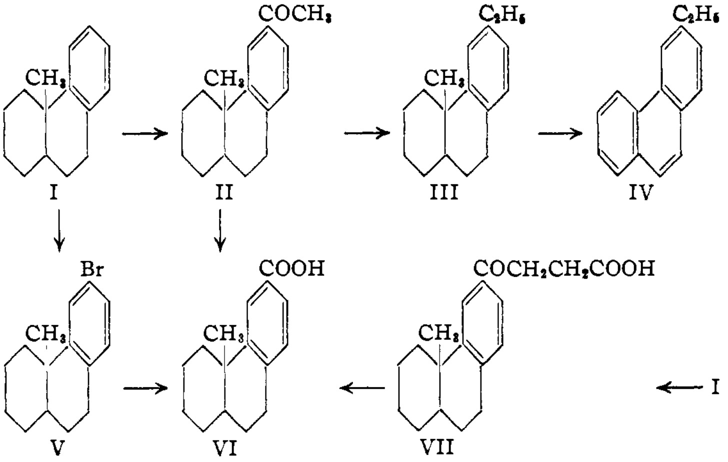
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Synthesis of Phenanthrenes. II. Substitution Reaction of 4a-Methyl-1,2,3,4,4a,9,10-10a-octahydrophenanthrene

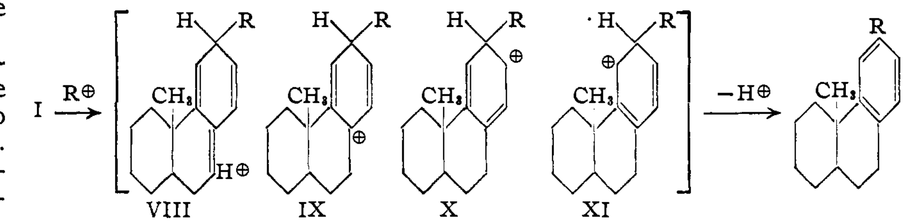
BY RODERICK A. BARNES AND ROY T. GOTTESMAN[1]

4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene has been prepared and its substitution reactions investigated. The bromination and Friedel–Crafts reactions have been found to take place almost exclusively at the 6-position. Furthermore only a single one of the two possible stereoisomers was isolated in each case. This observation together with a study of the oxidation product, 4a-methyl-9-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene, leads to the conclusion that the cyclization used to prepare this hydrocarbon was highly stereospecific.

Both the Bardhan–Sengupta[2] and Bogert–Cook[3] methods have been used to prepare a liquid substance believed to be 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (I). It has also been reported[3,4] that a closely related hydrocarbon, *as*-octahydrophenanthrene, prepared by the Bogert–Cook procedure, is really a mixture containing both *cis* and *trans* isomers and a spirane. The present work was initiated with the hope that some substitution reactions might furnish solid products which would indicate the exact nature of hydrocarbon I as prepared by the Bogert–Cook procedure.



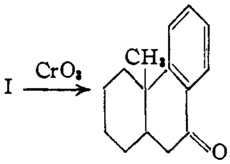
The Friedel–Crafts reaction using acetyl chloride introduced an acetyl group into the 6-position of I. This was proved by converting the ketone 4a-methyl-6-acetyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (II) to 3-ethylphenanthrene (IV). The structure of bromination product V was established by replacing the bromine atom by a carboxyl group to yield acid VI which was identical with the product obtained when II was subjected to the haloform reaction. The structure of ketoacid VII obtained from a Friedel–Crafts reaction with succinic anhydride was also proved by converting it to VI.



By analogy with tetralin[5] it might be predicted that hydrocarbon I would undergo substitution reactions predominately at the 6- and/or 7-position. An explanation for the observation that these reactions go exclusively to the 6-position may lie in the fact that structure VIII makes an appreciable contribution to the transition state for the substitution at this position. This would lower the energy of the transition state as compared with that for substitution at the 7-position where only structures analogous to IX, X and XI could contribute (the quaternary carbon eliminates the possibility of a structure analogous to VIII for this position).

The fact that the solid products obtained (VI, VII and carbonyl derivatives of II) were readily crystallized and had melting point ranges typical of homogeneous solids indicates that I also was a homogeneous substance rather than a mixture of *cis* and *trans* isomers. Further evidence for this view was obtained by oxidizing I with chromic acid to yield 4a-methyl-9-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XII). The 2,4-dinitrophenylhydrazone (XIIIa) and semicarbazone (XIVa) of XII like other crystalline substances prepared from hydrocarbon I were homogeneous.

A mixture of both isomers of XII had been synthesized by Newman and Farbman[6] and a semicarbazone (XIVb) prepared and recrystallized several times in an attempt to obtain a pure isomer.



XII

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[1] Abstracted from a thesis submitted by Roy Tully Gottesman to the Graduate Faculty for the Ph.D. degree, August, 1951.

[2] G. A. R. Kon, *J. Chem. Soc.*, 1081 (1933).

[3] D. Perlman, D. Davidson and M. T. Bogert, *J. Org. Chem.*, **1**, 288 (1936).

[4] J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944).

[5] Tetralin reacts almost exclusively at the 6- or 7-position in the Friedel–Crafts reaction: C. L. Hewett, *ibid.*, 293 (1940); R. T. Arnold and R. A. Barnes, THIS JOURNAL, **66**, 960 (1944). However, R. T. Arnold and R. A. Barnes, *ibid.*, **65**, 2393 (1943), have found that the chloromethylation of tetralin takes place to a considerable extent at the 5-position.

[6] M. S. Newman and M. D. Farbman, *ibid.*, **66**, 1550 (1944).

A mixture of XIVa and XIVb[7] melted somewhat lower than either substance alone.

A sample of ketone[7] containing both isomers was treated with 2,4-dinitrophenylhydrazine. Fractional crystallization of the product was not effective in separating the isomers. Chromatography on alumina produced fractions which were essentially pure XIIIa and XIIIb. The identity of XIIIa from the chromatography and directly from our sample of XII was definitely established by examining the X-ray powder photographs. This diagram was quite different from that of XIIIb. By comparing the X-ray powder diagram of the 2,4-dinitrophenylhydrazone of the mixture with the pure isomers, it is estimated that the ketone[7] contained about 30% of XII identical with that prepared in this work and 70% of its isomer. This constitutes the first completely unambiguous proof that I is not a spirane.[8]

We believe that conversion of I by a two-step process to pure XIIIa (free from XIIIb) was effected only by virtue of the fact that I itself was a pure isomer. This indicates that the cyclization reaction leading to I was highly stereospecific.[9] It is difficult to suggest a mechanism to explain this observation until it has been decided whether I is the *cis* or the *trans* isomer.[10]

Experimental[11]

4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (I).—A Grignard reagent was prepared from β-phenylethyl bromide (411.4 g., 2.23 moles) and treated with 2-methylcyclohexanone (249.3 g., 2.22 moles) according to the procedure of Perlman, Davidson and Bogert.[3] There was obtained 278.7 g. (57.4%) of 1-β-phenylethyl-2-methylcyclohexanol which boiled at 149–150.5° (5 mm.), $n^{24}\text{D}$ 1.5290. The cyclization of this alcohol was carried out as previously described[3] using 85% sulfuric acid (575 ml.). There was obtained 218.9 g. (85.5%) of hydrocarbon which boiled at 139–141° (9.5 mm.), $n^{20}\text{D}$ 1.5519.

This product was distilled through a 36-inch Todd fractionating column packed with glass helices. Eighteen fractions were collected and their refractive indices determined. The main product, pure I, comprised 71% of the distillate, b.p. 116–118° (1 mm.), $n^{25}\text{D}$ 1.5500 ± 0.0002, $\lambda_{\max}^{95\%\text{ alc}}$ 257 mμ (ε, 600). A forerun amounting to 7% of the distillate boiled at 114° (1 mm.), $n^{25}\text{D}$ 1.5488 ± 0.0002, $\lambda_{\max}^{95\%\text{ alc.}}$ 253 mμ (ε 1480). This substance was almost certainly the olefin obtained by dehydration rather than cyclization of 1-β-phenylethyl-2-methylcyclohexanol since permanganate oxidation converted it to benzoic acid.

4a-Methyl-6-acetyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (II).—To an ice-cooled mixture of powdered anhydrous aluminum chloride (16.7 g., 0.125 mole) in carbon disulfide (140 ml.) a solution of (I) (20 g., 0.1 mole) and acetyl chloride (8.7 g., 0.11 mole) in carbon disulfide (70 ml.) was added dropwise. The reaction mixture was stirred for 3.5 hours in the cold and then was allowed to stand at room temperature for four hours.

The carbon disulfide was distilled from the reaction mixture and ice-cold water added to the cooled residue. The yellow oil which separated was extracted with ether and washed with two portions of 5% sodium hydroxide solution. The ether extract was dried over anhydrous sodium sulfate. Following the removal of the ether, the product was distilled *in vacuo*. Redistillation gave 13.7 g. (56.6%) of product, b.p. 146–150° (0.63 mm.), $n^{25}\text{D}$ 1.5625.

Anal. Calcd. for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.32; H, 9.17.

The semicarbazone melted at 179–182° after recrystallization from dilute ethanol.

Anal. Calcd. for $C_{18}H_{25}N_3O$: C, 72.21; H, 8.42. Found: C, 72.27; H, 8.48.

The 2,4-dinitrophenylhydrazone melted at 205–207° after recrystallization from ethanol–ethyl acetate.

Anal. Calcd. for $C_{23}H_{26}N_4O_4$: C, 65.38; H, 6.20. Found: C, 65.42; H, 6.20.

4a-Methyl-6-bromo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (V).[12]—Hydrocarbon I (10 g., 0.05 mole) was dissolved in carbon tetrachloride (50 ml.) and a few grains of iron powder and one crystal of iodine were added. A solution of bromine (8 g., 0.05 mole) in carbon tetrachloride (20 ml.) was added while the temperature was maintained at 10°. The mixture was stirred until the color of bromine disappeared and then was allowed to stand overnight.

The mixture, after being washed with water and a saturated solution of sodium bicarbonate, was dried over anhydrous sodium sulfate. After removal of the solvent, the product was vacuum distilled. The main fraction of 10.0 g. (71.8%) boiled at 120–124° (0.25 mm.). A sample with b.p. 122° (0.25 mm.), $n^{23}\text{D}$ 1.5832 was submitted for analysis.

Anal. Calcd. for $C_{15}H_{19}Br$: C, 64.50; H, 6.86; Br, 28.64. Found: C, 64.96; H, 6.72; Br, 28.51.

β-6-(4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthroyl)-propionic Acid (VII).—To a mixture of powdered anhydrous aluminum chloride (13.4 g., 0.1 mole), and succinic anhydride (5.5 g., 0.055 mole) in nitrobenzene (30 ml.) cooled in an ice–salt-bath, there was added, over a period of one hour, a solution of I (10 g., 0.05 mole) in nitrobenzene (20 ml.). The dark reddish-brown mixture was stirred at 0–8° for 10 hours. It was then poured onto a mixture of ice and hydrochloric acid and was ether extracted. The organic layer was washed with 100 ml. of 6 *N* hydrochloric acid and then was shaken with 5% sodium hydroxide solution. The brown alkali extracts were washed with ether and acidified to *p*H 2. The oily yellow acid was ether extracted.

After removal of the solvent, the product was distilled *in vacuo*, b.p. 229–231.5° (0.45 mm.). There was obtained 7.3 g. (48.6%) of crude acid. This was decolorized with activated charcoal in benzene solution and then recrystallized from aqueous acetic acid. The product was obtained as white needle-like rods, m.p. 124.5–126°.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.78; H, 8.09.

4a-Methyl-6-carboxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VI). A. Haloform Reaction on II.—Ketone II (2.0 g.) was treated with iodine in alkaline solution.[13] From the alkaline solution 0.3 g. (15%) of a solid acid was isolated. After recrystallization from aqueous acetic acid it melted at 182–184° with sublimation noted at *ca.* 175°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.78; H, 8.75.

B. **Grignard Reaction** on V.—A solution of V (1.0151 g.) dissolved in anhydrous ether (2.0 ml.) was added to magnesium turnings (0.088 g.). When the reaction did not start easily, 2 drops of ethyl bromide were added to initiate the reaction. The Grignard reagent was added rapidly to a stirred slurry of Dry Ice (10 g.) in ether (10 ml.).[14] The

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[7] We wish to thank Prof. M. S. Newman of The Ohio State University for a sample of this semicarbazone and a generous quantity of the ketone from which it was prepared.

[8] The formation of phenanthrene by dehydrogenation of I has been interpreted as evidence for the structure assigned; ref. 2. The observation that spiranes rearrange to aromatic compounds under dehydrogenation conditions renders this evidence of questionable value as an absolute proof of structure; J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 365 (1934); G. R. Clemo and J. Ormston, *ibid.*, 325 (1933); M. Levitz, D. Perlman and M. T. Bogert, *J. Org. Chem.*, **6**, 105 (1941).

[9] On the basis of a planar carbonium ion intermediate in the cyclization a mixture of *cis* and *trans* forms would be expected.

[10] J. W. Cook, N. A. McGinnis and S. Mitchell, ref. 4, present evidence indicating that *cis-as*-octahydrophenanthrene is formed first and subsequently partly rearranged by aluminum chloride to the *trans* isomer.

[11] All melting points reported were determined on the Kofler hot-stage apparatus. Microanalyses were by W. Manser, Zurich, Switzerland.

[12] The authors wish to thank Doris E. Barnes for performing this experiment.

[13] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 138.

[14] A. S. Hussey, THIS JOURNAL, **73**, 1364 (1951).

TABLE I

v., very; s., strong; d., diffuse; m., medium; f., faint; w., weak

Line	Compound XIIIa			Line	Compound XIIIb		Inten-	Line	Mixture		
no.	θ	d/n, Å.	Intensity	no.	θ	d/n, Å.	sity	no.	θ	d/n, Å.	Intensity
1	2°53′	15.30	v.s.	1	3°41′	11.97	v.s.	1	2°55′	15.12	m.
2	5°43′	7.73	v.s.	2	4°43′	9.36	s.	2	3°43′	11.88	v.s.
3	6°37′	6.68	v.s.d.	3	5°44′	7.70	v.f.	3	4°37′	9.57	s.
4	7°12′	6.14	v.s.	4	7°02′	6.28	f.	4	5°42′	7.75	v.s.
5	8°43′	5.08	m.	5	7°52′	5.62	s.	5	6°37′	6.68	w.d.
6	9°26′	4.70	s.	6	8°19′	5,32	s.	6	7°49′	5.66	v.s.
7	10°04′	4.40	s.d.	7	9°04′	4.88	w.	7	8°53′	4.98	w.
8	11°01′	4.03	s.	8	9°31′	4.65	s.	8	9°25′	4.70	s.
9	11°41′	3.80	m.	9	9°54′	4.48	m.	9	10°32′	4.21	m.
10	13°01′	3.24	v.s.d.	10	10°35′	4.19	v.s.	10	10°59′	4.05	s.

acidified mixture was extracted with ammonia. Acidification of the ammoniacal extract followed by overnight cooling in the refrigerator gave 0.0296 g. of acid. After recrystallization from aqueous acetic acid this acid melted at 183–185°. A mixed melting point determination with a sample prepared by Method A showed no depression.

C. From VII.—Acid VII (0.6 g.) was dissolved in chloroform (3 ml.) and bromine (0.10 ml.) was added. The crude brominated product remaining after removal of the chloroform was heated at 100° with sodium acetate (0.5 g.) and acetic acid (1.0 ml.) for two hours. The reaction mixture was diluted with water and extracted with ether to yield, after distillation of the ether, a yellow glassy solid. This material was dissolved in aqueous acetone and oxidized with potassium permanganate solution (0.5 g. in 12 ml. of water). By processing the reaction mixture an acid of melting point 183–185.5° was obtained which proved to be identical with the sample obtained in part A.

4a-Methyl-6-ethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (III).—A mixture of granulated zinc (8 g.), water (12 ml.), concentrated hydrochloric acid (4 ml.) and mercuric chloride (0.8 g.) was shaken for 10 minutes. The solution was decanted and glacial acetic acid (10 ml.), toluene (8 ml.), ketone (II) (3 g.) and concentrated hydrochloric acid (14 ml.) were added. The mixture was refluxed for 24 hours during which time two 5-ml. portions of concentrated hydrochloric acid were added.

The toluene layer was separated and washed with water. The combined aqueous layers were washed with ether. Following the removal of the ether and toluene, the product was distilled *in vacuo* giving 2.04 g. (72.2%) of a clear colorless liquid, b.p. 101.5–104.5° (0.22 mm.), $n^{25}D$ 1.5474.

When water was used rather than acetic acid as a solvent in this reduction, a yield of only 32.8% of (III) was obtained even though the period of refluxing was 72 hours.

A sample of III was purified by dissolving it in petroleum ether and allowing the solution to stand over sodium for two days so as to remove any oxygen containing compounds. The solution (now brown in color) was filtered, the solvent evaporated and the residue distilled.

Anal. Calcd. for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.23; H, 10.44.

3-Ethylphenanthrene.—The dehydrogenation of III was carried out in an apparatus similar to that described by Linstead and co-workers.[15] A mixture of III (1.1097 g.) and 5% palladium-on-charcoal catalyst (0.222 g.) was heated at 300–320° for 12 hours. At the end of this time no further evolution of gas occurred. The mixture was extracted with ether and the catalyst removed by filtration. The ether was removed on a steam-bath under a stream of air leaving 0.9341 g. (92.3%) of a yellow liquid.[16] The product gave a blue fluorescence under ultraviolet light and could not be induced to crystallize upon cooling.

Oxidation of this liquid (0.3 g.) with chromium trioxide (0.66 g.) in glacial acetic acid (2.7 ml.) gave 0.08 g. of an orange solid, **3-ethyl-9,10-phenanthrenequinone.** After three recrystallizations from ethyl alcohol, the orange needles melted at 168–170°.[17] The quinone gave a green color in sulfuric acid which disappeared on dilution, as reported.[17]

4a-Methyl-9-keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XII).—A solution of chromium trioxide (11.5 g.) in 80% acetic acid (21.5 ml.) was added dropwise to an ice-cold solution of I (10 g.) in glacial acetic acid (95 ml.). The mixture was stirred for 10 hours in an ice-bath and then allowed to stand at room temperature for three days.

The reaction mixture was poured into 1200 ml. of water and was extracted with 400 ml. of ether and 200 ml. of benzene. The combined organic layers were washed and dried over anhydrous magnesium sulfate. Following the removal of the solvents, the product was distilled *in vacuo*. There was obtained 5.7 g. (53.3%) of material, b.p. 121–138° (0.55 mm.). Fractionation of the product gave purified ketone, b.p. 119–122° (0.64 mm.), $n^{25}D$ 1.5669.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.81; H, 8.31.

The semicarbazone (XIVa) prepared in the usual manner and recrystallized from ethanol melted at 199–200° with decomposition when the hot stage was heated rapidly and at 196–199.5° with decomposition when the rate of heating was 2 degrees per minute.

Anal. Calcd. for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80. Found: C, 70.76; H, 7.84.

A mixture of a sample of the semicarbazone (XIVb) of Newman and Farbman[7] which melted between 195–200° with a decomposition when heated at the rate of 2 degrees per minute with a sample of XIVa melted at 191–197.5°.

The 2,4-dinitrophenylhydrazone (XIIIa) recrystallized three times from ethyl alcohol–ethyl acetate as orange prisms and had a m.p. 182.5–184°.

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.93; H, 5.62. Found: C, 63.98; H, 5.61.

The 2,4-dinitrophenylhydrazone prepared from the ketone of Newman and Farbman[7] recrystallized three times from ethyl alcohol–ethyl acetate melted over the range from 166–184°. The melting point of a mixture of the two samples was 160.5–180°.

Separation of XIIIa and XIIIb.—A sample (102.5 mg.) of the 2,4-dinitrophenylhydrazone, m.p. 166–184°, described in the previous experiment was chromatographed using a 25-cm. column of 80–200 mesh acid washed alumina (15 g.). The sample was introduced in benzene solution and the chromatogram developed with a 45% solution of benzene in petroleum ether. Thirty-four fractions were collected by elution with this solvent mixture. Fractions 9, 10, 11, 12 and 13 (24.6 mg.) were combined and rechromatographed using 10 g. of alumina. The product so obtained gave an X-ray diffraction pattern identical with XIIIa. Fractions 31, 32, 33 and 34 (11.8 mg.) were combined and recrystallized, m.p. 186–190°. The X-ray diffraction pattern of this substance was quite different from XIIIa; this indicated that fractions 31–34 were fairly pure XIIIb. From the intensity of the lines in the X-ray pattern before chromatographing it is estimated that the original sample contained 30% of XIIIa and 70% of XIIIb.

The X-ray diffraction patterns were determined with a Debye camera (radius 5.71 cm.). The radiation was CuKα (λ 1.539 Å.) at 35 kilovolts and 20 milliamperes and the period of exposure was 10 hours. Table I gives the data for the first ten lines of each substance. The lattice spacings (d/n) calculated by the Bragg equation are estimated to be accurate within 0.2 Å.

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[15] R. P. Linstead, A. F. Millidge, S. L. S. Thomas and A. L. Walpole, *J. Chem. Soc.*, 1146 (1937).

[16] *Cf.* E. Mosettig and J. van de Kamp, THIS JOURNAL, **55**, 3442 (1933); M. T. Bogert and G. S. Stamatoff, *Rec. trav. chim.*, **52**, 584 (1933); R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1012 (1933).

[17] M. T. Bogert and C. S. Stamatoff, ref. 16, report 168.2–169°.