

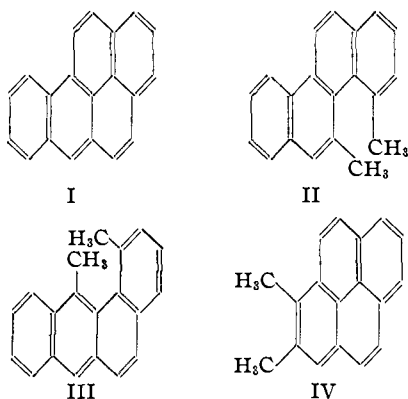
[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, AND THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Synthesis of 4,5-Dimethylchrysene<sup>1</sup>

BY MELVIN S. NEWMAN<sup>2</sup>

In seeking to understand the relationship between chemical constitution and cancer producing activity of hydrocarbons, it has long been of interest to determine to what extent a polycyclic hydrocarbon might be simplified without materially affecting its carcinogenic activity. Of particular interest is the comparison of the activity of pentacyclic compounds with that of tetracyclic ones containing two methyl groups at the points of attachment of the fifth ring.

In this connection the potent cancer producing hydrocarbon 3,4-benzpyrene, I, isolated from coal tar,<sup>3</sup> is of particular interest for it may be considered as being related to three hydrocarbons, namely, 4,5-dimethylchrysene, II, 1',9-dimethyl-1,2-benzanthracene, III, and 3,4-dimethylpyrene, IV.



It seemed desirable to apply the recently developed general method for the synthesis of chrysene derivatives,<sup>4,5</sup> to the synthesis of II, especially because of the theoretical interest in this type of compound (see discussion below). The synthesis of a hydrocarbon believed to be 4,5-dimethylchrysene, II, is herein reported. The reactions involved are indicated in the following chart.

The condensation of benzylmagnesium chloride with trioxymethylene was carried out on a

(1) Part of the work herein reported was aided by a grant from the Jane Coffin Childs Memorial Fund for Medical Research, Yale University.

(2) The Elizabeth Clay Howald Scholar at The Ohio State University, 1939-1940.

(3) Cook, Hewett, and Hieger, *J. Chem. Soc.*, 395 (1933).

(4) Newman, *THIS JOURNAL*, **60**, 2947 (1938).

(5) Newman, *ibid.*, **62**, 870 (1940).

large scale in order to determine the utility of this abnormal reaction<sup>6</sup> for the preparation of the required *o*-methylbenzyl alcohol, V. The alcohol fraction obtained amounted to 62% but time-temperature cooling curves showed it to be impure. By one fractionation in a heated packed column it was possible to obtain pure V (42%). A product of comparable purity was more easily obtained (55%) from the condensation of *o*-tolylmagnesium bromide with trioxymethylene. The further conversion of V into VII by standard methods went smoothly.<sup>7</sup>

The required 1-phenyl-2-bromopropane, VIII, was prepared from the corresponding carbinol, VII, which resulted from the condensation of phenylmagnesium bromide with propylene oxide.<sup>8</sup> To establish the structure of VIII it was converted (via the Grignard reagent) into benzylmethylacetic acid, the amide of which was found to be identical with an authentic sample.

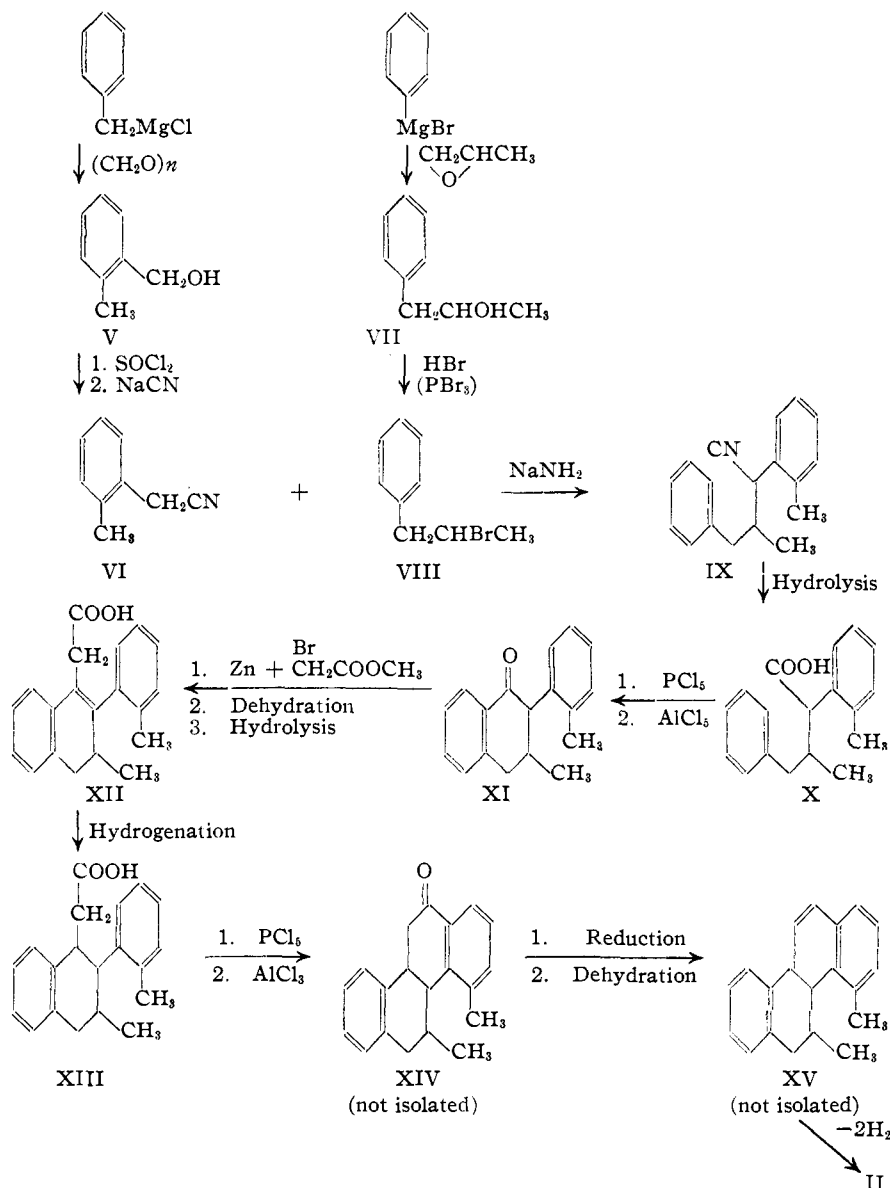
The alkylation of VI with VIII using sodium amide proceeded smoothly as in an analogous case<sup>5</sup> to yield the nitrile, IX, which was hydrolyzed to the acid, X, in high yield by long refluxing in acetic acid containing sulfuric acid. Cyclization of the acid chloride of X in benzene solution using aluminum chloride produced XI. Compounds IX, X and XI were all obtained as pale colored viscous oils. No prolonged efforts were made to secure them in crystalline form, for it was suspected that the presence of two asymmetric carbon atoms would make crystallization difficult. The amide of X, resulting from incomplete hydrolysis of IX, crystallized in white needles and melted over the range 105-116°.

No attempt was made to isolate the hydroxy ester obtained by the condensation of methyl bromoacetate and XI, the crude ester being dehydrated and hydrolyzed to yield a mixture of acids from which the desired 3,4-dihydro-3-methyl-2-(*o*-tolyl)-1-naphthaleneacetic acid, XII, was isolated in crystalline condition. The double

(6) (a) Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903), no yield; (b) Reichstein, Cohen, Ruth and Meldahl, *Helv. Chim. Acta*, **19**, 412 (1936), reported 50-55% of product, b. p. 115-120° at 14 mm., no melting point.

(7) Compare Hill and Short, *J. Chem. Soc.*, 1123 (1935).

(8) Levene and Walti, *J. Biol. Chem.*, **90**, 86 (1931).



bond is placed in the ring instead of the alternate position of conjugation with the carboxyl group because with this structure only one asymmetric carbon atom is present. Such a compound would be more apt to crystallize than the acid with a conjugated double bond, the latter requiring two asymmetric carbons. In addition to the crystalline acid there was also obtained a larger amount of non-crystalline isomeric acids.

The reduction of the crystalline acid, XII, was accomplished by high pressure hydrogenation over catalyst 37KAF<sup>9</sup> in dioxane solution at 200°. Although there was some loss due to decarboxyla-

(9) Connor, Folkers and Adkins, *THIS JOURNAL*, **54**, 1138 (1932).

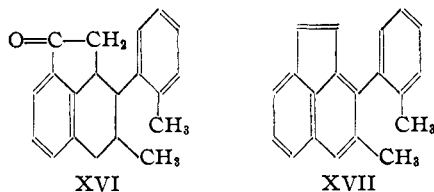
tion at this temperature, the desired acid, XIII, was obtained as a pale yellow glass which could not be crystallized. It may be noted that XIII contains three asymmetric carbon atoms.

The conversion of XIII into II was extremely difficult but was finally accomplished in 7.9% yield. The steps involved (1) cyclization of the acid chloride of XIII to XIV using aluminum chloride, (2) reduction to an alcohol using the aluminum isopropylate-isopropanol reagent,<sup>10</sup> (3) dehydration to XV by heating, and (4) dehydrogenation to II using sulfur at 230°. No appreciable amount of II was ever obtained when the

(10) Lund, *Ber.*, **70**, 1520 (1937).

liquid isomeric acids, XII, were reduced and treated in the same manner. On crystallization from benzene-alcohol, II was obtained as shiny colorless plates, m. p. 164.0–164.8°, having an intense blue-violet fluorescence in ultraviolet light. In two respects, 4,5-dimethylchrysenes differed markedly from other chrysenes derivatives prepared in this Laboratory.<sup>4,5</sup> It was not found possible to prepare an analytically pure picrate, for invariably either picric acid or hydrocarbon contaminated the orange-red picrate. Furthermore, the *s*-trinitrobenzene derivative melted at 131–132°, a full 33° lower than the melting point of II. All of the *s*-trinitrobenzene derivatives prepared previously by the author have melted higher than the parent hydrocarbon.

It should be mentioned that several attempts to convert XIII into II failed to give any of the desired material and in all cases considerable carbonization and resinification took place during the last step. This may be due partly to the formation of a product of the acenaphthylene type (see XVII below) and partly to the innate resistance to formation of compounds of the type in question (see Theoretical Discussion).



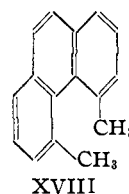
It was deemed possible that on cyclization the acid chloride of XIII might have yielded an acenaphthenone derivative, XVI, which on treatment as above described would have resulted in the formation of 2-(*o*-tolyl)-3-methylacenaphthylene, XVII. This possibility for the structure of the hydrocarbon obtained was ruled out on the basis of the absorption spectrum.<sup>11</sup>

The successful completion of the synthesis of II seems to the author to be due to two factors: (1) the methyl groups were introduced at a time when no resistance to their introduction was to be expected; and (2) the final ring closure to a hydro-

(11) Through the courtesy of Professor L. F. Fieser of Harvard University, Dr. R. N. Jones has measured the ultraviolet absorption spectrum of II. Their report reads, "Your 4,5-dimethyl(chrysenes) compound has an absorption curve definitely of the chrysenes type but with considerable loss of fine structure. The spectrum stands in much the same relationship to that of chrysenes as does the spectrum of 9,10-dimethyl-1,2-benzanthracene to benzanthracene." Their findings will be published shortly together with results on several other chrysenes derivatives. Significant points in their communication consist of maxima at 2740 Å. ( $\log E = 5.11$ ) and 3440 Å. ( $\log E = 4.34$ ) and a point of inflection at 3800 Å. ( $\log E = 2.87$ ).

aromatic chrysenes ketone, XIV, involved a portion of the molecule removed from the interfering methyl groups and therefore not directly affected by them. Indeed, it is possible to construct models of XIV and XV without undue straining of the bond angles. It was the final dehydrogenation to II in which the greatest resistance was encountered. It is noteworthy that no monomethyl chrysenes (4-methylchrysenes<sup>12</sup> in particular) was isolated. This would indicate that the methyl group linked to carbon 5 is not easily removed under the prevailing conditions. Rather, the entire molecule is disrupted, as evidenced by the large amount of carbonization. The possibility that during dehydrogenation the methyl group attached to carbon 5 had migrated to another position in the molecule also was considered. However, the author knows of no instance where such a migration has taken place during dehydrogenation with sulfur (230°).

**Theoretical Discussion Concerning Interferences between Substituents in Polynuclear Molecules.**—The compound 4,5-dimethylphenanthrene, XVIII, will be used as a model for the following discussion as any arguments which apply to it also apply to other compounds (*e. g.*, II and III) containing the same structural feature.



If a scale model is drawn or constructed in which the aromatic rings are coplanar and the methyl groups occupy the same volume as in toluene, the two methyl groups interfere with each other to a large extent.<sup>13</sup> Such calculations undoubtedly led to the predictions which have been made concerning the impossibility of preparation and existence of compounds of this type.<sup>14,15</sup> However,

(12) Bachmann and Struve, *J. Org. Chem.*, **4**, 456 (1939); Fieser and Johnson, *THIS JOURNAL*, **61**, 1647 (1939).

(13) The author is indebted to Drs. E. N. Lassetre and P. M. Harris for these calculations and for valuable advice in this connection.

(14) Haworth and Sheldrick, *J. Chem. Soc.*, 1950 (1934) "... it is impossible to introduce two methyl groups in the 4,5-positions of phenanthrene without introducing excessive strain in the molecule."

(15) Cook and Kennaway, *Am. J. Cancer*, **33**, 55 (1937). "It is a little doubtful, however, whether such a hydrocarbon (*i. e.*, 1',9 dimethyl-1,2-benzanthracene, III) could be obtained, as from stereochemical considerations it would appear that it would be impossible to introduce two methyl groups at the positions shown without distorting at least one of the valency directions of an aromatic ring out of the plane of the ring, and such deviation has rarely, if ever, been observed."

a search of the literature has revealed two instances in which compounds of the type in question have been prepared, namely, 2,2'-dimethyl-*meso*-benzanthrone<sup>16</sup> and 2,2'-dimethyl-*meso*-naphthodianthrone.<sup>17</sup> That the methyl groups in these compounds have the positions indicated is proved by their conversion into compounds containing a new ring formed by fusion of the two methyl groups.<sup>18</sup> In addition the author has recently described the preparation of other compounds containing analogously located methyl groups and their conversion into coronene.<sup>19</sup> The hydrocarbon, II, herein described may be cited as another case in point, although its structure has not yet been conclusively established by conversion into 3,4-benzopyrene, I.

Thus it must be considered as definitely proved that compounds of the 4,5-dimethylphenanthrene type are capable of existence and can be prepared. There is little doubt, however, that there is great resistance to their formation. As evidence of this resistance may be cited the unsuccessful attempts to prepare 4,5-dimethylphenanthrene, XVIII,<sup>14</sup> and 1',9-dimethyl-1,2-benzanthracene, III.<sup>20</sup> In addition the low yield of desired hydrocarbon and large amounts of carbonization in the dehydrogenation of XV also point to some feature lacking in similar conversions which proceeded in much better yields.<sup>4,5</sup>

The question then arises as to how the methyl groups are located in space. One (or a combination) of three alternatives is suggested: (1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings. Of these the latter seems more likely.<sup>18</sup> Should this indeed be the case, optical activity would be possible, for 4,5-dimethylphenanthrene (and similar compounds where certain groups must be forced out of the plane of the aromatic rings) can be represented in two non-superimposable forms which are mirror images.<sup>21</sup> Work designed to throw light upon this question is now in progress in this Laboratory.

(16) Scholl and Tanzer, *Ann.*, **433**, 172 (1923).

(17) German Patent 458,710, *Chem. Zentr.*, **99**, II, 399 (1928).

(18) Scholl and Meyer, *Ber.*, **67**, 1232 (1934); German Patent 456,583; *Chem. Zentr.*, **99**, I, 2011 (1928).

(19) Newman, *This Journal*, **62**, 1683 (1940).

(20) Fieser and Seligman, *ibid.*, **60**, 170 (1938); **61**, 136 (1939).

(21) The author is indebted to Dr. F. Y. Wiselogle of Johns Hopkins University for suggesting the possibility of optical activity in II.

## Experimental<sup>22,23</sup>

***o*-Methylbenzyl Alcohol, V.**—A Grignard reagent was prepared under nitrogen from 326 g. of freshly vacuum-distilled benzyl chloride in 2 liters of dry ether using 200 g. of magnesium. This solution was filtered using nitrogen pressure into another flask and there stirred and refluxed for one day with 160 g. of trioxymethylene which had been dried for two weeks over phosphorus pentoxide. After decomposing the reaction mixture with ammonium chloride solution there was obtained 193 g. (62.4%) of a colorless product, b. p. 107–115° at 12 mm. Time-temperature cooling curves showed the non-homogeneity of this material. On fractionation in a three-foot (1-meter) heated column packed with glass helices there was obtained 130 g. (42%) of pure V,<sup>6</sup> b. p. 109° at 12 mm., f. p. 35.0°. A cooling curve taken with this product showed a flat at 35.0° for twenty minutes when over 80% had solidified. The phenyl urethan melted at 79.0–79.6°.<sup>6a</sup> No pure crystalline urethan was obtained from the lower boiling fractions which were undoubtedly mixtures of V with  $\beta$ -phenylethanol.

The Grignard reagent from 608 g. of *o*-bromotoluene<sup>24</sup> and 86 g. of magnesium in 1200 cc. of ether was allowed to react with 150 g. of dry trioxymethylene without added heat for one day. The reaction mixture was decomposed with ammonium chloride solution and a 55% yield of pure V was obtained by two fractionations from a modified Claisen flask.

***o*-Methylbenzyl Chloride.**—In the best of several experiments in which the yields varied from 75 to 89%, 56 g. of V in 100 cc. of dry benzene was added dropwise during thirty minutes to 65 g. of thionyl chloride in 50 cc. of benzene containing one drop of pyridine. After warming on the water-bath for one hour the mixture was cooled and treated with ice water. The benzene was removed by distillation through a column and 57.5 g. (89%) of *o*-methylbenzyl chloride was obtained as a colorless lachrymatory liquid, b. p. 84° at 14 mm. (lit. ref. 6b reported b. p. 76–80° at 14 mm.). The remaining 11% was a polymeric resin.

***o*-Methylbenzylcyanide, VI.**—A solution of 140.5 g. of *o*-methylbenzyl chloride in 200 cc. of alcohol was added to a solution of 65 g. of sodium cyanide in 80 cc. of water and the mixture refluxed for four hours. After removing the precipitated salt by filtration and the alcohol by vacuum distillation, the product was isolated by ether extraction and distilled under reduced pressure. The nitrile, VI, b. p. 123.5–125.0° at 14 mm., was obtained as a colorless liquid in 86% yield. After purification by the method of Johnson,<sup>25</sup> with slight loss, the product boiled at 125.5° at 14 mm.

**1-Phenyl-2-propanol, VII.**—To a Grignard reagent prepared from 471 g. of bromobenzene and 74 g. of magnesium

(22) All melting points corrected.

(23) Analyses marked \* by Mr. D. Lester, Yale University. Analyses marked ‡ by Mr. J. H. Walker. Mr. O. Woolfolk aided in the preparation of V from *o*-tolylmagnesium bromide and trioxymethylene. The assistance of Messrs. Walker and Woolfolk was made possible through the Ohio State W. P. A. Project No. 65-1-42-89.

(24) Obtained from the Dow Chemical Company.

(25) "Organic Syntheses," Vol. 16, John Wiley and Sons, Inc., New York, N. Y., p. 89.

in 1400 cc. of ether was slowly added 180 g. of propylene oxide. After refluxing for twenty hours, the mixture was treated with ammonium chloride solution. The crude product, b. p. 90–110° at 14 mm., amounted to 280 g. On fractionation in the above-mentioned column there was obtained 244 g. (60%) of VII, b. p. 105.5–107.0° at 14–15 mm.,  $n_D^{20}$  1.5196.<sup>26</sup> The phenyl urethan melted at 88.2–88.8°.

**1-Phenyl-2-bromopropane, VIII.**—To a solution of 180 g. of phosphorus tribromide in 100 cc. of benzene was added with cooling 128 g. of VII during one hour. The mixture stood at room temperature for two hours and was then slowly heated and refluxed for ten minutes. The benzene layer was washed with water and dried over calcium chloride. The yield of twice distilled 1-phenyl-2-bromopropane, VIII, b. p. 112.5–114.0° at 20–21 mm.,  $n_D^{20}$  1.5416, was 118 g. (63%).<sup>27</sup> The same bromide was obtained in 60% yield by refluxing VII with an excess of 48% hydrobromic acid.

**Proof of Structure of VIII.**—A Grignard reagent was prepared from 22 g. of VIII and 3 g. of magnesium in 80 cc. of ether and poured on powdered solid carbon dioxide. The acid fraction thus produced distilled constantly to yield 7.6 g. (42%) of benzylmethylacetic acid, b. p. 172–173° at 23 mm.<sup>28</sup> The acid chloride was prepared with thionyl chloride and converted to the amide with aqueous ammonia. On crystallizing from ligroin the amide separated as colorless needles, m. p. 106–107°. This amide was shown to be identical with authentic benzylmethylacetamide,<sup>29</sup> m. p. 106–107°, prepared from pure diethyl methylmalonate<sup>30</sup> and benzyl chloride.

**$\alpha$ -(*o*-Tolyl)- $\beta$ -methyl- $\lambda$ -phenylbutyronitrile, IX.**—The alkylation of VI with VIII using sodium amide was carried out exactly as in the case of  $\alpha,\lambda$ -diphenylbutyronitrile.<sup>5</sup> Yields of IX, b. p. 159–160° at 1 mm., averaged 63%.

*Anal.\** Calcd. for C<sub>18</sub>H<sub>19</sub>N: C, 86.70; H, 7.68. Found: C, 86.95; H, 7.47.

**$\alpha$ -(*o*-Tolyl)- $\beta$ -methyl- $\lambda$ -phenylbutyric Acid, X.**—Alkaline hydrolysis of IX, even in an autoclave at 150° for seven hours, resulted only in the formation of a small amount of the amide of X, no acid fraction being formed. The amide was obtained in colorless needles, m. p. 105–116°, from benzene–ligroin. Two recrystallizations raised the melting range to 115–122°.

*Anal.\** Calcd. for C<sub>18</sub>H<sub>21</sub>ON: C, 80.86; H, 7.92. Found: C, 80.67; H, 7.60.

In the best of several experiments, a solution of 118.5 g. of IX, 60 cc. of water, 80 cc. of concentrated sulfuric acid, and 470 cc. of acetic acid was refluxed for sixty-two hours in a flask fitted with a ground-in condenser. After adding 100 cc. of water, most of the acetic acid was removed under reduced pressure and the residue extracted with benzene. The benzene extracts were well washed with water to remove acetic acid. The desired acid was then extracted with sodium carbonate solution, transferred to benzene

after acidification, and isolated as a yellow-orange viscous oil in 88% yield after removing the last traces of solvent by heating *in vacuo*. No attempts were made to purify this material for analysis. From the neutral fraction of the reaction products there was obtained 8.4 g. (6.6%) of crystalline amide.

**1-Keto-2-(*o*-tolyl)-3-methyl-1,2,3,4-tetrahydronaphthalene, XI.**—A solution of 112 g. of X in 100 cc. of benzene was added to 86 g. of phosphorus pentachloride. When this reaction was complete, the benzene and phosphorus compounds were removed under reduced pressure. The yellow-orange acid chloride was dissolved in 400 cc. of sulfur-free benzene and 58.5 g. of aluminum chloride was added in portions with stirring and cooling. As each addition of aluminum chloride was made, an orange color was formed on its surface followed immediately by disappearance of the color and brisk evolution of hydrogen chloride. After almost all of the aluminum chloride had been added, the reaction mixture still remained a yellow-orange solution. With the addition of the last portions of aluminum chloride the solution became deep red and there was no further brisk evolution of hydrogen chloride from the surface of the slight excess of reagent. After fifteen minutes at room temperature the solution was poured on ice and hydrochloric acid. The benzene layer was thoroughly washed with acid and alkali and the crude ketone was distilled under reduced pressure. There was obtained 94 g. (92%) of XI as an orange-yellow viscous oil, b. p. 170° at 0.5–1.0 mm. This material was distilled again with no lightening of color. No satisfactory semicarbazone could be isolated. A middle portion of the distillate was taken for analysis.

*Anal.\** Calcd. for C<sub>18</sub>H<sub>19</sub>O: C, 86.36; H, 7.25. Found: C, 86.16; H, 7.26.

**3,4-Dihydro-3-methyl-2-(*o*-tolyl)-1-naphthaleneacetic Acid, XII.**—In a typical run, 20 g. of freshly sandpapered zinc foil<sup>31</sup> was added to a solution containing 30 g. of XI and 37 g. of methyl bromoacetate in 120 cc. of sulfur-free benzene. The mixture was heated almost to boiling and a few crystals of iodine were added. The flask was then surrounded with several towels and the heat of reaction kept the benzene boiling. After the spontaneous reaction moderated the solvent was kept refluxing for fifteen minutes. The cooled reaction mixture was then decomposed with dilute hydrochloric acid. The entire residue remaining after removal of the benzene was heated (trace of iodine) at 210° under slightly reduced pressure to effect dehydration and was then distilled to yield 32.1 g. of an orange oil. This distillate was refluxed for sixteen hours with alcoholic potassium hydroxide. The neutral fraction, b. p. 168–170° at 1 mm., isolated from this reaction consisted of 12.2 g. (41%) of XI. From the acid portion was obtained 6.2 g. (17.7%, or 29.8% allowing for recovered ketone) of XII, m. p. 160–170°, in two crops from benzene–ligroin. A portion recrystallized several times melted at 180–182°.

*Anal.\** Calcd. for C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>: C, 82.16; H, 6.90. Found: C, 82.43; H, 6.93.

By removing all traces of solvent from the mother liquors

(31) Natelson and Gottfried, *THIS JOURNAL*, **61**, 970 (1939). The zinc foil was obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J.

(26) Columbic and Cottle, *THIS JOURNAL*, **61**, 996 (1939), give b. p. 92–93° at 8 mm.,  $n_D^{20}$  1.5221, m. p. of phenyl urethan, 86.5–87.0° uncor.

(27) Schroeter, Lichtenstadt and Irineu, *Ber.*, **51**, 1601 (1918).

(28) Conrad and Bischoff, *Ann.*, **204**, 177 (1880).

(29) Edeleanu, *Ber.*, **20**, 618 (1887), gave m. p. 109° uncor.

(30) Cox and McElvain, "Organic Syntheses," Vol. 17, John Wiley and Sons, Inc., New York, N. Y. p. 56.

of the acid crystallizations there was obtained an additional 12.0 g. (34.3%, or 57.7% allowing for recovered ketone) of a mixture of isomeric liquid acids, XII. For purification these were converted into ethyl esters and distilled, b. p. 215–223° at 7–8 mm. Hydrolysis of a portion of these esters gave an acid mixture from which no crystalline material could be obtained.

*Anal.* † Calcd. for  $C_{22}H_{24}O_2$ : C, 82.47; H, 7.55. Found: C, 82.48; H, 7.44.

**1,2,3,4-Tetrahydro-3-methyl-2-(*o*-tolyl)-1-naphthalene-acetic Acid, XIII.**—Shaking in alcohol solution with hydrogen and platonic oxide catalyst and prolonged contact with sodium amalgam in alkaline solution failed to change the acid, XII. A solution of 9.7 g. of XII, m. p. 178–181°, in 25 cc. of dioxane in a glass container was shaken over 1 g. of catalyst 37KAF<sup>9</sup> for five hours at 200° under hydrogen (initial pressure of 1900 lb.). The neutral fraction (1.2 g.) formed by decarboxylation was removed by ether extraction of an alkaline aqueous solution of the reduced acid. The acid was taken up in a small amount of benzene–ligroin. This solution was seeded with crystals of XII and kept at 0° for a week. There was thus obtained 0.13 g. of XII, showing that reduction had been essentially complete. No attempt at analysis of the reduced acid, XIII, was made. Evaporation of all solvent left a pale yellow viscous oil which set to a glass and weighed 8.15 g. (84%).

**4,5-Dimethylchrysene, II.**—A solution of 4.07 g. of XIII in 25 cc. of benzene was treated with 2.9 g. of phosphorus pentachloride. The pale yellow oil remaining after the benzene and phosphorus compounds were removed under reduced pressure was dissolved in 25 cc. of sulfur-free benzene and was treated with 1.9 g. of aluminum chloride at room temperature. The evolution of hydrogen chloride was brisk and took place immediately, a bromine colored solution being produced. After a total of thirty minutes the mixture was poured into dilute acid and the benzene layer separated and washed with dilute acid, water, and saturated sodium chloride solution. The solvent was removed and the clear orange-brown oil remaining dissolved in dry isopropanol and treated with aluminum isopropylate (from 0.5 g. of aluminum).<sup>10</sup> A deep red color was produced immediately. When the formation of acetone had ceased the mixture was treated with dilute acid and the organic product taken up in benzene, washed well with

acid and dilute carbonate solution, and finally vacuum distilled to give 2.82 g. (80%) of an orange-brown viscous oil. This material was treated as above with the Lund reagent<sup>10</sup> (more acetone being produced) and the product this time heated at 220–230° for ten minutes to effect dehydration. Then 0.64 g. of sulfur was added and the mixture heated at 230° for thirty minutes, when the evolution of hydrogen sulfide slackened. After adding a small amount of zinc dust, the product was vacuum distilled. The dark red distillate was carefully redistilled, the lower boiling fraction being collected separately and dissolved in a little benzene and alcohol. On cooling and scratching crystallization immediately began and there was obtained 0.386 g. of almost colorless small plates, m. p. 158–161°. After two recrystallizations from the same solvent mixture, 0.174 g. of white shining plates, m. p. 164.0–164.8°, was obtained. The melting point when mixed with 6-methylchrysene, m. p. 161°,<sup>4</sup> was depressed 40°.

*Anal.* † Calcd. for  $C_{26}H_{18}$ : C, 93.71; H, 6.29. Found: C, 93.80, 93.46; H, 6.22, 6.15.

The *s*-trinitrobenzene derivative was prepared from the mother liquors of the above recrystallizations. On two recrystallizations of this derivative from benzene–alcohol there was secured 0.194 g. (equivalent to 0.106 g. of II) of orange needles, m. p. 131.0–132.0°. The hydrocarbon obtained from a portion of this derivative by chromatographic procedure using activated alumina was identical with the II described above.

*Anal.* † Calcd. for  $C_{26}H_{18}O_6N_3$ : C, 66.52; H, 4.08; N, 8.95. Found: C, 66.72, 66.80; H, 4.02, 4.03; N, 8.65, 8.70.

### Summary

The preparation of a hydrocarbon believed to be 4,5-dimethylchrysene, II, is described. Evidence supporting this structure is presented as well as a theoretical discussion concerning the spatial location of the substituent groups in compounds of this type. The possibility is pointed out that, owing to a non-planar arrangement of groups, compounds of the 4,5-dimethylphenanthrene type may exist in optically active forms.

COLUMBUS, OHIO

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