

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.43; H, 7.02. Found: C, 74.20; H, 7.34.

Isomerization of 2,3-Dimethylene- $\Delta^{9(10)}$ -octalin (II).—A mixture of 2.0 g. of 2,3-dimethylene- $\Delta^{9(10)}$ -octalin (II) and 0.5 g. of palladium-on-carbon catalyst was heated under reflux for 30 hours. After the catalyst had been removed by filtration, the filtrate was oxidized with an excess of potassium permanganate according to the method of Coulson.²² Ethyl alcohol was added to the hot solution in order to decompose the excess potassium permanganate. The solution was then acidified and extracted with ether in an exhaustive ether extractor. Evaporation of the ether produced a solid residue which was recrystallized from an acetone-benzene mixture to yield 1.1 g. (34%) of pyromellitic acid (VI), m.p. 260–264° dec. (reported²² m.p. 260–264° dec.).

3,6-Dimethyl-1,2-dimethylene-4-cyclohexene (VIII).—At the rate of 1.5 g. per minute, 105 g. (0.413 mole) of 3,6-dimethyl-*cis*- Δ^4 -tetrahydrophthalyl diacetate (VII) was dropped through the vertical Vycor pyrolysis tube heated at 505° as described above. Because of the tendency of this compound to char the pyrolysis was interrupted at the midpoint and a clean pyrolysis tube was inserted in the apparatus. During the pyrolysis and before addition of the ester to either pyrolysis tube, a slow stream of oxygen-free nitrogen was introduced at the top of the apparatus. The pyrolysate was dissolved in 100 ml. of ether and the solution was extracted several times with distilled water. (Titration of an aliquot of the aqueous extracts indicated that 53% of two molar equivalents of acetic acid had been eliminated.) After the ether solution had been dried over anhydrous magnesium sulfate, the ether was removed by distillation under reduced pressure. The residue was fractionated through a 6-inch, helix-packed column to yield 14.3 g. (26%) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII), b.p. 49° (15 mm.), n_D^{25} 1.4884; 21.6 g. (27%) of 3,6-dimethyl-1-methylene-2-acetoxymethyl-4-cyclohexene (IX), b.p. 76° (1.5 mm.), n_D^{25} 1.4762; and 19 g. (18% recovery) of the starting diester VII. The yield of the triene VIII, based on unrecovered VII and IX, was 47%.

(22) E. A. Coulson, *J. Chem. Soc.*, 1305 (1938).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.79; H, 10.22. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.31.

5,8-Dimethyl- $\Delta^{6,9(10)}$ -hexahydronaphthalene-2,3-dicarboxylic Anhydride (X).—A mixture of 1.96 g. (0.02 mole) of maleic anhydride plus 2.68 g. (0.02 mole) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) in 50 ml. of ether was heated under reflux for 21 hours. After about half of the ether had been removed by evaporation, the concentrated solution was cooled to form a precipitate. The solid was removed by filtration and recrystallized from a chloroform-petroleum ether mixture to yield 1.1 g. (24%) of 5,8-dimethyl- $\Delta^{6,9(10)}$ -hexahydronaphthalene-2,3-dicarboxylic anhydride (X), m.p. 162–163°. Further evaporation of the ether filtrate gave a yellow oil that could not be crystallized.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.14; H, 6.84.

Isomerization of 3,6-Dimethyl-1,2-dimethylene-4-cyclohexene (VIII) to Prehnitene (XI).—A mixture of 7.6 g. (0.057 mole) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) and 0.2 g. of a 10% palladium-on-carbon catalyst was heated under reflux for 48 hours. The catalyst was removed by filtration and the filtrate was fractionated through a 6-inch, helix-packed column to yield 2.9 g. of a mixture (presumably triene VIII and prehnitene), b.p. 50–68° (20 mm.), n_D^{25} 1.4938, and 2.6 g. of slightly impure prehnitene (XI), b.p. 42–45° (0.9 mm.), n_D^{25} 1.5020–1.5072 (reported b.p. 75–75.5° (6.5 mm.)²³, n_D^{25} 1.5187²⁴).

By the procedure of Huntress and Autenrieth,²⁵ 1.0 g. of the impure prehnitene (XI) was converted to 2,3,4,5-tetramethylbenzenesulfonamide, m.p. 179–181° (reported²⁵ m.p. 183.5–184°), with chlorosulfonic acid.

(23) L. I. Smith with F. H. MacDougall, *THIS JOURNAL*, **51**, 3005 (1929).

(24) K. v. Auwers, *Ber.*, **55**, 26 (1922).

(25) E. H. Huntress and J. S. Autenrieth, *THIS JOURNAL*, **63**, 3416 (1941).

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Polynuclear Aromatic Hydrocarbons. IX.¹ The Synthesis of 3,4-Benzpyrene and 7-Methyl-3,4-benzpyrene

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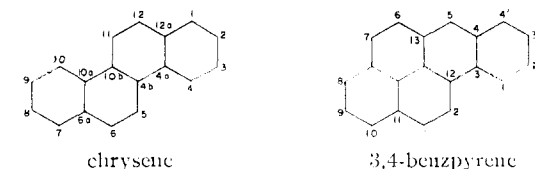
RECEIVED FEBRUARY 28, 1958

The synthesis of 3,4-benzpyrene (X) and 7-methyl-3,4-benzpyrene (XI) from 5-keto-5,6,6a,7,8,9,10,10a-octahydrochrysenes (I) is described. The ketone I was converted by the Reformatsky reaction to a mixture of the two unsaturated acids III and IV which were reduced and cyclized to the corresponding ketones VII and VIII. When either VII or VIII was reduced and dehydrogenated, 3,4-benzpyrene (X) was obtained. Treatment of VII with methylmagnesium iodide followed by dehydrogenation afforded 7-methyl-3,4-benzpyrene (XI), one of the two monomethyl-3,4-benzpyrenes whose synthesis has yet to be described. The attempted preparation of X by the cyclodehydrogenation of XI and XIII afforded chrysenes by the ejection of an ethyl group.

In a recent communication⁴ we reported the preparation of the keto-octahydrochrysenes (I) from naphthalene and *trans*-2-hydroxy-cyclohexanecarboxylic acid lactone. It became apparent that this ketone (I) could serve not only as a useful precursor to the chrysenes ring system but also to the im-

portant 3,4-benzpyrene (X) nucleus.⁵ Moreover, the synthetic scheme whereby we planned to elaborate X from I also seemed applicable to the preparation of 7-methyl-3,4-benzpyrene (XI), a hydrocarbon of considerable interest for biological

(5) These numbering systems are employed throughout this paper:



(1) Paper VIII, D. D. Phillips and T. B. Hill, *THIS JOURNAL*, **80**, 3663 (1958).

(2) To whom inquiries regarding this article should be sent. Shell Development Co., Modesto, Calif.

(3) Krishnagar College, Krishnagar, West Bengal, India. Fulbright Scholar, 1956–1958.

(4) D. D. Phillips and D. N. Chatterjee, *THIS JOURNAL*, **80**, 1360 (1958).

testing as it is one of the two monomethyl-3,4-benzpyrenes whose synthesis has yet to be described.⁶ In this paper the successful syntheses of X and its 7-methyl derivative XI are reported.

During the course of our earlier work⁴ there appeared an alternate synthesis of I in which *trans*-2- β -naphthylcyclohexaneacetic acid was cyclized to I in 93% yield by anhydrous hydrogen fluoride.⁷ In order to compare the properties of I prepared by the two different methods, we repeated the work of Buchta and Ziener⁷ and obtained significantly different results. Although the ketone I after crystallization had essentially the same m.p. (117–119°) as reported, we found that it was in fact a mixture containing no less than 20% of the isomeric keto δ octahydro-1,2-benzanthracene (II), m.p. 160–161°, and 80% of I, m.p. 126–127°, readily separable by chromatography. The structures of

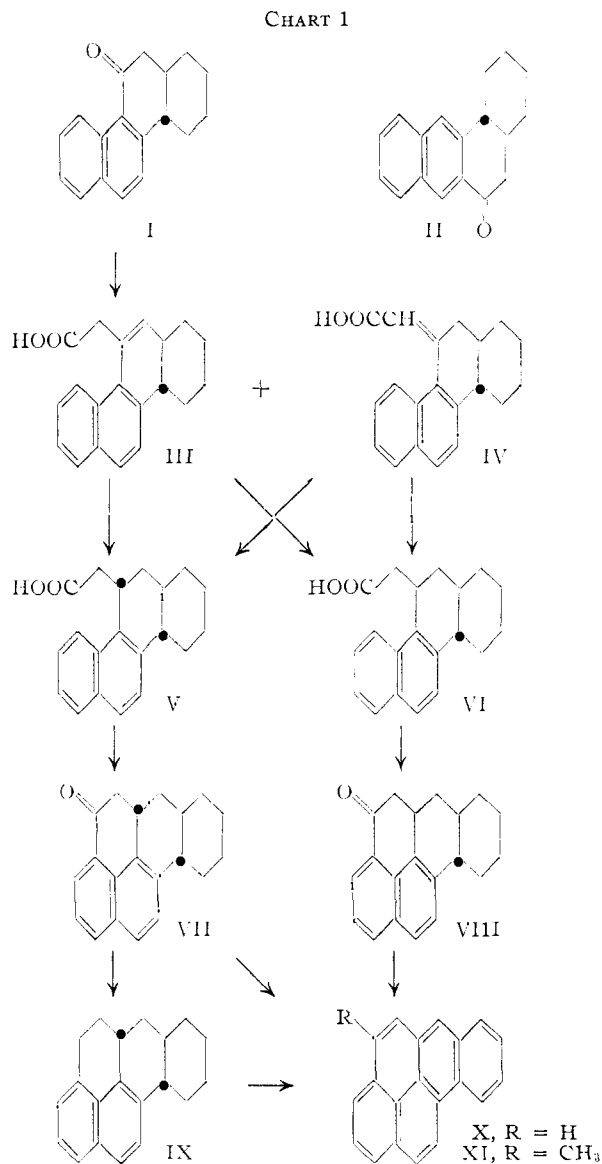
both ketones were established by reduction and dehydrogenation to 1,2-benzanthracene and chrysenes, respectively.

When pure ketone I was condensed with ethyl bromoacetate in the Reformatsky reaction there was obtained a 70% yield of a mixture of unsaturated acids from which about 60–65% of the pure β,γ -unsaturated isomer III could be isolated by fractional crystallization. Although a pure specimen of the α,β -unsaturated acid IV could not be obtained, its presence in the crystallization residues was inferred from the infrared absorption spectrum as well as by hydrogenation studies.⁸

The hydrogenation of III afforded a mixture of acids, m.p. 178–180°, from which pure V, m.p. 186–187°, was isolated by fractional crystallization. The *cis* configuration of the 4a- and 11-hydrogens (see footnote 5) has been assigned on the basis of an inspection of molecular models, from which it is clear that the 12a-hydrogen, by virtue of its proximity to the double bond, provides more steric hindrance to the attacking hydrogens than does the 4a-hydrogen. Consequently, the entering groups will approach from the same side as the 4a-hydrogen, resulting in the *cis* configuration. The same isomer (V) predominated in the hydrogenation of the mixture rich in IV, a result that may be rationalized by the same considerations. This same hydrogenation also afforded some of the other isomer (VI) whose structure was deduced by cyclization in anhydrous hydrogen fluoride to a ketone (VII) isomeric with that (VIII) obtained from the *cis* isomer V.⁹

When ketone VII was reduced with lithium aluminum hydride and the resulting alcohol was dehydrogenated, 3,4-benzpyrene (IX) was obtained in poor yield. An unidentified substance, probably phenolic, also was obtained in the reaction. When the ketone VII was reduced to the corresponding hydrocarbon IX, however, and this was subsequently dehydrogenated, 3,4-benzpyrene (X) was obtained in good yield. The same ketone (VII) condensed smoothly with methylmagnesium iodide to afford the methylcarbinol which was dehydrogenated to 7-methyl-3,4-benzpyrene (XI).¹⁰ The hydrocarbon XI possessed the typical ultraviolet absorption spectrum of a 3,4-benzpyrene derivative with the expected¹¹ small bathochromic shift being observed in most of the maxima.

Another route to 3,4-benzpyrene (X), based on I as starting material, was investigated but met



(6) J. W. Patton and G. H. Daub, *THIS JOURNAL*, **79**, 709 (1957). References to the preparation of ten of the possible twelve monomethyl-3,4-benzpyrenes are given in this paper.

(7) E. Buchta and H. Ziener, *Ann.*, **601**, 155 (1956).

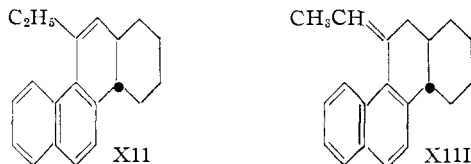
(8) It has been our experience that exocyclic α,β -unsaturated acids such as IV are hydrogenated much more rapidly than their endocyclic β,γ -counterparts (cf. III). Thus III required 10 hr. for the uptake of one mole of hydrogen under conditions where the mixture rich in IV required less than 0.5 hr. for the uptake of 50% of the theoretical amount and only 3.5 hr. for the full amount. These results have been confirmed by studies where both isomers were available in a pure form and will be the subject of a future communication.

(9) It is obvious that the isomers formed in each of the steps outlined in Chart 1 need not be separated if X and/or XI is the ultimate goal. In order to work with crystalline compounds, however, we effected the separations described above and, in general, the yields in subsequent transformations were higher when at least partial separations were made. We have run through the entire scheme without extensive purification and have obtained both X and XI but in significantly lower over-all yield.

(10) The same results were obtained with VIII, further establishing the isomeric nature of VII and VIII.

(11) R. N. Jones, *THIS JOURNAL*, **67**, 2127 (1945).

with little success. The ketone I was condensed with ethylmagnesium iodide and the resulting carbinol was dehydrated to a mixture of two hydrocarbons (XII and XIII). Because pyrenes have been prepared by the cyclodehydrogenation of



similarly constituted 4-alkyl-1,2-dehydrophenanthrenes,¹² it was thought that either or both XII and XIII would afford 3,4-benzpyrene (X) under the same conditions. When heated to 320° in the presence of 10% palladium-on-charcoal catalyst, both hydrocarbons suffered the loss of an ethyl group and chrysene was the only product isolated. There are a few analogies for this behavior¹³ although the successful dehydrogenation of a 5(11)-ethylhexahydrochrysene to the corresponding 5-ethylchrysene has been described.¹⁴

The carcinogenic activity of 7-methyl-3,4-benzpyrene (XI) is being examined and the results will be recorded elsewhere.

Acknowledgments.—The senior author (D.D.P.) is grateful to the Alfred P. Sloan Foundation for their support of this program during the period 1955–1958. D.N.C. wishes to thank the Damon Runyon Memorial Cancer Fund for a post-doctoral fellowship.

Experimental¹⁵

trans-5-Keto-5,6,6a,7,8,9,10,10a-octahydrochrysene (I).
a. From *trans*-2-Hydroxycyclohexanecetic Acid Lactone and Naphthalene.—This reaction has been described in detail⁴ and will not be repeated here.

b. From β -Naphthylmagnesium Bromide.⁷—Ethyl cyclohexanone-2-acetate¹⁶ was condensed with β -naphthylmagnesium bromide as described⁷ except for an additional 6-hr. stirring period at room temperature. This raised the yield of the lactone from 20 to 30%. The lactone was reduced to 2- β -naphthylcyclohexanecetic acid by the Clemmensen reduction. When this acid was cyclized by hydrogen fluoride, a ketone, m.p. 117–119°, was obtained in 86% yield. When chromatographed on acid-washed alumina this ketone, assumed to be homogeneous by Buchta and Ziener,⁷ was separated into two distinct compounds. Hexane-benzene (3:1) eluted 65% (based on the acid) of pure ketone I, needles from ethanol, m.p. 126–127°; λ_{\max} (log ϵ): 215 μ (4.68), 247 (4.38) and 315 (3.87).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.32; H, 7.15.

The 2,4-dinitrophenylhydrazone crystallized from benzene as red needles, m.p. 245–246°; lit. m.p. 230–232°,⁴ 222–225°.⁷

(12) D. N. Chatterjee, *THIS JOURNAL*, **77**, 5131 (1955).

(13) C. K. Bradsher and L. Rapaport, *ibid.*, **66**, 2181 (1944); W. E. Jones and G. R. Ramage, *J. Chem. Soc.*, 1853 (1938); W. Cocker, B. E. Cross and J. McCormick, *ibid.*, **72** (1952). The last reference lists a brief bibliography on the subject.

(14) M. S. Newman, *ibid.*, **62**, 870 (1940). The conditions (heating with sulfur at 230–240°) were much milder than those described in the Experimental section of this paper and failure to eject the ethyl group is not entirely unexpected.

(15) Melting points and boiling points are both uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol with a Beckman model DK automatic recording spectrophotometer. Infrared absorption spectra were obtained on a Perkin-Elmer model 21 double beam spectrophotometer. The solids were pressed in potassium bromide. Analyses are by Schwarzkopf Labs., Woodside 77, N. Y.

(16) C. M. Ma, *Ber.*, **68**, 871 (1935).

Elution with 50:50 benzene-hexane afforded 15% (based on the acid) of *trans*-4-keto-1',2',3',4',1,2,3,4-octahydro-1,2-benzanthracene (II) as colorless plates from benzene-methanol, m.p. 160–161°; λ_{\max} (log ϵ): 246 μ (4.65), 253 (4.70), 291 (3.94), 303 (3.94) and 344 (3.22).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.24; H, 7.42.

The 2,4-dinitrophenylhydrazone crystallized from benzene as red needles, m.p. 239–240°.

Anal. Calcd. for $C_{24}H_{22}O_4N_4$: N, 13.02. Found: N, 13.21.

trans-1,2,3,4,4a,11,12,12a-Octahydrochrysene.—A mixture of 0.25 g. (0.001 mole) of pure ketone I, m.p. 126–127°, 5 ml. of ethylene glycol and 1 ml. of 85% hydrazine hydrate was heated under reflux (150–160°) for 2 hr. The solution was cooled slightly, 0.5 g. of potassium hydroxide was added and the mixture was heated slowly to 220° where it was maintained for 4 hr. The usual workup afforded 0.1 g. (42%) of the hydrocarbon as colorless needles from methanol, m.p. 115–116°, lit.⁷ m.p. 110–111°; λ_{\max} (log ϵ): 229 μ (4.84), 275 (3.60), 284 (3.63), 291 (3.51), 307 (2.84), 312 (2.61) and 321 (2.70).

The structure of this hydrocarbon was established by its quantitative dehydrogenation to afford chrysene, m.p. 250–251°, undepressed on admixture with an authentic specimen.

trans-1',2',3',4',1,2,3,4-Octahydro-1,2-benzanthracene.—The reduction of 0.25 g. (0.001 mole) of the ketone II, m.p. 160°, by the Huang-Minlon method described above gave 0.18 g. (76%) of solid hydrocarbon which crystallized from ethanol as colorless needles, m.p. 77–79°; λ_{\max} (log ϵ): 229 μ (5.01), 274 (3.72), 284 (3.70), 294 (3.47), 307 (2.91), 318 (2.62) and 322 (2.89).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.52; H, 8.48. Found: C, 91.38; H, 8.58.

The dehydrogenation of 50 mg. of this hydrocarbon with 25 mg. of 10% palladium-on-charcoal at 300–320° for 2 hr. gave 25 mg. (52%) of 1,2-benzanthracene, m.p. 161–162°, identified by its characteristic ultraviolet absorption spectrum and by comparison with an authentic specimen.

The Reformatsky Reaction of *trans*-5-Keto-5,6,6a,7,8,9,10,10a-octahydrochrysene (I) with Ethyl Bromoacetate.—The ketone (1.25 g., 0.005 mole) was dissolved in a mixture of 25 ml. of dry benzene and 25 ml. of dry ether and to this mixture was added 0.6 g. of 20 mesh zinc, 1 ml. of ethyl bromoacetate and a trace of iodine. The reaction was heated under reflux with stirring for 8 hr. with the addition of 0.3 g. of zinc and 0.5 ml. of ethyl bromoacetate after 3 hr.

The reaction mixture was decomposed with dilute hydrochloric acid and the aqueous layer was extracted with 50 ml. of ether. The combined organic phases were washed with water and dried over sodium sulfate. Removal of the solvent under reduced pressure left a light yellow viscous oil which was dehydrated by warming with 5 ml. of formic acid on the steam-bath for 5 min. After the formic acid had been removed under reduced pressure, the residual oil was dissolved in benzene and passed through a column of alumina. Evaporation of the solvent left a viscous oil which was saponified by heating under reflux for 2 hr. with methanolic potassium hydroxide. The alcohol was removed under reduced pressure and the residue was diluted with water. Extraction of the alkaline solution with ether gave 0.15 g. of unreacted ketone. Acidification of the alkaline solution gave 0.95 g. (70% based on the ketone consumed) of a light brown mixture of solid acids. Crystallization of this material from benzene afforded 0.55 g. of *trans*-1,2,3,4,4a,12a-hexahydrochrysene-11-acetic acid (III), m.p. 220–222°. An additional 0.05 g. of the acid, m.p. 218–220°, was obtained from the mother liquor raising the total yield to 0.6 g. for this isomer.

Recrystallization from benzene-methanol afforded the analytical sample as stout cubes, m.p. 227–228° dec.; λ_{\max} (log ϵ): 229 μ (4.73) and 313 (4.01); 5.85 μ .

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.80. Found: C, 82.07; H, 6.81.

The mother liquor, after separation of the acid, m.p. 220–222°, was concentrated, but no crystalline isomeric acid IV could be isolated. Evaporation of the solution afforded 0.35 g. of a semisolid residue with an infrared absorption spectrum (λ_{\max} 5.89 μ) that indicated the presence of some

of the conjugated isomer IV. Evidently this acid mixture consists mainly of *trans* 1,2,3,4,4a,11,12,12a-octahydrochrysenylidene-11-acetic acid (IV), contaminated with a relatively small amount of the isomer III.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.80. Found: C, 81.75; H, 6.54.

1,2,3,4,4a,11,12,12a-Octahydrochrysen-11-acetic Acid (V).—At atmospheric pressure, 0.55 g. of the acid III, m.p. 220–222°, dissolved in 20 ml. of ethyl acetate was reduced in the presence of 0.1 g. of 10% palladium-on-charcoal catalyst. After 10 hr. at room temperature, when the theoretical amount of hydrogen had been absorbed, the solution was filtered and the solvent removed under reduced pressure. Crystallization of the solid residue from a benzene-hexane mixture afforded 0.4 g. (72%) of 1,2,3,4,4a,11,12,12a-octahydrochrysen-11-acetic acid (V) as short needles, m.p. 178–180°. Two further crystallizations from a benzene-methanol mixture provided an analytical sample of V as colorless needles, m.p. 186–187°. Its ultraviolet absorption spectrum (λ_{max} (log ϵ): 230 $m\mu$ (4.98), 275 (3.77), 285 (3.82), 306 (3.08), 313 (2.82) and 321 (2.83)) was typical of a substituted naphthalene.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.49. Found: C, 81.48; H, 4.37.

The semi-solid residue (0.35 g.) consisting of a mixture of III and IV was reduced catalytically under similar conditions. More than half of the theoretical amount of hydrogen was taken up within 0.5 hr. After 3.5 hr. at room temperature, it was worked up in the usual way to give a colorless solid which crystallized from a benzene-hexane mixture to afford 0.2 g. (55%) of impure V, m.p. 175–178°, identical with the impure sample, m.p. 178–180°, obtained above from III.

The combined mother liquor from both reductions on evaporation gave 0.3 g. (32%) of semi-solid mass which was evidently a mixture of the two isomers V and VI.

7-Keto-1',2',3',4',3,4,5,6,7,13-decahydro-3,4-benzpyrene (VII).—The cyclization of 0.58 g. (0.002 mole) of the acid, V, m.p. 178–180°, was accomplished by allowing it to stand at 0° for 20 min. in 10 ml. of anhydrous hydrogen fluoride. The dark red solution then was poured onto 200 g. of crushed ice. The organic material was extracted with ether, washed with water and sodium carbonate solution and dried over sodium sulfate to yield, on evaporation, 0.55 g. (100%) of solid ketone which was taken up in benzene and passed through a column of alumina. Concentration of the benzene eluents afforded 0.48 g. (90%) of the ketone VII as long colorless needles, m.p. 165–168°. An analytical sample obtained by recrystallization from a benzene-methanol mixture showed m.p. 172–173°; λ_{max} (log ϵ): 218 $m\mu$ (4.65), 250 (4.37) and 336 (3.68).

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.95; H, 7.24. Found: C, 86.61; H, 7.36.

The 2,4-dinitrophenylhydrazones crystallized from pyridine as red needles, m.p. 278–280° dec.

Anal. Calcd. for $C_{20}H_{20}O_4N_2$: N, 12.28. Found: N, 12.35.

The cyclization of 0.3 g. of the semi-solid mixture of V and VI under identical conditions afforded a pale yellow semi-solid product in 95% yield. Chromatography of this sample on alumina followed by elution with hexane gave 0.1 g. of a yellow fluorescent oil. Elution with 30% benzene in hexane gave 0.2 g. (72%) of a pale yellow solid which crystallized from a benzene-methanol mixture as light yellow needles, m.p. 135–142°. It exhibited an intense green fluorescence in solution. Fractional crystallization of this ketone mixture from methanol permitted its separation into the two isomeric ketones: (a) 30 mg. of colorless needles of VII, m.p. 172–183°, and (b) 0.1 g. of light yellow needles, m.p. 142–143°, evidently the other isomer (VIII). Its ultraviolet absorption spectrum (λ_{max} (log ϵ): 217 $m\mu$ (4.67), 251 (4.37) and 336 (3.70)) was very similar to that of VII.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.95; H, 7.24. Found: C, 87.45; H, 7.32.

The 2,4-dinitrophenylhydrazones crystallized from aqueous pyridine as orange needles, m.p. 279–280° dec.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: N, 12.28. Found: N, 12.52.

7-Hydroxy-1',2',3',4',3,4,5,6,7,13-decahydro-3,4-benzpyrene.—To a slurry of 0.23 g. of lithium aluminum hydride in 20 ml. of dry ether was added 0.11 g. of the ketone

VII, m.p. 172–173°. The solution was heated under reflux for 2 hr. and worked up in the usual manner. Crystallization from a benzene-methanol mixture afforded 94 mg. (85%) of the alcohol as fine needles, m.p. 175–176°. An analytical sample, obtained by crystallization from the same solvent, had m.p. 176–177°; λ_{max} (log ϵ): 232 $m\mu$ (5.00), 278 (3.72), 287 (3.77), 308 (3.14) and 324 (2.93).

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.33; H, 7.91. Found: C, 85.95; H, 7.74.

1',2',3',4',3,4,5,6,7,13-decahydro-3,4-benzpyrene (IX).—A mixture of 0.11 g. of the ketone VII, m.p. 172–173°, 5 ml. of ethylene glycol and 1 ml. of 85% hydrazine hydrate was heated under gentle reflux for 3 hr. The mixture was cooled, 0.5 g. of solid potassium hydroxide was added and the mixture slowly distilled until the bath temperature rose to 220° at which point it was heated under reflux for 4 hr. A small amount of the hydrocarbon IX codistilled with the solvent. The usual workup gave 0.1 g. of solid which was taken up in hexane and chromatographed on alumina. Elution with 100 ml. of hexane afforded 72 mg. (70%) of IX as soft silky needles, m.p. 123–124°. The ultraviolet absorption spectrum of this hydrocarbon (λ_{max} (log ϵ): 232 $m\mu$ (4.98), 278 (3.67), 287 (3.72), 309 (3.08), 318 (2.77) and 324 (3.07)) was typical of a substituted naphthalene derivative.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.48; H, 8.51.

3,4-Benzpyrene (X).—An intimate mixture of 50 mg. of the decahydrobenzpyrene IX and 20 mg. of 10% palladium-on-charcoal catalyst was heated to 300–320° for 2 hr. The hydrocarbon that sublimed into the air condenser was returned to the reaction tube and heated for an additional hour. After cooling, the hard cake was dissolved in hot benzene and chromatographed on alumina. The material obtained by evaporation of the eluent crystallized from benzene-methanol to yield 35 mg. (73%) of 3,4-benzpyrene (X) as pale yellow needles, m.p. 175–176°; lit. m.p. 178.5–179° (cor.),¹⁷ 176–176.5° (cor.).¹⁸

The ultraviolet absorption spectrum (λ_{max} : 225, 255, 267, 272, 283, 298, 330, 348, 363, 384 and 403 $m\mu$) was in excellent agreement with that reported.¹⁹

The *sym*-nitrobenzene complex crystallized from benzene-methanol as bright red needles, m.p. 226–227°, lit.¹⁷ m.p. 226–227°.

The dehydrogenation of 50 mg. of the alcohol (see above) under similar conditions gave 15 mg. (33%) of 3,4-benzpyrene, m.p. 175–176°. The low yield was presumably due to the formation of some phenolic product which was retained by the alumina column.

7-Methyl-3,4-benzpyrene (XI).—A Grignard reagent, prepared from 0.12 g. (0.005 g. atom) of magnesium and 1.2 g. (0.008 mole) of methyl iodide in 15 ml. of dry ether, was added slowly, at 5°, to a well-stirred solution of 0.27 g. (0.001 mole) of the ketone VII, m.p. 168–170°, in 15 ml. of dry benzene. After stirring at room temperature for 4 hr., the reaction mixture was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over sodium sulfate. Removal of the solvent left 7-hydroxy-7-methyl-1',2',3',4',3,4,5,6,7,13-decahydro-3,4-benzpyrene as a viscous yellow oil.

The crude alcohol was dehydrated and dehydrogenated by heating for 1 hr. at 300° with 0.1 g. of 10% palladium-on-charcoal catalyst. After cooling, the hard cake was dissolved in boiling benzene and the solution was chromatographed on alumina. Concentration of the benzene eluent yielded 0.12 g. of 7-methyl-3,4-benzpyrene (XI) as light yellow needles, m.p. 187–188°. The mother liquors afforded an additional 0.02 g. of the hydrocarbon, m.p. 185–187°, raising the total yield to 0.14 g. (54% from VII). An analytical sample was obtained from benzene as pale yellow needles, m.p. 188–189°.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.22; H, 5.84.

The ultraviolet absorption spectrum of 7-methyl-3,4-benzpyrene (XI) showed the following λ_{max} (log ϵ): 229

(17) L. F. Fieser and E. B. Hershberg, *THIS JOURNAL*, **60**, 1658 (1938).

(18) L. F. Fieser and M. Fieser, *ibid.*, **67**, 782 (1935).

(19) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, chart no. 554.

$m\mu$ (4.46), 255 (4.66), 266 (4.74), 274 (4.53), 285 (4.65), 298 (4.73), 332 (3.67), 345 (4.05), 364 (4.32), 378 (4.35), 385 (4.38) and 404 (3.48).

The picrate crystallized from benzene-methanol as purple needles, m.p. 188–189°.²⁰

Anal. Calcd. for $C_{27}H_{17}O_7N_3$: C, 65.45; H, 3.46. Found: C, 65.70; H, 3.37.

The *sym*-trinitrobenzene complex separated from benzene-methanol as bright red needles, m.p. 210–211°.

Anal. Calcd. for $C_{27}H_{17}O_6N_3$: N, 8.76. Found: N, 8.58.

trans-11-Ethyl-1,2,3,4,4a,12a-hexahydrochrysene (XII) and *trans*-11-Ethylidene-1,2,3,4,4a,11,12,12a-octahydrochrysene (XIII).—A Grignard solution prepared from 0.24 g. (0.01 g. atom) of magnesium and 1.6 g. of ethyl iodide in 20 ml. of dry ether was added dropwise, at 0°, to a stirred solution of 0.75 g. (0.003 mole) of the keto chrysene I in 20 ml. of dry benzene. After stirring at ordinary temperature for 2 hr., the solution was heated under gentle reflux for 2 hr. and decomposed with dilute hydrochloric acid. The usual workup afforded 0.8 g. of solid material which was de-

(20) After the submission of this paper we were informed of the synthesis of 7-methyl-3,4-benzpyrene and its picrate (Ph.D. dissertation of Joseph L. Comp, University of New Mexico, 1956). The properties of the hydrocarbon, m.p. 190–191°, and the picrate, purple needles, m.p. 187–187.5°, are in excellent agreement with those reported here and the ultraviolet absorption spectrum of the two hydrocarbons were essentially identical. We are grateful to Prof. Guido H. Dault for this information prior to its publication.

hydrated by heating for 10 min. at 100° with 5 ml. of anhydrous formic acid.

Removal of the formic acid under reduced pressure yielded a solid which was dissolved in benzene and chromatographed on alumina. Elution with 100 ml. of hexane gave 0.14 g. of XII as a colorless viscous oil, λ_{max} 296 $m\mu$, $\log \epsilon$ 3.87, and 232 $m\mu$, $\log \epsilon$ 4.74.

Anal. Calcd. for $C_{26}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.26; H, 8.68.

Elution with a second 100-ml. portion of hexane afforded 40 mg. of the ethylidene compound XIII as needles from methanol, m.p. 116–117°, depressed to 90° on admixture with *trans*-1,2,3,4,4a,11,12,12a-octahydrochrysene, m.p. 115–116° (see above). The ultraviolet absorption spectrum (λ_{max} $\log \epsilon$): 238 $m\mu$ (4.86), 315 (4.04), 328 (3.86) and 335 (3.87) was in accord with the structure assigned to this hydrocarbon.

Anal. Calcd. for $C_{26}H_{22}$: C, 91.60; H, 8.40. Found: C, 92.02; H, 7.84.

Elution of the chromatographic column with 50:50 benzene-hexane afforded 0.5 g. of unreacted ketone I, m.p. 123–124°.

When both of these hydrocarbons (XII and XIII) were heated to 300–320° with 10% palladium-on-charcoal catalyst as described above, there was obtained as the only isolable product a small yield of chrysene, m.p. and mixed m.p. 250–251°.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. X.¹ The Synthesis of 6,7-Acebenzo[c]phenanthrene

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RECEIVED MARCH 7, 1958

The synthesis of 6,7-acebenzo[c]phenanthrene (XI) from *trans*-2- α -naphthylcyclohexanecetic acid (V) is described. The acid V was cyclized to the ketone I which then was converted to the acetic acid derivative VII by the Reformatsky reaction. Cyclization of this acid (VII) afforded the ketone VIII which was converted to the corresponding hydrocarbon IX by Wolff-Kishner reduction. Aromatization of IX was extremely difficult but conditions were found whereby a 10% of XI could be obtained. The ultraviolet absorption spectrum of this interesting hydrocarbon is discussed.

It is now well established that the introduction of a dimethylene bridge into a polynuclear aromatic hydrocarbon that is either a weak carcinogen or is devoid of carcinogenic properties often imparts considerable activity to the compound. Examples in the 1,2-benzanthracene series are particularly striking in this respect⁴ and the effect of a similar structural change in other ring systems is therefore of considerable interest. In this regard, we have selected for study 6,7-acebenzo[c]phenanthrene (XI) and in this paper are described the synthesis

and some of the properties of this interesting hydrocarbon.

The starting material I was originally obtained from the cyclization of V, a minor product of the Friedel-Crafts reaction between naphthalene and *trans*-2-hydroxycyclohexanecetic acid lactone.⁵ Although the structure of I seemed to be adequately established in our earlier paper, the same structure recently has been assigned to a ketone with widely divergent properties.⁶ We therefore felt obligated to verify our assignment by an independent synthesis, which, at the same time, might also afford I in higher yields than we had realized previously.⁵

With this view in mind, α -naphthylmagnesium bromide was condensed with ethyl cyclohexanone-2-acetate to afford the lactone II. Our first attempts to reduce this lactone involved catalytic hydrogenation at 60° but concomitant reduction of one of the aromatic rings occurred and the tetralin acid III was obtained. That the unsubstituted ring had been reduced was verified by cyclization to a ketone IV which could be further reduced and dehydrogenated to benzo[c]phenanthrene. The lac-

(1) Paper IX, D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 4350 (1958).

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(4) The parent hydrocarbon, 1,2-benzanthracene, is very weakly carcinogenic whereas 5,10-dimethylene-1,2-benzanthracene (cholanthrene) and 6-methyl-5,10-dimethylene-1,2-benzanthracene (20-methylcholanthrene) are two of the most potent carcinogens known (I. Berenblum, *Cancer Research*, **5**, 561 (1945); M. J. Shear, *Am. J. Cancer*, **33**, 499, 519, 528 (1938)). The 4,10-dimethylene derivative is also carcinogenic (M. J. Shear, *ibid.*, **28**, 334 (1936); **33**, 499, 516, 517 (1938); C. E. Dunlap and S. Warren, *Cancer Research*, **6**, 454 (1946)) as are the 3,4-dimethylene (G. M. Badger, *et al.*, *Proc. Roy. Soc. London*, **B129**, 439, 443 (1940)) and 8,9-dimethylene (M. J. Shear, *Am. J. Cancer*, **28**, 334 (1936); L. F. Fieser, *et al.*, *ibid.*, **29**, 260 (1937)) derivatives.

(5) D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 1360 (1958).

(6) V. Klibansky and D. Ginsburg, *J. Chem. Soc.*, 1293 (1957).