ing anhydrous formic acid (90 cc.) for three hours. The precipitate was collected and recrystallized from methyl ethyl ketone. The m. p. of the prisms could be raised to 280°, but the mixed m. p. with the above sample proved the identity.

Summary

On heating 9,10-diphenyl-9,10-dichloro-9,10-dihydroanthracene is converted into 2-chloro-9,10-diphenylanthracene (and 1 mole of hydrochloric acid). This reaction is suggested to involve a *p*-quinolid tautomerization.

This mechanism is used for explaining certain known reactions of the anthracene series. It may be responsible, too, for the occurrence in nature of 2-methylanthraquinone in various oxidative stages with regard to the methyl group.

REHOVOTH, PALESTINE RECEIVED MARCH 4, 1937

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

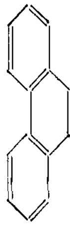
Synthesis of Triphenylene

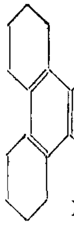
BY ERNST BERGMANN AND O. BLUM-BERGMANN

For spectroscopic purposes, we required a specimen of pure triphenylene (I). An easy way of synthesis has been devised by Mannich[1] and by Diels and Karstens[2] by dehydrogenation with selenium of dodecahydrotriphenylene (II), which is formed in relatively small yields (3 to 4 g. from 100 g. of cyclohexanone) on treating cyclohexanone with methyl alcoholic sulfuric acid. We thought it advisable to find a synthetic method proving at the same time the constitution of triphenylene, which so far has been based on mere analogy. The method to be described here gives not only the desired proof, but may be extended to include the synthesis of alkyl and aryl derivatives of triphenylene.

By the interaction of 9-phenanthrylmagnesium bromide and succinic anhydride according to the method of Weizmann and co-workers[3] β-(9-phenanthroyl)-propionic acid (III) is formed. It is converted, through its semicarbazone, into γ-(9-phenanthryl)-butyric acid (IV) which subsequently has been cyclized by means of phosphoric oxide to form 4-keto-1,2,3,4-tetrahydrotriphenylene (V). Clemmensen reduction afforded 1,2,3,4-tetrahydrotriphenylene (VI), which could be dehydrogenated easily to (I).

In preparing triphenylene by dehydrogenation of (II), occasionally an intermediate product $C_{18}H_{16}$ has been obtained, which was identified by mixed m. p. as tetrahydrotriphenylene (VI), for which our synthesis gives the exact formula. Obviously, the three hydrogenated rings in (II) lose their supernumerary hydrogen atoms stepwise.[3a]


I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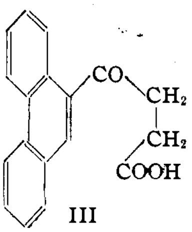

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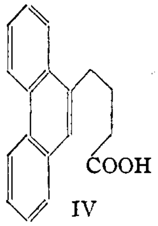

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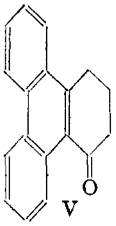
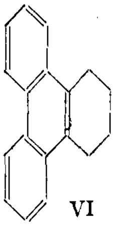


V


VI

Experimental

β-(9-Phenanthroyl)-propionic Acid (III).—When a solution of 9-phenanthrylmagnesium bromide (prepared from 5 g. of magnesium and 48.5 g. of 9-bromophenanthrene according to Bachmann[4]) was added to a boiling suspension of succinic anhydride (15 g.) in ether, a violent reaction took place. After one hour's boiling, the product was decomposed with ice and dilute sulfuric acid and the resulting acid extracted with alkali from its solution. The dark brown liquid, on acidifying, deposited an oil, which solidified quickly. The crystals were collected, kept with benzene at 0° for twenty-four hours, filtered, washed with ice-cold benzene and recrystallized from propyl alcohol; m. p. 176°; yield, 9 to 11.5 g. This acid dissolves in concentrated sulfuric acid with dark orange-red color. (Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.0. Found: C, 77.5; H, 5.1.)

The methyl ester, prepared by means of diazomethane in ethereal solution, boiled at 217–220° (1.5 mm.) and crystal-

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[1] Mannich, *Ber.*, **40**, 153 (1907); compare Pirrone, *Chem. Zentr.*, **107**, II, 2351 (1936).

[2] Diels and Karstens, *ibid.*, **60**, 2323 (1927).

[3] Weizmann and co-workers, *J. Chem. Soc.*, 1370 (1935).

[3a] Compare Cook and Hewett, *J. Chem. Soc.*, (370 1934), for the case of didecahydrobenzanthracene.

[4] Bachmann, THIS JOURNAL, **56**, 1363 (1934).

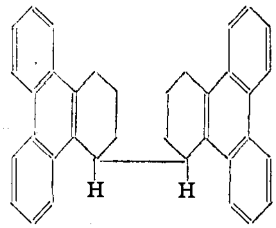
lized on trituration with alcohol; from methanol as needles, m. p. 88°. (Calcd. for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.6; H, 5.5.)

For the preparation of the **semicarbazone** of (III), the keto acid (18 g.) was dissolved in propyl alcohol (75 cc.) and after addition of fused sodium acetate (8.3 g.) in the minimum amount of alcohol and of semicarbazide hydrochloride (7.1 g.) in water, boiled for three and one-half hours. After twelve hours, the precipitate, consisting of yellowish grains and a white powder, was filtered, washed with water and dried; yield, 15–16 g.; m. p. 229° (dec.). For analysis, the semicarbazone was recrystallized from 75% acetic acid, whereupon the m. p. rose to 237°. (Calcd. for $C_{19}H_{17}O_3N_3$: C, 68.1; H, 5.1. Found: C, 68.5, 68.4; H, 5.5, 5.6.)

γ-(9-Phenanthryl)-butyric Acid (IV).—The semicarbazone (7.5 g.) was added to a solution of sodium (7.5 g.) in alcohol (100 cc.) and heated for six hours to 200° in an autoclave in hydrogen atmosphere. The alcohol was distilled off, the residue dissolved in water, filtered and precipitated by addition of acid; from glacial acetic acid, m. p. 173°; yield, 4.5 g. (Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.8; H, 6.4.)

4-Keto-1,2,3,4-tetrahydrotriphenylene (V).—The acid (IV) (10 g.) was heated with toluene (150 cc.) to 100° and phosphoric oxide (60 g.) added in small portions. The mass was then heated to 130° for two hours and decomposed with ice. The toluene layer was extracted with soda solution, dried and evaporated in a vacuum. The remaining oil, on trituration with light petroleum and acetone at 0°, crystallized and gave 5 g. of the desired ketone, which was recrystallized from methanol; prismatic leaflets, m. p. 101°. A second crop amounting to 1.3 g. separated from the watery phosphoric acid solution, which had been separated from the toluene layer, on standing. (Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 87.2, 86.9; H, 5.9, 5.6.)

1,2,3,4-Tetrahydrotriphenylene (VI).—The above ketone (6 g.) was heated with amalgamated zinc wool (60 g.) in glacial acetic acid (100 cc.) and concentrated hydrochloric acid added in small portions, until all the zinc disappeared. The reduction product crystallized on the surface of the acid liquid, and was extracted by means of ether and benzene. It crystallized, after evaporation of these solvents, on addition of methanol. The desired hydrocarbon (VI) dissolved in boiling propyl alcohol and crystallized on cooling in long silky needles, m. p. 120–121°; yield, 4 g. (Calcd. for $C_{18}H_{16}$: C, 93.1; H, 6.9. Found: C, 93.0, 93.3; H, 7.1, 7.2.) A small fraction, which proved insoluble in propyl alcohol, was recrystallized twice from ethyl malonate, giving octahedra, m. p. 300°. Analysis and molecular weight determination suggested the formula (VII) of *bis*-(1,2,3,4-tetrahydrotriphenylenyl-4,4'). Similar observations have been made in other cases in our Laboratory. (Calcd. for $C_{36}H_{30}$: C, 93.5; H, 6.5; mol. wt., 462. Found: C, 93.0; H, 6.2; mol. wt. (camphor), 506.)



(VII)

Triphenylene (I).—The tetrahydro compound (VI) (6 g.) was heated with selenium (9 g.) to 320° for ten hours. The mass was extracted with boiling butyl alcohol, which separated, on cooling, the desired hydrocarbon: from propyl alcohol needles, m. p. 198°.

The dehydrogenation of (II), m. p. 232°, according to Diels[1] has to be carried out at 320° for ten hours; the product may be worked up conveniently as above. If carried out at 290°, as suggested by Diels, a mixture was obtained which, by fractional crystallization from butyl alcohol, can be separated into the bent needles of triphenylene (I) and the much more soluble prismatic needles of its tetrahydro derivative (VI), m. p. 116–117°. Identification was by mixed melting points.

Summary

For the synthesis of triphenylene, a method has been devised which involves interaction of 9-phenanthrylmagnesium bromide with succinic anhydride.

In the dehydrogenation of dodecahydrotriphenylene an intermediary tetrahydro product may be isolated under certain conditions.

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