SYNTHESIS OF SOME COMPOUNDS OF POSSIBLE CARCINOGENIC ACTIVITY

by

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TO MY PARENTS

THIS THESIS IS

AFFECTIONATELY DEDICATED.

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INTRODUCTION

INTRODUCTION

The campaign against cancer has hardly any counterpart in the history of all the natural sciences, and there is hardly a branch of the natural sciences which has not been mobilized in this veritable crusade. If we inquire about the role of chemistry, and more specifically that of organic chemistry in this movement, we should probably start with the year 1775 when Percival Plott pointed out the possible connection between cancer, occupational disease of chimney sweepers, and soot. However, it was almost 150 years later when Passey (1) could prove this hypothesis by applying the ethereal extract of soot to the skin of a mouse and producing a malignant tumor on its back.

Rather than attempting to depict historically all the contributions of organic chemists, it seems to be more important to inquire what is expected in our times of the organic chemist, and what is the nature of his contribution which might ultimately help to solve the problem of cancer.

Obviously, there is no one simple, straightforward answer to this question, yet an attempt can be made to generalize, and then a seemingly simple reply can be formulated. What is necessary is a clearer and deeper insight into the realm of organic compounds and reactions, and, specifically, a better knowledge of some special fields of organic chemistry, namely, the field of polynuclear hydrocarbons.

Since the birth of organic chemistry an increasing number of scientists have tried and are still trying to fulfill the first part of this requirement. However, the real stimulus was felt in the field of polycyclic hydrocarbons and their derivatives, to a great extent due to the efforts and achievements of James Wilfred Cook and Erich Julius Clar. Although the emphasis seemed to be, especially during the period between the two World Wars, on the aromatic compounds, it was soon realized that saturated polynuclear hydrocarbons and especially their derivatives known as steroids, may play an equally important role in the chemistry of cancer.

Whatever direction the future development of this problem may take, the importance of the knowledge in the field of polynuclear hydrocarbons could not have been emphasized more strongly. It is inconceivable that a mode of biological or physiological action of a certain compound could be successfully found without knowing or possessing some means of describing, predicting, and explaining its reactions and behavior. A vast amount of data was accumulated, mainly in the last twenty years, but still many and many more reactions and compounds will have to be investigated before the state of knowledge will be brought to at least the present level of aliphatic compounds and their derivatives. New methods and techniques were and still have to be developed; that there is good hope for the future is substantiated by the truly great achievements of the past and present generations.

It is the purpose of this thesis to investigate further some of the reactions leading to the formation of polynuclear hydrocarbons, to prepare new compounds, describe their properties and preparation, and thus make a contribution to this important field of organic chemistry.

HISTORICAL

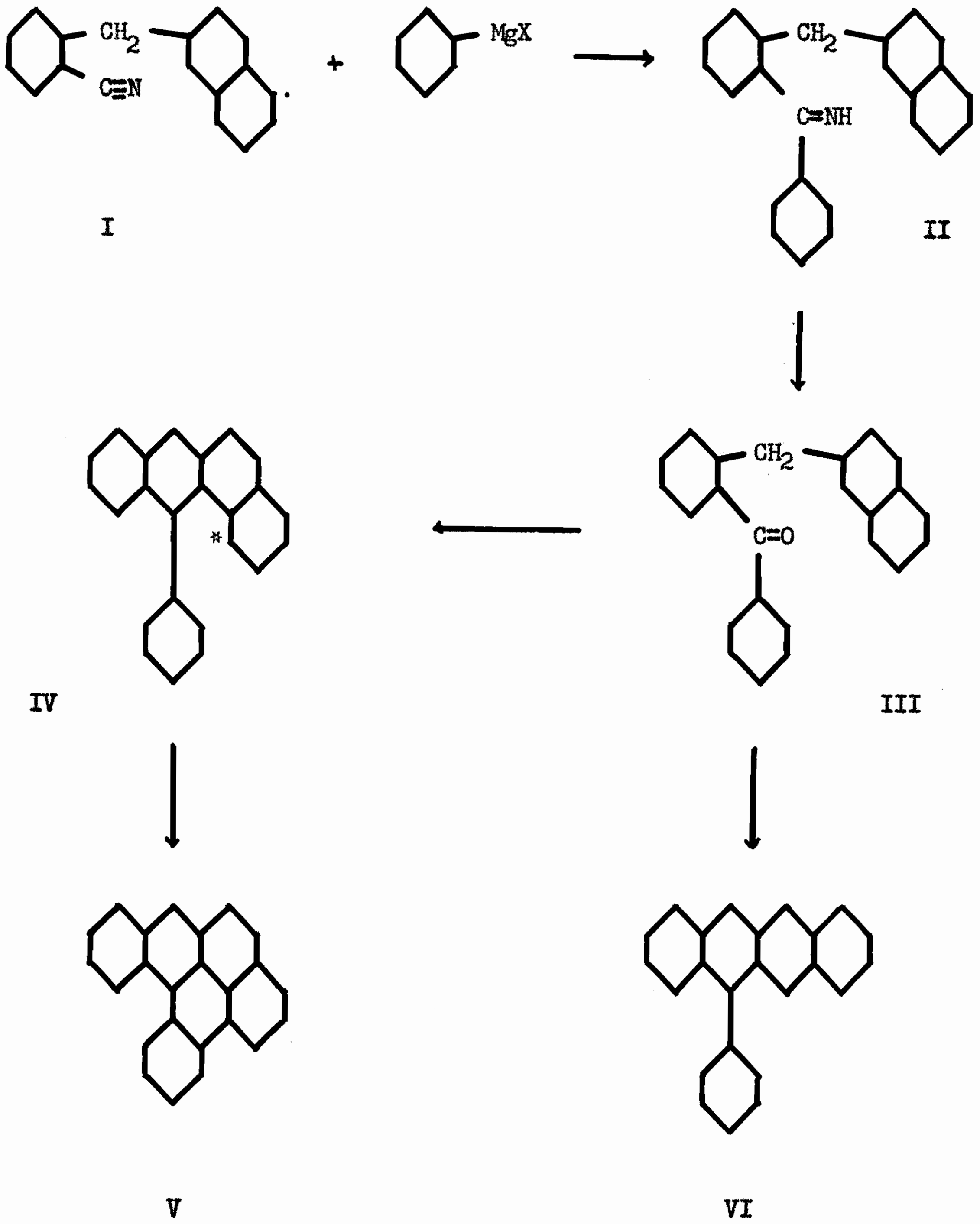
HISTORICAL

One of the most interesting and at the same time most extensive groups of compounds with known or suspected carcinogenic activity is the group of the derivatives of 1,2-benzanthracene. There seems to be nothing mysterious about the parent compound itself. It is a crystalline, colorless, only moderately reactive compound with practically no physiological activity (2), and yet some of its derivatives belong to the most potent carcinogens known at present. The chemistry of benzanthracene, although quite thoroughly investigated, cannot account for the peculiarities in the behavior of its derivatives, the sudden changes in their physiological activity, especially as far as cancer is concerned. Between the years 1930 and 1940 more than fifty alkylbenzanthracenes were prepared and tested, and an interesting observation was derived. The 10-, 5-, and 9-positions seemed to be most favorable for the appearance of carcinogenic properties (3, 4). Although these findings were published about twenty years ago and a considerable number of alkyl derivatives, especially in these points, had been synthesized, it is surprising indeed that only two aryl-substituted benzanthracenes appeared in literature before the work done at the Virginia Polytechnic Institute.

The synthesis of the 9- and 10- phenyl- and methylphenyl-1,2-benzanthracenes was of interest not only regarding their possible carcinogenic activity, but also as an extension of a special type of cyclodehydration of certain ketones which was introduced by Bradsher in 1940 (5).

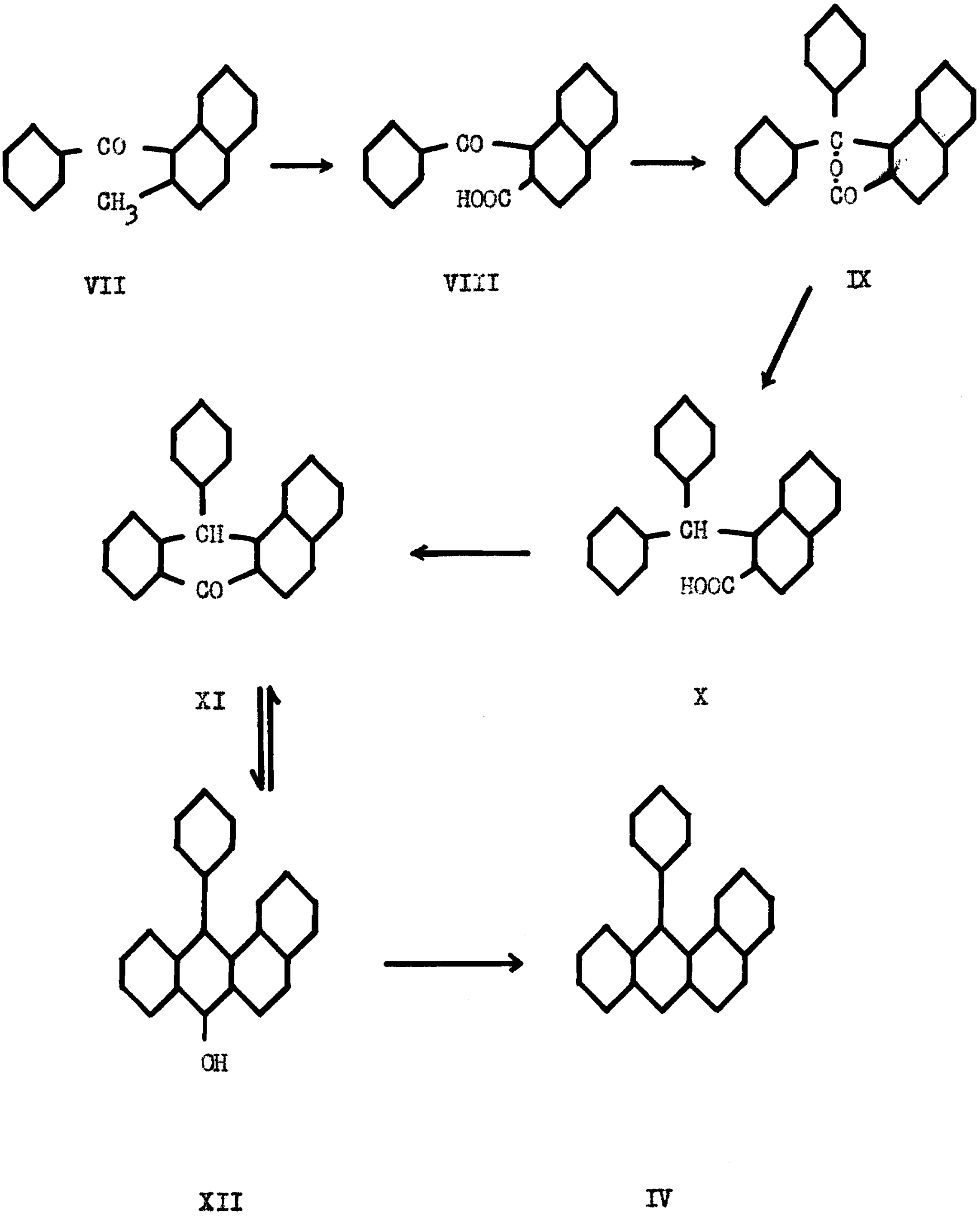
The hydrocarbons prepared by Bradsher were 9- and 10-methyl-1,2-benzanthracene, and the question whether an aryl group might be used in place of the alkyl group was of considerable interest. A preparation of 10-phenyl, 10-mono- and dimethylphenyl-1,2-benzanthracenes was already adequately described by Vingiello, Borkovec and Shulman (6, 7). The examination of the atomic models and the path of reaction (Chart I) indicated, however, possible difficulties in the preparation of the isomeric compounds in the 9-substituted series. The first two steps leading to the ketone (III) are analogous to reactions which were known to proceed satisfactorily. The cyclodehydration of the ketone, however, may theoretically take two different pathways : if the closure occurs at the α-position of the naphthyl ring, a benzanthracene (IV) will result; if the second β-position on the naphthyl ring will take part in the reaction, a tetracene derivative (VI) might be formed. Although the α-position is known to be relatively much more reactive than the β-, a scale model of the molecule IV reveals a certain strain and hindrance due to the closeness of the position designated by an asterisk and the phenyl ring. From this point of view the structure VI could be the preferred one, being relatively strainless. A further complication may arise due to the possibility of oxidation or dehydrogenation of the hydrocarbon IV which would then lead to dibenzpyrene, V. Such a reaction is known to occur by the action of aluminum chloride on IV at the temperature of boiling benzene, and the byproducts resulting from it were recently identified (8, 9). The previously

CHART I



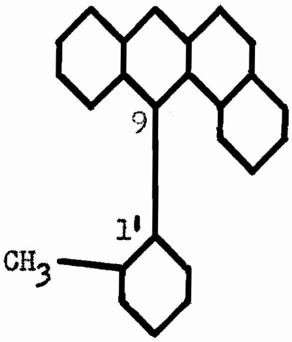
All rings are fully aromatic unless otherwise indicated.

CHART II

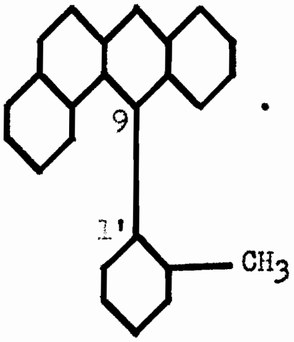


reported reaction (8) leading to IV (Chart II) starts with the easily accessible ketone VII which is oxidized by selenium dioxide in water at 220° to the acid VIII. This is transformed into its chloride which reacts in the pseudoform with benzene and aluminum chloride and forms the lactone IX which can be reduced by alcoholic potassium hydroxide and zinc dust to the acid X. The cyclization of X can be effected by sulfuric acid, and the resulting tautomeric compound XI, XII yields upon reduction by potassium hydroxide and zinc dust the 9-phenyl-1,2-benzanthracene (IV). Without mentioning the inherent difficulties due to the complicated sequence of reactions, it is obvious that this method can be used safely only for the preparation of the phenyl compound and not the methyl or dimethylphenyl analogues.

The methyl- and dimethylphenylbenzanthracenes are of considerable interest still from another point of view. The molecular models indicate and the evidence presented in this work proves quite conclusively that the phenyl ring in the 10- and in the 9- position is not coplanar with the benzanthracene part of the molecule. If a methylphenyl derivative (say, 9-(2'-methylphenyl)-1,2-benzanthracene(XIII)) is examined



XIII



XIV

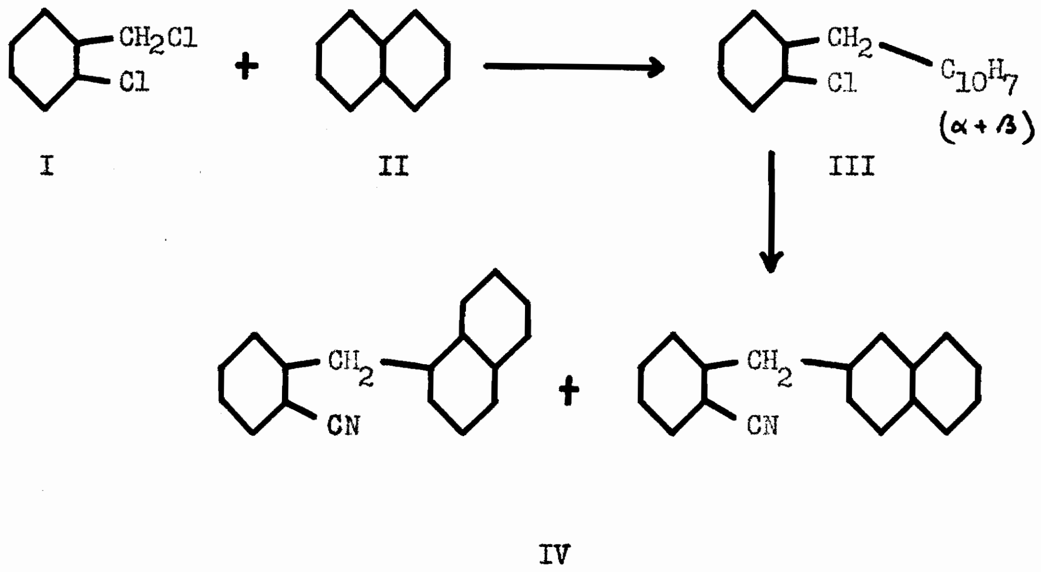
either as a scale model or just as indicated above, the possibility of the existence of the two enantimorphs XIII and XIV becomes obvious, assuming restricted rotation around the 9-1' pivot bond. Similar cases concerning the biphenyl derivatives were known (9 and references there), but only a few of them seem to be as illustrative as the example above. Although it is not within the scope of the present work to attempt the separation of these antipodes, the fact that they will be made relatively easily obtainable might be of importance.

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

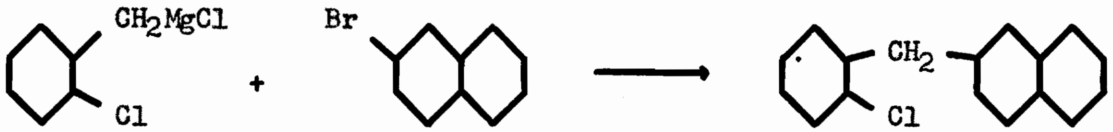
A. Preparation of Starting Materials

The new method for the preparation of the 2-(1-naphthylmethyl)-benzonitrile which was prepared by Borkovec (11), yielded as a by-product the 2-naphthylmethyl isomer which was quite valuable due to the high price of 2-bromonaphthalene. This reaction will be briefly described. A Friedel-Crafts type reaction is carried out between chloride I and naphthalene (II). A mixture of the two resulting isomeric chlorobenzylnaphthalenes III is transformed by means of a Rosenmund-von Braun reaction to the corresponding nitriles IV.



The yields in this reaction were between 35 - 70% of the mixture of the two isomers depending on the conditions used. Although the ratio of the two isomers also varied with the catalyst and temperature, the relative percentage of the β-isomer never exceeded 30%. There was a considerable difficulty with the separation of the two isomeric nitriles,and even though fractional crystallization from ethanol yielded the β-isomer in a reasonable quantity, it was not possible to recover it quantitatively, and the solution invariably turned light brown during the repeated evaporation of the solvent which was probably due to the partial polymerization of the nitriles. Chapman (12) suggested that strong light would enhance this process, but even when the solutions were kept in darkness the coloration appeared in sufficient intensity to prevent the crystallization and a total recovery of both isomers. It was desirable to develop a procedure which would yield a higher relative percentage of the β-isomer so that the former could be crystallized without removing the α-isomer first.

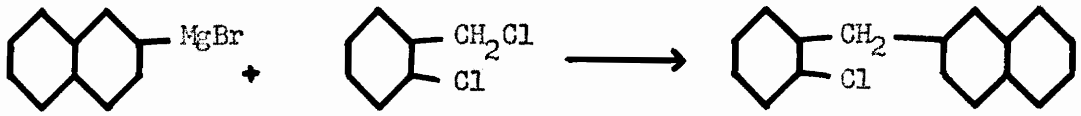
A satisfactory solution to this problem (11, 12)was found in using nitrobenzene as a solvent, aluminum chloride as a catalyst, and carrying out the Friedel-Crafts reaction under reduced pressure. The yields then amounted to 60-70%, the ratio of the two isomeric chlorocompounds being about 1:1. The chlorine was then replaced by a cyano group, and the resulting mixture of nitriles was carefully distilled in vacuo. Although it was not possible to separate the two nitriles quantitatively by fractional distillation (11),it was found that when the distillate was divided into three fractions (the first being the one collected at the beginning of the distillation, the third at the end ; the boiling point did not change appreciably during the entire process), the ratio of the α- to β-isomer was approximately 80:20 in the first, 50:50 in the second, and 20:80 in the third part. The β-isomer could then be crystallized quite easily from the third fraction dissolved in a mixture of ether-petroleum ether (3:7). Most of the nitrile used in this work was prepared by this method. The difficulty in the preparation of the two nitriles by the method used by Bradsher (5) was already described (11,12). Although the above method gave acceptable and quite economical results, other attempts were made in order to simplify the preparation of the β-isomer. A very attractive approach seemed to be the Grignard type reaction between the 2-chlorobenzylmagnesium chloride (V) and 2-bromonaphthalene (VI).



V VI VII

This reaction was attempted by adding the ethereal solution of the bromocompound to the Grignard reagent and by adding the Grignard reagent to the bromide; however, no reaction occurred in either case.

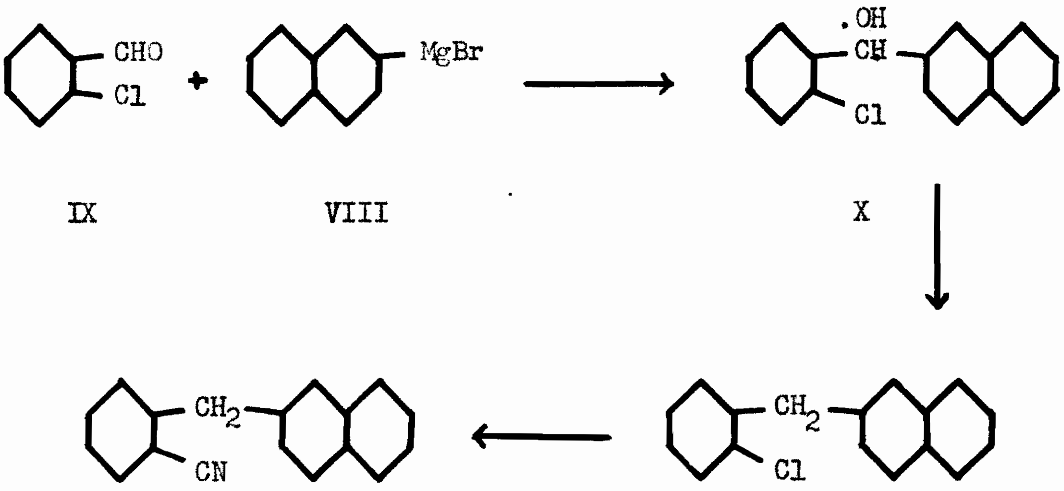
The second obvious possibility seemed to be the reaction between the 2-naphthylmagnesium bromide (VIII) and 2-chlorobenzylchloride (I):



VIII I VII

This reaction was conducted in the usual way and no desired products were obtained. However, 2,2-binaphthyl was isolated from the resulting mixture in good yield (55%).

The original procedure described by Bradsher (5) was also used for the preparation of some of the nitrile.



IX VIII X

XI VII

Although the reaction between the aldehyde (IX) and the Grignard reagent (VIII) seemed to proceed quite smoothly, considerable difficulties were encountered when an attempt was made to obtain the carbinol (X) in a pure state. Distillation of the reaction mixture yielded only about 50-60% of the expected carbinol, contaminated with a fraction which was collected immediately afterwards. The carbinol was then dissolved in acetone, and the impurity which crystallized as small yellowish plates was filtered. The filtrate which presumably contained only a small amount of the contaminant was distilled under reduced pressure, and again during the distillation quite a large fraction, corresponding to about 25% of the weight of the original material, was collected immediately after the carbinol fraction.

It seemed to be beyond doubt that the unknown compound resulted directly from the carbinol, but no plausible explanation was found. After repeated crystallization, the originally yellowish crystals were obtained as colorless plates, with strong blue fluorescence, slightly soluble in concentrated sulfuric acid, with a brown color. The unknown compound gave a bright orange precipitate with 2,4,7-trinitrofluorenone, but no color with picric acid. The Beilstein test was negative, however, no increase in pressure indicating elimination of hydrochloric acid was observed during the distillation. Much better results, as far as the yield in the overall reaction leading to the β-nitrile is concerned, can be obtained by reducing the crude carbinol and neglecting its purification.

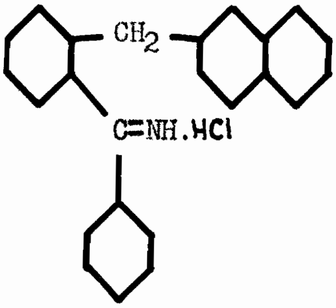
The reduction of the carbinol X to the chlorocompound VII by red phosphorus and iodine suffers from the same difficulties as the analogous reaction in the α-series previously described (11). The transformation of the compound VII to the nitrile XI by a Rosenmund-von Braun reaction is quite smooth and results in good yields.

Due to the high price of the 2-bromonaphthalene and the above described difficulties, only a small amount of the nitrile was prepared by this reaction.

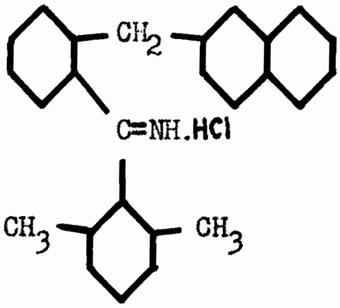
B. Preparation of 9-Aryl-1,2-benzanthracenes

The method used to prepare 9-phenyl-, the three isomeric 9-methylphenyl- and six isomeric 9-dimethylphenyl-1,2-benzanthracenes was essentially that used for the preparation of the 10-isomers (11), only 2-naphthylmethylbenzonitrile was used in place of the 1-isomer. The properties of the ketimines are quite similar to those in the α- series, i.e., the free ketimines are viscous oils or colorless crystalline substances of quite a low melting point, well soluble in common organic solvents, and they react with mineral acids to form the ketimine salts (hydrochlorides were mostly used in this and previous (11) work).

The hydrochlorides are colorless or slightly colored crystalline substances which melt with decomposition around 200°, are well soluble in ethanol, little or not at all in acetone, benzene, ether and ligroin; they can be transformed into the free imines by boiling them with dilute alkali, and hydrolyzed to the ketones by dilute mineral acids. The ease of hydrolysis, however, varies greatly with the structure of the compound, for example, the unsubstituted ketimine salt I,



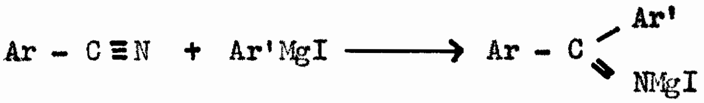
I



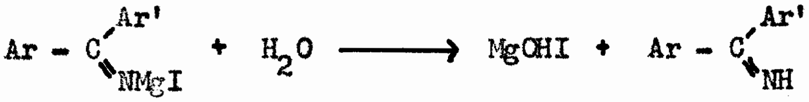
II

can be partially hydrolyzed by boiling water; the 2,6-dimethyl compound (II) was successfully hydrolyzed only by heating it with 40% sulfuric acid in a sealed Carius tube to 180° for eight hours. Steric hindrance was suggested (11) to account for these differences. The susceptibility to a partial hydrolysis seems to be specially developed in some of the unsymmetrical dimethyl compounds. Consequently, the preparation of an analytical sample was made so difficult that although all the ten ketimine hydrochlorides were isolated as such, only the phenyl- (I), three isomeric monomethylphenyl- and the 2,6-dimethylphenyl- compound (II) were successfully analyzed.

The hydroiodides seem to be in general less soluble, and their formation may sometimes lead to appreciable losses during the preparation. For example, in the preparation of the 2,6-dimethyl- compound (II), 2,6-dimethyliodobenzene was used as a starting material. During the decomposition of the mixture resulting from the Grignard reagent and the nitrile, the ketimine hydroiodide precipitated together with the magnesium salts and had to be recovered by quite a lengthy procedure. It was suggested already by Shulman (13) that such a precipitation might account for the occasional low yields in the preparation of the ketones with structure similar to those discussed here. This, however, seemed to apply only in the case where the starting material was an iodide (bromides were used in most cases in the present work). The following mechanism might possibly explain the differences :

1) 

$$\mathrm{Ar-C{\equiv}N + Ar'MgI \longrightarrow Ar-C(-Ar'){=}NMgI}$$

2) 

$$\mathrm{Ar-C(-Ar'){=}NMgI + H_2O \longrightarrow MgOHI + Ar-C(-Ar'){=}NH}$$

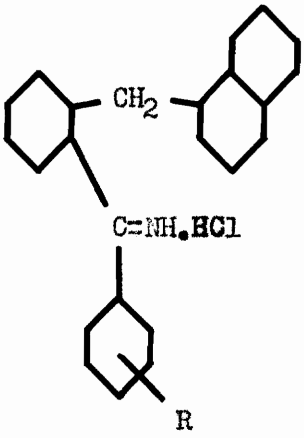
3) $\mathrm{MgOHI + H_2O \rightleftharpoons HI + Mg(OH)_2}$

4) 

$$\mathrm{Ar-C(-Ar'){=}NH + HI \longrightarrow Ar-C(-Ar'){=}NH . HI}$$

The equilibrium in step 3) which would be expected to favor the left side of the equation is probably shifted to the right due to the high affinity of the free imine (step 4) for the HI.

Four ketimine hydrochlorides of the type III (R = H, 2-CH_3, 3-CH_3, 4-CH_3)



III

were also prepared in order to complete previous work (6, 11). The usual method for preparation of the corresponding ketones consists of hydrolyzing the ketimine salt with a dilute mineral acid, and proceeds very smoothly with all the compounds with the exception of the 2,6-dimethyl compound (II). In previous work (11), before the sealed tube technique was developed, three compounds were isolated which had similar characteristics to those of the expected ketone, however, the C and H analyses were consistently high in both carbon and hydrogen. In the course of this work the previous experiments were repeated, and it was found that the compounds designated as Form I and Form III (the experiment yielding Form II could not be repeated) correspond to the free 2-(1-naphthylmethyl)-2',6'-dimethyl, diphenylketimine, Form I being a very pure sample of this compound, Form III containing some unknown impurity.The following table will be illustrative:

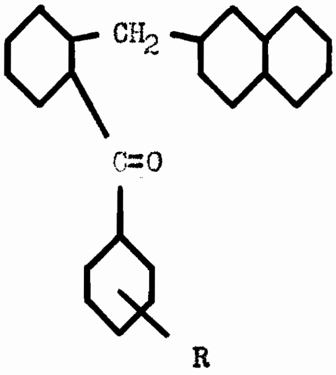
Table I

	Ketone % Calc.	Ketimine % Calc.	Form I % Found	Form III % Found	Ketone % Found
C	89.10	89.36	89.37	89.81	89.47
H	6.33	6.63	6.70	6.43	6.39
M.p. °C.			109.5-110	122-122.5	124.5-125.0

A satisfactory confirmation of the identity of the ketimine was achieved by dissolving the Form I in ether and mixing it with a few drops of ether saturated with hydrochloric acid. Ketimine hydrochloride which was identified previously precipitated immediately.

The presence of the free imine in place of the ketone can be easily explained. The attempts for hydrolysis of the ketimine salt were carried out in the presence of an organic solvent (benzene, toluene) in which it is very slightly soluble. After long reflux, the organic layer was separated and washed with water, 10% solution of sodium hydroxide, and then again with water to remove the traces of the acid. The alkali obviously had decomposed the small amount of dissolved ketimine salt, and the well soluble free imine was then isolated.

Ten other ketones of the type IV

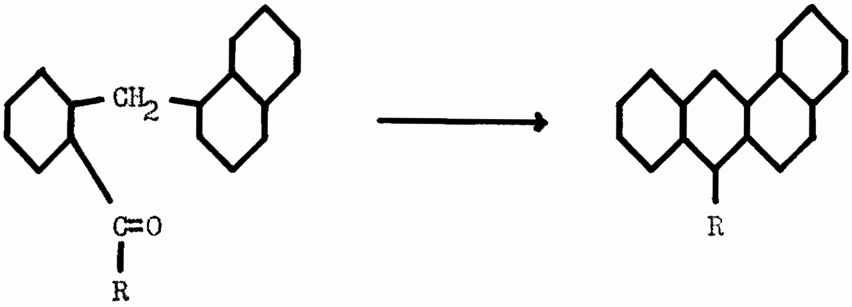


IV

(R = H; 2-CH_3; 3-CH_3; 4-CH_3; 2,4-CH_3; 2,5-CH_3; 2,6-CH_3; 3,4-CH_3; 3,5-CH_3)
2,3-CH_3
were prepared by the hydrolysis of the corresponding ketimines.

They form colorless crystals or very viscous oils of generally lower melting or boiling points than those in the 1-naphthyl series (11). During the distillation they acquire a strong yellowish-green fluorescence which disappears after a few days. This is probably due to a very small amount of impurity which can be removed by passing the ketone through activated alumina.

The cyclodehydration of the 2-(1-naphthylmethyl)acetophenone (V, R = CH_3) to the corresponding hydrocarbon VI (R = CH_3) was effected by Bradsher (5) by heating it under reflux with a mixture of acetic and hydrobromic acid.



V VI

The same procedure succeeded (6) for the ketone V, where R was phenyl or p-methylphenyl, but failed to yield satisfactory results with ketone V where R was o- or m-methylphenyl. The same difficulties were encountered in cases where R was a dimethylphenyl radical (11). The change in the relative concentration of HBr and the use of formic instead of acetic acid led to no appreciable differences in the reaction products. As discussed earlier (11), these and other considerations culminated in the development of a procedure where a higher temperature and minimum oxidation made the preparation of the 10-dimethylphenyl-1,2-benzanthracenes possible.

It may be briefly reviewed that this procedure consisted of heating a mixture of the ketone or ketimine with acetic and hydrobromic acid in a sealed glass tube (Carius tube) for several hours in a special furnace (Carius furnace). The temperature was automatically maintained at about 180° and the time was varied according to the structure of the ketone. It can be perhaps pointed out that, in general, the ketones having a methyl group in at least one of the ortho positions require longer heating periods than those with both methyl groups in the meta or meta and para positions. Prolonged heating at temperatures over 200° leads invariably to extensive charring of the material.

This method was now successfully applied to the cyclodehydration of the ketones V (R = o and m-methylphenyl), and the corresponding hydrocarbons were isolated in high yields.

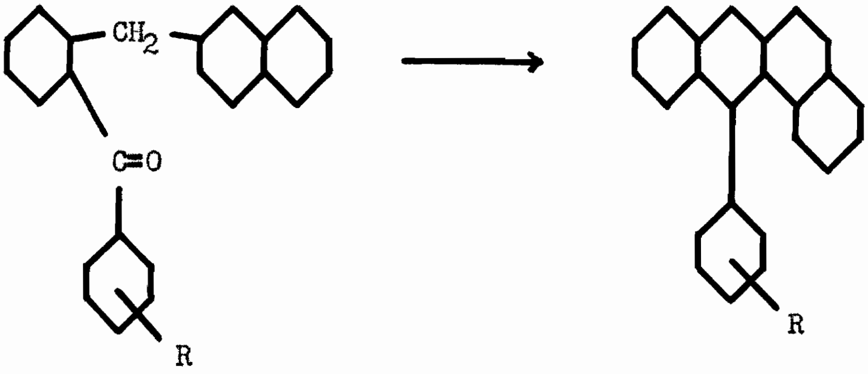
The cyclization in the 2-naphthyl series (ketones of the type IV) followed a very similar pattern, although as might be expected (see p.9), certain complications came up. The yields of the hydrocarbons were generally somewhat lower than those in the 1-naphthyl series (ketones of the type V), and there was always present a small amount (1-5%) of a deeply yellow material which could be separated only after many crystallizations, repeated chromatography,or by a method described below. This impurity possessed a very strong yellow fluorescence which disappeared after longer irradiation by short wave ultraviolet light, a perfect example of a high reactivity which probably prevented its recovery and crystallization. The solutions of this yellow material, and this was observed in every one of the concentrates resulting from the cyclization of all the ketones of type IV, lost their strong yellow fluorescence and turned deep orange after prolonged boiling or standing even when kept in relative darkness. The orange or brown compound which seemed to be non-homogeneous was then very strongly adsorbed by alumina, a good indication of its quinonoid nature.

The simplest way of separating these by-products from the benzanthracene seems to be Cook's method (14), which consists of heating the mixture in benzene solution with a small amount of maleic anhydride for a few hours, decomposing and removing the adduct with sodium hydroxide solution, and recovering the pure hydrocarbon from the organic layer. The preferential oxidation method, which is sometimes used for the same purpose cannot be used here because the 9-arylbenzanthracenes themselves are quite sensitive to oxidation. As will be discussed later, the molecular compound formation method is inapplicable, due to the structural features of the compounds involved.

Several other by-products were frequently found among the products of a cyclization reaction. The yellow fluorescing material seemed to be decidedly of hydrocarbon nature, being quite loosely bound to alumina in an adsorption column and comparatively easily eluted by petroleum ether.

There were, however, usually several other, possibly non-hydrocarbon fractions which were quite strongly adsorbed by alumina and could be eluted only by very powerful eluents as ether, acetone, etc. Their relative and absolute amounts varied with the ketone used and conditions during the reaction. The ketones of the type IV where R was H or CH_3, yielded very little of these by-products, a narrow red stripe being visible occasionally among others on top of the chromatography column. This, however, became exceptionally prominent in the chromatography of the cyclized ketones IV where R were two methyl groups. In some instances the amount of this deeply red material amounted to 10% of the yield, and could be isolated in crystalline form. The almost black, small needles had a very high melting point and their solution in benzene was decolorized by addition of maleic anhydride. Similar compounds were observed among the products of the ketones in the 1-naphthyl series, but no further investigation along this line was conducted.

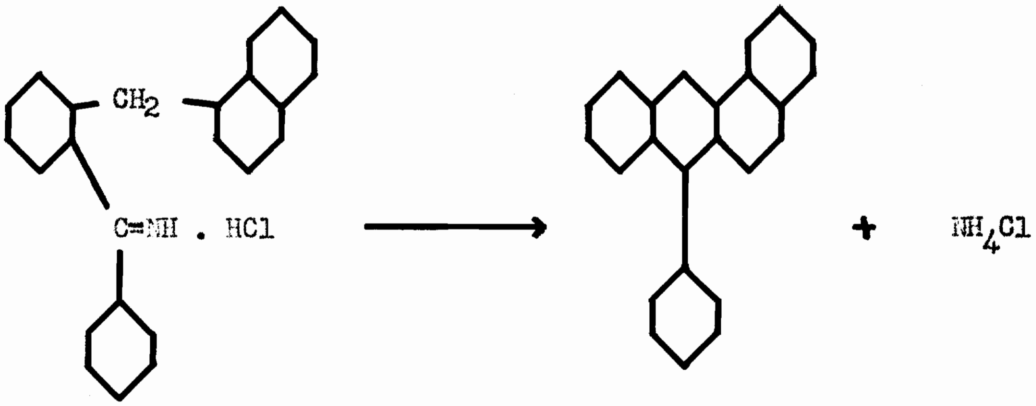
The two hydrocarbons of the type VII (R = H and p-CH_3)



IV VII

were prepared by the cyclodehydration of the corresponding ketones IV (R = H and p-CH_3) by heating them with the acid mixture under reflux for a short time. However, the bomb technique had to be used for the preparation of the other hydrocarbons of the type VII (R= 2'-CH_3; 3'-CH_3; 2',3'-CH_3; 2',4'-CH_3; 2',5'-CH_3; 3',4'-CH_3; 3',5'-CH_3), the starting materials being again the corresponding ketones IV.

In the previous work (11), several hydrocarbons were prepared directly from the ketimine salts by heating them with the usual acid mixture in a Carius tube. Two pathways were proposed for such reactions: 1) a hydrolysis of the ketimine and cyclization of the resulting ketone, 2) a direct cyclization of the ketimine hydrochloride with elimination of NH_4Cl. It was not then possible to decide which of these two possibilities was the preferred one, and several attempts along this line were undertaken later. It was found that the ketimine salt (VIII) can be quite easily cyclized just by heating it in a sealed tube in N_2 atmosphere for nine hours to 300°.



VIII

VII

The same experiment was then repeated with the ketone in place of the ketimine, but no reaction was noted. It cannot be, nevertheless, concluded that the acid cyclization of a ketimine is always a direct process (pathway 1). If moist ketimine is used in the thermal cyclization, a corresponding ketone, together with crystalline NH_4Cl, is recovered. Because the hydrolysis of most of the ketimines is a relatively easy process which yields the ketones under much milder conditions than the described thermal cyclization, it can be assumed that the acid catalyzed cyclization of the ketimines yields, in all probability, the corresponding ketones as intermediates (pathway 1). It was also attempted to cyclize thermally the sterically hindered ketimines (i.e., the 2',6'-dimethylphenyl compound). However, only some unidentified red oily compound was isolated from the reaction mixture. The lack of fluorescence clearly indicated the absence of the expected hydrocarbon.

The chromatographic separation of the reaction products deserves some mention here. Although there are several excellent reviews of this subject (53) which put the basic phenomenon on a firm physical basis, there is still a great deal of guesswork based on the experience and feelings of the experimentator necessary for obtaining optimal results. In general, the role of the polarity of the solvent is, at least qualitatively, well understood, but the fine details, mainly as far as mixtures of various solvents and their combination with different kinds of adsorbents is concerned, depend solely on personal imagination and experience. Fisher's Alumina (for chromatographic analysis), 80-200 mesh, was used exclusively throughout this work. The petroleum ether used was always carefully distilled and the fraction boiling between 50-90° collected. All other solvents were pure and anhydrous. A glass column, 60 cm. long, 1 cm. in diamater, was filled with petroleum ether and the alumina was slowly added (wet packing). The air bubbles were expelled by tapping the column gently with a rubber hammer. The excess solvent was then drained and the respective mixture dissolved in a minimum of benzene was carefully poured on top of the adsorbent. The usually deeply colored zone which was formed in the upper part of the column was then eluted by petroleum ether or mixtures of various other solvents. The progress of the operation was then usually traced by irradiating the column with ultraviolet light. Since many polycyclic aromatic hydrocarbons are sensitive to photoxidation, the irradiation time should always be minimized. It is recommended in general to perform the whole operation in relative darkness.

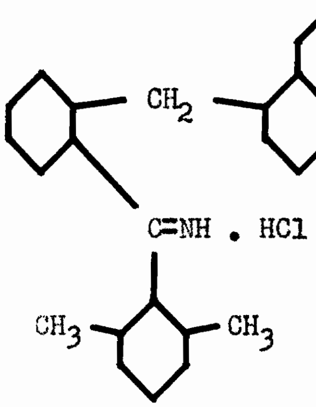
The individual fractions were then collected, the solvent distilled, and the remaining material crystallized. It must be emphasized that the separation, often amazingly efficient, is almost never quantitative. Usually there is a considerable amount of a "middle-fraction" consisting of variable amounts of the fraction which is being eluted and the one which immediately follows. Repeated chromatography must often be performed. The rate of elution is definitely connected with the efficiency of separation. The optimal resolution would be probably achieved by the smallest elution rate, however such a process would be extremely time consuming. A convenient compromise must then be made. Throughout this work the rate was kept mostly at about 30-50 drops per minute; even so the time necessary to complete one separation was about two to four days.

The 9-aryl-1,2-benzanthracenes are colorless solids which sometimes crystallize with considerable difficulty. So, for example, the 3,4-dimethyl compound was isolated as a colorless oil and resisted all attempts for cyclization for several months. Then, for no apparent reason, crystals formed and even slightly impure solutions of the same compound which were kept separately crystallized without seeding or any outside help. However, two members of this series (VII, R = $2',4'-CH_3$ and $2',5'-CH_3$) could not be crystallized as yet. All of these compounds possess a very strong blue fluorescence in both solid and dissolved states. Their ultraviolet adsorption spectra will be discussed later.

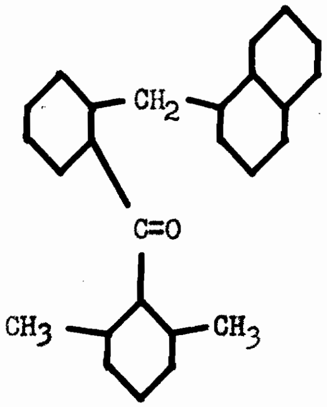
A very interesting property of some of these hydrocarbons is their ability to exist in polymorphic crystalline forms. At the same time, it complicates their isolation quite considerably, especially because the two forms only seldom can be obtained separately and at will, more often they both crystallize from the same solution, forming clusters of crystals with a melting point somewhere between those of the two pure modifications. One of the forms can and frequently has been easily mistaken for an impurity, which of course cannot be removed. The higher melting form seems to have a tendency to precipitate out of quite concentrated, warm solutions, whereas the lower melting form usually requires longer time and milder conditions for its formation. Some of the polymorphic forms were discovered under very peculiar conditions and were cause of grave concern to the author. For example, an alcoholic solution of one of the hydrocarbons was mixed with picric acid, in an effort to isolate the picrate. After several months and many vain attempts to obtain a crystalline addition product, a few colorless crystals appeared in the solution, but their melting point was very much different from that of the original compound. Since picrates are invariably deeply colored and are decomposed in contact with alumina, the possibility that this was a picrate was excluded. After spectral examination (the spectrum was identical with the original compound) and other considerations the crystals were recognized as a polymorphic form of the hydrocarbon.

C. Cyclodehydration of Some Highly Hindered Ketones.

In the previous work (11), it was indicated that the ketimines (IX) and ketones (X) of the following type



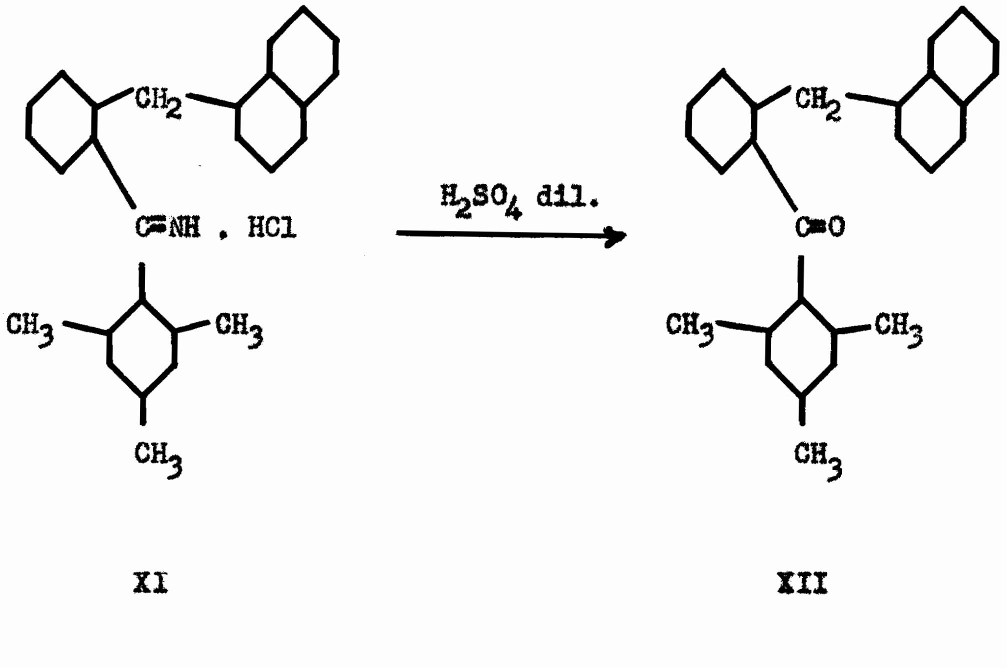
IX



X

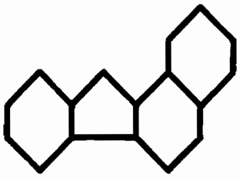
show an exceptional behavior as far as their reactivity is concerned. The difficulties connected with the hydrolysis of the ketimines were already adequately described (11) and explained by steric hindrance resulting from the two o-substituents. It is questionable whether this reasoning can be applied to the cyclodehydration of the ketimine or ketone. As will be discussed later, the phenyl ring which is attached to the benzanthracene nucleus cannot be coplanar with the rest of the molecule even if there were no substituents in the o- position. The only place where the two o- groups might exert their influence would be the carbonyl group which indeed (according to the mechanism proposed for this type of reactions by Bradsher and Vingiello (6)) plays an important role in the cyclization.

There were many attempts made in order to effect the cyclization of the ketimine (IX), and although no satisfactory procedure was developed, a small yield of unidentified colorless hydrocarbon was reported (11). Due to the improved technique in later experiments, substantial increase in the yield of this compound was achieved, but the analysis (C, 94.35; 94.51; 94.06; H, 5.65; 5.17; 5.43) showed an appreciable deviation from the calculated value (C, 93.94; H, 6.06) for the expected hydrocarbon. The high percentage of carbon suggested cleavage of either the methyl groups or the dimethylphenyl group, or a rearrangement. In order to gain more information, a trimethyl-substituted ketimine (XI)

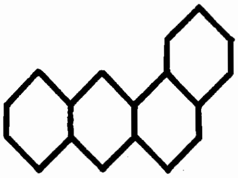


was prepared by the conventional method, hydrolyzed in a sealed tube to the ketone (XII) and the cyclization of this ketone was investigated.

Again, a colorless hydrocarbon was obtained which was proved to be identical with the one resulting from the attempted cyclization of the ketone X. It was then apparent that since the only part of the molecule where the two ketones (X and XII) differed was the methyl-substituted phenyl ring, the hydrocarbon product resulted from a cleavage of this ring. Two possibilities were then considered : 1,2-benzfluorene (XIII) and 1,2-benzanthracene (XIV).



XIII



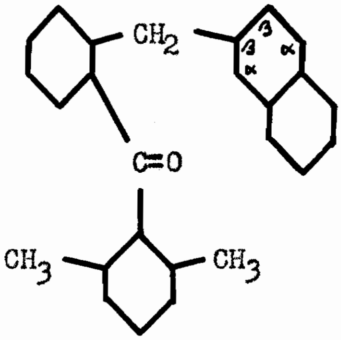
XIV

All the evidence indicated that the unknown hydrocarbon was identical with the latter. Some derivatives were prepared and the results are summarized in Table I.

Table I

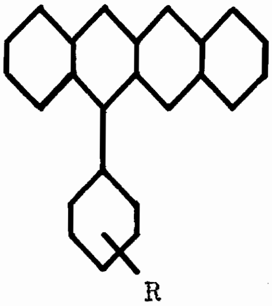
	1,2-benzanthracene	unknown compound
m. p. °C.	158-159 (7)	156-157
Solubility in H_2SO_4	Red, changes to blue (7)	Red (red fluorescence) changes to blue
Picric acid add.cpd.	141.5-142.5° (8,9)	140.5-141.5°
Trinitrofluorenone add.cpd.	223.6-224.0° (10)	223.0-223.5°

Spectral evidence will be discussed in part E. Very similar results were obtained when the cyclization of the ketone XV was attempted. 1,2-Benzanthracene was isolated as a reaction product, however no tetracene was obtained although it conceivably might have been formed by ring closure



XV

into the second β-position of the naphthalene nucleus. It was already mentioned that this possibility played a great role in the theoretical considerations concerning the cyclization of ketones derived from 2-substituted naphthalene.



XVI

Although the ring closure into the 2-position of naphthalene is very rare (16, 20) if the 1-position is available, some evidence was obtained that the tetracene derivatives (XVI) are formed in small amounts. The yellow fraction which accompanied every cyclization of the ketones in the 2-naphthalene series possessed a strong yellowish-green fluorescence which disappeared after irradiation by strong ultraviolet light, and formed an addition compound with maleic anhydride. Both of these phenomena can be observed already with unsubstituted tetracene, the first being presumably due to the formation of explosive photo oxides (16, 21) and the second to the easy formation of a colorless adduct (16, 22). The benzanthracenes are colorless, possess a blue fluorescence, and do not add maleic anhydride under the same conditions. It was attempted several times to isolate the yellow by-product in crystalline form, but without any success.

The cleavage of the hindered ketones indicated the necessity of devising a new method or at least of changing the conditions of the cyclization. Some unsuccessful efforts were described previously (11), others were made in the course of this work. Cold concentrated sulfuric acid led invariably to sulfonated, water soluble products, phosphorus pentoxide and 100% phosphoric acid yielded small amounts of green fluorescent oils which could not be crystallized. Finally a successful method was devised which followed a very unconventional line. The previous cyclizations were usually carried out in solution under catalysis by a strong mineral acid. The new method consisted of heating the ketone with powdered aluminum oxide to 240-280° under reduced pressure (0.5-3.0 mm.). Fisher's Alumina, dehydrated by heating to 300° for several hours under reduced pressure (the commercial product contains some water), was most often used. This procedure yielded excellent results in the cyclization of all the simple ketones in both the 1- and the 2-naphthyl series.

The hindered ketones were also successfully cyclized by this method, but the yields varied greatly from case to case. The ketones X and XII gave 45% and 80% yields of the corresponding hydrocarbon. The results of the cyclization of the ketone XV were quite poor, and the reaction seemed to be exceptionally difficult and complicated. However, some interesting observations were made during the attempts to improve the yields in this particular reaction. In the first group of experiments, Fisher's Alumina was used, the time of heating and temperature were varied, and the amount of strongly fluorescent fraction which appeared on the chromatography column was taken as a criterion for the efficiency of the catalyst. The optimal reaction time was two hours, shorter or longer periods of time gave lower results. The optimal temperature was between 260 and 280°, temperatures under 260° and over 280° gave lower yields. In the second group of experiments different kinds of aluminum oxide were used. Three sorts of Woelm alumina (designated as: "acid", "basic" and "non-alkaline") were compared with Fisher's Alumina. Under similar conditions the latter and Woelm "basic" alumina gave the best results, the "acid" alumina being surprisingly inefficient.

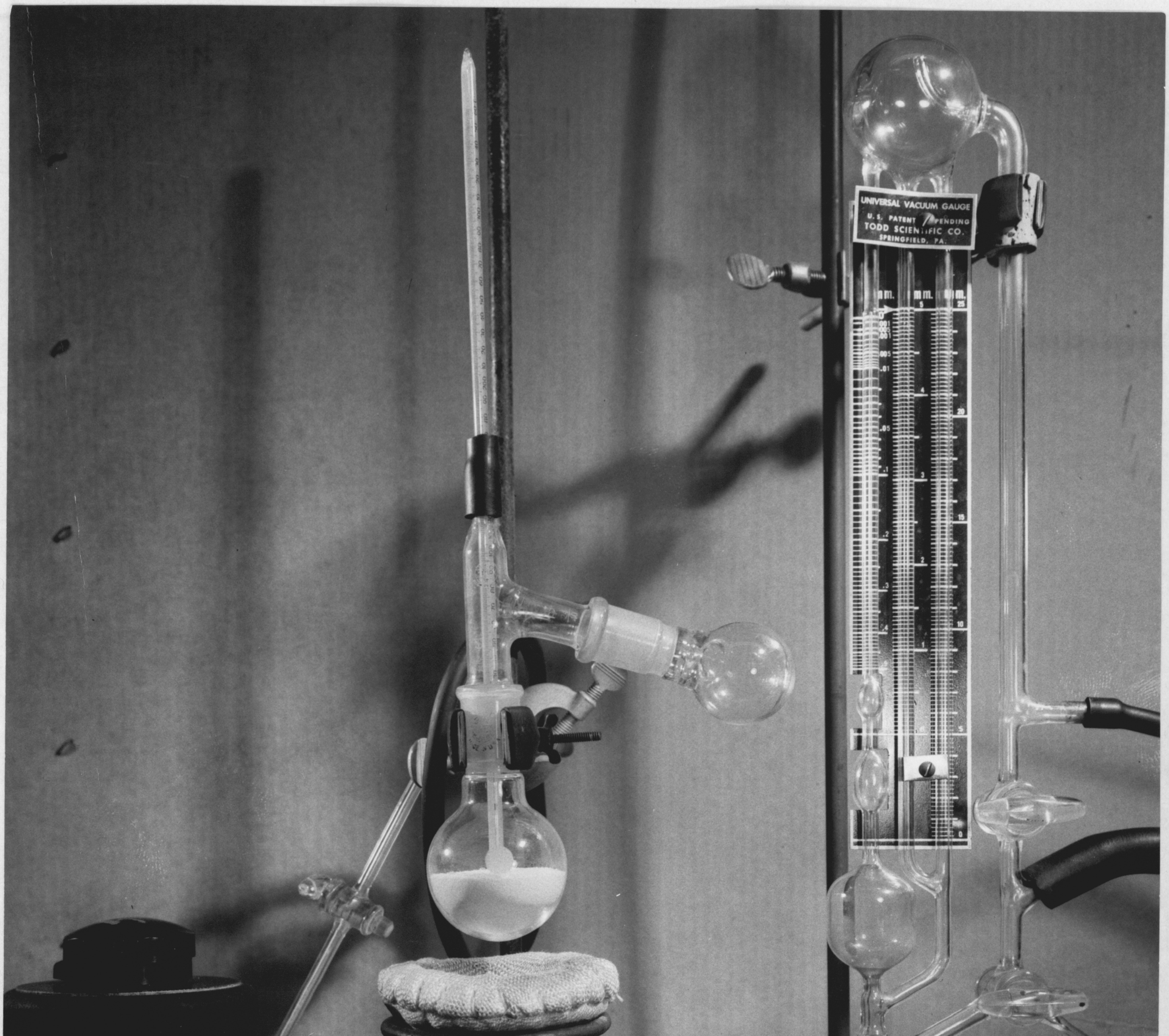
Even in the optimal case the amount of the strongly fluorescent fraction which could be eluted by petroleum ether was only 34% of the weight of the ketone. This fraction consisted invariably of four distinct regions which were easily recognizable on a chromatography column.

This does not imply that only four compounds were present. From the first colorless, blue fluorescent stripe which was eluted by petroleum ether two crystalline compounds were isolated, one of which was the expected 9-(2',6'-dimethylphenyl)-1,2-benzanthracene. Its identity was substantiated by taking its ultraviolet spectrum. The second compound was crystallized from ethanol as colorless prisms, m.p. 190-200°, and was insoluble in cold concentrated sulfuric acid. Even after six successive crystallizations the melting range was very broad. On heating, small colorless droplets formed around the crystal which became opaque at temperatures above 180°. This suggested that some chemical change was taking place during the melting process, but after cooling the molten crystals and repeating the melting point determination, the same phenomenon was observed. The analysis of this second product (C, 93.47; H, 6.56) showed appreciable deviation from the values for the expected benzanthracene derivative (C, 93.94; H, 6.06), but when compared to the calculated values (C, 93.37; H, 6.63) for a dihydroderivative, a surprising similarity was apparent. Some considerations concerning this case will be mentioned in part E.

D. General Remarks on Cyclodehydration by Means of Alumina

A photograph of the apparatus used in the Alumina reactions is shown on the next page. It consists of a round bottom flask, half-filled with the mixture of the alumina and the ketone, the thermometer being immersed in it without touching the glass. The upper smaller flask has a side-arm which is connected to the vacuum pump. The temperature is controlled by a variable transformer, and the pressure by a suitable vacuum gauge. During the reaction the material invariably turned deep yellow even when the compounds of the 1-naphthyl series were used and often quite vigorous "boiling" was observed. The high temperature was usually maintained for one to three hours, and after the flask cooled off the mixture was transferred into an adsorption column partially filled with alumina or other suitable adsorbent. The products were then eluted by petroleum ether or a mixture of benzene and petroleum ether. The path of the colorless hydrocarbon could easily be traced by irradiating the column with ultraviolet light; however, in the 9-substituted benzanthracene series a yellow impurity possessing a strong yellow fluorescence could not be separated quantitatively from the colorless fraction by this method.

The problem of a suitable mechanism for this reaction, although not pursued systematically, suggested an important question. Does the acid catalyzed cyclization of these ketones follow the familiar mechanism formulated by Bradsher and Vingiello (6) or does it undergo an Elbs-type ring closure? The importance of this consideration can be illustrated by the following scheme (Chart III).


UNIVERSAL VACUUM GAUGE
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mm.
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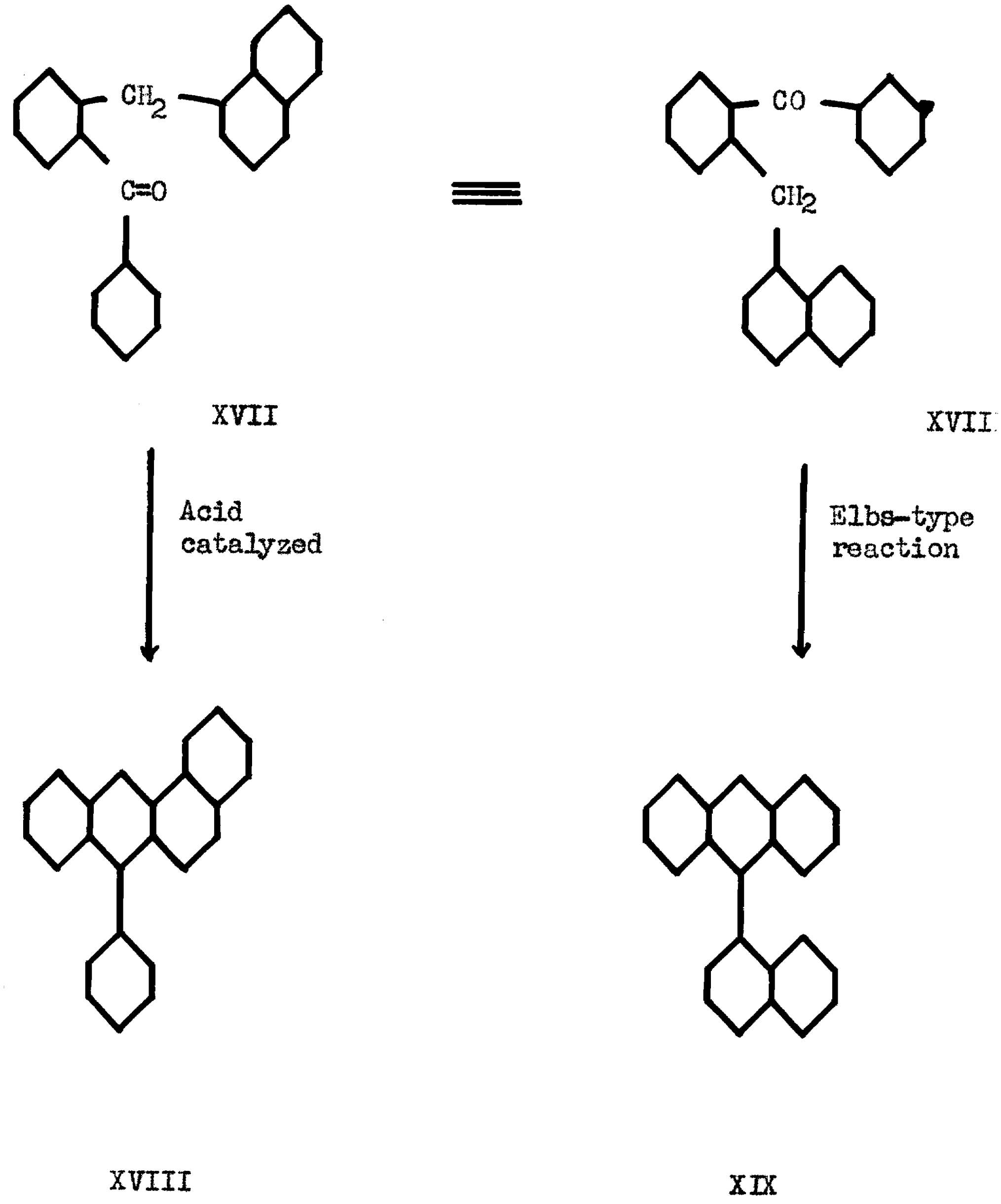
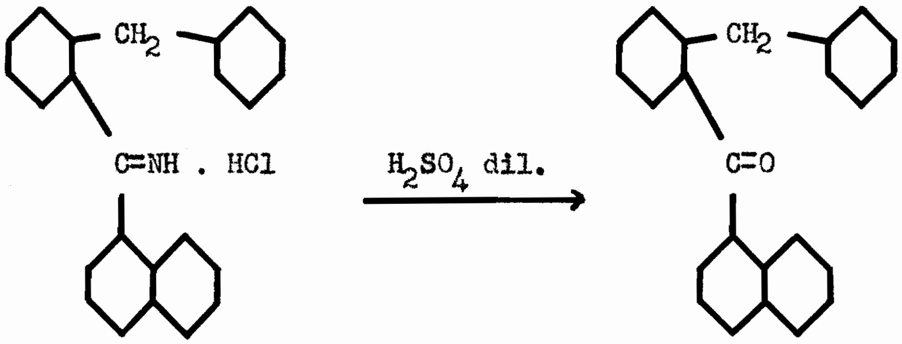
CHART III


CH$_2$
C=O
CO
CH$_2$
XVII
XVII
Acid catalyzed
Elbs-type reaction
XVIII
XIX

The acid cyclization of the ketone XVII yields a single hydrocarbon product which is identical with the main product resulting from the alumina cyclization of XVII. In order to gain a better insight into this question, the ketone XXI was prepared by hydrolyzing the ketimine salt XX and cyclized using both acid and alumina processes.

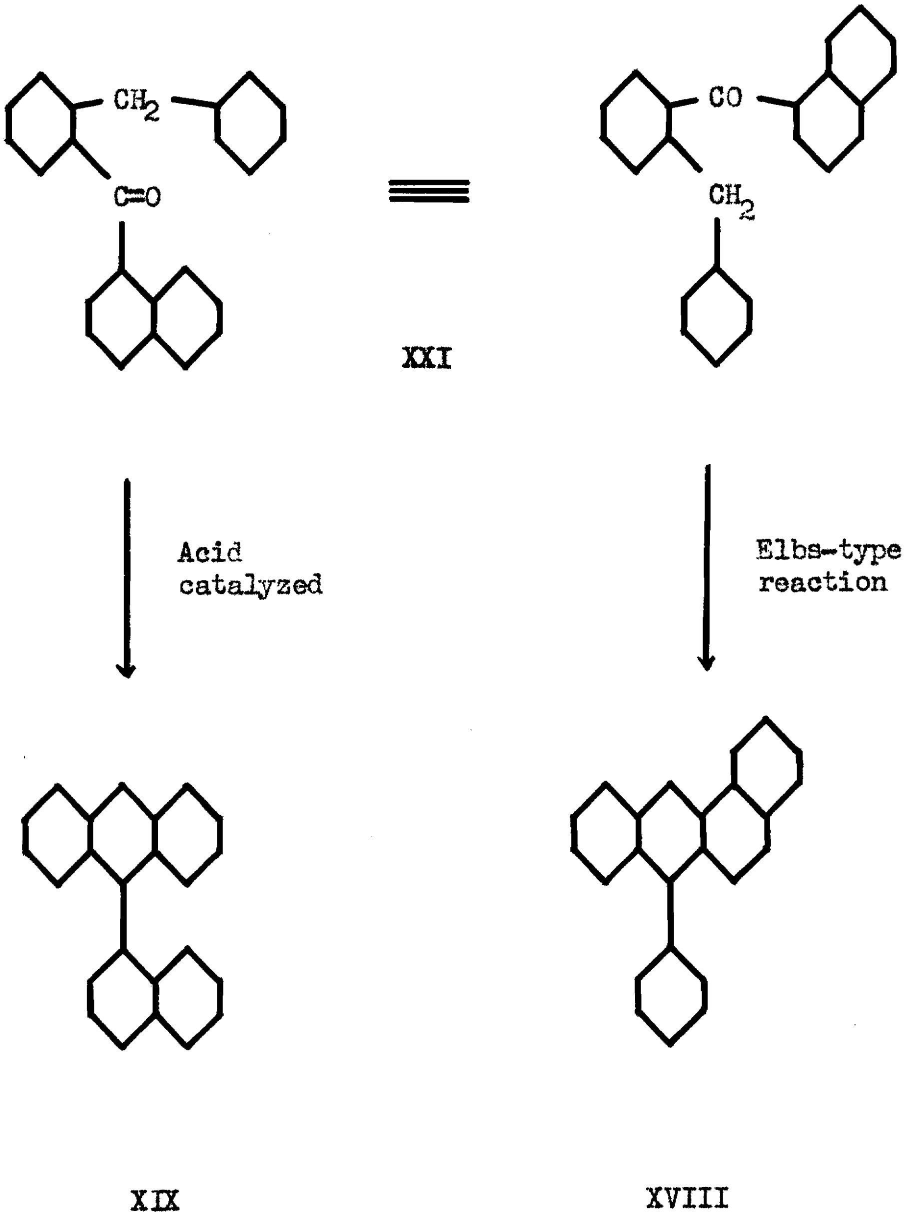


XX

XXI

The cyclization was difficult and the results quite surprising. There were two principal hydrocarbon products resulting in approximately equal amounts from the acid process. One was found to be identical with 10-phenyl-1,2-benzanthracene (XVIII) and the other with 9-(1-naphthyl)-anthracene (XIX). The following scheme (Chart IV) will be illustrative.

CHART IV


CH$_2$
C=O
CO
CH$_2$
XXI
Acid catalyzed
Elbs-type reaction
XIX
XVIII

The presence of the compound XIX was expected as a normal product of the cyclization of the ketone XXI according to all previously done work (6,7,23,24), however, the presence of XVIII was surprising indeed, the cyclization obviously followed a path similar to the Elbs-type reactions (25). Such reactions were thought to occur only at high temperatures and with no solvent or catalyst present.

The alumina cyclization, on the other hand, seems to be at least as far as the procedure is concerned, much close to the Elbs process. Actually, it was reported that ketones can be pyrolyzed by dropping the liquid into a metal tube packed with active alumina at about 400° (26). However, the effect of the catalyst was questioned by Fieser (25). Surprisingly enough, the cyclization of the ketone XXI by alumina yielded almost exclusively the hydrocarbon XVIII (i.e., a benzanthracene derivative) and only traces of the compound XIX (i.e., anthracene derivative). On the other hand, the alumina cyclization of the ketone XVII gave almost exclusively the hydrocarbon XVIII (benzanthracene derivative) but a very small amount of hydrocarbon XIX (anthracene derivative) was found as a by-product. It seems to be reasonable to conclude that the following generalizations can be considered in this type of cyclizations :

1) The well known cyclodehydration process as described by Bradsher and Vingiello is the preferred one.

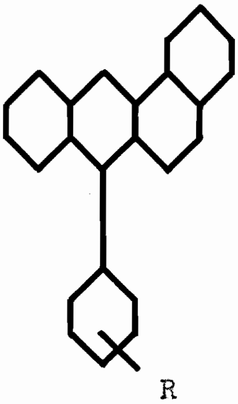
2) The Elbs type reaction can proceed simultaneously, but quantitatively it is only of secondary importance.

3) If the Elbs type cyclization involves a phenyl ring only very small amounts of Elbs type products are found.

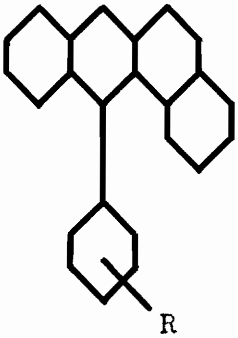
4) If the Elbs-type cyclization involves a naphthyl ring, a considerable increase in the relative quantity of the Elbs-type products may be found.

5) The above mentioned generalizations do not necessarily indicate the actual mechanism of each of the reactions.

As a result of later experiments it was quite easy to show that the acid cyclization follows, in general, the path of the accepted mechanism (6). All hydrocarbons of the general types XXII and XXIII



XXII

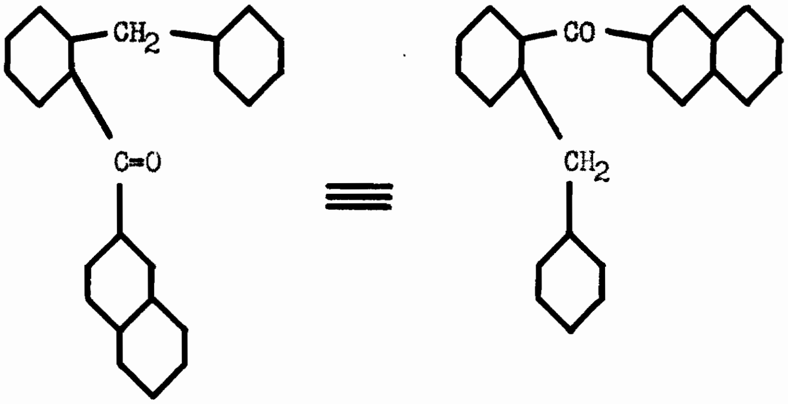


XXIII

prepared by the acid cyclization of the corresponding ketones were spectroscopically proved to be derivatives of 1,2-benzanthracene rather than anthracene, and the 9-phenyl-1,2-benzanthracene (XXIII, R = H) was identical with the one prepared by a different method (8).

The acid cyclization of the ketone XXI must then be considered as an exceptional case, being the only acid catalyzed reaction thus far known to yield Elbs-type products in such a considerable quantity.

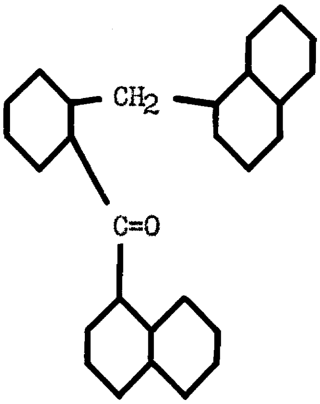
At this point it was very desirable to compare the reactivity and reactions of the ketone XXI with an isomeric ketone XXVIII, which was prepared by the usual method from the corresponding ketimine.



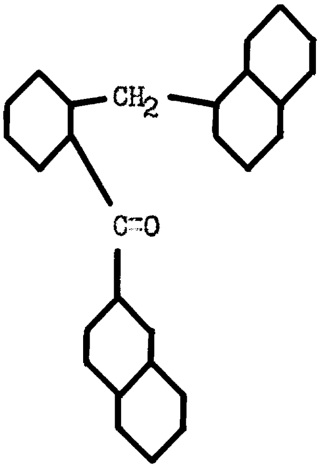
XXVIII

The difference was striking. It may be recalled that the cyclization of the corresponding 1-naphthylketone XXI was a relatively difficult process requiring high temperature and pressure (sealed tube technique). The ketone XXVIII, on the other hand, could be cyclized by the simple reflux method in excellent yields. The sealed tube technique gave almost quantitative yields of a very pure product; only traces of hydrocarbon by-products were detected. The question of by-products was in this case of special importance. The corresponding 1-naphthylketone XXI yielded up to 50% of hydrocarbon by-products resulting from the Elbs-type ring closure. It was therefore expected that more than a detectable amount of by-products might result from the cyclization of XXVIII (right-hand structure). Further complication was expected as a result of two non-equivalent positions on the naphthalene nucleus, each of which could conceivably yield a different hydrocarbon product (Elbs-type cyclization). In view of these considerations the results of the cyclization of XXVIII are very difficult to explain.

An attractive approach to the same problem was the comparison between the cyclization of the two ketones XXIX and XXX.

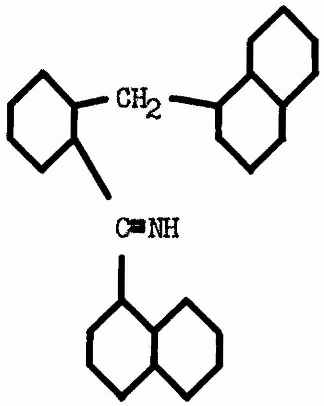


XXIX

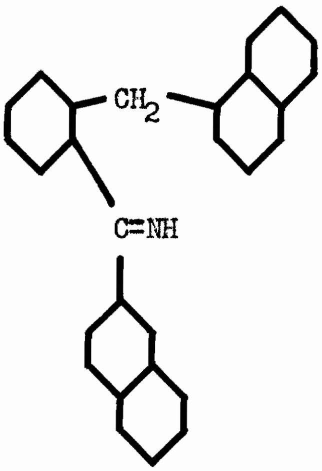


XXX

The corresponding ketimine salts were prepared by the conventional method and hydrolyzed in a sealed tube to the ketones. It was expected that the hydrolysis of the ketimine XXXII would be easier than the hydrolysis of XXXI. Both electronic and steric considerations would favor this hypothesis and the same reasoning can be applied to the case of the ketones XXI and XXVIII. Contrary to these expectations none of the ketimines can be hydrolyzed satisfactorily by simple reflux with dilute sulfuric acid; in all cases the sealed tube technique had to be used.

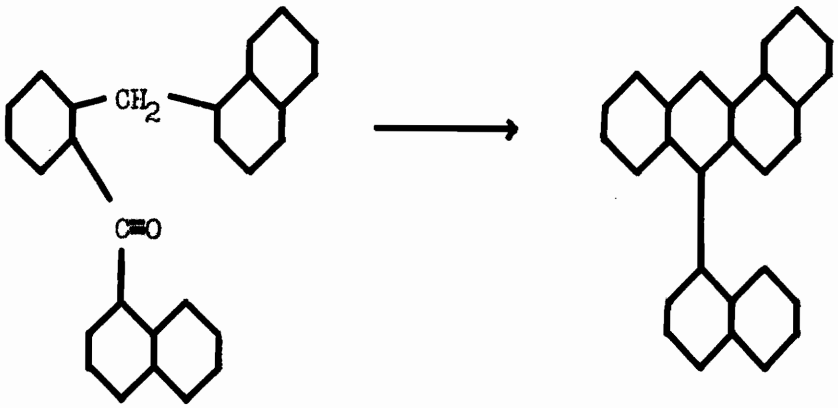


XXXI



XXXII

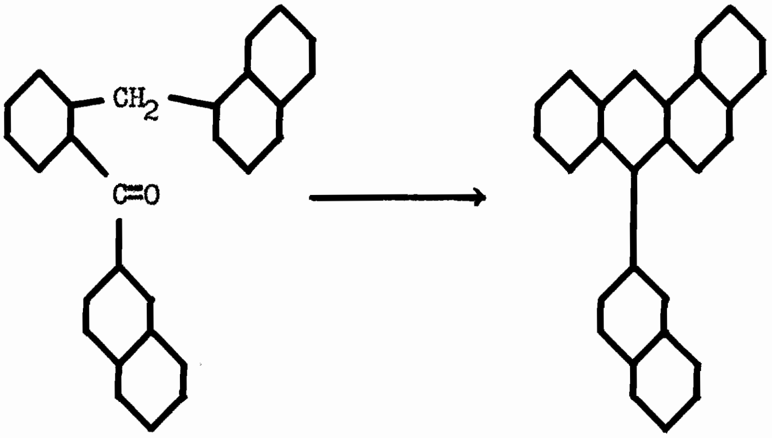
Nevertheless,the cyclization of these ketones (XXIX and XXX) proceeded according to all expectations. The sealed tube technique, using ketone XXIX, gave excellent yields of the corresponding hydrocarbon XXXIII.



XXIX XXXIII

This is easily understandable since both reaction paths (Bradsher-type, Elbs-type) would yield the same product.

As expected, the cylization of XXX to XXXIV was very smooth, and the simple reflux method gave high yields of the hydrocarbon.



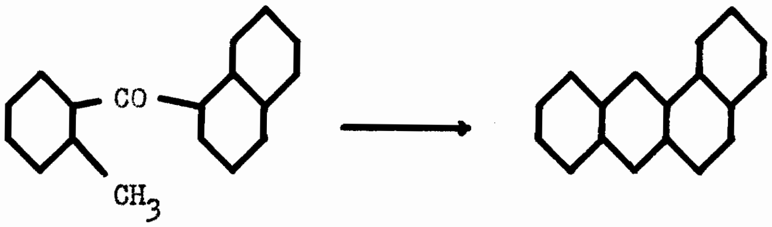
XXX XXXIV

Only traces of by-products (possibly those corresponding to the Elbs-type reaction) were detected. The same reaction was repeated using the sealed tube technique, and again high yields of XXXIV were realized. Although the amount of by-products increased, none of them could be properly identified.

The following evidence for the identity of the alumina cyclization products can be cited. All the hydrocarbons of the type XXII and XXIII prepared by the acid cyclization were identical with those prepared by the alumina method. The ketones where the phenyl ring was substituted by two methyl groups in ortho position cannot yield an Elbs-type product. Three such hydrocarbons were prepared and their spectra indicated their relationship with 1,2-benzanthracene. (See Section E.) However, it was hard to understand why the alumina cyclization of XIX yielded almost exclusively the Elbs-type product XVI, unless there were at least some tendency to favor or catalyze this type of reaction. Two experiments were performed in order to elucidate this question. To induce an Elbs-type reaction in 2-methylbenzophenone was always considered extremely difficult (27).

XXIV XXV

Therefore the ketone XXIV was subjected to the alumina method with the hope of obtaining better yields of anthracene (XXV). Only traces of anthracene were detected in the products of the reaction which was difficult to perform due to the relatively low boiling point of the ketone XXIV. In order to eliminate this difficulty as a possible reason for the negative results, another ketone, XVI, was prepared which is known to pyrolyze quite smoothly (28) giving good yields of benzanthracene XXVII.

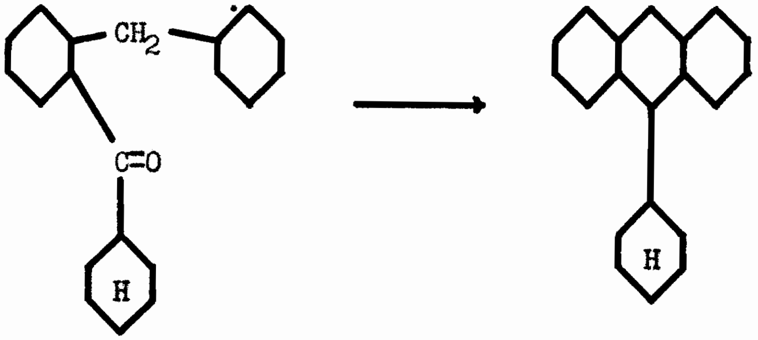


XXVI XXVII

However, even this reaction performed with alumina gave only traces of the product XXVII.

In view of this evidence, the conclusion that the alumina has no special tendency to act as a catalyst in an Elbs-type reaction, seems to be inevitable.

A further interesting extension of the applicability of the alumina cyclization was the successful attempt to cyclize the ketone XXXV



XXXV XXXVI

to the hydrocarbon XXXVI. A considerable amount of work was done in order to determine the structure of XXXVI (13), and the acid catalyzed cyclization of the ketone XXXV gave unsatisfactory results. The ketone was, nevertheless, very smoothly cyclized by the alumina method, and the resulting hydrocarbon was found to be identical with that isolated from the acid catalyzed cyclization.

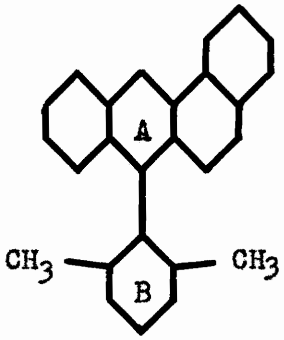
It has to be emphasized that the alumina cyclization reaction cannot be considered at present as a clear-cut procedure as far as the mechanism, scope and limitations are concerned. It can perhaps be argued that aluminum oxide, being able to act as a "Lewis acid" (21), simply replaces the function of the hydrobromic acid in the cyclization mixture. It is quite difficult, however, to imagine ionic processes in absence of a solvent. It seems more acceptable to regard the alumina only or mainly from the point of view of a large active surface acting in a similar fashion to the hydrogenation catalysts (30). This, on the other hand, is also open to serious objections and much more work will have to be done before this reaction will be fully understood.

Although in most of the cases mentioned alumina was used, it was found that other materials can also be used with some success. Florisil is the commercial name for an adsorbent material which is basically a complex magnesium silicate. When this material was used in place of alumina and mixed with a dimethyl-substituted ketone of the type XVII, a 30% yield of the corresponding hydrocarbon was obtained. However, there was a striking difference in the nature of the by-products. All the alumina cyclizations were characterized by the intensely yellow coloration of the reaction mixture. The yellow by-products, although never identified, accounted usually for not more than 10% of the amount of the ketone used. The Florisil cyclization, on the other hand, yielded over 40% of a deeply red oil which could be crystallized as almost black little needles which melted and decomposed over 250°. This by-product was at least superficially very similar to the red products invariably accompanying the acid catalyzed high temperature cyclizations of the dimethylketones. In concluding, it should be mentioned that no satisfactory results were obtained when the Florisil was used in an attempted cyclization of one of the di-ortho-substituted ketones.

E. Some Considerations Concerning the UV Spectra and Molecular Compounds of the Hydrocarbons Prepared.

The case of the cleavage of the highly hindered ketones leading to the formation of 1,2-benzanthracene (page 36) was quite revealing in that it indicated the insufficiency of some of the analytical data. It can be briefly reviewed that a compound $C_{26}H_{20}$ (corresponding to 9- or 10-(dimethylphenyl)-1,2-benzanthracene) contains 93.9% of carbon and compound $C_{18}H_{12}$ (corresponding to 1,2-benzanthracene) contains 94.7% of carbon. The usual reliability of C and H analysis is 0.3 - 0.5%. It is then evident that a value of 94.30% of carbon would fit any of the mentioned hydrocarbons, provided the reaction path and mechanism supports each of these possibilities. Consequently, some other evidence must be produced in order to substantiate one of the suggested structures. If at least one of the compounds in question was previously prepared and identified, a simple solution seems to be at hand, i.e., comparing the physical and chemical properties of the known and the unknown. However simple this solution sounds, there are often considerable difficulties in performing these simple comparisons. As far as the chemical properties of the compounds in question are concerned, aromatic hydrocarbons are often quite unreactive towards mild reagents and only seldom yield a well defined product after more drastic treatment (usually oxidation). This becomes especially important in cases where only a comparatively small amount of the substance is available. The most commonly known and used physical property is the melting point, the boiling point, if known, being only seldom of any real value, and other properties such as refractive index, solubility, etc. are in most cases unknown. However, polymorphism, which is quite common among polynuclear hydrocarbons must frequently be considered, and a melting point is then characteristic rather of the crystalline form than of the compound proper. This difficulty is often compensated by the ability of some hydrocarbons to form molecular compounds. Only little is known about the precise character of these usually highly colored crystalline substances, but it seems to be fairly well established that they owe their stability to electrostatic interactions, supposedly due to polarization of one component by the other (31, 32). The two prominent factors contributing to their stability are the amount of polarization that occurs between the donor (hydrocarbon) and acceptor molecule and their steric requirements (33, 34). To which extent these two factors influence the formation and stability of the molecular compound is hard to decide, but some interesting observations were made in the course of this work, and will be discussed subsequently. Returning briefly to the case of identity of the three mentioned compounds, 1,2-benzanthracene indeed forms well-defined molecular compounds with picric acid and trinitrofluorenone, but all attempts to isolate corresponding compounds of the substituted benzanthracenes failed.

This is in good agreement with the importance of the steric factor and its influence on the complex stability. Several x-ray diffraction studies (31, 35) have shown that, in general, the crystalline addition compounds consist of alternate layers of the two components. If the donor molecule is non-planar, the approach of the acceptor molecule is sterically hindered, and complex formation is then made more difficult because the non-planarity increases the distance through which the attractive forces must operate (34). This then suggests that the ring B (I) is not coplanar



I

with the ring system A, and it can also be amply demonstrated by constructing a model of the molecule (Fisher-Hirschfelder-Taylor kit can be used) showing the impossibility of the planar structure. It has to be emphasized that although no addition compound of I was isolated in a crystalline state, a deep red color always accompanied the mixing of the acceptor agent (picric acid, etc.) with the benzene solution of the hydrocarbon (alcoholic solutions sometimes show only deepening in brilliant yellow color of the picric acid). Further, it is worth mentioning that in a few cases crystalline red derivatives were obtained after many months, but these compounds showed a very low stability (i.e., they spontaneously decomposed into free picric acid, showed a broad melting point range, resisted all attempts at recrystallization, etc.) and could not be used as a routine means of identification and separation.

One of the physical properties which is becoming more and more important in hydrocarbon studies is the ability of their solutions to selectively absorb ultraviolet light. The resulting spectrum can then serve as a fingerprint for identification purposes. It is not within the scope of the present work to go deeper into the still little explored theories concerning the origin of this selective absorption and the connection between the spectral pattern and molecular structure. There is, however, one rule which was of importance in this investigation and therefore deserves a brief discussion here.

Let us consider an absorption spectrum of a polynuclear hydrocarbon, for example 1,2-benzanthracene. It can be expected that any substituent will produce a certain change in the position of the maximum absorption peaks (i.e., a hypsochromic or bathochromic shift) or eventually alter the entire form of the spectrum (36, 37). If the substituent were an aromatic group (as for example, phenyl or methylphenyl group in the cases discussed above), there can again be either a relatively small displacement of the spectral peaks, usually towards the longer wave lengths (bathochromic shift) or a deep change in the spectral form. There is a qualitative explanation for these two effects. Only a small displacement can be expected if the aromatic group (i.e., phenyl group) cannot be conjugated with the polynuclear system (i.e., benzanthracene), the reason for this being usually the non-planarity of the two components of the molecule. A detailed analysis of similar examples (9,10-diphenylanthracene (37), 2-methyldiphenyl (38)) can be found in the recent literature under the name of S (steric hindrance) effect. The second possibility, i.e.,a radical change in the appearance of the spectrum indicates an extensive conjugation between the two components and hence their coplanarity.

In view of previous attempts to prepare molecular compounds of 9- and 10-aryl-1,2-benzanthracenes and of the molecular models, it was not surprising to find that the spectra of all the hydrocarbons pertaining to this series were very closely similar to that of 1,2-benzanthracene.

A brief digression concerning this spectrum must be made. 1,2-Benzanthracene,naphthanthracene or tetraphene was first prepared by Elbs (39), and its melting point reported as 141° and 139°.Many other syntheses were later devised,and the most often reported melting point was 158-159° (16 and references there).The sample prepared during this work melted at 157-158° after at least fifteen recrystallizations from different solvents.The absorption spectrum was reported by Clar (40) with the following wave length maxima (Chart V) and by Friedel and Orchin (41) whose tabulated data (Chart V) are in good agreement with those obtained by the author (Chart V, Column III):

Chart V

E. Clar	Friedel & Orchin *	Indep. Sample
222.0	223.5	222.0
227.0	228.0	228.0
254.0	256.5	256.0
267.0	267.5	268.0
280.0	277.0	277.0
290.0	288.0	287.0
	300.0	300.0
316.0	315.0	314.0
329.0	326.5	327.0
344.0	341.5	342.0
359.0	358.0	358.0
	373.0	376.0
385.0	382.5	386.0

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* These data were obtained by extrapolation from reference 41,plate 499.

As an additional check, a purchased sample of 1,2-benzanthracene was purified by chromatography and crystallization, and the melting point, mixed melting point, and spectra were compared. Perfect agreement with the sample prepared in this work was found.

Two very interesting observations were made in comparing the spectra of the individual hydrocarbons.

1) The spectrum of 10-phenyl-1,2-benzanthracene is practically identical with any of the spectra of those compounds where the phenyl group is substituted by one, two or three methyl groups. The same was found in the 9-phenyl-1,2-benzanthracene series.

2) If the three spectra of 1,2-benzanthracene, 9-phenyl and 10-phenyl-1,2-benzanthracene are compared, a distinct bathochromic shift which is obviously due to the phenyl group is observed, this being more pronounced in the 10-phenyl series. The displacement is stronger in the α- than in the β- peaks.

The comparison of spectral patterns was of importance in several cases mentioned earlier in this discussion. The spectra of the hydrocarbon products of the acid catalyzed cyclizations of the two isomeric 2,6-dimethylketones and the 2,4,6-trimethylketone were found to be identical not only with each other but also with the independently prepared sample of 1,2-benzanthracene, hence their identity was adequately substantiated. The spectra of the products of the alumina cyclization of the same ketones, on the other hand, were found to be practically identical with the spectral patterns of the parent hydrocarbons (i.e., 9- and 10-phenyl-1,2-benzanthracene), which again strongly substantiated their identity.

Of a special importance were the spectral examinations of the two hydrocarbon products of the 2-(2-naphthylmethyl)-2',6'-dimethylbenzophenone. A decision had to be made as to which of the two colorless, crystalline compounds was the expected 9-(2',6'-dimethylphenyl)-1,2-benzanthracene. In view of the spectral patterns of the previously investigated hydrocarbons, it was expected that the spectral peaks of the 2',6'- compound would appear at the same wave length as those of the unsubstituted 9-phenyl-1,2-benzanthracene. Accordingly, it was found that the compound melting at 123.5° had a spectrum which was practically identical with that of the parent hydrocarbon; the other compound, melting at 190-200°, exhibited an entirely different spectral pattern, but some similar features were still recognizable.

A further case where spectral considerations were of importance was the identity of the products from the acid catalyzed cyclization of the 2-benzylphenyl-1-naphthylketone. The crystalline hydrocarbon, m. p. 182-183°, showed a typical 10-phenyl-1,2-benzanthracene spectrum. The second crystalline compound, m. p. 160°, had an entirely different spectrum with one very prominent peak at 247-253 $m\mu$. The spectrum of anthracene is very similar, the most prominent peak being at 243-250 $m\mu$. Similar correspondence could be found with the less prominent peaks in the longer UV region (300-380 $m\mu$).

Finally, a justification may perhaps be in order regarding the use of absorbencies instead of molar extinction coefficients which are preferred by some authors. The absorbency can be read directly from the dial of the instrument, which eliminates a considerable amount of work necessary for the extinction coefficient computation. Spectrophotometry is at present becoming more and more mechanized. Automatic recording spectrographs give only transmittancies or absorbencies, and since the mere comparing of the shape of the spectral curves is still one of the most important analytical tools in absorption spectroscopy, it seems to be reasonable to assume that the absorbencies will be used more in the future. These good points seem to sufficiently outweigh the inherent advantage of the molar extinction coefficient concerning the molar term which is included.

EXPERIMENTAL

EXPERIMENTAL [(a,b)]

2-Naphthylmethylchlorobenzenes (Friedel-Crafts reaction).

A mixture of 385 g. (3.0 moles) of naphthalene with 500 ml. of redistilled dry nitrobenzene, was stirred well in a 1500 ml. three-necked flask equipped with a dropping funnel. A magnetic stirrer can be used to advantage. After the naphthalene had dissolved 6.0 g. (0.045 mole) of aluminum chloride was added, the system was attached to an aspirator and the pressure reduced to about 30 mm. Then 240 g. (1.5 mole) of 2-chlorobenzylchloride was added dropwise. After the vigorous evolution of hydrogen chloride had subsided (about three hours), the aspirator was disconnected and 100 ml. of 20% hydrochloric acid was added slowly to the black mixture. The organic layer was then washed three times with water, dried over calcium chloride, and distilled at about 30 mm. pressure. The naphthalene and nitrobenzene distilled together between 100 - 170° and the residue (about 300 g.) was fractionated at 2 mm. pressure. A mixture of the two isomeric chlorocompounds was collected first, b.p. 186 - 192°, weight 230 g. (61%). The second fraction, b.p. 270 - 280°, weight 40 g., formed a slightly yellow, extremely viscous oil which consisted probably of a mixture of dialkylated naphthalenes.

2-Chlorophenyl-2-naphthylcarbinol.

A Grignard reagent was prepared from 12 g. (0.48 mole) of magnesium,

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(a) All melting points are corrected
(b) All the analyses reported here were done by the Micro-Tech Laboratories, Skokie, Illinois.

100 g. (0.48 mole) of 2-bromonaphthalene and 250 ml. of dry ether. When the reaction was complete, a solution of 65 g. (0.46 mole) of 2-chlorobenzaldehyde in 250 ml. of dry ether was added dropwise with stirring. A yellow precipitate appeared. The mixture was heated under reflux for one hour and then allowed to stand overnight at room temperature. It was then decomposed with 50 ml. of 20% ammonium chloride solution. The ethereal solution was decanted from the hard residue and the solution was washed twice with water, dried over "Drierite", and finally concentrated. The residue was fractionated under reduced pressure and the fraction distilling at 208-210° (1.5 mm.) was collected; yield 71 g. (57%). A portion of this viscous oil was refractionated and a sample was collected after half of the material had distilled; b.p. 200-201° (1 mm.).

Analysis : Calculated for $C_{17}H_{13}OCl$: C, 75.98; H, 4.88.
Found : C, 76.37; H, 4.88.

2-(2-Naphthylmethyl)chlorobenzene (Reduction of the carbinol).

A mixture of 120 g. (0.45 mole) of the 2-chlorophenyl-2-naphthylcarbinol, 25 g. (0.80 mole) of red phosphorus, and 25 g. (0.20 mole)of iodine in 1000 ml. of 90% acetic acid was heated under reflux for 25 hours. The hot solution was then filtered to remove the unreacted phosphorus, allowed to cool and mixed with 1000 g. of crushed ice. An iced 10% sodium hydroxide solution was then slowly added under stirring until the mixture showed an alkaline reaction. The red oily layer which appeared was extracted by ether, separated from the water layer and washed with a 20% solution of sodium hydroxide to remove free iodine. The organic layer was then again washed with water and dried over calcium chloride. The ethereal solution had a tendency to form quite stable emulsions with the washing agent. This was prevented or at least minimized by adding about 5-10% of petroleum ether to the mixture. The dry organic layer was then concentrated and fractionated under reduced pressure. The fraction distilling between 178-182° at 1.3 mm., (lit. (5) b.p. 189-192°, 2 mm.) was collected as a colorless oil; yield 80 g. (70%).

Attempted Synthesis of 2-(2-Naphthylmethyl)chlorobenzene.

A. A Grignard reagent was prepared from 4.9 g. (0.20 mole) of magnesium, 32 g. (0.20 mole) of 2-chlorobenzylchloride and a crystal of iodine in 300 ml. of dry ether. When the reaction was complete, 41 g. (0.20 mole) of 2-bromonaphthalene in 250 ml. of ether was added dropwise. No reaction was observed, even after several hours of reflux. The mixture was then decomposed by saturated ammonium chloride solution, the ethereal layer was separated, washed, concentrated and distilled. Unreacted 2-bromonaphthalene was recovered almost quantitatively.

B. A Grignard reagent was prepared from 3.0 g. (0.12 mole) of magnesium and 25 g. (0.12 mole) of 2-bromonaphthalene in 200 ml. of dry ether. After all the metal had dissolved, 19 g. (0.12 mole) of 2-chlorobenzylchloride in 150 ml. of dry ether was added dropwise. The originally brown reaction mixture turned yellow after two hours of reflux, but no magnesium salts precipitated. When the solution was allowed to stand overnight at room temperature, large yellow plates of 2,2'-dinaphthyl appeared in the flask. Recrystallization from hot benzene gave colorless plates, m.p. 180-181° * (lit. (43) m.p. 181°); yield 8.4 g. (55%). With picric acid orange needles were obtained, m.p. 182.5° (lit. (44) m.p. 184°).

2-(2-Naphthyl~~phenyl~~methyl)benzonitrile.

A. From Pure Chlorocompound

A mixture of 80 g. (0.30 mole) of the redistilled chlorocompound, 35 g. (0.40 mole) of cuprous cyanide, 0.10 g. of anhydrous cupric sulfate, and 20 ml. of dry pyridine in a 200 ml. round-bottom flask furnished with a long air condenser was heated for 22 hours in a metal bath maintained at 260-270°. The pyridine was allowed to escape slowly during the first two hours. After the reaction was complete, the condenser was replaced by a von Braun distilling head and the black material was crudely distilled at about 30 mm. pressure. The distillate was dissolved in ether and filtered through glass wool. The solution was then concentrated and distilled under reduced pressure. A slightly yellow oil distilling between 200-205° at 1.5 mm. was collected and crystallized from ethanol. It formed colorless prisms, m.p. 83-84° (lit. (5) m.p. 84.5-85.5°); yield 46 g. (60%).

B. From the Mixture of Two Isomeric Chlorocompounds

A mixture of 200 g. (0.80 mole) of the two isomeric chlorocompounds, 100 g. (1.1 mole) of cuprous cyanide, 0.20 g. of anhydrous cupric sulfate, and 60 ml. of dry pyridine, in a 500 ml. round-bottom flask furnished with a long air condenser, was heated for 17 hours in

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* All melting points are corrected.

a metal bath maintained at 260-270°. The nitrile was purified as described in the preceding section. The yield was 180 g. (92%) of the mixed nitriles. Some 150 g. of this mixture was cautiously refractionated at 2 mm. pressure using a 60 cm. long Vigreaux column. Three equal fractions were collected. The first one was crystallized from 95% ethanol, seeded with pure α-isomer and 30 g. of colorless crystals, m.p. 57-59° were collected (α-isomer). The second fraction was dissolved in a mixture of ether-petroleum ether (3:7), seeded with pure β-isomer, and 20 g. of colorless crystals m.p. 82-84° were collected (β-isomer). The third fraction was treated in the same manner and 35 g. of the β-isomer were recovered. The mother liquors from the crystallizations were combined, the solvent evaporated, 85 g. of a fresh mixture of nitriles was added and the whole process was repeated. From a total of 300 g. of the mixture, 130 g. of each isomer were isolated. Before using it in further reactions, the β-nitrile was recrystallized from hot 95% ethanol. Colorless crystals, m.p. 83-84°, resulted.

1-Bromo-2,3-dimethylbenzene.

Commercial 1-amino-2,3-dimethylbenzene hydrochloride was treated with sodium hydroxide and the free amine was extracted with ether. After removing the ether, the dark oil was purified by distillation; b.p.113° at 16 mm. A suspension of 53 g. (0.44 mole) of 1-amino-2,3-dimethylbenzene in 260 ml. of 40% hydrobromic acid (1.8 mole) was diazotized with 38 g. (0.55 mole) of sodium nitrite, added in two to five gram portions in a 1000 ml. flask. During the addition the temperature was kept below 5°, and the flask was shaken until the brown fumes were adsorbed. When the reaction was completed, five grams of copper turnings were added along with 200 ml. of water and the mixture was allowed to warm up until the evolution of nitrogen ceased. The product was then steam-distilled, separated, dissolved in ether, treated with sodium hydroxide solution, washed with water, and dried over calcium chloride. The solution was then concentrated and distilled under reduced pressure. A fraction distilling between 104-106° at 22 mm. (lit. (42) b.p. 213.8° at 760 mm.) was collected; yield 27 g. (30%).

1-Bromo-3,4-dimethylbenzene.

A mixture of 200 g. (1.9 mole) of 95% commercial o-xylene and 0.50 g. of iodine was treated with 250 g. (3.1 mole) of bromine. The temperature was kept between 0-5°. After two hours the evolution of hydrogen bromide ceased, and the liquid was washed with water, dried over calcium chloride, and fractionated at atmospheric pressure. The fraction distilling at 209-210°, 729 mm. (lit. (46) b.p. 214.5°,760 mm.) was a colorless oil which was subsequently redistilled twice; yield 230 g. (70%).

1-Bromo-3,5-dimethylbenzene.

A suspension of 210 g. (1.7 moles) of commercial 1-amino-2,4-dimethylbenzene (which was purified by distillation) in 1,400 ml. of cold concentrated hydrochloric acid was treated in a 5-liter three-necked flask with 280 g. (1.7 moles) of bromine dissolved in 1000 ml. of cold concentrated hydrochloric acid. The bromine solution was added dropwise over a two hour period to the contents of the flask which was equipped with a large separatory funnel and a mechanical stirrer. A reddish-orange product that formed at the end of the addition period was cautiously heated along with the other contents of the flask in a water bath until a completely white product formed (30 min.). The flask was then strongly cooled, the white crystalline compound filtered, and subsequently dissolved in hot water. After addition of excess of ammonium hydroxide, 1-bromo-2-amino-3,5-dimethylbenzene separated as an oil and was purified by distillation; b.p. 117-130° (5 mm.), weight 230 g. (67%).

A suspension of 85 g. (0.43 mole) of the above compound in a cold mixture of 280 ml. of ethanol and 69 ml. of concentrated sulfuric acid, was treated with 51 g. (0.74 mole) of sodium nitrite in 90 ml. of water. During the addition period (90 min.) vigorous stirring was maintained, and the temperature was not allowed to exceed 10°. After the addition was complete, the stirring was continued for 20 minutes. Nitrogen evolved evenly upon adding 12 g. (0.18 mole) of reduced copper powder, that had been washed with ether, and allowing the diazotized material to warm slowly. The mixture was then heated on a water bath until the evolution of nitrogen ceased. A liter of water was added to the resulting mixture, and the material was steam-distilled. An ether solution of the crude product was washed with sodium hydroxide solution, then with water, and finally dried over calcium chloride. The solution was then concentrated, washed with concentrated sulfuric acid and distilled under reduced pressure.

The fraction distilling between 75-76° at 5 mm. (lit. (45) b.p. 204°, 760 mm.) was collected; yield 48 g. (61%).

2-Methylbenzoic acid.

A Grignard reagent was prepared from 100 g. (0.58 mole) of 2-bromotoluene and 15 g. (0.62 mole) of magnesium in 500 ml. of dry ether. After the reaction was complete, the mixture was poured on 300 g. of finely crushed dry ice and stirred vigorously. The frozen mixture was allowed to stand for 20 min. at room temperature and then 100 ml. of 25% sulfuric acid was added while stirring. The ethereal layer was then separated, mixed with 100 ml. of benzene and extracted with sodium hydroxide solution twice. The combined water solutions were warmed and purified with charcoal. The acid was then precipitated by dilute sulfuric acid, filtered, and dried. It formed small colorless needles, m.p. 103-104° (lit. (47) m.p. 107-108°); yield 78 g. (93%).

2-Methylbenzoylchloride.

A mixture of 32 g. (0.23 mole) of 2-methylbenzoic acid in 100 g. (o.48 mole) of phosphorus pentachloride was slowly heated in a 300 ml. flask furnished with an efficient condenser. A quite vigorous reaction started immediately after the chloride began to melt. The hydrogen chloride was permitted to escape and the mixture was gently refluxed for an hour. The crystalline unreacted phosphorus pentachloride was separated from the cold reaction mixture and the liquid was distilled under reduced pressure. The acid chloride was collected between 115-120° (30 mm.) and redistilled under atmospheric pressure; b.p. 210-212° at 743 mm. (lit.(48) b.p. 206-208°, 760 mm.). The yield was 22 g. (62%).

2-Methylbenzophenone.

To a solution of 19 g. (0.14 mole of aluminum chloride in 150 ml. of benzene 22 g. (0.14 mole) of 2-methylbenzoylchloride were slowly added. The solution first turned yellow, then brown, and the reaction started slowly after gentle heating. The evolution of hydrogen chloride lasted about one hour and the mixture was then heated under reflux for 20 minutes. When a mixture of ice and 20 ml. of concentrated hydrochloric acid was added to the cold solution, the brown color changed back to yellow. The organic layer was separated, washed twice with sodium hydroxide solution, three times with water and dried over calcium chloride. Distillation under atmospheric pressure yielded 18.6 g. (66%) of colorless oil, b.p. 294-295°, 712 mm. (lit.(49),b.p. 309.5°, 762 mm.).

2-Tolunitrile.

A suspension of 125 g. (1.3 mole) of commercial cuprous chloride in 750 ml. of water was stirred and 165 g. (3.4 moles) of sodium cyanide was slowly added. The solution became clear with the evolution of heat, was cooled to 0° and mixed with 400 ml. of toluene in a 5 l. beaker. The diazonium salt was prepared in a 3 l. beaker from a suspension of 110 g. (1.0 mole) of 2-toluidine in 250 ml. of concentrated hydrochloric acid and 1000 g. of cracked ice. The mixture was vigorously stirred and a solution of 75 g. (1.1 mole) of sodium nitrite in 200 ml. of water was slowly added. The temperature was always kept under 5°. After all the nitrite was added, the solution was tested by starch-iodine paper for free nitrous acid and then neutralized to alkaline reaction (litmus) with about 50 g. of powdered sodium carbonate. This alkaline diazonium solution was then slowly added to the cyanide solution. During the addition which occupied about thirty minutes, such vigorous stirring was maintained that the toluene on the surface was constantly drawn to the stirrer and the temperature was kept below 5° by adding ice occasionally. As soon as the diazonium solution came into contact with the cuprous cyanide, a dark yellow oily precipitate was formed which at once began to give off nitrogen; the resulting nitrile was taken up by the toluene as soon as it was formed. When all the diazonium solution had been added, the temperature was held at 0 - 5° for thirty more minutes and then was allowed to rise to about 25° while the stirring was continued for two additional hours. The beaker was then warmed in hot water to about 50° without stirring, removed from the bath and allowed to stand until cool. The upper oily layer was transferred into a 3000 ml. round-bottom flask and distilled by steam until no more oil passed over. The toluene layer was then separated, washed with water, dried over calcium chloride and fractionated at 20 mm. pressure. The nitrile distilled between 93-95° and was redistilled under atmospheric pressure. A colorless fraction, b.p. 200° at 722 mm. (Lit. (50), 94-96°, 20 mm.) was collected; yield 76 g. (65%).

1-Naphthyl-2-tolylketone.

A Grignard reagent was prepared from 62 g. (0.30 mole) of 1-naphthylbromide and 7.3 g. (0.31 mole) of magnesium in 200 ml. of dry ether. After all the metal dissolved, the ether was replaced with a solution of 23 g. (0.20 mole) of the nitrile in 200 ml. of toluene. The mixture was then heated under reflux for 12 hours, cooled, decomposed by addition of 100 ml. of 10% hydrochloric acid, and boiled for six hours. The magnesium salts and the ketimine hydrochloride decomposed and the two clear layers were separated. The toluene layer was washed with water, dried over calcium chloride and fractionated under reduced pressure. The colorless ketone distilled at 183-184° (1 mm.) (lit.(51) 174° at 0.40 mm.); yield 45 g. (90%).

2-(1-Naphthylmethyl).diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium and 12 g. (0.080 mole) of bromobenzene in 100 ml. of dry ether. The solution was then placed in a 1000 ml. three-necked flask equipped with a mechanical stirrer, separatory funnel and a condenser with a thermometer, and 12 g. (0.050 mole) of 2-(1-naphthylmethyl)benzonitrile dissolved in 150 ml. of dry toluene was added dropwise. During the addition the flask was heated gently, and the ether was slowly distilled away. When the temperature of the vapors reached 105°, and all the nitrile was added, the solution was heated under reflux for 18 hours with stirring, and decomposed with 25 ml. of a 20% ammonium chloride solution. The strongly fluorescent solution was then separated and the residue in the flask washed twice with a mixture of benzene and petroleum ether (1:1). The combined extracts were washed with water and cooled to about 5°. The crude ketimine hydrochloride was precipitated by addition of 15 ml. of concentrated hydrochloric acid, separated and washed with petroleum ether; yield 12 g. (69%). The analytical sample was obtained by decomposing a part of the above described ketimine salt with 10% sodium hydroxide solution and taking up the free imine with benzene. The pure ketimine hydrochloride was then precipitated by gaseous hydrogen chloride and recrystallized from a mixture of chloroform and ether (1:5). It formed colorless prisms, m.p. 181°(dec.).

Analysis : Calculated for $C_{24}H_{20}NCl$: N, 3.92.

Found : N, 3.86.

2-(1-Naphthylmethyl)-2'-methyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium and 13 g. (0.080 mole) of 2-bromotoluene in 150 ml. of dry ether. After the reaction was completed, the ether was replaced with a solution of 12 g. (0.050 mole) of 2-(1-naphthylmethyl)benzonitrile in 150 ml. of dry toluene. The mixture was heated under reflux overnight and decomposed with 25 ml. of a 20% solution of ammonium chloride. The organic layer was decanted, the residue washed with benzene and the combined solutions mixed with enough concentrated hydrochloric acid to precipitate the ketimine salt. The yellow crystals were filtered, washed with ether, then acetone, and dried in vacuo at room temperature; yield 17 g. (93%). The analytical sample was prepared from the crude hydrochloride by recrystallization from an alcohol-acetone (1:6) mixture. The resulting slightly yellow plates melted and decomposed at 177°.

Analysis: Calculated for $C_{25}H_{22}NCl$: N, 3.76.
Found : N, 3.91.

2-(1-Naphthylmethyl)-3'-methyl,diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium and 13 g. (0.080 mole) of 3-bromotoluene in 150 ml. of dry ether. After the reaction was completed, the ether was replaced with a solution of 12 g. (0.050 mole) of 2-(1-naphthylmethyl)benzonitrile in 150 ml. of dry toluene. The mixture was then heated under reflux for five hours and decomposed with 25 ml. of a 20% solution of ammonium chloride. The organic layer was decanted, the residue washed with petroleum ether, then with acetone, the ketimine salt precipitated with concentrated hydrochloric acid, and the crystals were filtered. The resulting yellow powder was washed with petroleum ether and acetone and dried in vacuo; yield 16 g. (86%). The analytical sample was prepared by recrystallizing the crude hydrochloride from an alcohol-acetone (1:6) mixture. Lemon yellow prisms were obtained, which melted and decomposed at 185°.

Analysis : Calculated for $C_{25}H_{22}NCl$: C, 80.73; H, 5.98.
Found : C, 80.20; H, 6.03.

2-(1-Naphthylmethyl)-4'-methyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium and 13 g. (0.080 mole) of 4-bromotoluene in 150 ml. of dry ether. After the reaction was completed, the ether was replaced with a solution of 12 g. (0.050 mole) of 2-(1-naphthylmethyl)benzonitrile in 150 ml. of dry toluene. The mixture was then heated under reflux for five hours and decomposed with 25 ml. of a 20% solution of ammonium chloride. The organic layer was decanted, the residue washed with petroleum ether and benzene, and the ketimine salt was precipitated from the combined solutions with concentrated hydrochloric acid. The orange powder was filtered, washed with benzene and dried in vacuo; yield 13.5 g. (73%). The analytical sample was prepared by crystallizing the crude hydrochloride from an alcohol-ether mixture (1:5). Orange plates were obtained which melted and decomposed at 184°.

Analysis : Calculated for $C_{25}H_{22}NCl$: N, 3.76.
Found : N, 3.75.

2-(1-Naphthylmethyl)phenyl.1-naphthylketimine hydrochloride.

A Grignard reagent was prepared from 7.4 g. (0.30 mole) of magnesium and 63 g. (0.30 mole) of 1-bromonaphthalene in 400 ml. of dry ether. Some of the metal remained undissolved but disappeared during the subsequent replacement of the ether with 400 ml. of toluene. To the dark brown solution 49 g. (0.20 mole) of 2-(1-naphthylmethyl)benzonitrile in 100 ml. of toluene was added dropwise, and the mixture was heated under reflux overnight. The black solution was decomposed with 50 ml. of a 20% ammonium chloride solution. Because some of the ketimine salt precipitated together with the magnesium compounds, 100 ml. of a 25% sulfuric acid solution was added and the mixture heated under reflux for five hours. After all the magnesium precipitate had dissolved, the suspended ketimine salt was filtered, washed with water, then with ether, and mixed with 100 ml. of a 20% sodium hydroxide solution. The suspension was heated under reflux for three hours and 50 ml. of toluene was added. The heating was then continued until both layers became clear (two hours). The toluene layer was separated, washed with water, and mixed with ether saturated with hydrochloric acid. The ketimine hydrochloride precipitated as a lemon colored powder; yield 57 g. (70%).

The analytical sample was prepared by recrystallizing the crude hydrochloride from an alcohol-ether mixture (1:3). It formed lemon colored microscopic crystals, m. p. 186° (dec.).

Analaysis : Calculated for $C_{28}H_{22}NCl$: C, 82.44; H, 5.44.
Found : C, 82.42 ; H, 5.46 .

2-(1-Naphthylmethyl)phenyl, 2-naphthylketimine hydrochloride.

A Grignard reagent was prepared from 7.4 g. (0.30 mole) of magnesium and 63 g. (0.30 mole) of 2-bromonaphthalene in 400 ml. of dry ether, and the mixture was heated under reflux for three hours. Almost all of the metal dissolved and a solution of 49 g. (0.20 mole) of 2-(1-naphthylmethyl)-benzonitrile in 400 ml. of dry toluene was added dropwise. The ether was then distilled and the mixture heated under reflux overnight. The hot mixture was decomposed with 50 ml. of a 20% ammonium chloride solution.

The toluene layer was decanted and the ketimine salt precipitated with concentrated hydrochloric acid. It formed yellow micro-crystals,m.p.196° (dec.); yield 70 g. (87%). To prepare the analytical sample the ketimine hydrochloride was heated under reflux for two hours with 100 ml. of a 10% sodium hydroxide solution and 100 ml. of benzene. The benzene layer was separated, washed with water and mixed with ether, saturated with hydrochloric acid. The ketimine hydrochloride precipitated as a lemon colored powder, m. p. 206° (dec.).

Analysis : Calculated for $C_{28}H_{22}NCl$: C, 82.44; H, 5.44.

Found : C, ; H, .

2-(2-Naphthylmethyl)-diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium, 12 g. (0.080 mole) of bromobenzene and a small crystal of iodine in 100 ml. of dry ether. After all the metal dissolved, the ether was replaced with a solution of 12 g. (0.050 mole) of 2-(2-naphthylmethyl)-benzonitrile in 150 ml. of dry toluene. The milky yellow solution was heated under reflux overnight and decomposed with 25 ml. of a 20% solution of ammonium chloride. The green fluorescent organic layer was decanted, the residue washed with benzene, and the combined solutions cooled to about 5°. The crude ketimine was precipitated by addition of 10 ml. of concentrated hydrochloric acid, as a deeply orange viscous oil. The oil was separated and heated briefly with concentrated ammonium hydroxide. The free imine was then extracted with ether-petroleum ether (1:1) and passed through a short (20 cm.)chromatography column packed with alumina.

A slightly yellowish-green oil resulted after the evaporation of the solvent; yield 13 g. (80%).

A small amount of the free ketimine was dissolved in ether and 50 ml. of ether saturated with hydrogen chloride was added. The ketimine hydrochloride crystallized after scratching the flask with a glass rod as a colorless powder, m.p. 180° (dec.).

Analysis : Calculated for $C_{24}H_{20}NCl$: C, 80.54; H, 5.65.
Found : C, 80.28; H, 5.82.

2-(2-Naphthylmethyl)-2'-methyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium, a crystal of iodine and 13 g. (0.080 mole) of 2-bromotoluene in 150 ml. of dry ether. The ether was then replaced with a solution of 12 g. (0.050 mole) of 2-(2-naphthylmethyl)benzonitrile in 150 ml. of dry toluene, and the mixture was heated under reflux for six hours. The red liquid was decomposed with a 20% ammonium chloride solution,and the ketimine hydrochloride was precipitated with hydrogen chloride from the organic layer. The dark yellow crystals were filtered, washed with benzene, and dried; yield 17 g. (92%).

The analytical sample was prepared by recrystallizing the crude salt three times from alcohol-acetone (1:5). It formed slightly brown large prisms, m.p. 184°(dec.).

Analysis : Calculated for $C_{25}H_{22}NCl$: C, 80.73; H, 5.98.
Found : C, 80.78; H, 5.92.

2-(2-Naphthylmethyl)-3'-methyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium, a crystal of iodine and 13 g. (0.080 mole) of 3-bromotoluene in 150 ml. of dry ether. The ether was then replaced with 12 g. (0.050 mole) of 2-(2-naphthylmethyl)benzonitrile in 120 ml. of dry toluene. The milky solution was decomposed with ammonium chloride and the ketimine hydrochloride was precipitated after addition of concentrated hydrochloric acid and scratching the walls of the flask with a glass rod for 20 minutes; yield 13 g. (70%). The analytical sample was prepared by recrystallization of the crude salt three times from alcohol-acetone (1:5). It formed slightly yellow needles, m.p. 174°(dec.).

Analysis : Calculated for $C_{25}H_{22}NCl$: C, 80.73; H, 5.98.
Found : C, 80.65; H, 6.10.

2-(2-Naphthylmethyl)-4'-methyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 1.8 g. (0.080 mole) of magnesium, a crystal of iodine and 13 g. (0.080 mole) of 4-bromotoluene in 150 ml. of dry ether. The ether was then replaced with 12 g. (0.050 mole) of 2-(2-naphthylmethyl)benzonitrile in 150 ml. of dry toluene. The milky solution was decomposed with ammonium chloride and the ketimine hydrochloride precipitated with hydrochloric acid as a dark red oil. Crystals were obtained by washing the oil with cold water; yield 10 g. (55%).

The analytical sample was prepared by recrystallizing the crude salt, three times, from alcohol-acetone (1:5). It formed slightly orange needles, m.p. 193° (dec.).

Analysis : Calculated for $C_{25}H_{22}NCl$: C, 80.73; H, 5.98.
Found : C, 80.37; H, 6.03.

2-(2-Naphthylmethyl)-2',6'-dimethyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 63 g. (0.27 mole) of 2,6-dimethyliodobenzene and 6.6 g. (0.27 mole) of magnesium in 300 ml. of dry ether. After all the metal dissolved, the ether was replaced with 36.5 g. (0.15 mole) of 2-(2-naphthylmethyl)benzonitrile in 300 ml. of dry toluene and the solution was heated under reflux overnight. The brown solution was then decomposed with 30 ml. of a 20% ammonium chloride solution. The yellow precipitate was separated and boiled for two hours with 20% hydrochloric acid. The undissolved yellow ketimine hydroiodide was separated and recrystallized from dioxane petroleum ether (1:5); m.p. 220° (dec.). An additional amount of the ketimine salt was obtained from the toluene solution by precipitation with concentrated hydrochloric acid. The combined ketimine salts were decomposed by being heated under reflux with a 20% sodium hydroxide solution, and the free imine was extracted with benzene. The ketimine hydrochloride was precipitated from the benzene layer with concentrated hydrochloric acid; yield 49 g. (85%).

The analytical sample was prepared from the crude hydrochloride by crystallization from alcohol-acetone (1:10). It formed small lemon colored prisms, m.p. 192° (dec.).

Analysis : Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.26.
Found : C, 80.81; H, 6.24.

2-Benzylphenyl,1-naphthylketimine hydrochloride.

A Grignard reagent was prepared from 7.3 g. (0.30 mole) of magnesium, a crystal of iodine and 62 g. (0.30 mole) of 1-bromonaphthalene in 200 ml. of dry ether and 100 ml. of toluene. After all the metal had dissolved, the ether was replaced with 39 g. (0.20 mole) of 2-benzylbenzonitrile in 250 ml. of dry toluene and the mixture was heated under reflux overnight. The resulting deep red solution was decomposed with ammonium chloride, the organic layer was decanted and the residue washed twice with benzene. The ketimine hydrochloride was precipitated from the combined solutions with concentrated hydrochloric acid. The resulting yellow powder was filtered, washed with ether and dried; yield 70 g.(98%).

The analytical sample was prepared from the crude salt by crystallization from chloroform-ether (1:4). It formed large yellow prisms m.p. 169°(dec.).

Analysis : Calculated for $C_{24}H_{20}NCl$: N, 3.92.
Found : N, 4.35.

2-Benzylphenyl,2-naphthylketimine hydrochloride.

A Grignard reagent was prepared from 3.7 g. (0.15 mole) of magnesium, a crystal of iodine and 32 g. (0.15 mole) of 2-bromonaphthalene in 200 ml. of dry ether. The ether was replaced with 20 g. (0.10 mole) of

2-benzylbenzonitrile in 200 ml. of dry toluene, and the solution was heated under reflux overnight. The dark brown mixture was then decomposed with ammonium chloride solution and the toluene layer was decanted. The residue was washed twice with benzene and the combined solutions mixed with 10 ml. of concentrated hydrochloric acid. The orange ketimine hydrochloride precipitated and was filtered, washed and dried; yield 30 g. (80%).

The analytical sample was prepared by decomposing the crude hydrochloride with sodium hydroxide solution, extracting the free imine with benzene, precipitating the hydrochloride from the benzene layer with ether saturated with hydrogen chloride and recrystallizing it from alcohol-ether (1:5). It formed a yellow microcrystalline powder which melted and decomposed at 197°.

Analysis : Calculated for $C_{24}H_{20}NCl$: C, 80.54; H, 5.65.
Found : C, 80.07; H, 5.38.

2-(1-Naphthylmethyl)-2',4',6'-trimethyl.diphenylketimine hydrochloride.

A Grignard reagent was prepared from 3.7 g. (0.16 mole) of magnesium, a crystal of iodine and 30 g. (0.16 mole) of bromomesitylene in 200 ml. of dry ether. The slow reaction was initiated by a small amount of ethyl magnesium iodide. After eight hours all the metal dissolved, the ether was replaced with 12 g. (0.050 mole) of 2-(1-naphthylmethyl)benzonitrile in 200 ml. of dry toluene. The milky yellow solution changed to red-brown and was heated under reflux overnight. After adding 30 ml. of a 20% ammonium chloride solution, the mixture was boiled until it cleared, the deep red, fluorescent liquid was decanted, and the residue washed with benzene. The combined solutions were mixed with 20 ml. of concentrated hydrochloric acid, and the ketimine salt crystallized after scratching the flask with a glass rod. The crystals were filtered, washed with toluene, then with acetone, and dried; yield 18 g. (88%).

The analytical sample was prepared by decomposing the crude ketimine hydrochloride with sodium hydroxide solution, extracting the free ketimine with benzene, and precipitating the hydrochloride with concentrated hydrochloric acid. Crystallization from ethanol-acetone (1:10) and chloroform-ether (1:5) gave small, colorless crystals, m.p.195° (dec.).

Analysis : Calculated for $C_{27}H_{26}NCl$: N, 3.50.
Found : N, 3.33.

2-(1-Naphthylmethyl)-2',6'-dimethylbenzophenone.

A suspension of 2.0 g. of the corresponding ketimine hydrochloride in 25 ml. of water and 10 ml. of sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for six hours. The temperature was kept at 180-185°. The tube was then cooled to about 5°, opened, and the dark brown glassy solid was separated from the acid, dissolved in benzene, washed with water and dried over calcium chloride. The dry solution was then passed through a short column packed with Fisher's Alumina, the percolate concentrated, and the resulting brown oil was crystallized from a mixture of dioxane and ethanol (1:3). Large colorless prisms were obtained, m.p. 123.5-124.0°; yield 1.4 g. (77%).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 89.47; H, 6.39.

2-(1-Naphthylmethyl)-2',4',6'-trimethylbenzophenone.

A suspension of 2.0 g. of the corresponding ketimine hydrochloride in 25 ml. of water and 10 ml. of sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for six hours. The temperature was kept at 180°. The brown glassy material was separated, dissolved in a benzene-petroleum ether(8:2) mixture, and passed through a short column packed with Fisher's Alumina. The slightly yellow oil was crystallized from ligroin (60-90°), dioxane-ethanol (1:1), and finally from acetone. Colorless crystals, m. p. 159.5°, were obtained; yield 1.4 g. (77%).

Analysis : Calculated for $C_{27}H_{24}O$: C, 88.97; H, 6.64.
Found : C, 88.64; H, 6.82.

2-(2-Naphthylmethyl)benzophenone.

A mixture of 5.0 g. of the corresponding ketimine base, 50 ml. of 25% sulfuric acid, and 20 ml. of xylene was heated under reflux for four hours. The organic layer was separated, washed with water, dried over calcium chloride and distilled under reduced pressure after removing the solvent. A yellow, green fluorescent oil was collected at 236-238° (1.3 mm.); yield 4.9 g. (98%). To remove the traces of coloring materials, the oil was dissolved in benzene-petroleum ether (1:1) and passed through a short column packed with Fisher's Alumina. A colorless, viscous oil resulted after evaporation of the solvent.

Analysis : Calculated for $C_{24}H_{18}O$: C, 89.41; H, 5.63.
Found : C, 89.14; H, 5.68.

2-(2-Naphthylmethyl)-2'-methylbenzophenone.

A mixture of 15 g. of the corresponding ketimine hydrochloride, 50 ml. of 25% sulfuric acid and 20 ml. of toluene was heated under reflux for 17 hours. The toluene layer was separated, washed thrice with water and concentrated. The resulting brown viscous oil was dissolved in hot ethanol, purified with charcoal and cooled very slowly. Two crops of yellow crystals, m.p. 96-98°, were collected; yield 12 g. (88%). Four recrystallizations from acetone-ethanol (1:5) gave colorless plates, m.p. 97.5°.

Analysis : Calculated for $C_{25}H_{20}O$: C, 89.25; H, 5.99.
Found : C, 89.24; H, 6.16.

2-(2-Naphthylmethyl)-3'-methylbenzophenone.

A mixture of 10 g. of the corresponding ketimine hydrochloride, 40 ml. of 25% sulfuric acid, and 30 ml. of toluene was heated under reflux for two hours. The mixture was worked up as in the case of the 2-isomer. The resulting oil was distilled in vacuo and the ketone was collected as a yellow, green fluorescent, viscous oil at 236-238° (1.5 mm.); yield 8.4 g. (90%).

Analysis : Calculated for $C_{25}H_{20}O$: C, 89.25; H, 5.99.
Found : C, 89.18; H, 6.15.

2-(2-Naphthylmethyl)-4'-methylbenzophenone.

A mixture of 6.4 g. of the corresponding ketimine hydrochloride, 50 ml. of 25% sulfuric acid and 30 ml. of toluene was heated under reflux for one hour. The mixture was worked up as in the case of the 2-isomer. The resulting oil was distilled in vacuo, and the ketone was collected as a yellow, green fluorescent, viscous oil at 237-240° (1.5 mm.); yield 5.0 g. (86%).

Analysis : Calculated for $C_{25}H_{20}O$: C, 89.25; H, 5.99.
Found : C, 89.18; H, 6.15.

2-(2-Naphthylmethyl)-2',3'-dimethylbenzophenone.

A Grignard reagent was prepared from 3.6 g. (0.15 mole) of magnesium, 27 g. (0.15 mole) of 2,3-dimethylbromobenzene and 250 ml. of dry ether. The ether was replaced with 24 g. (0.10 mole) of 2-(2-naphthylmethyl)benzonitrile in 250 ml. of toluene, and the mixture was heated under reflux overnight. The solution was decomposed with ammonium chloride and the ketimine hydrochloride precipitated from the toluene layer with hydrochloric acid. The crystals were separated, mixed with 150 ml. of 30% sulfuric acid and 100 ml. of toluene, and the mixture was heated under reflux for four hours. The toluene layer was separated, the solvent removed and the resulting oil was distilled in vacuo. A fraction distilling between 261-264° (1.7 mm.) was collected and again distilled under reduced pressure. The ketone was recovered as a yellow oil, b.p.240-243° (1.0 mm.); yield 27 g. (77%).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 88.92; H, 6.31.

2-(2-Naphthylmethyl)-2',4'-dimethylbenzophenone.

A Grignard reagent was prepared from 3.6 g. (0.15 mole) of magnesium, 34 g. (0.15 mole) of 2,4-dimethyliodobenzene and 300 ml. of dry ether. The ether was replaced with 24 g. (0.10 mole) of 2-(2-naphthylmethyl)benzonitrile in 300 ml. of toluene, and the mixture was heated under reflux overnight. The solution was decomposed with ammonium chloride, but some of the ketimine hydroiodide precipitated together with the magnesium salts. Therefore, 100 ml. of 30% sulfuric acid was added, and the mixture was heated under reflux for 12 hours. The toluene layer was then separated, washed, dried and distilled in vacuo. A slightly yellow viscous oil was collected at 230-233° (1 mm.); yield 19 g. (53%). The analytical sample was obtained by redistilling the ketone, b.p. 235°(1.0 mm.).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 89.29; H, 6.11.

2-(2-Naphthylmethyl)-2',5'-dimethylbenzophenone.

A Grignard reagent was prepared from 5.6 g. (0.24 mole) of magnesium, 43 g. (0.23 mole) of 2,5-dimethylbromobenzene and 250 ml. of dry ether. The ether was replaced with 37 g. (0.15 mole) of 2-(2-naphthylmethyl)benzonitrile in 250 ml. of toluene, and the mixture was heated under reflux for five hours. The solution was decomposed with ammonium chloride, and the ketimine hydrochloride precipitated from the toluene layer with hydrochloric acid. The crystals were separated, mixed with 200 ml. of 30% sulfuric acid, and 100 ml. of toluene, and the mixture was heated under reflux for seven hours. The toluene layer was separated, the solvent removed, and the resulting oil distilled in vacuo. A fraction distilling at 242° (1.2 mm.) was collected and again distilled under reduced pressure. The ketone was recovered as a yellow viscous oil, b.p. 236-238° (1.0 mm.); yield 44 g. (84%).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 89.05; H, 6.54.

2-(2-Naphthylmethyl)-2',6'-dimethylbenzophenone.

A suspension of 10 g. of the corresponding ketimine hydrochloride in 50 ml. of 40% sulfuric acid was sealed in a Carius tube and heated in a Carius furnace at 180° for eight hours. The brown solid was separated, washed and recrystallized from acetic acid as brown prisms, m.p. 84-87°; yield 6.6 g. (73%). Several recrystallizations from ethanol gave colorless prisms, m.p. 86.5-87.0°.

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 89.33; H, 6.38.

2-(2-Naphthylmethyl)-3',4'-dimethylbenzophenone.

A Grignard reagent was prepared from 3.6 g. (0.15 mole) of magnesium, 27 g. (0.15 mole) of 3,4-dimethylbromobenzene and 300 ml. of ether. The ether was replaced with 24 g. (0.10 mole) of 2-(2-naphthylmethyl)benzonitrile in 300 ml. of toluene, and the mixture was heated under reflux overnight. The solution was decomposed with ammonium chloride and the ketimine hydrochloride precipitated from the toluene layer with hydrochloric acid as a red oil. The oil was separated, mixed with 75 ml. of 30% sulfuric acid and 100 ml. of toluene, and heated under reflux for five hours. The toluene layer was separated, the solvent removed, and the resulting oil distilled in vacuo. A fraction distilling at 235-238° (1.0 mm.) was collected, and again distilled under reduced pressure. The ketone was recovered as a yellow, green fluorescent oil, b.p. 238°(1.0 mm.); yield 28 g. (80%).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 89.01; H, 6.41.

2-(2-Naphthylmethyl)-3',5'-dimethylbenzophenone.

A Grignard reagent was prepared from 2.4 g. (0.10 mole) of magnesium, 18.5 g. (0.10 mole) of 3,5-dimethylbromobenzene and 200 ml. of ether. The ether was replaced with 16 g. (0.70 mole) of 2-(2-naphthylmethyl)benzonitrile in 200 ml. of toluene, and the mixture was heated under reflux overnight. The solution was decomposed with ammonium chloride, and the ketimine hydrochloride precipitated from the toluene layer with hydrochloric acid as a red-brown oil. The oil was separated, mixed with 100 ml. of 25% sulfuric acid and 100 ml. of toluene, and heated under reflux for seven hours. The toluene layer was separated, the solvent removed, and the resulting brown mass crystallized from ethanol as colorless prisms, m.p. 124.5-125.0°; yield 19 g. (82%).

Analysis : Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33.
Found : C, 88.74; H, 6.20.

2-Benzylphenyl-1-naphthylketone.

A mixture of 10 g. of the corresponding ketimine hydrochloride, 80 ml. of 25% sulfuric acid, and 50 ml. of toluene was heated under reflux for five hours. The toluene layer was separated and distilled in vacuo. A yellow, viscous oil was collected at 215-217° (0.8 mm.); yield 10 g. (76%).

Analysis: Calculated for $C_{24}H_{18}O$: C, 89.41; H, 5.63.
Found : C, 89.35; H, 5.45.

2-Benzylphenyl-2-naphthylketone.

A mixture of 10 g. of the corresponding ketimine hydrochloride and 50 ml. of 40% sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for five hours at 180°. The brown oil was separated and distilled in vacuo. A fraction distilling at 233-234° (1.5 mm.) was collected and crystallized from ethanol as colorless crystals, m.p. 83°; yield 7.7 g. (85%).

Analysis : Calculated for $C_{24}H_{18}O$: C, 89.41; H, 5.63.
Found : C, 89.30; H, 5.66.

2-(1-Naphthylmethyl)phenyl-1-naphthylketone.

A mixture of 10 g. of the corresponding ketimine hydrochloride and 50 ml. of 40% sulfuric acid was sealed in a Carius tube and heated in a Carius furnace for five hours at 180°. The brown oil was separated and distilled in vacuo. A fraction distilling at 285-287° (1.5 mm.) was collected, dissolved in benzene and passed through a column packed with Fisher's Alumina. The ketone was recovered after evaporation of the solvent as a slightly brown, viscous oil; yield 7.1 g. (78%).

Analysis : Calculated for $C_{28}H_{20}O$: C, 90.30; H, 5.41.
Found : C, 90.15; H, 5.43.

2-(1-Naphthylmethyl)phenyl-2-naphthylketone.

A mixture of 25 g. of the corresponding ketimine hydrochloride and 70 ml. of 40% sulfuric acid was sealed in a Carius tube and heated in a Carius furnace at 180° for six hours. The brown solid which separated on top of the mixture was separated, dissolved in benzene and the benzene solution washed with water and dried. The solvent was evaporated and the brown solid fractionated under reduced pressure. A fraction boiling between 277-279° (1.0 mm.) was collected; yield 21 g. (97%). Crystallization from ethanol gave colorless prisms, m.p. 99-100°.

Analysis : Calculated for $C_{28}H_{20}O$: C, 90.30; H, 5.41.
Found : C, 89.98; H, 5.17.

10-Phenyl-1,2-benzanthracene.

A. A Carius tube was flushed with nitrogen and 2.0 g. of the corresponding ketimine hydrochloride was carefully placed on the bottom. The tube was sealed and heated in a Carius furnace at 300° for nine hours. The brown solid was extracted with benzene and the insoluble residue (ammonium chloride) was dissolved in water and tested for NH_4^+ and Cl^-. The benzene extract was chromatographed on alumina with petroleum ether, the percolate concentrated, and the resulting reddish crystals resublimed twice in vacuo. White micro-crystals of the hydrocarbon resulted, m.p. 182.5-183.0° (lit.(13) m.p. 183-184°); yield 0.60 g. (35%).

B. The same experiment was repeated with the corresponding ketone. No reaction was observed and the ketone was recovered.

C. A mixture of 1.5 g. of the corresponding ketone and 25 g. of Fisher's Alumina was heated in vacuo (1.0 mm.) to 240-250° for one hour. The yellow powder was transferred into a chromatography column and the two hydrocarbon fractions were eluted with benzene-petroleum ether mixture (1:5). The first was a very small quantity of 9-(1-naphthyl)anthracene (about 0.01 g.), and the second was 10-phenyl-1,2-benzanthracene; yield 1.4 g. (99%). A small amount of a yellow substance which was firmly adsorbed by the alumina was not eluted. The 10-phenyl-1,2-benzanthracene forms a molecular compound with 2,4,7-trinitrofluorenone which can be recrystallized from hot ethanol. It was isolated as deep red micro-crystals, m.p. 193-194°.

10-(2'-Methylphenyl)-1,2-benzanthracene.

A. A mixture of 1.0 g. of the corresponding ketone, 45 ml. of 99.5% acetic acid and 150 ml. of 48% hydrobromic acid was heated under reflux for 21 hours. The black oil which separated on top of the solution was separated, purified with charcoal, and dissolved in ethanol. After seeding it with a tiny crystal of the hydrocarbon (see B.), 0.02 g. of the hydrocarbon was obtained; m.p. 130-132°.

B. A mixture of 1.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for 18 hours at 170°. The brown oil was separated and crystallized from ethanol. The hydrocarbon formed colorless plates, m.p. 131.5-132.0°; yield 0.70 g. (74%).

C. A mixture of 1.5 g. of the ketone and 25 g. of Fisher's Alumina was heated to 240-250° for one hour. The pressure was maintained at 1.0 mm. The hydrocarbon was eluted from the mixture on a column with benzene-petroleum ether mixture (1:2), m.p. 131.5-132.5°; yield 1.2 g. (82%).

Analysis : Calculated for $C_{25}H_{18}$: C, 94.30; H, 5.70.
Found : C, 94.57; H, 5.60.

10-(3'-Methylphenyl)-1,2-benzanthracene.

A. A mixture of 3.0 g. of the corresponding ketimine hydrochloride, 15 ml. of 48% hydrobromic acid and 30 ml. of acetic acid was sealed in a Carius tube and heated in a Carius furnace for two hours at 180°.

The brown oil was separated and chromatographed, using Fisher's Alumina as adsorbent and ether-petroleum ether (2:8) as solvent. White, silky micro-crystals, m.p. 109-110°, were obtained; yield 2.3 g. (88%).

B. A mixture of 1.5 g. of the corresponding ketone and 25 g. of Fisher's Alumina was heated under reduced pressure (1.0 mm.) to 240-250° for one hour. The hydrocarbon was eluted on a column with benzene-petroleum ether mixture (1:5); yield 1.3 g. (92%).

Analysis : Calculated for $C_{25}H_{18}$: C, 94.30; H, 5.70.
Found : C, 94.49; H, 5.73.

10-(4'-Methylphenyl)-1,2-benzanthracene.

A mixture of 1.5 g. of the corresponding ketone and 25 g. of Fisher's Alumina was heated in vacuo (1.0 mm.) for one hour at 240-250°. The yellow powder was transferred into a chromatography column and the hydrocarbon was eluted from the mixture with benzene-petroleum ether (1:5); m.p. 121-122° (lit. (6), m.p. 121-122°); yield 1.35 g. (96%).

Attempted Synthesis of 10-(2',3'-Dimethylphenyl)-1,2-benzanthracene.

A Carius tube was flushed with nitrogen and about 2.0 g. of the slightly moist corresponding ketimine hydrochloride was placed inside; the tube was sealed and heated in a Carius furnace at 300° for nine hours. The ammonium chloride crystals which appeared in the tube were extracted with water and tested for NH_4^+ and Cl^-. The residue was chromatographed on alumina using petroleum ether as a solvent. Only about 0.03 g. of some unidentified blue fluorescent material was recovered. As a second fraction (ether used as a solvent) 1.2 g. of the corresponding ketone, m.p. 71.5-72.5°, was obtained.

10-(2',6'-Dimethylphenyl)-1,2-benzanthracene.

A. A mixture of 2.0 g. of the corresponding ketimine hydrochloride, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace for 46 hours at 180°. The mixture was then diluted with water and extracted with benzene. The extract was washed with water, dried over calcium chloride, and chromatographed. The first fraction, eluted by ether-petroleum ether (3:7) yielded 0.40 g.(30%) of 1,2-benzanthracene, m.p. 157-158°. The second fraction (0.20 g.) was an unidentified deep red solid. The expected hydrocarbon could not be isolated.

B. The same reaction was carried out with 2.0 g. of the corresponding ketone. The first fraction, eluted with petroleum ether, gave thin colorless plates, m.p. 155-157°, which were identified as 1,2-benzanthracene; yield 0.70 g. (54%). The second fraction, eluted with benzene-petroleum ether (7:3) yielded 0.60 g. of a deep red oil which crystallized in almost black, small needles from acetone-ethanol (2:1), m.p. over 300° (dec.).

C. A mixture of 1.5 g. of the corresponding ketone with 30 g. of Fisher's Alumina was heated at 240-270° for three hours.The pressure was maintained at 1.0 mm. The hydrocarbon was recovered by chromatography as colorless crystals, m.p. 134.5-135.5°; yield 0.66 g. (46%).

Analysis : Calculated for $C_{26}H_{20}$: C, 93.93; H, 6.07.

Found : C, 93.57; H, 6.07.

10-(2',4',6'-Trimethylphenyl)-1,2-benzanthracene.

A. Attempted thermal cyclization. A Carius tube was swept with nitrogen and 4.0 g. of the corresponding ketimine hydrochloride was placed inside. The tube was sealed and heated at 300° for 20 hours. The black material was dissolved in benzene and chromatographed. Several red zones developed on the column, but no blue fluorescent colorless material could be recovered.

B. A mixture of 4.0 g. of the corresponding ketimine hydrochloride, 30 ml. of acetic acid and 15 ml. of 49% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace at 220° for six hours. The mixture was extracted with benzene and chromatographed. The first fraction, eluted with petroleum ether, yielded 0.85 g. (37%) of 1,2-benzanthracene, m.p. 157-158°. The second fraction, eluted with ether-petroleum ether (2:8), gave 1.4 g. of unidentified red oil. Several other fractions were not eluted.

C. A mixture of 2.0 g. of the corresponding ketone and 15 g. of Fisher's Alumina was heated at 240-250° under reduced pressure (0.5 mm.) for two hours. The hydrocarbon was recovered by chromatography, using petroleum ether as solvent. It formed colorless crystals, m.p.144.5-145.5°;

yield 1.5 g. (83%).

Analysis : Calculated for $C_{27}H_{22}$: C, 93.61; H, 6.39.

Found : C, 93.29; H, 6.70.

9-Phenyl-1,2-benzanthracene.

A. A mixture of 2.0 g. of the corresponding ketone, 30 ml. of acetic acid, and 15 ml. of 48% hydrobromic acid was heated under reflux for five hours. The mixture was extracted with benzene, the extract washed, dried and concentrated to 10 ml. volume. The solution was then poured in a column, packed with alumina. Two distinct zones appeared on the column, the lower one being colorless with a strong blue fluorescence, the upper one deeply yellow with a strong green fluorescence. The colorless substance, m.p. 153-154°, was identified as 9-phenyl-1,2-benzanthracene (lit.(8) m.p. 154-155°), and could be only partially separated from the yellow impurity when petroleum ether was used as solvent. Both fractions were eluted with petroleum ether, the solvent removed, and the glassy solid dissolved in 30 ml. of benzene. To the hot solution 0.3 g. of maleic anhydride was added, and the mixture was heated under reflux for three hours. About 20 ml. of a concentrated sodium hydroxide solution was then added, whereupon the yellow color disappeared. The benzene layer was separated, washed and the pure benzanthracene derivative isolated after evaporation of the solvent; yield 1.8 g.(96%). The hydrocarbon was sparingly soluble in concentrated sulfuric acid; the rosy solution turned brown after standing.

B. A mixture of 2.0 g. of the corresponding ketone and 25 g. of Fisher's Alumina was heated to 250-270° under reduced pressure (1.5 mm.) for 50 minutes. The hydrocarbon, mixed with a small amount of yellow impurity, was recovered by chromatography; yield 1.4 g. (74%).

9-(2'-Methylphenyl)-1,2-benzanthracene.

A. A mixture of 1.0 g. of the corresponding ketone, 30 ml. of acetic acid, and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for seven hours. The mixture was extracted with benzene and chromatographed on alumina. The hydrocarbon formed the first colorless fraction which was eluted with petroleum ether; yield 0.61 g. (65%). Several crystallizations from acetone-ethanol (1:5) gave colorless needles, m.p. 102.5-103.5°; it was soluble in concentrated sulfuric acid with a light violet color which changed to blue after standing. The second fraction, eluted with benzene-petroleum ether (1:4) was 0.15 g. of an unidentified yellow solid with a strong green fluorescence. The third fraction, eluted with benzene, was 0.15 g. of an unidentified deep violet solid. The remaining fractions were not eluted.

B. A mixture of 1.0 g. of the corresponding ketone and 30 g. of Fisher's Alumina was heated at 240-270° under reduced pressure (1.5 mm.) for two hours. Chromatography with benzene-petroleum ether (1:9) gave 0.40 g. (42%) of the hydrocarbon, m.p. 96-101°. The second fraction was 0.50 g. of an unidentified orange oil with a strong green fluorescence.

The remaining fractions were not eluted.

Analysis : Calculated for $C_{25}H_{18}$: C, 94.30; H, 5.70.

Found : C, 94.01; H, 5.67.

9-(3'-Methylphenyl)-1,2-benzanthracene.

A. A mixture of 1.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for three hours. The mixture was extracted with benzene and chromatographed on alumina. The hydrocarbon formed the first colorless fraction which was eluted with petroleum ether. Crystallization from acetone-ethanol (1:5) gave colorless, silky needles, soluble in sulfuric acid with a light pink color which changed to brown after standing, m.p. 131.5-132.5°; yield 0.90 g. (95%). The second fraction, eluted with benzene-petroleum ether (1:4) was 0.010 g. of an unidentified yellow solid with a strong green fluorescence. The third fraction, eluted with benzene-petroleum ether (3:7) was 0.050 g. of an unidentified purple solid.

B. A mixture of 1.0 g. of the corresponding ketone and 30 g. of Fisher's Alumina was heated at 240-250° under reduced pressure (1.2 mm.) for two hours. The yellow powder was chromatographed. The first fraction, eluted with petroleum ether, yielded 0.65 g. of the hydrocarbon, m.p. 130-132°. The second fraction, eluted with benzene-petroleum ether (3:7), gave a deeply yellow, glassy solid with an intensely green fluorescence, from which an additional 0.10 g. of the colorless hydrocarbon was isolated.

The remaining yellow compound changed to orange during the recovery of the hydrocarbon and could not be identified. The total yield of the hydrocarbon was 0.75 g. (80%).

Analysis : Calculated for $C_{25}H_{18}$: C, 94.30; H, 5.70.
Found : C, 93.93; H, 5.66.

9-(4'-Methylphenyl)-1,2-benzanthracene.

A mixture of 0.40 g. of the corresponding ketone, 26 ml. of acetic acid and 13 ml. of 48% hydrobromic acid was heated under reflux for 30 minutes. The red solid was separated and chromatographed. The first fraction, eluted with benzene-petroleum ether (1:9), gave, after crystallization from ethanol,0.25 g. of colorless long prisms,m.p. 115.5-116.5°. The second fraction was a deeply yellow oil which when dissolved in ethanol gave an additional 0.070 g. of the colorless hydrocarbon, and a small quantity of an unidentified yellow material. The total yield of the benzanthracene was 0.32 g. (85%). This hydrocarbon formed a dark red molecular compound with 2,4,7-trinitrofluorenone, m.p. 144-145°, which was prepared in the following way. Equal quantities (0.050 g.) of the hydrocarbon and 2,4,7-trinitrofluorenone were dissolved in 5 ml. of hot benzene (red solution), most of the solvent was evaporated and 10 ml. of ethanol was slowly added. Almost black, small needles formed when the solution was boiled.

Analysis : Calculated for $C_{25}H_{18}$: C, 94.30; H, 5.70.
Found : C, 94.58; H, 5.41.

9-(2',3'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of 4.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube, and heated at 180° in a Carius furnace for five hours. The mixture was extracted with benzene and chromatographed on alumina. The first colorless fraction, eluted with petroleum ether, gave 1.3 g. (34%) of colorless plates, m. p. 152-153°. The second fraction, eluted with benzene-petroleum ether (1:6) was 0.30 g. of an unidentified yellow solid with a strong green fluorescence. The third fraction, eluted with benzene, was 1.95 g. of an unidentified red solid.

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.06.
Found : C, 93.94; H, 6.14.

9-(2',4'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of 1.5 g. of the corresponding ketone and 30 g. of Fisher's Alumina was heated at 240-270° under reduced pressure (1.0 mm.) for 90 minutes and chromatographed on alumina. The first fraction, eluted with benzene-petroleum ether (1:5) gave 1.2 g. of a yellow solid which was dissolved in 10 ml. of benzene and mixed with a solution of 0.5 g. of maleic anhydride in 10 ml. of benzene. The mixture was then heated under reflux for three hours and mixed with 10 ml. of a 20% solution of sodium hydroxide. The yellow color disappeared and the benzene layer was separated, washed several times with water and dried over calcium chloride. After evaporating the solvent, 1.1 g. (75%) of a colorless, glassy solid, m.p. 59-65°, remained. All attempts to crystallize the hydrocarbon failed.

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.06.
Found : C, 93.61; H, 6.30.

9-(2',5'-Dimethylphenyl)-1,2-benzanthracene.

A. A mixture of 4.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for five hours. The mixture was extracted with benzene and chromatographed on alumina. The first fraction, eluted with petroleum ether, yielded 1.3 g. (34%) of a colorless glassy solid which resisted all attempts for crystallization. The second fraction, eluted with benzene-petroleum ether (1:7), gave 0.60 g. of intensely yellow, green fluorescent, glassy, unidentified material. The third, deeply red zone, was not eluted.

B. A mixture of 1.5 g. of the ketone and 25 g. of Fisher's Alumina was heated to 240-270° for two hours under reduced pressure (1.0 mm.). The yellow powder was chromatographed. The first fraction, eluted with petroleum ether, gave 0.66 g. (46%) of a colorless glassy solid, m.p. 65-70°, soluble in concentrated sulfuric acid with a weak red color. All attempts for crystallization failed. The second fraction, eluted with benzene-petroleum ether (1:4) yielded 0.60 g. of an unidentified yellow, green fluorescent glassy solid. The remaining yellow zones were not eluted.

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.06.
Found : C, 93.46; H, 6.28.

9-(2',6'-Dimethylphenyl)-1,2-benzanthracene.

A. A mixture of 2.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for 21 hours. The black mixture was extracted with benzene and chromatographed on alumina. The first fraction, eluted with petroleum ether, gave 0.63 g. (49%) of colorless plates of 1,2-benzanthracene, m.p. 158°. The second fraction, eluted with benzene-petroleum ether (1:4), yielded 0.50 g. of an unidentified brown solid. The third, deeply red zone, was not eluted.

B. A mixture of 1.0 g. of the ketone and 25 g. of alumina was heated under reduced pressure (1-2 mm.) for one to two hours. The yellow powder was then chromatographed, using benzene-petroleum ether (1:4) as a solvent, and the fluorescent fraction was collected. The results, obtained by varying the type of alumina, temperature and length of time, are tabulated below (Table I). The yield refers to the fluorescent (non-homogeneous) fraction.

TABLE I

Alumina	T°C	Time hrs.	Yield %
Fisher	220	2	14
Fisher	240-250	2	23
Fisher	240-270	2	29
Fisher	260-280	2	27
Fisher	280-300	1	10
* Florisil	260-290	2	2
Woelm, basic	240-280	2	34
Woelm, basic	270-280	2	27
Woelm, non-alkaline	280	2	29
Woelm, non-alkaline	280-300	2	16
Woelm, acid	240-280	1.5	4
Woelm, acid	260-280	2	15

* Florisil is a complex magnesium silicate of the following composition: MgO, 15.5 ± 0.5%; SiO_2, 84.0 ± 0.5%; Na_2SO_4, 0.5 ± 1.0%; pH = 8.4-8.5 (water suspension).

The yellow fluorescent fraction was chromatographed on alumina, and the colorless, blue fluorescent zone eluted with petroleum ether. Crystallization from ethanol first gave colorless prisms, m.p. 193-200°, insoluble in concentrated sulfuric acid, which were spectroscopically proven not to be the expected benzanthracene derivative. The analysis corresponds well to a dihydro-9-(2',6'-dimethylphenyl)-1,2-benzanthracene.

Calculated for $C_{26}H_{22}$: C, 93.37; H, 6.63.

Found : C, 93.47; H, 6.56.

The second product of crystallization was colorless plates, m.p. 123.5°, soluble in concentrated sulfuric acid with a red color which changed to blue and then to brown. The spectroscopic evidence and analysis indicated that this was the expected hydrocarbon.

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.06.

Found : C, 94.00; H, 6.25.

The remaining fractions could not be identified. The yield of the expected hydrocarbon was in the best case about 6%.

9-(3',4'-Dimethylphenyl)-1,2-benzanthracene.

A. A mixture of 2.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace at 180° for five hours. The mixture was extracted with benzene and distilled in vacuo. A fraction distilling between 253-255° (1.1 mm.), was collected and chromatographed on alumina. The first fraction, eluted with petroleum ether, was crystallized from ethanol. Two colorless polymorphic forms were obtained, m.p. 142-143° and 120-120.5°; combined yield 1.24 g. (65%). The higher melting form was less soluble in ethanol, acetone and ether than the lower melting one, and was preferentially formed from very concentrated, warm solutions. Both forms yielded a red solution with concentrated sulfuric acid; it turned greenish brown after long standing. The second, red fraction from the column, eluted with benzene, was combined with the second fraction from the distillation, b.p. 255-260° (0.9 mm.), and dissolved in ethanol. Unidentified deeply red crystals grew from the solution, m.p. 270-274° (dec.); yield 0.10 g.

B. A mixture of 1.5 g. of the ketone and 30 g. of Fisher's Alumina was heated at 240-270° for two hours under reduced pressure (1.2 mm.) and chromatographed. The first fraction, eluted with petroleum ether, gave 1.0 g. of a yellow solid which after recrystallization from ethanol yielded 0.97 g. (68%) of colorless crystals, m.p. 142-143°. The remaining yellow fractions were not eluted.

C. The above reaction was repeated, using Florisil instead of Fisher's Alumina. The mixture turned deeply red and was chromatographed on alumina using petroleum ether as a solvent; yield 0.39 g. (27%) of the expected hydrocarbon. The second fraction, eluted with benzene-petroleum ether (1:4) gave 0.02 g. of an unidentified yellow material. The third fraction, eluted with benzene, gave 0.62 g. of a deeply red solid, which after crystallization from ethanol yielded 0.21 g. of unidentified red crystals, m.p. 274-276° (dec.).

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.06.

Found : C, 93.72; H, 6.08.

9-(3',5'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of 2.0 g. of the corresponding ketone, 20 ml. of acetic acid and 10 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace at 180° for four hours. The mixture was extracted with benzene and chromatographed on alumina. The first fraction, eluted with petroleum ether, yielded 1.5 g. (79%) of colorless crystals, m.p. 230°. The second fraction, eluted with benzene-petroleum ether (1:4), gave 0.10 g. of unidentified yellow material. The third fraction, eluted with benzene, gave 0.25 g. of unidentified, deeply red material.

Analysis : Calculated for $C_{26}H_{20}$: C,93.94; H, 6.06.

Found : C,93.69; H, 6.07.

9-(1-Naphthyl)anthracene.

A. A mixture of 4.0 g. of the corresponding ketimine hydrochloride, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated in a Carius furnace at 200° for three hours. The mixture was extracted with benzene and chromatographed on alumina. The first fraction was 0.30 g. of naphthalene, the second fraction was 0,20 g. of unidentified bluish plates which melted and sublimed from 152° up; the analysis checked well with a calculated value for a dihydronaphthylanthracene.

Analysis : Calculated for $C_{24}H_{18}$: C, 94.07; H, 5.93.
Found : C, 94.02; H, 5.96.

The third fraction was 1.1 g. (32%) of the expected anthracene derivative. It formed colorless prisms, m.p. 160-161°, which dissolved in concentrated sulfuric acid with an intensely yellowish-green color. All these fractions were eluted with petroleum ether. The fourth fraction, eluted with benzene, yielded 0.90 g. (27%) of 10-phenyl-1,2-benzanthracene, m.p. 182-183°. Further fluorescent fractions were not eluted.

B. The same experiment was repeated with the corresponding ketone. Identical by-products were obtained. The yields of the two isomeric hydrocarbons, naphthylanthracene and phenylbenzanthracene were 45% and 36% respectively.

C. A mixture of 5.1 g. (0.020 mole) of 9-bromoanthracene, a crystal of iodine, 4.1 g. (0.020 mole) of 1-bromonaphthalene and 150 ml. of ligroin (b.p. 90-110°) was added to 1.0 g. (0.040 mole) of magnesium and heated under reflux for 70 hours. Since no reaction was observed, the ligroin was replaced with ether. After 30 hours of reflux almost all the metal dissolved and the mixture was decomposed with ammonium chloride. Only anthracene and naphthalene were recovered from the ethereal solution.

D. A mixture of 3.0 g. of the ketone and 20 g. of Fisher's Alumina was heated to 240-270° (1.0 mm.) for 2½ hours. The hydrocarbons were eluted with benzene and chromatographed on alumina. The first fraction, eluted with petroleum ether, yielded 0.10 g.(4%) of the naphthylanthracene, m.p. 157-158°. The second fraction, eluted with petroleum ether, gave 1.4 g. (49%) of the phenylbenzanthracene, m.p. 182-183°. Further fluorescent fractions were not eluted.

Analysis : Calculated for $C_{24}H_{16}$: C, 94.70; H, 5.30.
Found : C, 94.23; H, 5.36.

9-(2-Naphthyl)-anthracene.

A mixture of 1.5 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was heated under reflux for 15 hours. The hydrocarbon was extracted with benzene and crystallized from ethanol. It formed small, colorless leaflets, soluble in concentrated sulfuric acid with a green color, which changed to brown after a few hours, m.p. 200°; yield 1.26 g. (89%).

Analysis : Calculated for $C_{24}H_{16}$: C, 94.70; H, 5.30.
Found : C, 94.26; H, 5.43.

10-(1-Naphthyl)-1,2-benzanthracene .

A mixture of 2.0 g. of the corresponding ketone, 30 ml. of glacial acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for eight hours. The black solid was separated, dissolved in benzene, washed with water and concentrated to a 10 ml. volume. The concentrate was poured in a column packed with alumina, and eluted with benzene-petroleum ether (1:5). The percolate was concentrated and the hydrocarbon crystallized as colorless micro-crystals, m. p. 186°; yield 1.3 g. (68%). After four recrystallizations from benzene-ethanol (1:3), colorless crystals were obtained, m. p. 190°.

Analysis : Calculated for $C_{28}H_{18}$: C, 94.87; H, 5.13.
Found : C, 94.80 ; H, 5.24 .

10-(2-Naphthyl)-1,2-benzanthracene.

A. A mixture of 2.0 g. of the corresponding ketone, 40 ml. of acetic acid and 20 ml. of hydrobromic acid was heated under reflux for 12 hours. The white, crystalline solid which formed in the flask was separated and recrystallized from a mixture of benzene, acetone and ethanol (1:4:6). Slightly yellow micro-crystals possessing a strong green fluorescence were obtained, m. p. 172-173°; yield 1.7 g. (88%). Six recrystallizations from benzene-ethanol (1:10) gave colorless micro-crystals possessing a strong blue fluorescence, m. p. 174-175°. The mother liquor from the crystallizations contained a very small amount of an unidentified purple by-product.

B. A mixture of 2.0 g. of the corresponding ketone, 30 ml. of acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a Carius tube and heated at 180° in a Carius furnace for six hours. The black solid was separated, dissolved in a small quantity of benzene and poured in a column packed with alumina. The first fraction was eluted with benzene-petroleum ether (1:3). It formed, after evaporation of the solvent, a yellowish green solid with a strong green fluorescence, weight 1.82 g. Crystallization from benzene-ethanol (1:5) gave 1.8 g. (95%) of slightly yellow crystals, m.p. 172-174°. Three recrystallizations from the same solvent yielded colorless micro-crystals, m.p. 174-175°, possessing a strong blue fluorescence. The small quantity (about 0.020 g.) of the yellow, green fluorescent material could not be crystallized and identified. The second fraction was eluted with benzene. Crystallization of the deeply violet concentrate from ethanol gave a very small quantity of almost black micro-crystals, m. p. 184° (dec.). The nature of this compound was not investigated.

Analysis : Calculated for $C_{28}H_{18}$: C, 94.87; H, 5.13.
Found : C, 94.67; H, 5.23.

Catalytic Cyclization of 2-Methylbenzophenone.

A mixture of 5.0 g. of the ketone and 35 g. of Fisher's Alumina was heated at 200-250° under reflux for one hour. The pressure was kept at about 5 mm. The first fraction, eluted with petroleum ether, yielded 0.10 g. (2%) of anthracene, m.p. 211-213°. Several other colored fractions were collected, but no further amount of anthracene was recovered.

Catalytic Cyclization of 2-Naphthyl-1-tolylketone.

A mixture of 1.0 g. of the ketone and 30 g. of Fisher's Alumina was heated at 240° for one hour under reduced pressure (1.0 mm.). Only a trace of a fluorescent material was recovered by chromatography.

9-Cyclohexylanthracene.

A mixture of 8.0 g. of the ketone and 60 g. of Fisher's Alumina was heated at 250-280° for three hours under reduced pressure (20 mm.). The mixture was extracted with benzene and distilled in vacuo. A fraction, consisting of a mixture of both the unreacted ketone and the hydrocarbon distilling between 170-180° (2.0 mm.) was collected and mixed with 50 ml. of benzene and 4.0 g. of picric acid. The red picrate, m. p. 156° (lit. (13), m. p. 156-157°) crystallized from the solution, was separated and passed through a short column packed with alumina. The hydrocarbon was crystallized from ethanol in colorless prisms, m. p. 135-136° (lit. (52), m. p. 135-136°); yield 3.3 g. (44%).

Attempted Dehydrogenation of 9-(1-Naphthyl)-anthracene.

A. A mixture of 0.50 g. of the hydrocarbon, 4.0 g. of aluminum chloride, 4.0 g. of zinc chloride and a drop of pyridine was heated in a small beaker for ten minutes and decomposed with dilute hydrochloric acid. The black residue was extracted with benzene and chromatographed on alumina. Only 0.10 g. of anthracene and 0.10 g. of other noncrystalline products were isolated.

B. A mixture of 1.0 g. of the hydrocarbon and 1.5 g. of powdered selenium was heated in a test tube immersed in a metal bath for 30 hours. The temperature of the metal bath was maintained at 330°. The mixture was extracted with benzene and chromatographed on alumina. Only a very narrow red stripe appeared on the column, but it could not be isolated and identified. Most of the original hydrocarbon was recovered.

C. A mixture of 0.70 g. of the hydrocarbon, 70 ml. of benzene and 5.0 g. of aluminum chloride was heated under reflux for 70 minutes. After decomposing the mixture with dilute hydrochloric acid, the black mass was extracted with benzene and chromatographed on alumina. Four fluorescent fractions were eluted, but none of them corresponded to the expected dibenzpyrene.

Attempted Dehydrogenation of 9-Phenyl-1,2-benzanthracene.

A mixture of 0.50 g. of 9-phenyl-1,2-benzanthracene, 0.10 g. of a 10% platinum asbestos and 35 ml. of xylene was heated under reflux for five hours. Since no yellow coloration was observed (the expected dibenzpyrene is yellow), the solvent was evaporated and the mixture heated at 310° for two hours. The phenylbenzanthracene was recovered unchanged from the mixture.

RECOMMENDATIONS FOR FUTURE WORK

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1. The cyclodehydration of ketones by means of alumina which was discovered in the course of this work should be further explored from the following aspects:
    a) The application to other ketones, mainly in the benzylbenzophenone series.
    b) The nature of the by-products.
    c) The use of materials other than alumina.
    d) The mechanism of the reaction.
2. Some of the hydrocarbons prepared in this work could possibly be cyclodehydrogenated to hitherto unknown higher condensed systems. This concerns mainly the 9-phenyl-1,2-benzanthracene derivatives and the naphthylanthracenes and benzanthracenes.
3. The nature of the deeply colored by-products resulting from acid cyclization of the dimethyl substituted ketones in the 10-phenyl and 10-naphthyl-1,2-benzanthracene series and all the 9-substituted benzanthracene series should be investigated.
4. The resolution of the optical antipodes mentioned in the second part of this thesis should be attempted. It is suggested that the methyl derivatives be oxidized with selenium dioxide or other selective oxidizing agent to the corresponding acid which probably could be easy to resolve.

5. The by-products resulting from the synthesis of the (1- and 2-naphthylmethyl)chlorobenzene could be identified, converted to the nitriles and utilized for a synthesis of some angular polycyclic hydrocarbons.
6. The rates of cyclization of some of the simple 9- and 10-substituted 1,2-benzanthracenes should be measured, compared and the results used to substantiate the reaction mechanism.

SUMMARY

SUMMARY

1. The acid catalyzed cyclodehydration method was extended to the 9-aryl-1,2-benzanthracene and 9-naphthylanthracene series.

2. A new method of cyclodehydration was described.

3. The series of 10-mono- and 10-dimethylphenyl-1,2-benzanthracenes was completed. All the isomeric 9-mono- and 9-dimethylphenyl-1,2-benzanthracenes were prepared together with the corresponding ketones. Some highly hindered ketones were prepared and their cyclization realized. A total of 47 compounds, not previously reported in the literature, were synthesized.

4. The spectra of 24 hydrocarbons were recorded and the theory of nonplanarity of these compounds substantiated.

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VITA

VITA

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"The Preparation of Some 10-Dimethylphenyl-1,2-benzanthracenes", F. A. Vingiello, A. B. Borkovec, presented before the Chemistry Section of the Virginia Academy of Science, May 1953, Lexington, Virginia.

"A Study of the Reactions Between o-Chlorobenzylchloride and Naphthalene", F. A. Vingiello, A. B. Borkovec, presented before the

Chemistry Section of the Virginia Academy of Science, May 1954, Charlottesville, Virginia.

"The Synthesis of 10-Phenyl-1,2-benzanthracene and the Three Isomeric 10-Monomethylphenyl-1,2-benzanthracenes", F. A. Vingiello, A. B. Borkovec, J. Shulman, presented before the Division of Organic Chemistry of the American Chemical Society, September 1954,New York,N.Y.

"The Synthesis of the Six Isomeric 10-Dimethylphenyl-1,2-benzanthracenes", F. A. Vingiello, A. B. Borkovec, presented before the Division of Organic Chemistry of the American Chemical Society,October 1954, Birmingham, Alabama.

"The Synthesis of 9-Phenyl-1,2-benzanthracene and the Three Isomeric 9-Monomethylphenyl-1,2-benzanthracenes", F. A. Vingiello, A. B. Borkovec, presented before the Division of Organic Chemistry of the American Chemical Society, April 1955, Cincinnati, Ohio.

"Chromatographic Separation of Complex Polynuclear Hydrocarbon Mixture ", F. A. Vingiello, A. B. Borkovec, presented before the Chemistry Section of the Virginia Academy of Science, May 1955, Harrisonburg, Virginia.

"The Synthesis of 10-Phenyl-1,2-benzanthracene and the Three Isomeric 10-Methylphenyl-1,2-benzanthracenes", F. A. Vingiello, A. B. Borkovec, J. Shulman, J. Am. Chem. Soc. (in press).

"The Synthesis of the Six Isomeric 10-Dimethylphenyl-1,2-benzanthracenes, F. A. Vingiello, A. B. Borkovec, J. A. Chem. Soc.(in press).

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APPENDICES

EXPLANATION OF TABLES

The first group of tables (I to VI) comprises all the ketimines, ketones and hydrocarbons in the 9- and 10-phenyl-1,2-benzanthracene series and is intended to help in the location of a particular compound pertaining to this series. In the Reference Column, the plain number gives the reference as listed in this thesis (section literature) and the number in parentheses gives the page of the reference. TT refers to this thesis.

The second group of tables (VII - VIII) contains the adsorption maxima of all the investigated hydrocarbons. The number in the CH column refers to the hydrocarbons in tables I to VI, so that for example, CH 2 is the 10-(2'-methylphenyl)-1,2-benzanthracene, etc. A Beckman Spectrophotometer Model DU with 1 cm. quartz cells was used in this investigation. The concentration of the samples was 10 mg. per liter of 95% ethanol.

The third group of tables (IX to XI) deserves some more detailed explanation :

The table IX shows the spectra of the three related hydrocarbons: 1,2-benzanthracene, 9- and 10-phenyl-1,2-benzanthracene. The similarity of the spectral pattern and the shift in the positions of the adsorption peaks is clearly visible.

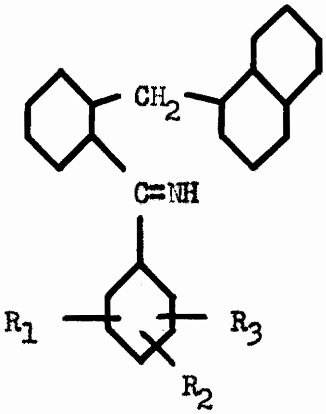
The table X shows a particular case of the two hydrocarbon products resulting from the alumina cyclization of 2-(2-naphthylmethyl)-2',6'-dimethylbenzophenone. The spectral pattern of the hydrocarbon CH I (9-(2',6'-dimethylphenyl)-1,2-benzanthracene) is clearly identical with the spectrum of 9-phenyl-1,2-benzanthracene. The spectral pattern of the hydrocarbon CH II (unknown by-product) shows a definite difference from the parent compound, although most of the adsorption peaks are maintained to a certain extent. It was suggested that this compound might be a dihydroderivative of CH I, but the spectral evidence, however satisfactory in deciding the structure of CH I, cannot be considered as sufficient to propose a significant structure for CH II.

The table XI shows the relationship between anthracene, 9-(1-naphthyl)- and 9-(2-naphthyl)anthracene. The similarity of these three spectral patterns is again highly significant. It can be recalled that both of the reactions leading to the two naphthyl-anthracenes could also yield benzanthracene derivatives (Elbs-type products). The contribution of the spectral pattern was of decisive importance here. Even a merely superficial comparison of a curve pertaining to the benzanthracene derivative shows very clearly a distinct difference between the isomeric hydrocarbons.

TABLE I

2-(1-Naphthylmethyl)diphenylketimines

prepared in the form of hydrochlorides.

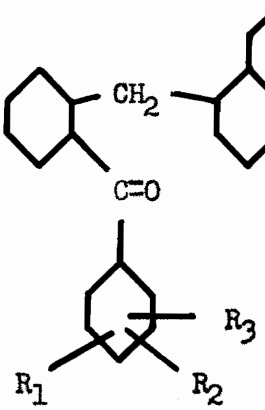


R_1	R_2	R_3	m. p.* °C.	Reference
H	H	H	181	TT (76)
2'-CH_3	H	H	177	TT (77)
3'-CH_3	H	H	185	TT (78)
4'-CH_3	H	H	202	TT (79)
2'-CH_3	3'-CH_3	H	185	11 (41)
2'-CH_3	4'-CH_3	H	173	11 (40)
2'-CH_3	5'-CH_3	H	176	11 (40)
2'-CH_3	6'-CH_3	H	176	11 (23, 39)
3'-CH_3	4'-CH_3	H	180	11 (42)
3'-CH_3	5'-CH_3	H	184	11 (41)
2'-CH_3	4'-CH_3	6'-CH_3	195	TT (86)

* All melt with decomposition.

TABLE II

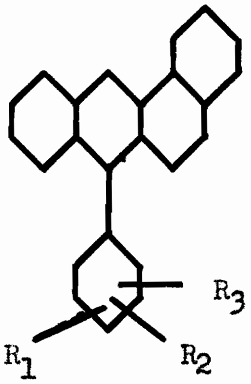
2-(1-Naphthylmethyl)benzophenones.



R_1	R_2	R_3	m. p. °C.	Reference
H	H	H	103.0-104.0	13 (55)
2'-CH_3	H	H	83.0-84.0	13 (56)
3'-CH_3	H	H	114.0-115.0	13 (57)
4'-CH_3	H	H	77.0-78.0	13 (58)
2'-CH_3	3'-CH_3	H	71.5-72.5	11 (45)
2'-CH_3	4'-CH_3	H	65.0-66.0	11 (45)
2'-CH_3	5'-CH_3	H	viscous oil	11 (43)
2'-CH_3	6'-CH_3	H	123.5-124.0	11(27,42), TT (87)
3'-CH_3	4'-CH_3	H	93.5-94.0	11 (44)
3'-CH_3	5'-CH_3	H	93.0-94.0	11 (44)
2'-CH_3	4'-CH_3	6'-CH_3	159.5	TT (88)

TABLE III

10-Phenyl-1,2-benzanthracenes.

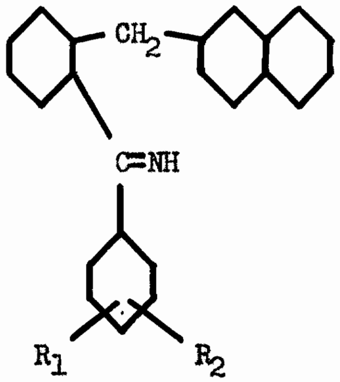


No.	R$_1$	R$_2$	R$_3$	m. p. ° C.	Reference
1	H	H	H	183 - 184	13 (56), TT (96)
2	2'-CH$_3$	H	H	131.5-132.0	TT (97)
3	3'-CH$_3$	H	H	109 - 110	TT (98)
4	4'-CH$_3$	H	H	121 - 122	6
5	2'-CH$_3$	3'-CH$_3$	H	175 - 176	11 (47)
6	2'-CH$_3$	4'-CH$_3$	H	107-108, 116-118	11 (47)
7	2'-CH$_3$	5'-CH$_3$	H	116 - 117	11 (48)
8	2'-CH$_3$	6'-CH$_3$	H	134.5-135.5	11 (25), TT (99)
9	3'-CH$_3$	4'-CH$_3$	H	117.5-118.5	11 (46)
10	3'-CH$_3$	5'-CH$_3$	H	118-120, 142-144	11 (46)
11	2'-CH$_3$	4'-CH$_3$	6'-CH$_3$	144.5-145.5	TT (100)

TABLE IV

2-(2-Naphthylmethyl)diphenylketimine hydrochlorides,

prepared in the form of hydrochlorides.

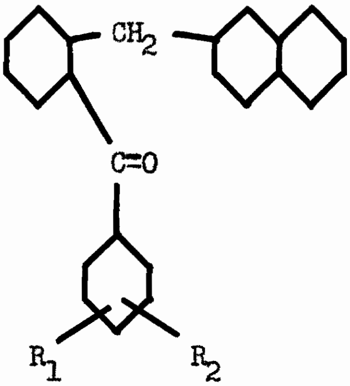


R_1	R_2	m. p.* °C.	Reference
H	H	180	TT (81)
2'-CH_3	H	184	TT (82)
3'-CH_3	H	174	TT (83)
4'-CH_3	H	193	TT (83)
2'-CH_3	6'-CH_3	192	TT (84)

* All melted with decomposition.

TABLE V

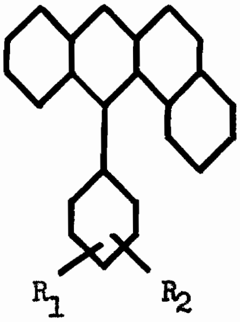
2-(2-Naphthylmethyl)benzophenone.



R_1	R_2	b. p. °C.	Reference
H	H	240 (1.5 mm.)	TT (88)
2'-CH_3	H	m. p. 97.5	TT (89)
3'-CH_3	H	236-238 (1.5 mm.)	TT (89)
4'-CH_3	H	237-240 (1.5 mm.)	TT (90)
2'-CH_3	3'-CH_3	240-243 (1.0 mm.)	TT (90)
2'-CH_3	4'-CH_3	235 (1.0 mm.)	TT (91)
2'-CH_3	5'-CH_3	236-238 (1.0 mm.)	TT (91)
2'-CH_3	6'-CH_3	m.p. 86.5-87.0	TT (92)
3'-CH_3	4'-CH_3	238 (1.0 mm.)	TT (92)
3'-CH_3	5'-CH_3	m. p. 124.5-125.0	TT (93)

TABLE VI

9-Phenyl-1,2-benzanthracenes.



No	R_1	R_2	m. p. °C.	Reference
12	H	H	154 - 155	8, TT (101)
13	2'-CH_3	H	102.5 - 103.5	TT (102)
14	3'-CH_3	H	131.5 - 132.5	TT (103)
15	4'-CH_3	H	115.5 - 116.5	TT (104)
16	2'-CH_3	3'-CH_3	152 - 153	TT (105)
17	2'-CH_3	4'-CH_3	58 - 64	TT (105)
18	2'-CH_3	5'-CH_3	64 - 69	TT (106)
19	2'-CH_3	6'-CH_3	123.5	TT (107)
20	3'-CH_3	4'-CH_3	119.0-119.5;142.5	TT (108)
21	3'-CH_3	5'-CH_3	230	TT (110)

TABLE VII

b

Adsorption Maxima of the Hydrocarbons Prepared

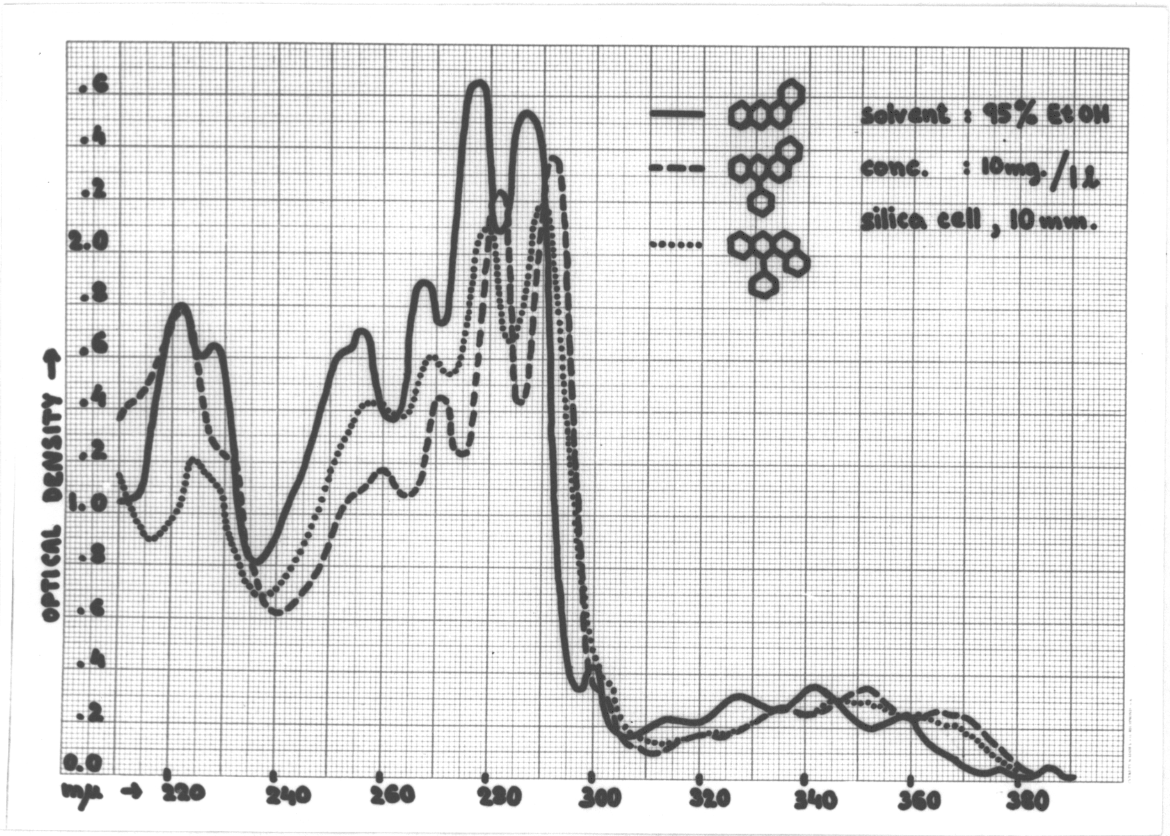
CH	λ_{max} in mμ								
1	222	260	271	281	292	322	336	352	365
2	222	260	270	281	292	320	335	351	366
3	222	260	271	281	292	321	336	351	365
4	222	259	271	281	292	321	336	351	365
5	222	259	271	281	292	322	336	350	366
6	222	259	271	281	292	322	336	351	365
7	222	259	270	281	292	322	335	351	366
8	221	259	271	281	291	321	335	352	366
9	222	260	271	281	292		336	351	366
10	222	260	271	281	292	321	336	351	366
11	222	259	271	281	292	320	335	351	368
12	224	258	270	279	290	336	346	352	361
13	225	258	270	279	290	335	347	352	361
14	225	259	269	278	289	336	346	351	
15	225	258	269	279	289	336	347		360
16	224	260	269	279	289	336	346		362
17	226	260	270	279	290	336		351	
18	224	260	269	279	289	336	346	351	362
19	223	260	269	279	290	337	346		362
20	226	259	269	279	290	337		351	362
21	226	260	269	279	290	337		350	362

TABLE VIII

Optical Density Values at the Adsorption Maxima

CH	Optical density at λ_{max}							
1	1.78	1.17	1.45	2.25	2.37	.17	.28	.35	.27
2	1.34	.98	1.16	2.05	2.32	.14	.23	.30	.22
3	1.51	.97	1.23	1.99	2.38	.14	.23	.29	.22
4	1.54	.98	1.20	1.89	2.30	.13	.22	.28	.22
5	1.50	.98	1.25	2.15	2.40	.15	.25	.31	.23
6	1.42	.91	1.16	2.01	2.32	.13	.23	.29	.23
7	1.51	.93	1.20	1.87	2.29	.14	.29	.30	.24
8	1.71	1.19	1.45	2.30	2.50	.17	.29	.36	.27
9	1.61	.91	1.15	1.83	2.20		.21	.27	.21
10	1.39	.84	1.11	1.82	2.20	.13	.21	.26	.20
11	1.47	1.03	1.18	1.88	2.20	.18	.20	.26	.19
12	1.20	1.43	1.60	2.10	2.19	.27	.30	.30	.25
13	1.04	1.28	1.42	1.95	2.17	.25	.27	.27	.26
14	.96	1.20	1.23	1.77	1.92	.20	.23	.23	
15	1.01	1.26	1.40	1.92	2.10	.23	.26		.22
16	1.27	1.53	1.64	2.31	2.36	.28	.31		.25
17	1.18	1.31	1.49	2.01	2.17	.24		.24	
18	1.40	1.53	1.68	2.29	2.35	.26	.29	.29	.24
19	.90	1.10	1.19	1.68	1.76	.19	.22		.18
20	1.21	1.14	1.13	1.56	1.62	.18		.20	.17
21	1.28	1.48	1.46	2.02	2.10	.26		.29	.24

TABLE IX



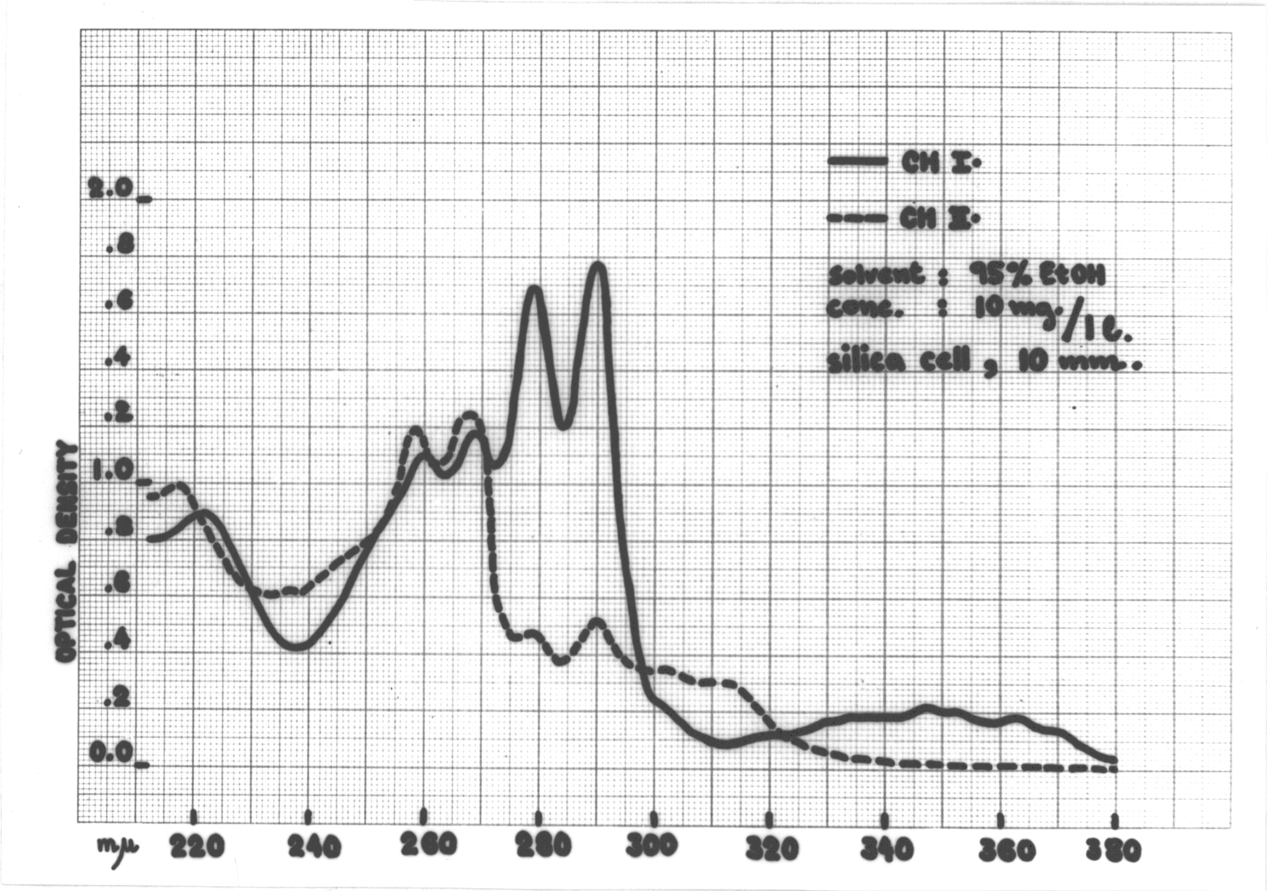
UV Spectra of

______ 1,2-Benzanthracene

\- - - 10-Phenyl-1,2-benzanthracene

..... 9-Phenyl-1,2-benzanthracene

TABLE X

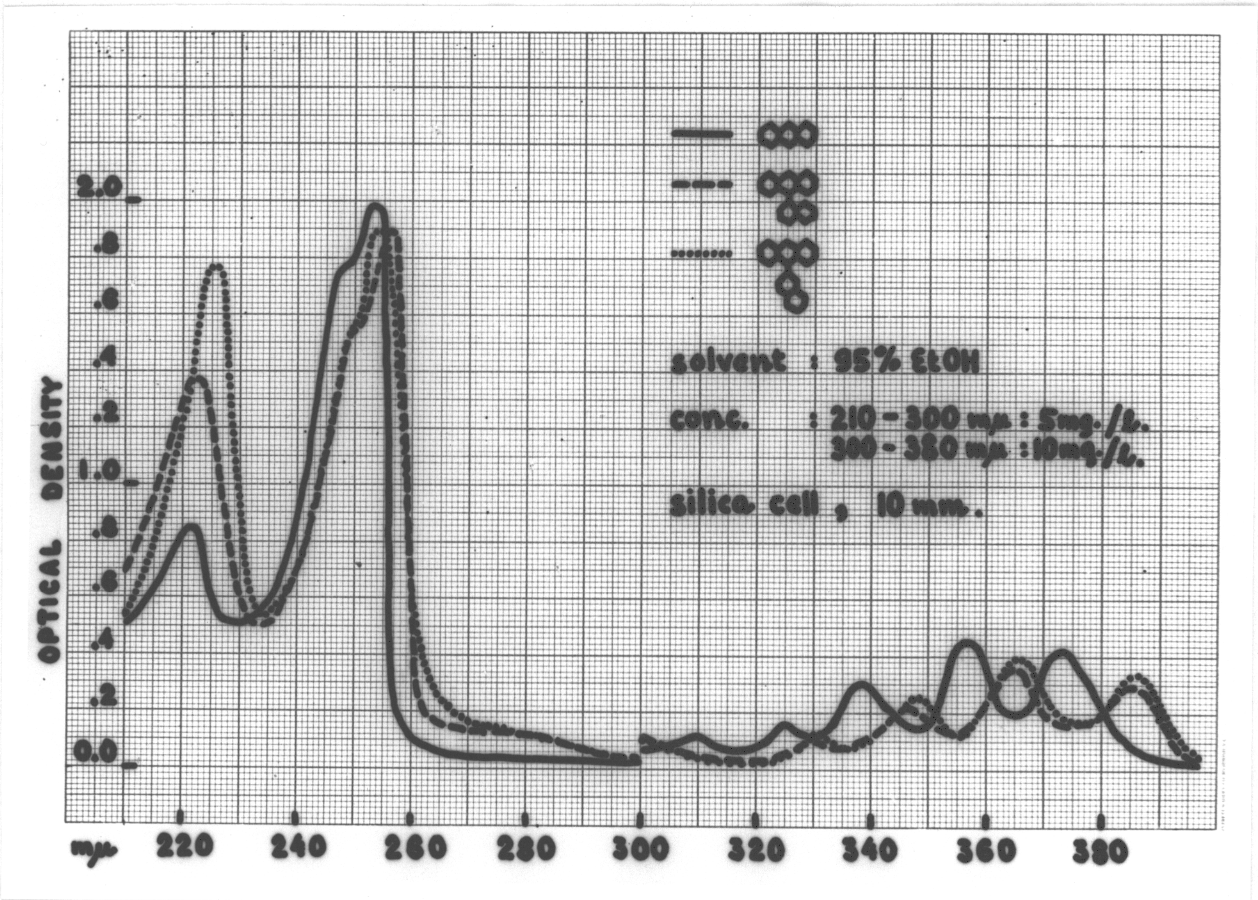


UV Spectra of

——— 9-(2',6'-Dimethylphenyl)-1,2-benzanthracene

- - - Unknown by-product

TABLE XI



UV Spectra of

——— Anthracene

- - - 9-(1-Naphthyl)anthracene

..... 9-(2-Naphthyl)anthracene