mμ (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 dehydrated 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 mμ, log ε 3.87, and 232 mμ, log ε 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 ε): 238 mμ (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°.

ITHACA, NEW YORK

[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. Daub for this information prior to its publication.

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

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

BY DONALD D. PHILLIPS[2] AND D. N. CHATTERJEE[3]

RECEIVED MARCH 7, 1958

The synthesis of 6,7-acebenzo[c]phenanthrene (XI) from *trans*-2-α-naphthylcyclohexaneacetic 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 respect[4] 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-hydroxycyclohexaneacetic 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-

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[1] Paper IX, D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 4360 (1958).

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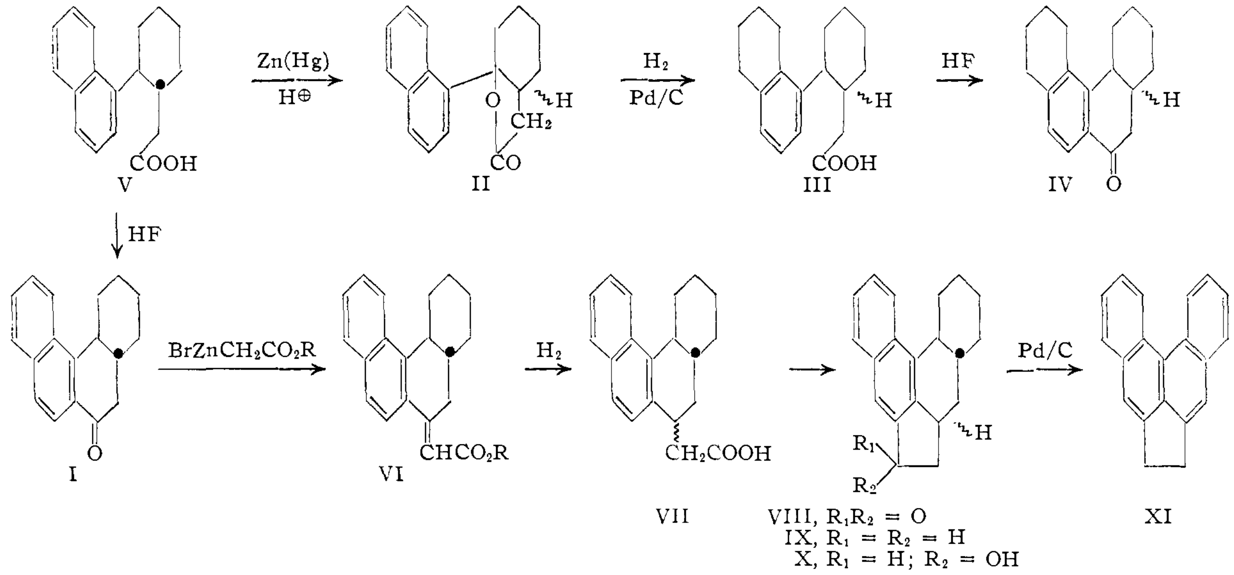
[3] Krishnagar College, Krishnagar, West Bengal, India. Fulbright Scholar, 1956–1958.

[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] Y. Klibansky and D. Ginsburg, *J. Chem. Soc.*, 1293 (1957).

CHART 1

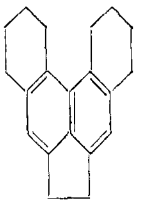


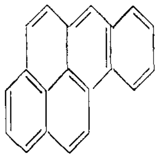
tone ring in II was successfully hydrogenolyzed by the Clemmensen method and the mixture of acids so obtained was separated into V and the corresponding *cis* isomer, m.p. 158–160° and 219–220°, respectively.[7] When the *trans* isomer V was cyclized by hydrogen fluoride, a ketone with identical properties to the I previously reported[5] was obtained,[8] thus establishing its structure.

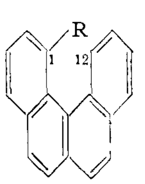
Ketone I condensed smoothly and in high yield with ethyl bromoacetate in the Reformatsky reaction to afford VI ($R = C_2H_5$), uncontaminated by any of the endocyclic isomer. When VI was catalytically reduced, one of the isomers corresponding to VII was obtained in a pure condition but the major product was a mixture of the two possible isomers. The pure compound and the mixture were both converted to XI by the route described below with essentially the same results, although the yields were corresponding better, as expected, when the pure isomer was employed.

The cyclization of pure VII afforded one of the isomeric forms of VIII, m.p. 164-165°, whereas the mixture of VII and its isomer yielded as the principal product the other stereoisomeric form of VIII, m.p. 168-169°. The loss on crystallization of this latter isomer was rather high, however, and the mixture from which it was obtained, m.p. 125–130°, was employed in future operations. When ketone VIII, m.p. 164–165°, was subjected to the Wolff–Kishner reduction, the corresponding hydrocarbon IX, m.p. 127–128°, was obtained in good yield. The same reduction of the 125–130° mixture of VIII afforded some of the 127–128° compound as well as the other isomer of IX, m.p. 109-110°.

The dehydrogenation of IX proved to be very difficult as complete destruction of the hydrocarbon occurred in our earlier experiments. We had anticipated some difficulty with this dehydrogenation in view of the unsuccessful efforts to synthesize XI from an isomeric hydrocarbon (XII).[9] However,


XII


XIII



XIV, R = H
XV, R = CH_3

when IX, m.p. 127–128°, was heated to 300–310° for one hour with 10% palladium-on-charcoal catalyst, the desired hydrocarbon XI, m.p. 125–126°, was obtained in 10% yield. Considerable fragmentation must have occurred during the dehydrogenation as XI was the only hydrocarbon that could be isolated except for a small amount of unreacted starting material. The results with the 109–110° isomer of IX were essentially the same except for the isolation of a small amount (2%) of 3,4-benzpyrene (XIII) along with XI. The formation of XIII may be ascribed to the presence of trace amounts of β-substituted naphthalenes in the starting materials as these have recently been shown to serve as convenient intermediates for the preparation of XIII.[10]

It may be seen from Fig. 1 that the ultraviolet absorption spectrum of XI, although similar in many respects to the parent hydrocarbon, benzo[c]phenanthrene (XIV), is distinctly different in some regions. The most striking difference may be

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[7] Klibansky and Ginsburg[6] report m.p. 84–86° for V.

[8] About 15% of an unknown ketone was also obtained in this reaction but was readily separated by careful fractional crystallization to afford I as *colorless* plates, m.p. 154–155°, λ_{max} 5.95 μ. Klibansky and Ginsburg[6] cyclized their V in the same manner but did not report the isolation of any other product except I which they describe as a *yellow* oil, λ_{max} *5.85* μ. We find these properties difficult to ascribe to a ketone with structure I and can only assume that the Israeli authors were dealing with a mixture. (Other discrepancies in products derived from I are recorded in the Experimental section.)

[9] L. F. Fieser, M. Fieser and E. B. Hershberg, THIS JOURNAL, **58**, 1463 (1936), report that complete destruction of XII occurred when heated with selenium, sulfur or platinum. We obtained similarly discouraging results when the corresponding alcohol X was dehydrogenated.

[10] D. D. Phillips and D. N. Chatterjee, *ibid.*, **80**, 4360 (1958).

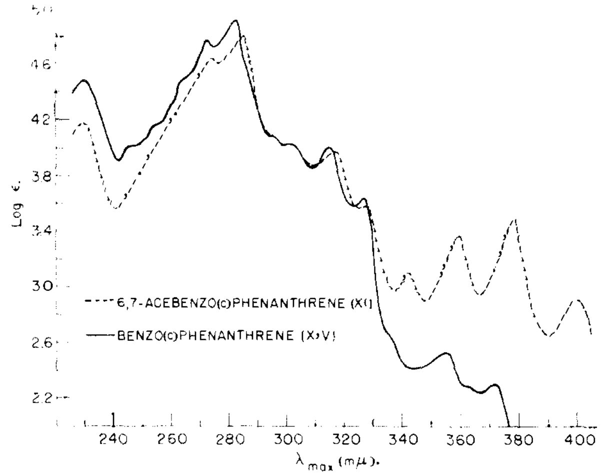

Fig. 1.

noted in the intensity of the bands from 342 to 399 mμ which have log ε values that are larger by a unit or more than those of the unsubstituted hydrocarbon XIV. A difference between the two compounds would be expected since the dimethylene bridge forces XI into a more rigid configuration.[11] A certain loss in fine structure is also observed in the spectrum of XI, particularly in the region between 230 and 274 mμ where the parent hydrocarbon XIV has three distinct bands. The same effect has been observed[12] in this region in 1-methylbenzo[c]phenanthrene (5-methyl-3,4-benzphenanthrene, XV) and may be attributed to the molecular overcrowding[13] that exists when groups are located in the 1-position of benzo[c]phenanthrene (XIV). On the other hand, the dimethylene bridge also exhibits a fine structure effect, observable in the 342–399 mμ region, analogous to that reported for 4,10-dimethylene-1,2-benzanthracene.[14]

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

Experimental[15]

2-α-Naphthyl-2-hydroxycyclohexaneacetic Acid Lactone (II).—A Grignard reagent from 2.4 g. (0.1 g. atom) of magnesium, 20.7 g. (0.1 mole) of α-bromonaphthalene in a mixture of 80 ml. of ether and 20 ml. of benzene was added with stirring, at 0°, to 18.4 g. (0.1 mole) of ethyl cyclohexanone-2-acetate[16] in 100 ml. of dry ether. After 2 hr. at 0° and 6 hr. at room temperature, the reaction mixture was decomposed and the organic material was extracted with ether.

The semi-solid residue left after evaporation of the solvent was saponified by heating for 3 hr. with 8 g. of potassium hydroxide in 100 ml. of methanol. The solvent was removed under reduced pressure and dilution of the viscous solution with a large volume of water led to the separation of a large amount of naphthalene and other neutral material which was extracted with ether. Acidification of the alkaline solution afforded 9 g. of acidic material which was distilled to give 2.2 g. of cyclohexanone-2-acetic acid, b.p. 125–130° (0.1 mm.), followed by 5.5 g. of a viscous oil, b.p. 195–200° (0.1 mm.), which slowly solidified on trituration with a little hexane. Crystallization from benzene–hexane afforded 3.2 g. (14%) of the lactone II as colorless plates, m.p. 131–133°. An analytical sample crystallized as plates from methanol, m.p. 133–134°, λ_{max} 5.68 μ.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.20; H, 6.76. Found: C, 81.29; H, 7.05.

2-α-Tetrylcyclohexaneacetic Acid (III).—In an electrically heated hydrogenation flask were placed 0.5 g. of the lactone II, 0.1 g. of 10% palladium-on-charcoal catalyst and 20 ml. of absolute ethanol. The mixture was shaken for 10 hr. at 60° under a hydrogen pressure of 43 lb. The catalyst was filtered and the solution was evaporated to a solid residue which was warmed with sodium carbonate solution. Extraction of the alkaline solution with ether gave 0.1 g. of unreacted lactone. Acidification of the alkaline solution afforded 0.4 g. of solid acid which, after two crystallizations from methanol, afforded one of the stereoisomeric forms of III as colorless cubes, m.p. 192–193°. Its ultraviolet absorption spectrum (λ_{max} 265 mμ, log ε 2.45) was very similar to that of α-methyltetralin.[17a]

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.41; H, 8.82. Found: C, 79.22; H, 8.98.

The cyclization of 50 mg. of the partially reduced acid III with 5 ml. of anhydrous hydrogen fluoride at 0° yielded 30 mg. of **6-keto-1,2,3,4,4a,5,6,9,10,11,12,13a-dodecahydrobenzo[c]phenanthrene** (IV) which crystallized from methanol as stout cubes, m.p. 120–121°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.04; H, 8.66. Found: C, 84.73; H, 8.47.

The 2,4-dinitrophenylhydrazone crystallized from benzene–methanol as red plates, m.p. 262–263°.

Anal. Calcd. for $C_{24}H_{26}N_4O_4$: N, 12.90. Found: N, 13.25.

***cis*- and *trans*-2-α-Naphthylcyclohexaneacetic Acids (V).**—A mixture of 3 g. of lactone II, 15 g. of amalgamated zinc, 10 ml. of toluene, 20 ml. of concd. hydrochloric acid and 10 ml. of water was refluxed gently for 72 hr. with the addition of 5 g. of amalgamated zinc and 10 ml. of concd. hydrochloric acid every 12 hr. The reaction mixture was diluted with water and extracted with ether. The ether solution was washed with water and the acidic matter was extracted with 5% sodium carbonate solution. Acidification of the alkaline solution afforded 2.7 g. (90%) of an acid mixture which slowly solidified. It crystallized from benzene–hexane as colorless needles, m.p. 125–130°.

Repeated crystallization of this mixture from methanol or hexane resulted in large losses without appreciable separation of the isomers. However, the separation was achieved by taking advantage of the low water-solubility of the sodium salt of the *trans*-acid. The acidic mixture was dissolved in hot sodium carbonate solution and the sodium salt that separated on cooling was crystallized from water. Acidification of an aqueous suspension of this precipitated salt afforded a solid acid that crystallized from aqueous methanol to give 1.6 g. (53%) of ***trans*-2-α-naphthylcyclohexaneacetic acid** (V) as long colorless needles, m.p. 150–152°. The analytical sample crystallized from methanol as needles, m.p. 158–160°. Its ultraviolet absorption spectrum ($\lambda_{max.}$ (log ε): 225 mμ (4.94), 273 (3.81), 282 (3.90) and 313 (2.65)) was very similar to that of α-methylnaphthalene.[17b]

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.95; H, 7.32.

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[11] R. N. Jones, THIS JOURNAL, **67**, 2127 (1945). It is highly significant that the same effect is observed in the spectrum of the next higher homolog, 6,7-trimethylenebenzo[c]phenanthrene, and that the "α/β" ratio is the same (1.33) for both hydrocarbons (E. Clar and D. G. Stewart, *ibid.*, **74**, 6235 (1952)).

[12] G. M. Badger and I. S. Walker, *J. Chem. Soc.*, 3238 (1954).

[13] F. H. Herbstein and G. M. J. Schmidt, *ibid.*, 3302 (1954); M. S. Newman and W. B. Wheatley, THIS JOURNAL, **70**, 1913 (1948).

[14] W. Dirschel and F. Hanusch, *Z. physiol. Chem.*, **233**, 13 (1935); R. N. Jones, *Chem. Revs.*, **32**, 29 (1943).

[15] Melting points and boiling points are both uncorrected. Infrared absorption spectra were measured on a Perkin–Elmer model 21B spectrophotometer. Ultraviolet absorption spectra were measured with a Beckman model DK automatic recording spectrophotometer in 95% alcohol as solvent. Analyses are by Schwarzkopf Labs., Woodside 77, N. Y.

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

[17] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Hydrocarbons," John Wiley and Sons, Inc., New York, N. Y., 1951; (a) chart no. 11, (b) chart no. 196.

The mother liquor that remained after separation of the insoluble sodium salt was acidified to give 1 g. of semi-solid acid which was dissolved in benzene. The solution slowly deposited 0.2 g. of the *cis*-acid as colorless plates, m.p. 190–195°. Two crystallizations from benzene–methanol afforded pure ***cis*-2-α-naphthylcyclohexaneacetic acid** (*cis*-V) as colorless plates, m.p. 219–220°. Its ultraviolet absorption spectrum was essentially superimposable on that of the *trans* isomer.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.60; H, 7.46. Found: C, 80.13; H, 7.40.

The benzene mother liquors, after separation of the *cis*-acid, m.p. 190–195°, were diluted with hexane. The solution slowly deposited 0.5 g. of colorless needles, m.p. 130–135°, evidently a mixture of the isomeric acids V.

***trans*-6-Keto-1,2,3,4,4a,5,6,13a-octahydrobenzo[c]phenanthrene** (I).—To 30 ml. of anhydrous hydrogen fluoride contained in a polyethylene bottle and immersed in an ice-bath was added 2.01 g. (0.0075 mole) of *trans*-acid V, m.p. 150–152°. The dark red solution was kept at 0° for 10 min. and then was poured onto 200 g. of crushed ice. The organic material was extracted with ether and the ether solution was washed several times with water and then with sodium carbonate solution. Removal of the solvent left 1.85 g. (98%) of solid ketonic material which was dissolved in benzene. After the removal of 0.3 g. of a ketonic by-product of unknown structure, the mother liquor was concentrated and diluted with hexane. The solution slowly deposited 1.45 g. of impure I, m.p. 140–145°. Vacuum sublimation followed by crystallization from benzene–methanol afforded 1.12 g. (60%) of ***trans*-6-keto-1,2,3,4,4a,5,6,13a-octahydrobenzo[c]phenanthrene** (I) as rectangular plates, m.p. 154–155°, λ_{max} 5.95 μ. The m.p. was undepressed on admixture with the ketone obtained from the reaction between *trans*-2-hydroxycyclohexaneacetic acid lactone and naphthalene.

The 2,4-dinitrophenylhydrazone crystallized from benzene as red needles, m.p. 272–273°, lit.[6] m.p. 186–188° (see Discussion).

***trans*-1,2,3,4,4a,5,6,13a-Octahydrobenzo[c]phenanthrene.**—Fifty milligrams of ketone I was refluxed gently for 2 hr. with 1 ml. of hydrazine hydrate solution and 5 ml. of ethylene glycol. To the cooled reaction mixture was added 0.5 g. of solid potassium hydroxide and the solution was slowly heated to a bath temperature of 220° at which it was maintained for 4 hr. The usual workup followed by chromatography on alumina afforded 40 mg. (85%) of the hydrocarbon which crystallized from methanol in colorless silky needles, m.p. 109–110°, lit.[6] m.p. 47° (see Discussion).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.52; H, 8.48. Found: C, 91.34; H, 8.72.

The dehydrogenation of 20 mg. of this hydrocarbon by heating for 1 hr. at 300–320° with 10 mg. of 10% palladium-on-charcoal catalyst gave 10 mg. of **benzo[c]phenanthrene** (XIV), m.p. 65–66°, identified by mixed m.p. comparison with an authentic sample.

Ethyl *trans*-1,2,3,4,4a,5,6,13a-Octahydro-6-benzo[c]-phenanthrylidene Acetate (VI, R = C_2H_5).—A mixture of 1.25 g. (0.005 mole) of ketone I, 25 ml. of dry benzene, 25 ml. of dry ether, 0.6 g. of 20 mesh zinc, 1 ml. of ethyl bromoacetate and a crystal of iodine was heated under reflux with stirring for 8 hr. After one hour a pale yellow complex separated from solution and after 4 hr. 0.5 g. of zinc and 9.5 ml. of ethyl bromoacetate were added.

The reaction mixture was hydrolyzed by dilute hydrochloric acid and the organic layer was washed with water and dried over sodium sulfate. Removal of the solvent left a viscous oil which was dehydrated by heating for 10 min. with 5 ml. of anhydrous formic acid. The semi-solid mass after removal of the formic acid was dissolved in benzene and passed through an alumina column. Concentration of the benzene eluents afforded 1.55 g. (97%) of the unsaturated ester VI (R = C_2H_5) as colorless needles, m.p. 125–126°. Recrystallization from benzene–hexane provided an analytical sample as soft, silky needles, m.p. 128°. Its ultraviolet absorption spectrum (λ_{max} (log ε): 221 mμ (4.33), 274 (4.52) and 312 (4.30)) was in agreement with the assigned structure.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.50; H, 7.50. Found: C, 82.39; H, 7.48.

Saponification of a part of the material afforded a quantitative yield of ***trans*-1,2,3,4,4a,5,6,13a-octahydro-6-benzo[c]phenanthrylideneacetic acid** (VI, R = H) which crystallized from absolute ethanol as colorless plates, m.p. 242° dec. The ultraviolet (λ_{max} (log ε): 221 mμ (4.32), 265 (4.55) and 310 mμ (4.29)) and infrared (λ_{max} 5.93 μ) absorption spectra were in agreement with its formulation as an α,β-unsaturated acid.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.80. Found: C, 82.23; H, 6.73.

1,2,3,4,4a,5,6,13a-Octahydrobenzo[c]phenanthrene-6-acetic Acid (VII).—A solution of 1.28 g. of the unsaturated ester VI, (R = C_2H_5), m.p. 125–126°, in 25 ml. of absolute ethanol was reduced at atmospheric pressure in the presence of 0.2 g. of 10% palladium-on-charcoal catalyst. The absorption of hydrogen was very rapid and about 90% of the theoretical amount was taken up in 1 hr.

After 3 hr. at room temperature, the solution was filtered and the viscous oil that remained after removal of the solvent was saponified by heating with methanolic potassium hydroxide. Removal of the alcohol under reduced pressure followed by dilution with water and acidification of the alkaline solution afforded 0.95 g. (81%) of colorless granules which were dissolved in benzene. The solution slowly deposited 0.3 g. (26%) of acid, m.p. 205–208°. Recrystallization from methanol afforded one of the stereoisomeric forms of **1,2,3,4,4a,5,6,13a-octahydrobenzo[c]phenanthrene-6-acetic acid** (VII) as colorless needles, m.p. 216–217°; λ_{max} (log ε): 232 mμ (4.87), 283 (3.68), and 323 (2.46); 5.86 μ.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.49. Found: C, 81.45; H, 7.53.

The benzene filtrate from the separation of the acid, m.p. 205–208°, was diluted with hexane. The solution deposited 0.5 g. (43%) of stout prisms, m.p. 159–160°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.49. Found: C, 82.05; H, 7.54.

In view of the subsequent experiments with this material, it appears to be a mixture of the stereoisomeric forms of VII, although the m.p. was unchanged on repeated crystallization.

1-Keto-4,5-tetramethylene-6,7-benzo-2a,3,4,5-tetrahydroacenaphthene (VIII).—The cyclization of 0.25 g. of the acid VII, m.p. 205–208°, was accomplished by treating with 10 ml. of anhydrous hydrogen fluoride at 0°. After 10 min. at ice temperature the dark red solution was poured onto 100 g. of crushed ice. The usual workup gave 0.24 g. of neutral material which was taken up in benzene and passed through an alumina column. Concentration of the benzene eluents afforded 0.21 g. (90%) of one of the isomeric forms of **1-keto-4,5-tetramethylene-6,7-benzo-2a,3,4,5-tetrahydroacenaphthene** (VIII) as colorless needles, m.p. 160–162°. Recrystallization from benzene–methanol afforded an analytical sample, m.p. 164–165°. It showed the characteristic infrared absorption of a conjugated 5-membered ring ketone at 5.85 μ. The ultraviolet absorption spectrum showed λ_{max} (log ε): 218 mμ (4.37), 252 (4.73), 297 (3.91), 308 (3.97) and 355 (3.44).

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.95; H, 7.24. Found: C, 86.73; H, 7.07.

The 2,4-dinitrophenylhydrazone crystallized from benzene as red plates, m.p. 255–256° dec.

Anal. Calcd. for $C_{26}H_{24}O_4N_4$: C, 68.42; H, 5.26; N, 12.28. Found: C, 68.40; H, 5.51; N, 12.41.

The cyclization of 0.7 g. of acid VII, m.p. 159–160°, with 10 ml. of anhydrous hydrogen fluoride as described above gave 0.5 g. (75%) of a mixture of the isomeric ketones VIII as colorless needles, m.p. 125–130°. Recrystallization of this material from hexane and finally from methanol afforded 0.15 g. of the other isomer of VIII as soft needles, m.p. 165–166°. The mixed m.p. with the 164–165° isomer (see above) was 140–145°. An analytical sample obtained by vacuum sublimation followed by crystallization from methanol had m.p. 168–169°, λ_{max} 5.85 μ.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.95; H, 7.24. Found: C, 87.35; H, 7.47.

The 2,4-dinitrophenylhydrazone crystallized from pyridine as red plates, m.p. 270–271°.

Anal. Calcd. for $C_{26}H_{24}O_4N_4$: N, 12.28. Found: N, 12.03.

The combined mother liquors, after separation of the 165–166° isomer of VIII, were concentrated to give 0.3 g.

of solid, m.p. 128–132°, evidently a mixture of the two stereoisomers (VIII).

1,2,3,4,4a,5,6,13a-Octahydro-6,7-acebenzo[c]phenanthrene (IX).—A mixture of 0.14 g. of ketone VIII, m.p. 164–165°, 1 ml. of 85% hydrazine hydrate and 5 ml. of ethylene glycol was refluxed gently for 3 hr. at 140–150°. After cooling, 0.5 g. of solid potassium hydroxide was added and the mixture was heated slowly to a bath temperature of 220°. The mixture was refluxed gently at that temperature for 2 hr. and the hydrocarbon was codistilled with three 10-ml. portions of ethylene glycol. The distillate was diluted with water and extracted with ether. The ether solution was washed with water and dried over sodium sulfate. Removal of the solvent left a colorless solid which crystallized from methanol to give 0.11 g. (83%) of one of the isomeric forms of **1,2,3,4,4a,5,6,13a-octahydro-6,7-acebenzo[c]phenanthrene (IX)** as colorless needles, m.p. 127–128°. The ultraviolet absorption spectrum of this hydrocarbon (λ_{max} (log ϵ): 232 mμ (4.95), 274 (3.71), 284 (3.77), 294 (3.65), 307 (2.99), 317 (2.66) and 321 (2.79)) was very similar to that of a substituted naphthalene.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.48; H, 8.62.

The reduction of 0.3 g. of a mixture of the isomeric ketones (VIII), m.p. 125–130°, was carried out by the Huang-Minlon method as described above. Distillation of the hydrocarbon with three 10-ml. portions of ethylene glycol afforded 0.1 g. of the hydrocarbon which crystallized from methanol as soft, feathery needles, m.p. 123–125°, identical with the hydrocarbon, m.p. 127–128°, obtained by reduction of the 164–165° isomer of VIII.

The non-volatile material from the Wolff–Kishner reduction was diluted with water and extracted with ether. The solid that remained after removal of the solvent was chromatographed on neutral alumina and eluted with hexane. Concentration of the hexane eluents yielded 0.1 g. (raising the total yield of hydrocarbon to 0.2 g. (70%)) of colorless granules, m.p. 98–100°. Two crystallizations from methanol afforded the other isomer of IX as clusters of short needles, m.p. 109–110°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.25; H, 8.61.

6,7-Acebenzo[c]phenanthrene (XI).—An intimate mixture of 0.1 g. of hydrocarbon IX, m.p. 127–128°, and 25 mg. of 10% palladium-on-charcoal catalyst was heated for 0.5 hr. at 300–310°. The hydrocarbon that sublimed into the air condenser was returned to the reaction tube and heating was continued for an additional 0.5 hr.

After cooling, the mass was dissolved in benzene and chromatographed on neutral alumina. Elution with hexane gave 10 mg. of unreacted hydrocarbon IX. Elution with 25% benzene in hexane afforded 10 mg. of 6,7-acebenzo[c]phenanthrene (XI) as a pale yellow, fluorescent solid which crystallized from methanol as microcrystalline needles with a faint yellow cast, m.p. 115–118°. Except for a small amount of fluorescent tarry material, no other products could be eluted with benzene.

For purification, the hydrocarbon XI was converted to the **2,4,7-trinitrofluorenone complex**, reddish needles from benzene–methanol, m.p. 192–193°. The analysis indicated that the ratio in this complex was not a simple one but agreed most closely with a ratio of 1.33:1 for XI and the reagent, respectively.

Anal. Calcd. for $4/3(C_{20}H_{14})\cdot C_{13}H_5N_3O_7$: C, 72.78; H, 3.65. Found: C, 72.42; H, 3.79.

The hydrocarbon XI was regenerated from the trinitrofluorenone complex by passing a benzene solution through an alumina column and crystallized from methanol as colorless needles, m.p. 125–126°.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.48; H, 5.52. Found: C, 94.35; H, 5.70.

The *sym*-trinitrobenzene complex crystallized from benzene–methanol as red needles, m.p. 184–185°.

Anal. Calcd. for $C_{26}H_{17}N_3O_6$: C, 66.81; H, 3.64. Found: C, 66.56; H, 3.83.

The ultraviolet absorption spectrum of the hydrocarbon XI (Fig. 1) showed the following maxima (log ϵ in parentheses): 230 mμ (4.18), 274 (4.63), 284 (4.79), 295 (4.10), 302 (4.03), 316 (3.97), 327 (3.58), 342 (3.10), 359 (3.37), 378 (3.48) and 399 (2.90).

The yield of hydrocarbon XI could not be improved by changing the reaction conditions. Essentially no product could be isolated by dehydrogenation of IX at higher temperatures for a shorter period or at lower temperatures for a longer period of time. Similar results were obtained from the dehydrogenation of the mixture of hydrocarbons IX obtained from ketone I without extensive purification of intermediates although the yields of XI were somewhat lower. Moreover, from the later fractions on the chromatogram there was isolated a small amount (2%) of **3,4-benzpyrene (XIII)**, m.p. 170–172°, identified by mixed m.p. with an authentic specimen.

An attempt was made to prepare the hydrocarbon XI from the corresponding alcohol X by the method successfully employed in the synthesis of cholanthrene.[18] Lithium aluminum hydride reduction of VIII, m.p. 166–165°, afforded a 60% yield of **1-hydroxy-6,7-benzo-4,5-tetramethylene-2a,3,4,5-tetrahydroacenaphthene (X)** as silky needles from hexane, m.p. 160–161°.

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

The alcohol was dehydrated by sublimation at 0.1 mm. and the sublimate was dehydrogenated by heating for 1 hr. to 300–310° with 10% palladium-on-charcoal catalyst. Complete destruction of the molecule occurred, however, and no hydrocarbons could be isolated from the reaction.

ITHACA, NEW YORK

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[18] W. E. Bachmann and M. Carmack, THIS JOURNAL, **63**, 1686 (1941).