

A STUDY OF THE PREPARATION OF SOME 10-DIMETHYLPHENYL-1,2-BENZANTHRACENES

by

Alexej B. Borkovec

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of


MASTER OF SCIENCE

in


CHEMISTRY

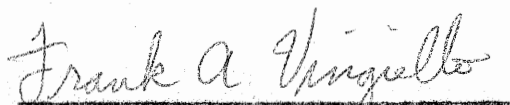
APPROVED:

APPROVED:


Director of Graduate Studies


Head of Department


Dean of Applied Science and
Business Administration


Director of Investigation

December, 1953

Blacksburg, Virginia

LD
5655
V855
1953
B674
C.2

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	3
HISTORICAL	6
DISCUSSION OF RESULTS.....	14
EXPERIMENTAL	34
SUMMARY	49
ACKNOWLEDGEMENTS	51
LITERATURE CITED	53
VITA	56
APPENDICES	58

CHARTS

CHART I	8
CHART II	9
CHART III	10
CHART IV	11
CHART V	21

INTRODUCTION

INTRODUCTION

Many hypotheses have been advanced to account for the unique properties of certain polycyclic aromatic hydrocarbons in producing tumor growths. The fact that most of the compounds in this class contain the phenanthrene ring system substituted by condensed aromatic rings and methyl groups, has led to the conception that some feature of this system may be necessary for and involved in the carcinogenic process. The 9,10-bond of phenanthrene activated by substitution in the phenanthrene ring system, in particular, may be an active part of the carcinogenic molecule (1, 2).

It was shown by T. W. Cook (3) that although 1,2-benzanthracene has only very weak carcinogenic properties, substitution in the 5, 6, 9 or 10 position can increase these properties substantially. The exact relationship, however, between the biological activity and the nature of the substituents is still not known. So for example, 10-methyl-1,2-benzanthracene shows a pronounced carcinogenic activity, whereas the disubstituted 3,10 and 4,10-dimethyl-1,2-benzanthracenes do not show any activity (4).

A large number of polycyclic hydrocarbons which were prepared in recent years not only gave a firm basis for the above mentioned consideration, but also broadened the way for the understanding of structural problems in polycyclic systems, and for the application of the newer electronic theories not only to simple aliphatic or aromatic compounds, but also to

systems where various electronic (resonance) and steric effects can influence the reaction simultaneously.

In practice some of the polycyclic hydrocarbons may find use as fuel moderators. Due to their high hydrogen content and in some cases outstanding thermal properties, they may serve as neutron moderators (5).

These were the main reasons that led to our systematic research on the preparation and properties of polycyclic hydrocarbons.

It was shown by Bradsher (6) that 9- or 10- substituted 1,2-benzanthracenes can be prepared by a method shown in Chart IV. Shulman (7) prepared 2-(1-naphthylmethyl)-benzophenone, 2'-methyl-, 3'-methyl- and 4'-methyl, 2-(1-naphthylmethyl)-benzophenones by this method. Two of these ketones were cyclized by Shulman (7) and Vingiello (8) to 10-phenyl and 10-(4'-methylphenyl)-1,2 benzanthracene respectively.

It is the purpose of this thesis to further investigate the reaction suggested by Bradsher, and the preparation of some 10-dimethylphenyl-1,2-benzanthracenes.

HISTORICAL

HISTORICAL

Basically there are three methods for the preparation of 9- or 10-substituted 1,2-benzanthracenes. The first method, which was developed by J. W. Cook (9) Chart I*, is based on the reaction of 1,2-benz-10-anthrone (I) on an appropriate Grignard reagent and dehydration of the resulting carbinol (II) to the hydrocarbon (III). 10-Isopropyl (9,11) methyl (10), methoxy (11), ethyl (11), n-propyl (11), allyl (11), n-butyl (11), n-amyl (11), and 9,10-dimethyl (12,13) 1,2-benzanthracenes were prepared by this method. This method which seems to be quite general, fails however, in attempts to prepare 9-substituted 1,2-benzanthracenes (10).

The second method shown in Charts II and III, is based on the reaction of 2-(1-naphthoyl)benzoic acid (IV) or 2-benzoyl-1-naphthoic acid (V) with an appropriate Grignard reagent, and cyclization of the resulting acid (VI) or anhydride (IX) to the corresponding anthrone (VII) and reduction to the hydrocarbon (VIII). 9-Methyl (10,14) and 10-methyl (15) 1,2-benzanthracenes were prepared by this method.

A third method which will be thoroughly discussed later was introduced by Bradsher (6) and is based (Chart IV) on a reaction of 2-(1- or 2-naphthylmethyl)benzotrile (X) with an appropriate Grignard reagent and cyclization of the resulting ketone (XI) to the corresponding hydrocarbon (XII). 9-Methyl-(6), 10-methyl-(6), 10 phenyl-(7), and 10-(4'-methylphenyl)-(8) 1,2 benzanthracenes were prepared by this method, which seems to be

* All rings are fully aromatic unless otherwise specified.

CHART I

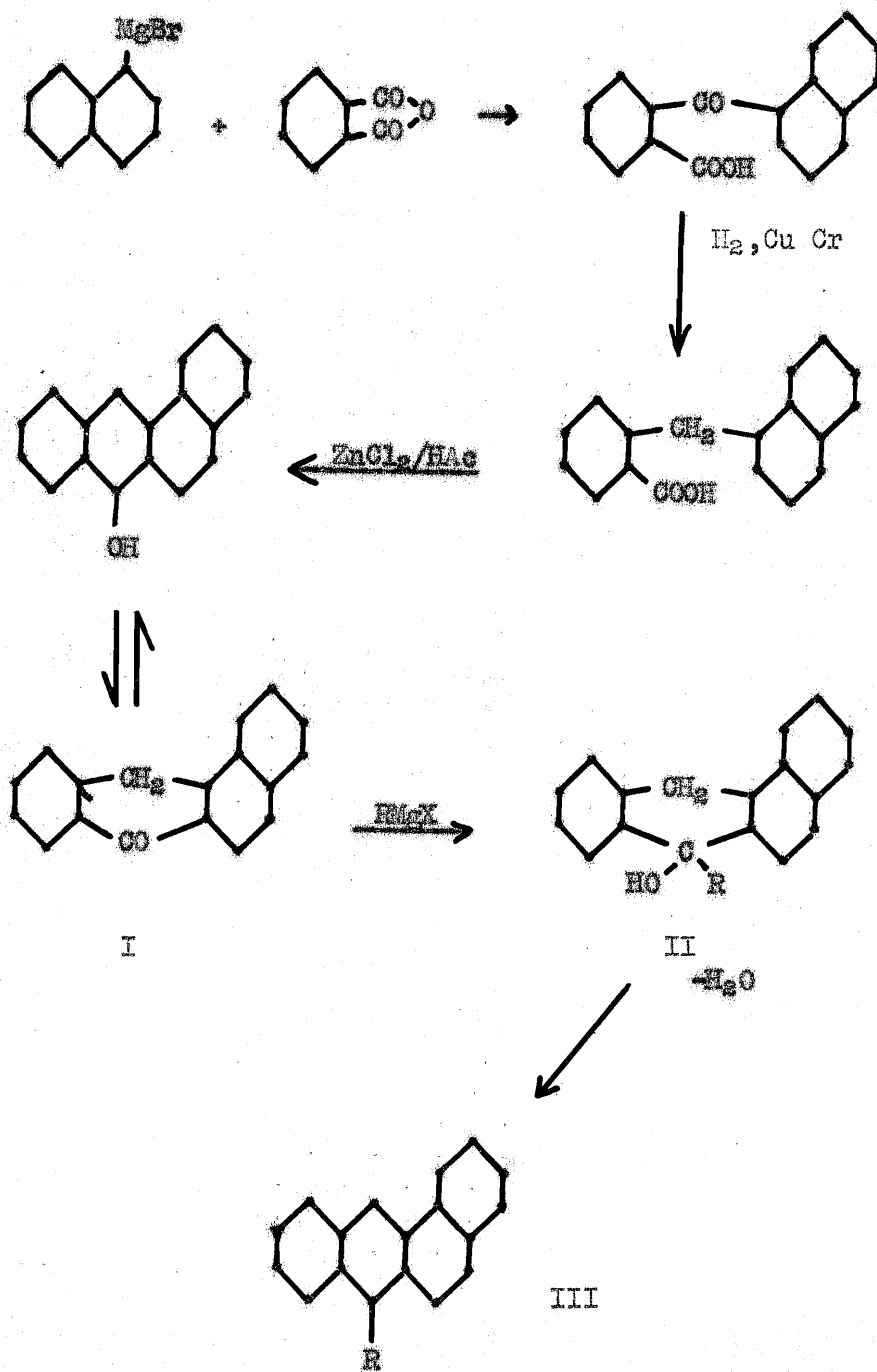


CHART II

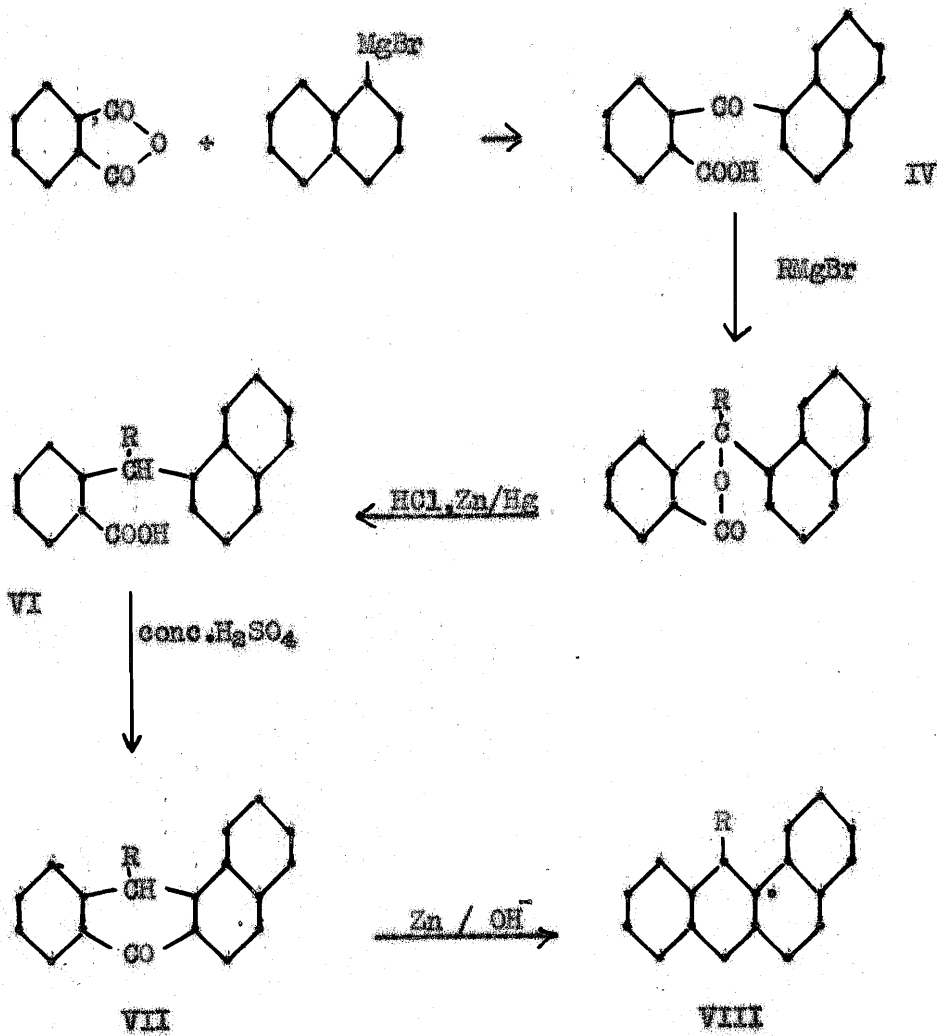


CHART III

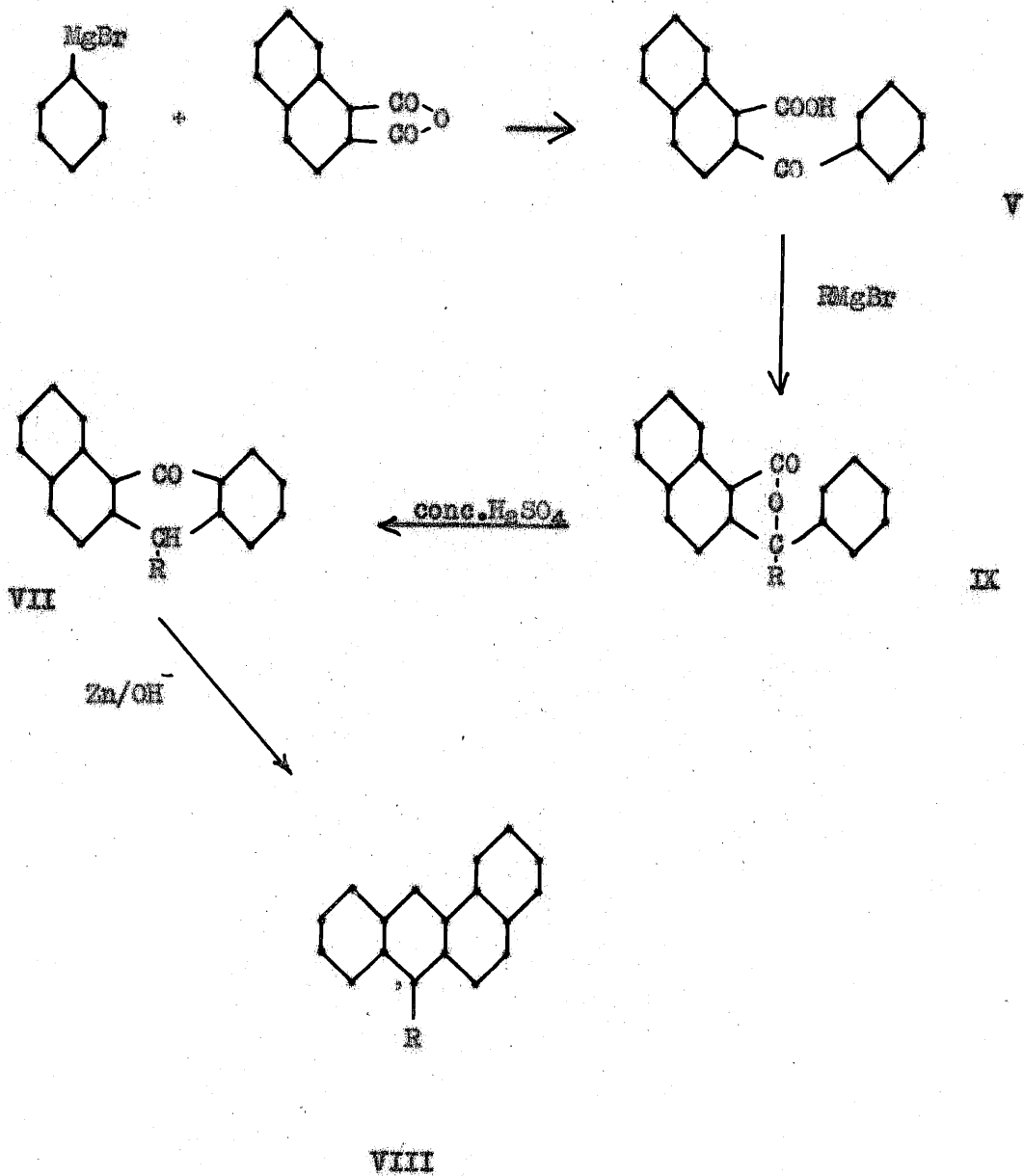
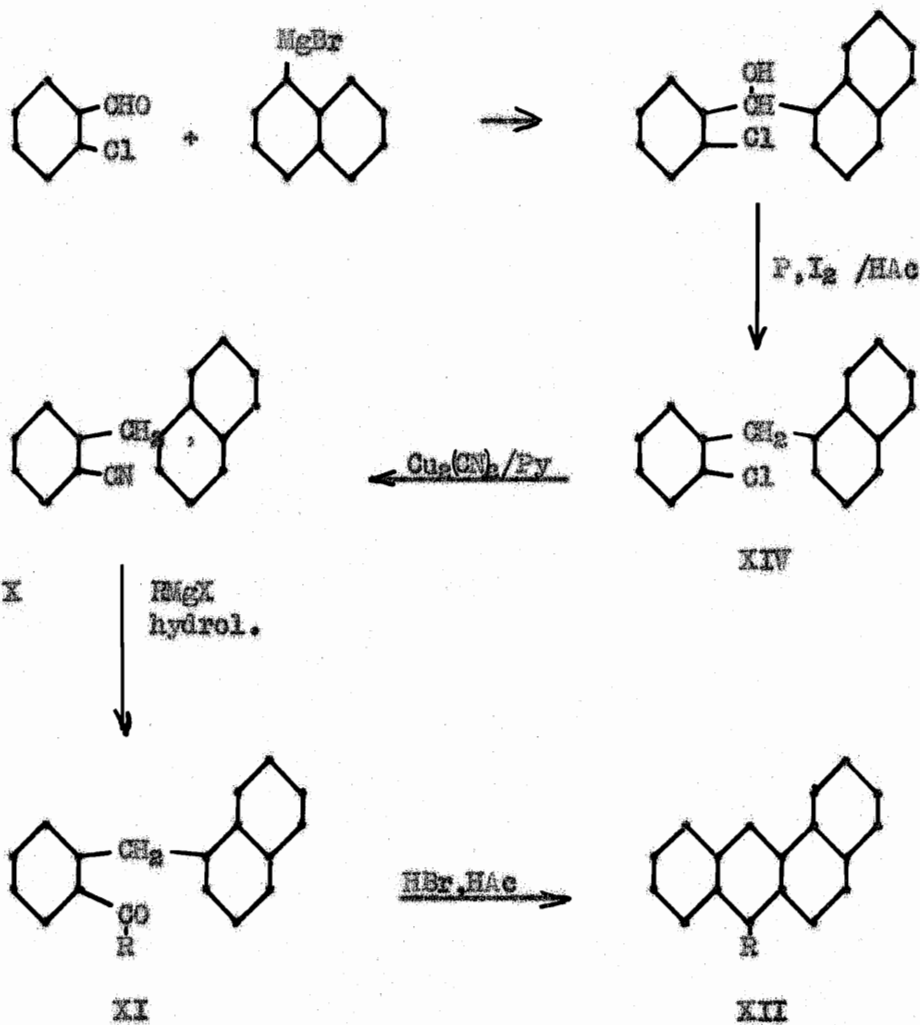


CHART IV



If 2-naphthylmagnesiumbromide is used in the first step 9-substitution results.

general not only for alkyl but also for aryl 9- or 10-substituted 1,2-benzanthracenes.

Although in all of the three methods mentioned the yields are considered "satisfactory", there is a marked difference in these, which can be shown in the example of 10-methyl-1,2-benzanthracene which was prepared by each of the three methods.

The overall yield of the hydrocarbon prepared by the first method is about 7% (calculations based on anthrone) (10). The overall yield in the second method was about 13% (15), and the last method yields about 29% overall yield of the hydrocarbon (6). It will be shown later that even such comparatively high yield can still be increased by eliminating one step from Bradsher's procedure, and that more than 30% yield of the hydrocarbon can be obtained also in the preparation of arylated 1,2-benzanthracenes. Unfortunately, none of the aryl-substituted, 1,2-benzanthracenes were prepared by the first and second methods, so that a comparison of the yields in such preparations is not available.

It was already stated that some of the 9- or 10- substituted 1,2-benzanthracenes exhibit a marked carcinogenic activity. Without going into details which would be beyond the scope of this thesis, it can be mentioned that there seems to be a connection between the character of the substituent and the biological activity of the substance. In the special case of 9- or 10-substituted 1,2-benzanthracenes, the carcinogenic potency decreases with the following change of substituents $\text{CH}_3/$ $\text{C}_2\text{H}_5/$ $n\text{-C}_3\text{H}_7/$ $n\text{-C}_4\text{H}_9$. This may be in connection with the suggestion of E. and F. Bergman (16) that the aromatic carcinogens possess a planar configuration. From

this point of view, none of the 1,2-benzanthracenes substituted in 9 or 10 position by an aryl group should exhibit any carcinogenic activity, since such compounds probably can not have a planar configuration, especially if such group has substituents in the ortho position.

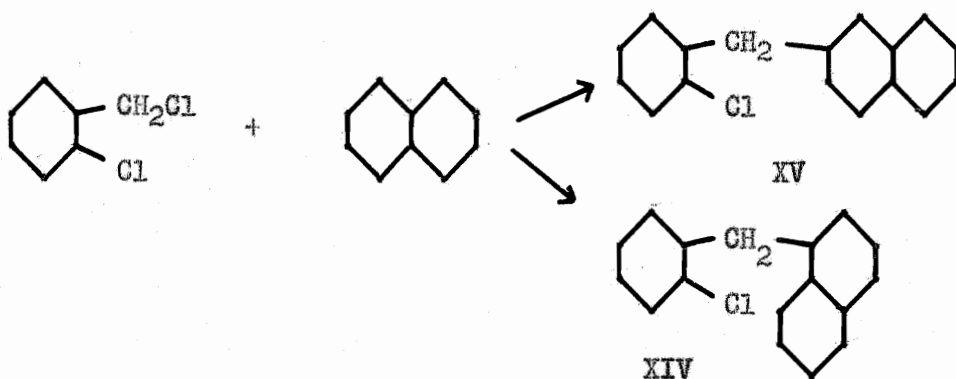
DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

A. Preparation of o-(Naphthylmethyl)benzonitrile

The procedure by which Bradsher (6) prepared 9- and 10-methyl-1,2-benzanthracene is shown in Chart IV. Although the first two steps result in quite high yields, the overall yield (60%) of o-chloro(1-naphthylmethyl)benzene (XIV) proved to be uneconomical for the preparation of large quantities of the nitrile (X) necessary for further reactions. Should 2-bromonaphthalene be used (for the preparation of 9-substituted benzanthracenes), the cost of the o-(2-naphthylmethyl)benzonitrile would be almost prohibitive. The attempts to improve the yields in the two mentioned reactions were not successful. A yield of 95% of pure carbinol was obtained in the reaction of o-chlorobenzaldehyde with 1-naphthylmagnesiumbromide, but in the following reaction (i.e. the reduction of the carbinol) the yields never exceeded 70%.

A different and more promising approach to the preparation of the chlorocompound (XIV) was made by a Friedel-Crafts reaction between o-chlorobenzylchloride and naphthalene, both cheap and available in large quantities, using different solvents, catalysts, and temperatures.



The following criteria were considered in the choice of a proper solvent : 1) speed of reaction, 2) 1- or 2- substitution. From the first point of view, all other common solvents (CS_2 , petrolether, ligroin, tetrachloroethane) are superior to nitrobenzene, but the latter distinctly favors (17) 2-substitution. Since one of the main reasons for this investigation was to find an economical way for the preparation of o-(2-naphthylmethyl)chlorobenzene, nitrobenzene was chosen for the solvent. For this particular reaction aluminium chloride, which forms a soluble labile complex with nitrobenzene, was used as a catalyst.

The temperature during the alkylation was kept in the neighborhood of 0° to minimize the polyalkylation, although a higher temperature would probably favor 2-substitution.

The results of this mode of preparation were not favorable. The reaction lasted almost 40 hours, a large quantity of nitrobenzene was necessary to dissolve at least part of the naphthalene (at 0°), and after vacuum fractionation of the resulting dark oil only 31% boiled in the proper range of the expected chlorocompound ($182-184^\circ/1 \text{ mm.}$), and about 40% consisted of an extremely viscous transparent oil (b.p. $260-268^\circ/1 \text{ mm.}$)- which was supposed to be a mixture of isomeric dialkylated naphthalenes.

More promising results were obtained when the reaction between naphthalene and o-chlorobenzylchloride was carried out without any solvent. Commercial production of benzylnaphthalene (18) was taken as an example, and three different catalysts (AlCl_3 , ZnCl_2 , Zn) were used. The difference among the yields resulting from the differently catalyzed reactions is shown in Table I (one mole of o-chlorobenzaldehyde is taken as the basis).

Table I

Catalyst (mole)	C ₁₀ H ₈	T °C.	Yield of Mono- substituted C ₁₀ H ₈	Yield of Poly- substituted C ₁₀ H ₈
ZnCl ₂ (0.2)	1.0	120°	-	30%
Zn (0.25)	2.0	100°	50%	15%
Recycled Zn (0.25)	2.0	100°	79%	18%
AlCl ₃ (0.001)	2.0	160°	48%	20%
Recycled AlCl ₃ (0.001)	2.0	160°	70%	29%

With the exception of ZnCl₂, the yields in single reactions were not too satisfactory; a substantial improvement was achieved, however, when the unreacted material from one reaction, together with the polysubstituted naphthalene were added to the material for the next reaction. In this manner the yield was increased to 70-80%, and the formation of polysubstituted naphthalenes was suppressed to a minimum.

The reaction itself is exceptionally simple. The mixture of 1 mole of o-chlorobenzylchloride and 2 moles of naphthalene is heated in a large beaker to the proper temperature, and the catalyst is cautiously added. In both cases the evolution of HCl is quite violent. After the reaction the hot mixture is filtered through glass wool, washed with water, dried and distilled under reduced pressure. The mixture of chlorocompounds is usually collected as a colorless oil (boiling range 185-195°/ 1 mm.)

Generally 20-30% of the yield is a slightly yellow, extremely viscous oil (boiling range 255-265°/1 mm.), which is supposed to consist entirely of o-chlorobenzyl-naphthalenes. There are ten possible isomeric disubstituted naphthalenes; it is very probable, however, that only a few of them are present in larger quantities in the mixture. So, for example, it was possible to separate by fractional crystallization, using acetone as solvent, one of the isomers as colorless prisms (m.p. 162-164°*),

Analysis** : Calculated for $C_{24}H_{18}Cl_2$: C, 76.39; H, 4.81; Cl, 18.79
 Found : C, 76.30; H, 5.15; Cl, 19.0)

and it was found that about 18-23% of this isomer is present in the mixture. These twice substituted naphthalenes can serve as very interesting material for future syntheses of angular polycyclic hydrocarbons which would be difficult to obtain by any other method.

The main problem in the preparation of monosubstituted naphthalenes was the separation of the isomeric 1- and 2- naphthyl compounds. Both the 1- and 2- chlorocompounds (XIV and XV) are colorless oils of b.p. 189 - 192° (2 mm.) and 203-204° (3 mm.) respectively. It was attempted to separate a mixture of 70% 1- and 30% 2-chlorocompound (XIV and XV) by distillation in Todd Precise Fractionation Assembly, by means of which separation of compounds with boiling points as close as 5.9° is claimed. This attempt, however, proved to be unsuccessful.

Therefore, a von Braun reaction was carried out with the mixture, and both nitriles (X) were isolated as a slightly yellow viscous oil. The boiling points of the 1- and 2- nitriles are 216-217° (3 mm.) and 223-226° (3 mm.) respectively. Again, the attempt to separate this mixture by

* All melting points are corrected.

** All analyses by Micro-Tech. Laboratories, Skokie, Ill.

fractional distillation was unsuccessful. The nitriles, however, if pure, are crystalline compounds of melting points $59-60^{\circ}$ for the 1- compound, and $84.5 - 85.5^{\circ}$ for the 2- compound. It can then be presumed that fractional crystallization might be the proper mode of separation. Of the numerous solvents which were tried, 90% ethyl alcohol proved to be the most suitable. The mixture of nitriles was dissolved in hot ethyl alcohol to obtain an almost saturated solution which was allowed to cool off gradually over a period of two to five days. The lower melting *o*-(1-naphthylmethyl)benzotrile crystallized out in almost pure form (m. p. $57-60^{\circ}$), and after one recrystallization from ethyl alcohol, colorless large prisms (m.p. $58.5 - 59.5^{\circ}$) were easily obtained. A mixed melting point of this nitrile and the nitrile prepared by Bradsher's method showed no appreciable depression (mixed m. p. $59.0-59.5^{\circ}$). The mother liquor was then concentrated to a smaller volume, and allowed to cool slowly over a period of five to ten days. *o*-(2-Naphthylmethyl)benzotrile crystallized out, after seeding, in large colorless monoclinic crystals, which after three successive recrystallizations melted at $84.5 - 85.5^{\circ}$. Even better results for the preparation of 2- nitrile were obtained when alcohol was replaced in the mother liquor with a mixture of 30% ether and 70% petroleum ether (b.p. $30-60^{\circ}$). By this method large quantities of very pure 1- and 2- nitrile can be prepared easily, the only disadvantage being the comparatively long time necessary for fractional crystallization.

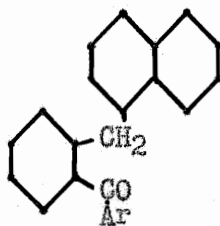
Separation by chromatographic adsorption with alumina as adsorbent and petroleum ether or ethyl alcohol as solvents, was tried for both the chlorocompound and the nitrile, without success. It is quite possible that a

proper choice of solvent and adsorbent might lead to satisfactory results. If larger quantities are involved, however, chromatographic methods require even more time, and are more laborious than fractional crystallization.

Most of the *o*-(1-naphthylmethyl)benzointrile used for the preparation of dimethylphenyl-1,2-benzanthracenes was, however, prepared by the original Bradsher method.

b. Preparation of *o*-(1-Naphthylmethyl)dimethylbenzophenones.

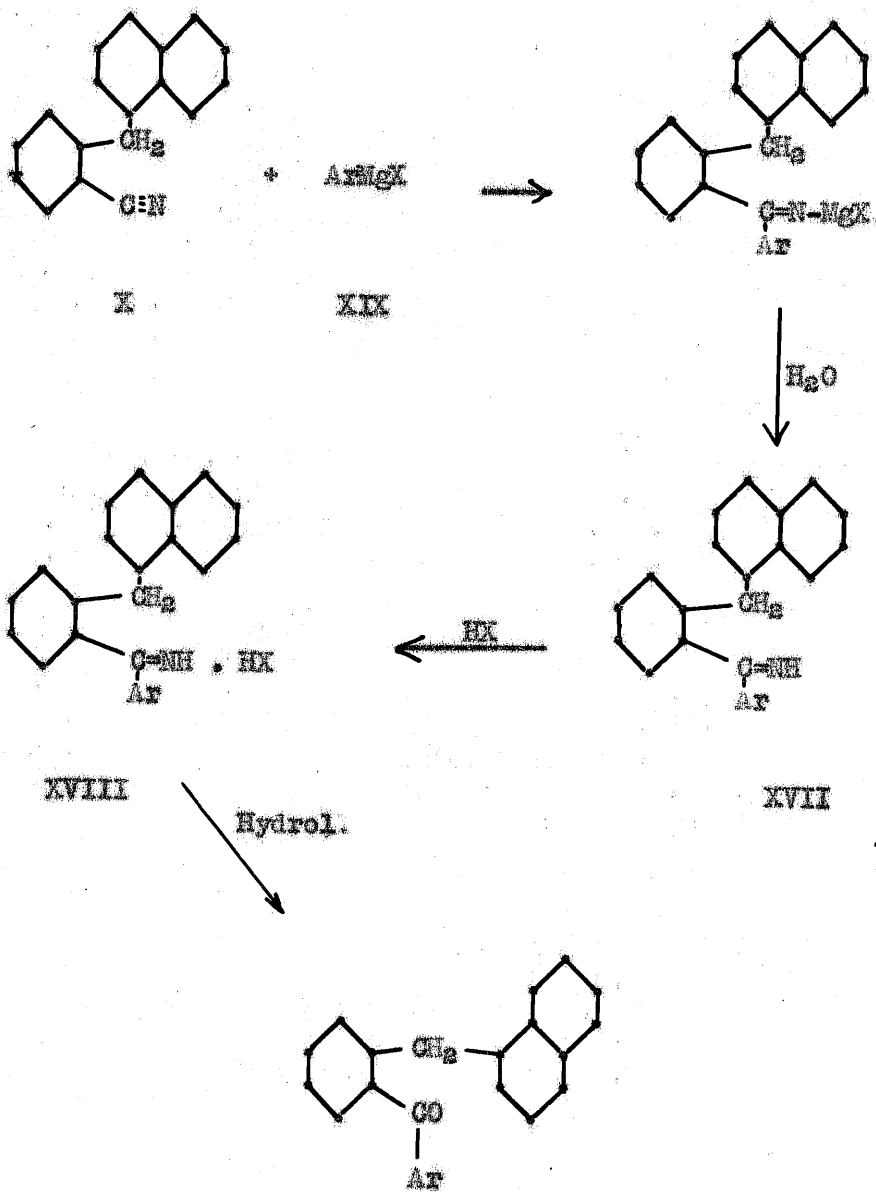
Compounds of the general type



XVI

where Ar is phenyl, *o*-, *m*-, and *p*-methylphenyl, were prepared by Shulman (7) who used Bradsher's procedure (Chart IV) with minor changes in the hydrolysis of the Grignard addition compounds. From the detailed scheme of the reaction (Chart V), it can be seen that the hydrolysis of the magnesium complex proceeds in three phases, yielding in each phase quite stable compounds which can be isolated. The initial low yields of ketone were accounted for by Shulman (7) by the use of ammonium chloride for the decomposition of the Grignard mixture. This was probably due to

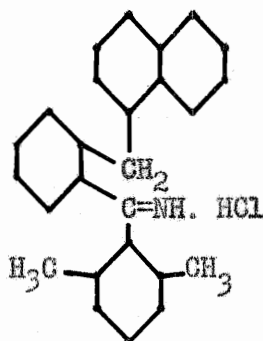
CHART V



an incorrect assumption that the free ketimine was insoluble and could coprecipitate with the magnesium salts. Upon the addition of 20% ammonium chloride solution and subsequent reflux for one to three hours, the ketimine (XVII) is freed and dissolved quantitatively in the toluene layer. However, if an acid is added to this solution, the ketimine molecule (XVII) combines with one molecule of the acid and eventually crystallizes out, since the salt of the ketimine (XVIII) is almost insoluble, not only in toluene, but also in ether, acetone, benzene, etc. (Chart V). Usually the Grignard reaction and the hydrolysis were carried out in the following manner: (Chart V). Ether in the Grignard reagent solution (XIX) was replaced with toluene, and a solution of nitrile (X) in toluene was added and heated under reflux overnight. The ratio of the Grignard reagent to the nitrile was in most cases three to one. It was observed, however, that even a ratio of three to two gives satisfactory results. The mixture was then decomposed with a 20% solution of ammonium chloride and heated under reflux for one to three hours. The clear, strongly fluorescent toluene layer was then decanted, and the residue washed twice with fresh toluene. The hard residue was completely soluble in dilute hydrochloric acid, which was a satisfactory check that all of the ketimine was extracted with toluene. Concentrated hydrochloric acid was then added to the toluene solution, and small yellowish crystals of the ketimine hydrochloride crystallized out after scratching the flask with a glass rod. The crystals were separated and freed of impurities by boiling with acetone. For the preparation of an analytical sample, the ketimine hydrochloride was decomposed with 10% sodium hydroxide solution, free imine extracted with benzene, and

precipitated again with hydrochloric acid. Almost white crystals were then recrystallized from a mixture of ethyl alcohol and acetone. Pure ketimine hydrochlorides formed small, hard, almost white crystals, with strong yellow or green fluorescence, which started to decompose at 180 - 190°. The yields in this reaction were between 65 and 95%.

The hydrolysis of ketimine hydrochlorides to ketones was accomplished by heating a suspension of the ketimine in 25% sulfuric acid and toluene under reflux. This method, however, failed in the case of the 2,6-dimethyl compound (XX).



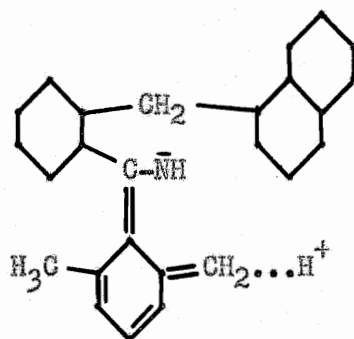
XX

It can be readily seen, even from its planar structural formula (XX) that the ketimino group is highly hindered by both the orthomethyl groups and the naphthylmethyl groups.

J. B. Culbertson (19), in a recently published study on the hydrolysis of substituted diphenylketimines, suggests two factors which influence the sensitiveness of ketimines toward hydrolysis: (1) a ketimine -

enamine tautomerism and/or resonance, (2) steric hindrance (ortho-effect).

In cases where the two benzene rings adjacent to the ketimino group are substituted by a hydroxyl or amino group, the ketimine-enamine tautomerism or resonance are possible, and may then largely influence the rate of hydrolysis. However, if the substituents as in (XX) are alkyl groups, only the hyperconjugated form XXI



XXI

would stabilize the enamine form. Such a form (XXI) would contribute very little, if anything at all, to the stability of the enamine resonance structure. It seems, therefore, more probable that the marked difference in the hydrolysis of the ketimine (XX) can be attributed mainly to the steric hindrance or ortho-effects of the two methyl groups.

According to the electronic theory of the English school (20), the probable mechanism of this acid catalyzed hydrolysis is based on three steps :

- 1) Electrophilic attack on the polarized ketimino group

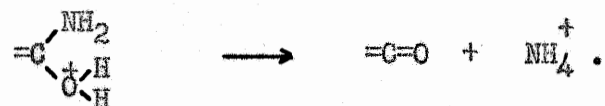


which results in the formation of a carbonium ion.

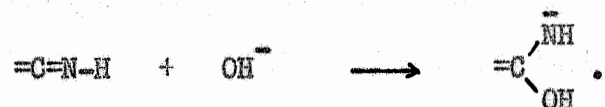
2) Hydration of the carbonium ion, and



3) Transformation of the unstable oxonium complex to a ketone



If the reaction were base catalyzed, the first probable step would be a nucleophilic attack on the polarized ketimino group

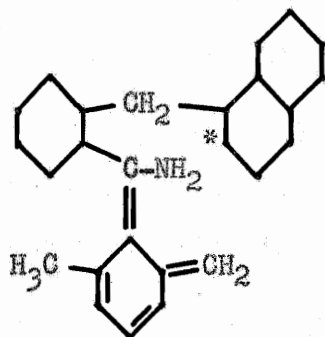


Considering the steric conditions of both carbon and nitrogen atoms which form the ketimino group and their "degree of hindrance", it can be concluded that, if the above considerations are valid, the acid catalyzed reaction should be preferable.

After a series of unsuccessful attempts, the ketimine (XX) was hydrolyzed by heating it under reflux for 60-80 hours with 40% sulfuric acid. All attempts at hydrolysis in alkaline media failed.

In the course of the hydrolysis with 40-60% sulfuric acid in the presence of toluene, a strong blue fluorescence developed in the toluene layer. Since this effect was probably due to the presence of a small amount of the respective hydrocarbon, it was concluded that sulfuric acid in such concentration may function as a cyclization agent, either for the ketone or directly for the ketimine. It was observed by Collie (21) and others (22,23) that ketimines which display a "ketimine-enamine-tautomerism"

are able to split ammonia, especially if in the presence of a compound with activated hydrogen (in the cited case the amino form reacts with the ketimino hydrogen). If at least a small amount of the amino form (XXI or XXII)



XXII

of the ketimine were present in the hydrolyzing mixture, it might well eliminate ammonia and cyclize, since the hydrogen atom on naphthalene nucleus (marked by *) can be considered as activated or labile (24). It was impossible, however, to reach any satisfactory conclusion in the hydrolysis or cyclization when sulfuric acid of greater strength than 40% was used, because of the extensive oxidation of the mixture. Even later, when these difficulties were eliminated and good yields of the hydrocarbons were obtained directly from the ketimines, it was difficult to decide if the hydrocarbons were formed by direct cyclization of the ketimine, or if the ketimine is first hydrolyzed to the ketone and this cyclodehydrated to the hydrocarbon.

Although the experimental evidence is not conclusive, it seems to be probable that both reactions may take place simultaneously, depending on the ratio of the tautomeric forms (XX, XXII), or if resonance effects

are involved, depending on the resonance energy which each of the structures (XK, XXI) contributes to the total resonance energy of the molecule (25).

In total twenty-seven reactions were carried out in attempts to hydrolyze the o,o-ketimine. Pure acids (sulfuric, phosphoric, hydrochloric, hydrobromic), acid mixtures (sulfuric and acetic, sulfuric and formic, sulfuric and hydrochloric, hydrobromic and acetic, etc.), and bases (sodium and potassium hydroxide) were used, but the ketone was isolated only in three cases.

a) Hydrolysis with 40% sulfuric acid.

After heating the mixture of the ketimine and 40% sulfuric acid under reflux for 70 hours, a small quantity of brown oil separated and was extracted with toluene. After purification, colorless prisms of m.p. 109.5-110.0° (Form I) were isolated; yield three to five percent. This reaction was repeated with similar results.

b) Hydrolysis with 40% sulfuric acid in presence of toluene.

After heating the mixture under reflux for 60 hours, a small quantity of colorless prisms of m.p. 124-125° (Form II) was separated, after purification, from the toluene layer; yield three percent. This reaction could not be repeated.

c) Hydrolysis with 48% hydrobromic acid and glacial acetic acid in a glass bomb.

In this reaction, which will be described later, two products were obtained: colorless prisms of m.p. 109.5-110° (Form I - yield 10-15%) and reddish brown transparent plates of m.p. 122.0-122.5° (Form III, yield

three to four percent).

The analyses of these three isolated forms were :

Calculated for $C_{26}H_{22}O$:	C, 89.10;	H, 6.33.
Found: Form I	:	C, 89.37;	H, 6.70.
Form II	:	C, 89.53;	H, 6.52.
Form III	:	C, 89.81;	H, 6.43.

No depression in the mixed melting points was observed in any case, and no interconversion occurred after many crystallizations from different solvents and cross-seeding. It will not be attempted now to explain this peculiarity, but further experiments which may lead to a satisfactory explanation are underway.

All the other dimethyl substituted ketones were crystalline solids with melting points between 60-120°, which did not display any fluorescence in solid form or solution. The yields in the hydrolyses were quite high (70-95%).

c. Preparation of 10-substituted 1,2-benzanthracenes.

In Bradsher's procedure (6), the ketone was cyclized in a very high yield by being heated under reflux for some time with a mixture of hydrobromic and acetic acid. Shulman (7) and Vingiello (8) prepared the phenyl- and 4-methylphenyl-1,2-benzanthracenes in the same manner. However, this method of preparation failed not only in the synthesis of 2-methylphenyl-, but also in all the dimethylphenyl-1,2-benzanthracenes. The formation of these hydrocarbons can be traced very easily by radiating the reaction mixture with ultraviolet light, and since all the hydrocarbons in question possess a strong blue fluorescence, their presence in the

solution can be easily determined. It was found by this method that if a mixture of 0.5 gram of a ketone, 45 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid was heated under reflux for eight days, a small amount of the corresponding hydrocarbon was probably formed, but since most of the ketone decomposed, and the mixture turned black, it was not possible to separate and isolate the minute amount of the hydrocarbon.

It was already mentioned that the ketimine hydrochlorides could be prepared in high yields and in a very pure form. Theoretically it should be possible, under proper conditions, to cyclize the ketimines directly to hydrocarbons without interrupting the reaction in the ketone stage. As was already stated, even if some hydrocarbon is formed in the cyclization mixture, the reaction is very slow and the conditions for destructive oxidation of the material favorable, so that no pure hydrocarbon can be obtained. To accelerate the reaction and eliminate the effect of air, a mixture of two grams of ketimine hydrochloride, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid was sealed in a glass bomb, and immersed (3 cm.) into a metal bath which was heated to 250-270°. The temperature inside the bomb was estimated at 160-180°. After some time, depending upon the ketimine used, the hydrocarbon separated on top of the liquid as a heavy oil which was easily isolated. To eliminate the influence of air completely, the glass bomb was in some cases swept with nitrogen and sealed. However, no difference in the results was observed.

This method proved to be not only suitable for direct cyclization of the ketimine, but it was also successfully used for the preparation of the o,o-ketone (XX), since in this case the reaction did not proceed to

the hydrocarbon stage.

Purification of the Hydrocarbons.

The purification of the hydrocarbons proved to be, in most cases, very difficult. After the reaction, the cyclization mixture in the bomb consisted invariably of two layers. The lower acid layer contained small amounts of unreacted ketimine and traces of the dissolved ketone and hydrocarbon. The upper dark oily layer, which solidified after cooling, contained impure hydrocarbon and varying amounts of the corresponding ketone.

The acid layer was diluted and partially neutralized, a small amount of solid material separated and combined with the dark oily layer. This was then dissolved in benzene, washed with water to remove the remaining acid, dried over calcium sulfate, and finally, the benzene was replaced by petroleum ether (b.p. 30-60°), and the solution was chromatographed.

A 40-cm. high column of the usual type (diameter 1.5 cm.) was wet-packed with Fisher's Alumina (80-200 mesh), and the hydrocarbon was eluted with petroleum ether. It was observed that direct daylight and fluorescent tube light in shorter wave lengths cause a brown coloration of the material absorbed in the column, and the chromatography was therefore performed in a dark place. The separation of the hydrocarbon from other impurities, mainly from the ketone, is very satisfactory. If pure petroleum ether is used as a solvent, the hydrocarbon can be separated quantitatively from the ketone, whose affinity for the absorbent is much higher. So, for example, from three grams of a mixture of a hydrocarbon

with its corresponding ketone, the former was quantitatively eluted with four liters of petroleum ether, whereas the ketone was not even partially eluted after using 15 liters of the same solvent.

The hydrocarbons were isolated from the petroleum ether solution as colorless non-crystalline solids with a strong blue fluorescence. Their crystallization proved to be very difficult. More than forty solvents and mixtures of solvents were tried, and none of them could be applied successfully for the whole series of isomers. A mixture of varying amounts of ethyl ether, ethyl alcohol and water was used for the crystallization of 2,3-, 3,4- and 3,5- hydrocarbons, but could not be used for 2,4-hydrocarbons, which resisted all attempts of crystallization. Since this hydrocarbon turned slightly yellow during the chromatography, it was rechromatographed in a dark place. Even then, however, the resulting colorless solid material resisted all attempts of crystallization. It was possible to obtain from 90% alcohol a decidedly crystalline mass which had all the characteristics of a mixture of two crystalline compounds, i.e. melting point range 74-82°, microscopic crystals formed on the walls of the flask, etc. It was therefore decided to distill the hydrocarbon in vacuo, and eventually separate the components of the mixture. The distillation of four grams of the substance was performed in a nitrogen atmosphere, and 0.5 mm./Hg, and only one fraction (b.p. 252-256°) was collected. All attempts to crystallize the resulting resinous solid failed. In order to establish if the supposed mixture was composed of substances of the same or of different chemical composition, 0.2 grams of the resinous solid was vacuum sublimated, and the white sublimate dissolved in alcohol and carefully precipitated by

adding water. The semicrystalline precipitate was dried and analyzed.

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

Found : C, 93.47; H, 6.34.)

It was therefore supposed that only hydrocarbons were present in the sample. The hydrocarbon was then chromatographed again under the same conditions as previously, and the resulting colorless oil was successfully crystallized from petroleum ether as large colorless prisms, m.p. 115-118°. Because of this comparatively large melting point range, the hydrocarbon was recrystallized from a mixture of ether, ethyl alcohol and water. Two different crystalline forms appeared in the solution and were separated by hand. One form were large colorless prisms, identical with those isolated previously (m.p. 115-117°), the other form were colorless small plates (m.p. 107-109°). Since the mixed melting point of these two forms showed no depression (111-116°), it was apparent that both were isomorphic forms of the same hydrocarbon; however, no interconversion was observed, inasmuch as a solution of one form seeded with a crystal of the other form yielded the original form again. Both forms were, therefore, recrystallized 27 times and their interconversion of one form into the other occurred without seeding or any other outside assistance. The melting point of the purest lower melting form A was 107.5-108.5°, and of the higher melting form B was 116-118°. Form A is more soluble in alcohol and other mixed solvents, and can be transformed into B by quick cooling of the saturated hot solution of A or B. Form B which is very slightly soluble in alcohol, can be transformed into A by slowly cooling a hot saturated solution of B (or A). It can be often observed, however,

that both forms crystallize out of the same solution, and that in a saturated solution, containing crystals in A form, after long standing both A and B forms appear.

Similarly as the 2,4-hydrocarbon, also the 3,4- and 3,5-hydrocarbons indicated the presence of some chemically similar substance of a different crystalline form. By accident three such compounds were isolated. One of the general methods for purifying hydrocarbons is to isolate them as picrates, and recover the hydrocarbon by chromatography. Although this method did not bring the expected results in the case of the hydrocarbons studied, it was found that all the mono- and dimethyl hydrocarbons in benzene solution yield a deep red color with a saturated benzene solution of picric acid. This complex is probably stable only in benzene solution, since after cooling the picric acid crystallizes out. Other solvents were therefore used (petroleum ether and alcohol, alcohol), but in such cases only a very slight deepening in the yellow color of the solution was observed. However, when the alcoholic solution of picric acid and a hydrocarbon (3,4- or 3,5-) was allowed to stand and was slowly cooled, two types of crystals appeared: deep red crystals typical for picrates (only in the case of the 3,4- compound), and slightly yellow crystals (in both cases) which had identical properties with the original hydrocarbon, with the exception of melting points which were in both cases considerably higher than those of the original compound.

EXPERIMENTAL

EXPERIMENTAL2-Chlorophenyl-1-naphthylcarbinol.

A Grignard reagent was prepared from 11.6 g. (0.48 mole) of magnesium, 100 g. (0.48 mole) of redistilled 1-bromonaphthalene, and 250 ml. of dry ether. When the reaction was complete, a solution of 55.3 g. (0.39 mole) of *o*-chlorobenzaldehyde in 300 ml. of dry ether was added dropwise with stirring. The mixture was stirred overnight at room temperature, and then heated under reflux for one hour, and finally the milky yellow solution was decomposed with 75 ml. of cold 20% ammonium chloride solution. The ethereal solution was decanted from the hard residue, and the residue was washed twice with ether. The combined ether solutions were washed with water, dried over calcium chloride, and finally concentrated. The residue was fractionated under reduced pressure in a nitrogen atmosphere, and the fraction distilling at 203-207° (0.8 mm.) was collected; yield 100 g. (95%). It formed a slightly yellow viscous oil which solidified and crystallized after standing. Crystallization from ethanol gave white needles of m. p. 95-96°. (Lit. (26) m.p. 96-97°).

2-Chlorophenyl-1-naphthylmethane (XIV).

A solution of 100 g. (0.37 mole) of 2-chlorophenyl-1-naphthylcarbinol in 825 ml. of 90% acetic acid, 20 g. red phosphorus, and 20 g. of

iodine was heated under reflux with stirring for 28 hours. After the reaction, the excess phosphorus was filtered off the hot solution with suction, the filtrate mixed with two kilograms of ice and 500 ml. of ether and neutralized with a 10% solution of sodium hydroxide. The ethereal layer was separated, washed three times with dilute sodium hydroxide, twice with water, dried over calcium chloride, and distilled under reduced pressure in a nitrogen atmosphere. The fraction distilling at 175-185° (0.4 mm.) was collected as a slightly yellow, viscous oil; yield 64 g. (67%). (Lit. (6) m.p. 189-192°, 2 mm.).

2-(1-Naphthylmethyl)benzotrile (X).

A mixture of 100 g. (0.396 mole) of 2-chlorophenyl-1-naphthylmethane, 44 g. of cuprous cyanide, 25 ml. of dry pyridine and cca. 0.01 g. of anhydrous cupric sulfate, was heated in a 200 ml. flask in a metal bath for 25 hours. The pyridine was allowed to escape gradually through a tall air condenser while the temperature of the metal bath was kept between 250-270°. The resulting black mixture was then crudely distilled under reduced pressure using a von Braun distilling head, and finally fractionated. A slightly yellow heavy oil which solidified after seeding was collected at 198-200° (1.5 mm.), and was then crystallized from ethanol as colorless prisms m.p. 59.5-60.0°. (Lit. (6) m.p. 59-60°). The yield was 85 g. (88%).

Preparation of o-chlorophenylnaphthylmethanes (XIV) by a Friedel Crafts type reaction.

A mixture of 128 g. (1 mole) of naphthalene and 80.5 g. (0.5 mole) of o-chlorobenzylchloride was heated in a 1000 ml. beaker to 100°, and 8.2 g. (0.12 mole) of zinc dust were cautiously added. After the evolution of hydrogen chloride had ceased, the hot mixture was filtered through glass wool, washed three times with water and dried over calcium chloride. The product was then fractionated under reduced pressure and a fraction distilling between 185-195° (1 mm.) was collected. The other two fractions, one boiling below 180° and the other above 200°, were combined and mixed again with one mole of naphthalene and 0.5 mole of o-chlorobenzylchloride, and the whole reaction was repeated four times. The total amount of naphthalene used was 512 g. (4 moles), o-chlorobenzylchloride 322 g. (2 moles) and zinc 33 g. (0.5 mole). The yield of o-chlorophenylnaphthylmethane in this cycle was 400 g. (79%).

When aluminium chloride was used as a catalyst, the reaction was performed in the same manner, only the amount of aluminium chloride used in each reaction was about 0.1 g. The yield in this cycle was 70%.

1-Bromo-3,4-dimethylbenzene.

A mixture of 200 g. (1.88 mole) of 95% commercial o-xylene and 0.5 g. iodine was brominated with 246 g. (3.08 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 $109-110^{\circ}$ (729 mm.) was a colorless oil which was subsequently twice redistilled; yield 233 g. (70.5%).

1-Bromo-2,3-dimethylbenzene.

Commercial 1-amino-2,3-dimethylbenzenehydrochloride was treated with 20% sodium hydroxide solution and the free xylidine extracted with ether. A suspension of 60.6 g. (0.5 mole) of the xylidine in 293.5 ml. (2 moles) of 40% hydrobromic acid was diazotized in a 1000 ml. flask with 39 g. (0.83 mole) of crystalline sodium nitrite, 5 to 8 g. added at a time. The temperature was kept at $5-8^{\circ}$, and after each addition the flask was shaken until all the red fumes were adsorbed. After the reaction, two grams of fine copper turnings were added to the mixture, a reflux condenser was attached to the flask, and the contents were cautiously heated until the first signs of the reaction appeared. The flask was then placed on ice and the nitrogen was allowed to escape slowly. After the evolution of nitrogen subsided, the mixture was heated gently for thirty minutes, 300 ml. of water was added, and the contents of the flask were steam distilled for two hours. The distillate was made alkaline and the dark orange oil was separated, washed with water and concentrated sulfuric acid, then again with water, and dried over calcium chloride. The yield of the crude product was 35 g. (38%). This compound was twice redistilled at atmospheric pressure (b.p. $208-209^{\circ}$ at 231 mm.). (Lit. (28) b.p. 213.8° at 760 mm.).

2-(1-Naphthylmethyl)-2',6'-dimethyl,diphenylketiminehydrochloride

A Grignard reagent was prepared from 3.5 g. (0.14 mole) of magnesium and 34 g. (0.15 mole) of 2,6-dimethylbenzene in 125 ml. of dry ether. Some magnesium remained unreacted after the mixture had been heated under reflux for one hour. The reagent was then placed in a 1000 ml. three-neck flask equipped with a mechanical stirrer, separatory funnel and a condenser with a thermometer, and a solution of 12.2 g. (0.05 mole) of 2-(1-naphthylmethyl)benzotrile in 200 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 contents of the flask turned milky yellow), the solution was heated under reflux for 18 hours under stirring, and decomposed with 25 ml. of a 20% ammonium chloride solution. The clear red liquid was then separated and the residue in the flask washed twice with fresh benzene. The combined extracts were washed with water, and 20 ml. of concentrated hydrochloric acid were added. After scratching the walls of the flask with a glass rod, the crude iminehydrochloride crystallized out, was separated and washed with water, and boiled for one hour with a 20% sodium hydroxide solution. The free imine was extracted with benzene, washed with water, and again precipitated with concentrated hydrochloric acid; yield 14.5 g. (75%).

To prepare an analytical sample, the iminehydrochloride was again decomposed with a sodium hydroxide solution, precipitated with hydrochloric acid, and crystallized from a mixture of 10% ethanol and 90% acetone.

The resulting white crystals melted at 176-179° with decomposition.

Analysis: Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.27.

Found : C, 80.49; H, 6.42.

2-(1-Naphthylmethyl)-2',5'-dimethyl, diphenylketiminehydrochloride.

A Grignard reagent was prepared from 4.8 g. (0.2 mole) of magnesium, 37.3 g. (0.2 mole) of 1-bromo-2,5-dimethylbenzene, and 200 ml. of ether which was replaced after reaction with a solution of 17 g. (0.07 mole) of the nitrile in 250 ml. of toluene. The reaction was then carried out as in the case of the 2',6'- isomer. The yield was 27 g. (70%). After reprecipitation and crystallization from a mixture of ethanol and acetone (one to nine), it formed slightly yellow prisms which melted with decomposition at 176°.

Analysis : Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.27.

Found : C, 80.72; H, 6.53.

2-(1-Naphthylmethyl)-2',4'-dimethyl, diphenylketiminehydrochloride

A Grignard reagent was prepared from 28.6 g. (0.123 mole) of 1-iodo-2,4-dimethylbenzene, 3 g. (0.123 mole) of magnesium, and 150 ml. of ether, which was replaced after reaction with a solution of 10 g. (0.041 mole) of the nitrile in 150 ml. of toluene. The reaction was then carried out as in the case of the 2',6'- isomer. The yield was 9.8 g. (62%). After reprecipitation and crystallization from a mixture of ethanol and acetone (one to nine), it formed slightly yellow crystals which melted

with decomposition at 173°.

Analysis: Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.27.

Found : C, 81.05; H, 6.38.

2-(1-Naphthylmethyl)-2',3'-dimethyl,diphenylketiminehydrochloride.

A Grignard reagent was prepared from 2.9g.(0.12 mole) of magnesium, 26.8 g.(0.145 mole) of 1-bromo-2,3-dimethylbenzene and 150 ml. of ether, which was replaced after reaction with a solution of 19 g. (0.08 mole) of the nitrile in 150 ml. of toluene. The reaction was then carried out as in the case of the 2',6'- isomer. The yield was 28.6 g. (92%). After reprecipitation and crystallization from a mixture of ethanol and acetone (one to nine), it formed slightly yellow crystals which melted with decomposition at 185°.

Analysis: Calculated for $C_{26}H_{24}NCl$: N, 3.63.

Found : N, 3.91.

2-(1-Naphthylmethyl)-3',5'-dimethyl,diphenylketiminehydrochloride.

A Grignard reagent was prepared from 2.2 g. (0.09 mole) of magnesium, 18.5 g. (0.1 mole) of 1-bromo-3,5-dimethylbenzene and 150 ml. of ether, which was replaced after reaction with a solution of 12.2 g.(0.05 mole) of the nitrile in 200 ml. of toluene. The reaction was then carried out as in the case of the 2',6'- isomer. The yield was 14.5 g. (75%). After reprecipitation and crystallization from a mixture of ethanol and acetone (one to nine), it formed slightly yellow crystals which melted with

decomposition at 184° .

Analysis: Calculated for $C_{26}H_{24}NCl$: N, 3.63.

Found : N, 3.92.

2-(1-Naphthylmethyl)-3',4'-dimethyl-diphenylketiminehydrochloride.

A Grignard reagent was prepared from 28 g. (0.15 mole) of 1-bromo-3,4-dimethylbenzene, 3.6 g. (0.15 mole) of magnesium and 150 ml. of ether, which was replaced after reaction with a solution of 12.2 g. (0.05 mole) of the nitrile in 100 ml. of toluene. The reaction was then carried out as in the case of the 2',6' isomer. The yield was 13.5 g. (70%). After reprecipitation and crystallization from a mixture of ethanol and acetone (one to nine), it formed white needles which melted with decomposition at 180° .

Analysis: Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.27.

Found : C, 79.88; H, 6.44.

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

A. A suspension of 2 g. of the corresponding ketimine in 50 ml. of 40% sulfuric acid was heated under reflux for 60 hours. The ketone was extracted with toluene and crystallized from ethanol in colorless prisms, m.p. $124-125^{\circ}$ (Form II). The yield was 0.05 g. (3%).

B. A suspension of 2 g. of the corresponding ketimine in 50 ml. of 40% sulfuric acid and 20 ml. of acetic acid was heated under reflux for 70 hours. The ketone was extracted with benzene and crystallized from ethanol

in colorless prisms, m.p. 109.5-110.0° (Form I). The yield was 0.1 g. (5%).

C. A solution of 2.5 g. of the corresponding ketimine in a mixture of 15 ml. 48% hydrobromic acid and 38 ml. of glacial acetic acid was sealed in a glass tube and immersed into a metal bath which was kept at 250-270° for 60 hours. The mixture was then neutralized with sodium hydroxide, extracted with benzene, and chromatographed. A small amount of strongly fluorescent material was eluted with petroleum ether, and the adsorbed ketone was eluted with a mixture of petroleum ether and ether (seven to three); yield 0.6 g. (27%). It was possible to recrystallize this material from ethanol and separate by hand two kinds of crystals: form I, as colorless prisms m.p. 109.5-110°, and form III, - reddish brown transparent plates, m.p. 122.0 - 122.5°.

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

Found :	Form I	: C, 89.37; H, 6.70.
	Form II	: C, 89.53; H, 6.52.
	Form III	: C, 89.81; H, 6.43.

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

Two grams of the corresponding ketimine were heated under reflux with 40 ml. of 25% sulfuric acid and 35 ml. of toluene for a period of three hours. The ketimine hydrolyzed completely and dissolved in the toluene layer which was separated, washed three times with water, dried over calcium chloride, filtered over charcoal, and the toluene was replaced by petroleum ether (b.p. 30-60°). Chromatography in a column packed with Fisher Alumina (80-200 mesh) was carried out, a mixture of

petroleum ether and carbon tetrachloride (seven to three) being used as an eluant. The resulting ketone was a colorless, very viscous oil; yield 1.6 g. (88%). All attempts at crystallization failed.

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

Found : C, ; H,

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

A mixture of 1.5 g. of the corresponding ketimine, 40 ml. of 25% sulfuric acid, and 30 ml. of toluene, was heated under reflux for a period of two hours. The toluene layer was separated, washed with water, dried over calcium chloride, charcoaled and crystallized from ethanol; yield 1.2 g. (87%). The analytical sample was obtained by three recrystallizations from ethanol as slightly pink prisms, m.p. 93-94°.

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

Found : C, 88.74 ; H, 6.20.

2-(1-Naphthylmethyl)-3',4'-dimethylbenzophenone.

A mixture of 2 g. of the corresponding ketimine, 30 ml. of 25% sulfuric acid, and 30 ml. of toluene, was heated under reflux for a period of three hours. The toluene layer was separated, washed with water, dried over calcium chloride, charcoaled and crystallized from ethanol; yield 1.6 g. (88%). The analytical sample was obtained by three recrystallizations from ethanol as slightly yellow prisms, m.p. 93.5-94°.

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

Found : C, 89.00 ; H, 6.49.

2-(1-Naphthylmethyl)-2',4'-dimethylbenzophenone

A mixture of 2.0 g. of the corresponding ketimine, 30 ml. of 25% sulfuric acid, and 30 ml. of toluene, was heated under reflux for three hours. The dark orange toluene layer was separated, washed with water, dried over calcium chloride, charcoaled and crystallized from ethanol; yield 1.7 g. (93%). The analytical sample was obtained by six recrystallizations from ethanol, and formed colorless prisms, m.p. 65-66°.

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

Found : C, 89.07; H, 6.29.

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

A mixture of 3.0 g. of the corresponding ketimine, 40 ml. of 25% sulfuric acid, and 30 ml. of toluene, was heated under reflux for four hours. The toluene layer was separated, washed with water, dried over calcium chloride, charcoaled and crystallized from ethanol; yield 1.8 g. (64%). The analytical sample was obtained by three recrystallizations from ethanol as colorless prisms, m.p. 70.5-71.5°.

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

Found : C, 88.84; H, 5.49.

10-(3',5'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of two grams of the corresponding ketimine, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid, was sealed in a glass tube and heated in a metal bath maintained at 250-270° for a period of four hours. A red, heavy oil which appeared on top of the solution was treated as in the case of the 2',5'- isomer; yield 1.65 g. (96%). The analytical sample was obtained by recrystallization of the resulting material from a mixture of ether and petroleum ether as small, colorless plates, m.p. 118-120°.

Analysis : Calculated for $C_{26}H_{20}$: C, 93.94; H, 6.07.

Found : C, 93.95; H, 6.23.

10-(3',4'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of two grams of the corresponding ketimine, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid, was sealed in a glass tube and heated in a metal bath maintained at 250-270° for a period of 13 hours. A heavy, red oil which appeared on the top of the solution was treated as in the case of the 2',5'- isomer; yield 1.3 g. (77%). The analytical sample was obtained by rechromatographing the resulting material twice and recrystallization from ethanol, ether, water mixture as colorless plates, m.p. 126-127°.

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

Found : C, 93.99; H, 6.37.

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

A mixture of two grams of the corresponding ketimine, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid, was sealed in a glass tube and heated in a metal bath maintained at 250-270° for a period of 25 hours. A black heavy oil which appeared on the top of the solution was treated as in the case of the 2',5'- isomer; yield 1.0 g. (59%). The analytical sample was obtained by chromatographing the resulting glassy solid three times, and recrystallizing it 27 times. Two isomorphous forms grew from the solution : A, small, colorless needles, m.p. 107.5 - 108.5°, and B, large, colorless prisms, m.p. 116.0 - 118°.

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

Found : C, 93.47; H, 6.34.

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

A mixture of two grams of the corresponding ketimine, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid, was sealed in a glass tube and heated in a metal bath maintained at 250-270° for a period of 25 hours. A black, heavy oil which appeared on the top of the solution was treated as in the case of the 2',5'- isomer; yield 0.7 g. (41%). The analytical sample was obtained by recrystallizing the resulting material three times from ether, ethanol, water mixture as colorless plates, m.p. 175-176° (sublimes).

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

Found : C, 94.04; H, 6.27.

10-(2',5'-Dimethylphenyl)-1,2-benzanthracene.

A mixture of two grams of the corresponding ketimine, 30 ml. of glacial acetic acid, and 15 ml. of 48% hydrobromic acid, was sealed in a glass tube and heated in a metal bath maintained at 250-270°, for a period of five hours. A green, heavy oil which appeared on the top of the solution was separated, dissolved in benzene, washed with water, and dried over calcium chloride. The benzene was replaced by petroleum ether and the solution was chromatographed. The resulting slightly yellow, transparent, strongly fluorescent oil was crystallized from a mixture of ethanol, ether, and water. The following technique was used: The hydrocarbon was completely dissolved in boiling ether, about a double amount of ethanol was added, and the solution was brought to boiling. Then a drop of water was added, and if the white precipitate which was immediately formed dissolved readily, another drop was added and the solution was allowed to cool slowly. The yield was 0.9 g. (53%). The analytical sample was obtained by rechromatographing the crude product, and crystallizing the resulting transparent oil from an ethanol, ether, water mixture. It formed colorless prisms, m. p. 116-117°.

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

Found: C, 93.7; H, 6.15.

SUMMARY

SUMMARY

1. A new method of preparation of 1-naphthylmethylbenzotriles was described.
2. Eighteen compounds, not previously reported in the literature, were synthesized.
3. Reasonably conclusive evidence was found that some of the hydrocarbons may exist in different polymorphic forms.

ACKNOWLEDGMENTS

ACKNOWLEDGEMENTS

The author wishes to express his appreciation of the continuous guidance, encouragement, and assistance given by Dr. Frank A. Vingiello throughout this work.

He also wishes to acknowledge his gratitude to his wife for her constant help.

This work was made possible by the grant of the Office of Ordnance Research U.S. Army, for which the author feels greatly indebted.

LITERATURE CITED

LITERATURE CITED

- (1) G. Wolf, J. A. C. S., 75, 2673 (1953).
- (2) C. L. Hewett, J. Chem. Soc., 1951, 299.
- (3) J. W. Cook, J. Chem. Soc., 1930, 1087.
- (4) E. Clar, Aromatische Kohlenwasserstoffe, p.190.
- (5) S. Glasstone, Sourcebook on Atomic Energy.
- (6) C. Bradsher, J. A. C. S., 62, 1077 (1940).
- (7) J. Shulman, M. S. Thesis, Virginia Polytechnic Institute (1950).
- (8) F. A. Vingiello, private communication.
- (9) J. W. Cook, J. Chem. Soc., 1932, 457.
- (10) J. W. Cook, A.M. Robinson, F. Goulden, J. Chem. Soc., 1937, 393.
- (11) L. F. Fieser, E. B. Hershberg, J. A. C. S., 59, 1028 (1937).
- (12) R. B. Sandin, L. F. Fieser, J. A. C. S., 62, 3098 (1940).
- (13) G. M. Badger, F. Goulden, F. L. Warren, J. Chem. Soc., 1941, 18.
- (14) M. S. Newman, J. A. C. S., 59, 1003 (1937).
- (15) L. F. Fieser, M. S. Newman, J. A. C. S., 58, 2376 (1936).
- (16) F. Bergman, Cancer Research, 2, 660 (1942).
- (17) L. F. Fieser, Experiments in Organic Chemistry, 2nd Ed., D. C. Heath
1941, 5, 690.
- (18) Beilsteins Handbuch der organischen Chemie, 4th Ed., 1944, 5, 689 (341).
- (19) J. B. Culbertson, J. A. C. S., 73, 4818 (1951).
- (20) A. E. Remick, Electronic Interpretations of Organic Chemistry, 2nd
Ed., Wiley, 1949.
- (21) J. N. Collie, J. Chem. Soc., 71, 299-311 (1897).

LITERATURE CITED - Continued

- (22) S. R. Best, J. F. Thorpe, J. Chem. Soc., 95, 1506 (1909).
- (23) K. V. Auwers, W. Susseml, Ber., 63, 1072 (1930).
- (24) J. G. Van Oot, Ph.D. Thesis, Virginia Polytechnic Institute, (1950).
- (25) G. W. Wheland, The Theory of Resonance, Wiley (1949).
- (26) F. A. Vingiello, J. A. C. S., 73, 1887 (1951).
- (27) Jacobsen, Ber., 17, 2372 (1884).
- (28) Stallard, J. Chem. Soc., 89, 809.

VITA

VITA

Alexej B. Borkovec was born in Prague, Czechoslovakia in October 1925.

He graduated from the Czech Polytechnic Institute in Prague (Geske vysoke uceni technicke, vysoka skola chemicko-technologickeho inzenyrstvi) in June 1949. From 1949 to 1951 he was employed with the United Nations in Munich, Germany, and from 1951 to 1952 with the Biochemical Institute and the Banco Minero in La Paz, Bolivia.

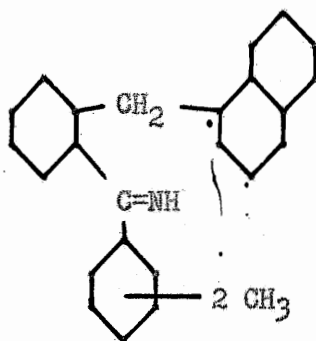
He entered the Virginia Polytechnic Institute in the fall of 1952 and has been there until the present time.

Alexej B. Borkovec

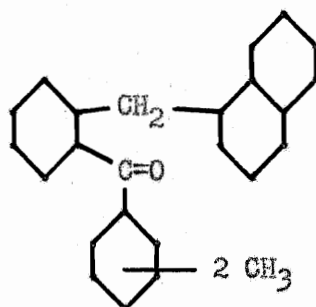
APPENDICES

2-(1-Naphthylmethyl)dimethyl, diphenylketimines

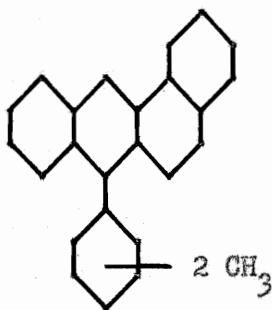
prepared in the form of hydrochlorides.



Position of CH ₂ groups	Reference page
2',3'	41
2',4'	40
2',5'	40
2',6'	23, 39
3',4'	42
3',5'	41

2-(1-Naphthylmethyl)dimethylbenzophenones.

Position of CH ₃ groups	Reference page
2',3'	45
2',4'	45
2',5'	43
2',6'	27, 42
3',4'	44
3',5'	44

10-(Dimethylphenyl)-1,2-benzanthracenes.

<u>Position of CH₃ groups</u>	<u>Reference page</u>
2',3'	47
2',4'	47
2',5'	48
2',6' ?	25
3',4'	46
3',5'	46