystals. After that it was cooled to room temperature. The solid product was filtrated, washed with water, dried, and recrystallized as pale yellow crystals from 95% ethanol. Yield 0.71 g, 75%. After chromatographing on a column packed with neutral alumina and petroleum ether 30-60° and crystallizing three times, the product was collected as pale yellow crystals, mp 175-176°.

1. Anal. Calculated for $C_{24}H_{15}F$: C, 89.44; H, 4.65; F, 5.90

Found C, 89.48; H, 4.43; F, 5.59

2. U.V. spectrum. Page 85 No: 2

3. I.R. spectrum. Page 96 No: 23

7-Fluorodibenzo(a,e)fluoranthene (66)

In a 250 ml, round-bottomed flask equipped with a condenser 3.00 g of anhydrous aluminum chloride in 120 ml of anhydrous benzene was heated gently, and to it was added 0.5 g (0.0015 mole) of 7-(4-fluorophenyl)-benz(a)anthracene in 25 ml of hot anhydrous benzene (the red brown color appeared directly after the addition). The solution was heated under reflux for 24 hours, cooled to room temperature, and poured into a beaker containing about 100 ml of 10% hydrochloric acid solution. The organic

layer was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to about 5 ml and crystallized as reddish crystals from 95% ethanol. The product was chromatographed through a column packed with neutral alumina (mesh 80-200). An eluent of petroleum ether 30-60° was used to wash down the blue band. After all the band had been removed the eluent was changed to benzene to wash down the desired yellow band. The red material was left at the top of the column. Then the second eluent was concentrated to a few ml and crystallized from 95% ethyl alcohol. After the fourth crystallization the product was tiny yellow crystals, mp 256-257°. Yield 0.23 g, 46%.

1. Anal. Calculated for $C_{24}H_{13}F_1$: C, 90.00; H, 4.06; F, 5.93.

Found C, 90.06; H, 4.05; F, 5.38.

2. U.V. spectrum. Page 86 No: 3

3. I.R. spectrum. Page 98 No: 26

2-(1-Naphthylmethyl)-3-fluorobenzophenone (32)

A Grignard reagent was prepared from 1.8 g (0.075 g atom) of magnesium turnings and 13 g (0.075 mole) of 3-fluorobromobenzene in 150 ml of anhydrous ethyl ether in a 1 liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and take-off condenser. After the reaction was completed, most of the ether was removed. A solution of 12 g (0.05 mole) of 2-(1-naphthylmethyl)benzonitrile in 150 ml of dry toluene was added slowly to the Grignard reagent. After the addition was completed the mixture was heated under reflux for 18 hours, then cooled to room temperature and decomposed with a solution of 20% ammonium

chloride (100 ml). After that the organic layer was separated, washed twice with water, combined with 100 ml of a solution of 25% sulfuric acid, and heated under reflux for 22 hours, then cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate and concentrated. The organic material was chromatographed (the column was packed with neutral alumina 80-200 mesh). The eluent was petroleum ether 30-60° mixed with a little benzene. The product was a viscous yellow oil and was crystallized as yellow crystals from petroleum ether with a few drops of benzene, mp 101-102°. Yield 10 g, 60% of fine pale yellow crystals.

1. Anal. Calculated for $C_{24}H_{17}O_1F_1$: C, 84.7; H, 5.00; F, 5.58;
O, 4.41

Found C, 84.78; H, 5.07; F, 5.36; O, 4.79

2. I.R. spectrum. Page 94 No: 18

7-(3-Fluorophenyl)benz(a)anthracene (31)

In a round-bottomed flask equipped with a condenser 1.00 g of 2-(1-naphthylmethyl)-3-fluorobenzophenone and 50 ml of glacial acetic acid with 15 ml of 48% hydrobromic acid solution was heated under reflux for 3 hours. After that it was cooled to room temperature, and the product was precipitated as beige crystals, which were filtrated from the acid solution, washed with water to remove the acidity, and recrystallized as white crystals from 95% ethyl alcohol. mp 160-161°. Yield 0.8 g, 85%.

1. Anal. Calculated for $C_{24}H_{15}F_1$: C, 89.44; H, 4.65; F, 5.90.

Found C, 89.43; H, 4.91; F, 5.75

2. U.V. spectrum. Page 85 No: 1
3. I.R. spectrum. Page 97 No: 24

8-Fluorodibenzo(a,e)fluoranthene (65)

In a 250 ml, round-bottomed flask equipped with a condenser, 3.00 g of anhydrous aluminum chloride in 120 ml of anhydrous benzene was heated gently, and to it was added 0.5 g (0.0015 mole) of 7-(3-fluorophenyl)benz(a)anthracene in 25 ml of hot anhydrous benzene (the red brown color appeared directly after the addition of the fluoro hydrocarbon to the aluminum chloride). The solution was heated under reflux for 24 hours, cooled to room temperature, and poured into a beaker containing around 100 ml of 10% hydrochloric acid solution. The organic layer was separated. The aqueous layer was extracted twice with benzene and combined with the other organic layer. The organic material was washed twice with water, dried over anhydrous magnesium sulfate, concentrated to about 5 ml and crystallized as orange crystals from 95% ethyl alcohol. The product was chromatographed as in the case of its isomer (7-fluoro-dibenzo(a,e)fluoranthene (66)). The product was collected as tiny yellow crystals. mp 235-236°. Yield 0.32 g, 62%. The analytical sample was crystallized four times after being chromatographed twice.

1. Anal. Calculated for $C_{24}H_{13}F_1$: C, 90.00; H, 4.06; F, 5.93

Found C, 90.23; H, 4.18; F, 5.18

2. U.V. spectrum. Page 86 No: 4

3. I.R. spectrum. Page 97 No: 25

o-Bromotoluene

A solution of 162 g (1.5 mole) of commercial o-toluidine in 880 ml (6 mole) of 40% commercial hydrobromic acid in a 3 l, three-necked flask fitted with a mechanical stirrer was cooled to 10° and diazotized with

116 g (1.7 mole) of sodium nitrite added in about 10 g increments at a time. After each addition it was left until all the red fumes were absorbed. The temperature was kept below 10°. When diazotization was completed, 5 g of copper powder was added. The flask was attached to a reflux condenser and heated very cautiously. As soon as the first sign of reaction was observed the flask was cooled with ice. Nitrogen was evolved vigorously. When the reaction subsided, the mixture was heated for one-half hour on the steam bath. Then 1 liter of water was added, and the mixture was steam distilled until about 1.5 l had passed over. The distillate was made alkaline with about 10 g of powdered sodium hydroxide, and the red bottom layer of crude o-bromotoluene was separated. The crude product was washed with concentrated sulfuric acid, which removed almost all the color, and then twice with water. It was dried over calcium chloride, filtrated and distilled from a modified claisen flask. The yield of the product boiling between 170-180° was 120 g, 47%. (Lit³⁹ bp 178-181°, 110-120 g, 42-47%).

2-Bromobenzyl bromide

A solution of 94.3 g (0.55 mole) of o-bromotoluene and 2.2 g benzoyl peroxide in 160 ml of dry benzene was brought to vigorous reflux in a 2 l, three-necked flask fitted with a stirrer and an efficient reflux condenser. A mixture of 98 g (0.55 mole) of N-bromosuccinimide and 2.2 g of benzoyl peroxide was added portionwise through a wide-mouthed adapter. The dry powder was added as rapidly as the violent foaming would permit and was worked down through the stem of the adapter with a stirring rod. Refluxing benzene washed the lower part of the adapter continuously. As soon as the foaming from the last addition of

N-bromosuccinimide had subsided, the flask was cooled, first with a water bath and then with an ice bath. The succinimide was filtered off and washed with dry benzene. The product was concentrated, and the residue was distilled under reduced pressure (8 mm 124-127°). The yield was a colorless liquid 100 g 74%. It was kept in the refrigerator. (Lit⁴⁰ 127-133°, 15.5 mm.)

2-(1-Naphthylmethyl)bromobenzene

A Grignard reagent was prepared by the addition of 142.2 g (0.6 mole) of 1-bromonaphthalene in 400 ml of dry ether to 14.6 (0.6 g atom) of magnesium turnings in a 2 l, three-necked, round-bottomed flask equipped with a mechanical stirrer and reflux condenser. After the addition was completed, the solution was heated at reflux temperature for 30 minutes. The ether was replaced with anhydrous benzene, and a solution of 100 g (0.4 mole) of 2-bromobenzylbromide in 200 ml of anhydrous benzene was added dropwise over a period of three hours. The solution was heated at reflux temperature for two additional hours. The complex was cooled and hydrolyzed with 10% hydrochloric acid solution. The organic layer was separated and dried over magnesium sulfate, then distilled under reduced pressure (0.5 mm 160-170°). The yield was a colorless liquid 60 g, 52%. (Lit⁴¹ 220-223° 2-3 mm.)

2-(1-Naphthylmethyl)-2'-fluorobenzophenone

A Grignard reagent was prepared by the addition of 11.8 g (0.04 mole) of 2-(1-naphthylmethyl)bromobenzene in 100 ml of dry ethyl ether to 1.22 g (0.05 g atom) of magnesium turnings in a 500 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer. After the reaction was completed, it was added slowly to a boiling solution

of 6.4 g (0.04 mole) of 2-fluorobenzoyl chloride in 100 ml of dry toluene in a 500 ml, three-necked, round-bottomed flask. After the addition was completed, the ether was allowed to distill until the boiling point of the solution reached 105°. Then the solution was heated an additional three hours. The solution was cooled to room temperature and decomposed with 25% sulfuric acid. The organic layer was separated, washed twice with water, dried over magnesium sulfate and concentrated. The product oil (dark) was chromatographed (neutral alumina and a mixture of benzene and petroleum ether as an eluent). The final product was a yellowish oil pure enough to be used for the next step. Yield 6.0 g, 43%. (Lit⁴² 3.55 g, 20%.)

7-(2-fluorophenyl)benz(a)anthracene (30)

A mixture of 1.00 g (0.003 mole) of 2-(1-naphthylmethyl)-2'-fluorobenzophenone, 60 ml of glacial acetic acid and 15 ml of 48% hydrobromic acid solution was sealed in a carius tube and heated for seven hours at 180°. The tube was allowed to cool to room temperature, and the organic material was extracted with benzene, separated, neutralized with sodium carbonate solution, washed twice with water, dried over magnesium sulfate, and concentrated. The product was chromatographed on a column packed with neutral alumina and a mixture of benzene and petroleum ether as an eluent. This product was collected as a yellow oil, crystallized from 95% ethanol as pale yellow crystals which melted at 155-156°. Yield 0.6 g, 63%. (Lit⁴² 87%. mp 154-155°.)

Attempted cyclization of 7-(2-fluorophenyl)benz(a)anthracene (30)

A. In a 250 ml, round-bottomed flask fitted with a condenser 3.00 g

of anhydrous aluminum chloride in 120 ml of dry benzene was heated gently. To it was added 0.5 g (0.0015 mole) of 7-(2-fluorophenyl)benz(a)anthracene in 25 ml of dry hot benzene. The solution was heated under reflux for 24 hours, cooled to room temperature, and poured into a flask containing about 100 ml of 10% hydrochloric acid solution. The organic layer was separated. The aqueous layer was extracted with benzene and combined with the other organic layer. The organic material was washed with water, dried over anhydrous magnesium sulfate and concentrated to a red-brown oil. The oil was chromatographed as in the case of its isomer (7-fluorodibenzo(a,e)fluoranthene). On the column were a blue band, a very short yellow band and at the top the red material. The blue band was removed by using petroleum ether, and the eluent was evaporated to yield a colorless oil that gave the characteristic ultraviolet spectra of the starting material. The short yellow band was removed with benzene but did not show the right spectra of fluoranthene (probably because it was not pure). The yield was very poor and it was therefore difficult to purify.

B. A mixture of 0.5 g of 7-(2-fluorophenyl)benz(a)anthracene and 3.00 g of anhydrous aluminum chloride in 1.50 ml of dry benzene was heated under reflux for 36 hours, cooled to room temperature and treated as mentioned before in part A. The blue band was removed and the eluent evaporated. The yield was a colorless oil and did not give the characteristic spectra of the starting material. There was no indication that we had the desired compound or the starting material.

2-(1-Naphthylmethyl)-4'-chlorobenzophenone

A Grignard reagent was prepared from 14.0 g (0.75 mole) of 4-chlorobromobenzene and 1.8 g of magnesium turnings in 100 ml of dry ethyl

ether in a 1 liter, three-necked flask fitted with a mechanical stirrer and an efficient reflux condenser. After the reaction was completed, the ether was removed, and 10.0 g of 2-(1-naphthylmethyl)benzonitrile in 100 ml of dry benzene was added slowly. The mixture was heated under reflux and stirring for 18 hours, then cooled to room temperature and decomposed with a solution of 20% ammonium chloride. The organic layer was separated, washed twice with water and combined with 75 ml of a solution of 25% sulfuric acid and heated under reflux for 20 hours, then cooled to room temperature. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, concentrated, and distilled under reduced pressure (260-270° 1.5 mm). The product was collected as a viscous oil and crystallized from 95% ethanol. Yield 30 g, 75%. (Lit⁴³ 265-268° 1.5 mm, 37 g 92%.)

7-(4-Chlorophenyl)benz(a)anthracene (32)

A mixture of 1 g of 2-(1-naphthylmethyl)-4'-chlorobenzophenone and 10 g of phenyl acid phosphate was heated under reflux for two hours at 140°. The mixture was cooled to room temperature and washed with water until all the phenyl acid phosphate was removed. The residual oil was dissolved in 95% ethanol and treated with charcoal. The ethanolic solution yielded 0.5 g 65%. (Lit⁴³ 0.72 g 78%.)

7-Chloro-dibenzo(a,e)fluoranthene (68)

In a round-bottomed flask (500 ml) 6 g of anhydrous aluminum chloride in 150 ml of dry benzene was heated gently, and to it was added 1 g of 7-(4'-chlorophenyl)benz(a)anthracene in 50 ml of hot dry benzene. Then it was heated under reflux for 18 hours, cooled to room temperature

and poured into a flask containing 10% hydrochloric acid solution. Then the organic layer was separated, and the acid layer was extracted with benzene and combined with the main product. The organic material was washed with water, dried over anhydrous magnesium sulfate, concentrated to a few ml and crystallized from 95%. After that it was chromatographed (benzene as an eluent and neutral alumina as packing material) and the solvent evaporated and crystallized as tiny yellow crystals from 95% ethanol with a few ml of benzene. The yield was 0.5 g, 50%. mp 237-238°.

1. Anal. Calculated for $C_{24}H_{13}I_1$: C, 85.5; H, 3.95; I, 10.55

Found C, 85.75; H, 4.03; I, 10.50

2. U.V. spectrum. Page 87 No: 5

3. I.R. spectrum. Page 96 No: 22

8-Chloro dibenzo(a,e)fluoranthene (67)

In a round-bottomed flask (500 ml) 6 g of anhydrous aluminum chloride in 150 ml of dry benzene was heated gently, and to it was added 1.00 g of 7-(3'-chlorophenyl)benz(a)anthracene in 50 ml hot dry benzene. Then it was heated under reflux for 18 hours, cooled to room temperature and poured into a flask containing 10% hydrochloric acid solution. Then the organic material was washed with water, dried over anhydrous magnesium sulfate, concentrated to a few ml and crystallized from 95% ethanol. After that it was chromatographed and was evaporated the eluent and crystallized the product as tiny yellow crystals from 95% ethanol and a few drops of benzene. The yield was 0.55 g, 55.5%, mp 217-218°.

1. Anal. Calculated for $C_{24}H_{13}I$: C, 85.50; H, 3.95; I, 10.55
Found C, 85.69; H, 4.08; I, 10.26
2. U.V. spectrum. Page 87 No: 6
3. I.R. spectrum. Page 95 No: 21

2-(1-Naphthylmethyl)-4'-methoxybenzophenone

A Grignard reagent was prepared from 22.5 g (0.12 mole) of P-bromoanisole, 2.9 g (0.12 g atom) of magnesium and 150 ml of dry ethyl ether in a 1 liter, three-necked, round-bottomed flask equipped with a mechanical stirrer and take-off condenser. After the reaction was completed, the ether was distilled off and 13. g (0.062 mole) of 2-(1-naphthylmethyl)benzonitrile in 125 ml of dry benzene was added dropwise. After all the nitrile had been added, the mixture was heated under reflux for 20 hours, then cooled to room temperature and decomposed with a solution of 20% ammonium chloride. The organic layer was separated. The residue was extracted with benzene and the extracts combined with the organic layer. This organic solution was washed twice with water, combined with 75 ml of a solution of 25% sulfuric acid and heated under reflux for 20 hours, then cooled to room temperature. The organic layer was separated, washed twice with water, dried over anhydrous magnesium sulfate, concentrated, and chromatographed (neutral alumina oxide and benzene). The yellow oil was crystallized as white crystals from petroleum ether 30-60°. Yield 19 g, 90%. (Lit⁴³ yield 90% after distillation under reduced pressure 254-262° 3 mm.)

7-(4-Methoxyphenyl)benz(a)anthracene

A mixture of 1 g of 2-(1-naphthylmethyl)-4'-methoxybenzophenone and 10 g of phenyl acid phosphate in a round-bottomed flask (100 ml) was

heated under reflux for three hours at 140-145°. The mixture was cooled to room temperature, extracted with benzene, washed with water at least three times to remove the phenyl acid phosphate, dried over anhydrous magnesium sulfate, concentrated, and crystallized from 95% ethanol. The product was obtained as slightly yellow crystals, mp 187-188°. Yield 0.57 g, 60%. (Lit⁴³ yield 54% mp 188-189°.)

Attempted cyclization of 7-(4'-methoxyphenyl)benz(a)anthracene

A. In a round-bottomed flask fitted with a condenser 1.5 g of anhydrous aluminum chloride in 60 ml of dry benzene was heated gently. To it was added 0.5 g of 7-(4'-methoxyphenyl)benz(a)anthracene in 30 ml of dry hot benzene. The gray color developed immediately. The solution was heated under reflux 30 minutes, cooled to room temperature and decomposed with 10% hydrochloric acid solution. The organic layer (pale yellow color) was separated and concentrated. Then it was chromatographed on a column packed with neutral alumina with petroleum ether as the eluent. The column developed one blue fluorescent band which gave the characteristic spectra of the starting material and no indication of the desired compound.

B. The same conditions as used in part A were employed except that the refluxing time was two and one-half hours. Also, only the starting material was discovered.

C. The same conditions as used in part A were employed except that the refluxing time was nine hours. We got a product of around 10% with a long range melting point. This crude product showed ultraviolet spectra different than the starting material and not exactly as the dihydro compound as was the case in product.

Isomerization of 12-(phenyl)benz(a)anthracene

A. In a round-bottomed flask fitted with a condenser 300 mg of anhydrous aluminum chloride in 25 ml of hot dry benzene was prepared, and to it was added 100 mg of 12-(phenyl)benz(a)anthracene in 25 ml of hot dry benzene. The mixture was heated under reflux for ten minutes, cooled to room temperature, decomposed with 10% hydrochloric acid, and concentrated to give a heavy, dark brown oil. A sample of the oil was dissolved in benzene. The gas liquid was chromatographed (Micro-Tek Model 1600 with hydrogen flame detector and 4' x 1/8" column packed with 2.5% SE-52 on Gas Chrom Z operated at column temperature 225), which was used to analyze the products of this reaction, showed around 50% of 12-(phenyl)benz(a)anthracene, 30% of 7-(phenyl)benz(a)anthracene, 20% of benz(a)anthracene and a very small amount of dibenzo(a,e)fluoranthene.

B. In a round-bottomed flask 300 mg of anhydrous aluminum chloride in 25 ml of hot dry benzene was prepared. To it was added 100 mg of 12-(phenyl)-benz(a)anthracene in 25 ml of hot dry benzene. The mixture was heated under reflux for 15 minutes and cooled to room temperature. The product was treated as mentioned before in part A. The analysis showed around 35% of 7-(phenyl)benz(a)anthracene, nothing of the starting material, 48% of benz(a)anthracene, and some dibenzo(a,e)fluoranthene with some unknown by-products.

C. In a round-bottomed flask the same materials that were used in part A of this experiment were heated under reflux for 30 minutes. The analysis showed around 37% of 7-(phenyl)benz(a)anthracene, 23% of benz(a)-anthracene, and the rest were some dibenzo(a,e)fluoranthene with unknown by-products.

SUMMARY

VI. SUMMARY

A. The two new ketones 2-(1-naphthylmethyl)-3-fluoro and 4-fluoro benzophenone were cyclodehydrated to 7-(3-fluoro, and 4-fluorophenyl)-benz(a)anthracene in a mixture of glacial acetic acid and 48% hydrobromic acid.

B. Cyclodehydrogenation of 7-(2'-methyl, 3-methyl, 4-methyl 3,4-dimethyl, 3,5-dimethyl, 2,3-dimethyl and 2,4-dimethylphenyl)benz(a)-anthracene to the corresponding dihydro compounds was done using anhydrous aluminum chloride in dry benzene in a ratio of 3:1. These interesting new dihydro-compounds have not been previously reported and apparently were overlooked by previous workers⁶⁰. In addition to providing valuable models for spectral studies and physiological activity-molecular structure correlations, these new intermediates help shed light on the mechanism of cyclodehydrogenation reactions. The dihydro compounds were dehydrogenated by 2,3-dichloro-5,6-dicyanobenzoquinone (D.D.Q.) to the corresponding polycyclic aromatic hydrocarbons, 9-methyldibenzo(a,e)fluoranthene, 8-methyldibenzo(a,e)fluoranthene, 7-methyldibenzo(a,e)fluoranthene, 7,8-dimethyldibenzo(a,e)-fluoranthene, 6,8-dimethyldibenzo(a,e)fluoranthene, 8,9-dimethyldibenzo(a,e)fluoranthene and 7,9-dimethyldibenzo(a,e)fluoranthene, respectively.

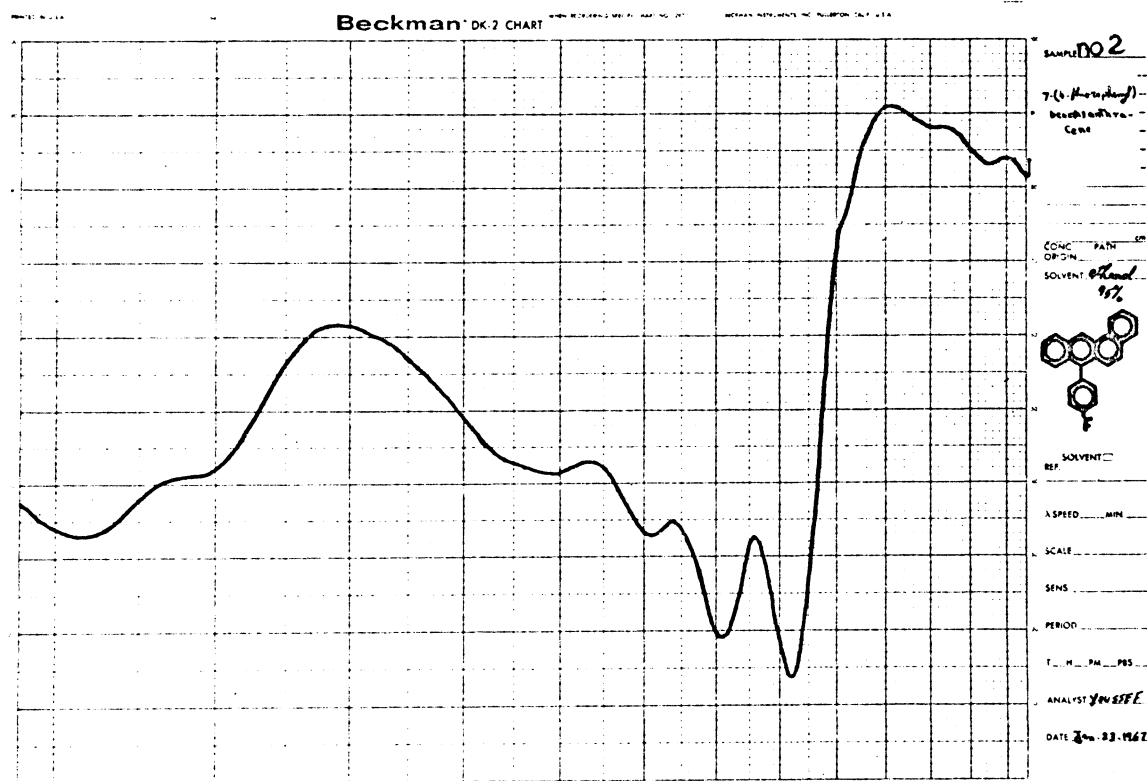
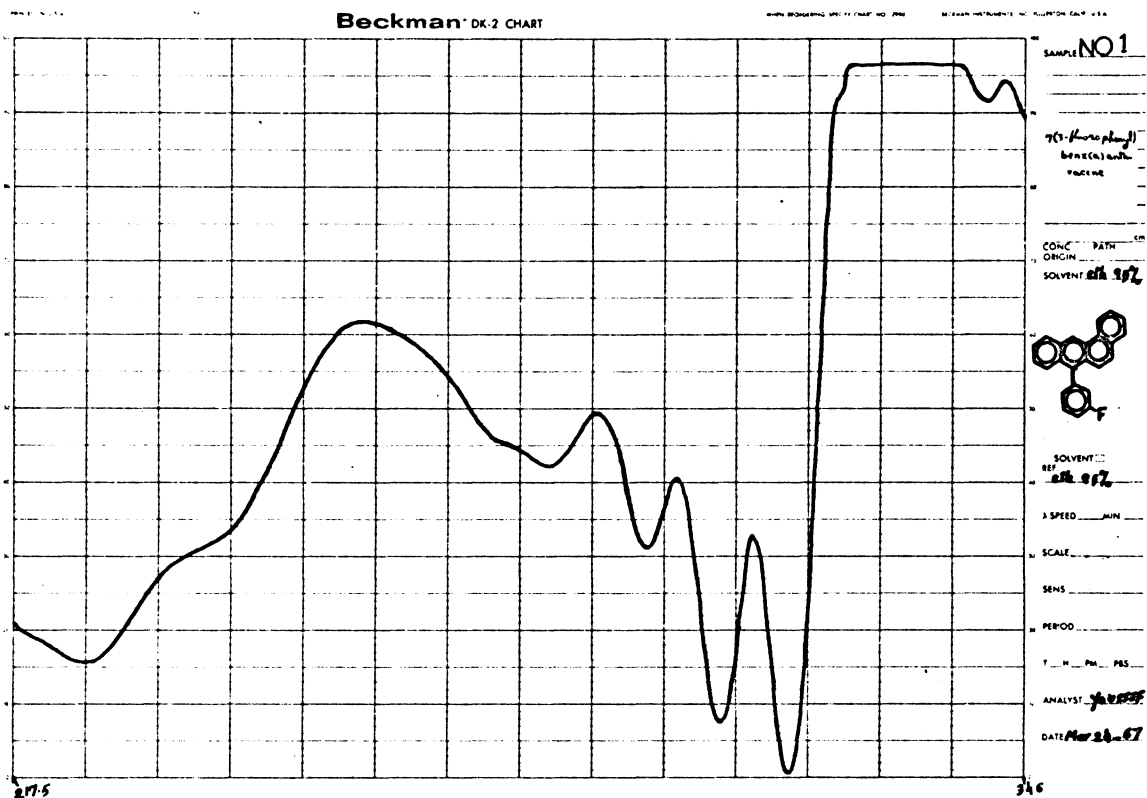
C. Cyclodehydrogenation of 7-(3-fluoro, 4-fluoro, 3-chloro, 4-chloro and 4-bromophenyl)benz(a)anthracene was done using anhydrous aluminum chloride in dry benzene in a ratio of 6:1, giving the corresponding fluoranthene derivatives without separation of intermediate dihydro

compounds 8-fluorodibenzo(a,e)fluoranthene, 7-fluorodibenzo(a,e)-fluoranthene, 8-chlorodibenzo(a,e)fluoranthene and 7-chlorodibenzo-fluoranthene.

D. Study of the rearrangement (isomerization) of 12-phenylbenz(a)-anthracene to 7-phenylbenz(a)anthracene was done using gas liquid chromatograph Micro Tek Model 1600.

During the course of this investigation 24 new compounds were prepared and characterized by elemental analysis, infrared absorption spectra and ultraviolet spectrum.

APPENDIX

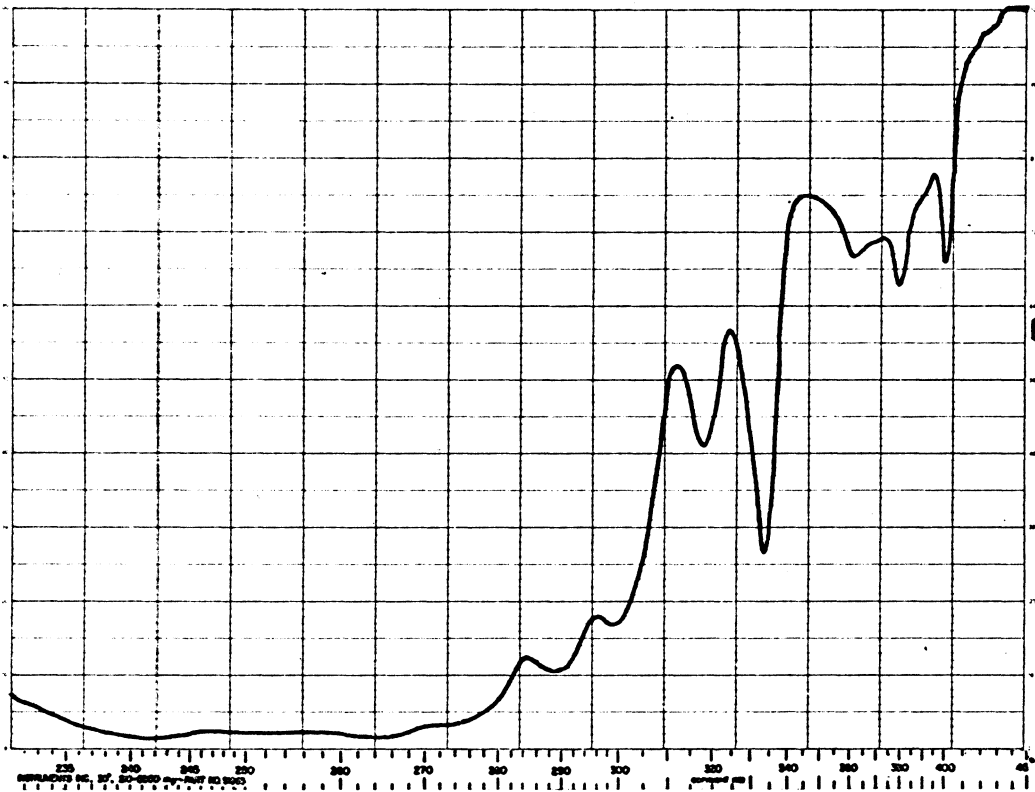


MODEL N. 174

Beckman DK-2 CHART

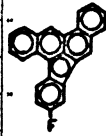
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BECKMAN INSTRUMENTS INC. FULLERTON CALIF. U.S.A.



SAMPLE NO 3
8-chloro dibenzofluorene
(a.s.) Fluorenone

CONC. PATH
ORIGIN
SOLVENT 85% 952



SOLVENT
REF. 85% 952

λ SPEED MIN

SCALE

SENS.

PERIOD

T. H. PM. PAS.

ANALYST B. J. JONES

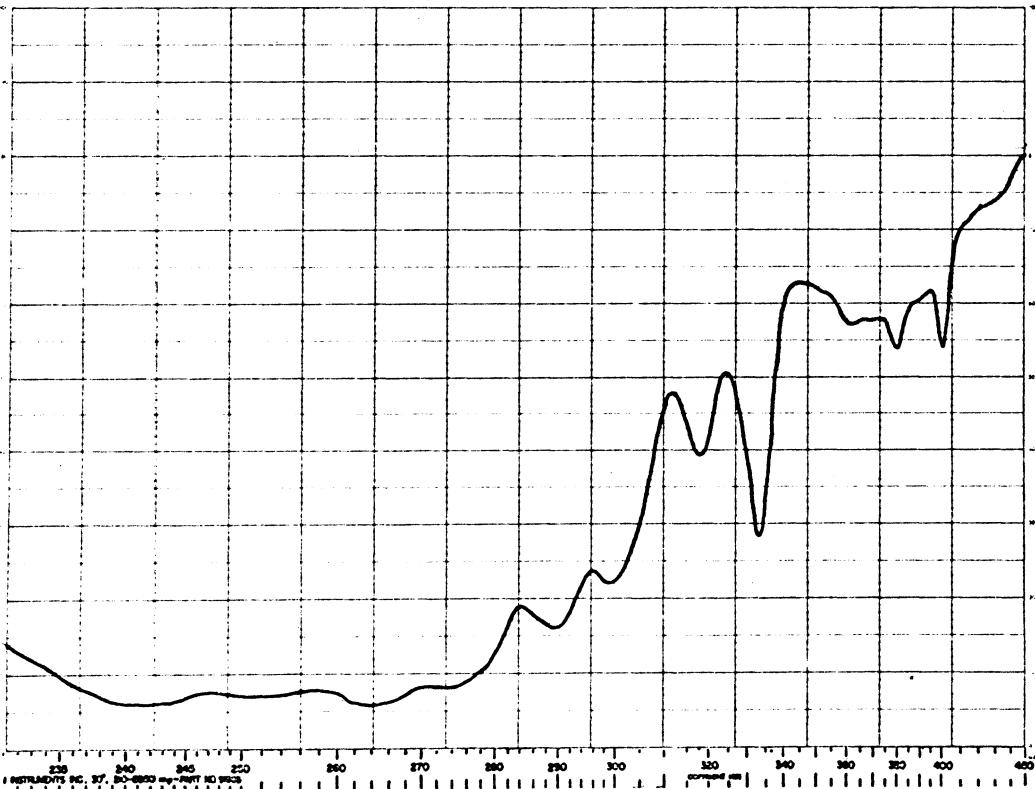
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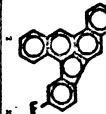
WHEN RECORDING SPLIT FLOW NO. 1788

BECKMAN INSTRUMENTS INC. FULLERTON CALIF. U.S.A.



SAMPLE NO 4
8-chloro dibenzofluorene
(a.s.) Fluorenone

CONC. PATH
ORIGIN
SOLVENT 85% 952



SOLVENT
REF. 85% 952

λ SPEED MIN

SCALE

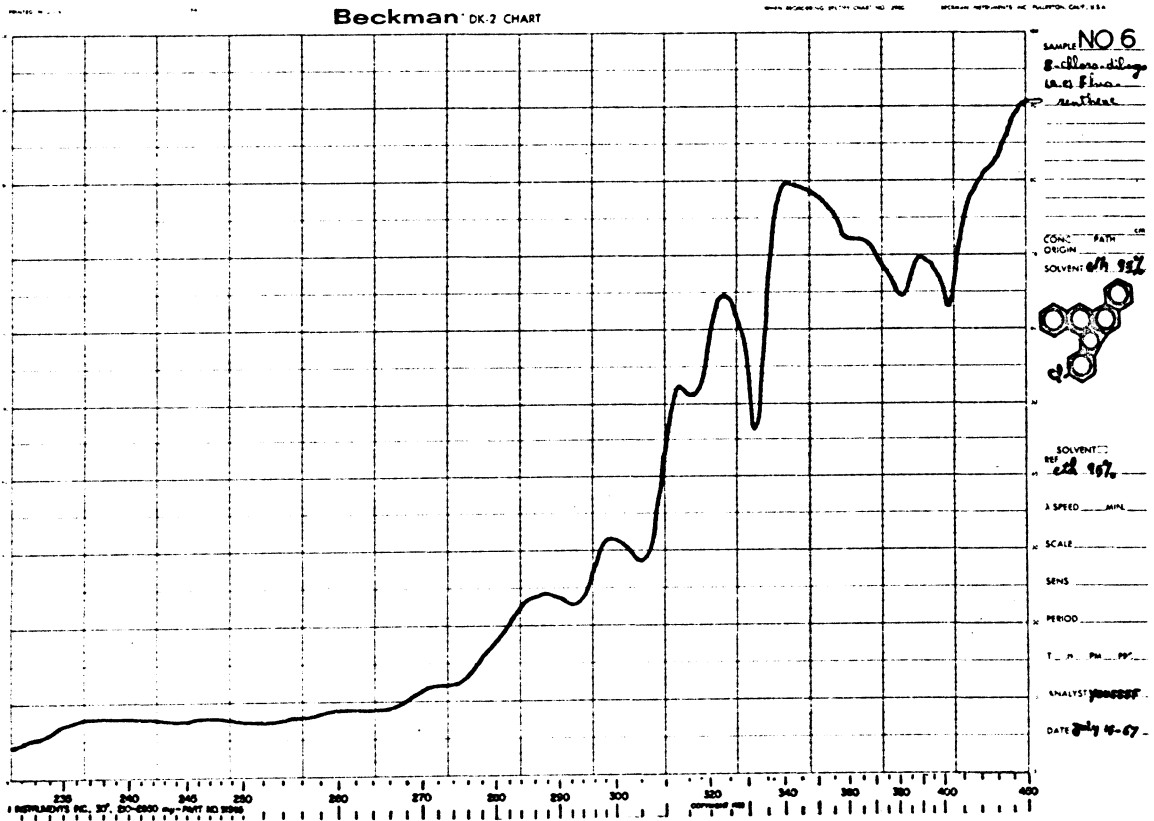
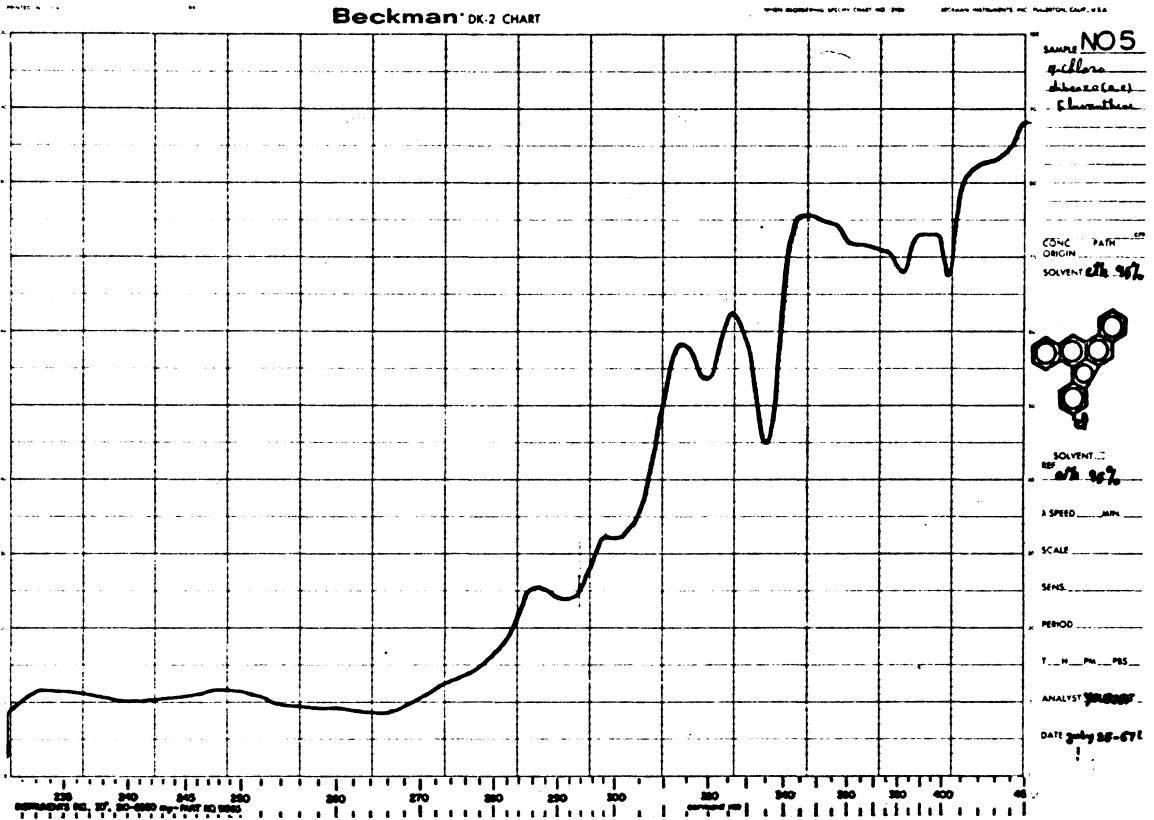
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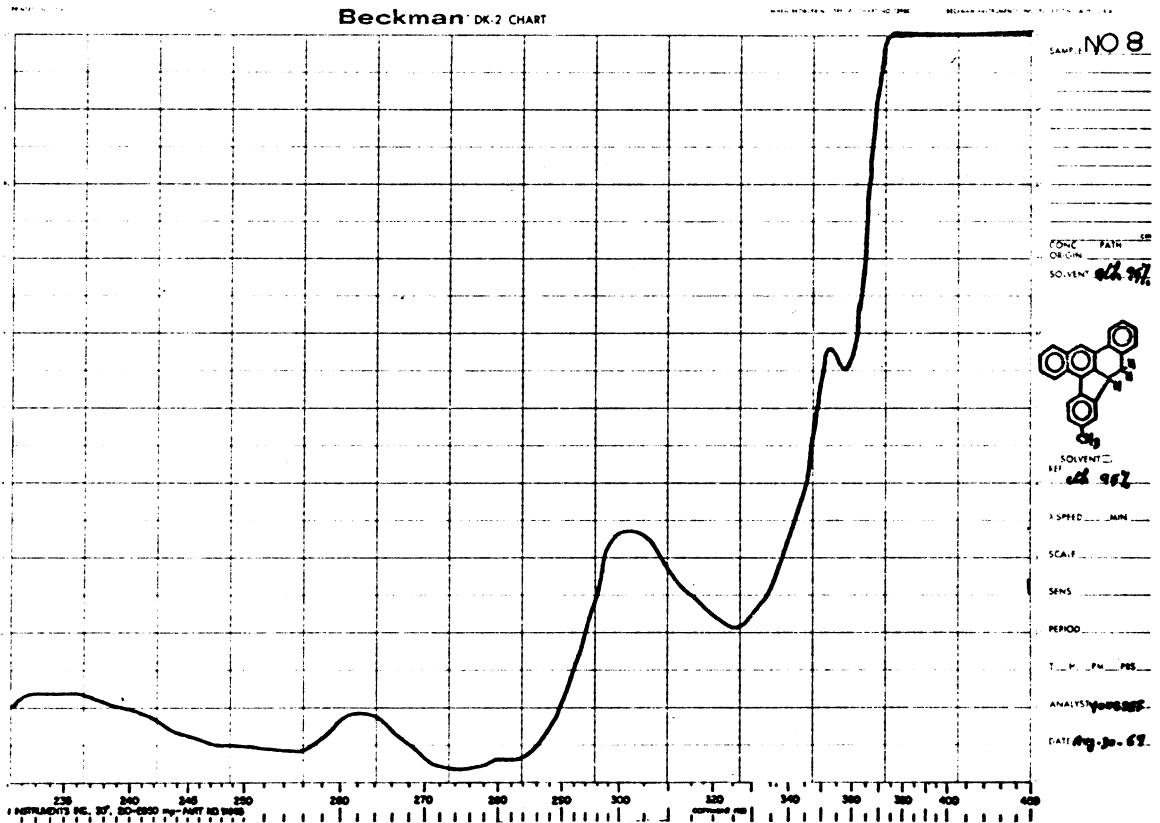
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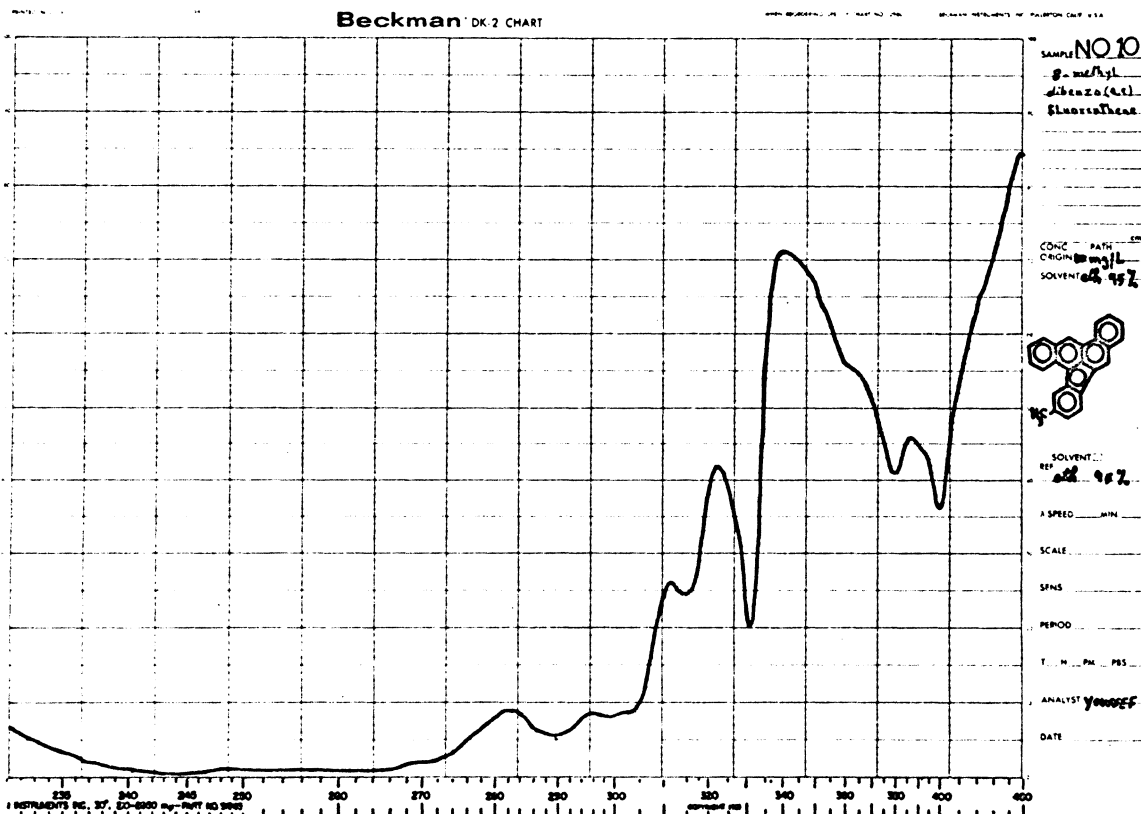
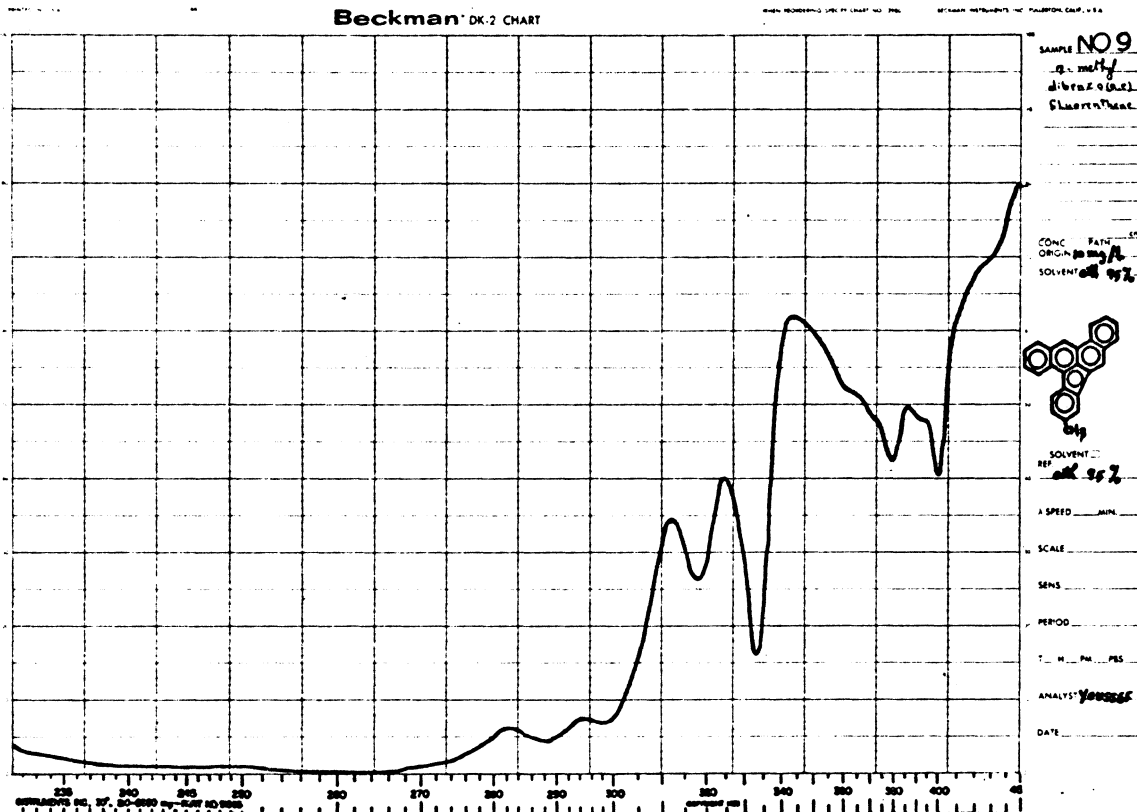
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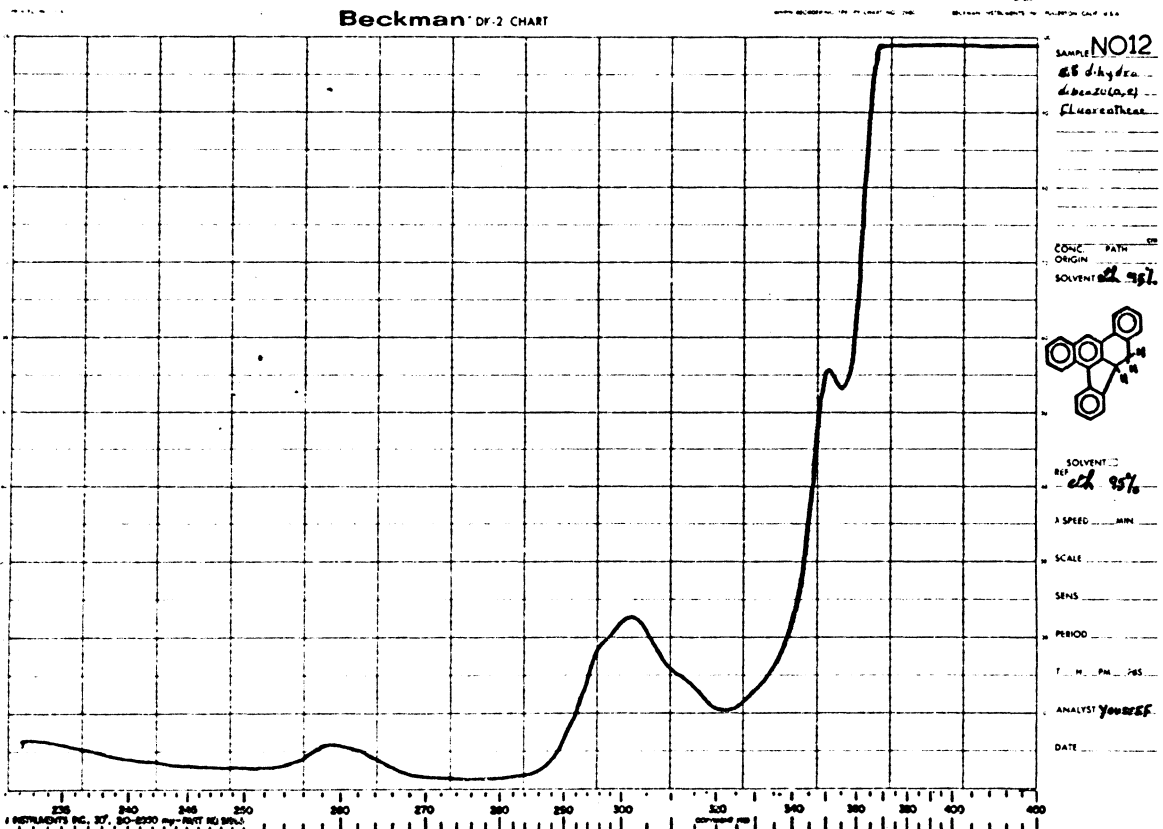
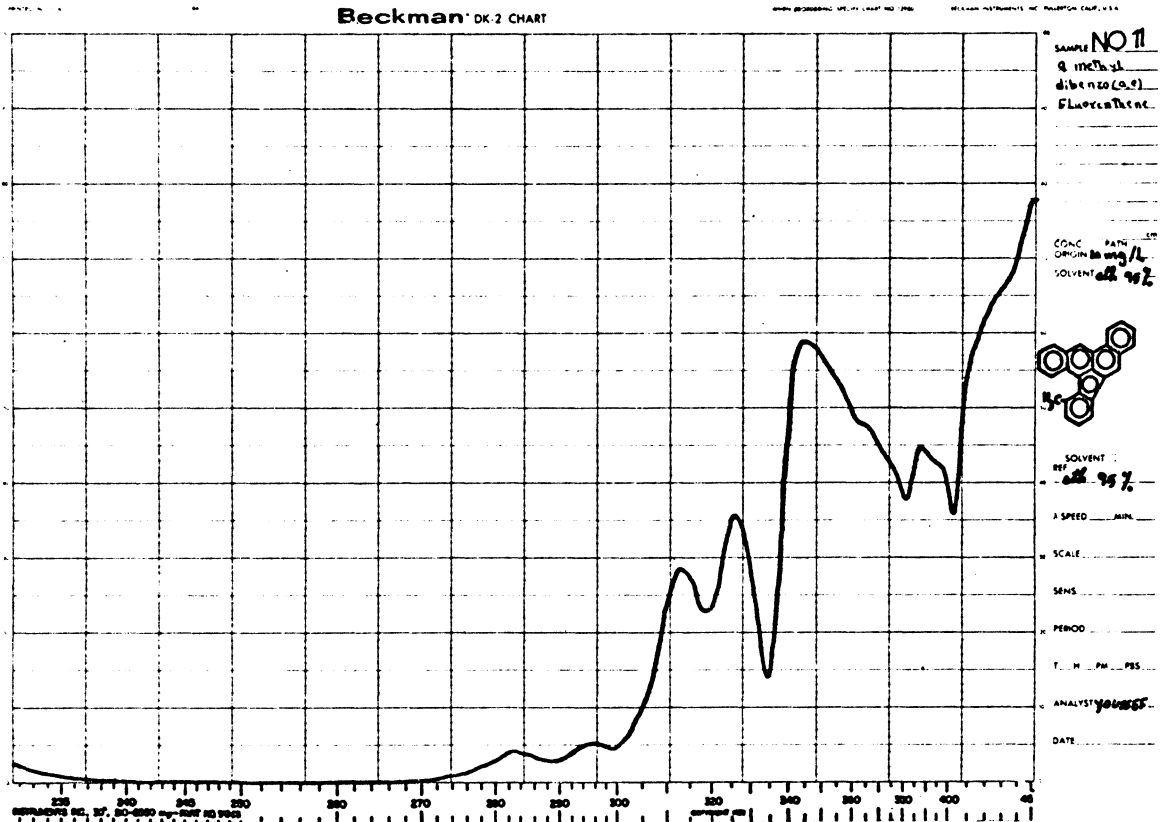
ANALYST J. JONES

DATE FEB 28-67

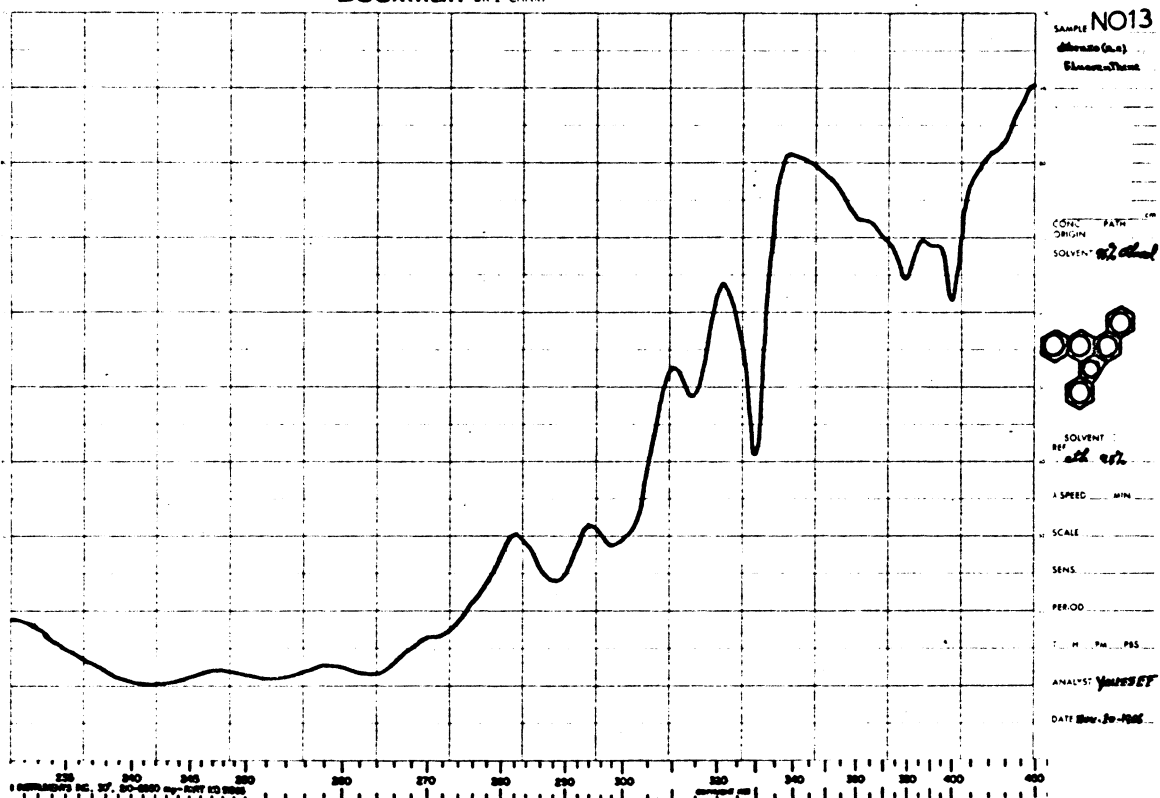




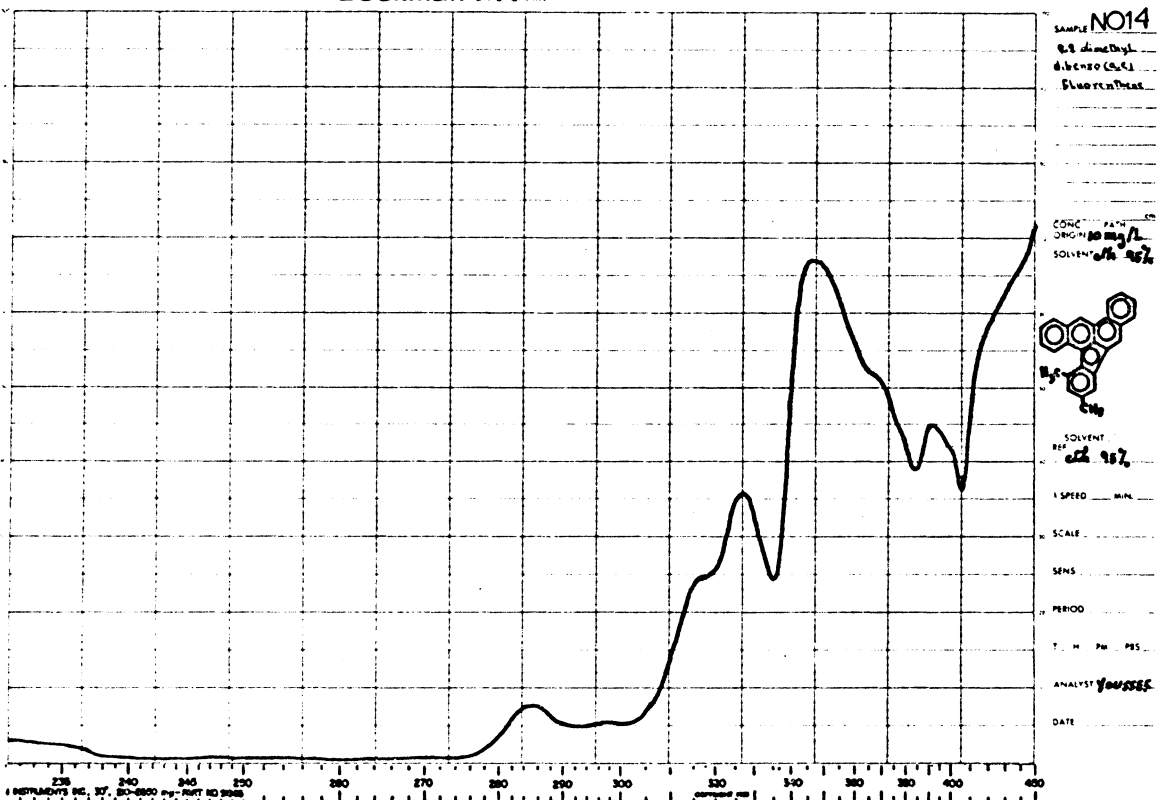




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Beckman DK-2 CHART

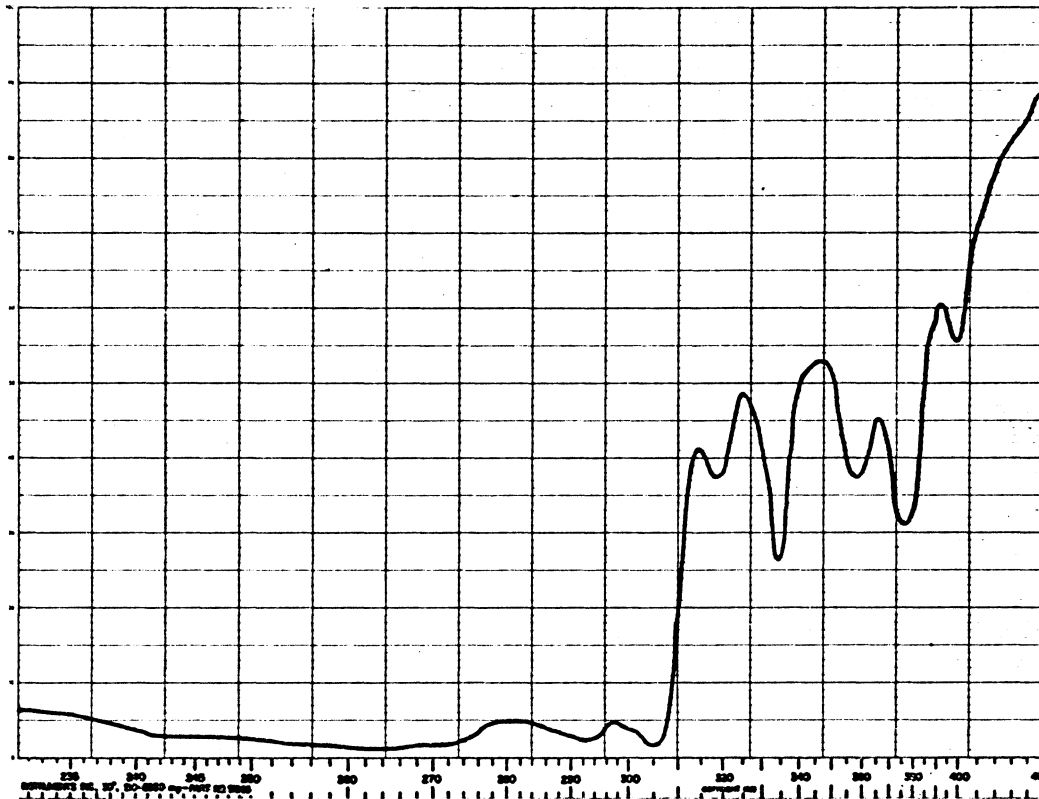


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Beckman DK-2 CHART

UVEN RECORDING SPECT CHART NO. 7266

BECKMAN INSTRUMENTS, INC. FULLERTON, CALIF. U.S.A.



SAMPLE **NO15**
g.g. dimethyl
dibenz (a,e)
fluorene

CONC. 1.0 PATH 1.0
 ORIGIN Beckman
 SOLVENT 95% CH₂Cl₂

Cc1ccc2c(c1)ccc3c2c(c4ccccc4)cc5ccccc35

SOLVENT ☐ REF. 95% CH₂Cl₂

A. SPEED MIN.

SCALE 1

SENS. 1

PERIOD 1

T. 1 H. 1 PM 1 P.S.

ANALYST Youssey

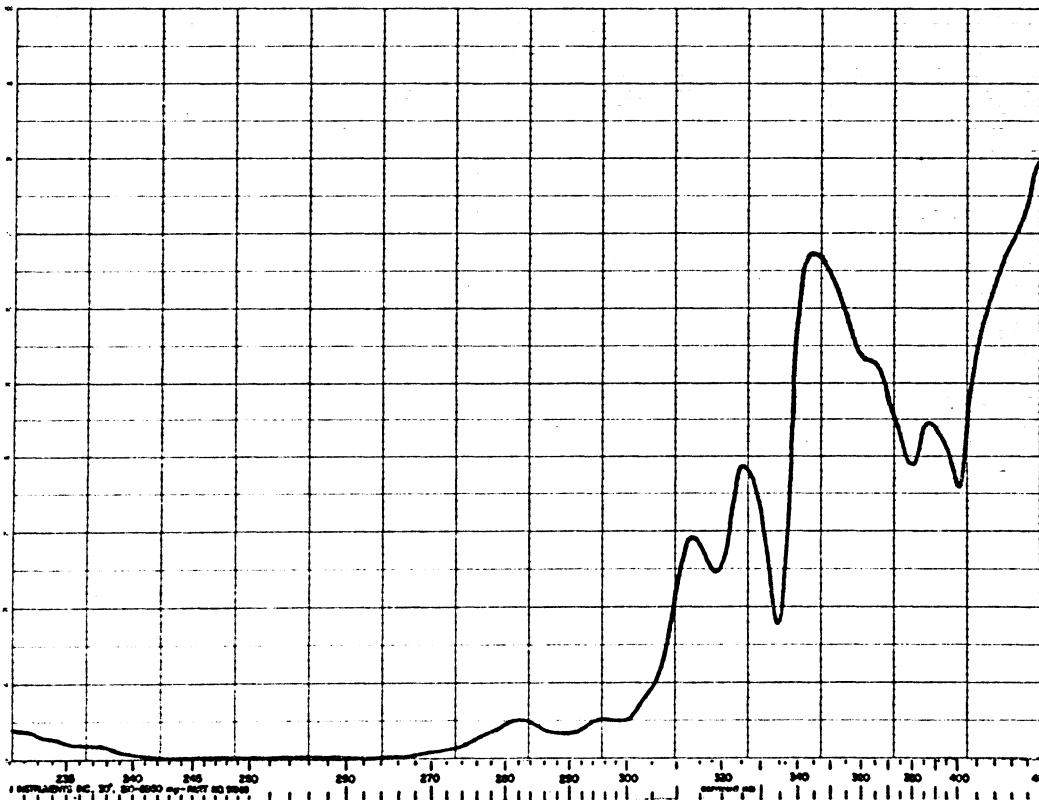
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Beckman DK-2 CHART

UVEN RECORDING SPECT CHART NO. 7266

BECKMAN INSTRUMENTS, INC. FULLERTON, CALIF. U.S.A.



SAMPLE **NO16**
g.g. dimethyl
dibenz (a,e)
fluorene

CONC. 1.0 PATH 1.0
 ORIGIN Beckman
 SOLVENT 95% CH₂Cl₂

Cc1ccc2c(c1)ccc3c2c(c4ccccc4)cc5ccccc35

SOLVENT ☐ REF. 95% CH₂Cl₂

A. SPEED MIN.

SCALE 1

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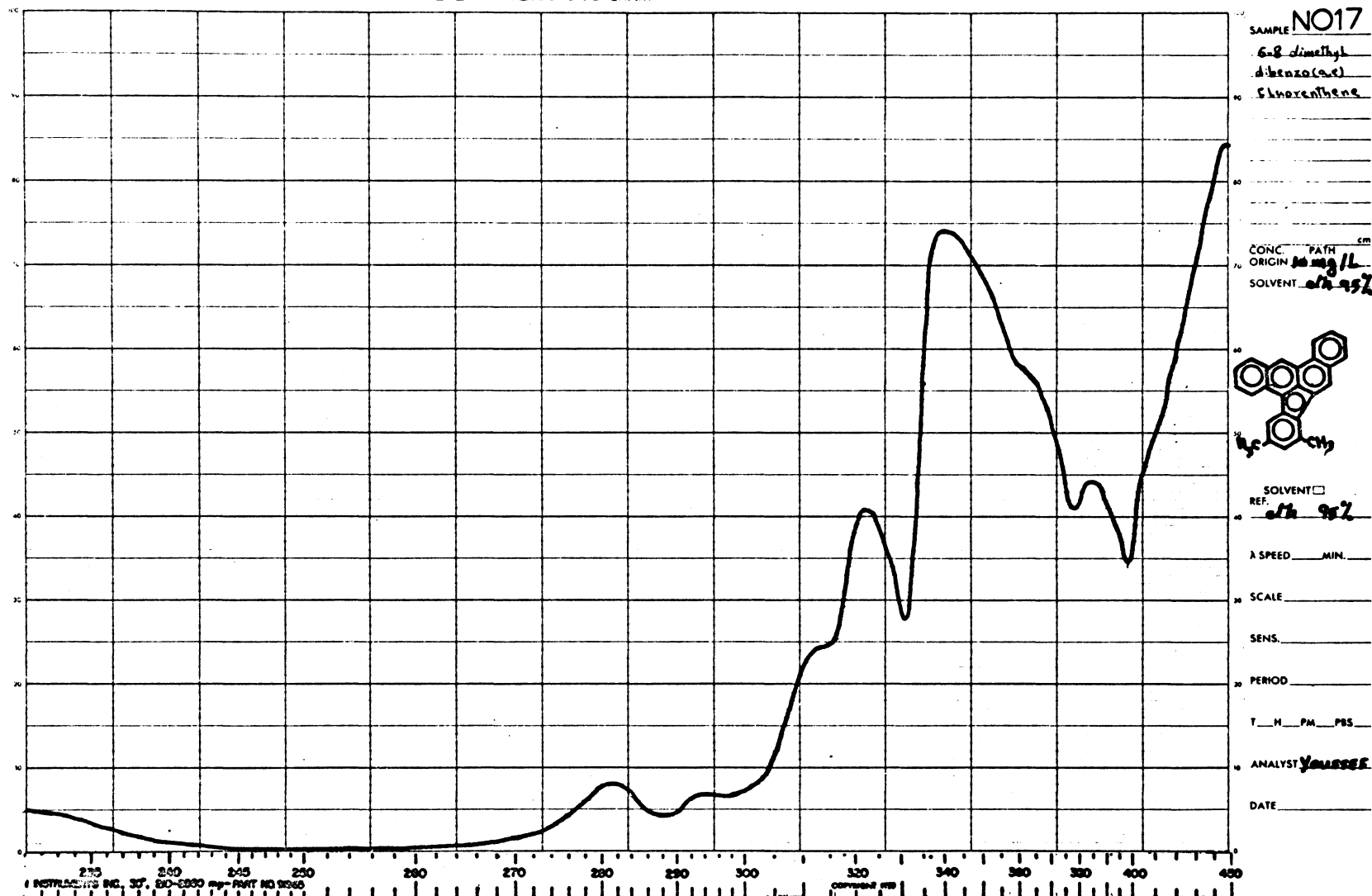
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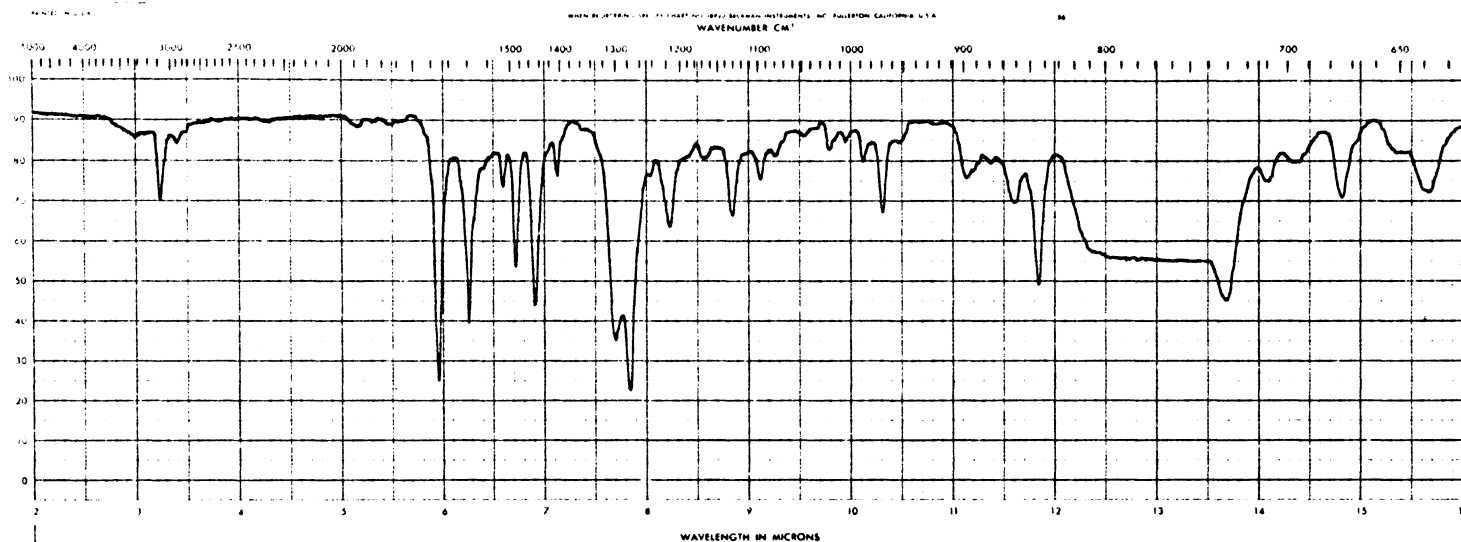
DATE 10/1/68

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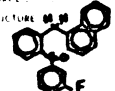
SPECTRUM NO **NO 18**

DATE **Nov 24-1967**

SAMPLE **2(1-naphthyl**

methyl) 4-fluorobenzophenone

SOURCE **benzophenone**

STRUCTURE 

PATH **cc**

SOLVENT **cc**

CONCENTRATION **Conc**

PHASE **Conc**

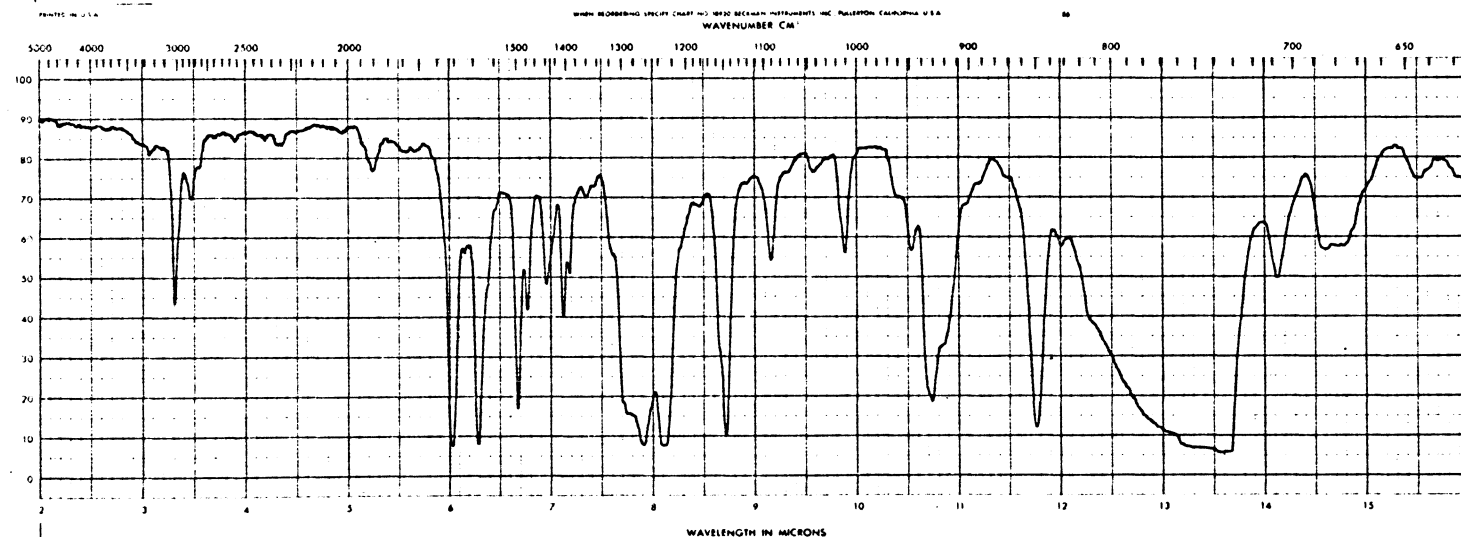
COMMENTS

ANALYST **A.K. YOUSSEF**

Beckman

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SPECTROPHOTOMETER



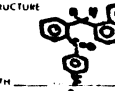
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DATE **Nov 24-1967**

SAMPLE **2(1-naphthyl**

methyl) 4-fluorobenzophenone

SOURCE **benzophenone**

STRUCTURE 

PATH **cc**

SOLVENT **cc**

CONCENTRATION **Conc**

PHASE **Conc**

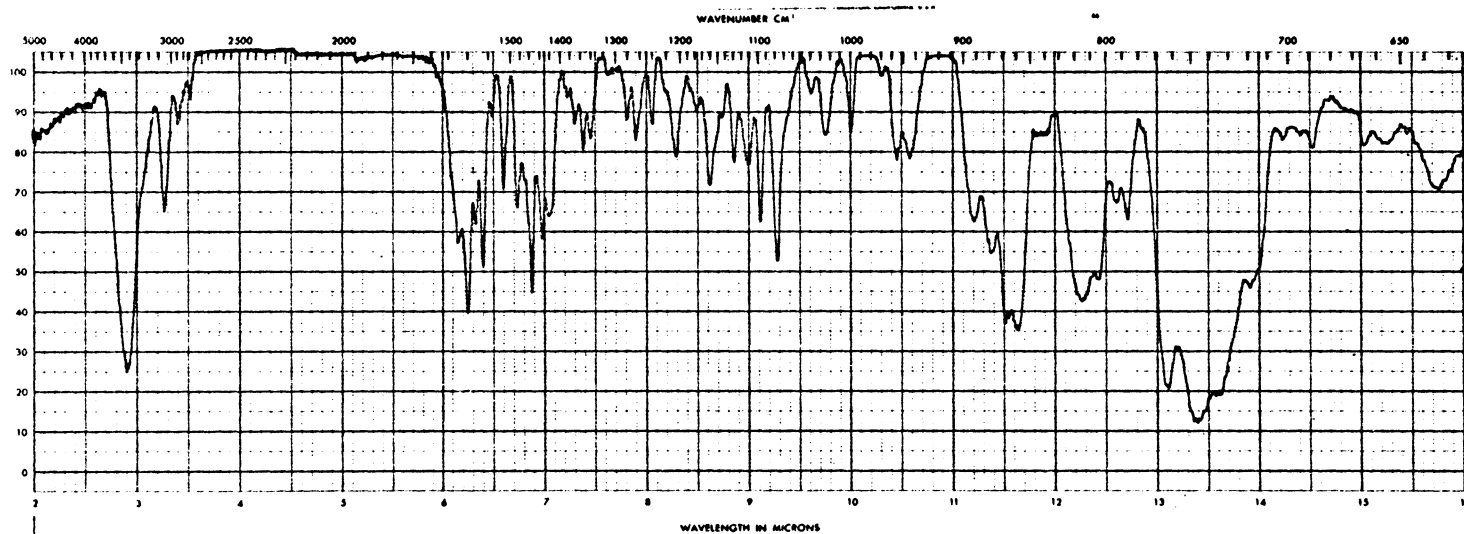
COMMENTS

ANALYST **A.K. YOUSSEF**

Beckman

INFRARED

SPECTROPHOTOMETER



SPECTRUM NO **NO 21**

DATE _____

SAMPLE 2-chloro

dibenz(a,h)

fluorene

SOURCE _____

STRUCTURE



PATH _____

SOLVENT KBr

CONCENTRATION 0.1g/2

PHASE _____

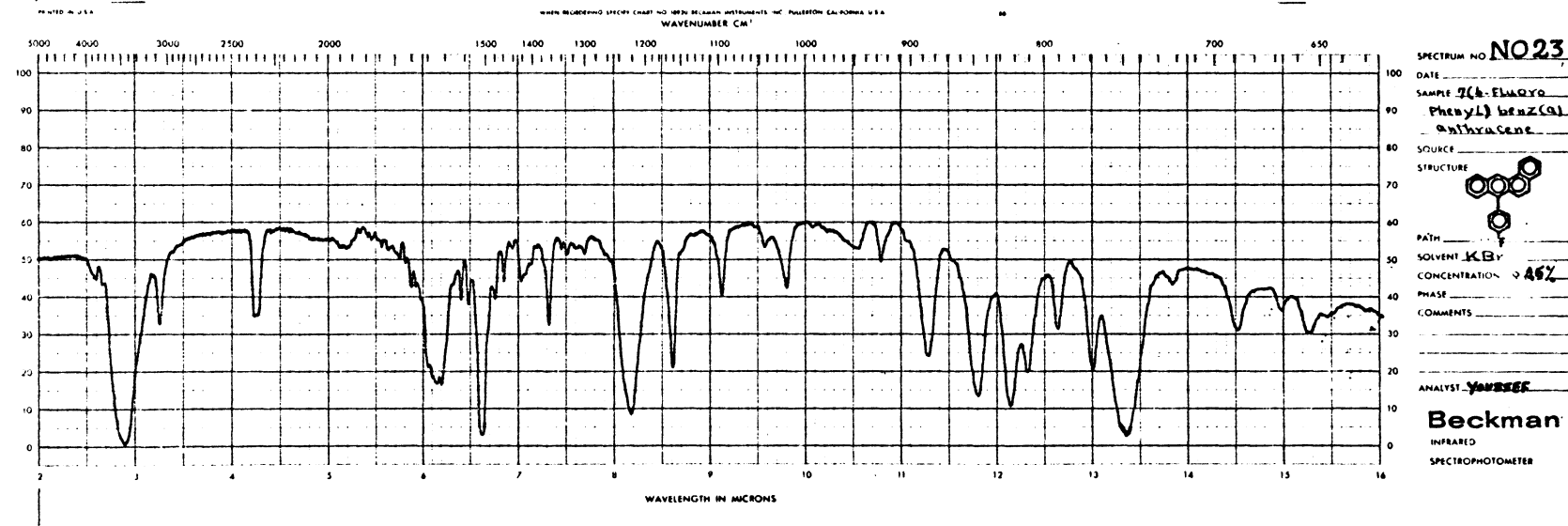
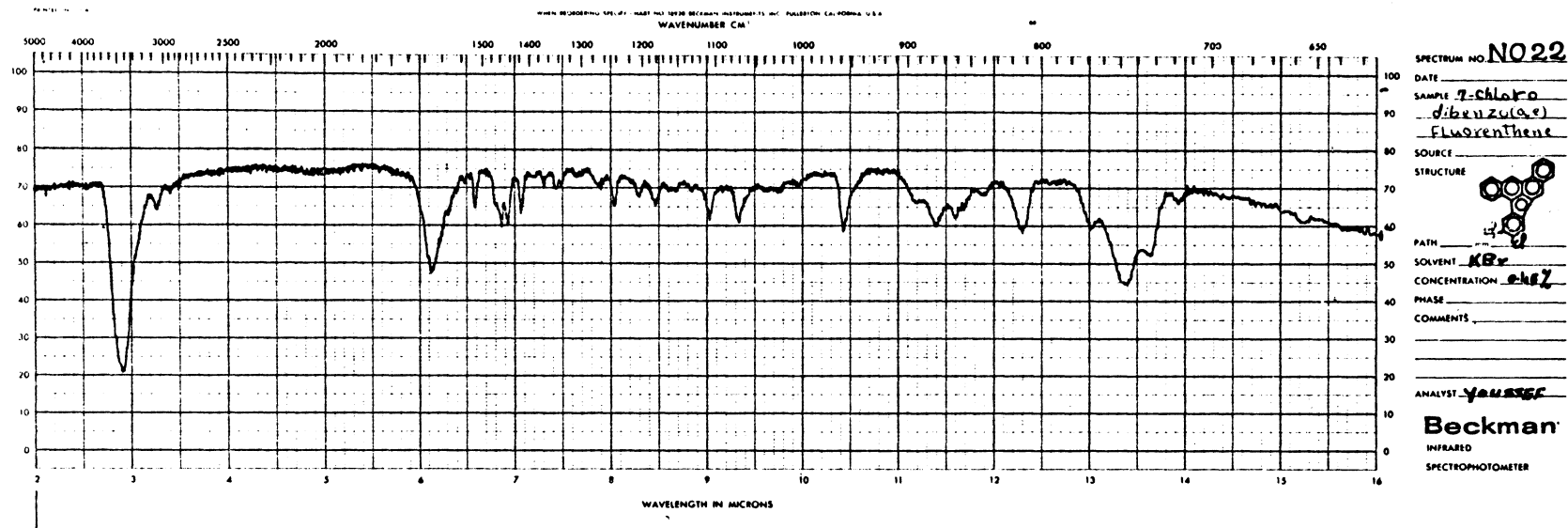
COMMENTS _____

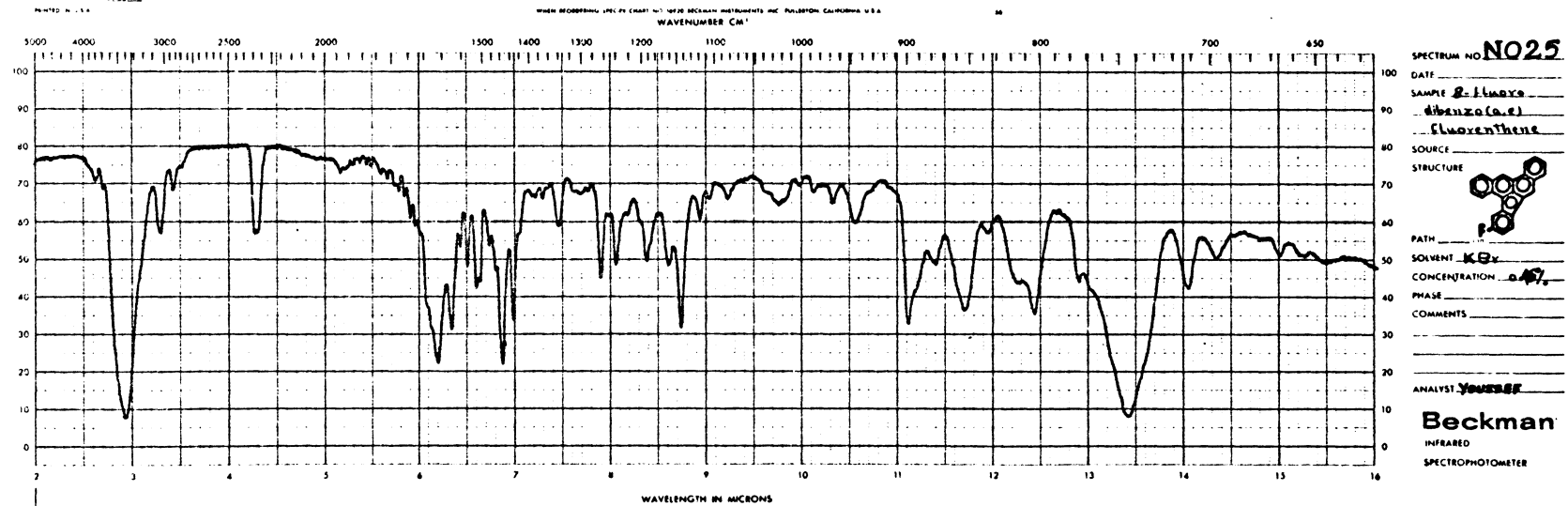
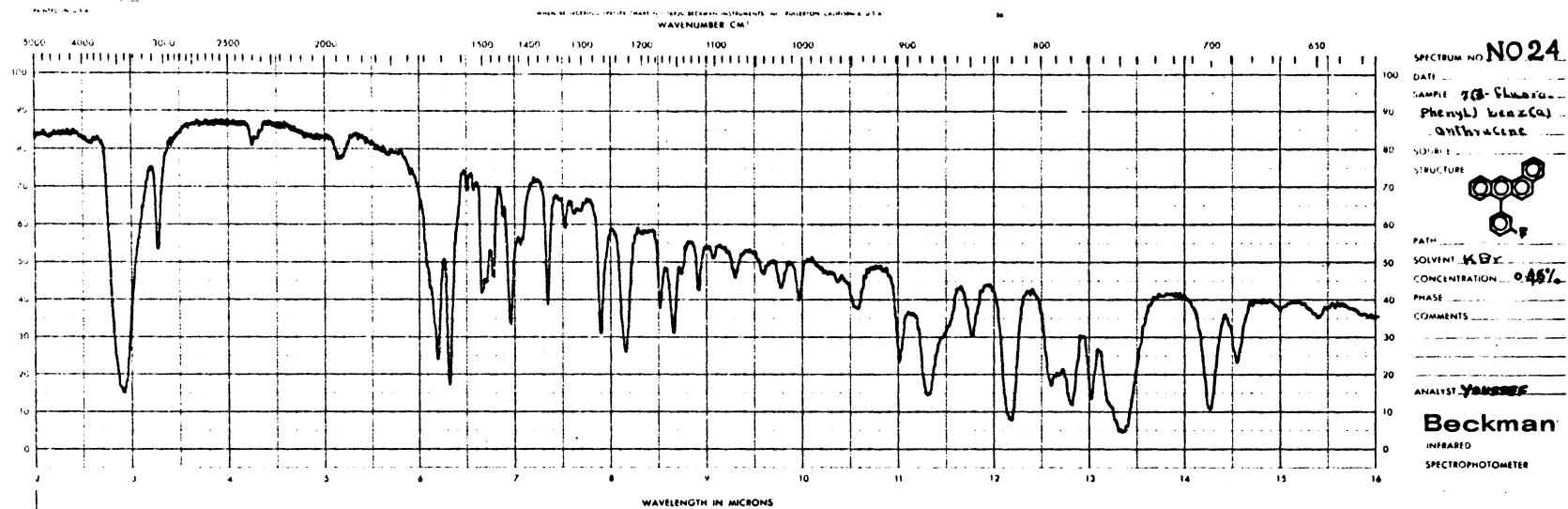
ANALYST Youssef

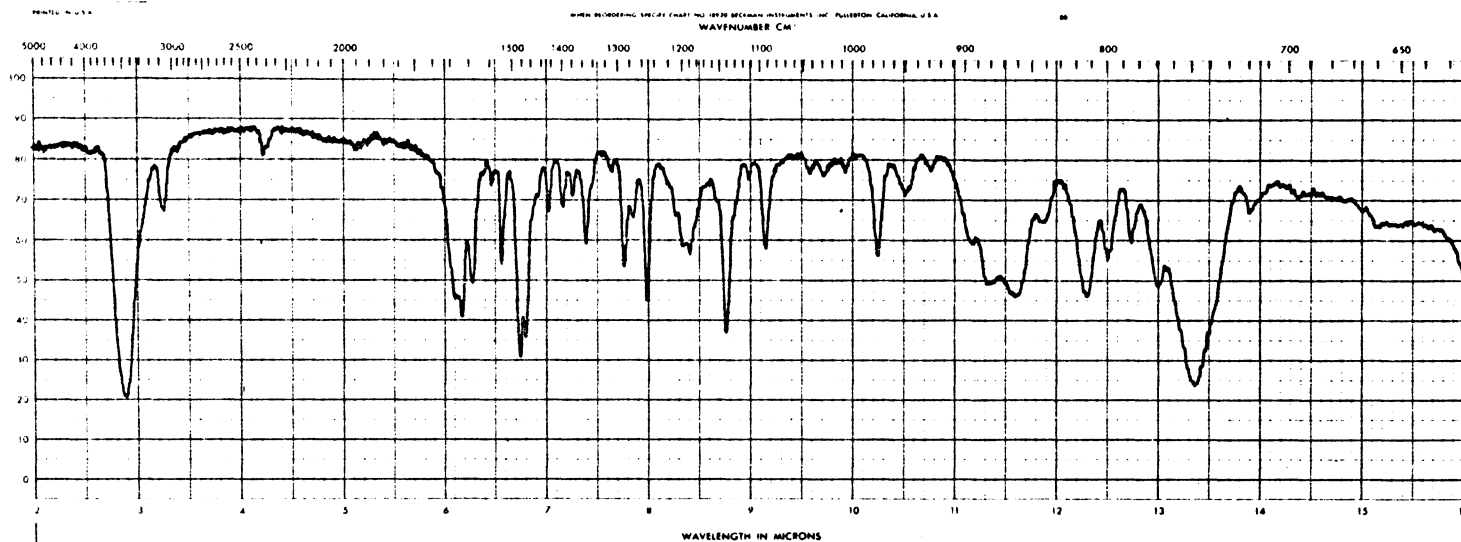
Beckman

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SPECTROPHOTOMETER







SPECTRUM NO. **NO 26**

DATE _____

SAMPLE 9-fluorenyl

dibenzo(a,e)

fluorene

SOURCE _____

STRUCTURE 

PATH _____

SOLVENT KBr

CONCENTRATION 0.4%

PHASE _____

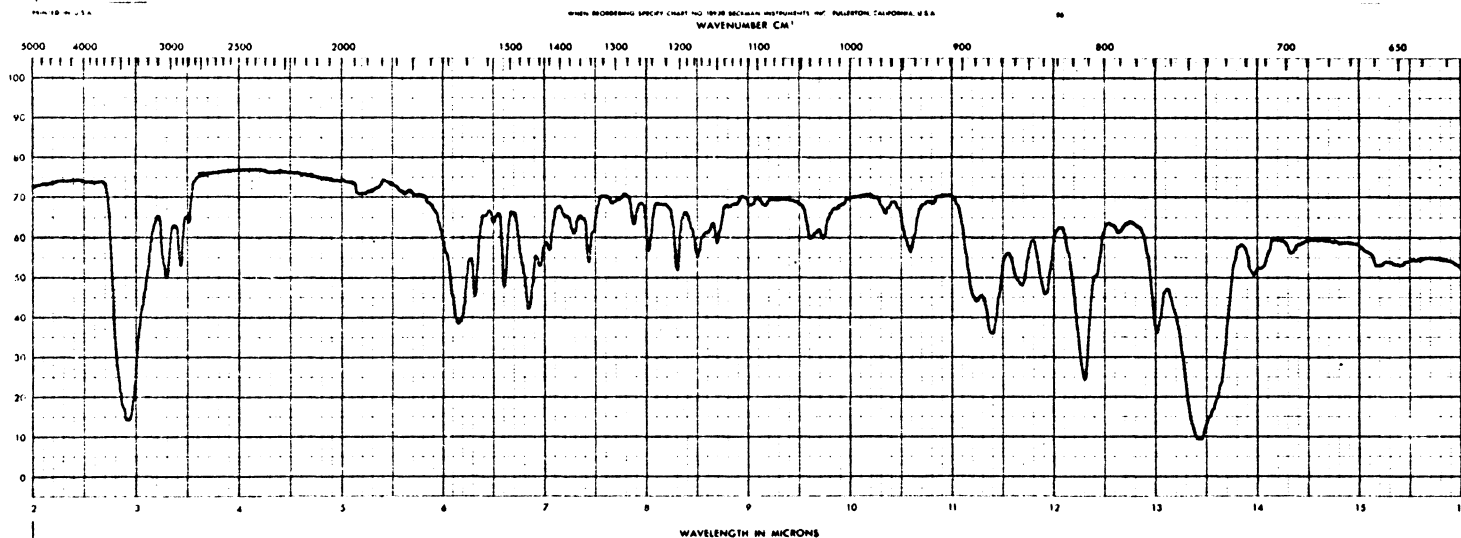
COMMENTS _____

ANALYST Young

Beckman

INFRARED

SPECTROPHOTOMETER



SPECTRUM NO. **NO 27**

DATE _____

SAMPLE 9-methyl

dibenzo(a,e)

fluorene

SOURCE _____

STRUCTURE 

PATH _____

SOLVENT KBr

CONCENTRATION 0.4%

PHASE _____

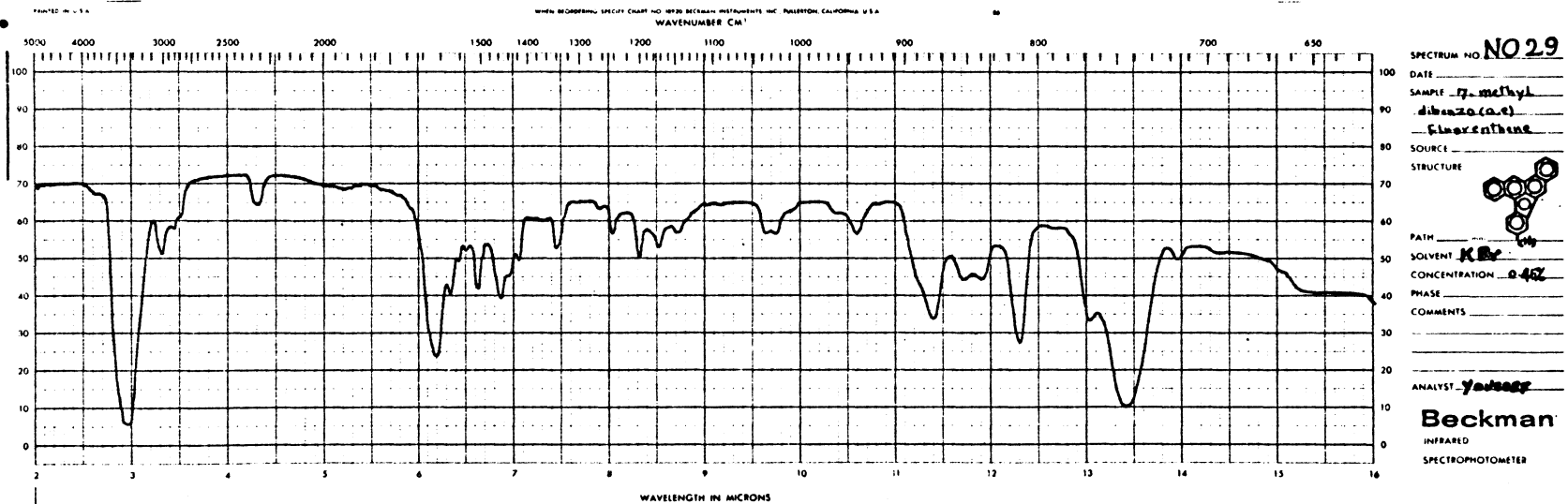
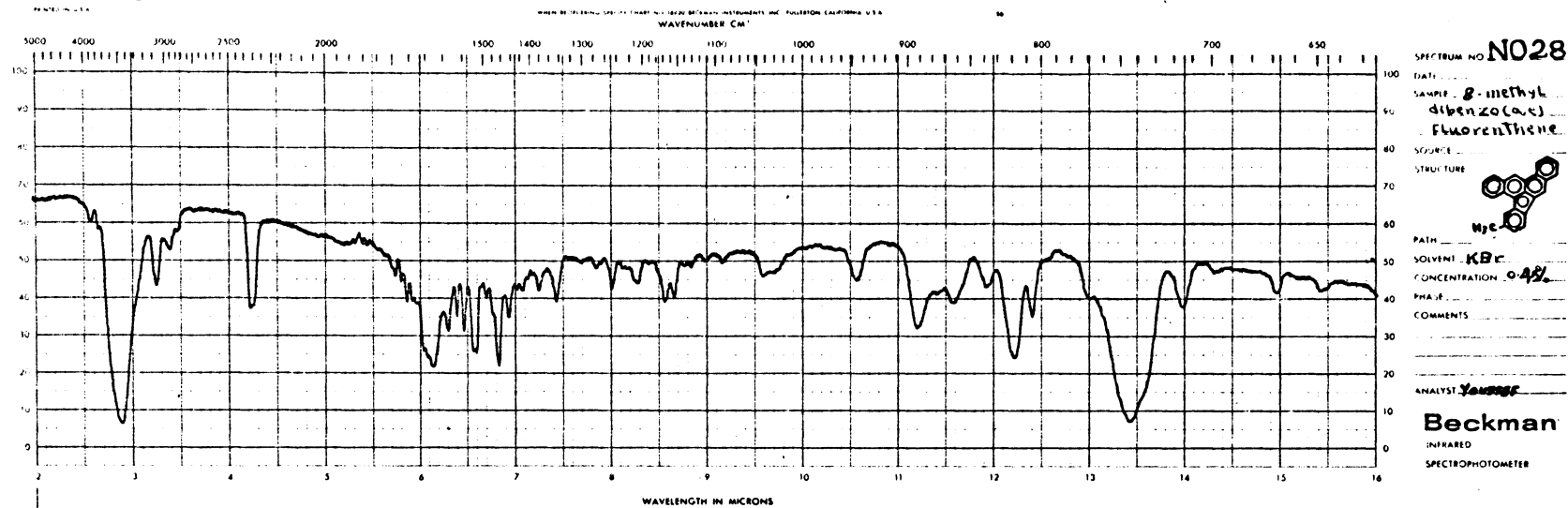
COMMENTS _____

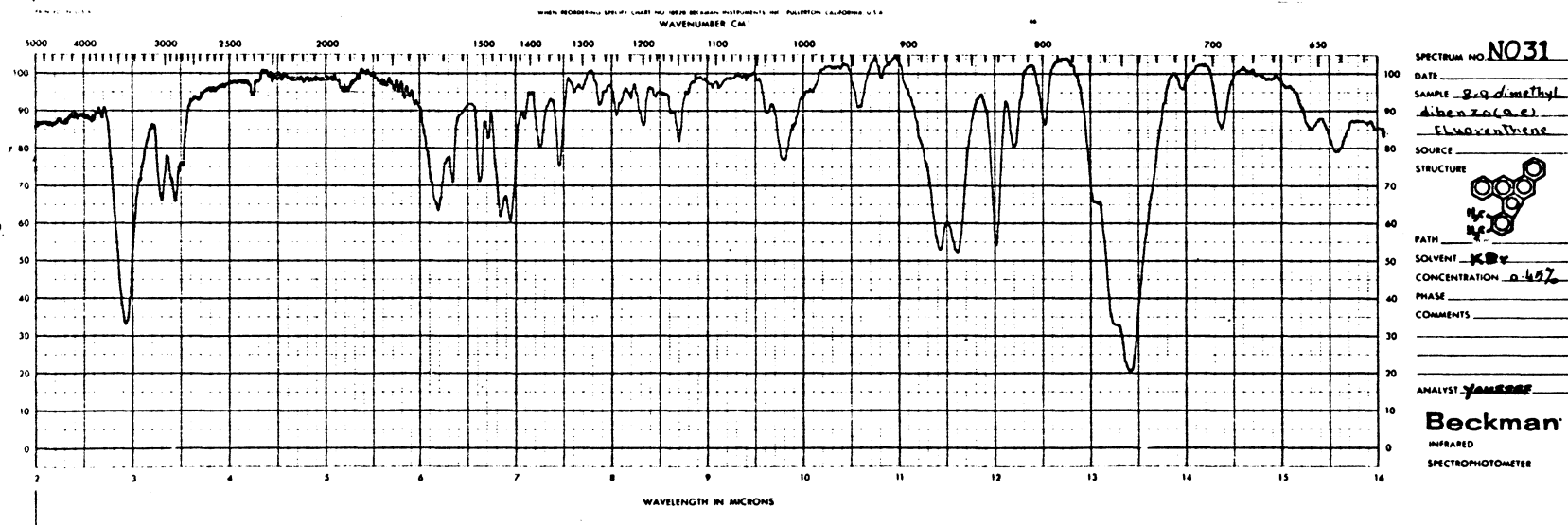
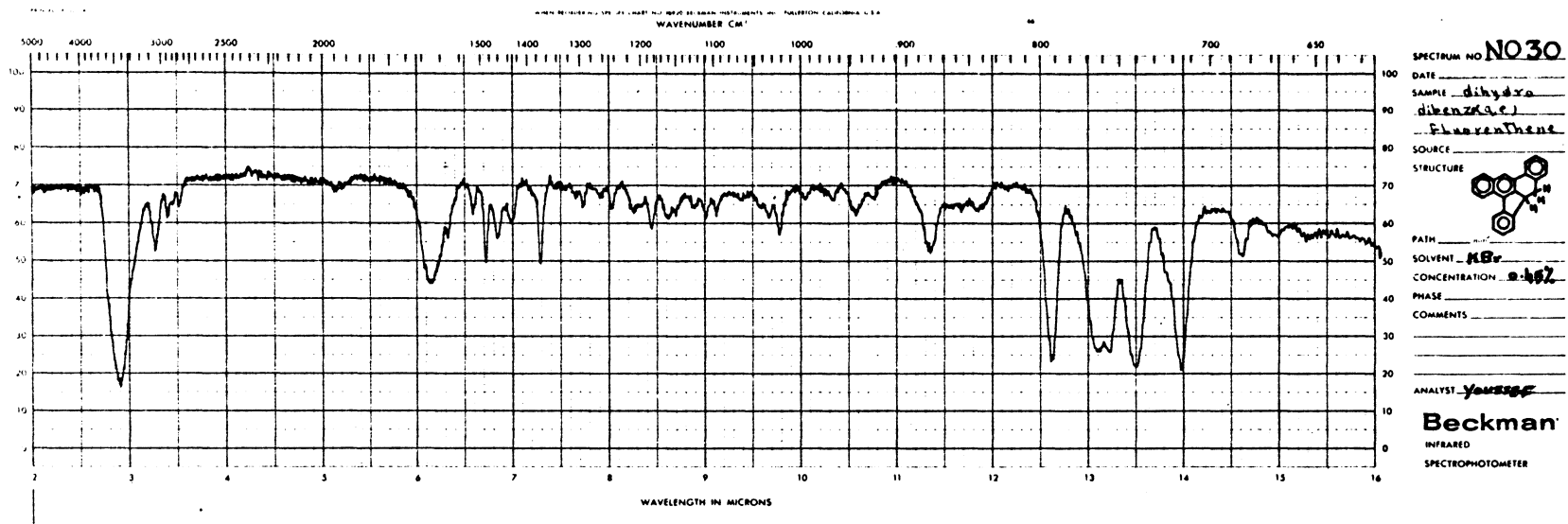
ANALYST Young

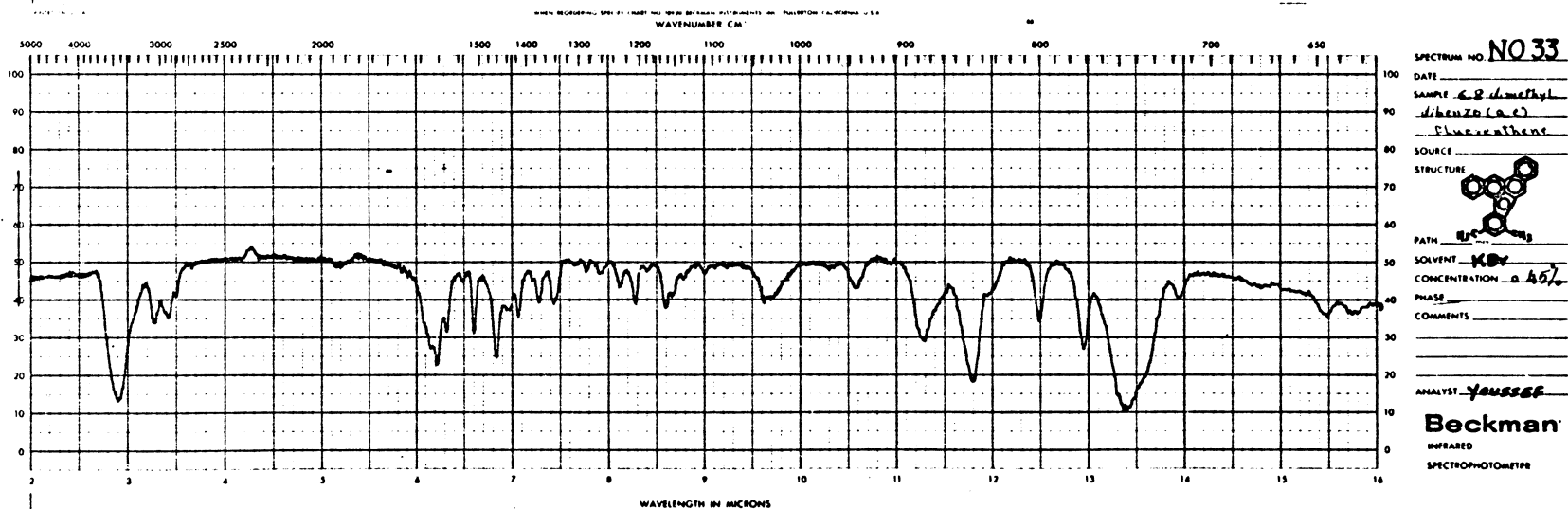
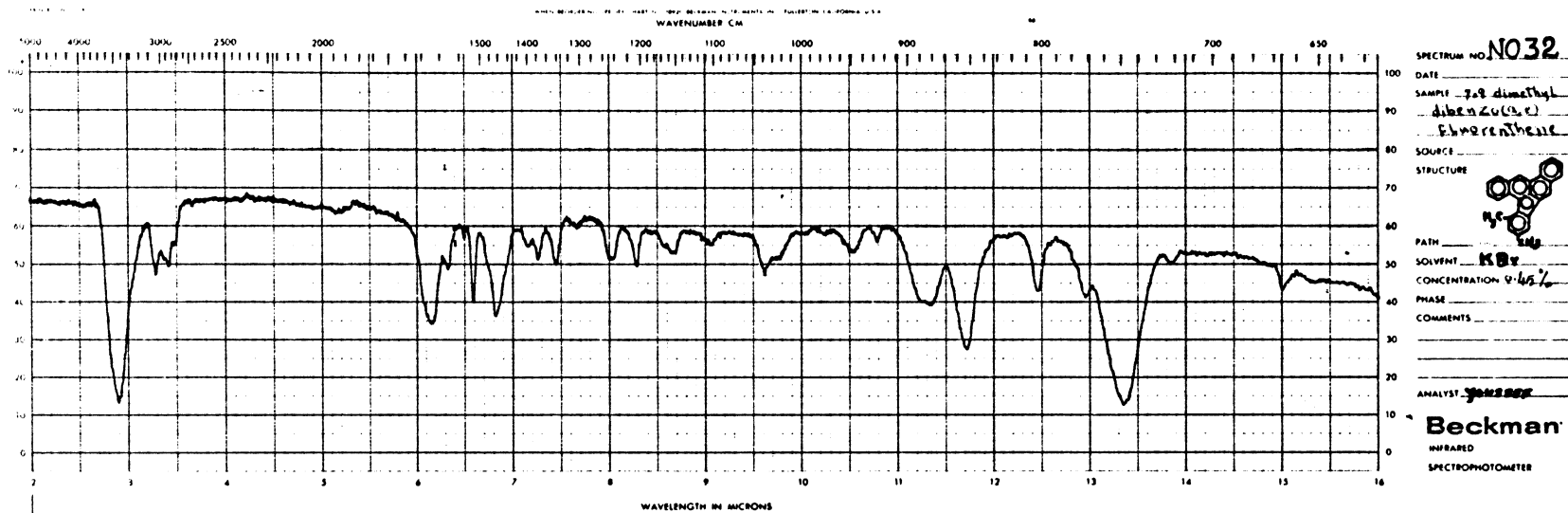
Beckman

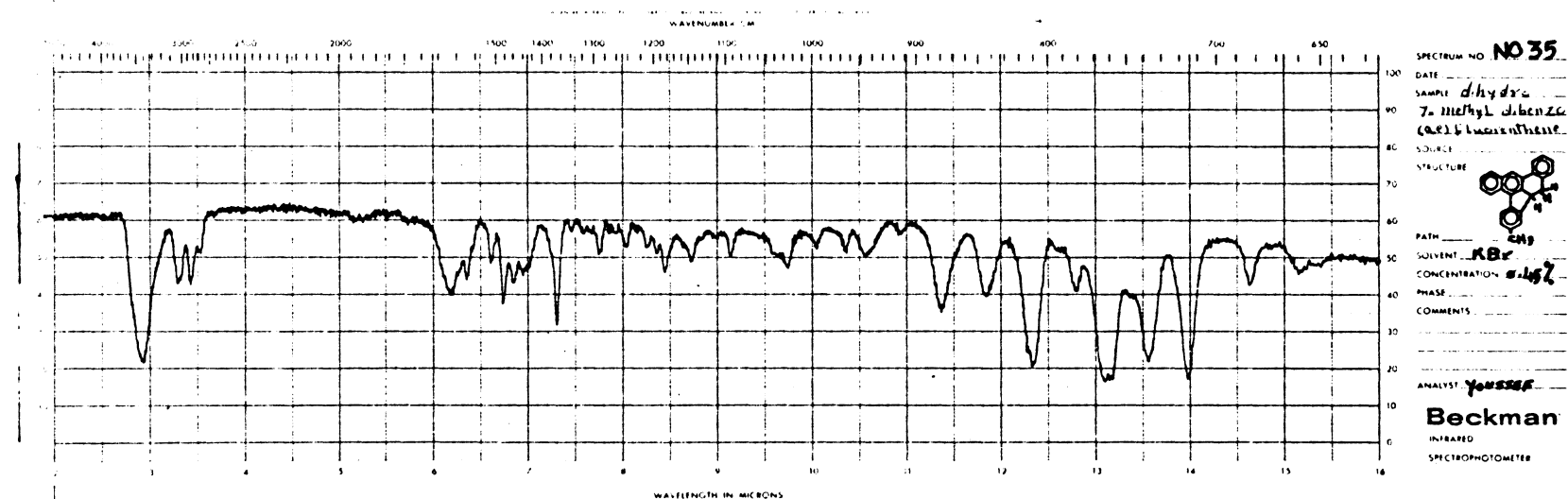
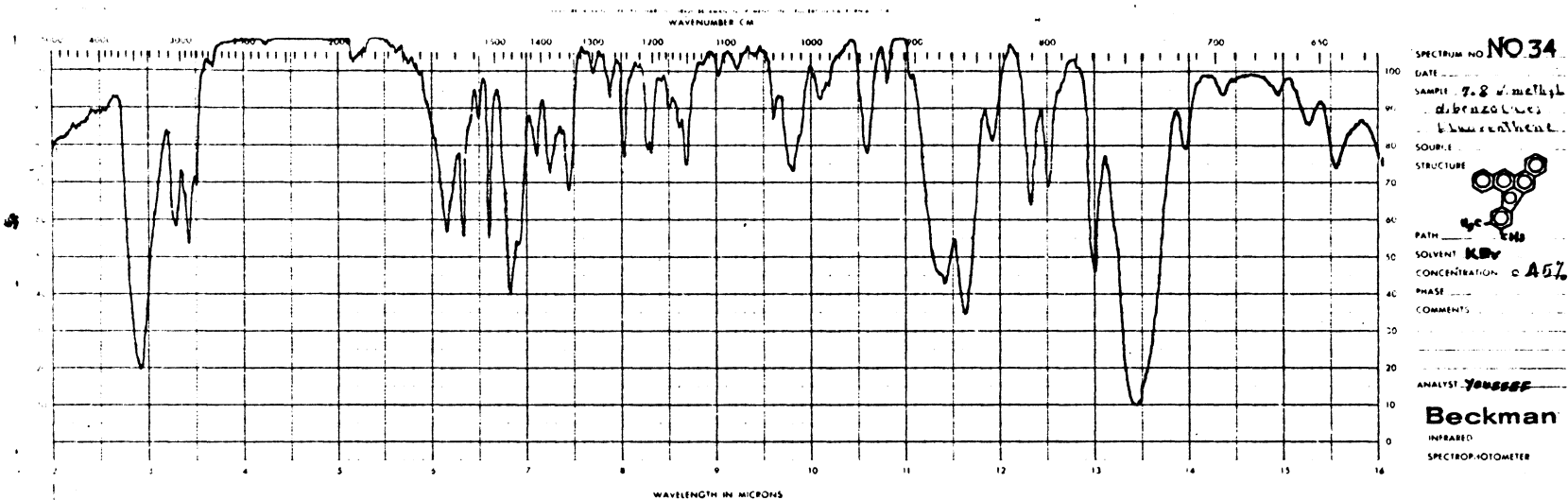
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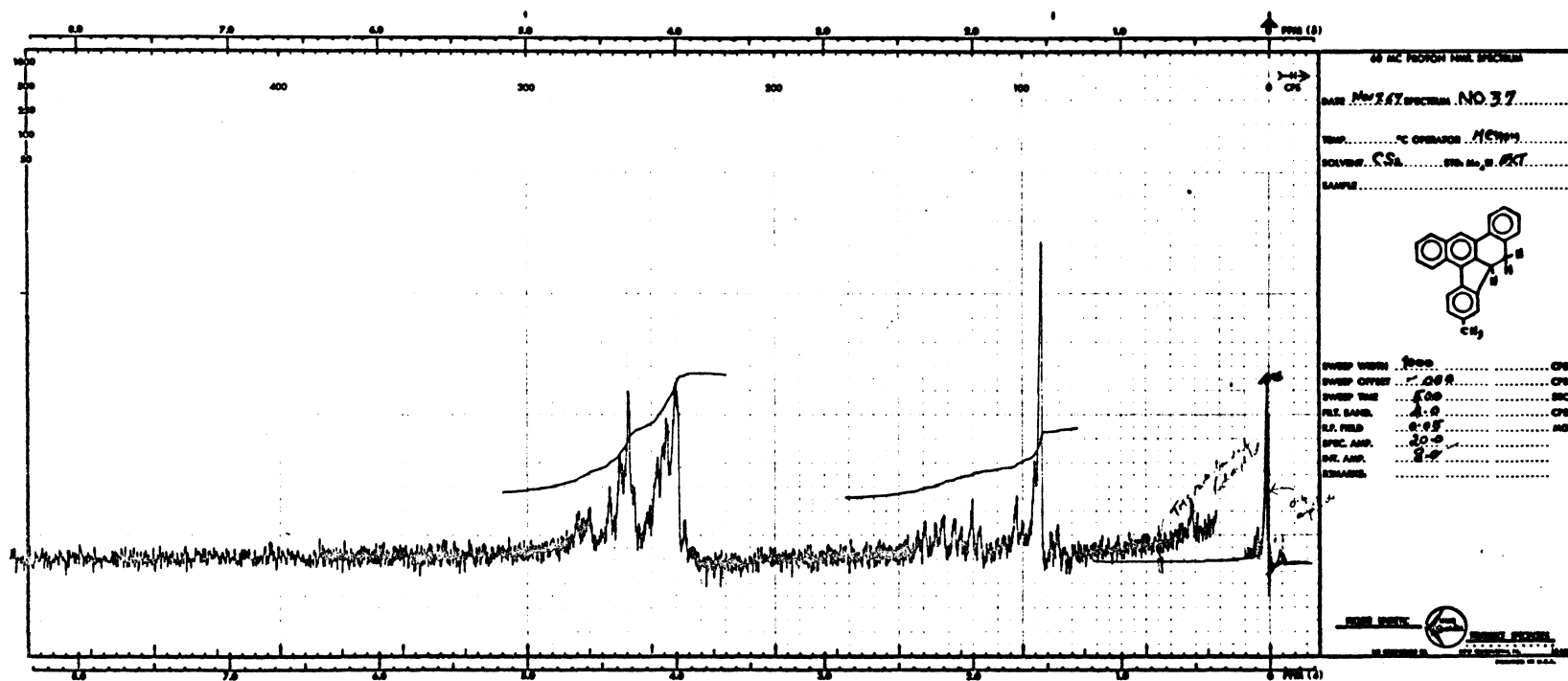
SPECTROPHOTOMETER











LITERATURE CITED

VIII. LITERATURE CITED

1. K. Yamagiwa and K. Ishikawa, Mitt. med. fak. Tokio 15: 295 (1915).
J. Cancer Research 31 (1918) Cited in cancer bulletin by R. W. Cumely, Vol. 9, p. 15 (1955).
2. Tsutsui, Gann 12, 17 (1918).
3. J. Thomas, B. Tabbens, M. Mukai and E. Sanborn, Anal. Chem. 29: 1835 (1957).
4. J. W. Cook, J. Am. Chem. Soc., 1087 (1930).
5. D. Lavit-Lamy and N. P. Buu-Hoi, Chem. Comm., 92 (1966); Bull. Soc. Chim. France, 2613, 2619 (1966).
6. F. A. Vingiello and A. K. Youssef, Chem. Comm., 863 (1967).
7. E. Clar and D. G. Stewart, J. Chem. Soc., 687 (1951).
8. E. L. Kennaway, Brit. Med. J., ii, 1 (1925).
9. E. Clar, Ber. dtsch. Chem. Ges. 62; 350 (1929).
10. I. Heiger, Biochem. J., 24: 505 (1930).
11. Shou-Sin Sung, C. R. Acad Sci (Paris) 257(6): 1425-1427 (1963).
12. O. Schmidt, Z. Phys. Chem., 42: 83 (1939).
13. A. Pullman and B. Pullman, "Cancerisation par les Substances chimiques et Structure moleculaire" Masson, Paris (1955).
14. G. M. Badger, Brit. J. Cancer 2, 309 (1948).
15. E. Clar. Ber. dtsch. Chem. Ges. 72, 1645 (1939). Amer. Patent No. 2172020.
16. E. Clar. Ber. 81 (1948). J. Chem. Soc., 2013, 2440 (1949).
17. C. K. Bradsher. Chem. Revs. 38, 447 (1946).
18. J. Cook and H. Hewett. J. Chem. Soc., 398 (1933).
19. E. Clar et al, J. Chem. Soc., 2652 (1956).

20. R. Scholl and J. Mansfield, Ber. 43: 1737 (1910).
21. A. Homer, J. Chem. Soc., 1103 (1907).
22. R. Scholl and C. Seer, Ann., 394: 111 (1912).
23. G. Kranzlein "Aluminum chloride in der organischen Chemie", 3rd ed. Verlag Chemie, Berlin, p. 146 (1939).
24. G. A. Olah, "Friedel-Crafts and Related Reactions", Vol. 2, Part II, p. 980.
25. B. Baddeley, J. Chem. Soc., 994 (1950).
26. C. D. Nenitzescu and A. T. Balaban, Chem. Ber. 91: 2109 (1958).
27. F. G. Baddar and F. L. Warren, J. Chem. Soc., 944 (1939).
28. F. A. Vingiello, W. W. Zajac and L. C. Mahone, J. Org. Chem., 28: 3253 (1963).
29. F. A. Vingiello and T. J. Delia, J. Org. Chem. 29: 2180 (1964).
30. F. A. Vingiello and P. D. Henson, J. Org. Chem., 30: 2842 (1965).
31. F. A. Vingiello and A. K. Youssef, Chem. Comm., 1152
32. C. K. Bradsher, J. Am. Chem. Soc., 62: 1077 (1940).
33. S. G. Quo, Ph.D. Thesis, V.P.I., (1960).
34. C. F. Koelsch and A. G. Whitney, J. Org. Chem., 6: 795 (1941).
35. L. Friedman and H. Shechter, J. Org. Chem., 26: 2522 (1962).
36. M. S. Newman and H. Boden, J. Org. Chem., 26: 2525 (1962).
37. M. S. Newman and D. K. Philips, J. Am. Chem. Soc., 81: 3667 (1959).
38. A. E. Remick "Electronic Interpretation of Org. Chem." 2nd ed. John Wiley and Sons, Inc., 1949.
39. L. A. Bigelow, Org. Synth., Vol. 9, p. 22 (1923). John Wiley and Sons, Inc., New York, N.Y.
40. R. L. Lestinger and J. H. Skoog, J. Am. Chem. Soc., 77: 5176 (1955).

41. E. Greenwood, Ph.D. Thesis, V.P.I., p. 91 (1966).
42. F. A. Vingiello, L. Ojakaar and R. Kelsey, J. Med. Chem. 8, 144 (1965).
43. F. A. Vingiello and R. K. Stevens, J. Am. Chem. Soc., 80, 5256 (1958).
44. R. K. Stevens, M.S. Thesis, V.P.I., p. 29 (1957).
45. C. K. Bradsher and F. A. Vingiello, J. Am. Chem. Soc., 71, 1434 (1949).
46. F. A. Vingiello, J. G. Van Oot and H. H. Hannabas, Ibid. 74, 4546 (1952).
47. F. A. Vingiello and J. G. Van Oot, Ibid. 73, 5070 (1951).
48. G. J. Buese, M.S. Thesis, V.P.I. (1951).
49. J. E. Bondurant, M.S. Thesis, V.P.I. (1950).
50. F. A. Vingiello, M. O. L. Spangler and J. E. Bondurant, J. Org. Chem., 25, 2091 (1960).
51. F. A. Vingiello, L. Ojakaar and R. Kelsey, J. Med. Chem., 8, 144 (1965).
52. F. A. Vingiello and R. K. Stevens, J. Am. Chem. Soc., 80, 5257 (1958).
53. F. A. Vingiello and A. Borkovec, J. Am. Chem. Soc., 77, 4823 (1955).
54. F. A. Vingiello and A. Borkovec, J. Am. Chem. Soc., 78, 1240 (1956).
55. F. A. Vingiello, A. Borkovec and J. Shulman, J. Am. Chem. Soc., 77, 2320 (1955).
56. E. Clar "Polycyclic hydrocarbons", Vol. II. Academic Press, New York, N.Y. 1964.
57. F. A. Vingiello and W. W. Zajac, J. Org. Chem., 26, 2228 (1961).
58. F. A. Vingiello and T. J. Delia, J. Org. Chem., 29, 2180 (1964).

59. E. Clar and D. Stewart, J. Chem. Soc., 687 (1951).
60. D. Lavit-Lamy and N. P. Buu-Hoi, Chem. Comm., 92 (1966).
61. D. Lavit-Lamy et N. P. Buu-Hoi. Bulletin de la Societé Chimique de France, No. 8, p. 2613 (1966).
62. A. B. Borkovec, M.S. Thesis, V.P.I. p. 44-46 (1953).
63. F. A. Vingiello, J. Am. Chem. Soc., 73, 1887 (1951).
64. E. Clar "Polycyclic Hydrocarbons", Vol. II, Academic Press, New York, N.Y., 1964.

VITA

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SYNTHESIS OF SOME NEW SUBSTITUTED
DIBENZO(a,e)FLUORANTHENES

BY

Abdullatif K. Youssef

ABSTRACT

The following compounds, 9-methyldibenzo(a,e)fluoranthene, 8-methyldibenzo(a,e)fluoranthene, 7-methyldibenzo(a,e)fluoranthene, 7,8-dimethyldibenzo(a,e)fluoranthene, 6,8-dimethyldibenzo(a,e)fluoranthene, 8,9-dimethyldibenzo(a,e)fluoranthene, and 7,9-dimethyldibenzo(a,e)-fluoranthene, were prepared by the cyclization reaction using anhydrous aluminum chloride (by ratio 1:3 by weight) in hot dry benzene, then heated under reflux for 30 minutes.

The intermediate dihydro compounds, which resulted from these reactions, were separated and characterized by n.m.r. spectra, ultraviolet spectra, infrared spectra, and elemental analysis. The molecular weight was checked by mass spectra. All of these dihydro compounds were dehydrogenated (aromatized) by using D.D.Q. (2,3-dichloro-5,6-dicyanobenzocuinone) to give the above new compounds with a quantitative yield from the dehydrogenation reaction. All of these new compounds were characterized by infrared spectra, ultraviolet spectra, and elemental analysis. In the case of preparing the following new halo compounds, 7-chlorodibenzo(a,e)fluoranthene, 8-chlorodibenzo(a,e)-fluoranthene, 7-fluorodibenzo(a,e)fluoranthene, and 8-fluorodibenzo(a,e)-

fluoranthene, which were prepared by the same procedure used above, except the refluxing time was longer (24 hours), it was not possible to separate the intermediate dihydro compounds, presumably due to the refluxing time and to the electronic effect of the halogen atoms. All of these halo compounds were characterized by ultraviolet spectra, infrared spectra, and elemental analysis. Some of these compounds were sent for biological studies.