

THE SYNTHESIS OF PICENE

By

Warren C. McVey

Thesis Submitted to the Faculty of the Graduate School
of the University of Maryland in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy

1938

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To Dr. N. L. Drake
is extended appreciation for his
aid and guidance during this investigation.

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I. Historical Survey.

"Picene" was the name given by Burg (2) to a hydrocarbon which he isolated from lignite tar. The same substance had been isolated about seven years earlier by Rasenack (3) from coal tar residues, but Rasenack, noting its close resemblance to chrysene, concluded that it was an isomer of chrysene.

Graebe and Walter (4) obtained picene by a destructive distillation of still residues from the rectification of California petroleum. They checked the $C_{22}H_{14}$ formula proposed by Burg by a molecular weight determination by the method of Victor Meyer.

The first instance of a synthetic preparation of picene is recorded by Lispieau (5), who isolated it from the products obtained by the action of ethylene bromide on naphthalene in the presence of aluminum chloride. It was also prepared by Hirn (6) by passing the vapors of α,α' -dinaphthyl stilbene through a red hot tube. More recently, Freidman (7) heated α -methyl naphthalene with sulfur in a closed tube for 72 hours at $300^{\circ} C.$, and obtained a little high melting substance which he thought was picene.

The first really clear cut synthesis, however, was due to Ruzicka and Hosli (8). They reacted the Grignard compound of β -(naphthyl-1) ethyl chloride with α -tetralone and obtained α,β -(dinaphthyl-1) ethane, which underwent cyclization and dehydrogenation to form picene when heated with anhydrous aluminum

chloride in CS₂ solution. Similar syntheses have been carried out by Ruzicka and Morgeli (8) to produce 3,9,10-trimethyl piceene and 3,8-dimethyl piceene, and more recently by both Ruzicka and Hoffman (10) and by Howard (11) to yield 1,8-dimethyl piceene.

Waldmann and Pitschak (12) condensed *o*-xylyl dicyanide with *o*-nitro-benzaldehyde, and saponified the resulting di-(*o*-nitro-benzal)-*o*-phenylene dicyanide to the di-carboxylic acid. This was reduced to the diamino compound, and cyclized by means of a Pechorr condensation to form piceene-12,13-dicarboxylic acid which was decarboxylated to give piceene.

II. Introduction .

In the final proof of the structure of an organic compound, no evidence is quite so satisfactory as a synthesis of the substance in question. The synthesis of one of its degradation or dehydrogenation products is somewhat less conclusive, but still a very valuable contribution to the evidence upon which a proposed structure may be based. Especially is this true if it is possible to follow all steps in the synthesis from the starting material to the finished product.

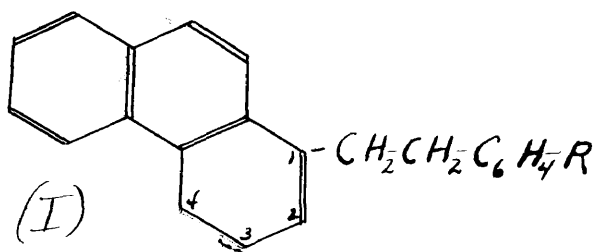
The picene skeleton has been found to be present in many triterpenes, and certain dehydrogenation products of triterpenes have been shown to be derivatives of picene (13) (14)(15)(16)(17)(18)(19). As an aid in the proof of the structure of these compounds therefore, methods suitable for the synthesis of picene, and more especially its alkyl derivatives, are extremely desirable. The syntheses of Ruzicka and co-workers (8)(9)(10), of Howard (11), and of Waldmann and Pitschak (12), while meeting the requirement that they should be clear cut and capable of being followed step by step, leave something to be desired with regard to several particulars. First the necessary intermediates are often not available and are difficult to prepare, or do not lend themselves to convenient modifications. In the second place, the yields are generally very poor.

III. The Aim

The aim of this research therefore, is first to develop another synthesis for piene which may be readily modified to enable various alkylated pienes to be prepared. Also it seems desirable to study the conditions under which cyclisation may occur, with the view of future modification of the intermediates or of the procedure.

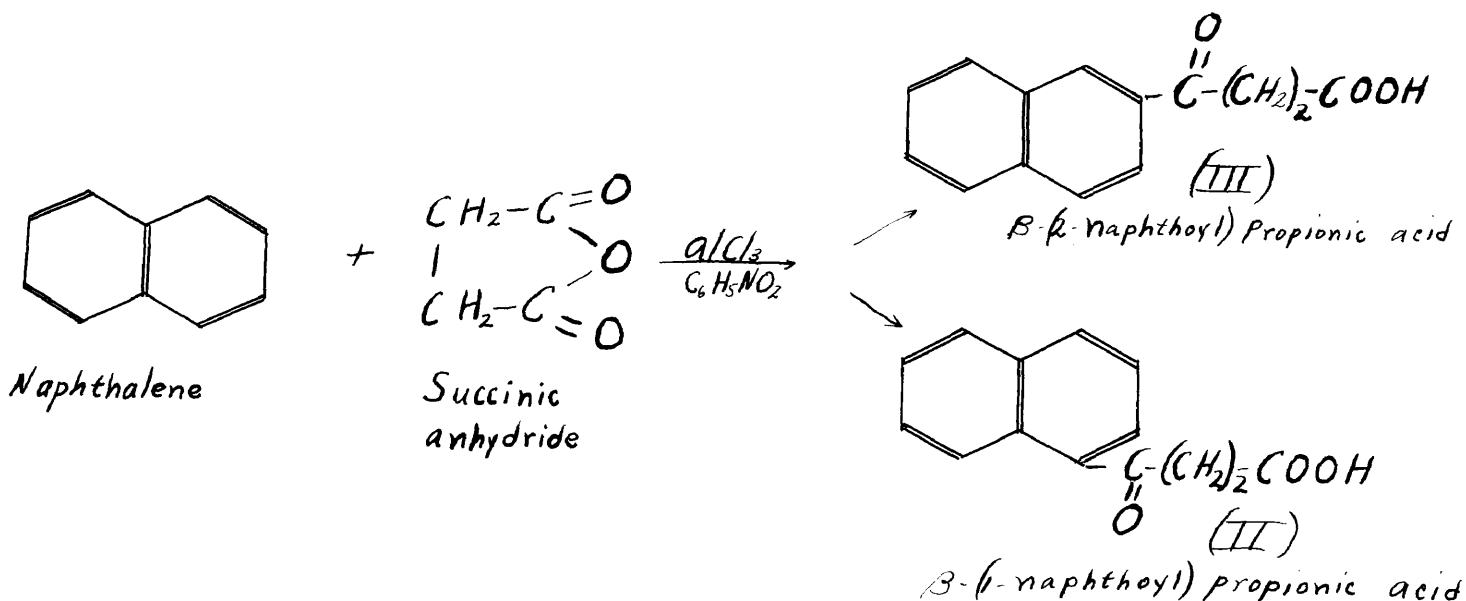
IV. Outline of the Procedure Investigated

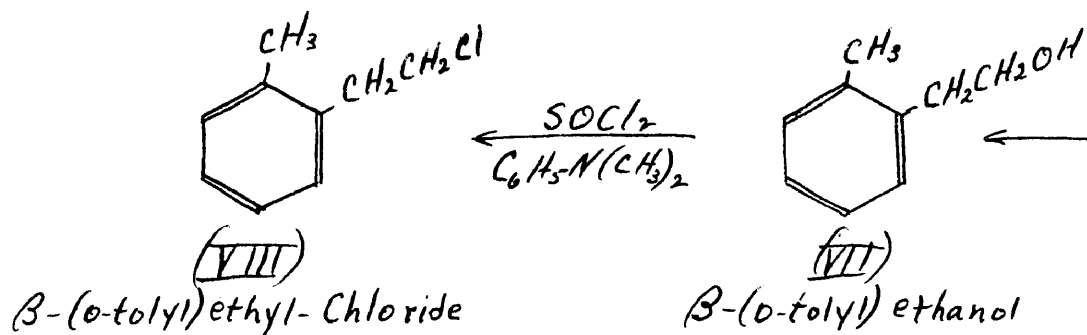
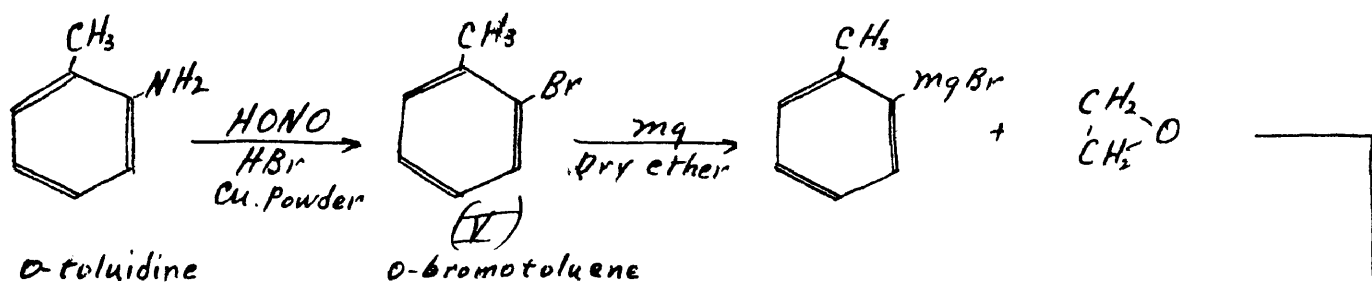
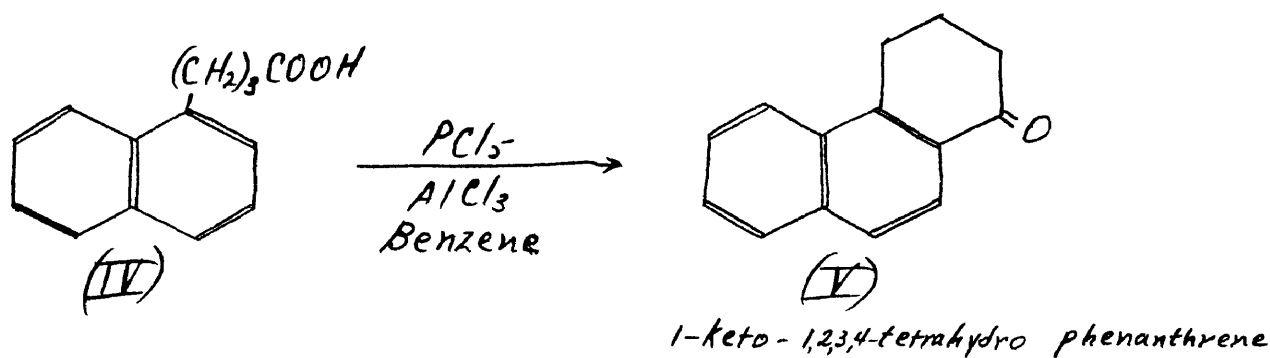
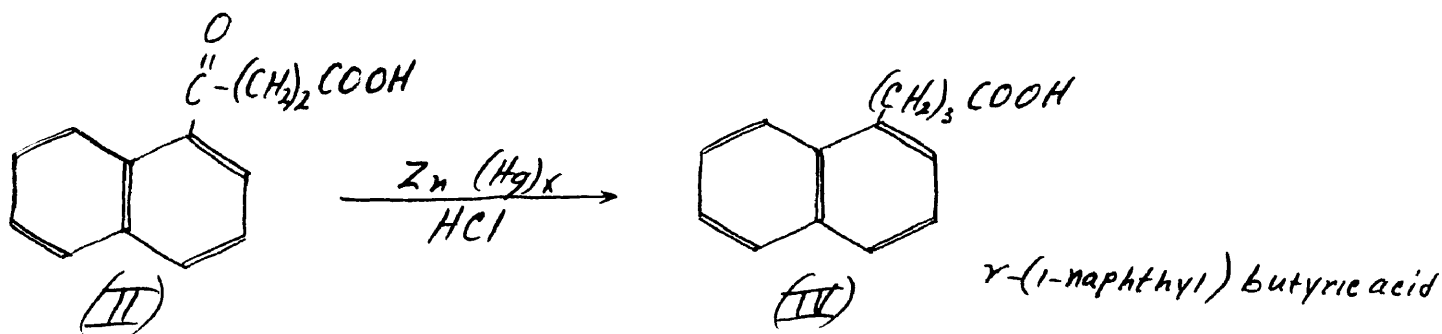
The synthesis investigated divides itself sharply into two parts. The first is the preparation of a 3,4-dihydro-1- β -(aryl)ethyl phenanthrene (I).

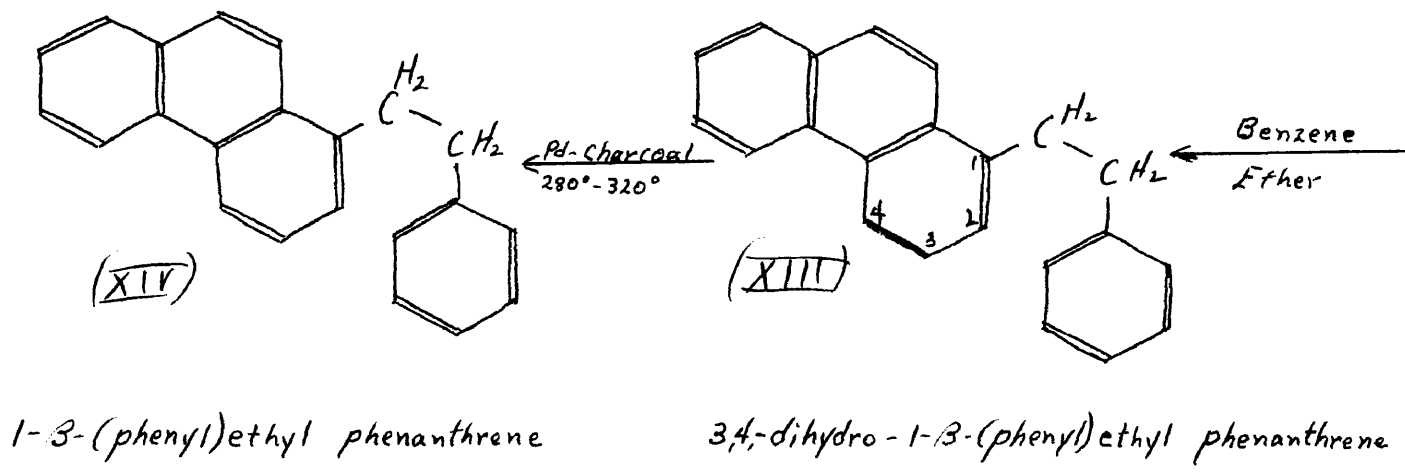
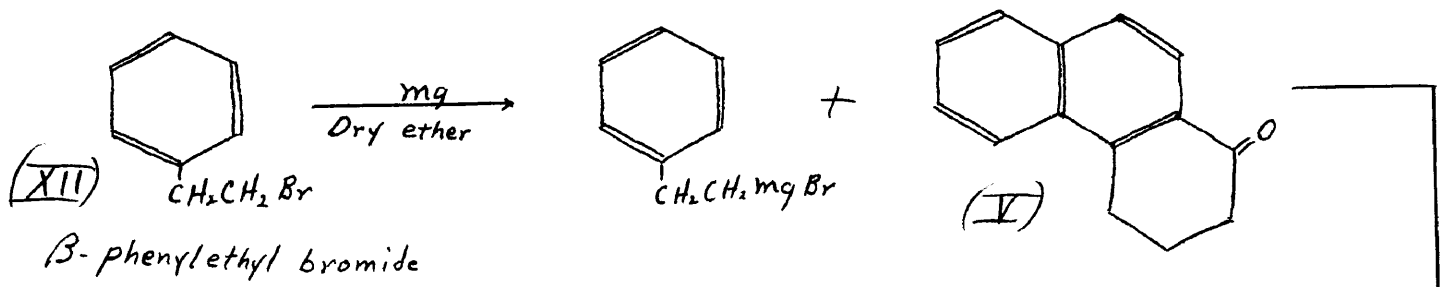
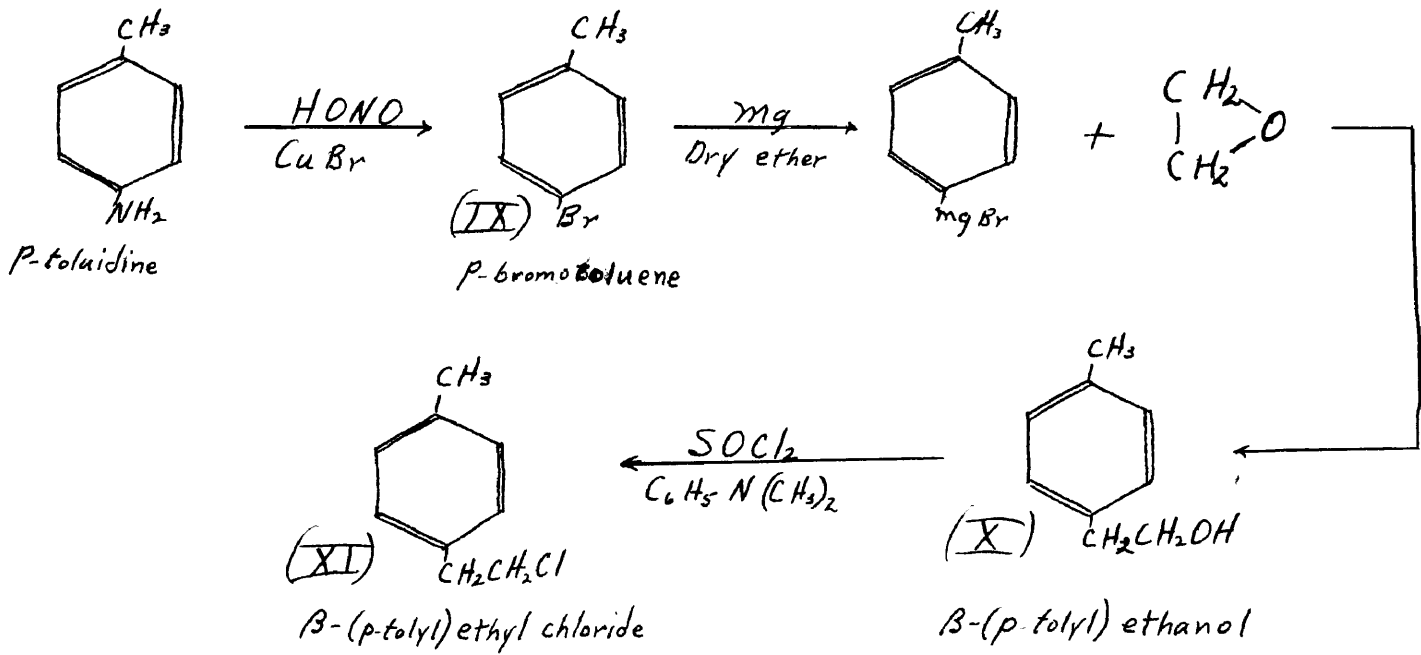


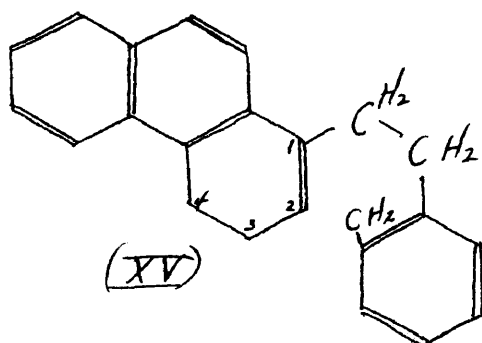
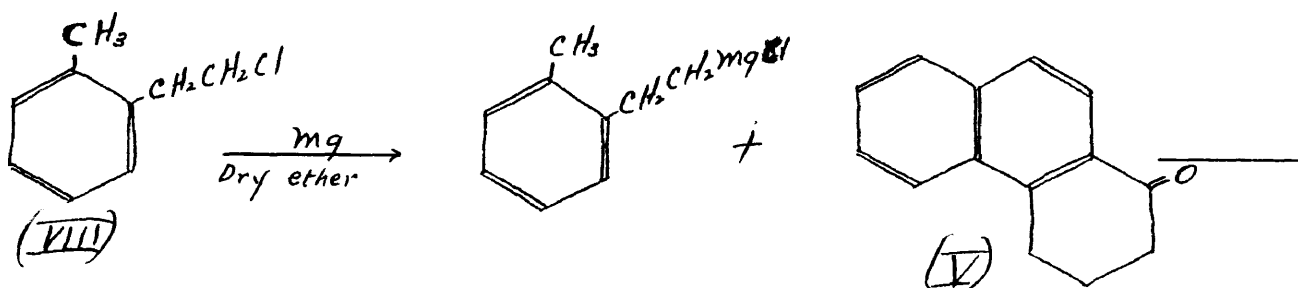
The second is the cyclization of (I) and its dehydrogenation to form picene.

The procedures followed in the synthesis of three 3,4-dihydro-1- β -(aryl)ethyl phenanthrenes are shown in the following scheme of diagrams. The Roman numerals accompanying the intermediates are reference numbers used for convenience and brevity in the experimental part of this thesis.

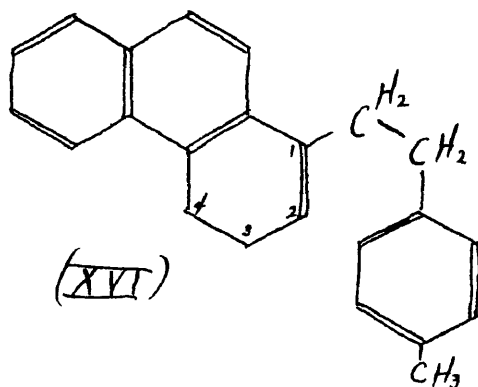
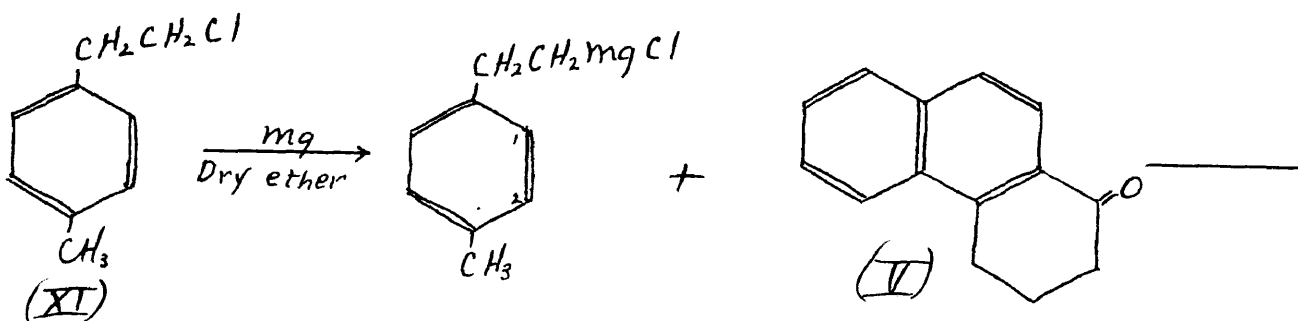








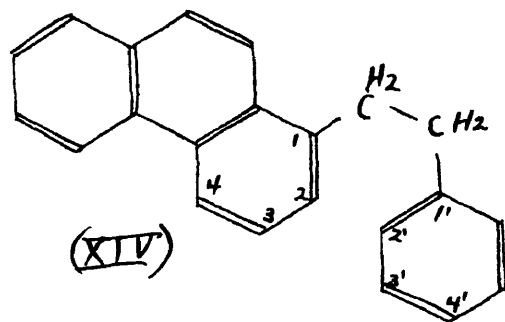
3,4-dihydro-1-B(o-tolyl)ethyl phenanthrene



3,4-dihydro-1-B(p-tolyl)ethyl phenanthrene

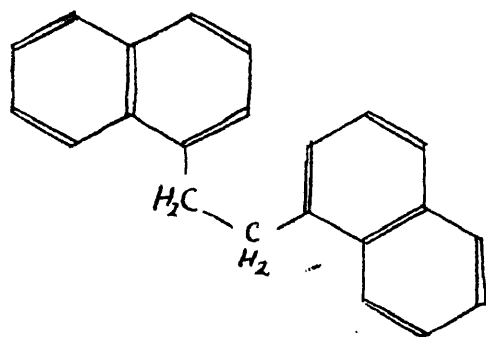
In the separation of the two isomeric β -(naphthoyl) propionic acids (II) and (III), advantage is taken of the fact that (II) is both more soluble and more highly dissociated than (III). To a suspension of the mixed acids in water was added a quantity of sodium hydroxide sufficient to convert about one-third of the mixture into their sodium salts. The resulting solution consists chiefly of the sodium salt of the β -(1-naphthoyl) propionic acid (II), and may be filtered from the undissolved acids and recovered by precipitation with an acid.

When 1- β -(phenyl)ethyl phenanthrene (XIV),



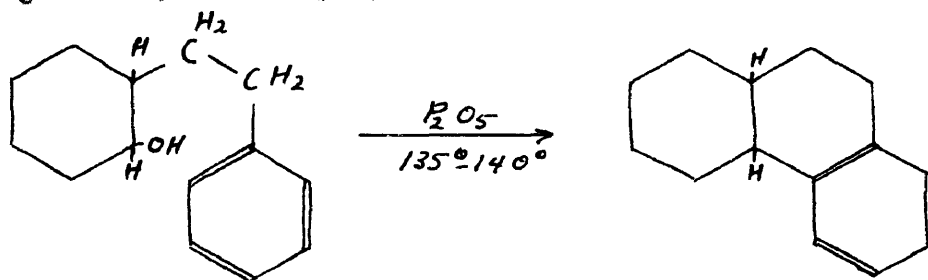
in CS_2 solution was reacted with anhydrous aluminum chloride in an attempt to bring about a cyclization between the 2 and the 2' carbon atoms, a tarry polymerized product was obtained from which no picene could be isolated. It is evident that the reaction proceeds differently than in the case of the

supposedly analogous α/β -di-(naphthyl-1) ethane,

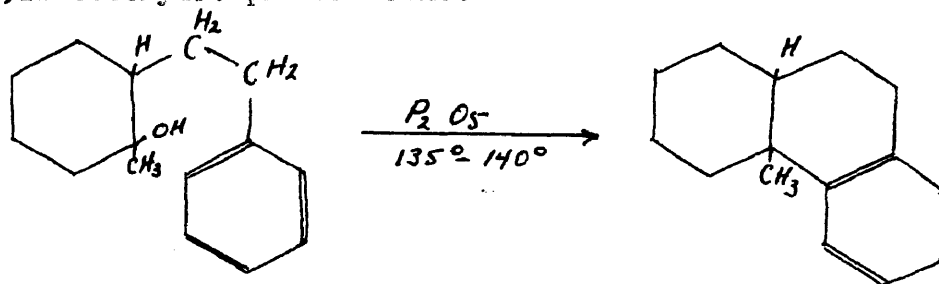


which Ruzicka and Hosli (8) cyclicized into picene in this manner. So a brief survey was made of the various cyclization reactions and procedures used by other investigators.

Bardhan and Sengupta (20) cyclicized 2- β -(phenyl)ethyl cyclohexanol into 1,2,3,4,9,10,11,12-octahydro phenanthrene using P_2O_5 as a cyclizing agent.

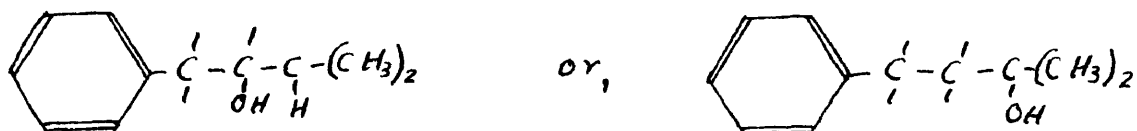


Kon (21), by the same means, cyclicized 1-methyl-2- β -(phenyl)ethyl cyclohexanol to form 12-methyl-1,2,3,4,9,10,11,12-octahydro phenanthrene.

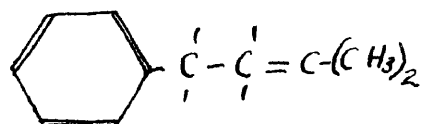


These authors assumed that the cyclization occurred as the result of a dehydration of the intermediate by the P_2O_5 .

Bogert and Davidson (22) found that by dehydrating mono-phenylated alcohols of the type,

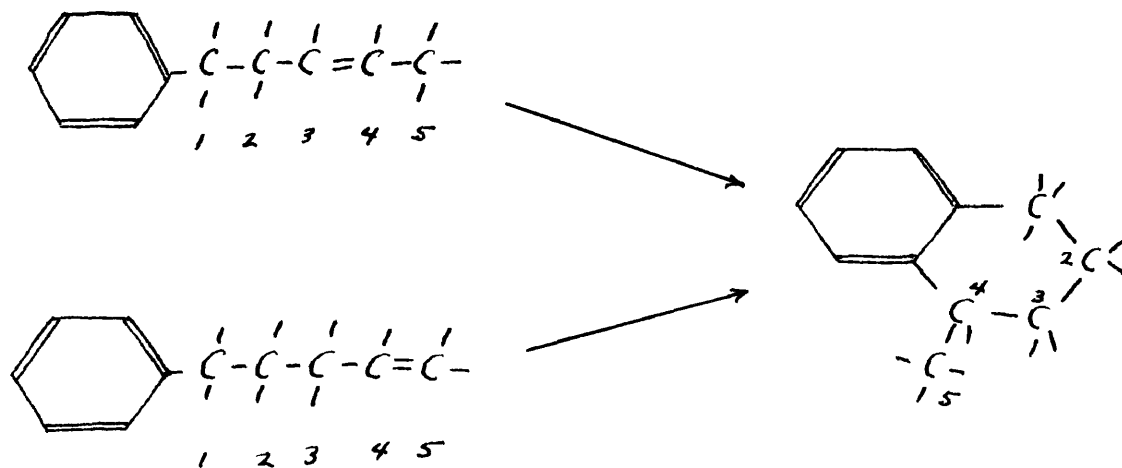


with 85% sulfuric acid, indanes were produced instead of the expected olefins of the type,



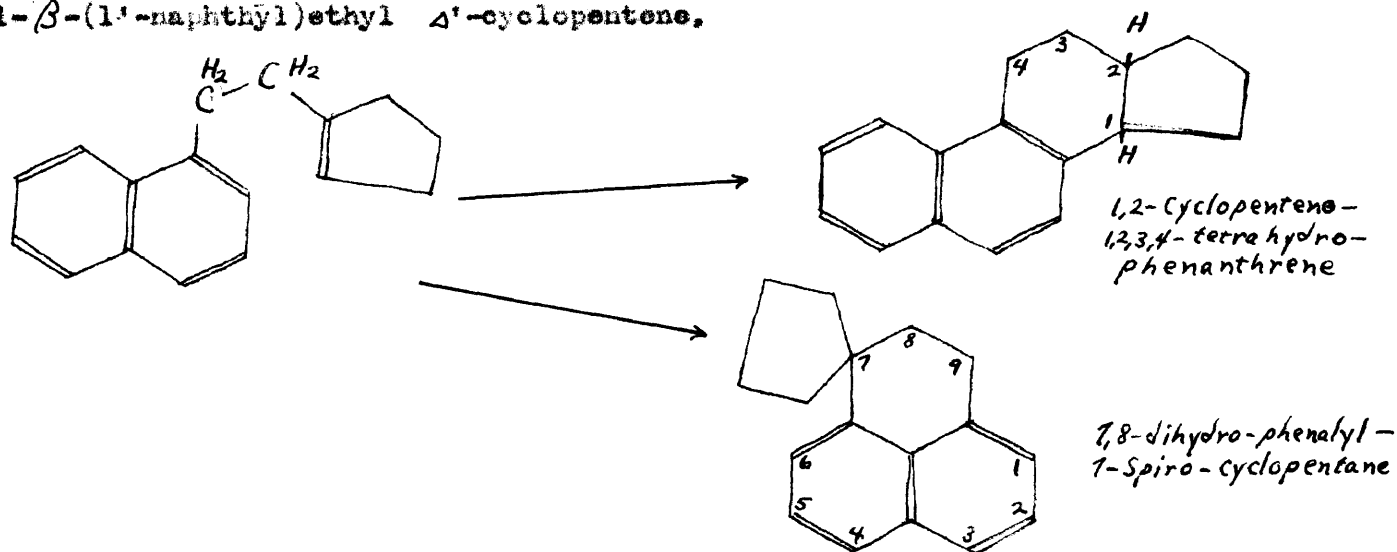
The intermediate olefins, where they could be isolated, were also found to give indanes when treated with 85% sulfuric acid. Working along similar lines, Bogert and co-workers (23)(24) confirmed these results, namely, that the alcohols pass first into one or more olefins which then polymerize to form cyclic compounds.

From the work cited above, and the additional work of Cook and others (25)(26)(27)(28), we may conclude that in any chain of carbon atoms attached to an aromatic group, cyclization to form a new six carbon ring may take place whenever an olefinic linkage occurs either between the third and fourth, or between the fourth and fifth carbons distant from the aromatic group.

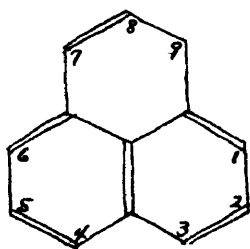


When the unsaturation is between the third and fourth carbon atoms, this cyclization may take place even though the olefinic bond is a part of another hydro-aromatic cycle, but if the olefinic linkage forms a part of another aromatic ring, the cyclization is generally greatly impeded or prevented altogether. The cyclization by Kuzicka and Bosli (8) of α/β -di-(naphthyl-1)ethane to picene is the only instance found of cyclization between two aromatic rings.

When Cook and Hewitt (29) attempted to cyclize 1- β -(1'-naphthyl)ethyl Δ^1 -cyclopentene,

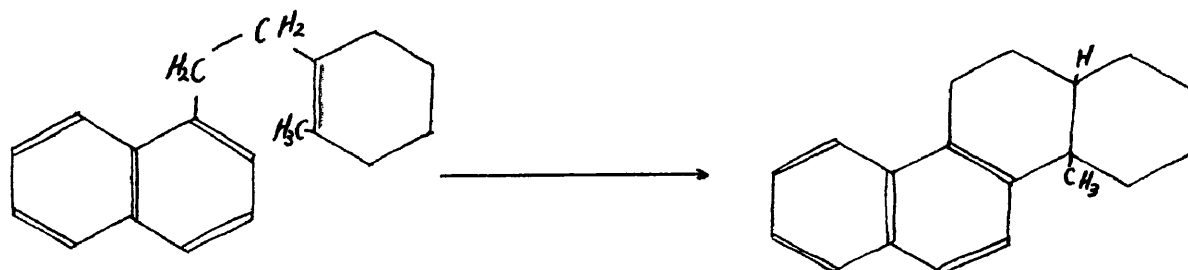


they obtained besides a small yield of the expected 1,2-cyclopenteno-1,2,3,4-tetrahydro phenanthrene, a considerable yield of an isomeric hydrocarbon which they considered to be 7,8-dihydrophenalyl-7-spirocyclopentane. Cook and Hewitt (29) gave the name "phenalene" to the following hydrocarbon,



Hence, its derivatives were termed "phenalyl" derivatives.

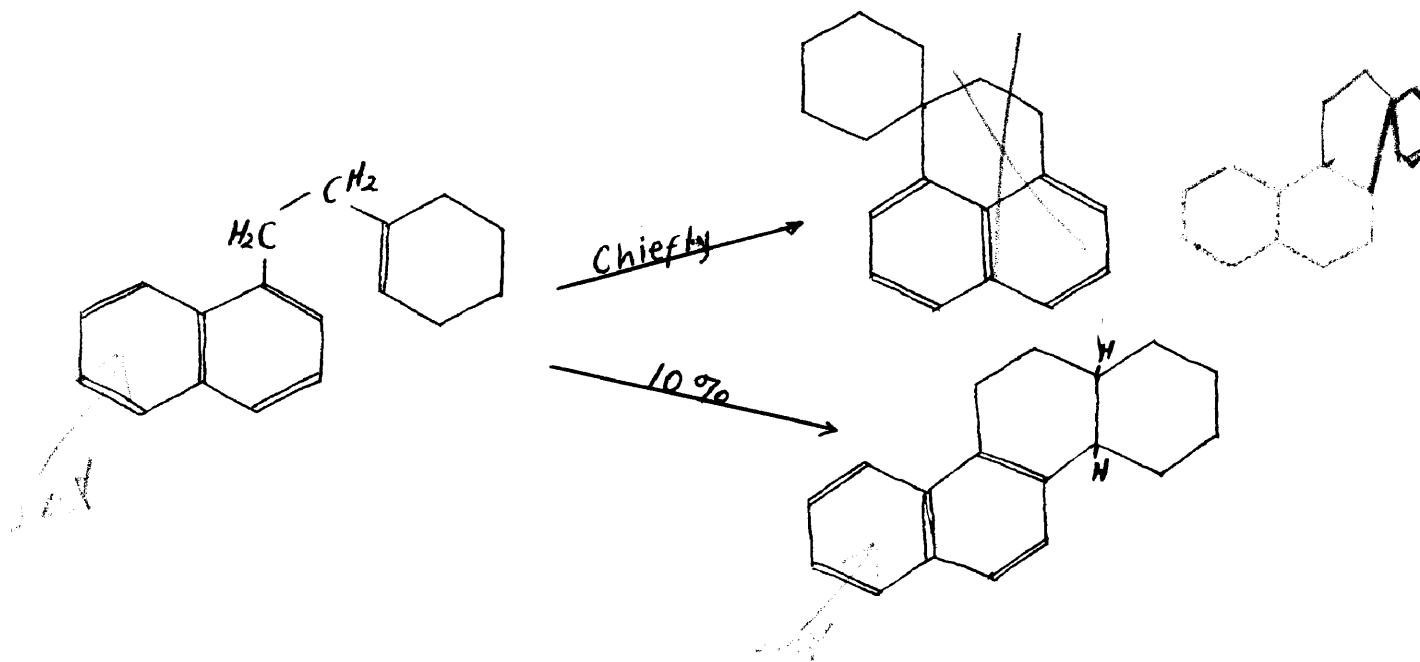
Cook and co-workers thoroughly investigated this phenomenon of spiran formation which they found rather general in this type of compound, and stated that if an alkyl group were present at the point on the hydro-aromatic ring where cyclization was expected to occur, the cyclization was directed to the carbon holding the alkyl group. Thus a quaternary alkyl group was created and spiran formation was generally prevented. For example, they found that if α -(naphthyl-1)- β -(2-methyl-1,2-cyclohexene-1)ethane were subjected to treatment with anhydrous aluminum chloride in CS_2 at $0^\circ C.$, a good yield of methyl-octahydro chrysene was obtained which gave chrysene on dehydrogenation.



α -(naphthyl-1)- β -(2-methyl-1,2-cyclohexene-1) ethane

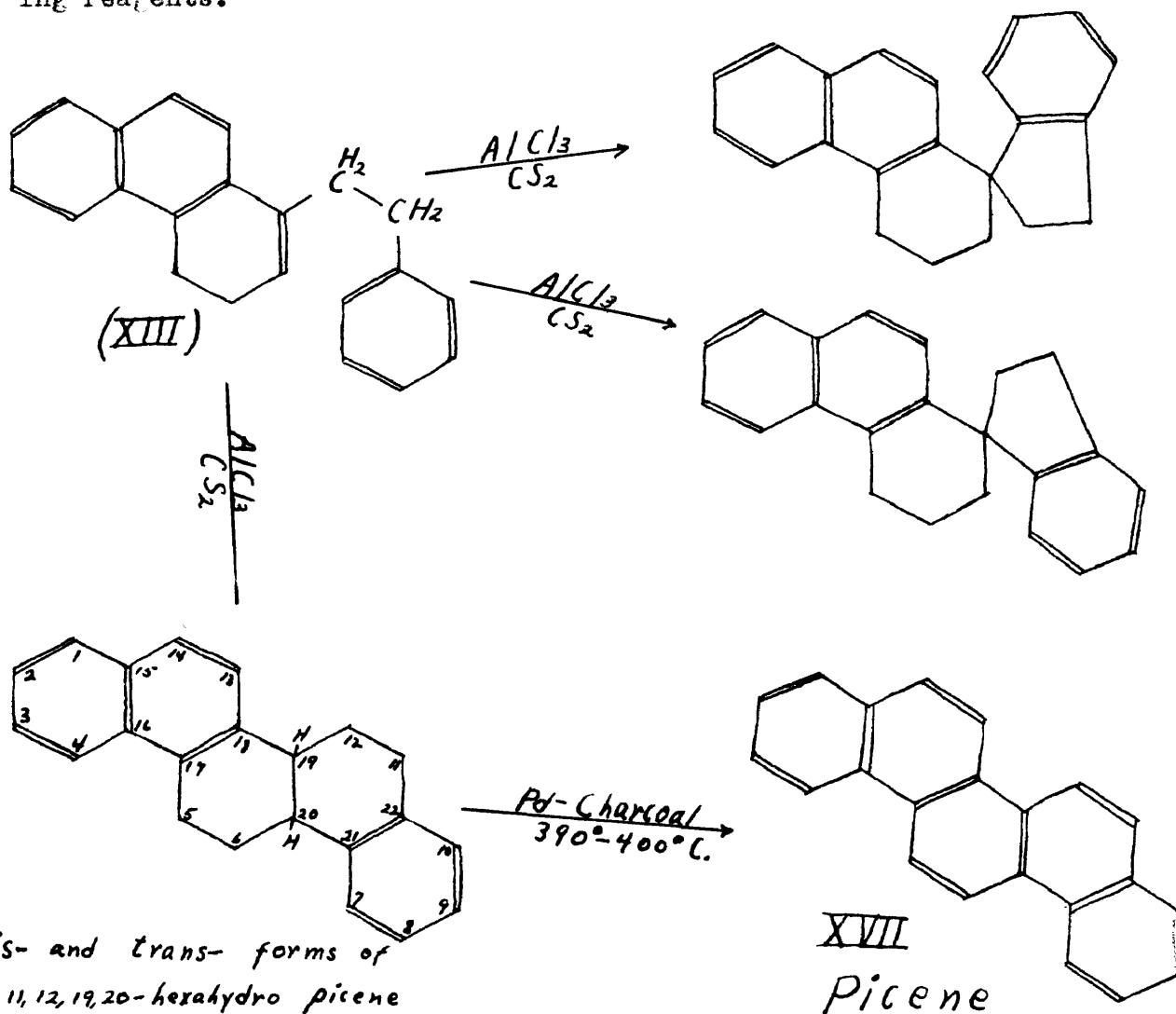
α methyl octahydrochrysene

If however, the non-methylated compound, α -(naphthyl-1)- β -(1,2-cyclohexene-1)ethane were cyclized in the same manner, two products were obtained.



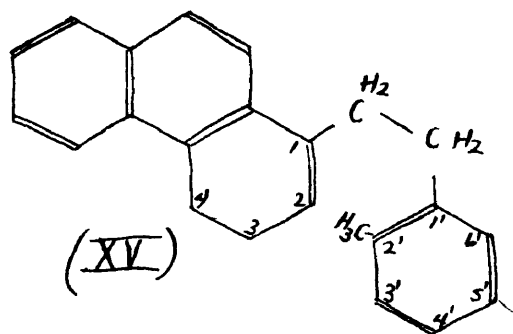
In 1- β -(phenyl)ethyl phenanthrene (XIV), while it has an olefinic linkage in an acceptable position for cyclization, the unsaturation which must take part in the cyclization forms a part of an aromatic system. In the case of 3,4-dihydro-1- β -(phenyl)ethyl phenanthrene (XIII) however, the unsaturation which disappears during the

cyclization forms a part of a hydro-aromatic ring, and in light of the investigations cited, should be more readily cyclicized than (XIV). It will be noted however, that (XIII) has no alkyl group attached to the hydro-aromatic ring at the point where cyclization should occur. Therefore according to Cohen, Cook, Hewitt and Girard (30), we might expect extensive spiran formation upon treating (XIII) with cyclizing reagents.



When in this investigation, (XIII) was subjected to treatment with anhydrous aluminum chloride in CS_2 as described in the experimental part, a viscous oil was obtained from which no pure substance could be isolated. Taking into account the probability of spiran formation, this was not surprising, as at least four compounds could reasonably be expected, and are shown in the above series of diagrams. When this viscous oil was dehydrogenated by heating with palladium adsorbed on charcoal, picene was obtained in yields slightly better than one percent. The remainder of the viscous oil was apparently not affected by the dehydrogenation.

With regard to the intermediate 3,4-dihydro-1- β -(o-tolyl)ethyl phenanthrene (XV),

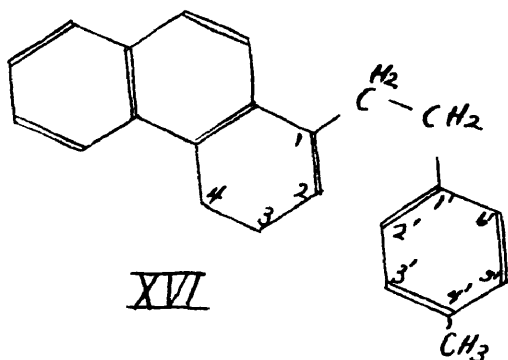


it will be seen that the methyl group is not attached at the 2-position on the hydro-aromatic ring where its presence would probably retard spiran formation, but that it is located at the 2'-position on the aromatic ring. If (XV) is to cyclicize so as to produce a quaternary methyl group, it will

be necessary to break the 1',2'-double bond in the aromatic ring. The probability of this happening is believed to be small. If, however, (XV) should cyclicize with the breaking of the 1,2-double bond in the hydro-aromatic ring, which is the usual course of such cyclizations, two possibilities must be considered. The cycle might close between carbons 2 and 6' to yield a cyclization product which would give a 10-methyl picene on dehydrogenation, or it might close between carbons 2 and 2', losing the methyl group in the process and giving the same intermediate as was obtained by the cyclization of (XIII). In this investigation, when (XV) was treated with anhydrous aluminum chloride in CS₂ at 0° C., and the product dehydrogenated, only picene could be isolated from the reaction products, and the yield of picene (4³/₅%) was better than when (XIII) was used as an intermediate.

The loss of the alkyl group during the cyclization may be explained by considering the analogy between the reaction in this case and the reaction of toluene and an olefin such as ethylene, using aluminum chloride as a catalyst (34). Considerable ethyl benzene was produced, the methyl group was lost, and the reaction took place with greater ease than with benzene. With free toluene and an olefin, considerable substitution also occurred at the carbons ortho or para to the methyl group, but in (XV), the preferential formation of a six-membered ring prevents any cyclization involving these carbons and the probability of reaction at the carbon holding the methyl group is increased.

In this investigation, the treatment of 3,4 dihydro-1- β -(p-tolyl) ethyl phenanthrene (XVI),



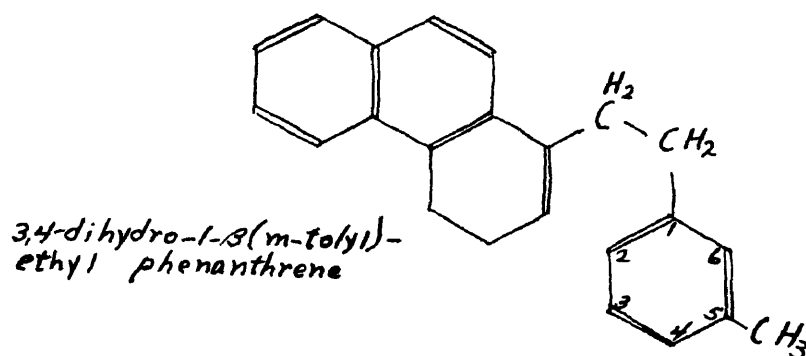
with aluminum chloride in CS_2 at $0^\circ C$. gave the usual viscous oil, but which when dehydrogenated, yielded none of the expected product, 8-methyl picene. The probable explanation is that the methyl group in the 4'-position exerts a definite directing influence toward reaction at the ortho carbons (3' and 5') and against cyclization at the meta carbons (2' and 6') which are the only ones available for cyclization.



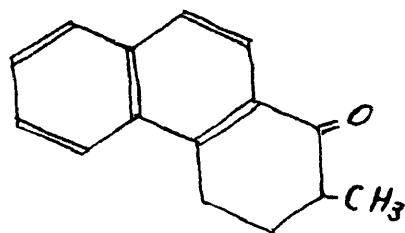
V. Conclusions

From this investigation we may conclude that the preparation of the intermediates (XIII), (XV) and (XVI) offer no serious difficulties. The yield of picene from (XV), while never better than 5%, is sufficiently promising to warrant further investigation. The following suggestions for further investigation are respectfully offered:

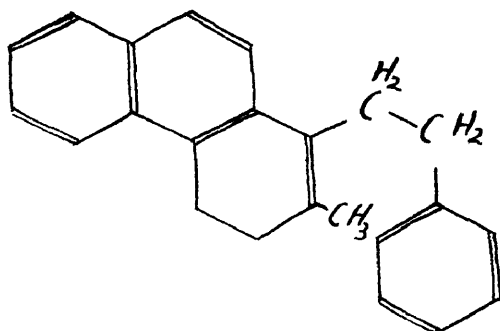
1. From β -(m-tolyl)ethyl chloride and 1-keto-1,2,3,4-tetrahydro phenanthrene (V), prepare 3,4-dihydro-1- β -(m-tolyl)ethyl phenanthrene. It is believed that the ortho and para directing influence of the methyl group in this position would tend to activate either the 2 or the 6 carbon atom sufficiently to promote cyclization at this point.



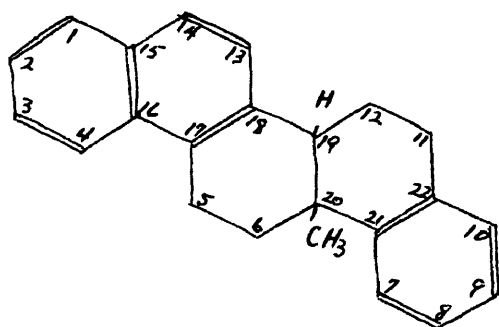
2. From naphthalene and the anhydride of methyl succinic acid prepare 1-keto-2-methyl-1,2,3,4-tetrahydro phenanthrene,



and react it with the Grignard compound of β -phenylethyl bromide. This will yield 3,4-dihydro-2-methyl-1- β -(phenyl)ethyl phenanthrene.



This intermediate has an olefinic linkage properly located with respect to the aromatic ring, and also has a methyl group attached to the hydro-aromatic ring at the point where cyclization is expected to occur. According to the previously mentioned work of Cook and co-workers, this compound would be expected to cyclize to form 5,6,11,12,19,20-hexahydro-20-methyl picene.



with a reduction in the spiran forming side reaction. This product would yield picene on dehydrogenation.

VI. Experimental part.

All temperatures listed in this investigation were taken with calibrated thermometers, and have been corrected for exposed stem.

β -1-naphthoyl propionic acid (II), and β -2-naphthoyl propionic acid (III).

The method used is a modification of that used by Fieser and Peters (36). To a 3-liter 3-necked round bottomed flask, fitted with a mercury sealed stirrer, a thermometer, and a dropping funnel, was added 116 grams naphthalene dissolved in 350 ml. dry nitrobenzene. One hundred grams succinic anhydride was then added, which did not completely dissolve. Keeping the contents of the flask below 5°C. by means of an ice and salt bath, a solution of 266 grams anhydrous aluminum chloride in 700 ml. dry nitrobenzene was slowly dropped into the well stirred mixture. Two to three hours were required for this operation. The resultant dark red solution was held at about 5°C. for five days, being protected from moisture by means of a calcium chloride tube.

The solution was then poured into a mixture of 1 kg. crushed ice and 250 ml. concentrated HCl in a 5-liter flask, and the nitrobenzene removed by distillation with steam. Six to seven hours distillation was necessary to remove all of the nitrobenzene. The mixture of crude acids remained in the flask as a heavy oily layer which solidified on cooling. After cooling, the aqueous layer was

decanted off, the hard cake of mixed acids broken up and washed several times with water, and the acids collected on a filter. The acids were dissolved in 1500 ml. hot 10% Na_2CO_3 solution, filtered from any insoluble material, and after cooling, the solution was carefully acidified with HCl. The crude acids were filtered off and dried overnight at 100°C. The yield of crude mixed acids, consisting of approximately equal amounts of each isomer, was 205 grams.

Separation of the mixed naphthoyl propionic acids.

Sixty-eight grams of the finely pulverized crude acids was placed in a 3-liter flask and suspended in 1500 ml. warm water, and 50 ml. of 2N NaOH solution was slowly added with shaking. This is one-third the theoretical quantity necessary to dissolve the acids. The mixture was held at 50-60°C. for several hours, or preferably overnight, with occasional shaking, then cooled to room temperature and filtered. The filtrate which should be clear and pale yellow in color was acidified with a slight excess of dilute HCl. The milky fluid so obtained was shaken momentarily, allowed to stand for a few minutes, then shaken again. The white acid, consisting almost entirely of β -1-naphthoyl propionic acid, separated in a flocculent form and was easily filtered. After several recrystallizations from 20% acetic acid, the acid was obtained in a white crystalline form melting at 132-133°C.

The residue of undissolved acids was returned to the flask and treated with another 50 ml. of the 2N NaOH in the same manner as before. This yielded a mixture of both isomers, but free from tarry impurities. The acids so obtained were added to the next batch of starting material, and the treatment with alkali carried out as before.

The residue undissolved by the two treatments with NaOH consists almost exclusively of β -2-naphthoyl propionic acid, contaminated with considerable tarry material. It may be purified by crystallization from acetic acid after boiling with decolorizing carbon.

γ -1-naphthyl butyric acid(IV)

The modified Clemmensen procedure of Martin(37) was used. One hundred grams mossy zinc and 10 grams $HgCl_2$ were placed in a 1-liter round bottomed flask, covered with 60 ml. 5% HCl, and shaken for 5 minutes. The dilute acid was decanted off, and 175 ml. concentrated HCl and 75 ml. water added, followed by 100 ml. toluene. Fifty grams β -1-naphthoyl propionic acid(II) was then carefully added so that it all remained in the toluene layer and did not come into contact with the zinc. The contents were not stirred or shaken. The flask was fitted with a reflux condenser and the contents refluxed for 30-40 hours.

After cooling slightly, the layers were decanted from the residual zinc into a large separatory funnel. The zinc was washed thoroughly with toluene, and the washings added to the separatory funnel. The acid layer was drawn off and extracted with toluene. The combined toluene layers were shaken vigorously with several grams of "Nuchar", filtered into a distilling flask, and the water removed by distilling off 25-50 ml. of the toluene. The remaining solution was chilled and γ -1-naphthyl butyric acid separated. Thirty grams were obtained which after recrystallization from benzene, melted at 107.5-108.5°C.

1-keto-1,2,3,4-tetrahydro phenanthrene. (V)

A modification of the cyclization method of Adelson and Bogert (38) was used. Fifty grams γ -1-naphthyl butyric acid was suspended in 500 ml. dry benzene in a 2-liter 3-necked flask fitted with a mercury sealed stirrer and a reflux condenser with a trap for HCl. Fifty grams PCl_5 was added and the stirring commenced. The acid passed into solution within a few minutes with the evolution of heat, and was then refluxed for 1½ hours.

The solution was cooled to 0-5°C. by means of an ice bath, and maintained at this temperature during the addition of 34 grams of pulverized anhydrous aluminum chloride in small portions with stirring, over a period of about 30 minutes. The mixture was then allowed to warm up to room temperature, and kept at this temperature overnight without

stirring. It was then refluxed for 2½ hours, and after cooling poured onto 300 grams ice and 50 ml. concentrated HCl. After warming on the steam bath for ½ hour, the mixture was transferred to a large separatory funnel and the acid layer drawn off and discarded. The benzene layer was washed thoroughly with water (avoiding too vigorous shaking which forms emulsions), and then washed with successive portions of 5% Na₂CO₃ solution until the aqueous layer was colorless. Then after washing with water, the benzene was removed by distillation, and the residue distilled in vacuum. The yield of product distilling at 145-150°C. at 1 mm. was 37 grams, or 81%. The melting point after recrystallization from methanol was 95-96°C.

Analysis:

Calculated for C₁₄H₁₂O₄: H, -6.17%, C - 85.67%

Found - H -6.13%, C - 85.49%

The 2,4-dinitro-phenylhydrazone was prepared by dissolving one part 2,4-dinitro-phenylhydrazine and one part l-keto-1,2,3,4-tetrahydro phenanthrene in 200 parts boiling ethanol. After filtering, a few drops concentrated HCl were added and the solution boiled for a few minutes. The brilliant red dinitro-phenylhydrazone separated almost quantitatively from the hot alcohol, and after cooling, the solution was filtered. The 2,4-dinitro-phenylhydrazone was recrystallized from pyridine. Melting point, 283-285°C., with decomposition.

Analysis: *

Calculated for $C_{20}H_{16}N_4O_4$:— K= 14.69%

Found — N= 14.80%, 14.62%

β -(*o*-tolyl) ethanol (VII).

The *o*-bromotoluene (VI) was prepared from *o*-toluidine as described in Organic Syntheses, Vol. 9, page 22, and was converted into β -(*o*-tolyl) ethanol by a modification of the procedure for synthesis of *n*-hexyl alcohol, Organic Syntheses, Vol. 6, page 54. β -(*o*-tolyl) ethanol had been previously prepared by a slightly different method by Grignard (39).

Twenty grams magnesium was covered with 175 ml. dry ether in a 3-liter 3-necked flask. A mercury sealed stirrer, a reflux condenser, and a dropping funnel were attached. A few milliliters of *o*-bromotoluene were added and the reaction started by the addition of a crystal of iodine and gentle warming. Then 100 ml. additional dry ether was added and the remainder of 150 grams *o*-bromotoluene added through the dropping funnel at a rate sufficient to cause the mixture to reflux. The addition required about 3½ hours, and the mixture was refluxed for ½ hour longer on the steam bath.

The Grignard solution was then cooled to 5°C. by an ice bath and 40 grams ethylene oxide distilled through a U-tube filled with soda-lime,

* The writer is indebted to Mr. Thomas H. Harris for this analysis.

and through a condenser packed in ice and salt, and allowed to drop into the stirred solution in the flask. The reflux condenser was replaced by a thermometer. The ethylene oxide was distilled at such a rate that the temperature of the stirred mixture remained between 0° and 5° C. Toward the end of the addition of the ethylene oxide, the mixture becomes viscous and began to solidify. After all the ethylene oxide had been added, the mixture was warmed on the steam bath and 65 ml. ether distilled off. Sixty-five milliliters dry benzene was then added and more ether distilled off until the temperature of the material in the flask reached 65°C.

Then after cooling, 150 gms. ice and 150 ml. benzene were added, and the magnesium compounds dissolved by addition of 150 ml. concentrated HCl. The two layers were separated and the aqueous layer extracted with benzene. After washing the combined solvent layers with water and NaHCO₃ solution, the benzene and ether were removed by distillation on the steam bath, and the alcohol distilled in vacuum. The yield of β -(o-tolyl) ethanol was 64 grams, or 62%. The alcohol was a syrupy water-white liquid distilling at 99°-105° at 1 mm. Boiling point at atmospheric pressure was 237°C. Density 20/20° - 1.0195. n_D (20°) - 1.5349. Grignard (39) found, density 4°/14.8° - 1.0098 and n_D - 1.5347.

Analysis:

Calculated for C₉H₁₁O: H - 8.88%, C - 79.37%

Found: H - 8.95%, 8.77%, C - 79.14%, 79.20%

The 3,5-dinitrobenzoate formed by heating together equivalent quantities of the alcohol and of 3,5-dinitrobenzoyl chloride and recrystallizing the resulting product from ethanol, melted at 126°-128°C.

Analysis:

Calculated for $C_{16}H_{14}O_6N_2$: H - 4.27%, C - 58.12%
Found: H - 4.34%, 4.18%, C - 58.83%, 58.41%

β -(p-tolyl) ethanol (X).

p-bromotoluene (IX) was prepared from p-toluidine according to the method described in Organic Syntheses, Vol. 5, page 21. It was converted into β -(p-tolyl) ethanol by a procedure similar to that described for the preparation of β -(o-tolyl) ethanol (VII). In the preparation of the Orignard reagent, it was necessary to mix a little dry ether with the p-bromotoluene in the dropping funnel to prevent it from solidifying. β -(p-tolyl) ethanol had been prepared by several investigators in the past, using methods differing from the one described here. (59)(40)

The yield of β -(p-tolyl) ethanol, a syrupy white liquid of aromatic odor, obtained from 146 grams p-bromotoluene was 62 grams, or 53%. The material distilled at 100° - 106°C. at 1 mm. Two redistillations were necessary as a small quantity of di-p-ter-tolyl (M.P. 120°-121°) formed as a by-product of the reaction tended to sublime over and contaminate the distilled material. Boiling point

of the purified material at atmospheric pressure - 235°C.

Density 20°/20° = 1.0008. $n_D(20^\circ)$ = 1.5282. Grignard (39)

found: Density 4°/13° = 1.0028. n_D = 1.5299.

Analysis:

Calculated for $C_9H_{10}O$: H = 8.88%, C. = 79.39%

Found: H = 9.02%, C. = 79.29%

The 3,5-dinitrobenzoate was formed by heating together equivalent quantities of the alcohol and of 3,5-dinitrobenzoyl chloride. The ester was recrystallized from ethanol, as yellowish needles. Melting point - 147°-149°C.

Analysis:

Calculated for $C_{16}H_{14}N_2O_6$: H = 4.27%, C. = 58.18%

Found: H = 4.31%, 4.25%, C. = 58.32%, 58.29%

β -(o-tolyl)ethyl chloride (VIII).

In a 500 ml. flask were placed 34 grams β -(o-tolyl) ethanol (VII) and 61 grams dry dimethyl aniline. The flask was placed in an ice and salt bath and 60 grams thionyl chloride added slowly to the cold stirred mixture. The resultant black viscous liquid was allowed to stand overnight at room temperature, then heated on the steam bath for one hour. Water (150 ml.) was then added, and after cooling, 150 ml. ether. The contents were transferred to a separatory funnel, mixed thoroughly, and allowed to stand until no further separation of the stubborn emulsion occurred. The aqueous layer was drawn off, leaving

any emulsion with the ether layer. The aqueous layer was again extracted with ether and the combined ether extracts were washed with several portions of concentrated HCl which generally broke the remaining emulsion. The ether layer was now washed with water, several times with NaHCO_3 solution, then with water again, and finally dried over anhydrous CaCl_2 to which a piece of KOH had been added. After filtering, the ether was removed by distillation on a steam bath, and the β -(o-tolyl)ethyl chloride distilled under vacuum. The boiling point was 80° - 84° at 1 mm., and 223° at atmospheric pressure. It is a clear water-white liquid when distilled, but becomes red on standing. The yield was 32.7 grams or 85%. Density $20^\circ/20^\circ = 1.0553$. $n_D(20^\circ) = 1.5313$.

Analysis:

Calculated for $\text{C}_9\text{H}_{11}\text{Cl}$: Cl - 22.93%

Found: Cl - 22.73%, 23.07%

β -(p-tolyl)ethyl chloride (XI).

Thirty-four grams β -(p-tolyl) ethanol (X) was mixed with 61 grams dimethyl aniline, and 60 grams thionyl chloride added in a manner identical with that described for β -(o-tolyl)ethyl chloride (VIII). The β -(p-tolyl)ethyl chloride so obtained distilled at 81° - 85° at 1 mm. A yield of 32.8 grams, or 85% of the theoretical was obtained. The boiling point was 222°C . at atmospheric pressure. Density $20^\circ/20^\circ = 1.0370$. $n_D = 1.5251$.

Analysis:

Calculated for $C_9H_{11}Cl$: Cl - 22.93%

Found: Cl - 22.96%, 22.85%

3,4-dihydro-1- β -(phenyl)ethyl phenanthrene (XIII).

Six grams magnesium and 80 ml. anhydrous ether were placed in a 1-liter 3-necked flask equipped with a mercury sealed stirrer, a reflux condenser, and a dropping funnel. Thirty-seven grams β -phenylethyl bromide (Eastman's No. 1869) was placed on the dropping funnel, a small quantity of which was now dropped into the reaction flask. The reaction was started by adding a crystal of iodine and warming. Then, while warming gently to keep the reaction from stopping, the remainder of the β -phenylethyl bromide was slowly added. Refluxing was continued for four hours after the last of the bromide had been added.

The Grignard reagent was then cooled in an ice bath, and 32 grams (39.2 gms. theory) of 1-keto-1,2,3,4-tetrahydrophenanthrene (V), dissolved in 200 ml. of a mixture of one part anhydrous ether and one part anhydrous benzene, was slowly dropped into the stirred mixture. The ice bath was then removed and the mixture was refluxed for one hour, after which ether was distilled from the mixture until the temperature reached 75°C. as shown by a thermometer dipping into the boiling solution. Then refluxing was resumed and continued 5 hours longer, adding a little dry ether if necessary to prevent the temperature of the liquid from rising above 75°C.

After cooling, the solution was decomposed by the addition of 300 grams of ice and 100 ml. concentrated HCl, and the acid layer drawn off and extracted with ether. The combined ether-benzene layers were washed with water and NaHCO₃ solution, dried over anhydrous CaCl₂, and the solvent distilled off. The residue was distilled under vacuum. The tertiary alcohol which was formed by interaction of the ketone and the Grignard reagent was completely dehydrated to a hydrocarbon (XIII). A fore-run of 8 grams, distilling between 135°-170° at 0.5 - 1 mm. was chiefly unchanged ketone (V). 3,4-dihydro-1-β-(phenyl)ethyl phenanthrene distilled at 185°-187° at 0.5-1 mm., as a viscous yellow oil which solidified after standing for several days. The yield of distilled material was 24.0 grams. This represents a yield of 52% of the basis of ketone added, or 69% on the basis of the ketone actually utilized. The material was difficult to crystallize, but fair results were obtained by crystallization from 95% ethanol. After numerous recrystallizations, a small quantity was obtained which melted at 62°-63°C.

Analysis:

Calculated for C₂₂H₂₀: H = 7.09%, C. = 92.91%

Found: H = 6.97%, 7.24% C. = 93.01%, 92.60%

The trinitrobenzolate was prepared by dissolving equimolecular quantities of 3,4-dihydro-1-β-(phenyl)ethyl phenanthrene and symmetrical trinitrobenzene in a small volume of hot 95% alcohol. The orange trinitrobenzolate separated upon cooling, and after four recrystallizations

from alcohol, it melted at 91°-92°C.

Analysis:

Calculated for $C_{23}H_{23}N_3O_6$; H - 4.66% C - 67.60%

Found; H - 4.71% C - 67.81%

3,4-dihydro-1- β -(o-tolyl)ethyl phenanthrene (XV)

The procedure is the same as described for (XIII). β -(o-tolyl)ethyl chloride (VIII) (32.7 grams) was reacted with 5.7 grams magnesium in 75 ml. dry ether. Thirty-four grams (V), dissolved in 200 ml. ether-benzene mixture, was added. The vacuum distillation was carried out at 0.5 - 1 mm., which yielded a 14 gram fore-run, from which 10.9 grams unreacted ketone was recovered, and 27.8 grams of 3,4-dihydro-1- β -(o-tolyl)ethyl phenanthrene distilling at 190°-195°. This represented a yield of $51\frac{1}{2}\%$ on the basis of the ketone added, and 79% on the basis of the ketone actually utilized. (XV) distilled in the form of a yellow viscous oil, which did not solidify after several days at 5°C. It crystallized readily from 95% ethanol however, and formed small well defined crystals which after several recrystallizations from ethanol melted at 57°-58°C.

Analysis:

Calculated for $C_{23}H_{22}$; H - 7.43% C - 92.57%

Found; H - 7.43%, 7.34% C - 92.83%, 92.58%

The trinitrobenzolate was formed as described for the trinitrobenzolate of (XIII). After several recrystallizations

from ethanol, the orange trinitrobenzolate melted at 101.5°-102.5°C.

Analysis:

Calculated for $C_{29}H_{25}N_3O_6$: H - 4.93% C - 68.09%

Found; H - 4.85% C - 68.29%

3,4-dihydro-1- β -(p-tolyl)ethyl phenanthrene (XVI)

By the same procedure as described for the two previous syntheses, 15.4 grams β -(p-tolyl)ethyl chloride (XI) was reacted with 3 grams magnesium, and 17 grams (V) added to the resulting Grignard reagent. After decomposing the magnesium compounds as previously described, 15.4 grams 3,4-dihydro-1- β -(p-tolyl)ethyl phenanthrene, distilling at 200°-205°C. at 0.5 - 1 mm. was obtained. This represented a yield of 59.5% on the basis of the ketone added or 63% on the basis of the ketone utilized. The 3,4-dihydro-1- β -(p-tolyl)ethyl phenanthrene distilled as a yellow viscous liquid which solidified on standing. It crystallized readily from ethanol, and after several recrystallizations, melted at 79.5°-81°C.

Analysis:

Calculated for $C_{23}H_{22}$: H - 7.43% C - 92.57%

Found; H - 7.29%, 7.46% C - 92.66%, 92.59%

The picrate was formed by dissolving equimolecular quantities of the hydrocarbon and of picric acid in a small volume of hot 95% ethanol. Upon cooling, the vermillion

picrate separated. After several recrystallizations from ethanol, it melted at 101°-102°C.

Analysis:

Calculated for $C_{29}H_{25}N_3O_7$: H - 4.78% C - 66.02%

Found; H - 4.98% C - 66.08%

Preparation of the palladium-charcoal catalyst

A suspension of 27 grams 100-200 mesh activated carbon in 180 ml. distilled water was mechanically stirred in a 1-liter beaker. Five grams pulverized palladium chloride was placed in a 150 ml. beaker and covered with 50 ml. boiling water. After stirring for about a minute, the supernatant liquid was decanted into the stirred carbon suspension. The residual palladium chloride was leached with another portion of boiling water and the solution decanted into the carbon suspension, and the procedure repeated until all the palladium chloride had been dissolved and added. The carbon suspension was then warmed to 50°C. and maintained at this temperature for two hours while a vigorous current of hydrogen was bubbled through the stirred suspension. It was then filtered in a large Buchner funnel and sucked as dry as possible. The carbon was returned to the original beaker and again stirred with distilled water and filtered, and this procedure repeated until a portion of the filtrate gave but a slight turbidity with silver nitrate. The carbon was now dried in a dessicator over

CaCl_2 and KOH, and kept in a well stoppered bottle.

3,4-dihydro-1-β-(phenyl)ethyl phenanthrene
1-β-(phenyl)ethyl phenanthrene (XIV)

Thirteen grams 3,4-dihydro-1-β-(phenyl)ethyl phenanthrene (XIII) was mixed with 5 grams palladium catalyst and placed in a 200 ml. round bottomed flask which was connected, by means of a ground glass joint, to a vertical section of large bore glass tubing about two feet in length. A bubble-counter was attached at the top of this glass column. The flask was heated in a fused salt bath composed of two parts sodium nitrite and one part sodium nitrate. The temperature of the bath was 270°C. at the beginning of the dehydrogenation, and was so heated as to gradually increase the temperature to 300°C. by the end of the first hour and to 320°C. by the end of the second hour. After cooling, the contents of the flask were extracted by boiling with successive portions of 95% ethanol and filtering. Upon concentrating these combined filtrates, crude yellow 1-β-(phenyl)ethyl phenanthrene separated. It was then dissolved in petroleum ether and the solution passed through a column 9 inches in length packed with 100-200 mesh aluminum oxide (Hydralo), which had been activated by heating to 250°C. under vacuum. The column was washed with successive portions of hot petroleum ether until a portion of the filtrate evaporated to dryness on the steam bath showed that no more material was being extracted. By this procedure almost all of the yellow

impurity remained in the first few centimeters of aluminum oxide at the top of the column. The combined petroleum ether filtrates were evaporated to dryness and the 1- β -(phenyl)ethyl phenanthrene was recrystallized several times from methanol. Melting point - 86.5°-89.5°. The yield of purified material was 9.2 grams from 10.8 grams crude product.

Analysis:

Calculated for $C_{22}H_{18}$: H - 6.43% C - 93.57%

Found; H - 6.50%, 6.49%. C - 93.38%, 93.34%

The Di-trinitrobenzolate. One equivalent of (XIV) and two equivalents of symmetrical trinitrobenzene were warmed with 95% ethanol. The yellow di-trinitrobenzolate formed almost immediately and required a large volume of boiling ethanol to dissolve it. It separated from ethanol in fine canary yellow needles. Melting point 149°-151°.

Analysis:

Calculated for $C_{34}H_{24}N_6O_{12}$: H - 3.41% C - 57.63%

Found; H - 3.66%, 3.57%, 3.56%, 3.62%

C - 57.67% 57.96% 57.83% 57.79%

Attempted cyclization of 1- β -(phenyl)ethyl phenanthrene

(XIV)

One gram (XIV) was dissolved in 10 ml. CS_2 (distilled from P_2O_5), and 0.5 grams pulverized anhydrous aluminum chloride added. An immediate darkening of the aluminum chloride particles occurred. The mixture was refluxed gently

for two hours, and the CS₂ then removed by evaporation on the steam bath. The residue was decomposed with ice and HCl, and the red tarry material filtered off and leached with successive portions of boiling ether until no more colored substances were extracted. The brown powder which remained was soluble with difficulty in benzene or pyridine, but nothing could be induced to crystallize from these solutions. After evaporation of the solvent, the tarry residue was subjected to vacuum sublimation at temperatures as high as 350° C., but no picene (XVII) could be obtained.

The cyclization was again attempted, using the procedure of Ruzicka (10) and of Howard (11). At the close of the three-day period of shaking, the solution and the tarry deposit were decomposed with ice and HCl as before. But again no picene could be isolated from the tarry reaction product.

Cyclization and dehydrogenation of 3,4-dihydro-1-β-(phenyl)ethyl phenanthrene (XIII) to form Picene (XVII).

3,4-dihydro-1-β-(phenyl)ethyl phenanthrene (XIII) (3.7 grams) was dissolved in 37 ml. dry CS₂. The solution was cooled to 0° C. by means of an ice and salt bath, and 3.7 grams pulverized anhydrous aluminum chloride was added in small portions, with shaking, over a period of 30 minutes. The mixture was kept overnight at 5° C. and then decomposed with ice and HCl, and the CS₂ removed by a distillation with steam. The viscous red oil which separated was

dissolved in ether, washed first with concentrated HCl, then with 20% NaOH solution, and finally with water, and dried over anhydrous CaCl₂. After removing the solvent, the residual oil was distilled in vacuum. Boiling point-205°-215° C. at 0.5-1 mm. An exceedingly viscous oil (2.9) grams was obtained, which after several weeks becomes opaque and finally solidified to a pasty solid of a consistency approximating that of soap. Repeated attempts to crystallize this material were unsuccessful. It did not form a picrate or a trinitrobenzolate.

Two and four-tenths grams of this viscous yellow oil was mixed with 1.2 grams palladium catalyst, and subjected to a dehydrogenation using the bath and apparatus described under (XIV). The temperature of the bath was maintained at 390°-400° C. for two hours. After cooling, the residue in the flask was leached with ether until no more colored material was extracted, then placed in a Soxhlet extractor, and extracted with CHCl₃ for 20 hours. The chloroform solution was evaporated to dryness and the residue again leached with ether. The brown ether-insoluble residue was sublimed in vacuum at 270°-290°. The sublimate was dissolved in chloroform, in which it was slightly soluble, and upon cooling, picene separated in glistening white plates. The yield of crystalline picene was 29.5 milligrams. The melting point taken by means of a calibrated 400° thermometer, was 367°-368.5° C.

Analysis:

Calculated for $C_{22}H_{14}$: H - 5.07% C - 94.74% ⁹³

Found; H - 5.08%, 5.29%. C - 94.72%. 94.74%

Cyclization and dehydrogenation of 3,4-dihydro-1- β -
(o-tolyl)ethyl phenanthrene (XV) to form Picene (XVII).

The cyclization of 3,4-dihydro-1- β -(o-tolyl) ethyl phenanthrene was carried out by the same procedure as for 3,4-dihydro-1- β -(phenyl)ethyl phenanthrene. A viscous yellow oil (7.5 grams) was obtained from 9.7 grams starting material. The boiling point was 205°-210° C. at 0.5 - 1 mm. Like the cyclization product in the previous synthesis, this yellow oil could not be crystallized, and did not show any evidence of solidification after several months. It formed no picrate nor trinitrobenzolate. Density 20°/20° - 1.097. $n_D - 1.6440. // 20^\circ$

A mixture of 5.4 grams of this cyclization product and 2.7 grams palladium catalyst was dehydrogenated as previously described at a bath temperature of 380°-400°C. for two hours, then extracted as in the previous synthesis. The yield of sublimed and recrystallized picene obtained from 5.4 grams cyclicized material was 230 milligrams. Melting point 367°-369°.

Analysis:

Calculated for $C_{22}H_{14}$: H - 5.07% C - 94.93% ✓

Found; H - 5.25%, 5.24% C - 94.76%, 94.93%

The picene obtained from the two intermediates (XIII) and (XV) showed no depression of the melting point when mixed.

Attempted cyclization and dehydrogenation of 3,4-dihydro-1- β -(p-tolyl)ethyl phenanthrene (XVI) to form 8-methyl-picene

The cyclization of 3,4-dihydro-1- β -(p-tolyl) ethyl phenanthrene was carried out as described under the cyclization of (XIII) and (XV). Five grams 3,4 dihydro-1- β -(p-tolyl) ethyl phenanthrene in 50 ml. CS₂ was cyclized with 5 grams anhydrous aluminum chloride. Upon decomposing the reaction mixture as previously described, 4 grams of an exceedingly viscous oil was obtained which distilled at 210°-220° at 0.5 - 1 mm. It solidifies into a pasty mass on standing but like the cyclization products already described, all attempts to separate any pure compounds by crystallization were unsuccessful.

Three grams of the cyclization product was dehydrogenated as previously described, but no trace of any picene derivative could be isolated from the reaction products.

VII. Summary

The literature on the subject of picene has been reviewed, and a new synthesis for picene has been developed. Various cyclization reactions used by other investigators in other researches have been studied. The analogy has been extended to cover the intermediates used in this synthesis, and suggestions for improvement are offered.

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