THE SYNTHESIS AND REACTIONS OF 2-(1-NAPHTHYLMETHYL)-2'-CARBOXYBENZOPHENONE

by

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MASTER OF SCIENCE
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THIS THESIS IS AFFECTIONATELY

DEDICATED TO MY WIFE AND PARENTS

ACKNOWLEDGEMENTS

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Appreciation is also extended to the other members of the faculty and to the graduate students for their many valuable suggestions.

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Finally, the author wishes to express his appreciation of the help and encouragement provided by his wife which was essential to the successful completion of this work.

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INTRODUCTION

INTRODUCTION

During the past few decades, much research has been carried out on the synthesis, reactions and properties of polynuclear aromatic hydrocarbons. Much of this interest has been stimulated by the fact that some of these compounds are known to possess carcinogenic activity.

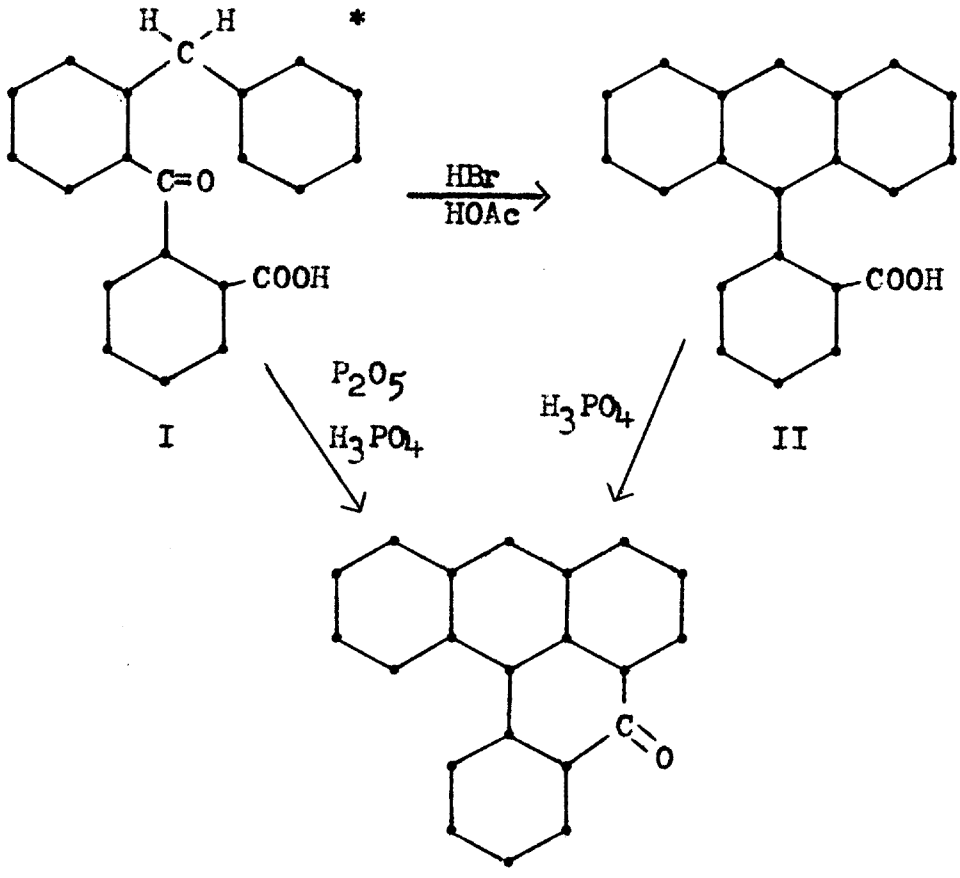
Historically, polycyclic hydrocarbons were the first known carcinogens. The first correlation of carcinogenic activity and structure came when Cook and coworkers (1,2) discovered that some of the most potent carcinogens contain the benz[a]anthracene nucleus with a carbon substituent at either of the meso positions, 7 or 12.

This evidence, plus the fact that certain polynuclear hydrocarbons have been effective as anti-cancer agents (3), has produced significant initiative in organic chemists to prepare a number of related compounds of this type, so that further insight can be made on the relation of structure and mechanics of physiological activity.

Previous work in This Laboratory has been mainly concerned with the synthesis and reactions of 7- and 12-aryl-benz[a]anthracenes.

In 1948, Bradsher and Vingiello (4) synthesized 9-(2-carboxyphenyl)anthracene (II) via the cyclodehydration of 2-benzyl-2'-carboxybenzophenone (I) with a hydrobromic

and acetic acid mixture. Further cyclization of 9-(2-carboxyphenyl)anthracene (II) to coeranthrone (III) was effected by using phosphoric acid. They found that coeranthrone (III) could also be prepared directly from 2-benzyl-2'-carboxybenzophenone (I) by a double cyclodehydration reaction with a mixture of phosphoric acid and phosphorus pentoxide.



III

* Throughout this thesis, all rings are aromatic unless otherwise indicated.

An interesting expansion of this work would be to attempt this same sequence of reactions in the benz[a]anthracene series as shown in Chart I.

The purpose of this investigation was to prepare 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV), and undertake its cyclodehydration to 7-(2-carboxyphenyl)benz[a]-anthracene (V) with further cyclodehydration to benzcoeranthrone (VI)[a].

A problem arises here, in that the cyclodehydration of the acid (V) can lead to two possible structural isomers, VIa and/or VIb, depending on whether the cyclization took place at the No. 6 or No. 8 carbon atom of benz[a]anthracene. Although an unequivocal synthesis of each isomer would be the only conclusive proof of which compound was formed, spectral studies of the product obtained have given an indication as to which position was involved in the cyclization.

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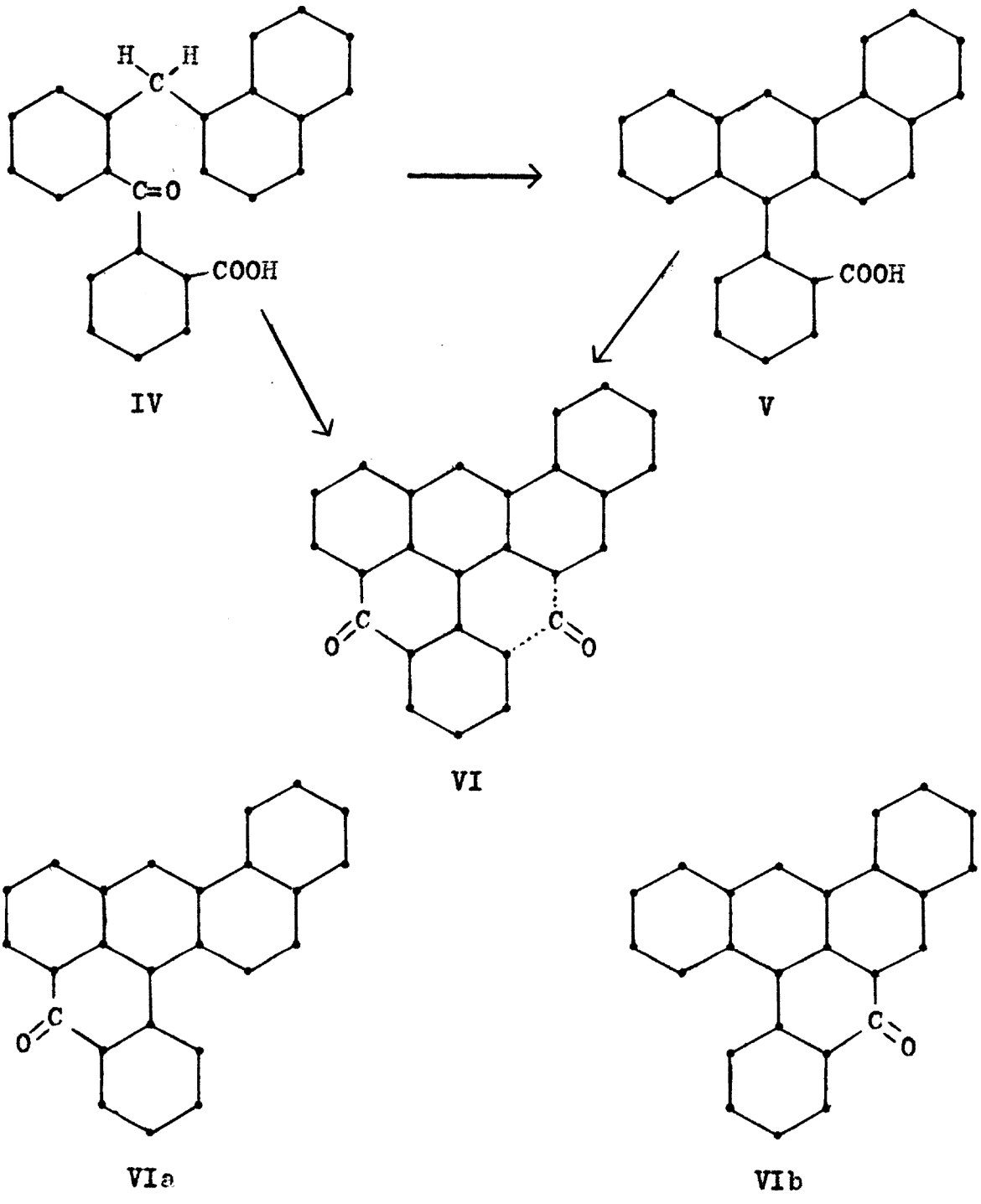
a. Benzcoeranthrone is a trivial name for either structure VIa or VIb. The correct nomenclature adopted by the American Chemical Society is given on pages 11 and 12.

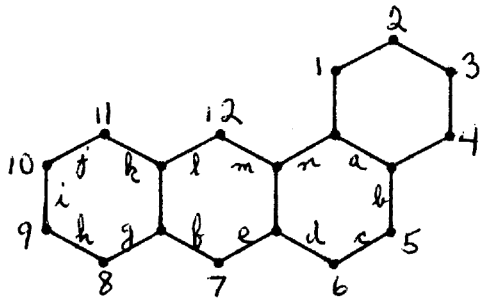
CHART I



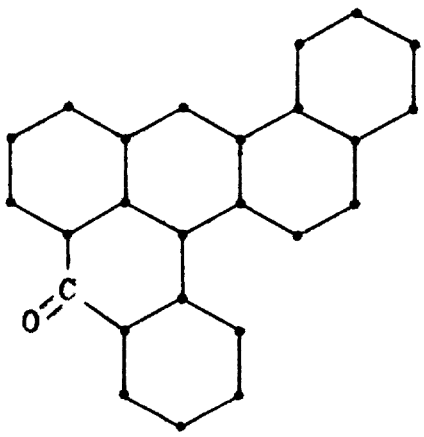
NOMENCLATURE

NOMENCLATURE

The nomenclature presented throughout this thesis is in accordance with the "Definitive Rules for Nomenclature" set forth in the Journal of the American Chemical Society.* Examples are given below:



Benz[a]anthracene



Naphtho[1,2,3-fg]benz[a]anthracene-11-one

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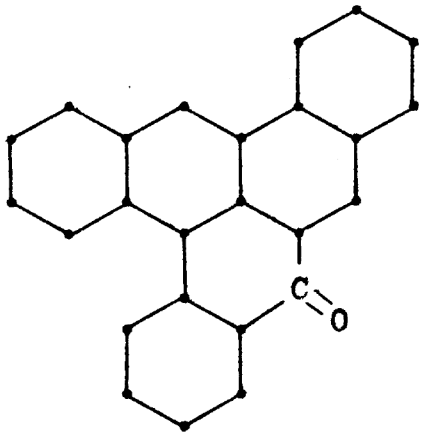
* See J. Am. Chem. Soc., 82, 5545 (1960).



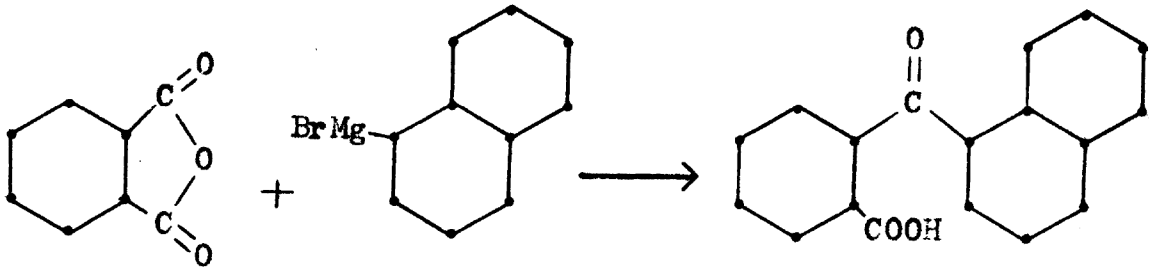
Naphtho[3,2,1-fg]naphthacene-11-one

HISTORICAL

HISTORICAL

A. Synthesis of keto acids using Grignard reagents and aromatic anhydrides.

In 1904, Werzmann and Pickles first observed that keto acids could be prepared by the reaction of anhydrides with Grignard reagents (5). Their experiments involved the reaction of phthalic anhydride with phenyl- or 1-naphthyl-magnesium bromide, which upon hydrolysis, gave 2-benzoyl- or 2-(1-naphthoyl)benzoic acid (VII).



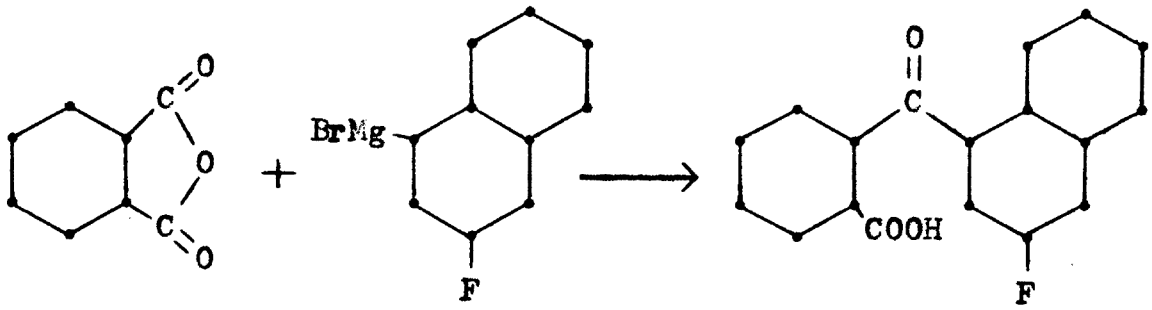
VII

Werzmann and coworkers extended their work in 1935 (6) by preparing a large series of aromatic keto acids by the reaction of such symmetrical anhydrides as phthalic anhydride, tetrachlorophthalic anhydride, and 2,3-naphthalic anhydride with the Grignard reagents of 2-bromonaphthalene, 9-bromo-phenanthrene, 1,4-dibromobenzene, etc.

This novel route to aromatic keto acid proved to be a very useful and important synthesis of intermediates in

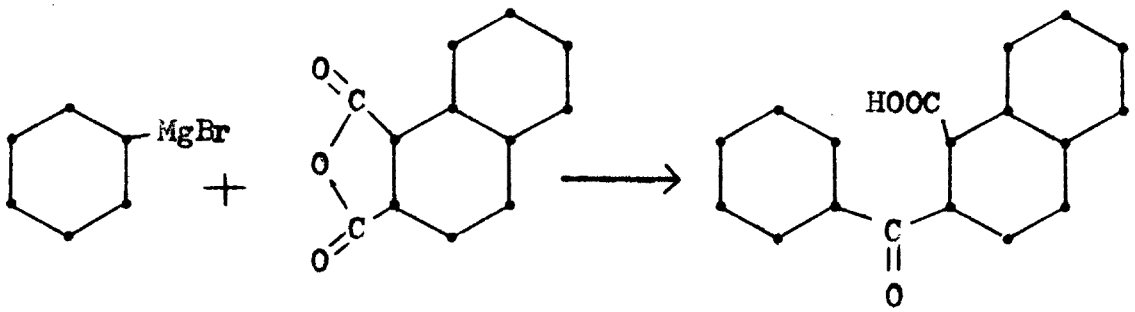
the preparation of certain polynuclear hydrocarbons, but only during the past 25 years had this reaction received any great attention.

Newman and coworkers (7,8) found this synthesis useful in the preparation of precursors of certain fluoro-substituted methylbenz[a]anthracenes. This was done by reacting phthalic anhydride with various bromofluoro-naphthalenes to give the expected fluoro-keto acid (VIII).



VIII

Fieser and Newman (9) have synthesized substituted benz[a]anthracenes by preparing the intermediate 2-benzoyl-1-naphthoic acid (IX) from the condensation of 1,2-naphthalic anhydride and phenylmagnesium bromide.



IX

Here there is a possibility of two products due to the asymmetry of the anhydride, but the only product obtained is the one indicated. By application of the "electronic theory of the English school," the position of cleavage of an asymmetrical anhydride may be predicted. Since this problem was not encountered in this work, it will not be discussed.

B. Synthesis of 7-substituted benz[a]anthracenes.

Many routes to the 7-substituted benz[a]anthracenes have been attempted with varying degrees of success. The route which is currently of greatest interest and which in many instances affords a higher yield of product, is the cyclodehydration of various 2-(1-naphthylmethyl)benzophenones with a mixture of hydrobromic and acetic acids.

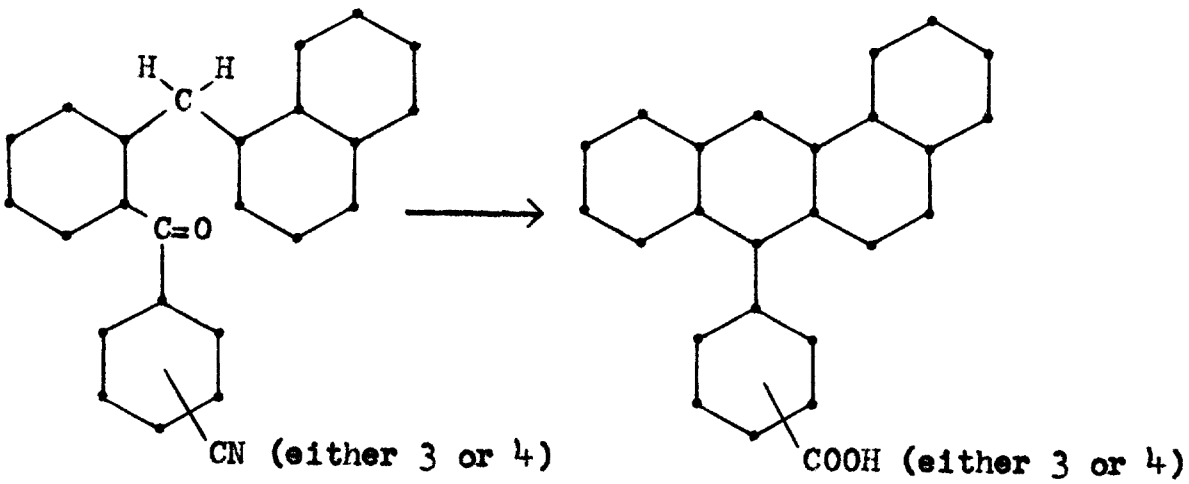
This type reaction was first reported by Bergmann in 1939. In attempting to hydrolyze the acetal of o-benzylbenzaldehyde with boiling hydrochloric acid, Bergmann not only obtained the expected aldehyde, but he also obtained a small quantity of anthracene.

Bradsher (11) in 1940, utilized this valuable observation and synthesized 9-methyl-, 9-ethyl-, and 9-phenylanthracene by heating the respective ketones in a mixture of 48% hydrobromic and glacial acetic acids. Further investigation by Bradsher (12,13) and Berliner (14) found application

of this reaction in the preparation of anthracenes substituted in both meso positions, as well as in the preparation of substituted 9-aryl anthracenes (4).

The application of this synthetic method was extended to the preparation of 7- and 12-substituted benz[a]anthracenes with encouraging results. Vingiello and coworkers (15,16,17,18) synthesized 7- and 12-monomethylphenyl and 7- and 12-dimethylphenyl benz[a]anthracenes.

As was mentioned in the Introduction, 9-(2-carboxyphenyl)anthracene (II) was prepared by this cyclization procedure. In the benz[a]anthracene series, analogous compounds were prepared by investigators in This Laboratory. Stevens (19) and Kunkel (20) prepared 7-(4-carboxyphenyl)- and 7-(3-carboxyphenyl)benz[a]anthracene respectively, as shown below.



Their method, which differs somewhat from that used in this investigation to prepare 7-(2-carboxyphenyl)benz[a]-

anthracene (V), involves the simultaneous cyclization of the ketone and hydrolysis of the cyano group to the carboxy group. The cyclization media employed was either a mixture of hydrobromic and acetic acids or phenyl acid phosphate.*

C. Anhydrous hydrogen fluoride and polyphosphoric acid as cyclodehydrating agents.

In 1939, it was observed that anhydrous liquid hydrogen fluoride was an excellent agent for effecting intramolecular acylation of aryl-substituted aliphatic acids (21).

Since that time, a number of cyclizations have been performed with this reagent.

The general procedure consists in allowing a solution of the acid in liquid hydrogen fluoride to stand for a few hours in an open vessel at room temperature. The advantages of this method lie in the simplicity of manipulation and in the good results obtained.

The success of HF as a cyclizing agent may be attributed in part to the fact that it manifests only a

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* Phenyl acid phosphate is a mixture of mono- and dihydrogen phosphate esters containing varying amounts of polyphosphates.

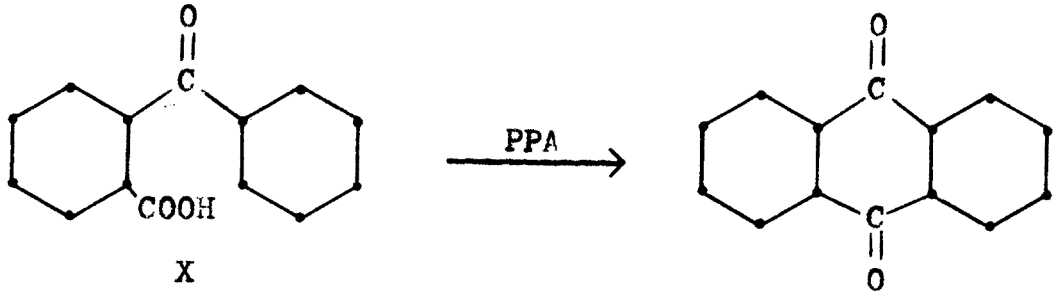
comparatively slight tendency to promote ketonic condensations and other undesirable side reactions.

The use of polyphosphoric acid as a cyclodehydrating agent is rapidly expanding. Much of the increased application of this reagent is due to the cleaner products obtained, and, in many cases, the better yields afforded.

Polyphosphoric acid is a very viscous liquid at room temperature and can be obtained commercially or prepared in the laboratory by the addition of phosphorus pentoxide to phosphoric acid.

Because of its tendency to be a good solvent for oxygen containing compounds, polyphosphoric acid has found great application in the cyclization of aromatic ketones and acids.

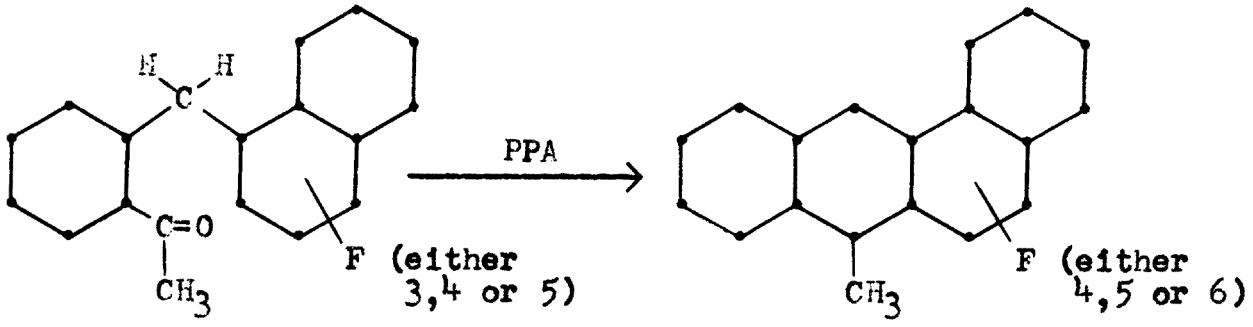
Snyder and Werber (22) used this reagent to prepare anthraquinone (XI) quantitatively by the cyclization of 2-benzoylbenzoic acid (X).



X XI

Benz[a]anthraquinone was also prepared in an appreciable yield by an analogous cyclization.

Newman and coworkers (7,8) prepared a series of fluromethyl benz[a]anthracenes using polyphosphoric acid as the cyclizing agent.



This reagent gave better yields of product than that achieved from the use of hydrobromic and acetic acids, and an appreciable yield was obtained from the ketone which gave no product whatsoever with hydrobromic and acetic acids.

The strong cyclizing power and mild destructive nature of polyphosphoric acid give it a definite advantage over the harsh degradation and sulfonation effects of sulfuric acid on aromatic oxygen compounds.

Both hydrogen fluoride and polyphosphoric acids were used to advantage in this investigation.

DISCUSSION OF RESULTS

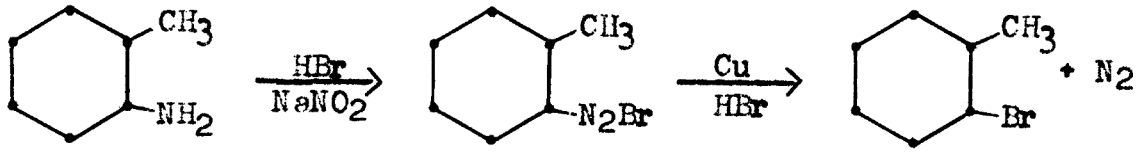
DISCUSSION OF RESULTS

A. Preparation of Starting Materials.

At the beginning of this investigation, the synthetic method outlined in Chart II was chosen as the most practicable procedure for the preparation of synthetic intermediates up to and including 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV).

Due to the great increase in price of o-bromotoluene (XII) experienced shortly after the outset of this work, it became necessary to prepare this intermediate in the laboratory, since it was needed in large quantities.

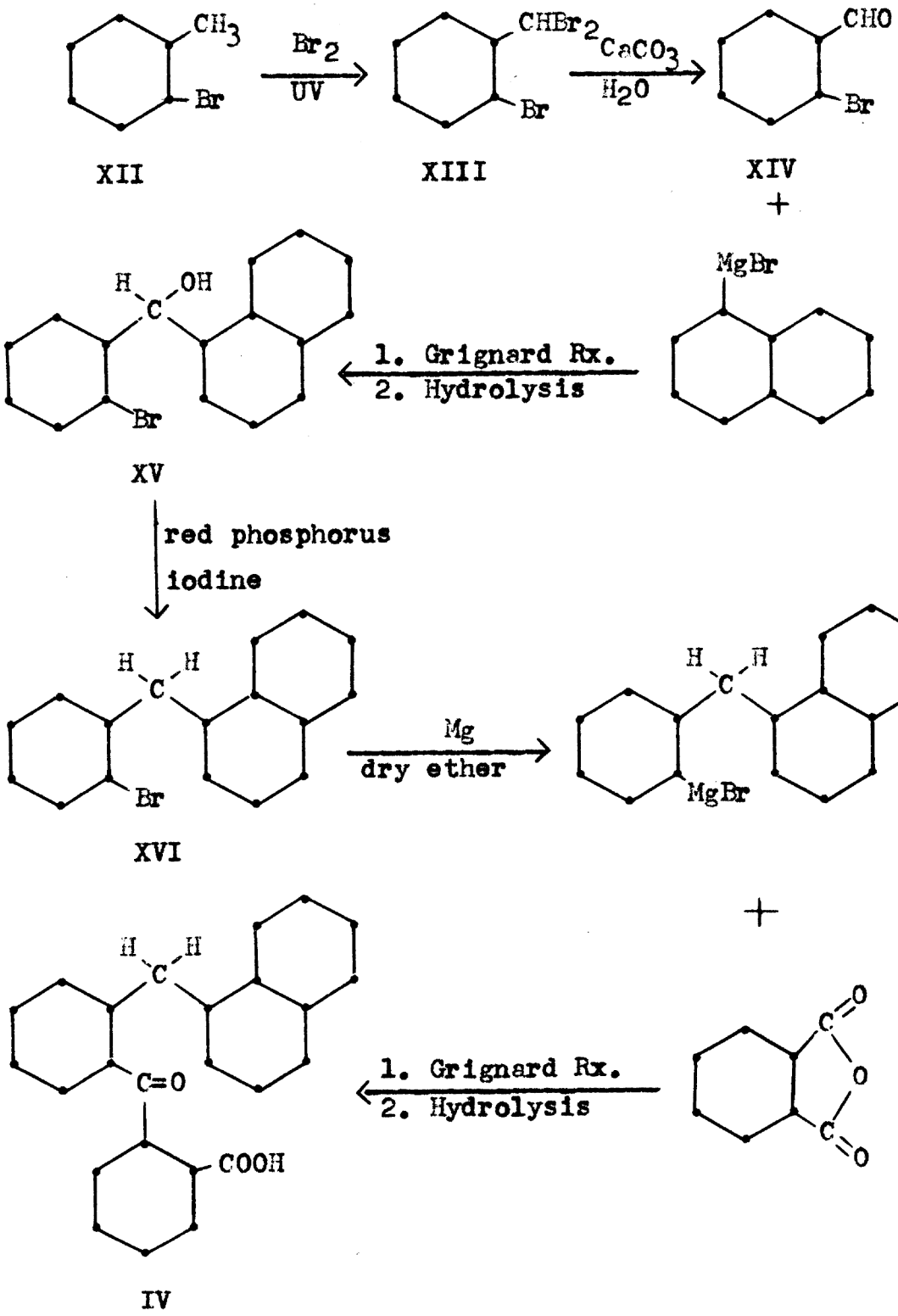
The particular method chosen was that employed by Bigelow (23), which involves the diazotization of o-toluidine (XVII) with sodium nitrite and hydrobromic acid. The resulting diazonium salt was decomposed with metallic copper



XVII XII

and yielded the desired product (XII). Yields of between 42-47% have been reported for this reaction, and those actually obtained in This Laboratory were slightly below these values. The only difficulty encountered in this

CHART II


CH3
Br
Br2
UV
CHBr2
Br
CaCO3
H2O
CHO
Br
XII
XIII
XIV
+
H
C
OH
Br
1. Grignard Rx.
2. Hydrolysis
MgBr
XV
red phosphorus
iodine
H
C
H
Br
Mg
dry ether
H
C
H
MgBr
XVI
+
H
C
H
C=O
COOH
1. Grignard Rx.
2. Hydrolysis
C=O
O
C=O
IV

preparation was the manipulation of the large equipment necessary for the preparation of large quantities of product. The average yield of between 80 and 100 g. of o-bromotoluene necessitated the use of 880 ml. of hydrobromic acid contained in a three liter flask. Any attempt to scale up the reaction would make the necessary handling of the reaction flask quite cumbersome. Therefore, several runs were required to acquire a sufficient quantity of product.

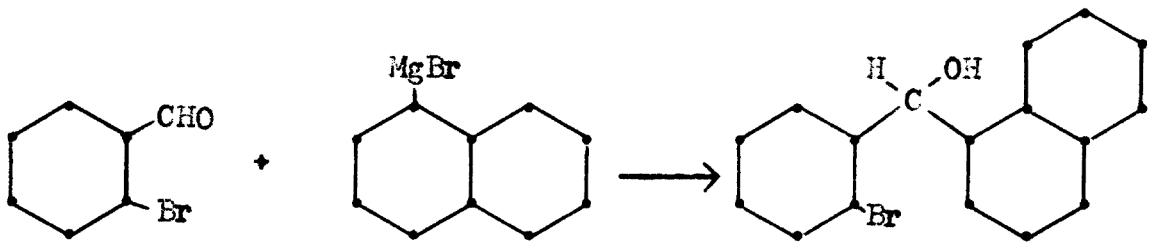
Prior to this work, two general procedures were employed in the preparation of o-bromobenzaldehyde (XIV) from o-bromotoluene (XII). One method utilizes the chromic acid oxidation of (XII) to the diacetate, which is converted to the aldehyde (XIV) upon hydrochloric acid hydrolysis (24,25). The average yield of this method has been reported to be about 40%.

The other technique, which is shown in Chart II, embodies the bromination of o-bromotoluene, followed by the hydrolysis of the benzal bromide (XIII) to the aldehyde (XIV) in reported yields of 80% (26). Although the bromination procedure is more tedious, it was employed because of the assumption of the higher yields obtained. However, this was found not to be the case, because, after several runs, the highest yield obtained was around 45%. Other workers in This Laboratory (27,28) have also reported similar results. One answer to the problem could lie in the techniques employed

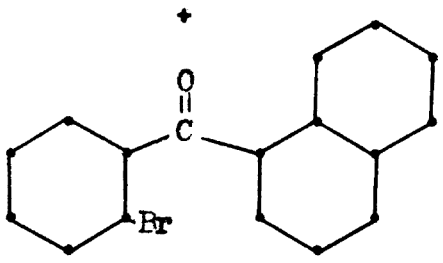
in the work up. o-Bromobenzaldehyde (XIV) is very easily air oxidized to o-bromobenzoic acid and prolonged periods of exposure to air such as drying the ethereal solutions overnight may facilitate such a major transformation as to affect the yield of aldehyde appreciably.

Recently, a much simpler approach to the preparation of the aldehyde (XIV) using 2-nitropropane has been attempted (29) with encouraging results. This procedure involves the bromination of o-bromotoluene (XII) to produce o-bromobenzyl bromide, which is reacted further with 2-nitropropane and sodium ethoxide to produce the aldehyde (XIV) in yields approaching 70% (30).

The next synthetic procedure employed was the reaction of o-bromobenzaldehyde with 1-naphthylmagnesium bromide. The usual product in the reaction of a Grignard reagent with an aldehyde is a secondary alcohol. This was found not to be entirely true in the reaction of the aldehyde (XIV) with 1-naphthylmagnesium bromide. In addition to the expected carbinol, 2-bromophenyl-1-naphthylcarbinol (XI), a study of the infrared spectrum of the product revealed the presence of a small quantity of the ketone (XVII). The relative nearness of the boiling points of these two products makes separation by distillation impractical.



XIV XV



XVII

Much of the information about this reaction and the products obtained has been contradictory and confusing. Delia (28) reported the presence of very little carbinol (XV), but instead, he indicated the products to be a mixture of ketone (XVII) and the reduced compound (XVI). He has suggested the possibility of auto oxidation-reduction of the carbinol (XV). Since the presence of the reduced compound (XVI) was not established at this point in this work, some other explanation for this phenomenon other than auto oxidation-reduction is required.

Kunkel (20) indicates the possibility of the carbinol being oxidized by the peroxides present in the ether during work-up, and he suggests the desirability of washing the ethereal extract of the carbinol with an aqueous solution of a reducing agent (e.g. $FeSO_4$).

It is needless to say that the exact route to the observed products of this reaction is still obscure, and further investigation is necessary.

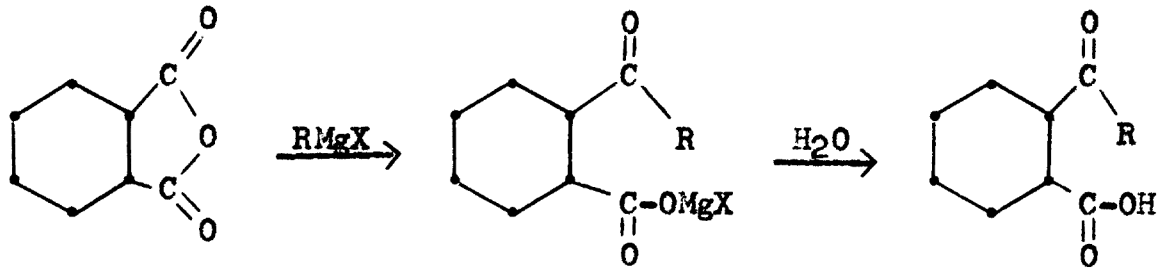
The carbinol was reduced to 2-(1-naphthylmethyl)-bromobenzene (XVI) by the use of red phosphorus and iodine in 90% acetic acid. The general procedure was to run the reduction on the crude unpurified carbinol, thereby eliminating the distillation step. The overall yield of reduced compound (XVI) based on the aldehyde (XIV) was 56%.

A much easier and less time consuming route to the reduced compound (XVI) than that described above is the Grignard coupling reaction between 1-naphthylmagnesium bromide and o-bromobenzylbromide. The yield of this recently studied (31) approach is about 50%, and it will probably replace the older method via the carbinol in the future preparation of compounds of this type.

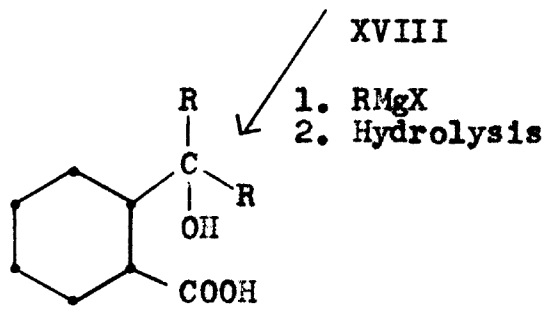
B. Preparation and Cyclization of 2-(1-naphthymethyl)-2'-carboxybenzophenone.

The preparation of the keto-acid, 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) proceeded satisfactorily from the reaction of the Grignard reagent of 2-(1-naphthylmethyl)bromobenzene (XVI) with phthalic anhydride. (See Chart II.) The reaction produced about 51% of white, feathery needles melting at 159-160°.

The presumed mechanism of this reaction involves



XVIII



XIX

the intermediate (XVIII) which is hydrolyzed to the corresponding keto-acid (6). The position in which the anhydride molecule enters is determined by the position of the MgX group, and no subsidiary reaction would be expected.

There is, however, the possibility that the keto-acid salt (XVIII) could react further with the Grignard reagent to give a hydroxy acid (XIX) or its lactone, but this can usually be prevented by using an excess of the anhydride, that is, by adding the Grignard reagent solution to the anhydride ("inverse-addition"). This "inverse-addition" procedure was accomplished easily by transferring the Grignard reagent under dry nitrogen pressure to a dropping funnel set in a flask containing phthalic anhydride in a solution of boiling benzene.

The structure of the keto-acid (IV) was substantiated by a satisfactory carbon-hydrogen analysis. The infrared spectrum of this compound is indicative of its structure by the appearance of the double carbonyl absorption bands at 1680 and 1665 cm^{-1}, which are the bands of the acid carbonyl and ketone carbonyl groups respectively. (a,b) (See Fig. I) There are also present the carboxylic hydroxyl absorption bands at 2660 and 2550 cm^{-1}.

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a. All infrared spectra were made using a Beckman IR-5 spectrophotometer.

b. The infrared spectra of all solid compounds were made using potassium bromide discs. The discs were prepared by combining a weighed sample of the organic compound with an appropriate weight of dry potassium bromide. The mixture was thoroughly mixed in a motor driven shaker and then pressed into a disc by means of a hydraulic press at 20,000 lbs./sq. in.

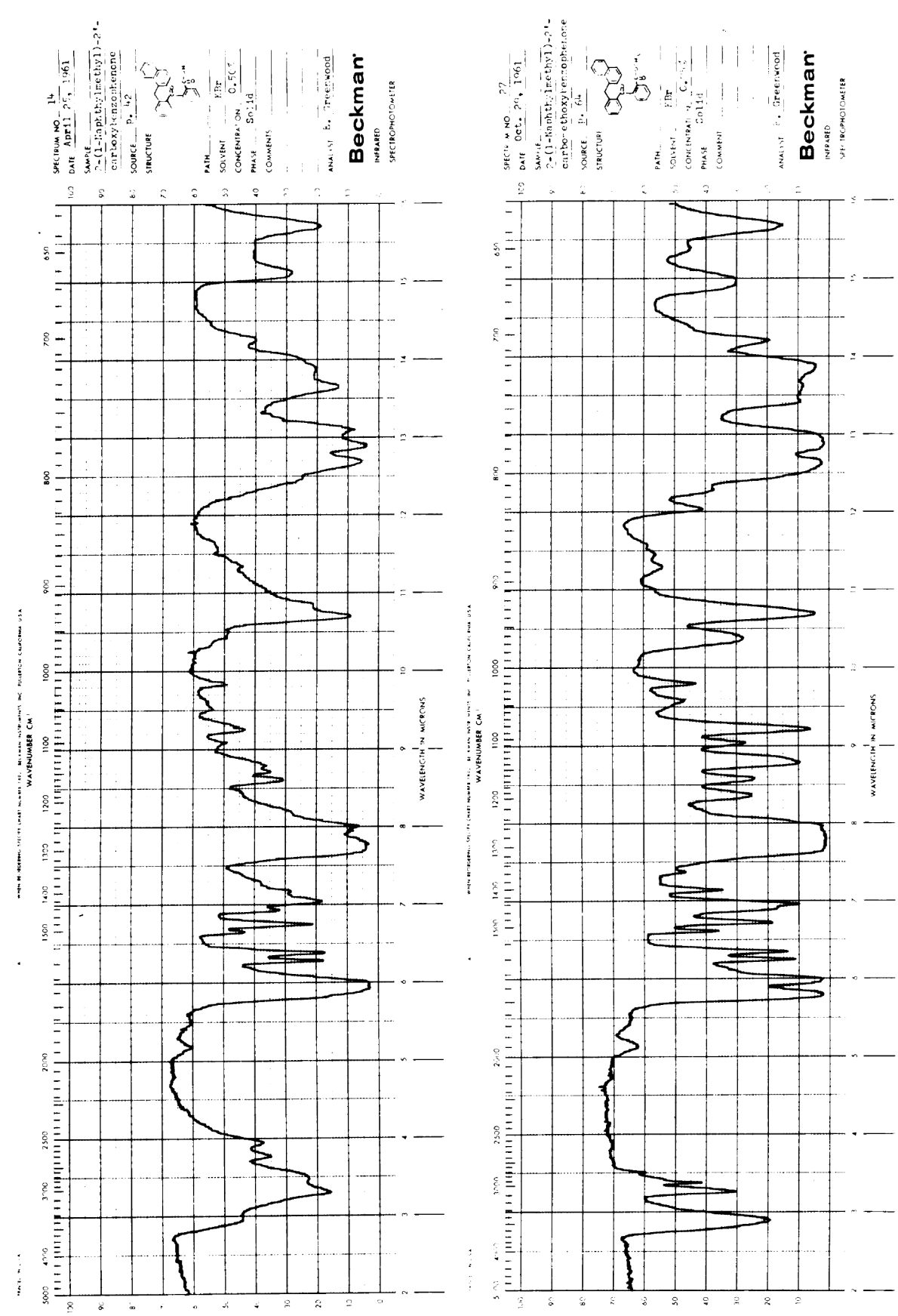

Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS
Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS

Fig. I

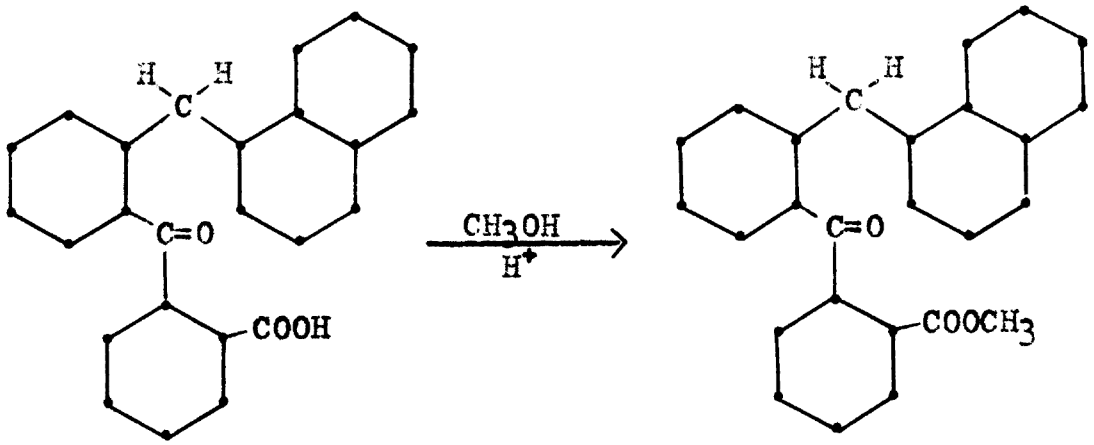
To further substantiate the structure of the keto-acid (IV), a neutralization equivalent titration was run and the equivalent weight was determined. The calculated equivalent weight for the keto-acid is 366 and the value obtained by experiment was 356.

The final phase of structure proof of the keto-acid (IV) was the preparation of its methyl ester, 2-(1-naphthylmethyl)-2'-carbomethoxybenzophenone (XX), which is shown in Chart III. The technique employed to advantage was that of allowing an acidic solution of the keto-acid in methanol to reflux for a period of 360 hours. This produced about 86% of the ester (XX) melting at 88-89°. A satisfactory carbon-hydrogen analysis was obtained on this compound and the infrared spectrum further established the structure by the appearance of absorption bands at 1730, 1300, and 1360 cm^{-1}. (See Fig. I.)

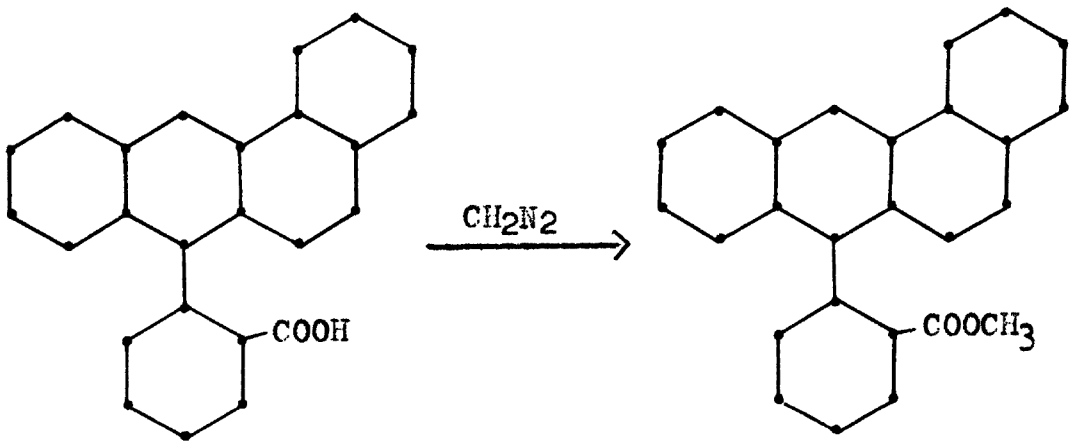
A procedure which was attempted without success in the preparation of the ester (XX) was that which involved the dissolution of the keto-acid (IV) in cold concentrated sulfuric acid followed by the addition of methanol. This reaction, attributed to Newman (32), was of interest because of the short reaction time required and the excellent yields obtained.

This reaction has only been applicable in the esterification of hindered aromatic acids such as 2,4,6-trimethylbenzoic acid, whereas, compounds like benzoic acid remain

CHART III

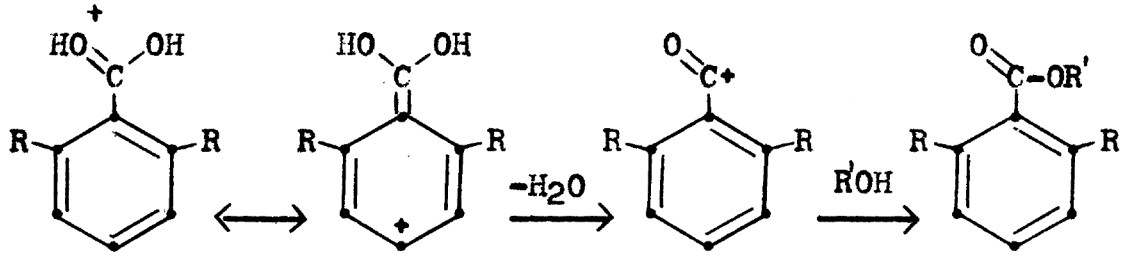


IV XX



V XXI

unaffected. The interpretation of this observation is that both the hindered and unhindered acid react with the sulfuric acid to form the protonated conjugate acid (A) which



(A) (B) (C) (D)

is stabilized by the resonance structure (B). These resonance structures, (A and B), require coplanarity of all the carbon and oxygen atoms, and when the R group is large like methyl, the interference between R and hydroxyl groups enhances the tendency for expulsion of water and the formation of the acyl carbonium ion (C), which reacts with the alcohol to form the ester (D). In the absence of this steric factor, structures (A) and (B) are stable and have no tendency to expel water. This is apparently the situation with the keto-acid (IV), as the only product obtained was the cyclized aromatic acid (V), which resulted as the consequential cyclization product of the acid catalysis.

The cyclization of the keto-acid (IV) to 7-(2-carboxyphenyl)benz[a]anthracene (V) as indicated in Chart I, proceeded with great ease by allowing the keto-acid (IV) to be heated to reflux with a mixture of hydrobromic and acetic

acids for a period of one hour. The yield of acid (V) obtained from this reaction was about 90%.

When Bradsher and Vingiello (4) attempted this type of cyclization on their analogous keto-acid (I), the yield of about 80% of the aromatic acid (II) was only obtained after a reflux period of around twenty hours. This greater ease of cyclodehydration in the naphthylmethylbenzophenone system as compared with that taking place in the o-benzylbenzophenone system can best be interpreted by an explanation of the electronic mechanism of this reaction.

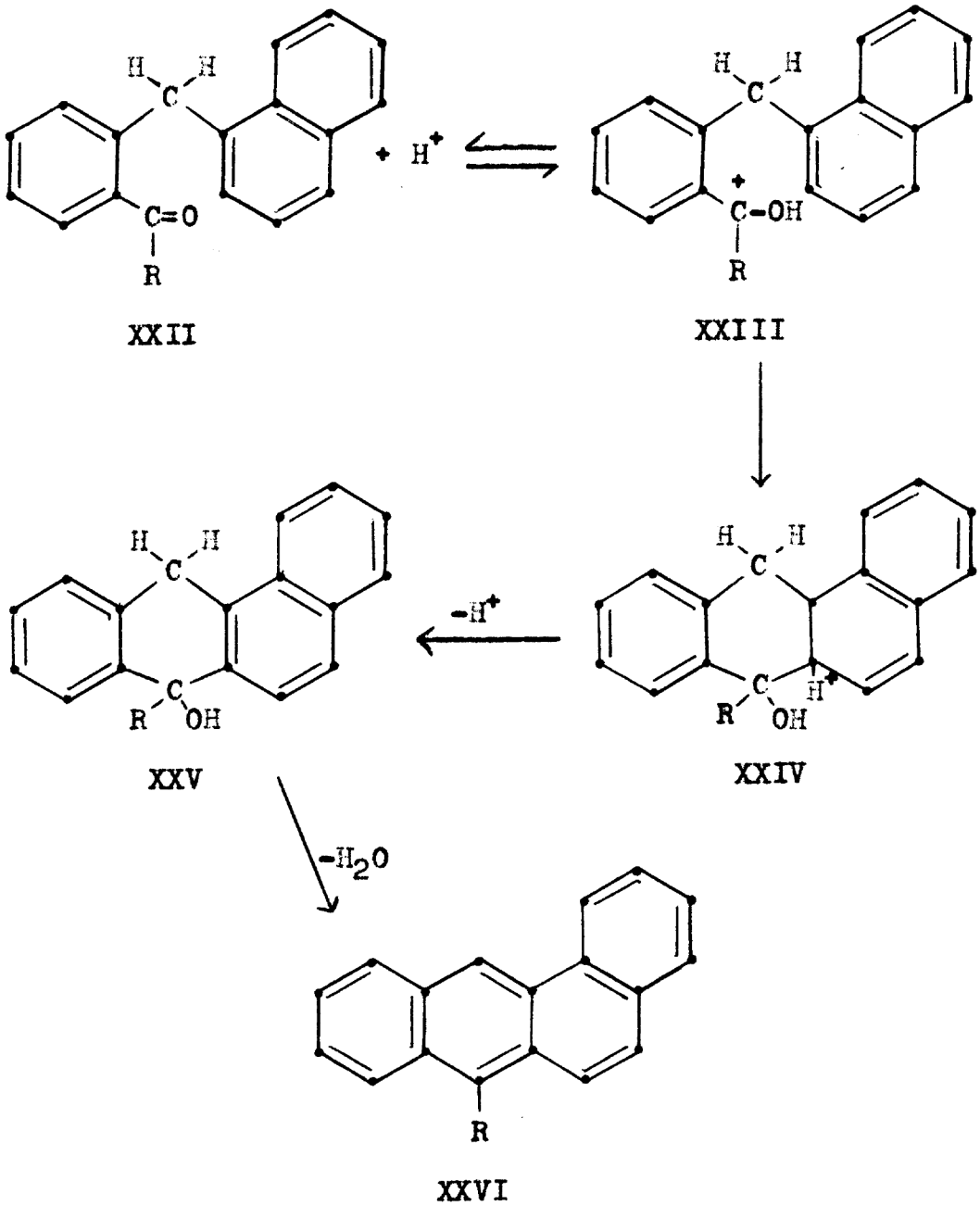
We must first assume that the mechanism proposed by Bradsher and Vingiello (13) for the cyclization of o-benzylbenzophenones is applicable to the cyclization of the keto-acid (IV) prepared in this investigation.

The mechanism shown in Chart IV involves:

1) The protonation of the ketone (XXII) to form the conjugate acid (XXIII).
2) The electrophilic attack of the carbonium ion on the 2-naphthyl carbon to form (XXIV).
3) The release of the proton to form (XXV).
4) The elimination of a molecule of water to give the conjugated aromatic system (XXVI).

From this it can be seen that the rate of cyclization should depend upon the following factors:

CHART IV



1) The position of equilibrium between the ketone and the conjugate acid (XXII $\rightleftharpoons$ XXIII).

2) The relative stability of the carbonium ion of the conjugate acid.

3) The electron density of the position into which cyclization takes place.

4) The steric effect of the R group.

5) The number of positions available for cyclization.

It is obvious that the only factor listed above which is of significant importance and which would show the greatest difference in the two systems in question is the one involving the electron density of the position into which cyclization occurs. All other factors could be considered nearly equal.

Since the reaction involves the electrophilic attack of a carbonium ion, it is understandable that the rate of cyclization into a naphthyl ring would tend to be greater than that into a phenyl ring due to the "electron rich" character of, in this case, the 2-position of the naphthyl ring.

In general, all cases of cyclization into the 2-position of the naphthyl system proceed with greater ease than that into a phenyl system. (19,20,29,33).

As mentioned previously, the cyclization of the keto-acid (IV) to (V) was accomplished fortuitously in a 60%

yield in the esterification attempt, by simply allowing a solution of the keto-acid in concentrated H_2SO_4 to stand for a few minutes at approximately -40°. This further illustrates the ease of this reaction.

A satisfactory carbon-hydrogen analysis of 7-(2-carboxyphenyl)benz[a]anthracene (V) was at first difficult to obtain. Experience has indicated that this type of compound very often leads to unacceptable carbon and hydrogen analyses. The acid (II) prepared by Bradsher and Vingiello (4) gave a poor carbon-hydrogen analysis, and 7-(4-carboxyphenyl)benz[a]anthracene prepared by Stevens (19) also furnished questionable analytical data.

The problem of this observed discrepency was soon attributed to the fact that aromatic acids of this type possess a strong tendency to hydrate. When the acid (V) was prepared for analysis, it was presumed that the sample could be thoroughly dried by allowing it to be heated in an evacuated container which was surrounded by refluxing methanol (b.p.65°). The melting point of this material was 132-135° and the conditions employed for drying were those usually used for a compound of this melting point. This procedure failed to completely remove the water of hydration even after many days of application, and erratic analytical data resulted. By increasing the drying temperature by the employment of refluxing toluene (b.p.110°), the water of

hydration was completely freed from the acid and an excellent carbon-hydrogen analysis was obtained. The melting point of the anhydrous product is 199-200°.

A neutralization equivalent was run on this completely dry compound and the experimentally determined equivalent weight of the acid was found to be 341, which agrees well with the calculated value of 348.

In order to make an approximate determination of the amount of water present in the hydrated compound, a known weight of sample was heated to constant weight at 110° in vacuo over a period of 48 hours. From the amount of weight lost during drying, the percentage of water present in the hydrated acid was found to be 9.6%. A neutralization equivalent titration of the hydrated acid indicated an equivalent weight of 384. This suggests that the acid (equiv. wt. of 348) hydrates with two moles of water to give the value of 384. The percentage of water here would be 9.4%. This agrees very well with the value of 9.6% obtained by the difference in weights of the hydrated and anhydrous materials, and suggests that the acid is hydrated with two moles of water.

The structure of 7-(2-carboxyphenyl)benz[a]anthracene was further established by the use of infrared and ultraviolet absorption spectra.[a]

In the infrared region, the carboxylic acid group exhibits characteristic absorption bands at 1350-1450 and 1660-1740 cm^{-1}. The location of these bands in the recorded spectra (See Fig. II) verify the presence of this functional group.

The ultraviolet absorption spectra of polycyclic aromatic compounds are complex and have become the subject of extensive study (34,35).

According to Badger (36), the ultraviolet absorption spectrum of benz[a]anthracene can be divided into three main regions. These regions are designated by the appearance of absorption maxima at 220-300 mμ, 310-360 mμ, and 360-390 mμ. The absorption in each of the regions is attributed to different types of electronic excitations. In general, the absorption maxima in the 220-300 mμ region are associated with electronic polarization along the horizontal axis of the system, while the 310-360 mμ and higher regions exhibit maxima due to vertical polarization.

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a. All ultraviolet absorption spectra were obtained with a Perkin-Elmer Model 3000 Spectracord (1 cm., quartz cell) at a concentration of about 5 mg. per liter in 95% ethanol.

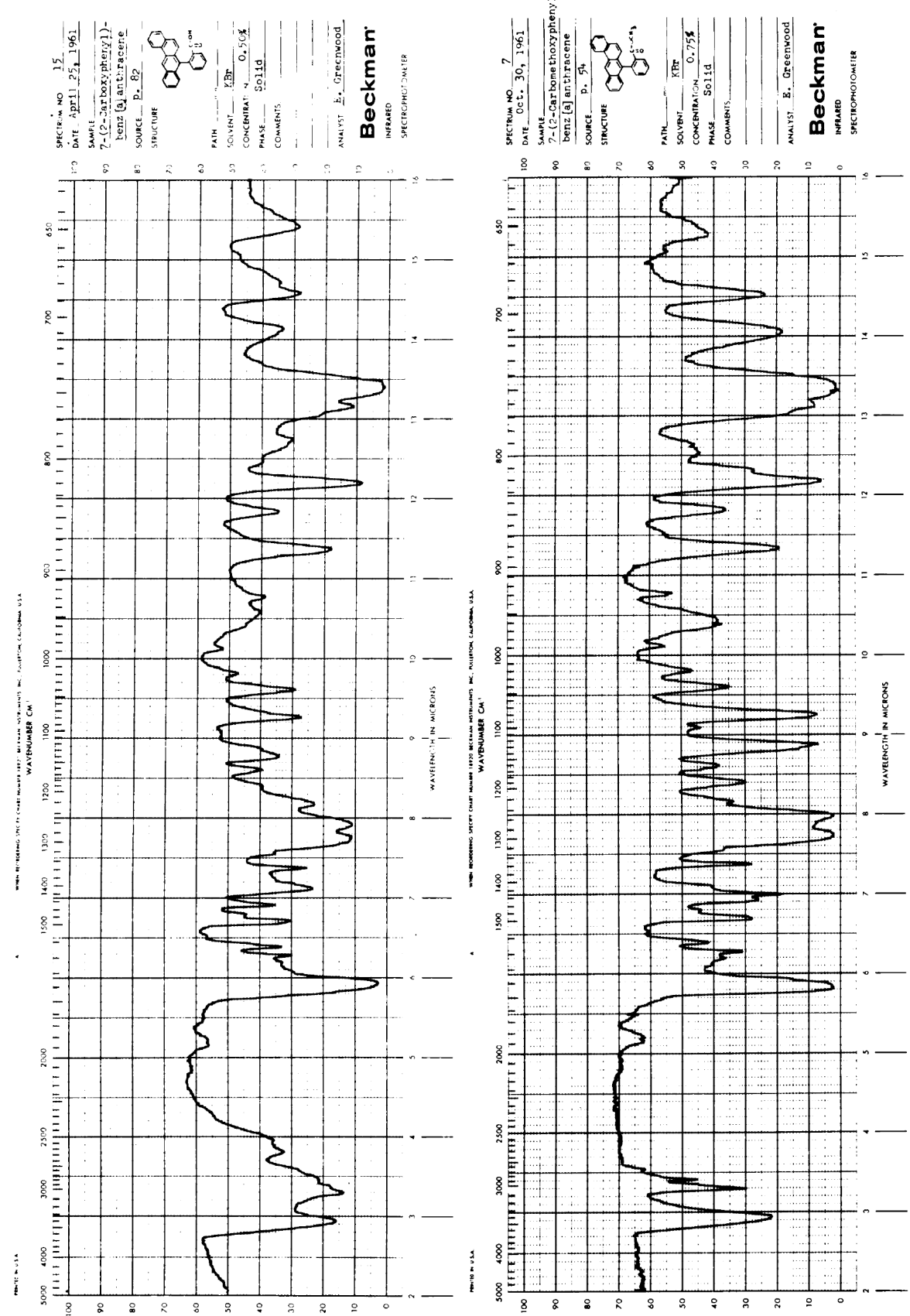

SPECTRUM NO 15
DATE April 25, 1961
SAMPLE 7-(2-Carboxyphenyl)-benz[a]anthracene
SOURCE p. 82
STRUCTURE
PATH
SOLVENT KBr
CONCENTRATION 0.50%
PHASE Solid
COMMENTS
ANALYST E. Greenwood
Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS
SPECTRUM NO 7
DATE Oct. 30, 1961
SAMPLE 7-(2-Carbomethoxyphenyl)-benz[a]anthracene
SOURCE p. 54
STRUCTURE
PATH
SOLVENT KBr
CONCENTRATION 0.75%
PHASE Solid
COMMENTS
ANALYST E. Greenwood
Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS

Fig. II

Substituted polycyclic aromatic compounds have absorption spectra which, in general, are very similar to those of the parent hydrocarbons except that the bands are displaced towards longer wavelengths (bathochromic shift). The magnitude of the shift depends on the position of substitution and on the nature of the substituent. There seems little doubt that the shift is largely due to the mesomeric or resonance effect of the substituent; that is, with the degree of conjugation of the substituent with the aromatic ring system.

In order to determine whether the cyclization product (V) contained the expected benz[a]anthracene structure, an ultraviolet absorption spectrum was run and the absorption maxima were measured and compared to that of benz[a]anthracene. (See Fig. III) The data is tabulated below:

Absorption maxima in millimicrons

Benz[a]anthracene (37)	7-(2-carboxyphenyl)-benz[a]anthracene (V)
222	222
227	231
254	259
267	271
280	281
290	292
316	321
329	335
344	352
359	365

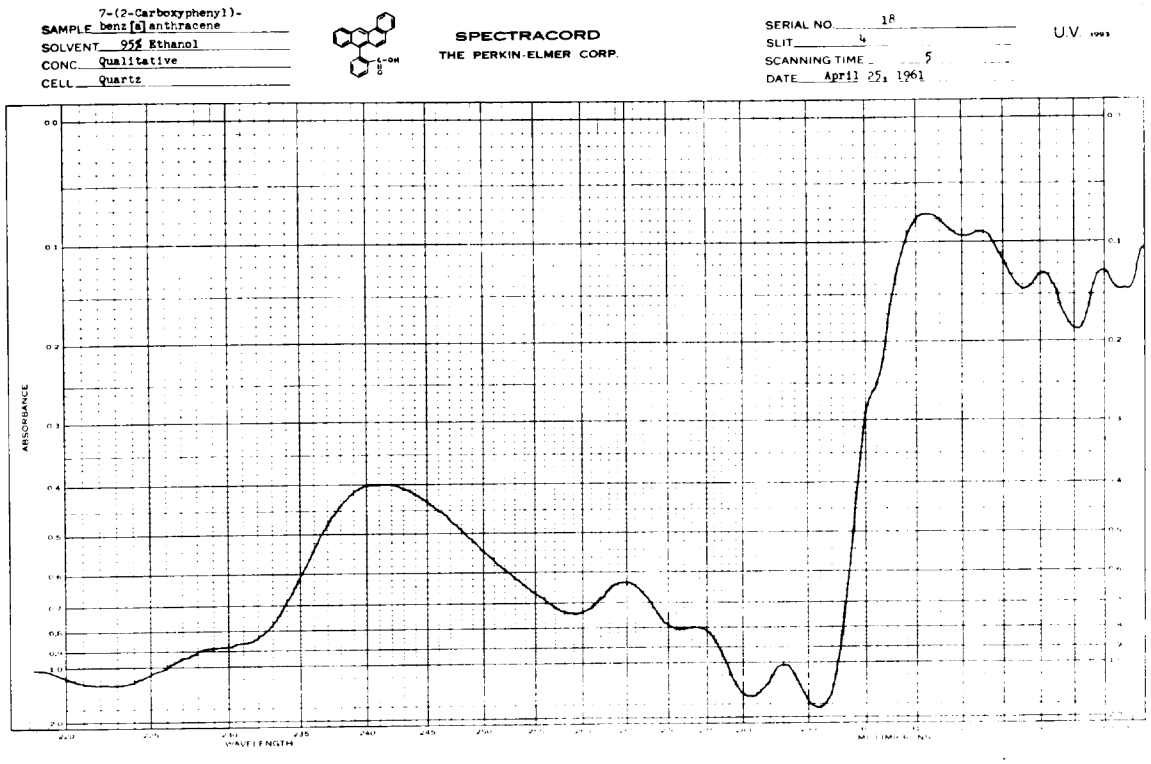

7-(2-Carboxyphenyl)-
SAMPLE benz[a]anthracene
SOLVENT 95% Ethanol
CONC. Qualitative
CELL Quartz
SPECTRACORD
THE PERKIN-ELMER CORP.
SERIAL NO. 18
SLIT 4
SCANNING TIME 5
DATE April 25, 1961
U.V.
ABSORBANCE
WAVELENGTH

Fig. III

As would be expected, the ultraviolet spectrum of 7-(2-carboxyphenyl)benz[a]anthracene is very similar to that of benz[a]anthracene. It is observed that there is a slight bathochromic shift which can only be attributed to the attached carboxyphenyl substituent.

It is a well known fact that in a system such as 7-(2-carboxyphenyl)benz[a]anthracene, there is enough steric hindrance of the hydrogen atoms on the No. 6 and No. 8 carbon atoms of benz[a]anthracene with the ortho hydrogen and ortho substituent on the attached phenyl group, that free rotation about the bond of attachment is restricted. An examination of the Fisher-Taylor-Hirschfelder models makes this obvious. Although this lack of coplanarity of the phenyl and benz[a]anthracene systems should bring about an inhibition of resonance, there is still a slight mesomeric effect or conjugation present which is accounted for by the presence of the bathochromic shift observed. The reason for this is not known.

The fact that the two ring systems are not coplanar suggests that, in the case of 7-(2-carboxyphenyl)benz[a]-anthracene (V), there can exist two stereo isomers; one isomer having the carboxyl group out in front of the benzanthracene plane, and the other with the carboxyl group behind the plane. Resolution of these two forms is necessary to verify this supposition.

The preparation of a methyl ester derivative of 7-(2-carboxyphenyl)benz[a]anthracene (V) was accomplished easily and swiftly by the employment of diazomethane. (See Chart III) Because of the instantaneous nature of this reaction, it is greatly preferred over the technique employed in the esterification of the keto acid (IV).

An ethereal solution of diazomethane was prepared by the hydrolysis of N-methyl-N-nitroso-p-toluenesulfonamide (commercially obtainable as "Diazald") with alcoholic potassium hydroxide (38). By allowing the acid (V) to stand in the ethereal solution for a few minutes, the ester was obtained in an 86% yield.

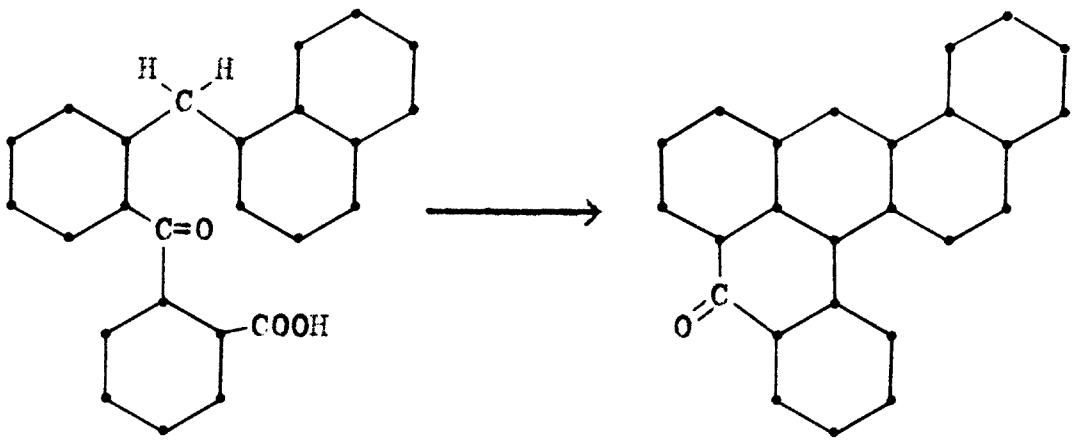
The structure of 7-(2-carbomethoxy)benz[a]anthracene (XXI) was established by a satisfactory carbon-hydrogen analysis, and by ultraviolet and infrared absorption spectra. (See Fig. II) The ester group displays itself by the absorption bands at 1730, 1260, and 1135 cm^{-1}. The ultraviolet spectrum of the ester (XXI) as expected, is similar to that of 7-(2-carboxyphenyl)benz[a]anthracene (V).

C. Preparation of Naphtho[1,2,3-fg]benz[a]anthracene-11-one.

As was mentioned in the Introduction, the cyclodehydration of 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) or 7-(2-carboxyphenyl)benz[a]anthracene (V) could lead to the formation of two possible products; naphtho[1,2,3-fg]-benz[a]anthracene-11-one (VIa) and/or naphtho[3,2,1-fg]-naphthacene-11-one (VIb). See Chart I. It is believed that the former product (VIa) is the only identifiable material obtained from this cyclodehydration reaction, and naphtho[1,2,3-fg]benz[a]anthracene will be the name applied to the cyclization product throughout the remainder of this discussion. The assumption that (VIa) is the product obtained was derived from a study of the infrared absorption spectra and electron density and localization energy of the benz[a]-anthracene system. This will be discussed in detail later.

The cyclodehydration of 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) to naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) was accomplished with varying degrees of success using polyphosphoric acid. The results are summarized in Table I. The method of heating the keto-acid (IV) with polyphosphoric acid in an open flask was attempted first. The optimum reaction time of 4 1/2 hours at 190-200° and 1 1/4 hours at 250° produced the best yield of 64%. The procedure of heating the reaction mixture at 190-200° and then at 250° which was used by Bradsher and Vingiello (4) in their analogous

TABLE I



IV VIa

POLYPHOSPHORIC ACID

Reaction Condition	Time (hrs.)	Temp. (°C)	Yield
open flask	1 3/4 1/4	190-200 250	10%
open flask	2 1/2 3/4	190-200 250	31%
open flask	4 1/2 1 1/4	190-200 250	64.2%
Carius tube	4 1/4	180	44.4%
Carius tube	5 1/4	180	55.3%
Carius tube	6 1/4	180	49%
Carius tube	8	180	33%

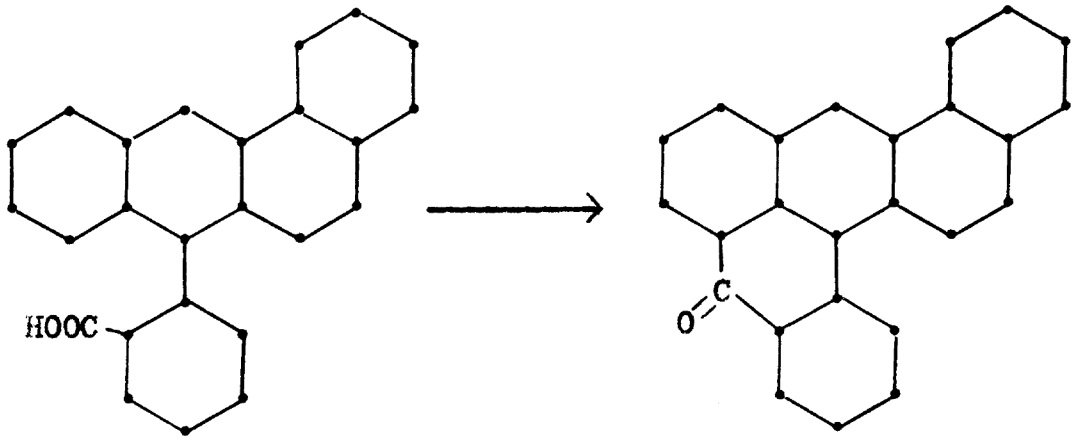
cyclization, presumably aids the two step cyclization of the keto-acid (IV) to (VIa) via the intermediate 7-(2-carboxyphenyl)benz[a]anthracene (V).

The open flask technique was replaced by the use of the Carius tube, which produced comparable results. The Carius tube technique was preferred over the former because of the cleaner product obtained, thereby making work-up simpler. As is seen in Table I, an increase in reaction time beyond 5 1/4 hours causes a decrease in yield presumably due to the increased formation of decomposition products.

The reagent which was not used extensively because of the hazards involved, but which gave the best yield of product in this cyclization was anhydrous hydrogen fluoride. The yield of 84% was realized with this cyclizing agent and the product was much purer than that achieved from the polyphosphoric acid reaction.

Another approach to naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) was made by the cyclodehydration of 7-(2-carboxyphenyl)benz[a]anthracene (V). The results of this cyclization using different concentrations of phosphoric acid are summarized in Table II. The attempted cyclization using 85% phosphoric acid (used by Bradsher and Vingiello (4) in their analogous cyclization) yielded only a high percentage recovery of starting material. It is believed that this incompleteness of reaction is due to the apparent insolubility

TABLE II



V VIa

Reaction Condition	Time (hrs.)	Temp. (°C)	Yield
open flask[a]	2 1/2	195	0%
open flask[b]	2	200	16.7%
Carius tube[b]	13 1/2	170	12.5%
Carius tube[b]	5 1/4	250	45%

a. 85% Phosphoric acid

b. 100% Phosphoric acid

of the acid (V) in the cyclizing media.

Clar (39), in preparing coeranthrone (III) from 5-(2-carboxyphenyl)anthracene (II), improved the yield of (III) somewhat over that obtained by Bradsher and Vingiello (4), by using 100% phosphoric acid instead of the 85% acid. When this reagent was used the yield was increased slightly, but it was not until the reaction was run in a Carius tube at higher temperatures, that the yields were increased appreciably to around 45%. It is interesting to note that when the reaction was carried out for 13 1/2 hours at 170°, very little product was obtained, but when the temperature was increased to 250°, an appreciably greater yield was realized only after 5 1/4 hours of reaction time. This observation reinforces the assumption of the very slight solubility of the acid (V) in the cyclizing media at the temperature of usual reaction conditions.

As was the case with the keto-acid (IV), anhydrous hydrogen fluoride was also a very effective reagent in the cyclization of the acid (V) to naphtho[1,2,3-fg]benz[a]-anthracene-11-one (VIa) in a yield of 90%.

From both the cyclization of the keto-acid (IV) or the acid (V), the product (VIa) was initially obtained as a red amorphous material melting at 180-184°. Usually after two or three recrystallizations from benzene-ethanol, a crystalline product was obtained with little loss in weight

as red needles melting at 218-220°. It appears that polymorphic forms are present and the presence of a certain amount of impurity favors the formation of the lower melting amorphous form. Accordingly, a similar case of polymorphism was reported by Newman (40) in which he found that the melting point of an aromatic acid and that of its analytical sample differed by some twenty degrees.

It was, indeed, a very difficult task to prepare a sample of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) which was pure enough for analysis. Repeated crystallizations of the material melting at 218-220° with acetic acid or benzene-ethanol gradually narrowed and raised the melting range, but the tendency of this high molecular weight compound to bind solvent and impurities made the purification very difficult. Finally, a sample which melted at 221-222° was prepared. It gave very good analytical data. The infrared spectrum of this compound (see Fig. IV) reveals the presence of the carbonyl group by the appearance of the carbonyl absorption band at 1650 cm^{-1}.

In order to give further support to the proposed structure of the cyclization product (VIa), a reduction derivative and a 2,4,7-trinitrofluorenone molecular complex were prepared and analytical data was obtained. See Chart V.

The procedure for the reduction of (VIa) to 11-H-naphtho[1,2,3-fg]benz[a]anthracene (XXVII) was first attempted

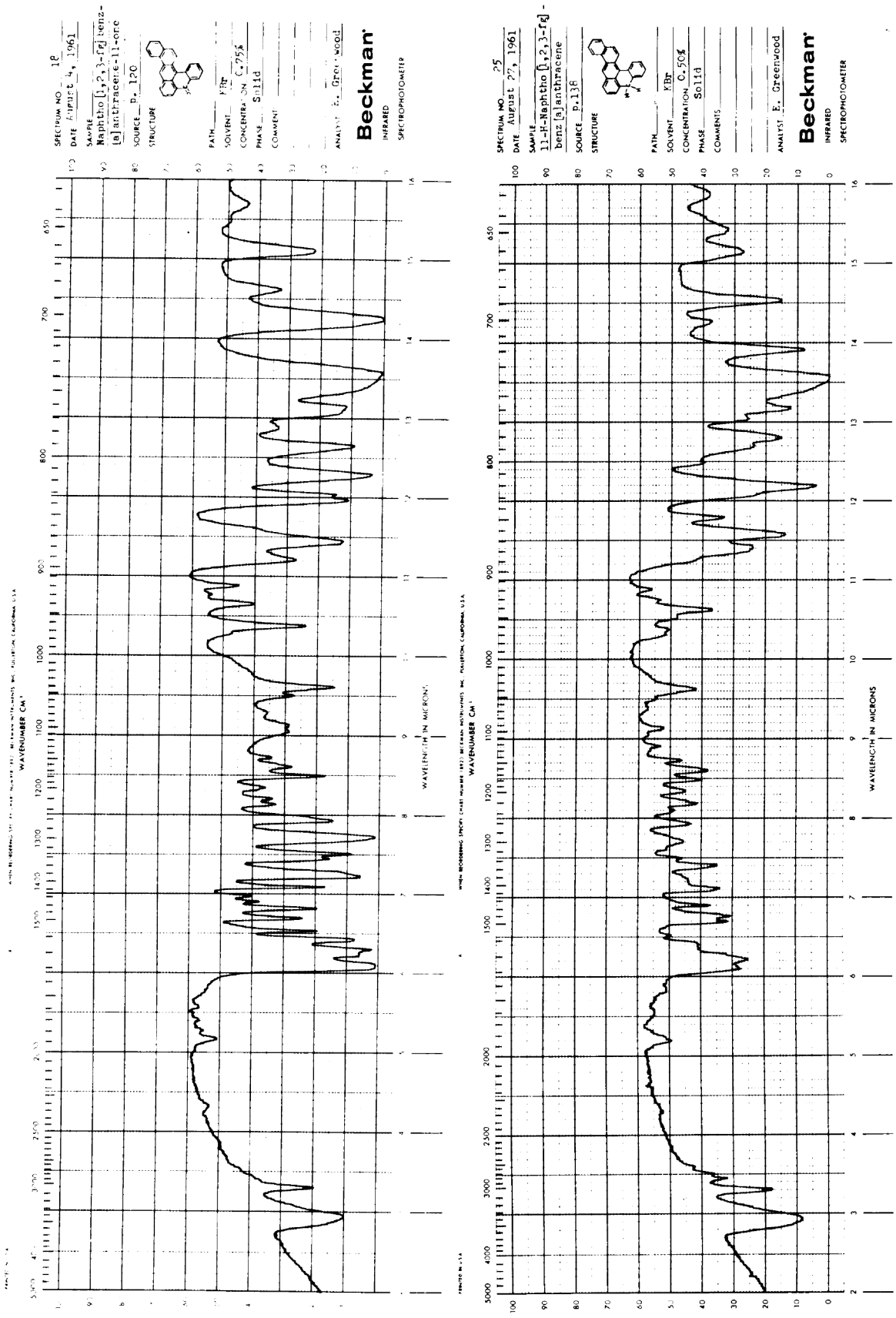
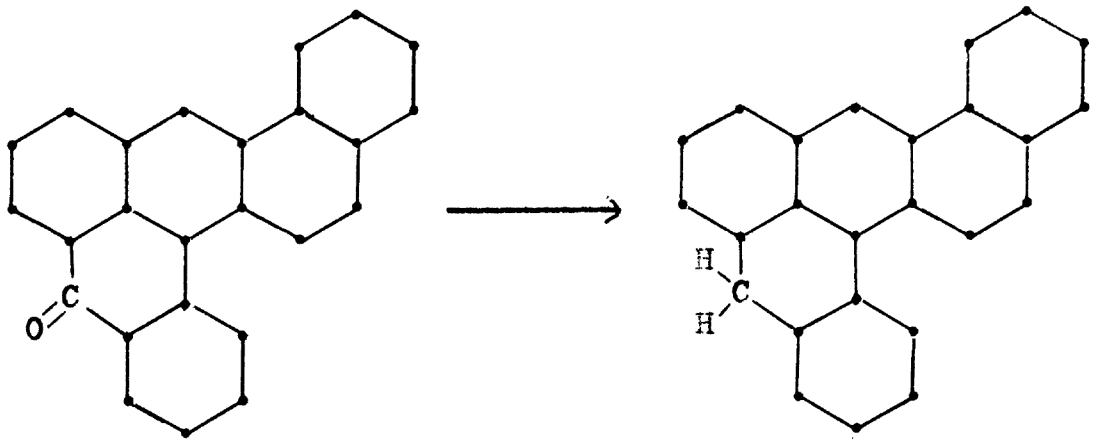

SPECTRUM NO. 18
DATE August 4, 1961
SAMPLE Naphtho[1,2,3-fg]benz-[a]anthracene-11-one
SOURCE p. 120
STRUCTURE
PATH
SOLVENT KBr
CONCENTRATION 0.75%
PHASE Solid
COMMENT
ANALYST E. Greenwood
Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS
SPECTRUM NO. 25
DATE August 27, 1961
SAMPLE 11-H-Naphtho[1,2,3-fg]-benz[a]anthracene
SOURCE p.136
STRUCTURE
PATH
SOLVENT KBr
CONCENTRATION 0.50%
PHASE Solid
COMMENTS
ANALYST E. Greenwood
Beckman
INFRARED
SPECTROPHOTOMETER
WAVENUMBER CM⁻¹
WAVELENGTH IN MICRONS

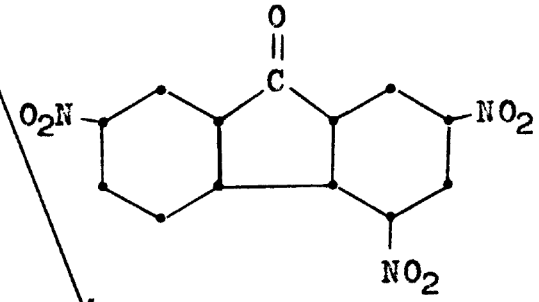
Fig. IV

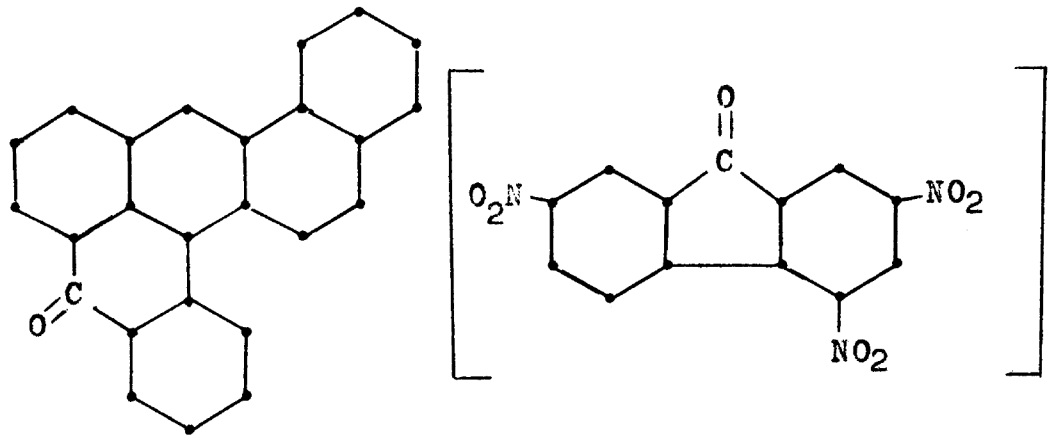
CHART V



VIa

XXVII



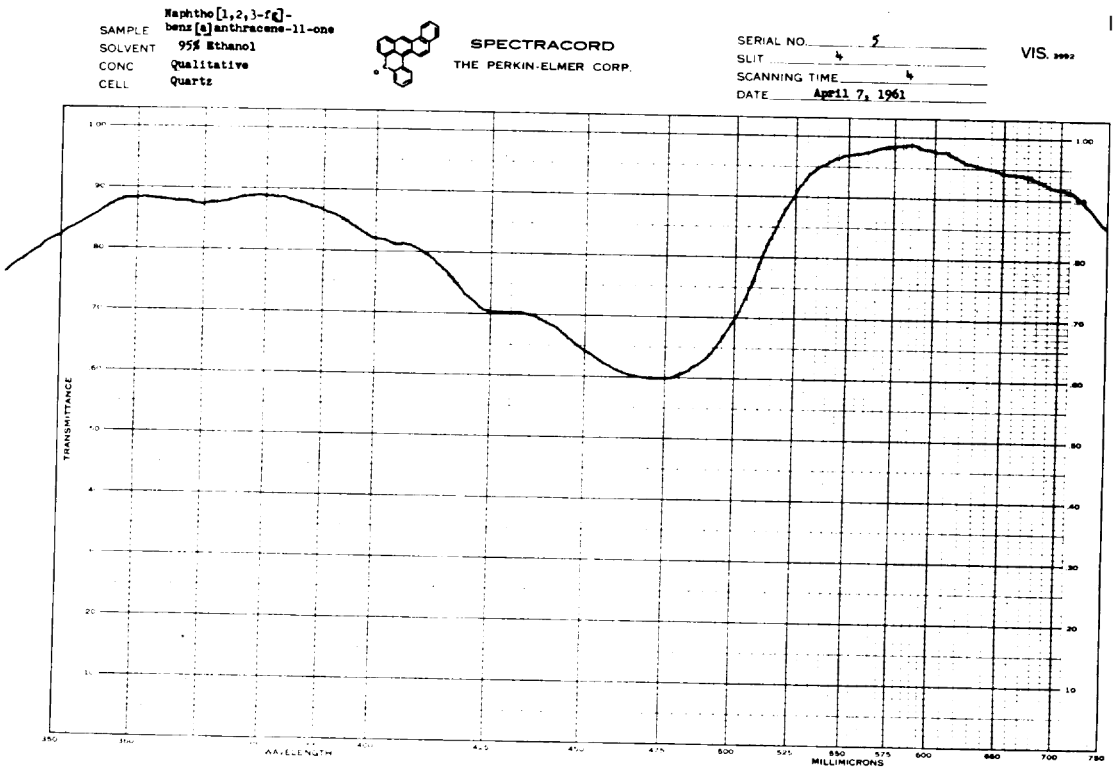


XXVIII

by the use of zinc dust in alkali. This technique worked very well for Clar (39) in the reduction of coeranthrone (III), but when applied to the reduction of (VIa), only starting material resulted. A modification of the zinc dust reduction was also attempted using zinc which had been activated with $CuSO_4$ (41), but again, only starting material resulted.

The reduction was finally performed by the use of lithium aluminum hydride and aluminum chloride. This produced 58% of 11-H-naphtho[1,2,3-fg]benz[a]anthracene (XXVII), which melted at 157-158°. The carbon-hydrogen analysis of this bright orange hydrocarbon was in good agreement with its structure. A study of the infrared spectrum (see Fig. IV) of this compound reveals the absence of the carbonyl absorption band at 1650 cm^{-1}, and the appearance of the absorption band for aliphatic carbon-hydrogen linkages at 2900 cm^{-1}.

Since both the carbonyl (VIa) and reduced (XXVII) compounds are colored, it was necessary to record not only the ultraviolet spectra, but also the visible absorption spectra, and thereby take into account the whole wavelength span of 220 to 750 millimicrons. See Figs. V and VI for the spectra of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) and 11-H-naphtho[1,2,3-fg]benz[a]anthracene (XXVII) respectively. The spectral data is tabulated below:


SAMPLE Naphtho[1,2,3-fg]-benz[a]anthracene-11-one
SOLVENT 95% Ethanol
CONC Qualitative
CELL Quartz
SPECTRACORD
THE PERKIN-ELMER CORP.
SERIAL NO. 5
SLIT 4
SCANNING TIME 4
DATE April 7, 1961
VIS.
TRANSMITTANCE
WAVELENGTH
MILLIMICRONS

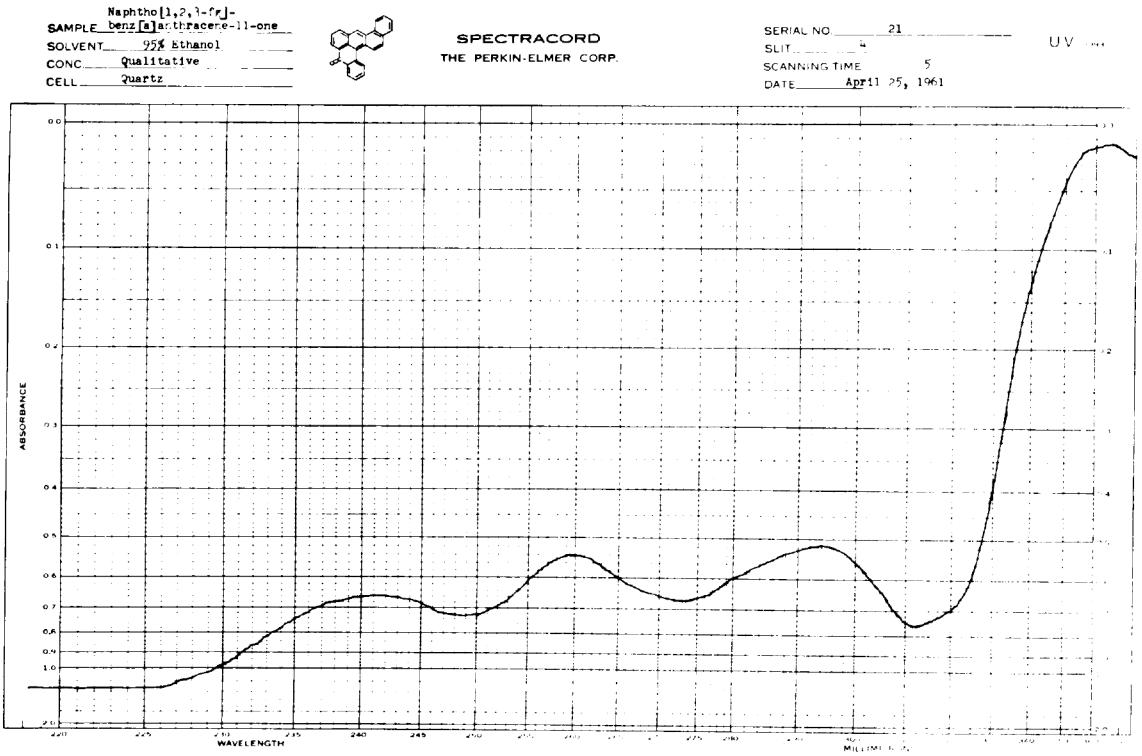
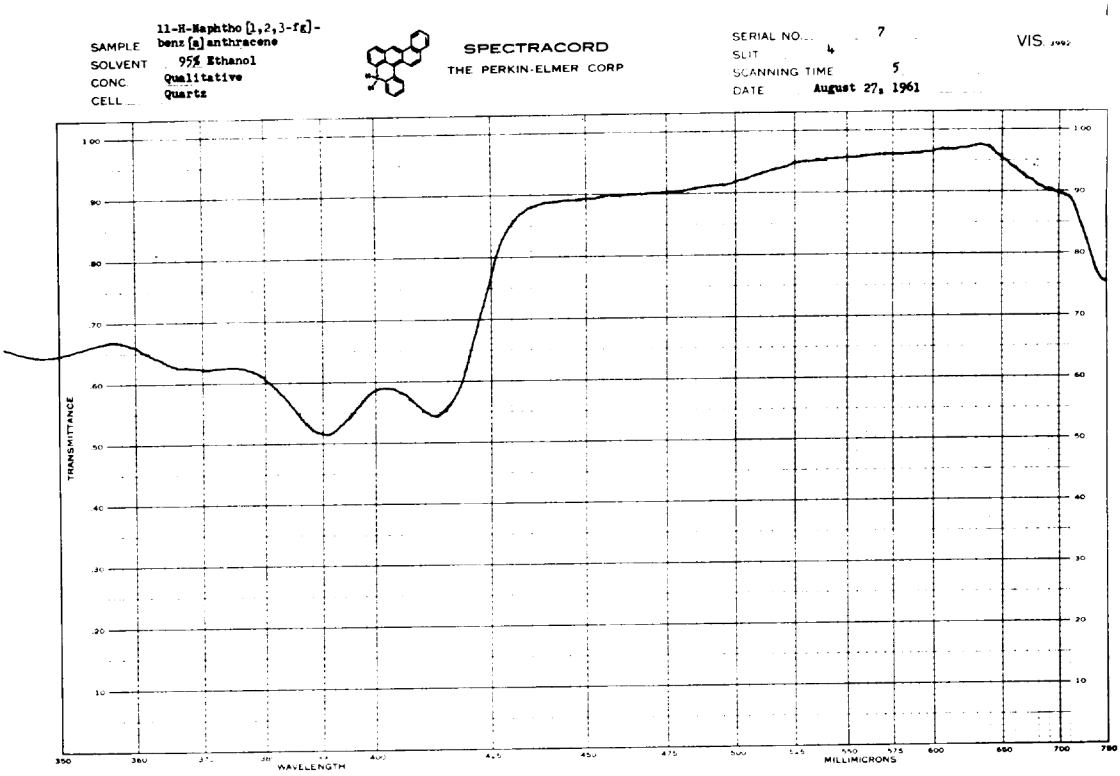

SAMPLE Naphtho[1,2,3-fg]-benz[a]anthracene-11-one
SOLVENT 95% Ethanol
CONC Qualitative
CELL Quartz
SPECTRACORD
THE PERKIN-ELMER CORP.
SERIAL NO. 21
SLIT 4
SCANNING TIME 5
DATE April 25, 1961
UV
ABSORBANCE
WAVELENGTH

Fig. V


SAMPLE 11-H-Naphtho [1,2,3-fg]-benz [a] anthracene
SOLVENT 95% Ethanol
CONC. Qualitative
CELL Quartz
SPECTRACORD
THE PERKIN-ELMER CORP
SERIAL NO. 7
SLIT 4
SCANNING TIME 5
DATE August 27, 1961
VIS.
TRANSMITTANCE
WAVELENGTH
MILLIMICRONS

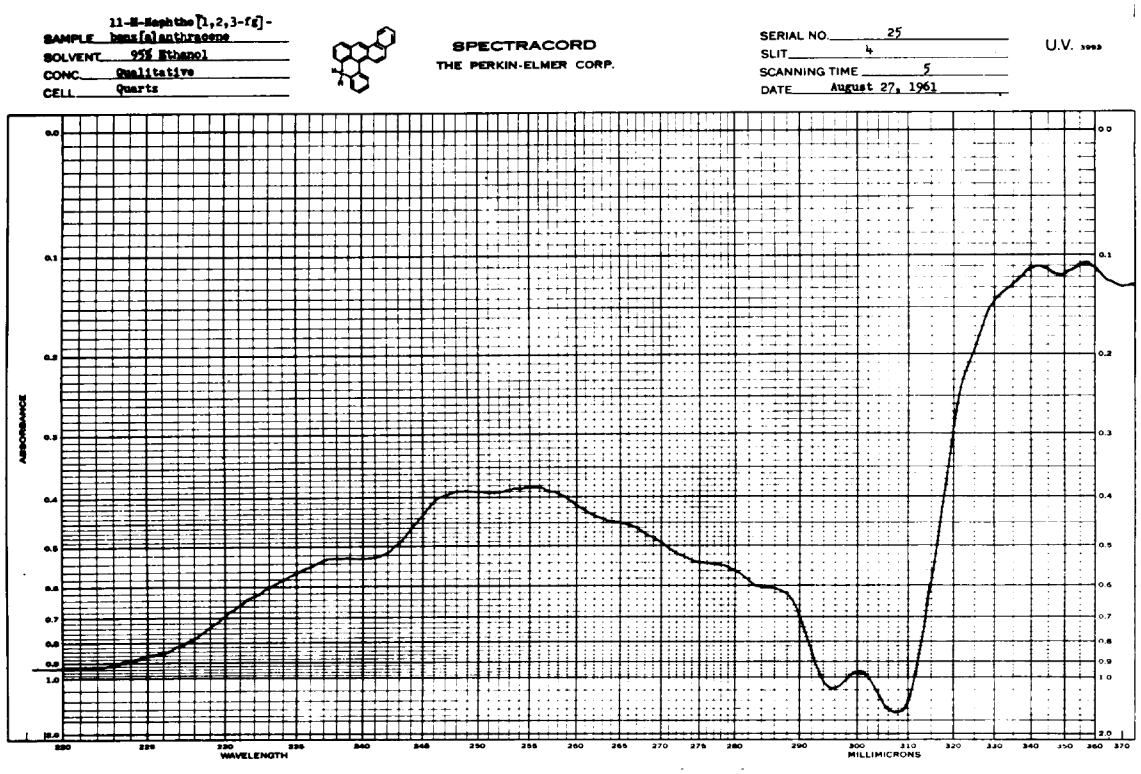

SAMPLE 11-H-Naphtho [1,2,3-fg]-benz [a] anthracene
SOLVENT 95% Ethanol
CONC. Qualitative
CELL Quartz
SPECTRACORD
THE PERKIN-ELMER CORP.
SERIAL NO. 25
SLIT 4
SCANNING TIME 5
DATE August 27, 1961
U.V.
ABSORBANCE
WAVELENGTH
MILLIMICRONS

Fig. VI

Absorption maxima in millimicrons	
Naphtho[1,2,3-fg]-benz[a]anthracene-11-one	11-H-naphtho[1,2,3-fg]-benz[a]anthracene
225	222
249	240
273	275
-	284
-	296
312	308
370	350
405	370
425	390
475	412

As can be seen in Fig. VI, the ultraviolet absorption spectrum of 11-H-naphtho[1,2,3-fg]benz[a]anthracene (XXVII) is very similar to that of 7-(2-carboxyphenyl)benz[a]anthracene (V) (see Fig. III) with the exception of a large bathochromic shift. This similarity would be expected, since the presence of the CH_2 group in 11-H-naphtho[1,2,3-fg]-benz[a]anthracene (XXVII) causes a decrease in the conjugation of the lower phenyl ring. This would thereby produce a system favoring phenyl-benz[a]anthracene rather than naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa), and therefore the absorption spectrum of 11-H-naphtho[1,2,3-fg]benz[a]-anthracene (XXVII) should be similar to the composite spectral curve of benz a anthracene and the phenyl ring.

One of the most outstanding properties of aromatic hydrocarbons is their ability to form molecular complexes with polynitro compounds. These complexes are usually

formed in a ratio of 1:1, but this is not always the case. The complexes are all highly colored and the depth of color seems to parallel their stability. The complexes are formed by electronic interactions due to the polarization of one component by the other; the hydrocarbon is the donor and the polynitro compound is the acceptor.

The reaction of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) with 2,4,7-trinitrofluorenone to form the molecular complex proceeded smoothly in a 1:1 ratio. See Chart V. The color of the complex (XXVIII) was deep red, which was not much different from that of the aromatic compound (VIa). The complex melted at 201.5-202° and the carbon, hydrogen, and nitrogen analysis was in very good agreement with the 1:1 ratio structure.

D. Spectral Data and Electron Density and Localization Energy Calculations Supporting the Naphtho[1,2,3-fg]benz[a]anthracene (VIa) Structure.

Infrared absorption spectra has largely been utilized as a means of identifying certain functional groups by the study of their characteristic absorption of energy at an appropriate frequency. More recently (42), however, infrared spectrophotometry has been applied as a useful tool in the confirmation of structural features of fused aromatic systems.

In applying the use of infrared absorption spectra to the problem of determining whether the cyclization of 7-(2-carboxyphenyl)benz[a]anthracene (V) formed naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) or naphtho[3,2,1-fg]naphthacene-11-one (VIb) (see Chart I), we must first consider the benz[a]anthracene system.

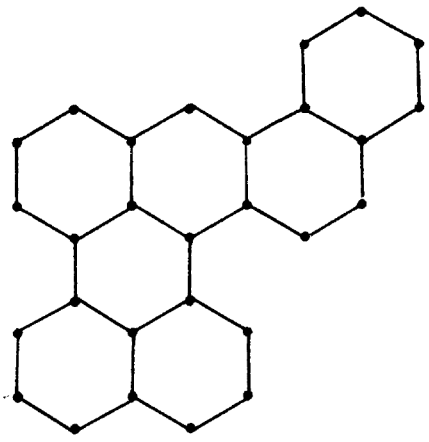
The general features of the infrared spectra of the benz[a]anthracenes are a number of strong bands between 700 and 900 cm^{-1} and a complex arrangement of bands between 1200 and 1700 cm^{-1} (43). The vibrations giving rise to the intense bends at 700-900 cm^{-1} include the out of plane deformations of C-H bonds in the substituted aromatic system. The region between 790 and 850 cm^{-1} contains at least one strong band for all compounds but 5 and 6 substituted

benz[a]anthracenes. It is this region which is of interest here. In various methyl substituted benz[a]anthracenes, for example, it is found that infrared spectra of all compounds substituted in various positions around the ring system exhibit strong absorption bands in the region 790-850 cm^{-1} except when there is substitution in the 5 or 6 position.

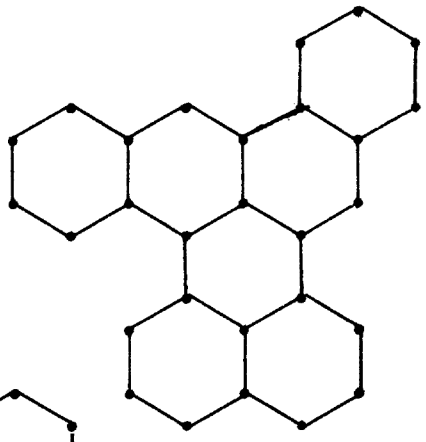
If we consider the infrared spectrum of the 7-(2-carboxyphenyl)benz[a]anthracene (V) system (Fig. II), certain bands in the 790-850 cm^{-1} region should be present, since there is no substitution in the 5 or 6 position. Two bands which are present in this region are located at 820 and 845 cm^{-1}. It seems logical that if the cyclization of 7-(2-carboxyphenyl)benz[a]anthracene took place at the No. 6 carbon of benz[a]anthracene, then these bands should disappear from the infrared spectrum of the cyclized product, but if cyclization took place at the No. 8 carbon atom, these bands should remain in the spectrum of the product. By examination of the infrared spectrum of the cyclization product (Fig. IV) it can be seen that both bands remain in this region, with only a slight shift to 813 and 835 cm^{-1} Therefore, it is assumed that the cyclization took place into the No. 8 carbon of benz[a]anthracene with the formation of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa).

Supporting evidence for this assumption was obtained

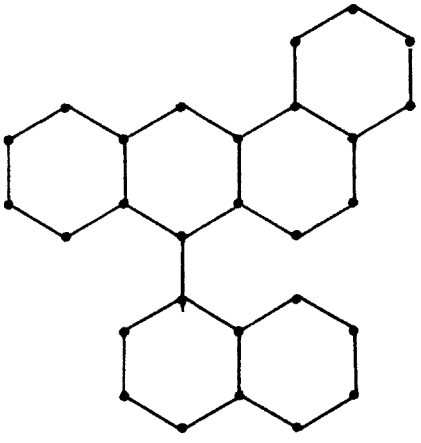
from the study of the infrared spectra of naphtho[2',1'-a]-perylene (XXIX) and 1,2,4,5-dibenzoperylene (XXX), as compared with that of 7-(1-naphthyl)benz[a]anthracene (XXXI).



XXIX



XXX



XXXI

The observations of the presence or absence of absorption bands in the 790-850 cm^{-1} region made in this study agreed with the previously maintained assumption.

One of the more recent achievements of quantum mechanics is the development of the theory in exploring the orientation of groups involved in substitution of aromatic molecules.

The application of this theory in the treatment of

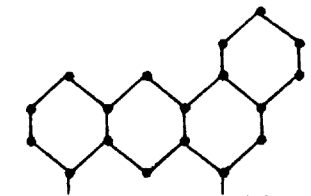
this problem may be roughly classified into two methods. The one, which can be called the "static method" is based on the hypothesis that the position of higher calculated π electron density is more easily attacked by electrophilic reagents. The other, which may be called the "dynamic method", consists of two parts: 1) the localization theory which is related to the calculation of the difference in unsaturation energy of the hypothetical transition complexes (44), and 2) the delocalization theory, which is based on the assumption that an electron in the highest molecular orbital of a substrate can undergo further delocalization due to the lowest unoccupied molecular orbital of the reagent.

A study of the electronic structure of the benz[a]-anthracene system lends further support as to which direction the cyclization in question takes place.

Dewar (45) has determined the relative reactivity of the various positions of substitution in benz[a]anthracene in terms of localization energy. It is assumed that the transition state in aromatic substitution involved a change in hybridization of the carbon atom undergoing attack from sp^2 to sp^3, and therefore, this carbon atom is consequently removed from conjugation. From this assumption, the localization energy is defined as the difference in π electron binding energy between the initial and transition states,

and represents the energy required to localize reactive electronic groupings at specific atoms in aromatic systems. The smaller the localization energy, the more readily should substitution occur.

An examination of the calculated localization energies pertinent to this discussion shows that the No. 8 carbon atom has a lower localization energy than the No. 6

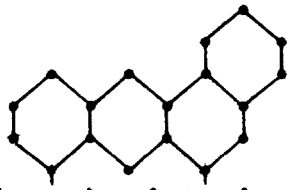


carbon atom, and therefore, of these two, the No. 8 carbon atom should be the more reactive position in substitution reactions.

The calculation of the localization energies for the 7-(2-carboxyphenyl)benz[a]anthracene (V) system is complex and remains to be attempted. It can, nevertheless, be assumed that the localization energy values for this system are nearly the same as those of the benz[a]anthracene system. This assumption is based on the fact that the attached phenyl ring would not contribute a mesomeric effect because of lack of conjugation due to steric inhibition of resonance. The phenyl ring, however, would be expected to exhibit a slight inductive effect, and the relatively small change in localization energy from this

effect would be the same for both the No. 6 and No. 8 carbon atoms because of the same bond distance between each of these positions and the position of attachment of the phenyl ring (46).

The afore-mentioned reasoning is also applicable to the calculated frontier electron density method (44) and similar conclusions about the position of cyclization of 7-(2-carboxyphenyl)benz[a]anthracene (V) can be drawn. By this method, the greater the frontier electron density, the more susceptable is that position to aromatic substitution. Appropriate values are given below.



(.209) (.177)

Here again, it can be seen that substitution at the No. 8 carbon atom is preferred over that at No. 6.

It should be pointed out that the difference in the values obtained by the frontier electron method for the No. 6 and No. 8 positions are more significant than those obtained by the localization method, since the values of the latter differ only by 0.03 units.

Although the proof of structure of naphtho[1,2,3-fg]-benz[a]anthracene-11-one (VIa) presented heretofore is not rigorous, it will have to suffice, nevertheless, until such time that compound (VIa) can be synthesized unequivocally.

EXPERIMENTAL

EXPERIMENTAL[a,b,c]

o-Bromotoluene (XII) (23).

To 880 ml. (6 moles) of 40 percent hydrobromic acid in a three liter Erlenmeyer flask was added 162 g. (1.5 moles) of commercial o-toluidine and the solution was cooled to 10°. To this cold solution was added 116 g. (1.7 moles) of sodium nitrite in 10 g. quantities. After each addition, the flask was stoppered and shaken until all the red fumes were absorbed. The temperature was carefully maintained below 10°. When the diazotization was complete, 5 g. of copper powder was added, the flask was attached to a long reflux condenser and heated very cautiously. As soon as the first sign of reaction was observed, the flask was cooled with ice. After the vigorous evolution of nitrogen, the mixture was heated for one-half hour on a steam bath. About 1 liter of water was added and the mixture was steam distilled until about 1.5 liters of condensate was collected. The distillate was made alkaline with about 10 g. of sodium hydroxide and the red, bottom layer of crude o-bromotoluene

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a. All analyses were performed by Geller Laboratories, Bardonia, New York.

b. All melting points were obtained using a Fisher-Johns melting point apparatus and are corrected.

c. All temperatures are expressed in degrees centigrade.

was separated, washed once with concentrated sulfuric acid, which removed almost all the color, and then twice with water. The product was dried over calcium chloride and distilled from a modified Claisen flask. The product distilling at 176-180° Lit.(23), b.p. 178-181° was collected; yield 103.3 g. (40.4%).

o-Bromobenzaldehyde (XIV) (26).

Into a 500 ml. three-necked flask equipped with a mechanical stirrer, reflux condenser, and a dropping funnel was placed 171 g. (one mole) of o-bromotoluene. The o-bromotoluene was heated to 130° with stirring and 160 g. (one mole) of bromine was added dropwise directly in front of a source of ultraviolet light.* Upon the completion of this addition, a second mole of bromine was added dropwise at 165°, after which the solution was allowed to reflux at this temperature for an extra hour. The resulting brown solution was placed in a two liter round bottom flask containing 150 g. of calcium carbonate and 500 ml. of water, and the contents were heated to reflux for 10 hours. The mixture was then steam distilled and the distillate

* The ultraviolet light source was obtained from the "Blak-Ray" Long Wave Ultraviolet Lamp, manufactured by Ultra-Violet Products, Inc., San Gabriel, California.

was extracted several times with ethyl ether. The ethereal solution was dried over anhydrous magnesium sulfate, concentrated, and the residual oil was distilled under reduced pressure. The fraction distilling between 57-67° at 0.6 mm. Lit.(26), b.p. 118-119°, 12 mm. was collected; yield 85.2 g. (46%).

2-Bromophenyl-1-naphthyl carbinol (XV).

A Grignard reagent was prepared from 82 g. (0.39 mole) of 1-bromonaphthalene and 9.6 g. (0.39 g. atoms) of magnesium turnings in 200 ml. of anhydrous ethyl ether. Upon complete formulation of the Grignard reagent, 73 g. (0.39 mole) of o-bromobenzaldehyde in 100 ml. of anhydrous ethyl ether was added dropwise. After the addition was complete, the mixture was stirred overnight, after which it was decomposed with 70 ml. of a 20% ammonium chloride solution. The ethereal layer was separated and the aqueous layer was extracted several times with ether. During the extractions, a thick emulsion formed in the aqueous layer which was broken with dilute hydrochloric acid. The ethereal solutions were combined and concentrated. The resulting impure carbinol was not distilled, but was saved for reduction in the following experiment.

2-(1-Naphthylmethyl) bromobenzene (XVI).

Into a one liter three-necked round bottom flask, equipped with a mechanical stirrer and reflux condenser, was placed 630 ml. of glacial acetic acid, 70 ml. of water, 20 g. of red phosphorus, and 20 g. of iodine. To this was added the 2-bromophenyl-1-naphthyl carbinol prepared in the previous experiment, and the mixture was heated to reflux for 40 hours. After refluxing, the solution was filtered while hot to remove the excess phosphorus, and the filtrate was poured over ice and carefully neutralized with sodium carbonate. The neutralized solution was extracted with ethyl ether until the extracts were almost colorless. The ethereal solutions were combined, dried over anhydrous $CaCl_2$ overnight, concentrated, and the residual oil was distilled under reduced pressure. The fraction distilling at 174-184° at 0.5 mm Lit.(47), b.p. 186-200°, 25 mm. was collected; yield 65.6 g. (56.5%).

2-(1-Naphthylmethyl)-2'-carboxybenzophenone (IV).

To 1.64 g. (0.0674 g. atom) of magnesium turnings in a 250 ml. round bottom, three-necked flask, equipped with a magnetic stirrer, was added 20 g. (0.0674 mole) of 2-(1-naphthylmethyl)bromobenzene dissolved in about 150 ml. of dry ethyl ether. A drop of methyl iodide was added to initiate the reaction. The Grignard reagent was slow to form and the mixture was allowed to reflux

overnight. The Grignard reagent was slowly transferred under nitrogen pressure to a dropping funnel set in a three-necked, 500 ml. round bottom flask, equipped with a mechanical stirrer and a reflux-take-off condenser. The Grignard reagent was slowly added to a solution of 8.95 g. (0.0605 mole) of phthalic anhydride in 200 ml. of boiling benzene. During the addition the ether flashed off. After the addition was complete, 150 ml. of anhydrous benzene was slowly added, and any remaining ether was distilled over. The mixture was allowed to reflux for three hours at 75°, after which the complex was decomposed by pouring the contents of the flask into a beaker containing 250 g. of ice, 150 ml. of water, and 40 ml. of concentrated sulfuric acid. This was stirred until the benzene layer became very thick with yellow material. The benzene layer was extracted five times with a 10% sodium carbonate solution. The extracts were combined and carefully acidified with sulfuric acid. The resulting crude material was dissolved in benzene and dried over magnesium sulfate overnight. The benzene solution was concentrated, and the product recovered was treated with charcoal and recrystallized twice from a 1:3 mixture of petroleum ether and benzene to yield 11.4 g (51.6%) of white, feathery needles melting at 159-160°.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.95; H, 4.95.
Found: C, 81.54; H, 5.09.

Neutralization Equivalent of 2-(1-Naphthylmethyl)-2'-carboxybenzophenone (IV).

A 0.200 g. sample of 2-(1-naphthylmethyl)-2'-carboxybenzophenone was dissolved in 95% ethanol. This solution was titrated with a 0.104 N sodium hydroxide solution, using bromthymol blue as the indicator, and 5.4 ml. of base were required to reach the end point.

$$\text{Equivalent weight} = \frac{(0.200)\ (1000)}{(5.4)\ \ (0.104)}$$

Equivalent weight = 356

Calculated Equivalent weight = 366

2-(1-Naphthylmethyl)-2'-carbomethoxybenzophenone (XX).

To 0.5 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone in a 50 ml. round bottom flask equipped with a reflux condenser, was added 25 ml. of methyl alcohol and six drops of concentrated sulfuric acid. The mixture was heated under reflux for 360 hours, then it was allowed to cool and the product precipitated. The resulting white material was recrystallized from methyl alcohol, which produced 0.45 g. (86.5%) of white needles which melted at 75-77°. Further recrystallization from methyl alcohol

produced the more stable white rhombic crystals which melted at 88-89°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30.
Found: C, 82.09; H, 5.41.

Attempted Preparation of 2-(1-Naphthylmethyl)-2'-carbomethoxybenzophenone (XX).

Into a 150 ml. beaker was placed 25 ml. of concentrated H_2SO_4 and this was cooled in a dry ice-acetone bath until the acid became pasty. To this paste was added 0.5 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone, and this mixture was stirred until solution was complete. The mixture became very deep red. To this was slowly added, with stirring, 35 ml. of methyl alcohol, which was previously cooled in a dry ice-acetone bath. The color changed from red to white. After being stirred for five minutes, the mixture was poured into a beaker containing 300 ml. of water, which diluted the H_2SO_4 and precipitated the solid. The precipitate was filtered by suction and recrystallized from methyl alcohol to yield 0.3 g. (63%) of 7-(2-carboxyphenyl)benz a anthracene (V).

7-(2-Carboxyphenyl)benz[a]anthracene (V).

To 0.50 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone was added four ml. of 48% hydrobromic

acid, one ml. of water, and 15 ml. of glacial acetic acid. The mixture was heated to reflux for one hour, after which, upon cooling, a white crystalline material precipitated. The product was filtered and washed with water to remove any residual hydrobromic and acetic acids. The product was treated with charcoal and recrystallized twice from ethanol to yield the hydrated acid which melted at 133-135°. Drying at 110° in vacuo produced 0.43 g. (90%) of fine white crystals which melted at 199-200°.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.19; H, 4.63.

Found: C, 86.12; H, 4.54.

Neutralization Equivalent of 7-(2-Carboxyphenyl)benz[a]-anthracene (V).

A 0.200 g. sample of 7-(2-carboxyphenyl)benz[a]-anthracene was dissolved in 95% ethanol. This solution was titrated with a 0.101 N sodium hydroxide solution, using bromthymol blue as the indicator, and 5.8 ml. of base were required to reach the end point.

$$\text{Equivalent weight} = \frac{(0.200)\ (1000)}{(5.8)\ (0.101)}$$

$$\text{Equivalent weight} = 341$$

$$\text{Calculated Equivalent weight} = 348$$

Ethereal-alcoholic solution of diazomethane (38).

To a solution of five g. of potassium hydroxide in eight ml. of water was added 25 ml. of 95% ethanol. This solution was placed in a 100 ml. round bottom, three-necked flask equipped with a magnetic stirrer, dropping funnel, thermometer, and a water cooled condenser set downward for distillation. The condenser was connected to two 250 ml. receiving flasks in series, the second of which was cooled to 0°. The second flask contained 30 ml. of ethyl ether and the inlet tube dipped below the surface of the liquid. The apparatus was set up in the hood. The alcoholic-alkali solution was heated to 65° and a solution of 21.5 g. of N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) in about 130 ml. of ethyl ether was added slowly. After the addition was complete, 20 ml. of ether was added and the distillation was continued until the distillate became colorless. The yellow ethereal solutions of diazomethane in the receiving flasks were combined and kept in an ice bath until needed.

7-(2-Carbomethoxyphenyl)benz[a]anthracene (XXI).

To 25 ml. of an ethereal solution of diazomethane at 0° was added 0.5 g. (0.00144 mole) of 7-(2-carboxyphenyl)-benz[a]anthracene. The solution was allowed to come to room temperature, after which it was heated on a steam bath to drive off the excess diazomethane and distill off

the ether. A pale yellow crystalline substance precipitated which was recrystallized twice from methanol to yield 0.45 g. (86.5%) of very pale yellow crystals which melted at 138-139°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01.

Found: C, 85.72; H, 5.01.

Naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa).

A. From 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV).

1. To 0.5 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone was added five ml. of 85% phosphoric acid. Phosphorus pentoxide was added until the mixture had a pasty consistency. The mixture was heated in a metal bath at 190-200° for 4 1/2 hours, and at 250° for 1 1/4 hours. The mixture was allowed to cool, after which it was poured over 100 g. of ice contained in a 400 ml. beaker. After the ice had melted, the resulting red-brown precipitate was filtered, dissolved in acetic acid, and the solution filtered. The solution was concentrated and 95% ethanol was added to lower the solubility. The resulting deep red material weighed 0.29 g. (64.2%) and melted at 180-185°. Further recrystallization from benzene-ethanol gave red needles melting at 218-220°. The analytical sample was obtained after several recrystallizations

from benzene-ethanol and melted at 221-222°.

Anal. Calcd. for $C_{25}H_{14}O$: C, 90.89; H, 4.27.
Found: C, 90.42; H, 4.53.

2. To 0.5 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone in a Carius tube was added five ml. of 85% phosphoric acid and enough phosphorus pentoxide to make the mixture pasty. The tube was sealed and heated at 180° for 5 1/4 hours. Upon cooling, the resulting dark green mixture was poured into a 400 ml. beaker and upon the addition of 150 ml. of water, a brick red precipitate came out of solution. The precipitate was boiled in ammonium hydroxide and filtered. Recrystallization from benzene-ethanol yielded 0.25 g. (55.3%) of red material which melted at 188-191°. Further recrystallization from benzene-ethanol gave red needles melting at 218-220°.

3. Into a small polyethylene bottle, equipped with a magnetic stirrer, was placed 0.5 g. (0.00137 mole) of 2-(1-naphthylmethyl)-2'-carboxybenzophenone. The apparatus was placed in the hood and the bottle was filled about three-fourths full (200 ml.) with anhydrous hydrogen fluoride. The mixture was allowed to stand with stirring for one day. After all the HF had passed out of the bottle, the resulting black residue was dissolved in benzene. To this heated solution was added 95% ethanol, and upon

cooling, 0.40 g. (83.5%) of deep red material precipitated, which melted at 180-185° and 203-206°. Further recrystallization from benzene-ethanol gave red needles which melted at 221-222°.

B. From 7-(2-carboxyphenyl)benz[a]anthracene (V).

1. To 0.25 g. (0.00072 mole) of 7-(2-carboxyphenyl)-benz[a]anthracene in a 50 ml. flask was added a mixture of 20 ml. of 85% phosphoric acid and eight g. of phosphorus pentoxide. The mixture was heated at 200° for two hours. After cooling, it was poured into 100 ml. of cold water. The resulting deep red material was filtered by suction, boiled in ammonium hydroxide, and filtered again. Recrystallization from acetic acid produced 0.04 g. (16.7%) of red material which melted at 180-185°.

2. To 0.21 g. (0.0006 mole) of 7-(2-carboxyphenyl)-benz[a]anthracene in a Carius tube was added a mixture of 20 ml. of phosphoric acid and eight g. of phosphorus pentoxide. The tube was sealed and heated at 250° for 5 1/4 hours. The resulting green solution was poured into 100 ml. of water and 100 ml. more of water was used to rinse out the tube. The resulting deep red precipitate was filtered and recrystallized from acetic acid-water to give 0.09 g. (45.2%) of product which melted at 178-180°.

3. Into a small polyethylene bottle, equipped with a magnetic stirrer, was placed 0.25 g. (0.00072 mole) of 7-(2-carboxyphenyl)benz[a]anthracene. The apparatus was placed in the hood and about 200 ml. of anhydrous hydrogen fluoride was added. The mixture was allowed to stand, with stirring, for 36 hours. After all the HF had passed out of the bottle, the remaining black residue was dissolved in benzene. The solution was concentrated and 95% ethanol was added. Upon cooling, 0.22 g. (91%) of deep red material precipitated which melted at 185-188° and 210-212°.

Attempted Preparation of 11-H-Naphtho[1,2,3-fg]benz[a]-anthracene (XXVII).

A. To a 10% NaOH solution which was covered with a layer of 10 ml. of n-octyl alcohol, was added 0.3 g. (0.00091 mole) of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) and five g. of zinc dust. The mixture, which was contained in a 100 ml. round bottom flask, was heated to reflux for six hours. The octyl alcohol was distilled off and the remaining mixture was poured into concentrated hydrochloric acid. The resulting red precipitate was filtered by suction and washed in hot water. This crude material was dried in a vacuum desiccator overnight and was vacuum sublimed. Some decomposition occurred during the sublimation.

The sublimate was chromatographed on basic alumina to remove decomposition products and the eluate was concentrated to yield an appreciable amount of starting material melting at 218-222°. No other product was obtained.

B. In a 100 ml. round bottom flask, 2.5 g. of zinc dust was allowed to stand for a few minutes with an aqueous solution of 0.01 g. of cupric sulfate crystals. The solution was poured off, and to the activated metal was added 40 ml. of a 2 N NaOH solution, 10 ml. of toluene, and 0.1 g. (0.0003 mole) of naphtho[1,2,3-fg]benz[a]anthracene. The mixture was heated to gentle reflux for 13 hours, after which, it was allowed to cool and 10 ml. of benzene was added. The contents of the flask were poured into a separatory funnel and the organic layer was separated. Concentration of the organic layer and addition of some ethanol facilitated the precipitation of an appreciable amount of starting material which melted at 220-221°. No other product was obtained.

11-H-Naphtho[1,2,3-fg]benz[a]anthracene (XXVII) (48).

Into a 50 ml. three necked flask, equipped with a mechanical stirrer, reflux condenser, and dropping funnel, was placed a slurry of 0.029 g. (0.00075 mole) of lithium aluminum hydride in two ml. of anhydrous ethyl ether.

Through the dropping funnel, a solution of 0.100 g. (0.00075 mole) of aluminum chloride in two ml. of anhydrous ether was added rapidly. Five minutes later, a solution of 0.2 g. (0.0006 mole) of naphtho[1,2,3-fg]benz[a]anthracene-11-one and 0.081 g. (0.0006 mole) of aluminum chloride in 25 ml. of benzene was introduced at a rate such as to produce gentle reflux. Twenty minutes after the last addition, three ml. of water were added slowly, followed by three ml. of a 6 N H_2SO_4 solution. The solution was transferred to a separatory funnel and after removing the organic layer, the aqueous layer was extracted once with benzene. The organic solutions were combined and taken to dryness by evaporation of the solvent with dry nitrogen. The residue was recrystallized twice to yield 0.1105 g. (58%) of fine orange needles which melted at 157-158°.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.10.
Found: C, 94.62; H, 5.31.

TNF of Naphtho[1,2,3-fg]benz[a]anthracene-11-one (XXVIII).

In two separate 25 ml. flasks 0.05 g. (0.0002 mole) of naphtho[1,2,3-fg]benz[a]anthracene-11-one and 0.048 g. (0.0002 mole) of 2,4,7-trinitrofluorenone were dissolved in about 15 ml. of benzene and ethanol, respectively. When the solutions were boiling, they were simultaneously

poured into a 50 ml. beaker. Upon cooling, deep red crystals precipitated which melted at 195-197°. Recrystallization from benzene-ethanol yielded fine red needles which melted at 201.5-202°.

Anal.

Calcd. for $C_{38}H_{19}N_3O_8$: C, 70.69; H, 2.97; N, 6.51.

Found: C, 70.73; H, 2.67; N, 6.35.

SUMMARY

SUMMARY

The preparation of 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) was accomplished by the reaction of phthalic anhydride and the Grignard reagent of 2-(1-naphthylmethyl)bromobenzene. This keto-acid (IV) was cyclized to 7-(2-carboxyphenyl)benz[a]anthracene (V) by the use of a mixture of hydrobromic and acetic acids. Methyl esters of both 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) and 7-(2-carboxyphenyl)benz[a]anthracene (V) were prepared. Neutralization equivalent titrations were run on both the keto acid (IV) and the acid (V), and the resulting experimentally determined equivalent weights agreed with the calculated values for the two compounds.

Naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) was prepared by the cyclization of the keto-acid (IV) with anhydrous hydrogen fluoride or polyphosphoric acid. The cyclization of the acid (V) to naphtho[1,2,3-fg]benz[a]-anthracene-11-one (VIa) was also affected by the use of anhydrous hydrogen fluoride or 100% phosphoric acid in a Carius tube.

Although the structure of naphtho[1,2,3-fg]benz[a]-anthracene-11-one (VIa) can not be proven by synthesis, because of the availability of two possible cyclization positions, the structure (VIa) is strongly supported by infrared

spectral studies and by electron density and localization energy calculations.

A reduction derivative and a 2,4,7-trinitrofluorenone molecular complex of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) were prepared.

The structures of the six new compounds and the TNF molecular complex were substantiated by satisfactory elemental analyses. The infrared and ultraviolet absorption spectra of the six new compounds were recorded.

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LITERATURE CITED

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ABSTRACT

The preparation of 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) was accomplished by the reaction of phthalic anhydride and the Grignard reagent of 2-(1-naphthylmethyl)bromobenzene. This keto-acid (IV) was cyclized to 7-(2-carboxyphenyl)benz[a]anthracene (V) by the use of a mixture of hydrobromic and acetic acids. Methyl esters of both 2-(1-naphthylmethyl)-2'-carboxybenzophenone (IV) and 7-(2-carboxyphenyl)benz[a]anthracene (V) were prepared. Neutralization equivalent titrations were run on both the keto-acid (IV) and the acid (V), and the resulting experimentally determined equivalent weights agreed with the calculated values for the two compounds.

Naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) was prepared by the cyclization of the keto-acid (IV) with anhydrous hydrogen fluoride or polyphosphoric acid. The cyclization of the acid (V) to naphtho[1,2,3-fg]benz[a]-anthracene-11-one (VIa) was also affected by the use of anhydrous hydrogen fluoride or 100% phosphoric acid in a Carius tube.

Although the structure of naphtho[1,2,3-fg]benz[a]-anthracene-11-one (VIa) can not be proven by synthesis, because of the availability of two possible cyclization positions, the structure (VIa) is strongly supported by infrared

spectral studies and by electron density and localization energy calculations.

A reduction derivative and a 2,4,7-trinitrofluorenone molecular complex of naphtho[1,2,3-fg]benz[a]anthracene-11-one (VIa) were prepared.

The structures of the six new compounds and the TNF molecular complex were substantiated by satisfactory elemental analyses. The infrared and ultraviolet absorption spectra of the six new compounds were recorded.