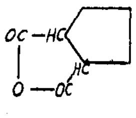
While this work was in progress, Bachmann[2] reported some preliminary experiments on the cyclization of (3-phenanthryl)-propionic acid. The cyclization product was assumed to be 1'-keto-2,3-cyclopentenophenanthrene, the isomeric formula of 1'-keto-3,4-cyclopentenophenanthrene being assumed to be less likely. According to the evidence presented by Hillemann[3] the latter formula should be preferred. It will be interesting to compare our substance (V) with 2,3-dimethylphenanthrene which is available by two independent methods.[4]



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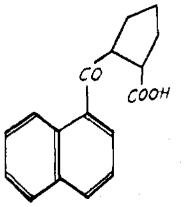

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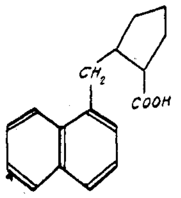

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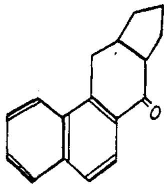

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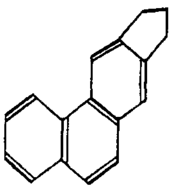

V

Experimental

Cyclopentane-1,2-dicarboxylic acid anhydride (I) was prepared according to Wassermann[5] from the acid with boiling acetic anhydride.

1-(α-Naphthoyl)-cyclopentane-2-carboxylic Acid (II).—The Grignard solution prepared from bromonaphthalene (8.5 cc.) and magnesium (1.4 g.) was added to an ethereal solution of the above anhydride (7.2 g.). The violent interaction produced a white crystalline precipitate, which after three hours of boiling was decomposed with cold dilute sulfuric acid. Most of the keto acid (7.1 g.) separated spontaneously; a second crop (1.25 g.) was extracted from the ethereal layer with soda solution, acidified and triturated with methanol and ether. The keto acid contains water of crystallization. (Found at 80° *in vacuo:* H_2O, 9.1. Calcd. for $C_{17}H_{16}O_3 + 1.5\ H_2O$: H_2O, 9.1). By recrystallization from methyl alcohol, it is obtained in prismatic hexagons, which give perfect analytical figures, but melt at 169–170° after prolonged sintering. We ascribe this fact to spontaneous conversion into the hydroxylactone form. (Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 75.7; H, 6.0.)

1-(α-Naphthyl-methyl)-cyclopentane-2-carboxylic Acid (III).—The keto acid (II) (12 g.) and amalgamated zinc wool (120 g.) were heated with a mixture of concentrated hydrochloric acid and water (1:1), until the metal had completely disappeared, from time to time some more concentrated acid being added. The acid (III) was extracted with ether and crystallized spontaneously, on evaporation of the solvent, yield, 9.2 g. It was triturated with petroleum ether, collected and recrystallized from a small quantity of ethyl acetate to rhombic crystals, m. p. 99–101°. (Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.0; H, 7.2.)

1-Keto-2,3-cyclopentano-1,2,3,4-tetrahydrophenanthrene (IV).—(a) The acid (III) (2 g.) was heated at 115–120° for two hours (oil-bath) with tin chloride (3 cc.) and toluene (4 cc.) and poured out into ice-cold concentrated hydrochloric acid. The toluene solution, additioned with ether, was washed with hydrochloric acid of decreasing concentration, then with soda solution and water. On evaporation of the solvent, the residue crystallized spontaneously. Triturated with methanol, it gave the ketone in a nearly pure condition (0.25 g.). It was recrystallized from propyl alcohol; needles, m. p. 163–164°. (Calcd. for $C_{17}H_{16}O$: C, 86.4; H, 6.8. Found: C, 86.3, 85.7; H, 6.5, 6.5.)

(b) The acid (III) (0.5 g.) in benzene (7.5 cc.) was heated on the water-bath for three hours with phosphoric oxide (3 g.). The mass was decomposed with ice, ether was added and the organic layer extracted with soda solution. On evaporation of the ether and the benzene, the ketone remained in pure, crystalline state (0.05 g.). This method proved to be the most convenient one.

(c) Cyclization with sulfuric acid gave variable results.

2,3-Cyclopentano-1,2,3,4-tetrahydrophenanthrene.—The above ketone (IV) (0.7 g.) was reduced with zinc wool (7 g.) according to the method described above. The hydrocarbon crystallized spontaneously (0.5 g.) and was recrystallized from petroleum ether; broad needles, m. p. 119–121°. (Calcd. for $C_{17}H_{18}$: C, 91.9; H, 8.1. Found: C, 92.0, 92.2; H, 8.2, 8.3.)

2,3-Cyclopentenophenanthrene (V).—The tetrahydro compound (0.5 g.) was heated to 320–340° with selenium (2 g.) for twenty-four hours (sealed tube). The product was extracted with boiling mixture of ether and acetone and the solvent evaporated. The residue was distilled at 0.05 mm., whereupon it crystallized spontaneously; yield 0.38 g. Recrystallization from ethyl alcohol, diluted with some propyl alcohol, gave prismatic plates, m. p. 85–85.5°. (Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.1, 93.0; H, 6.8, 6.8.)

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Synthesis of Methylcholanthrene

BY ERNST BERGMANN AND O. BLUM-BERGMANN

Among the aromatic degradation products of sterols, bile acids and similar substances two are of special interest, since they contain nearly all the carbon atoms of the starting materials: the hydrocarbon $C_{22}H_{20}$ from cholic acid and its

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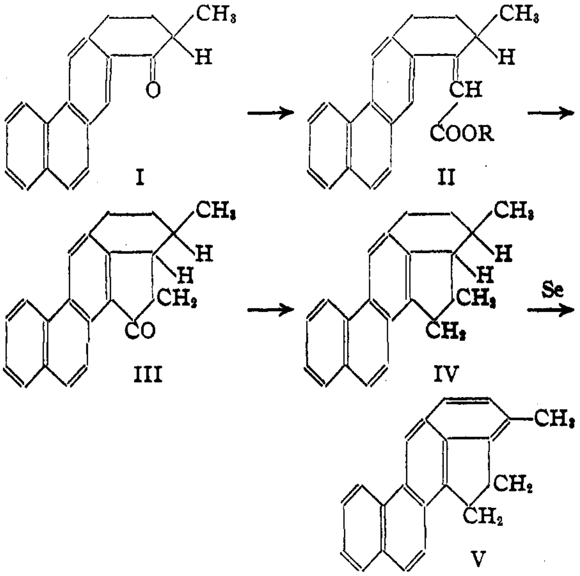
[2] Bachmann, THIS JOURNAL, **57**, 1381 (1935).

[3] Hillemann, *Ber.*, **69**, 2610 (1936).

[4] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934); Fieser and Hershberg, THIS JOURNAL, **57**, 1508 (1935).

[5] Wassermann, *Helv. Chim. Acta*, **13**, 207, 228 (1930); see there for references.

analogs,[1] and the so-called methylcholanthrene, $C_{21}H_{16}$.[2] Their synthesis therefore is of considerable interest. But while four methods are available for the synthesis of cholanthrene,[3] the synthesis of methylcholanthrene has so far been accomplished only by a pyrolytic process.[4] This paper describes a non-pyrolytic synthesis of methylcholanthrene according to the following scheme



Our synthesis applies to the adnexion of the five-membered ring to the benzphenanthrene system, by the Reformatzky reaction. This reaction has proved to be useful in the synthesis of 3'-methyl-1,2-cyclopentenophenanthrene by Bergmann and Hillemann[5] and since then in the preparation of similar substances.[6] The above scheme is self-explanatory; it is the reversal of the degradative formation of the ketone I from methylcholanthrene.[2] The methylcholanthrene obtained in the course of the above synthesis has been identified by analysis and by direct comparison with a sample for which we are indebted to the courtesy of Professor J. W. Cook (London). With regard to the formation of (I) from the corresponding γ-(3-phenanthryl)-isovaleric acid, it may be noted that this cyclization involves the position 2 of the nucleus only and not the position 4, although the latter one is connected with C 3 by a double bond and therefore should be favored. Apparently, this is due to an effect of steric hindrance,[7] which as a matter of fact has not been observed in a similar case reported recently by Hillemann.[8]

Experimental

The synthesis of the ketone (I) was effected according to Cook,[2] but the separation of methyl β-(2-phenanthroyl)- and β-(3-phenanthroyl)-isobutyrates proved a matter of extreme patience and accuracy. The methylsuccinic anhydride, required in the first stage of the synthesis, was not prepared via methylsuccinic acid, but by catalytic hydrogenation of citraconic anhydride, which is easily available today. The hydrogenation was effected in glacial acetic acid with palladized barium sulfate as catalyst, and the anhydride isolated by direct distillation in a vacuum; b. p. 127–129° (16 mm.); yield, quantitative.

(2 - Methyl - 5,6 - benzo - 1,2,3,4 - tetrahydroanthrylidene-1)-acetic Acid (II).—The above ketone (9 g., m. p. 137–138°), methyl bromoacetate (7.8 cc.), zinc-copper-couple (12 g.)[9] and benzene (30 cc.) were heated together until reaction took place. When the spontaneous reaction ceased, the green mass was heated for four and one-half hours, after addition of some more benzene (10 cc.), and decomposed with ice-cold dilute sulfuric acid. The reaction product showed a marked tendency to disproportionate, when heated with 85% formic acid as usual. Therefore the following procedure was adopted.[10]

After decomposition, ether was added and the organic solution extracted with soda. The soda solution was acidified, the precipitated acid dissolved in ether, after evaporation triturated with alcohol and acetone and recrystallized from benzene or ethyl acetate: short bent needles; m. p. 231–233° (slight dec.); yield 0.3 g. Concentrated sulfuric acid gave a violet color reaction. (Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.5, 83.0, 82.9; H, 6.2, 6.6, 5.8.). The neutral residue of the organic layer was dissolved in alcohol (60 cc.) and benzene (40 cc.) and after addition of sodium sulfate (40 g.) treated at ice-temperature for two hours with dry gaseous hydrochloric acid. The mass was poured out into water, ether added, the solution washed with soda solution, dried and evaporated. Distillation *in vacuo* (1.5–2 mm.) gave the **methyl ester** of (II), as a viscous yellow oil; b. p. 240–245°; yield 6 g. (Calcd. for $C_{22}H_{20}O_2$: C, 83.5; H, 6.3. Found: C, 83.5; H, 6.2.) A sample of the ester (1.2 g.) on saponification with potassium hydroxide (0.22 g.) gave the above acid, m. p. 227° (dec.).[11]

Reduction.—The above ester (6 g.) in boiling glacial acetic acid (40 cc.) was hydrogenated in presence of palladized barium sulfate; the reaction did not proceed to the

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[1] Diels, Gaedke and Koerding, *Ann.*, **459**, 1 (1927); Ruzicka and co-workers, *Helv. Chim. Acta*, **16**, 216, 812 (1933); **17**, 200 (1934); Cook and co-workers, *J. Chem. Soc.*, 1319 (1935); 54 (1936).

[2] Wieland and Dane, *Z. physiol. Chem.*, **219**, 240 (1933); Cook and Haslewood, *J. Chem. Soc.*, 428 (1934).

[3] Cook, Haslewood and Robinson, *ibid.*, 667 (1935); Cook and Haslewood, *ibid.*, 767, 770 (1935); Fieser and Seligman, This Journal, **57**, 2174 (1935).

[4] Fieser and Seligman, *ibid.*, **57**, 228, 942 (1935); **58**, 2482 (1936).

[5] Bergmann and Hillemann, *Ber.*, **66**, 1302 (1933); *cf.* Hillemann, *ibid.*, **68**, 102 (1935).

[6] See, *e. g.*, Cook and Haslewood, *J. Chem. Soc.*, 767 (1935).

[7] Fieser, This Journal, **51**, 1898, 1938 (1929); Fieser, Fieser and Hershberg, *ibid.*, **58**, 2322 (1936).

[8] Hillemann, *Ber.*, **69**, 2610 (1936).

[9] Gladstone and Tribe, *J. Chem. Soc.*, **35**, 567 (1879).

[10] Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, [2] **135**, 265 (1932).

[11] It has not been proved whether the acid has the structure (II) or the isomeric β,γ-unsaturated formula.

end; therefore the product was isolated by evaporation of the solvent and hydrolyzed by means of 15% methyl alcoholic potassium hydroxide solution (10 cc.). The mixture of acids obtained was treated with ether. A first crop of the unsaturated acid (II) (1.2 g.) remained insoluble; from the mother liquor a second crop of the same substance was obtained (0.8 g.); then the saturated **(1,2,3,4-tetrahydro-2-methyl-5,6-benzanthryl-1)-acetic acid** separated and was recrystallized from ethyl alcohol: hexagonal leaflets, m. p. 192–194.5°, which gave a yellow color reaction with concentrated sulfuric acid. (Calcd. for $C_{21}H_{20}O_2$: C, 82.9; H, 6.6. Found: C, 83.0, 83.3; H, 6.8, 7.2.) The hydrogenation of the regenerated unsaturated acid (II) was accomplished by means of palladium black in ethyl acetate.[12]

Synthesis of (III).—1,2,3,4-Tetrahydro-2-methyl-5,6-benzanthryl-1)-acetic acid (0.46 g.) was dissolved in boiling benzene (10 cc.) and, after addition of phosphoric oxide (3 g.), boiled for three hours. The mass was poured onto ice, extracted with ether and washed with soda solution. The ether residue crystallized spontaneously; it was triturated with acetone and some petroleum ether (80–100°) and collected. It crystallized from ligroin containing some benzene, and then from propyl alcohol as needles, m. p. 168–170°; yield, 0.22 g. (Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 87.7; H, 6.3.) Concentrated sulfuric acid gives an orange-yellow solution with green fluorescence.

Tetrahydromethylcholanthrene (IV).—The above ketone (0.2 g.) was reduced with amalgamated zinc wool (2 g.) and concd. hydrochloric acid. The product was isolated with ether and distilled at 0.15 mm. The yellowish oil which exhibited a violet fluorescence was triturated with acetone and methanol, collected and recrystallized from ethyl alcohol; fluorescent leaflets, m. p. 97–99°; yield, 0.12 g. (Calcd. for $C_{21}H_{20}$: C, 92.7; H, 7.3. Found: C, 92.2; H, 7.0.)

Methylcholanthrene (V).—The tetrahydro derivative (0.1 g.) was heated with selenium (2 g.) in a sealed tube at 330° for forty-eight hours. The product was extracted with ether and benzene and after evaporation of these solvents distilled at 0.05 mm. in presence of sodium metal. The orange-yellow distillate crystallized spontaneously and was triturated with a mixture of methyl and ethyl alcohols: from benzene, yellow rhombic crystals, m. p. 175–177°. The m. p. of Professor Cook's preparation was not depressed by admixture of our product; yield, 0.067 g. (Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.7; H, 6.2.)

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(12) Reduction experiments with sodium amalgam failed owing to the insolubility of the alkali salts of (II).

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Structurally Equivalent Units and the Classification of Normal and Abnormal Liquids

BY RAYMOND H. EWELL

Certain liquids have long been designated as abnormal or "associated" liquids. This designation was made because they did not obey certain physical rules, such as the rule of rectilinear diameters, Trouton's rule, the Ramsay–Shields equation, etc., which the so-called normal liquids did obey. Abnormal liquids also have much higher boiling points and viscosities than would be expected by analogy with normal liquids. The following classification is a somewhat more explicit one than is at present in the literature, as far as the writer is aware:

1. *Abnormal liquids.*—Compounds containing OH or NH groups, *i. e.*, compounds which form hydrogen bonds, giving rise to a positive intermolecular structure. Included are water, ammonia, alcohols, organic acids, phenols, primary and secondary amines, amides, etc., and also hydrogen fluoride.
2. *Intermediate group.*—Compounds containing C=O, C≡N or N=O groups, including ketones, esters, anhydrides, nitriles, nitro derivatives, etc.
3. *Normal liquids.*—All others (except molten metals and molten salts, which occupy separate categories altogether), including non-metallic elements, hydrocarbons and their halogen derivatives, ethers, tertiary amines, sulfides, mercaptans, fourth group tetrahalides, SO_2, S_2Cl_2, PCl_5, CS_2, HCl, HBr, HI, ICl, CO_2, etc.

The following table illustrates in part the basis of the classification.

	B. p., °C.	Viscosity at 25° (in millipoises)
$C_4H_9CH_3$	36	2.3
$C_4H_9NH_2$	78	6.8
C_4H_9OH	118	26.0
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle CH_2$	35	2.3
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle NH$	55.5	3.67
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle O$	34.5	2.35
$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\rangle CH$	93	3.6
$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\rangle N$	90	3.6
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle C{=}H_2$	66	. . .
$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\rangle C{=}O$	102	. . .
$C_4H_9C{\equiv}CH$	71.5	. . .
$C_4H_9C{\equiv}N$	141	. . .