[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XVII.[1] 9-Methyl- and 10-Methyl-1,2,3,4-dibenzophenanthrenes

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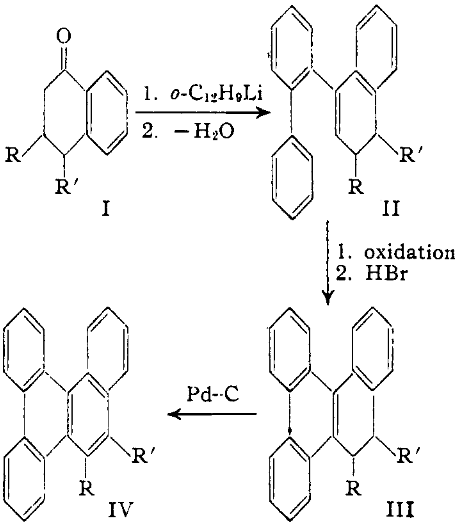
The announcement by Hewett[2] of the carcinogenic action of 1,2,3,4-dibenzophenanthrene has made it of interest to prepare some methyl derivatives[3] of this hydrocarbon for testing. In an earlier communication,[4] we described a new method for the synthesis of the parent hydrocarbon (IV, R and R′ = H). This involves the preparation of 1-(2-biphenylyl)-3,4-dihydronaphthalene (II, R and R′ = H) by the reaction of *o*-phenylphenyllithium with α-tetralone, followed by oxidation to the olefin oxide with perphthalic acid, cyclization to the 9,10-dihydro-1,2,3,4-dibenzophenanthrene (III, R and R′ = H) and finally dehydrogenation to the fully aromatic derivative (IV, R and R′ = H).



While this synthesis should lend itself readily to the preparation of a number of homologs, the present communication deals with those which may be prepared from α-tetralones containing methyl groups in the alicyclic ring. Starting with 4-methyltetralone-1[5] (I, R = H; R′ = CH_3), 9-methyl-1,2,3,4-dibenzophenanthrene was obtained in an over-all yield of 37%. The isomeric 3-methyltetralone-1[6] (I, R = CH_3; R′ = H) in the same way led to 10-methyl-1,2,3,4-dibenzophenanthrene (IV, R = CH_3; R′ = H). When 3,4-dimethyltetralone-1[5] (IV, R and R′ = CH_3) was used, the synthesis proceeded as usual as far as the 9,10-dimethyl-9,10-dihydro-1,2,3,4-dibenzophenanthrene (III, R and R′ = CH_3), but dehydrogenation to the fully aromatic hydrocarbon (IV, R and R′ = CH_3) could not be accomplished. When the dihydro compound was heated with palladium–charcoal, about the usual volume of gas was evolved, but the only crystalline product which could be isolated was 9-methyl-1,2,3,4-dibenzophenanthrene[7] (IV, R = H; R′ = CH_3). Dehydrogenation with sulfur gave essentially the same result, while chloranil seemed to be without effect.

One other observation of interest is the apparent ability of 9-methyl-1,2,3,4-dibenzophenanthrene to absorb oxygen as evidenced by the decline in carbon and hydrogen content[8] of the sample upon storage. While oxygen absorption by polycyclic aromatic hydrocarbons is by no means unusual, the known examples are confined to those hydrocarbons containing the anthracene nucleus.[9]

Experimental

9-Methyl-1,2,3,4-dibenzophenanthrene

1-(2-Biphenylyl)-4-methyl-3,4-dihydronaphthalene (II, R = H; R′ = CH_3).—An ether solution containing 13 g. of 4-methyltetralone-1[5] was added slowly to a solution of *o*-phenylphenyllithium, prepared in ether from 1.5 g. of lithium and 28.6 g. of *o*-iodobiphenyl. After refluxing overnight, the product was decomposed with water in the usual way and purified by distillation. The distillate was obtained as a viscous oil, b. p. 215–218° (6–7 mm.); yield 15.5 g. (64.5%) .

Anal.[10] Calcd. for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.12; H, 6.77.

9-Methyl-9,10-dihydro-1,2,3,4-dibenzophenanthrene (III, R = H; R′ = CH_3).—Oxidation of the above hydrocarbon was accomplished by the use of an excess of perphthalic acid as described previously[4] for the parent hydrocarbon. The crude oxide obtained from 15.5 g. of 1-(2-biphenylyl)-4-methyl-3,4-dihydronaphthalene was dissolved in 125 cc. of acetic acid, 75 cc. of 34% hydrobromic acid added, and the mixture refluxed for forty-eight hours. At the end of this period, the solution was diluted, extracted with benzene, and the washed benzene solution concentrated and distilled *in vacuo*. The product was a hard yellow resin which could not be crystallized; yield 13.8 g. (89.5%). The hydrocarbon could be converted to a picrate in acetic acid solution, yielding bright red needles, m. p. 170.5–171°.

Anal. Calcd. for $C_{29}H_{21}N_3O_7$: N, 8.03. Found: N, 8.01.

9-Methyl-1,2,3,4-dibenzophenanthrene (IV, R = H; R′ = CH_3).—One gram of the dihydro compound above

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[1] For the preceding communication of this series see THIS JOURNAL, **66**, 1280 (1944).

[2] Hewett, *J. Chem. Soc.*, 1286 (1938).

[3] For an analysis of the possible carcinogenic action of alkyl 1,2,3,4-dibenzophenanthrenes, see Bergmann and Eschinazi, THIS JOURNAL, **65**, 1413 (1943).

[4] Bradsher and Rapoport, *ibid.*, **65**, 1646 (1943).

[5] Kloetzel, *ibid.*, **62**, 1708 (1940).

[6] Tishler, Fieser and Wendler, *ibid.*, **62**, 2866 (1940).

[7] Other instances of the elimination of a methyl group during dehydrogenation are known, *e. g.*, Jones and Ramage, *J. Chem. Soc.*, 1853 (1938).

[8] The authors are indebted to Dr. T. S. Ma, of the University of Chicago, for his kind coöperation and advice on this aspect of the problem.

[9] Bergmann and McLean, *Chem. Rev.*, **28**, 367 (1941).

[10] Microanalyses by Dr. T. S. Ma, University of Chicago.

was heated for two hours in an atmosphere of carbon dioxide with 0.1 g. of 30% palladium-charcoal at 310–350° The volume of hydrogen evolved was 70–80% of the theoretical. The product was obtained as hexagonal prisms from benzene–alcohol, m. p. 147–148.5°; yield 0.64 g. (64%; 37% over-all from the tetralone). Recrystallized the product was white, m. p. 150.5–151.5°.

Anal. Calcd. for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found[11]: C, 94.10; H, 5.56.

Oxidation of the hydrocarbon by sodium dichromate in glacial acetic acid yielded 1,2,3,4-dibenzophenanthraquinone,[12] m. p. 237–239°, which gave no depression of melting point when mixed with an authentic sample (ref. 4).

The picrate of the hydrocarbon was obtained as small dark red needles from benzene–alcohol, m. p. 207.5–208.5°.

Anal. Calcd. for $C_{29}H_{19}N_3O_7$: N, 8.06. Found: N, 7.64.

Decline in Carbon and Hydrogen Content of Samples of 9-Methyl-1,2,3,4-dibenzophenanthrene.—The results shown in Table I are obtained from two different preparations of the hydrocarbon. The first sample, A, was subjected to recrystallization and sublimation between analyses, while sample B was merely allowed to stand for approximately four weeks before a second analysis was performed. It will be noted that in each case, the carbon and hydrogen content declines with increasing age of the sample.

TABLE I

Sample	Analyses, % C	Analyses, % H	Total C and H, %
A (analytical sample)	93.90	5.78	99.68
A (above recrystallized)	93.31	5.71	99.02
A (above resublimed)	90.31	5.37	95.68
B (analytical sample)	91.11	5.49	96.60
B (above sample after standing four weeks)	88.45	5.40	93.85

10-Methyl-1,2,3,4-dibenzophenanthrene

β-Methyl-γ-phenylbutyric acid was prepared in 75% yield by the Martin–Clemmensen reduction[13] of β-benzoylbutyric acid[14] and cyclized to **3-methyltetralone-1** as described by Tishler and co-workers.[6]

1-(2-Biphenylyl)-3-methyl-3,4-dihydronaphthalene (II, R = CH_3, R′ = H) was prepared in essentially the same manner as the 4-methyl isomer. From 12.2 g. of 3-methyltetralone, 27 g. of *o*-iodobiphenyl, and 1.4 g. of lithium, the desired hydrocarbon was obtained as a viscous oil, b. p. 218–220° (8–9 mm.); yield 14.7 g. (65%). This material crystallized on standing and an analytical sample was prepared by recrystallization from alcohol as white needles, m. p. 77–78°.

Anal. Calcd. for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.00; H, 6.62.

10-Methyl-9,10-dihydro-1,2,3,4-dibenzophenanthrene (III, R = CH_3; R′ = H).—The above hydrocarbon (14 g.) was oxidized in the usual way with an excess of perphthalic acid. The crude oxide was added to a mixture of 150 cc. of acetic acid and 90 cc. of 34% hydrobromic acid and refluxed for forty-eight hours. Worked up in the usual way, the desired hydrocarbon was obtained as shiny white plates from benzene–alcohol, m. p. 149–151°; yield 10.2 g. (73%). An analytical sample melted at 151–152°.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 94.01; H, 6.02.

The hydrocarbon formed a red picrate, m. p. 117.5–119°, in acetic acid, but this decomposed on attempted recrystallization. The trinitrobenzene derivative proved more stable and was obtained as fine orange crystals from benzene–alcohol, m. p. 138.5–139.5° (with previous softening).

Anal. Calcd. for $C_{29}H_{21}N_3O_6$: N, 8.28. Found: N, 8.14.

10-Methyl-1,2,3,4-dibenzophenanthrene (IV, R = CH_3; R′ = H).—One gram of the dihydro compound and 0.1 g. of palladium-charcoal were heated for two hours at 300–330° in an atmosphere of carbon dioxide. The hydrogen evolved amounted to 90% of the theoretical volume. The aromatic hydrocarbon was obtained from benzene–alcohol as pale yellow hexagonal prisms, m. p. 159–160°; yield 0.7 g. (70%; 33% of the theoretical from the tetralone). Recrystallization gave pure white crystals, m. p. 163.5–164°.

Anal. Calcd. for $C_{23}H_{16}$: C, 94.48; H, 5.52. Found: C, 94.53; H, 5.64.

The picrate formed red needles, m. p. 150.5–151.5°, but could not be recrystallized. The trinitrobenzene derivative was obtained as orange needles from benzene–alcohol, m. p. 161–162°.

Anal. Calcd. for $C_{29}H_{19}N_3O_6$: N, 8.31. Found: N, 8.07.

Attempted Preparation of 9,10-Dimethyl-1,2,3,4-dibenzophenanthrene

1-(2-Biphenylyl)-3,4-dimethyl-3,4-dihydronaphthalene (II, R and R′ = CH_3) was prepared as in the case of its homologs. From 14.7 g. of 3,4-dimethyltetralone-1,[5] 30 g. of *o*-iodobiphenyl and 1.55 g. of lithium, 16.1 g. (61.5%) of a very viscous oil was obtained, b. p. 217–218° (8 mm.). A sample was prepared for analysis by crystallization from alcohol as white rhombs, m. p. 78–79.5°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.86; H, 7.14. Found: C, 92.88; H, 7.31.

9,10-Dimethyl-9,10-dihydro-1,2,3,4-dibenzophenanthrene (III, R and R′ = CH_3).—The hydrocarbon above was oxidized by the action of an excess of perphthalic acid and the crude oxide cyclized with hydrobromic and acetic acids. Worked up in the usual way and purified by vacuum distillation, the product was obtained as a yellow resin.

This material formed a picrate in alcohol, m. p. 154–154.5°.

Anal. Calcd. for $C_{30}H_{23}N_3O_7$: N, 7.82. Found: N, 7.36.

Attempted Dehydrogenation of 9,10-Dimethyl-9,10-dihydro-1,2,3,4-dibenzophenanthrene.—One gram of the dihydro compound was heated for two hours at 310–350° with palladium-charcoal in an atmosphere of carbon dioxide. The volume of the gas evolved was 80% of the theoretical. On working up the mixture, the only solid compound obtained was proved, by a mixed melting point determination, to be 9-methyl-1,2,3,4-dibenzophenanthrene (m. p. 149–150°).

Dehydrogenation with sulfur at 250° failed to yield any pure isolable compound, but a picrate, identical with that of 9-methyl-1,2,3,4-dibenzophenanthrene, was obtained from the reaction product.

When chloranil was used, only the starting material could be isolated as a picrate.

Summary

By the use of suitably substituted tetralones, the olefin oxide cyclization has been used to prepare 9-methyl- and 10-methyl-1,2,3,4-dibenzophenanthrene.

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[11] This sample was rapidly recrystallized and kept under vacuum until time of analysis.

[12] Hewett, *J. Chem. Soc.*, 193 (1938).

[13] Martin, THIS JOURNAL, **58**, 1438 (1936).

[14] Higginbotham, Lapworth and Simpson, *J. Chem. Soc.*, **125**, 2339 (1924).