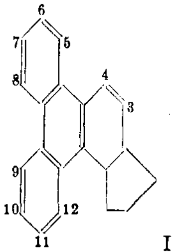
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

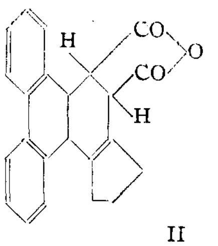
1,2-Cyclopentenotriphenylene. II

BY ERNST BERGMANN AND FELIX BERGMANN

In a previous paper,[1] synthetic experiments had been reported expected to yield 1,2-cyclopentenotriphenylene (I). In the course of this synthesis, three hydrocarbons were isolated, to which, on the basis of mere analogies, the following formulas were assigned: "cyclopentenotriphenylene" m. p. 171–172.5°; picrate, m. p. 172–173°; "9-methyl-3,4-benzpyrene,"[2] m. p. 157.5–159.5°; picrate, m. p. 153–155°; "1,2,3,4-dibenzfluorene," m. p. 115–116°; picrate, m. p. 165–167°. In order to determine definitely the structure of the three products, we have tried both chemical and physical methods. A possible synthesis of 1,2-cyclopentenotriphenylene by an unambiguous method was suggested by our observation[3] that this hydrocarbon system can be obtained easily by the diene reaction of 9-cyclopentenylphenanthrene and maleic anhydride. When the condensation product (II) was treated with lead tetraacetate[4] four hydrogen atoms were removed, leaving 1,2-cyclopentenotriphenylene-3,4-dicarboxylic acid anhydride (III). Direct decarboxylation proved difficult, but eventually two different stepwise methods have been worked out. (a) With quinoline and basic cupric carbonate,[5] a monocarboxylic acid "A" was formed, m. p. 299–300° (methyl ester, m. p. 197–198°), the potassium salt of which was decarboxylated thermally with relative ease, giving the desired cyclopentenotriphenylene (I).[6] (b) The anhydride (III), on heating with soda-lime, gave an isomeric cyclopentenotriphenylene carboxylic acid (3 or 4) "B," m. p. 249° (methyl ester, m. p. 117°). This, when treated with basic cupric carbonate in quinoline, gave again the desired hydrocarbon (I). The substance was identified in each case by the characteristic orange-yellow picrate, m. p. 165–167°. Therefore, the hydrocarbon formerly supposed to be 1,2,3,4-dibenzfluorene, actually is 1,2-cyclopentenotriphenylene.



I



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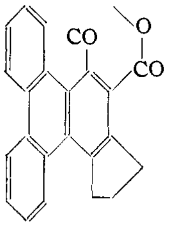

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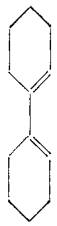

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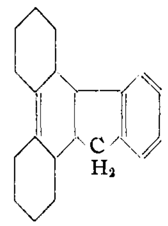

V

The spectrum of the substance formerly supposed to be cyclopentenophenanthrene ($C_{21}H_{16}$) shows even on qualitative examination[7] so close a resemblance to 3,4-benzpyrene[8] that we definitely may assign to it the structure of 9(?)-methyl-3,4-benzpyrene,[9] ($C_{21}H_{14}$). The intense green-yellow fluorescence of our substance points in the same direction; even the melting point of our hydrocarbon is almost identical with that of 3,4-benzpyrene[10] and is not depressed by its admixture.[11,12]

The third of the above hydrocarbons (m. p. 157.5–159.5°) finally has been identified as 1,2,3,4-dibenzfluorene. After some unsuccessful attempts, reported in the experimental part, it was synthesized by a method based on a recent observation by Alder and Rickert.[13] Dicyclohexenyl (IV)

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[1] Bergmann and O. Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936).

[2] This hydrocarbon was previously called 7-methyl-1,2-benzpyrene; this name has been changed according to the suggestions of Cook and co-workers, *Amer. J. Cancer*, **29**, 279 (1937).

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

[4] (a) Haworth and co-workers, *J. Chem. Soc.*, 635, 643 (1935); (b) 352, 1000 (1936); (c) Weizmann, Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

[5] Fieser, Fieser and Hershberg, *ibid.*, **58**, 2324 (1936).

[6] The same result was obtained when the monocarboxylic acid A was distilled over zinc dust *in vacuo*.

[7] The detailed report on the spectrographic analysis will be published later.

[8] Mayneord and Roe, *Proc. Roy. Soc.* (London), **152B**, 299 (1935).

[9] The analytical figures for $C_{21}H_{14}$ and $C_{21}H_{16}$ and for the respective picrates are relatively similar, so that a definite decision on the basis of the combustion analyses was not to be expected.

[10] Compare Cook and Hewett, *J. Chem. Soc.*, 403 (1933). The two respective picrates, although almost identical in appearance, have different m. p's. (172–173° as against 197–198°).

[11] The possibility that the methyl group is situated at C_8 of the pyrene skeleton has to be borne in mind, in view of the observation by Vollmann [*Ann.*, **531**, 36 (1937)], that in the synthesis of 1,2-cyclopentenophenanthrene 3-methyl-pyrene is formed along with the 4-isomer.

[12] The same conclusion on the structure of our hydrocarbon has been expressed recently by Hewett, *J. Chem. Soc.*, 193 (1938).

[13] Alder and Rickert, *Ber.*, **71**, 379 (1938).

was condensed with indene by heating at 180°[14] to give the dodecahydro derivative (V) of 1,2,3,4-dibenzfluorene, which could be dehydrogenated easily. The hydrocarbon so obtained melted at 158–159°; picrate, m. p. 153–155°. The melting points were not depressed by admixture of the appropriate preparations described in our previous paper on the subject.

Experimental

1,2 - Cyclopentenotriphenylene - 3,4 - dicarboxylic Acid Anhydride (III).—(a) A solution of the tetrahydro compound (II)[3] (1 g.) in glacial acetic acid (25 cc.) and acetic anhydride (25 cc.) was cooled to 75° and added to a suspension of lead tetraacetate[15] (25 g.) in glacial acetic acid (10 cc.). The reaction mixture, immediately turning yellow, is kept on the water-bath for twenty minutes and then in the refrigerator for two hours. The melting point (296°) of the crystals is not raised by recrystallization from xylene, decalin or ethyl benzoate; yellow needles, yield 100 mg. (*Anal.* Calcd. for $C_{23}H_{14}O_3$: C, 81.7; H, 4.2. Found: C, 81.9, 81.8; H, 4.6, 4.4.) (b) A somewhat less pure product was obtained when the anhydride (15 g.) suspended in glacial acetic acid (100 cc.) was mixed with lead tetraacetate (30 g.) in glacial acetic acid (100 cc.) and the mass heated for two hours on the water-bath. The yield in this case was 8.5 g., but the product had to be recrystallized several times.

1,2 - Cyclopentenotriphenylene - 3(4?) - carboxylic Acid ("A").—The above anhydride (III, 4 g.) was boiled for two hours with quinoline (25 cc.) and basic cupric carbonate (0.8 g.). The reaction product was poured into dilute sulfuric acid, extracted with ether and isolated by vacuum distillation. The brown oil, b. p. 245–255° (0.7 mm.), solidified on trituration with acetone and was recrystallized from butyl acetate or ethyl benzoate: clusters of needles, m. p. 299–300°. (*Anal.* Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.1. Found: C, 84.4; H, 5.5.) The **methyl ester** prepared by means of diazomethane can be recrystallized most conveniently from acetic anhydride, giving needles, m. p. 197–198°. (*Anal.* Calcd. for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5. Found: C, 84.7; H, 5.6.)

1,2 - Cyclopentenotriphenylene - 4(3?) - carboxylic Acid ("B").—The anhydride (III, 6 g.) was heated with soda-lime (18 g.) to 180° for one hour and to 300° for two hours in a sealed tube. The product was poured into hydrochloric acid and extracted with chloroform. The residue of this solution crystallized spontaneously; it was triturated with methyl alcohol and recrystallized from a mixture of butyl acetate and ligroin: shiny needles, m. p. 249°. (*Anal.* Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.1. Found: C, 83.7; H, 5.9.) The **methyl ester**, prepared as above, does not crystallize well. It was obtained as a sirupy mass, which was distilled in high vacuum and then treated with a mixture of isopropyl alcohol and acetone; m. p. 117°.

1,2-Cyclopentenotriphenylene (I).—(a) The methyl ester (0.6 g.) of the monocarboxylic acid ("A") was boiled for one hour with alcoholic potassium hydroxide (2 mols). The alcohol was distilled off and the residue heated to 320–250° for four hours in a sealed tube. Water and ether were added and the product isolated by high vacuum distillation; b. p. 250–330° (0.3 mm.). The distillate was dissolved in benzene and directly converted into a picrate by means of alcoholic picric acid solution: orange needles, m. p. and mixed m. p. with the product of E. Bergmann and O. Blum-Bergmann, 165–167°. (b) The monocarboxylic acid ("B") (0.6 g.) was boiled with quinoline (15 cc.) and basic cupric carbonate (1.2 g.) for twenty-four hours and the mass worked up as usual. The product boiled at 260–280° (2.5 mm.) and again was converted into the characteristic picrate; m. p. and mixed m. p. 165–167°, after recrystallization from a mixture of benzene and alcohol. (c) The monocarboxylic acid ("A") (0.2 g.) was mixed with zinc dust (20 g.) and distilled slowly at 30 mm. The distillate was taken up with acetone and the acetone residue distilled at 25 mm. and converted into the picrate; m. p. 165–167°.

Dodecahydro-1,2,3,4-dibenzfluorene (V).—Dicyclohexenyl (IV, 50 g.) and indene (25 g.), both freshly distilled, were mixed and heated at 180° for twenty hours in a sealed tube, and the product fractionated in vacuum (0.3 mm.). The condensation product was secured in two portions, the first one boiling at 180–185° (14 g.) and the second at 185–190° (12 g.). It may be that they represent different steric forms of the condensation product (V), although diene condensations generally take place in a sterically homogeneous manner (Fraction I: Calcd. for $C_{21}H_{26}$: C, 90.7; H, 9.3. Found: C, 90.5; H, 9.2. Fraction II: Found: C, 90.5; H, 9.0). Both gave the same results on dehydrogenation.

1,2,3,4-Dibenzfluorene.—The dodecahydro derivative (V) (6 g.) was heated with selenium (20 g.) at 300° for twenty hours. The reaction product was removed mechanically from the excess selenium and recrystallized several times from isopropyl alcohol and butyl alcohol; needles, m. p. 158–159°; the picrate, prepared according to E. Bergmann and O. Blum-Bergmann,[1] melted at 153–155°; yield 3.8 g.

Unsuccessful Experiments to Synthesize 1,2,3,4-Dibenzfluorene.—We applied to our problem the chrysene synthesis devised by Ruzicka, Ehmann, Goldberg and Hoesli,[16] which has been utilized in the analogous case of 1′,2′-naphtha-2,3-fluorene by Cook, Dansi, *et al.*[17] 9-Chloromethylphenanthrene, which was prepared easily from 9-phenanthrylcarbinol, reacted with the sodium derivative of ethyl cyclohexanone-2-carboxylate to yield ethyl 2-(9′-phenanthryl-methyl)-cyclohexanone-2-carboxylate (VI), but unfortunately cyclization according to the scheme

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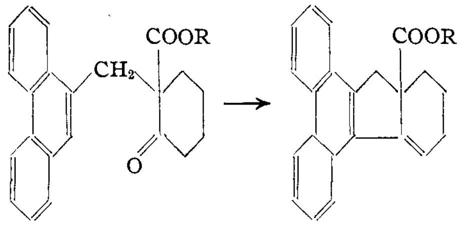
(14) For other diene reactions with dicyclohexenyl, see ref. 4c.

(15) For the preparation of lead tetraacetate, the following method has proved very convenient. To glacial acetic acid (250 cc.), minium (75 g.) is added in small portions at room temperature, while the mass is stirred thoroughly. The operation takes about thirty minutes; the product starts crystallizing during this time. The mass is kept in the icebox for two hours and filtered. The crystals, containing only traces of unchanged minium, are transferred, while still wet, to a desiccator. Working at room temperature permits a much quicker addition of minium, as no decomposition is to be feared.

(16) Ruzicka, Ehmann, Goldberg and Hoesli, *Helv. Chim. Acta*, **16**, 833 (1933).

(17) Cook, Dansi, *et al.*, *J. Chem. Soc.*, 1319 (1935).



(VI) (VII)

occurred to a negligible extent only.

9-Phenanthrylcarbinol[18] (14 g.) (from benzene as needles, m. p. 150°) is mixed with dimethylaniline (12 g.) and benzene (40 cc.) and treated at 0° with thionyl chloride (7 cc.). The crystalline cake formed is kept for ten hours at room temperature and then heated to 100°, until the evolution of sulfur dioxide ceases. On addition of water and ether, part of the 9-chloromethylphenanthrene separates spontaneously; the remainder was obtained by evaporation of the ethereal layer. From light petroleum the m. p. is 98°; it is useful to induce crystallization by scratching; yield 12 g.[19]

Ethyl 2-(9′-Phenanthrylmethyl)-cyclohexanone-2-carboxylate (VI).—9-Chloromethylphenanthrene (3.7 g.) was added to ethyl sodio-cyclohexanone-2-carboxylate (from 0.4 g. of sodium and 3.1 g. of the ester, b. p. 119° (26 mm.)) in toluene (25 cc.) and the whole boiled for six hours. After treatment with dilute sulfuric acid, the toluene was evaporated and the oily residue triturated with methanol and acetone. It gave 2.5 g. of the desired product, which was recrystallized from light petroleum as dimorphous white needles and yellow stout prisms; m. p. 118–119°. (*Anal.* Calcd. for $C_{24}H_{24}O_3$: C, 80.0; H, 6.7. Found: C, 79.3; H, 6.)

Cyclization VI → VII.—The foregoing ester (10 g.) was heated at 140° for twelve hours with water (100 cc.) and concentrated sulfuric acid (55 cc.). The organic material was extracted with ether and benzene and distilled *in vacuo*. At 230° (0.03 mm.) a viscous, nearly colorless oil distilled and on treatment with glacial acetic acid gave a crystalline mass (2.9 g.). It consisted almost completely of the starting material, which was recovered by recrystallization from propyl alcohol. A small amount of material proved insoluble in this solvent and was subsequently recrystallized from ethyl malonate. The analysis of the prisms, m. p. 250°, so obtained, was consistent with (VII). (*Anal.* Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 83.8; H, 6.2.) From the glacial acetic acid mother liquor no homogeneous material could be isolated, even after dehydrogenation with platinum black at 320–340°.

Summary

The three hydrocarbons, previously obtained from 9-phenanthrylmagnesium bromide and cyclopentanone, are now identified as 1,2-cyclopentenotriphenylene, 9(?)-methyl-3,4-benzpyrene and 1,2,3,4-dibenzfluorene, respectively.

1,2-Cyclopentenotriphenylene was synthesized from the addition product of 9-cyclopentenylphenanthrene and maleic anhydride by dehydrogenation and subsequent stepwise decarboxylation.

For the synthesis of 1,2,3,4-dibenzfluorene, dicyclohexenyl was condensed with indene and the addition product dehydrogenated by means of selenium. The attempt to apply Ruzicka's chrysene synthesis to the case of 1,2,3,4-dibenzfluorene was unsuccessful.

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

[19] Compare v. Braun, *Ber.*, **70**, 984 (1937).

[CONTRIBUTION FROM THE CELLULOSE DEPARTMENT, CHEMICAL FOUNDATION, BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.]

Optical Properties of Cellulose Dispersed in Cuprammonium Hydroxide Solution[1]

BY JACK COMPTON

The current concept regarding the nature of the colloidal solutions resulting from the dispersion of cellulose by cuprammonium hydroxide solution, Schweizer's reagent, depends on the theories of cellulose fiber structure, namely, the continuous, or macromolecular, theory, and the discontinuous, or micellar, theory.

The continuous, or macromolecular, theory, developed by Staudinger on the basis of viscosity measurements, may be summed up in the following statement:[2] "Accordingly cellulose and its derivatives are molecular colloids and on the length and form of their macromolecules depends the colloidal behavior of their solutions." The macromolecules in cellulose fibers are considered regularly lined up under the influence of covalent forces in a direction parallel to the fiber axis.

The discontinuous, or micellar, theory, postulated by von Nägeli[3] and extended to cellulose by Karrer[4] in 1921, assumes that the micelle of cellu-

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[1] Presented before the Division of Cellulose Chemistry at the 94th meeting of the American Chemical Society, Rochester, N. Y., Sept. 9, 1937.

[2] H. Staudinger, *Ber.* **70**, 2514 (1937).

[3] C. von Nägeli, "Die Stärkekörner," Friedrich Schulthess, Zurich, 1858.

[4] P. Karrer and F. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921).