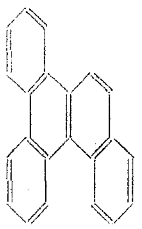
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

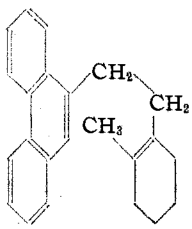
1,2,3,4-Dibenzophenanthrene. I

BY ERNST BERGMANN

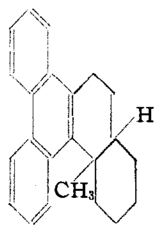
Of the possible aromatic systems consisting of five benzene rings, three are unknown so far: 1,2,3,4-dibenzophenanthrene (I), 1,2,5,6-dibenzophenanthrene and 1′,2′-naphtha-1,2-anthracene.[1] We have undertaken their synthesis and report here experiments for the preparation of (I), which followed the lines worked out for the isolation of the similar 1,2-cyclopentenotriphenylene[2] (I is 1,2-benzotriphenylene). The magnesium derivative of β-(9-phenanthryl)-ethyl chloride reacted upon 2-methylcyclohexanone to give α-(9-phenanthrylethyl)-β-methyl-Δ^{α}-cyclohexene (II), which was cyclized by means of anhydrous stannic chloride. As the product formed by subsequent selenium dehydrogenation gave only very small amounts of an aromatic hydrocarbon of the desired analytical composition, the cyclization product of (II) seems not to be 5,6,7,8,9,10,11,12-octahydro-11-methyl-1,2,3,4-dibenzophenanthrene (III), but a spirane, and the aromatic hydrocarbon, which forms a yellow picrate, a rearrangement product.[3]



I



II



III

In the experimental part some more unsuccessful experiments to synthesize (I) are recorded. The investigation is being continued.[3a]

Experimental

α - (9 - Phenanthryl - ethyl) - β - methyl - Δ^{α}-cyclohexene (II).—When *o*-methylcyclohexanone (10 g.) was added to the solution of β-(9-phenanthryl)-ethylmagnesium chloride (from 2.5 g. of magnesium turnings and 24 g. of the chloride),[2] a vivid reaction took place, which was completed by boiling for three hours. On decomposition with dilute acid, some 1,4-di-(9′-phenanthryl)-butane (1.4 g.) separated. The ether residue decomposed partly when heated on the water-bath, giving off water, and therefore it was heated with potassium hydrogen sulfate (20 g.) to 160° for one hour. Distillation in a good vacuum (0.01 mm.) gave after a small head fraction, which probably was 9-ethylphenanthrene, the desired product (10 g.) as a colorless, viscous oil, b. p. 220°, which could not be induced to crystallize (Calcd. for $C_{23}H_{24}$: C, 92.0; H, 8.0. Found: C, 92.1; H, 8.3). The **picrate**, prepared in concentrated benzene solution, precipitated on chilling as an orange-red powder. From propyl alcohol it formed silky needles, which melted at 124–125° to a dark-red liquid (Calcd. for $C_{29}H_{27}O_7N_3$: C, 65.8; H, 5.1. Found: C, 66.0, 66.0; H, 5.3, 5.5).

Bromine Titration.—0.6594 and 1.3185 g. of the hydrocarbon absorbed 0.3260 and 0.7056 g. of bromine, the theoretical amounts required for 1 double bond being 0.3517 and 0.7032 g., respectively.

Cyclization.—A solution of the foregoing hydrocarbon (II) (15 g.) in benzene (150 cc.) was saturated with dry hydrogen chloride, treated with stannic chloride (6 g.), and kept at room temperature for forty-eight hours. Decomposition with ice and concentrated hydrochloric acid gave the spiranic cyclization product; colorless oil, b. p. 220° (0.01 mm.); yield, 12 g. (Calcd. for $C_{23}H_{24}$: C, 92.0; H, 8.0. Found: C, 91.6; H, 7.9). On mixing its benzene solution with the equivalent amount of picric acid in benzene, a red solution was obtained, which deposited the **picrate** on evaporation. From propyl alcohol this formed orange-red, prismatic needles, m. p. 172° (Calcd. for $C_{29}H_{27}O_7N_3$: C, 65.8; H, 5.1. Found: C, 65.9; H, 5.2).

Cyclization of (II) by means of aluminum chloride did not always give satisfactory results.

Dehydrogenation of the Presumable Spirane.—The above hydrocarbon (3 g.) was heated with selenium (5 g.) at 300–320° for twenty hours in a sealed tube. The reaction product was extracted with chloroform and the residue purified by distillation in a high vacuum (0.01 mm.). After a small head fraction at 160–190° bath temperature, the desired product distilled at a bath temperature of 260–280°. It solidified spontaneously and was triturated with petroleum ether (b. p. 80–100°) and recrystallized from the same solvent, giving faintly yellow, star-like aggregates of prismatic needles, m. p. 184°; yield 1–3%. (Calcd. for $C_{22}H_{14}$: C, 95.0; H, 5.0. Found: C, 95.0; H, 5.1%). The picrate separated from its dark yellow benzene solution in silky, yellow needles, m. p. 220°.

The head fraction mentioned above crystallized from methyl alcohol in the form of leaflets of m. p. 99° and was identified as **phenanthrene**. Its formation is due to thermolytic fission. An analogous observation has been made recently in our laboratory[4] in the dehydrogenative preparation of 2′,1′-naphtha-1,2-fluorene.[5] Its 10-methyl-3,4,9,10-tetrahydro derivative, when heated with selenium, gives partly 3,4-dihydrophenanthrene.

Several other synthetic methods for the preparation of

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[1] Barry, Cook, *et al.*, *Proc. Roy. Soc.* (London), **117B**, 318 (1935).

[2] E. Bergmann and O. Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936); E. Bergmann and F. Bergmann, *ibid.*, **60**, 1805 (1938).

[3] Compare Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, p. 162.

[3a] (I) has recently been synthesized by Hewett, *J. Chem. Soc.*, 193 (1938).

[4] Unpublished results.

[5] Bachmann, Cook, Hewett and Iball, *J. Chem. Soc.*, **54** (1936).

(I) have been tried without success. Dicyclohexenyl (4.5 cc.)[6] and 1,2-naphthoquinone (10.4 g.) condensed at 180° to form an unworkable black resin, and 3-bromo-1,2-naphthoquinone (1.6 g.) did not react at all with this hydrocarbon (1.1 g.) when heated at 100° for four hours in the presence of *sym*-tetrachloroethane[7] (10 cc.). The potassium derivative of ethyl cyclohexanone-*o*-carboxylate could not be coupled with β-(9-phenanthryl)-ethyl chloride, even on prolonged heating,[8] and finally the fact may be recalled,[9] that 9-cyclohexenylphenanthrene does not react with maleic anhydride to form a derivative of 1,2,3,4-dibenzophenanthrene.

Summary

By interaction between 2-methylcyclohexanone and the Grignard derivative of β-(9-phenanthrylethyl) chloride and subsequent cyclization, a spirane is formed instead of the expected octahydro-methyl-1,2,3,4-dibenzophenanthrene. Its dehydrogenation gave small amounts of an aromatic hydrocarbon. Several other methods of synthesis also failed.

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[6] Compare Weizmann, Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

[7] Compare, for this method, Fieser and Dunn, *ibid*,, **59**, 1016, 1021, 1024 (1937).

[8] With this reaction, we intended to utilize the method of Ruzicka, Ehmann, Goldberg and Hoesli [*Helv. Chim. Acta*, **16**, 833 (1933)] for the synthesis of chrysene and 1,2-cyclopentenophenanthrene.

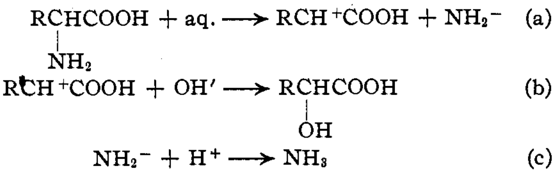
[9] E. Bergmann and F. Bergmann, THIS JOURNAL, **59**, 1443 (1937).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Photochemical Deamination of Amino Acids in Water Solution. II

BY CH. WEIZMANN, Y. HIRSHBERG AND ERNST BERGMANN

In the first paper on the subject,[1] we were able to demonstrate that under the influence of ultraviolet light water solutions of amino acids undergo hydrolysis according to the scheme



$$\underset{\displaystyle NH_2}{RCHCOOH} + aq. \longrightarrow RCH^{+}COOH + NH_2^{-} \qquad (a)$$

$$RCH^{+}COOH + OH' \longrightarrow \underset{\displaystyle OH}{RCHCOOH} \qquad (b)$$

$$NH_2^{-} + H^{+} \longrightarrow NH_3 \qquad (c)$$

In order to see how the nature of the group R influences the speed of the reaction, we compared alanine and phenylalanine under identical conditions. Phenylalanine decomposes about 2.7 times as quickly as alanine, in 0.1 *N* solution, and 2.2 times as quickly in 0.05 *N* solution. This influence of the phenyl group may be due to two effects, to its loosening the C–N bond and to the increase in light absorption,[2] both effects perhaps being connected in some way. The necessary measurements could be made only in the first stage of the reaction, as phenylalanine undergoes a side reaction, leading to an insoluble coating on the quartz walls and to the formation of an unpleasantly smelling volatile product. In the first minutes of irradiation, however, only ammonia is formed, according to the above scheme. The same complication as with phenylalanine occurs in the case of phenylglycine, $C_6H_5CH(NH_2)COOH$, the decomposition of which therefore could not be studied. Apparently, these side reactions are due to the presence of the aromatic nucleus, as similar observations have been made before with tyrosine solutions.[3]

The constitutional change brought about by coupling alanine with glycine to form alanylglycine also increases the speed of the photochemical deamination. Alanylglycine is hydrolyzed 4.2 times as quickly as alanine in 0.1 *N* solution, and 2.6 times as quickly in 0.05 solution. It is difficult to explain this difference, but it may be assigned to the greater distance between the amino and the free carboxyl group enhancing the ionization of the C–N bond, or to the increased light absorption[4] or to both effects. It may be added that we think it safe to ascribe the ammonia formed exclusively to the decomposition of the $-C-NH_2$ and not of the amide group, since the amide group, as far as we know, is much stabler toward photochemical hydrolysis.[5] It appears that peptides are attacked in the same way as amino

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[1] Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **58**, 1675 (1936).

[2] Compare Allen, Steiger, Magill and Franklin, *Biochem. J.*, **31**, 195 (1937).

[3] Compare Part I. The ultraviolet absorption spectra of tyrosine and phenylalanine are practically identical: Feraud, Dunn and Kaplan, *J. Biol. Chem.*, **112**, 323 (1935).

[4] Magill, Steiger and Allen, *Biochem. J.*, **31**, 188 (1937).

[5] Compare, *e. g.*, the experiments of Paternò, *Gazz. chim. ital.*, **44**, I, 237 (1914). Allen, Steiger, Magill and Franklin[2] have stated recently that in acylated amino acids and peptides hydrolysis of the –CO–NH-group occurs on irradiation. While that may be true in the case of acylated amino acids, which do not contain the amino group necessary for photolysis, there apparently is no need for that assumption with regard to peptides.