[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SYNTHESIS OF 1′,9-DIMETHYL-1,2-BENZANTHRACENE

JAMES CASON AND DONALD D. PHILLIPS

Received October 15, 1951

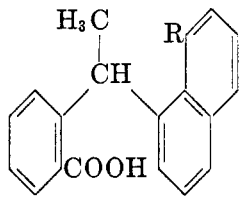
Synthetic routes to 1′,9-dimethyl-1,2-benzanthracene (X) were originally investigated because of interest in testing the possible carcinogenic properties of this hydrocarbon. Its structural relationship to the powerfully carcinogenic 3,4-benzpyrene is apparent (1). Difficulties encountered (1, 2) in attempts to prepare this compound have now made the synthesis itself of considerable theoretical interest. As late as 1938, Cook and Kennaway expressed serious doubt as to the possibility of ever obtaining 1′,9-dimethyl-1,2-benzanthracene because stereochemical relationships necessitate the distortion out of the plane of the ring of at least one of the valence bonds between methyl and an aromatic ring (3). At that time, such a deviation had not been observed. More recently, however, Newman and his collaborators have synthesized 4,5-dimethylchrysene (4), 4,5-dimethylphenanthrene (5), and 4,5,8-trimethyl-1-phenanthrylacetic acid (6). The latter compound was obtained in an optically active form. The asymmetry in this molecule is ascribed to the methyl groups being forced out of the plane of the ring in such a way as to overlap each other. The unequivocal nature of the synthetic schemes employed by Newman and his coworkers has strongly indicated the possibility of synthesizing 1′,9-dimethyl-1,2-benzanthracene and, indeed, such a synthesis has now been accomplished and the structure of the final product has been verified beyond reasonable doubt.

The final step in the synthetic sequence leading to 1′,9-dimethyl-1,2-benzanthracene (X) was dehydrogenation of 1′,9-dimethyl-1′,2′,3′,4′-tetrahydro-1,2-benzanthracene (VIII) with palladium on charcoal at 330°. The possibility of rearrangement or demethylation during this process has been examined most rigorously. Analyses of the hydrocarbon as well as the complexes formed with 2,4,7-trinitrofluorenone (7), *sym*-trinitrobenzene, and picric acid[1] have all supported the expected molecular formula. The ultraviolet absorption spectrum (Fig. 3) was very similar to that of 9-methyl-1,2-benzanthracene (IX) and all of the characteristic maxima, A–K, of the 1,2-benzanthracene system were clearly visible (9). In order to verify the fact that the 1′-methyl group had not migrated during the dehydrogenation (10, 11), hydrocarbon X was oxidized to a quinone (m.p. 188.0–189.6°) which failed to depress the melting point (189.6–190.6°) of an authentic sample of 1′-methyl-1,2-benzanthraquinone[2] (1), and depressed the

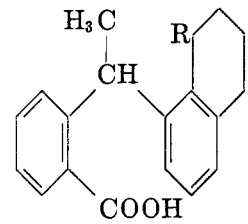
[1] It is of interest that the melting point of this picrate (123.2–124.4°) falls below that of the hydrocarbon (131.5–132.0°). Orchin (8) has ascribed such a behavior to the results of steric interference between substituents in the 1′- and 9-positions, but has mentioned that such an interpretation is probably an oversimplification. Additional significant factors must actually be involved; otherwise, the isolation of a picrate of 1′,9-dimethyl-1,2-benzanthracene would hardly be expected.

[2] These comparisons were made possible through the generosity of Dr. M. S. Newman who supplied us with samples of 1′-methyl- and 2′-methyl-1,2-benzanthracene.

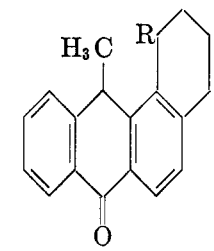
melting point (190.8–191.8°) of an authentic sample of 2′-methyl-1,2-benzanthraquinone[2] (12). The 4′-methyl-1,2-benzanthraquinone (12) has a much higher melting point (220°). Furthermore, the hydrocarbon depressed the melting points of authentic samples of 1′-methyl-1,2-benzanthracene and 2′-methyl-1,2-benzanthracene. The picrate of 1′,10-dimethyl-1,2-benzanthracene (1) melts about 24° above that of hydrocarbon X.



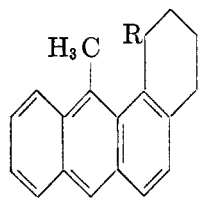
I R = H
II R = CH_3



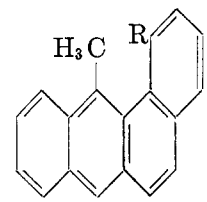
III R = H
IV R = CH_3



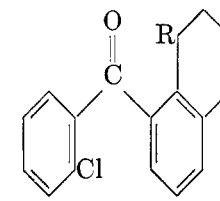
V R = H
VI R = CH_3



VII R = H
VIII R = CH_3



IX R = H
X R = CH_3



XI R = H
XII R = CH_3

In a recent attempted synthesis of 1′,9-dimethyl-1,2-benzanthracene (X) Cason and Wordie prepared acid II but were unable to cyclize it by any of a variety of powerful cyclization procedures (13). From a study of models, these authors suggested that failure to cyclize was due to steric interference between the two methyl groups. Such an interference would prevent the two aromatic systems from approaching the same plane and thus keep the carboxyl group out of the vicinity of the 2-position of the naphthalene moiety. These authors also suggested that if the tetrahydro acid, IV, could be prepared, cyclization should be much more hopeful because the methyl group in the tetralin ring would be out of the plane of the rest of the molecule. Anthrone VI could then be converted to hydrocarbon VIII, and strain would not be introduced until the dehydrogenation of VIII. Since this latter step involves the formation of no new carbon-carbon bonds, chances of success should be good. These expectations have now been realized by the facile cyclization of acid IV to anthrone VI, reduction of the anthrone, and dehydrogenation to X.

When acid IV was cyclized in acetic anhydride-acetic acid mixture according to the method of Fieser and Hershberg (14), the anthrone (VI) was obtained directly, instead of the expected acetate of the anthranol. The anthrone (VI) was likewise obtained when anhydrous hydrogen fluoride (22) was the cyclizing

agent. The identity of the anthrone was established by combustion analysis and ultraviolet absorption spectrum (Fig. 1). This unprecedented[3] failure to enolize in the presence of refluxing acetic anhydride indicates that the keto-enol equilibrium is energetically displaced far in favor of the keto form. A study of models indicates that such a behavior is reasonable, for steric interference of the methyls is much more pronounced in the anthranol form. In fact, it was also indicated that the hydrogens on the tetralin ring would offer serious interference with the enolization of 9-methyl-1,2-benz-10-anthrone (V). This suggested behavior was

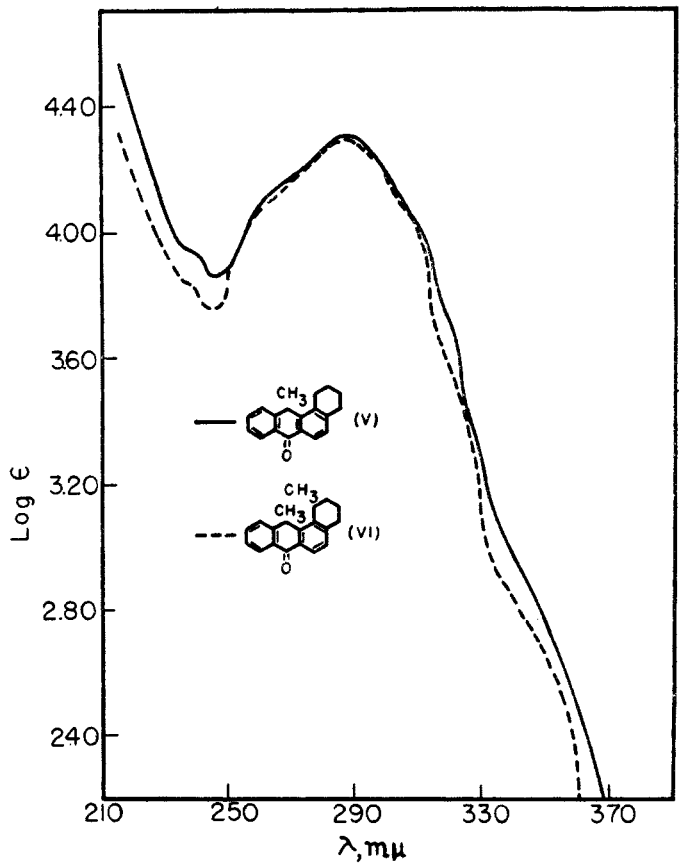


FIGURE 1. ABSORPTION SPECTRA OF ANTHRONES

tested by the synthesis of acid III and subsequent cyclization to the anthrone (V), whose ultraviolet absorption spectrum (Fig. 1) was identical to that of VI. It has previously been reported (15) that 1′,2′,3′,4′-tetrahydro-1,2-benz-10-anthrone enolizes in a normal manner.

[3] Fieser and Kilmer, *J. Am. Chem. Soc.*, **61**, 863 (1939), obtained 9-methyl-1,2,5,6-dibenz-10-anthrone from a cyclization with acetic anhydride and zinc chloride, but this appeared due to the insolubility of this anthrone, for it could be converted to the anthranyl acetate in acetic anhydride solution. Our compounds were entirely soluble in the reaction mixture used for cyclization.

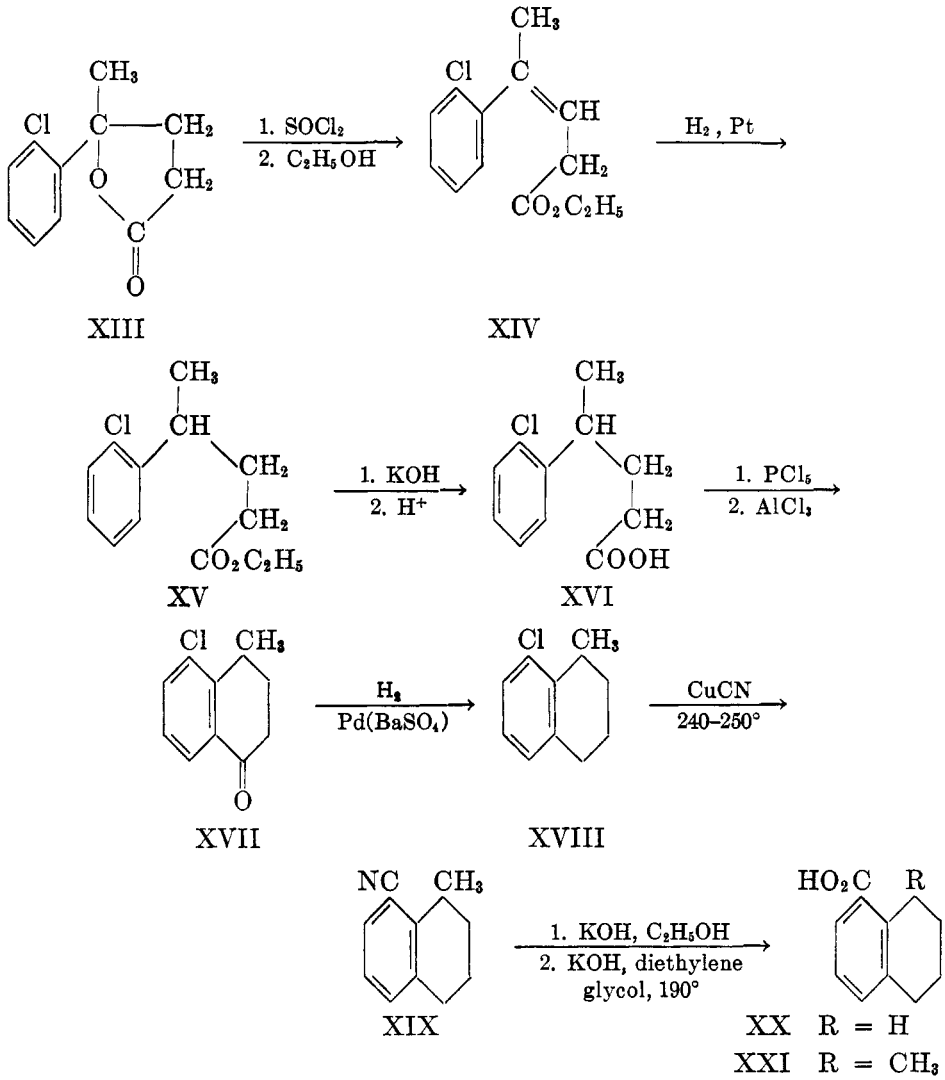
The synthesis of acid IV was accomplished by a sequence of reactions analogous to that employed by Cason and Wordie for acid II (13). An important intermediate in this sequence was the chloroketone, XII, and this ketone has been prepared from 8-methyl-5,6,7,8-tetrahydro-1-naphthoic acid (XXI). Although this acid has been isolated in low yield from the hydrogenation products of naphthalic anhydride (16), such a procedure appeared impractical for the preparation of the substantial quantities required for the multi-step synthesis of X. For this reason, an alternate scheme involving the sequence of reactions shown by formulas XIII–XXI was developed, and it yielded quantities of acid XXI that were sufficient for the ultimate synthesis of X.

The inverse addition of *o*-chlorophenylmagnesium bromide to ethyl levulinate gave lactone XIII in 39% yield. Extensive enolization of the keto ester, which was evidenced by the considerable amounts of it that were recovered from the reaction mixture, appears responsible for the low yield of lactone XIII. This yield could not be improved under a variety of experimental conditions. In another approach to the lactone, both methyllithium and methylmagnesium bromide were allowed to react with methyl β-(*o*-chlorobenzoyl)propionate but the principal product isolated (62% yield) in both experiments was β-(*o*-chlorobenzoyl)propionic acid (17). The lactone (XIII) was obtained in only 10% yield. Although this lactone, in contrast with expectations, proved resistant to high pressure hydrogenation in the presence of copper chromite catalyst and could not be opened under the conditions of the Clemmensen reduction, it was easily converted to the unsaturated ester (XIV) in 86% yield by ring-opening with thionyl chloride according to the procedure (18) developed in the aliphatic series. The unsaturated ester (XIV) was hydrogenated and saponified to yield acid XVI.

Acid XVI was cyclized to the tetralone (XVII) by the inverse Friedel and Crafts reaction according to Johnson and Glenn (19). Although nearly quantitative yields are reported for this reaction, even for compounds having an unreactive aromatic nucleus, our best yields were about 80%. Optimum conditions for the reaction were found to include the use of 1.4 equivalents of aluminum chloride and allowing the acid to stand for at least one hour in the presence of excess phosphorus pentachloride.

Ketone XVII was best converted to the tetralin (XVIII) by hydrogenolysis in ethanolic solution in the presence of 5% palladium-on-barium sulfate catalyst. Yields in this procedure were of the order of 75%, as compared to 70% obtained from the Huang-Minlon modification of the Wolff-Kishner reduction (20). The competing reaction in the catalytic reduction appeared to be the simultaneous hydrogenolysis of the chlorine atom to give appreciable amounts of 1-methyltetralin. When tetralone XVII was hydrogenated in the presence of copper chromite at 150° and 180 atmospheres pressure, there was obtained in 70% yield a mixture of the stereoisomeric 4-methyl-5-chloro-1-tetralols, m.p. 68–70°. This result is in agreement with the observations of Nightingale and Radford (21) who were able to reduce aromatic ketones selectively to either the secondary carbinol or the hydrocarbon, depending on the temperatures used. The hydrogenation of XVII was not carried out at higher temperatures on account of likelihood of hydrogenolysis of halogen; instead, the mixture of alcohols was hydrogenated at

low pressure to tetralin XVIII in the presence of 5% palladium-on-barium sulfate catalyst.



XIII XIV XV XVI XVII XVIII XIX

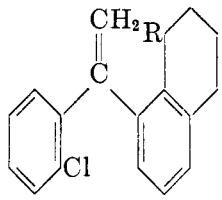
XX R = H

XXI R = CH_3

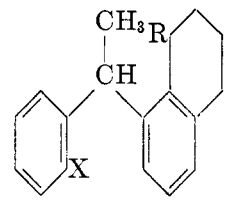
The chlorotetralin (XVIII) was converted in 81% yield to the cyano derivative (XIX) which was obtained as a low-melting solid, m.p. 43.0–44.0°. When this cyano derivative was hydrolyzed directly at 190° in basic diethylene glycol the acid (XXI), obtained in 95% yield, was found to melt at 115.1–116.0°, and this melting point could not be improved by further recrystallization. Cason and Wordie (16) reported the melting point of XXI as 118.9–119.6°. The principal contaminant in the present preparation was believed to be the isomeric 5-methyl-5,6,7,8-tetrahydro-2-naphthoic acid which would result from the *p*-chlorobromobenzene present as an impurity in the *o*-chlorobromobenzene used for the

synthesis of XIII. Since it was desirable to verify the identity of the acid of Cason and Wordie, there was used a two-step hydrolysis which took advantage of the absence of steric hindrance in the 5-methyl isomer. The contaminating isomer was hydrolyzed to the acid in basic ethanolic solution, while the desirable nitrile (XIX) was hydrolyzed only as far as the amide. This neutral amide was easily separated and further hydrolyzed to acid XXI, m.p. 118.1–119.1°. On admixture with a sample of the acid prepared by Cason and Wordie (m.p. 118.9–119.6°), there was no depression in melting point.

In order to keep chloroketone XII and subsequent compounds free from isomers, bis-(*o*-chlorophenyl)cadmium was prepared from carefully purified *o*-chlorobromobenzene and allowed to react with the acid chloride of XXI that had been obtained from selective hydrolysis of XIX as described above. A pure sample of chloroketone XII was readily obtained in 74% yield, m.p. 80.0–80.9°.



XXII R = H
XXIII R = CH_3



XXIV R = H, X = Cl
XXV R = CH_3, X = Cl
XXVI R = H, X = CN
XXVII R = CH_3, X = CN

This ketone was converted, *via* the chloroalkene (XXIII) to the chloroalkane (XXV) in 65% over-all yield by the methods previously described (13). When heated in an autoclave at 240–250° with cuprous cyanide and pyridine, the chloroalkane was readily converted in 70% yield to the corresponding nitrile (XXVII), m.p. 106.7–108.0°. The nitrile was hydrolyzed to the acid (IV), m.p. 185.1–186.0°, by heating for 24 hours at 190–200° in basic diethylene glycol solution. A low yield (41%) of the acid was obtained on account of conversion of 40% of nitrile XXVII to a neutral solid, m.p. 232–234°, which could not be hydrolyzed with potassium hydroxide at temperatures as high as 240°. Its ultraviolet absorption spectrum showed a weak absorption peak at 277mμ (log ε 3.43), the same wave-length at which the acid (IV) has its principal absorption maximum (log ε 3.26). A much more pronounced absorption maximum was observed at 330 mμ (log ε 2.93), where the acid (IV) shows no maximum. The structure of this compound has not been rigorously established, but it is probably the lactam with a seven-membered ring resulting from cyclodehydrogenation of the amide. An analogous compound was not obtained from hydrolysis of nitrile XXVI which does not have a methyl in the aliphatic ring.

The anthrone (VI), m.p. 130.2–131.3°, obtained from the cyclization of acid IV was reduced under a variety of conditions. The best of these involved the use of aluminum isopropoxide in xylene. A 93% yield of crude hydrocarbon was obtained by this procedure, which appears to have been used for a compound of

this type on only one previous occasion (23). The ultraviolet absorption spectrum (Fig. 2) indicates that the crude reduction product is nearly one-half the anthracene derivative, VIII; however, an analytically pure sample could not be obtained. In view of this difficulty, anthrone V, lacking the methyl group in the angular ring, was reduced under similar conditions to give a 91% yield of the known hydrocarbon, VII, m.p. 121.7–122.2° (24). This compound was readily

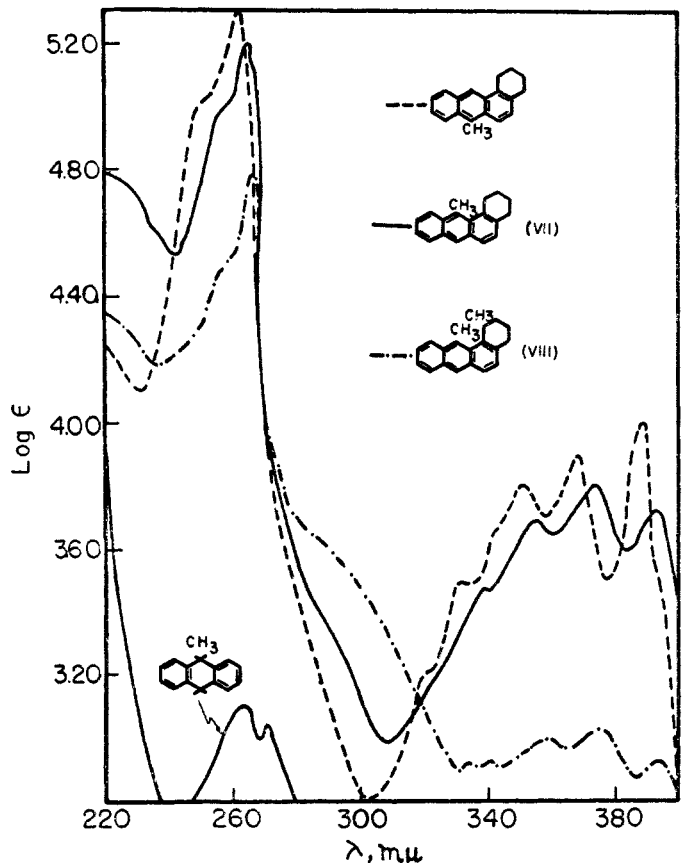


FIGURE 2. COMPOUND VII, $\lambda_{max.}$ (log ϵ): 264 (5.22); 340 (3.48); 354 (3.70); 374 (3.82); 394 (3.73).
COMPOUND VIII, $\lambda_{max.}$ (log ϵ): 264 (4.82); 340 (2.92); 357 (2.99); 376 (3.03); 394 (2.92).

obtained in a pure condition, and its ultraviolet absorption spectrum is also shown in Fig. 2 along with that reported by Fieser and Hershberg (25) for an analogous compound, 10-methyl-1′,2′,3′,4′-tetrahydro-1,2-benzanthracene. The similarity between the 9- and the 10-methyl derivatives is immediately apparent, while the lower values of log ϵ for VIII indicate the presence of a considerable amount of weakly absorbing substances, possibly the 9,10-dihydro-10-anthranol and the 9-10-dihydroanthracene. The absorption of 9-methyl-9,10-dihydro-

anthracene (Fig. 2) is far less intense than that of the anthracene derivatives. If the impurities in crude VIII are the 9,10-dihydro derivatives this makes reasonable the relatively satisfactory dehydrogenation of the crude reduction product to the fully aromatic hydrocarbon, X. Maleic anhydride adducts (26) were obtained from both VII and VIII, but that from VIII was separated in small

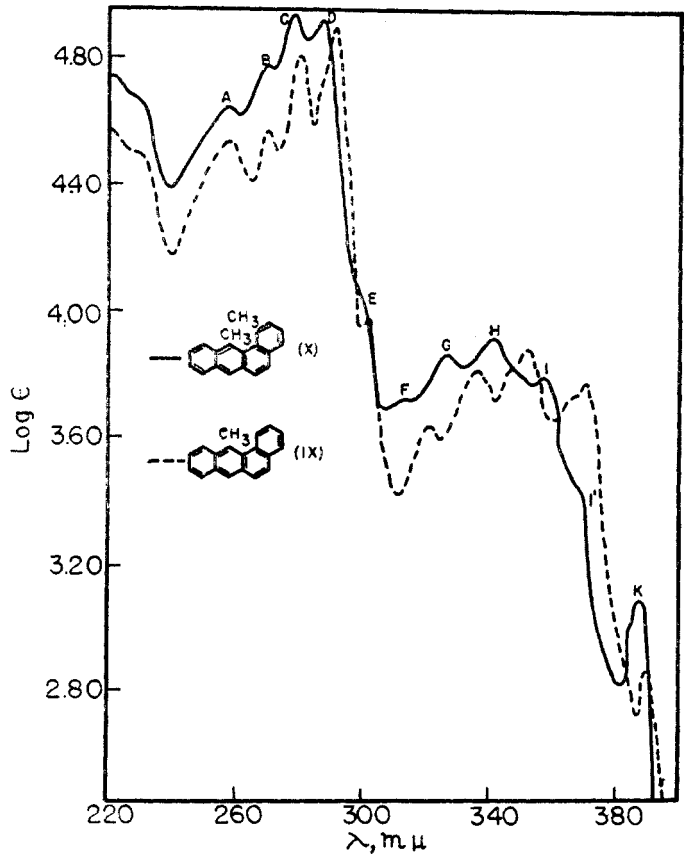


FIGURE 3. COMPOUND IX, $\lambda_{max.}$ (log ϵ): A, 259 (4.54); B, 271 (4.57); C, 281 (4.81); D, 292 (4.89); E, 302 (3.97); F, 322 (3.63); G, 337 (3.81); H, 352 (3.87); I, 370 (3.77); K, 390 (2.87).
COMPOUND X, $\lambda_{max.}$ (log ϵ): A, 258 (4.63); B, 270 (4.76); C, 278 (4.92); D, 287 (4.91); E, 300 (4.03); F, 314 (3.71); G, 326 (3.85); H, 341 (3.91); I, 356 (3.78); I′, 370 (3.29); K, 387 (3.07).

amount and was not obtained in a pure condition. Since steric interference of the two methyl groups in VIII is increased by formation of the fully aromatic anthracene nucleus, it is not surprising that VIII forms with considerably more difficulty than does VII.

When anthrone VI was reduced according to Huang-Minlon's modification of the Wolff-Kishner reduction (20), compound VIII (identified as its 2,4,7-trinitrofluorenone complex) was again obtained. Since the Huang-Minlon modifi-

cation reputedly prevents the formation of the alcohol as a side reaction (27), the mechanism for the formation of VIII by this procedure remains obscure. If the alcohol is an intermediate, it may be visualized as losing the elements of water to form VIII. A further anomaly was observed in the zinc and alkali reduction (28) of anthrone VI. The principal product isolated (44%) was not the expected hydrocarbon (VIII), but the alcohol, 1′,9-dimethyl-1′,2′,3′,4′,9,10-hexahydro-1,2-benz-10-anthranol. These abnormal reactions of anthrone VI, although inexplicable in part, are most probably a result of the unusual keto-enol equilibrium which has been shown to be energetically far in favor of the keto form, even in refluxing acetic anhydride.

Although the monomethyl compound, VII, was dehydrogenated in excellent yield by heating with sulfur to 245°, a similar treatment of the dimethyl compound, VIII, gave intractable tars. Compound VIII was successfully dehydrogenated by heating for one hour at 330–335° in the presence of 30% palladium-on-charcoal catalyst (29); compound X was obtained in 50% yield, based on the 2,4,7-trinitrofluorenone complex isolated (7). The purified complex was readily decomposed on alumina to give 1′,9-dimethyl-1,2-benzanthracene (X) as brilliant yellow needles, m.p. 131.5–132.0°, with an apparent change of state at 123°. When the dehydrogenation was carried out in benzene with a 30% palladium-on-charcoal catalyst according to the procedure of Adkins and England (30), a 23% yield of X was obtained.

As indicated by formulas I–XII, model experiments were run with 5,6,7,8-tetrahydro-1-naphthoic acid (XX) being used in place of acid XXI. The physical properties of the compounds obtained in this sequence of reactions are listed in the experimental section.

EXPERIMENTAL

All melting points are corrected and all boiling points are uncorrected. Analyses are by the Microanalytical Division of the Department of Chemistry of the University of California.

The ultraviolet absorption spectra were obtained from measurements made with a Beckman model DU quartz spectrophotometer and in all cases the solvent was 95% ethanol. Concentrations were adjusted so that all readings of optical density were in the range 0.1–1.5.

γ-(o-Chlorophenyl)-γ-valerolactone (XIII). *A. From o-chlorophenylmagnesium bromide and ethyl levulinate.* The Grignard complex from 3.3 moles of magnesium and 3.3 moles of *o*-chlorobromobenzene (31) was prepared in the usual manner in 1500 ml. of ether and added in a nitrogen atmosphere to a cooled (−2°) solution of 432 g. (3.0 moles) of ethyl levulinate in 1 l. of dry benzene. With vigorous stirring, the addition usually required 2.5 hours, during which time a very viscous semisolid complex precipitated. After addition of ice and acid, the organic phase was washed with sodium bicarbonate solution and water, and the product was distilled rapidly in a Claisen flask, then fractionated through a 65-cm. Podbielniak type column to give 127 g. (30%) of ethyl levulinate and 175 g. (39%) of lactone XIII, b.p. 151–153° (5 mm.). A center cut was retained for analysis, b.p. 151.5° (5.3 mm.), n_D^{20} 1.5520.

Anal. Calc'd for $C_{11}H_{11}ClO_2$: C, 62.71; H, 5.26; Cl, 16.83.
Found: C, 62.35; H, 5.18; Cl, 16.98.

B. From methyl β-(o-chlorobenzoyl)propionate and methylmagnesium bromide. A solution

of methylmagnesium bromide (0.077 mole) in 50 ml. of ether was added at 0° with stirring to 15.9 g. (0.07 mole) of methyl β-(*o*-chlorobenzoyl)propionate (17) in 50 ml. of benzene. After stirring had been continued for one hour, the clear yellow solution was decomposed with ice and acid. Since the starting keto ester and the desired lactone are not separable by fractional distillation, the crude reaction product was saponified, and the material obtained after acidification was extracted with alkali. From the alkaline extract was obtained 9.14 g. (60%) of β-(*o*-chlorobenzoyl)propionic acid, m.p. 70.2–72.0° (17). The neutral material gave, on distillation through a 65-cm. Podbielniak column, 1.33 g. (10%) of lactone XIII, b.p. 134–136° (2.3 mm.). The same yield was obtained when methyllithium was used in place of methylmagnesium bromide.

Ethyl 4-(o-chlorophenyl)-3-pentenoate (XIV). A mixture of 41.0 g. (0.195 mole) of lactone XIII and 67.8 g. (0.57 mole) of purified thionyl chloride (b.p. 77.0–77.1°) in 69 ml. of dry benzene was heated under reflux for four hours, then added with stirring, over a period of 20 minutes, to 200 ml. of absolute ethanol (temperature rise from 12–24°). The excess ethanol and diethyl sulfite were fractionated through a 65-cm. Podbielniak type column, and the residual chloroester was dehydrohalogenated by heating to 180° for one hour (18). Fractionation through the same column gave 40.0 g. (86%) of colorless unsaturated ester, b.p. 135–137° (3.8 mm.), and 1.2 g. of starting lactone, b.p. 152° (3.8 mm.). A small center cut of the main fraction was retained for analysis, b.p. 136.0° (3.8 mm.), n_D^{20} 1.5233.

Anal. Calc'd for $C_{13}H_{15}ClO_2$: Cl, 14.85. Found: Cl. 14.60.

When lactone XIII was hydrogenated at 200° and 4000 p.s.i. in the presence of a copper chromite catalyst (36), hydrogenolysis of the *ortho*-chlorine took place but no acidic material was isolated. Under the conditions of the modified Clemmensen reduction (28), lactone XIII was recovered unchanged.

Ethyl 4-(o-chlorophenyl)pentanoate (XV). A solution of 82.9 g. (0.35 mole) of freshly distilled XIV in 250 ml. of 95% ethanol was hydrogenated at room temperature and 3 atm. pressure in the presence of 1.8 g. of commercial platinum oxide catalyst. One molar equivalent of hydrogen was absorbed in three hours and the filtered solution was concentrated to a colorless oil. Fractionation through a 65-cm. Podbielniak type column gave a small forerun of dechlorinated product followed by 76.1 g. (91%) of colorless saturated ester, b.p. 136–138° (4 mm.). A small center cut was retained for analysis, b.p. 137.5–138.0°, n_D^{20} 1.5121.

Anal. Calc'd for $C_{13}H_{17}ClO_2$: C, 64.86; H, 7.12; Cl, 14.73.

Found: C, 65.08; H, 6.92; Cl, 15.02.

4-(o-Chlorophenyl)pentanoic acid (XVI). A mixture of 148.7 g. (0.618 mole) of ester XV and 70 g. (1.06 moles) of 85% potassium hydroxide in 500 ml. of 95% ethanol was heated under reflux for three hours, cooled, and poured into 2500 ml. of water. Fractionation of the resultant acid through a 65-cm. Podbielniak type column gave 123.6 g. (94%) of colorless oil, b.p. 170–173° (5 mm.). A small center fraction was retained for analysis, b.p. 171.5° (5.2 mm.), n_D^{20} 1.5324.

Anal. Calc'd for $C_{11}H_{13}ClO_2$: Eq. wt., 212.5. Found: Eq. wt., 213.6.

4-Methyl-5-chloro-1-tetralone (XVII). The acid chloride from 50.0 g. (0.235 mole) of XVI and 54.0 g. (0.26 mole) of phosphorus pentachloride was prepared according to the procedure of Johnson and Glenn (19) and allowed to stand one hour with frequent shaking to ensure complete reaction. The acid chloride in 100 ml. of dry benzene was then added with stirring, over a period of 20 minutes, to a cooled slurry of 44.0 g. (0.33 mole) of aluminum chloride in 250 ml. of dry benzene; the dark brown complex was stirred at 25° for 18 hours. The product was then worked up in the usual manner (19) and distilled through a 65-cm. Podbielniak type column to yield 30.4 g. (80%) of colorless tetralone, b.p. 127–128.5° (4 mm.). A small sample crystallized from acetone-hexane in stout prisms, m.p. 65.0–65.4°.

Anal. Calc'd for $C_{11}H_{11}ClO$: C, 67.81; H, 5.70; Cl, 18.21.

Found: C, 67.46; H, 5.66; Cl, 17.93.

1-Methyl-8-chloro-1,2,3,4-tetrahydronaphthalene (XVIII). A solution of 51.0 g. (0.26 mole) of ketone XVII in 250 ml. of 95% ethanol was hydrogenated at room temperature

and 3 atm. pressure in the presence of 20.0 g. of 5% palladium-on-barium sulfate catalyst. The hydrogenation was interrupted after the absorption of two molar-equivalents of hydrogen and the filtered catalyst digested with 100 ml. of hot alcohol. The combined alcohol solutions were concentrated and the residual oil distilled through a 65-cm. Podbielniak type column to give 3.7 g. of 1-methyltetralin, b.p. 83–85° (7 mm.), n_D^{20} 1.5352 (37), followed by 35.4 g. (75%) of colorless XVIII, b.p. 107–109° (7 mm.). A small sample was retained for analysis, b.p. 107.5° (7 mm.), n_D^{22} 1.5550.

Anal. Calc'd for $C_{11}H_{13}Cl$: C, 73.14; H, 7.25.

Found: C, 73.44; H, 7.47.

The modified Wolff-Kishner reduction (20) of ketone XVII gave XVIII in 70% yield.

High pressure hydrogenation of XVII was carried out at 2500 p.s.i. and 150° in the presence of a copper chromite catalyst (36). One mole of hydrogen was rapidly absorbed. The usual workup gave on distillation a 70% yield of the stereoisomeric 4-methyl-5-chloro-1-tetralols, b.p. 144–145° (4.5 mm.), m.p. 68.0–70.0°. Analysis of the crude solid indicated the presence of dechlorinated material as contaminant.

Anal. Calc'd for $C_{11}H_{13}ClO$: C, 67.17; H, 6.66; Cl, 18.03.

Found: C, 67.82; H, 6.62; Cl, 16.94.

The mixture of alcohols was slowly (15 hours) hydrogenated in 95% ethanol as described above for XVIII and compound XVIII was obtained in 50% yield.

1-Methyl-8-cyano-1,2,3,4-tetrahydronaphthalene (XIX). A mixture of 70.8 g. (0.39 mole) of XVIII, 39.8 g. (0.44 mole) of cuprous cyanide (dried at 100° in a vacuum), 9.1 ml. of acetonitrile (distilled from phosphorous pentoxide), and 107 ml. of pyridine (distilled from barium oxide) was heated with shaking to 240–250° for 33 hours. When worked up as previously described (13) and distilled through a 65-cm. Podbielniak type column, there was obtained 53.6 g. (81%) of colorless nitrile, b.p. 123–124° (5 mm.). A small sample crystallized from methanol in colorless plates, m.p. 43.0–44.0°.

Anal. Calc'd for $C_{12}H_{13}N$: N, 8.18. Found: N, 8.09.

Conversions of XVIII ranged from 72–77% and yields of XIX were of the order of 55–70% when only one equivalent of cuprous cyanide was used and the reactants were heated in a sealed tube without shaking.

8-Methyl-5,6,7,8-tetrahydro-1-naphthoic acid (XXI) (16). *A. Direct hydrolysis.* A mixture of 10.0 g. (0.06 mole) of XIX, 75 g. (1.1 moles) of 85% potassium hydroxide, and 380 ml. of diethylene glycol was heated to 190° for 14 hours in a steel flask; the ammonia was titrated as has been described (33). The cooled mixture was poured into 1.5 l. of water and the *amide* (0.15 g.) filtered; m.p. 187.8–188.4° (crystallized from hexane).

Anal. Calc'd for $C_{12}H_{15}NO$: N, 7.40. Found: N, 7.59.

Acid XXI (10.5 g., 95%) was precipitated on acidification of the filtrate, and after three recrystallizations from acetone-hexane formed colorless needles, m.p. 115.1–116.0°.

B. Two-step hydrolysis. A mixture of 53.6 g. (0.313 mole) of XIX, 168 g. (2.64 moles) of 85% potassium hydroxide, and 600 ml. of 80% ethanol was heated under reflux until ammonia evolution had ceased (31 hours). The mixture was poured into 3 l. of water and the precipitated amide (49.5 g.) was collected, m.p. 184.2–187.0°. This material was next hydrolyzed as described in (*A*) to give 47.7 g. (96%) of crude acid XXI, which after three recrystallizations from 50% ethanol formed colorless needles, m.p. 118.1–119.1°. On admixture with the acid prepared by Cason and Wordie (16) (m.p. 118.9–119.6°), the m.p. was 118.0–119.8°.

1-(o-Chlorobenzoyl)-8-methyl-5,6,7,8-tetrahydronaphthalene (XII). The *o*-chlorobromobenzene was prepared from *o*-chloroaniline which had been carefully distilled through a 3-ft. helix-packed column, b.p. 116.5–116.7° (46 mm.). The amine was converted (31) to *o*-chlorobromobenzene of b.p. 84.0–85.0° (16 mm.), n_D^{21} 1.5804.

A Grignard reagent was prepared from 0.74 mole of magnesium and 0.80 mole of *o*-chlorobromobenzene in 500 ml. of ether and converted to the cadmium reagent with 0.45 mole of anhydrous cadmium chloride in the usual manner (32). The cadmium reagent was allowed to react with the acid chloride from 0.247 mole of acid XXI and 0.50 mole of

thionyl chloride, as previously described (13). Distillation of the products through a 65-cm. Podbielniak type column yielded 50.4 g. (74%) of the desired ketone, b.p. 192–195° (2.5 mm.). A small sample recrystallized four times from hexane gave colorless plates, m.p. 80.0–80.9°.

Anal. Calc'd for $C_{18}H_{17}ClO$: Cl, 12.45. Found: Cl, 12.72.

1-(o-Chlorophenyl)-1-(8-methyl-5,6,7,8-tetrahydro-1-naphthyl)ethene (XXIII) was prepared from 10.0 g. (0.035 mole) of ketone XII and methyllithium as previously described for the fully aromatic analog (13). Distillation of the products through a 65-cm. Podbielniak type column gave the ethylene in 85% yield as a colorless glass, b.p. 183–187° (2.3 mm.). A small center cut was analyzed; b.p. 184.0° (2.3 mm.).

Anal. Calc'd for $C_{19}H_{19}Cl$: Cl, 12.54. Found: Cl, 12.38.

1-(o-Chlorophenyl)-1-(8-methyl-5,6,7,8-tetrahydro-1-naphthyl)ethane (XXV). A solution of 9.33 g. (0.033 mole) of the ethylene XXIII in 75 ml. of acetic acid was hydrogenated at room temperature and 3 atm. pressure in the presence of 0.3 g. of commercial platinum oxide catalyst. Hydrogenation was complete in 3 hours and the filtered solution was distilled through a 65-cm. Podbielniak type column to give 7.05 g. (76%) of XXV, b.p. 178–180° (2.5 mm.). A small center cut, b.p. 179.5° (2.5 mm.), was retained for analysis.

Anal. Calc'd for $C_{19}H_{21}Cl$: Cl, 12.44. Found: Cl, 12.08.

1-(o-Cyanophenyl)-1-(8-methyl-5,6,7,8-tetrahydro-1-naphthyl)ethane (XXVII). The chloroalkane (XXV) was converted to the corresponding nitrile as described above for XIX and was obtained in 70% yield as a colorless oil, b.p. 190–192° (2.5 mm.). A small sample crystallized from hexane as colorless, powdery crystals, m.p. 106.7–108.0°.

Anal. Calc'd for $C_{20}H_{21}N$: C, 87.23; H, 7.70.

Found: C, 86.86; H, 7.60.

1-(o-Carboxyphenyl)-1-(8-methyl-5,6,7,8-tetrahydro-1-naphthyl)ethane (IV). Nitrile XXVII (24.0 g., 0.087 mole) was hydrolyzed by the direct method described above for acid XXI. There was obtained from the diluted reaction mixture 10 g. of a *neutral material*, m.p. 232.0–234.0°, which could not be hydrolyzed by heating to 240° for 24 hours. The analysis is in excellent agreement with that calculated for the *lactam*.

Anal. Calc'd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.82; Mol. wt., 291.

Found: C, 82.60; H, 7.40; N, 4.96; Mol. wt. (Rast), 252.

Acid IV (10.4 g., 41%) was obtained from the acidified filtrate, and after two recrystallizations from hexane it formed colorless needles, m.p. 185.1–186.0°.

Anal. Calc'd for $C_{20}H_{22}O_2$: Equiv. wt., 294.4. Found: Equiv. wt., 296.4.

1′,9-Dimethyl-1′,2′,3′,4′-tetrahydro-1,2-benz-10-anthrone (VI). A mixture of 600 mg. (2.0 millimoles) of IV, 9.0 ml. of glacial acetic acid, and 3.0 ml. of acetic anhydride was treated as described by Fieser and Hershberg (14). The crude anthrone (VI) was chromatographed on alumina and recrystallized from 95% ethanol to give 466 mg. (83%) of colorless needles, m.p. 130.2–131.3°.

Anal. Calc'd for $C_{20}H_{20}O$: C, 86.90; H, 7.29.

Found: C, 86.68; H, 7.34.

The ultraviolet absorption spectrum (Fig. 1) showed a maximum at 288 mμ (log ε 4.30). The same compound was obtained in 83% crude yield by cyclizing with anhydrous hydrogen fluoride (22).

1′,9-Dimethyl-1′,2′,3′,4′-tetrahydro-1,2-benzanthracene (VIII). A mixture of 378 mg. (1.4 millimoles) of anthrone VI in 10 ml. of dry xylene containing 392 mg. (1.9 millimoles) of aluminum isopropoxide was heated under reflux for 48 hours. The acetone formed in the reaction was codistilled with isopropyl alcohol. The yellow, gelatinous residue was taken up in benzene and washed with sulfuric acid, ammonia, and water. The washed solution was concentrated to 10 ml. and passed through a small column of alumina. Concentration of the fluorescent eluate gave 335 mg. (93%) of a pale yellow oil which failed to crystallize.

Anal. Calc'd for $C_{20}H_{20}$: C, 92.25; H, 7.75.

Found: C, 90.73; H, 8.34.

The *complex* with 2,4,7-trinitrofluorenone (TNF) (7) crystallized from acetic acid as jet-black needles, m.p. 201.0–202.0°.

Anal. Calc'd for $C_{20}H_{20}\cdot C_{13}H_5N_3O_7$: C, 68.83; H, 4.38.
Found: C, 68.86; H, 4.13.

Cleavage of this TNF complex did not yield analytically pure hydrocarbon VIII.

Compound VIII was obtained in 55% yield (based on the TNF complex) when VI was reduced under the conditions of the modified Wolff-Kishner method (20).

Zinc and alkali reduction of anthrone VI. When anthrone VI was reduced according to Martin's modification (28), the crude reduction product was chromatographed and sublimed to give a 44% yield of an oil which failed to crystallize and formed no complex with TNF (7). Its analysis most closely approximated that of 1′,9-dimethyl-1′,2′,3′,4′,9,10-hexahydro-1,2-benz-10-anthranol.

Anal. Calc'd for $C_{20}H_{22}O$: C, 86.30; H, 7.96.
Found: C, 85.95; H, 7.60.

1′,9-Dimethyl-1,2-benzanthracene (X). The crude hydrocarbon (VIII) (300 mg., 1.15 millimoles) was intimately mixed with 70 mg. of 30% palladium-on-charcoal catalyst (29) and heated for one hour at 330–335°. The melt was taken up in benzene and chromatographed on alumina to give a strongly fluorescent eluate which on concentration gave 272 mg. (93%) of an orange, fluorescent oil. The *TNF complex* (7), made in the usual way, crystallized from benzene as brick-red needles, m.p. 225–230°. The crude yield was 330 mg. (50%). A small sample of this complex was recrystallized from benzene and obtained as brick-red needles, m.p. 234.5–235.6°.

Anal. Calc'd for $C_{20}H_{16}\cdot C_{13}H_5N_3O_7$: C, 69.33; H, 3.70.
Found: C, 69.25; H, 3.58.

The complex (116 mg.) was chromatographed on alumina. Concentration of the fluorescent benzene eluate gave 46 mg. of X as pale yellow clusters, m.p. 123.0–126.2°. Recrystallization from 3 ml. of 95% ethanol gave X as brilliant yellow needles. At 123.0°, the crystals changed to an opalescent melt which cleared sharply at 131.5–132.0°.

Anal. Calc'd for $C_{20}H_{16}$: C, 93.72; H, 6.28.
Found: C, 93.87, 94.18; H, 5.83, 6.01.

On admixture of X with authentic samples of 1′-methyl- and 2′-methyl-1,2-benzanthracene, the melting points were in both instances considerably depressed (35).

The *picrate of X* crystallized from methanol in red warts, m.p. 123.2–124.4°. This picrate was prone to dissociation, and recrystallization resulted in large losses.

Anal. Calc'd for $C_{20}H_{16}\cdot C_6H_3N_3O_7$: C, 64.33; H, 3.95.
Found: C, 64.47; H, 3.72.

The *sym-trinitrobenzene complex* crystallized from methanol in long, scarlet needles, m.p. 145.0–147.0°.

Anal. Calc'd for $C_{20}H_{16}\cdot C_6H_3N_3O_6$: C, 66.52; H, 4.08.
Found: C, 66.35; H, 4.13.

Compound X was obtained in 23% yield (based on the TNF) when dehydrogenation was carried out in benzene in the presence of 30% palladium-on-charcoal catalyst, according to the procedure of Adkins and England (30).

Oxidation of compound X. When 43 mg. of X was oxidized in glacial acetic acid containing 60 mg. of potassium dichromate and the product chromatographed on alumina there was obtained from the yellow zone 30 mg. (66%) of crude quinone, m.p. 180–188°. After two recrystallizations from methanol the quinone formed brilliant yellow plates, m.p., 188.0–189.6°. On admixture with an authentic sample of similarly prepared 1′-methyl-1,2-benzanthraquinone (1) (m.p. 189.6–190.6°) the melting point was 188.0–190.5°. However, on admixture of the quinone from X with an authentic sample of 2′-methyl-1,2-benzanthraquinone (12) (m.p. 190.8–191.8°) the melting point was depressed to 154.5–165.0°.

5,6,7,8-Tetrahydro-1-naphthoic acid (XX) was prepared in 80% yield, according to the procedure of Dauben, Hiskey, and Markhart (34), by hydrogenation of 1-naphthoic acid

in acetic acid with commercial platinum oxide catalyst. The melting point of the crude acid was 147.0–149.5°.

1-(o-Chlorobenzoyl)-5,6,7,8-tetrahydronaphthalene (XI). The acid chloride from 60.0 g. (0.34 mole) of XX was allowed to react with 0.5 mole of bis-(*o*-chlorophenyl)cadmium as described for XII and there was obtained 58.4 g. (70%) of chloroketone XI, b.p. 203–206° (3 mm.). The compound readily crystallized from 95% ethanol as colorless needles, m.p. 82.7–83.5°.

Anal. Calc'd for $C_{17}H_{15}ClO$: Cl, 13.10. Found: Cl, 13.22.

1-(o-Chlorophenyl)-1-(5,6,7,8-tetrahydro-1-naphthyl)ethene (XXII). The ketone XI was converted in 68% yield to the alkene as described above for XII. The ethene was a colorless oil, b.p. 173–175° (2.5 mm.).

Anal. Calc'd for $C_{18}H_{17}Cl$: Cl, 13.19. Found: Cl, 13.14.

1-(o-Chlorophenyl)-1-(5,6,7,8-tetrahydro-1-naphthyl)ethane (XXIV). The alkene was hydrogenated as described above for the analogous compound and XXIV was obtained in 93% yield as a colorless glass, b.p. 184–186° (4.5 mm.).

Anal. Calc'd for $C_{18}H_{19}Cl$: Cl, 13.09. Found: Cl, 13.27.

1-(o-Cyanophenyl)-1-(5,6,7,8-tetrahydro-1-naphthyl)ethane (XXVI). Chloroalkane XXIV was converted in 90% yield to the nitrile as described for the preparation of XIX, and the nitrile was obtained as a colorless oil, b.p. 199–201° (5 mm.).

Anal. Calc'd for $C_{19}H_{19}N$: N, 5.36. Found: N, 5.13.

1-(o-Carboxyphenyl)-1-(5,6,7,8-tetrahydro-1-naphthyl)ethane (III). Nitrile XXVI was hydrolyzed to III in 63% yield as described for the preparation of IV, and the acid was crystallized from 75% ethanol as colorless needles, m.p. 136.3–136.7°.

Anal. Calc'd for $C_{19}H_{20}O_2$: Equiv. wt. 280.4. Found: Equiv. wt. 286.4.

9-Methyl-1′,2′,3′,4′-tetrahydro-1,2-benz-10-anthrone (V). When acid III was cyclized in acetic acid-acetic anhydride (14) as described for the preparation of VI, anthrone V was obtained in 92% yield, and a small sample recrystallized twice from 80% ethanol gave small, colorless needles, m.p. 114.4–114.9°, $\lambda_{max.}$ 288 mμ, log ε 4.30 (Fig. 1).

Anal. Calc'd for $C_{19}H_{18}O$: C, 86.96; H, 6.92.
Found: C, 86.80; H, 6.78.

9-Methyl-1′,2′,3′,4′-tetrahydro-1,2-benzanthracene (VII). Anthrone V was reduced in 91% yield to VII using aluminum isopropoxide and xylene as described for the reduction of VI, and the hydrocarbon was crystallized from ethanol as orange needles, m.p. 121.7–122.2°, [reported (24) 122.6–124.2°].

Anal. Calc'd for $C_{19}H_{18}$: C, 92.66; H, 7.34.
Found: C, 92.09; H, 7.43.

The *complex with 2,4,7-trinitrofluorenone* (7) crystallized from acetone as jet-black needles, m.p. 200.8–201.3°.

Anal. Calc'd for $C_{19}H_{18}\cdot C_{13}H_5N_3O_7$: C, 68.42; H, 4.13.
Found: C, 68.62; H, 4.41.

The *maleic anhydride adduct* (26) crystallized from benzene as colorless blades, m.p. 288.4–290.2°.

Anal. Calc'd for $C_{23}H_{20}O_3$: C, 80.19; H, 5.85.
Found: C, 80.45; H, 5.73.

When *anthrone V was reduced* according to the modified (20) Wolff-Kishner reduction, VII, m.p. 121.3-122.0°, was obtained in 30% yield.

9-Methyl-1,2-benzanthracene (IX) (35). Hydrocarbon VII was dehydrogenated in quantitative yield by heating with sulfur to 245° for one hour, and IX was obtained as a tan powder, m.p. 130–135°. The *2,4,7-trinitrofluorenone derivative* crystallized from acetic acid as brick-red needles, m.p. 234.5–235.0°.

Anal. Calc'd for $C_{19}H_{14}\cdot C_{13}H_5N_3O_7$: C, 68.92; H, 3.43; N, 7.54.
Found: C, 68.88; H, 3.56; N, 7.84.

A small sample of IX was purified by chromatographing the recrystallized TNF (7)

and was obtained from benzene as colorless plates, m.p. 138.0–139.0°. The reported melting point is 138.6–139.6° (35). This carefully purified sample was used for the ultraviolet absorption spectrum (Fig. 3). The "E" maximum, not previously reported (9) for this compound, was observed.

SUMMARY

1′,9-Dimethyl-1,2-benzanthracene has been synthesized from 8-methyl-5,6,7,8-tetrahydro-1-naphthoic acid. The final step, in which strain was introduced into the molecule, was dehydrogenation of 1′,2′,3′,4′-tetrahydro-1′,9-dimethyl-1,2-benzanthracene. The structure of the final product has been checked rigorously.

There are reported several interesting chemical properties of the intermediate anthrone, 1′,2′,3′,4′-tetrahydro-1′,9-dimethyl-1,2-benz-10-anthrone.

BERKELEY, CALIFORNIA

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