reaction was isopropylation of benzene. Substantially no alkylation of isobutane occurred; however, isobutane reacted, yielding *t*-butylbenzene and *m*- and *p*-*t*-butylisopropylbenzenes. The composition of the product showed that benzene reacted approximately 350 times as readily as isobutane.

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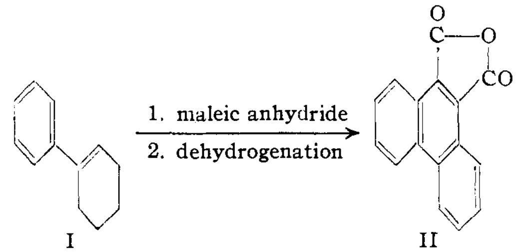
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Condensation of Phenylcycloalkenes with Maleic Anhydride. I. Synthesis of 7-Methoxy-3,4-benzphenanthrene

BY JACOB SZMUSZKOVICZ[1] AND EDWARD J. MODEST

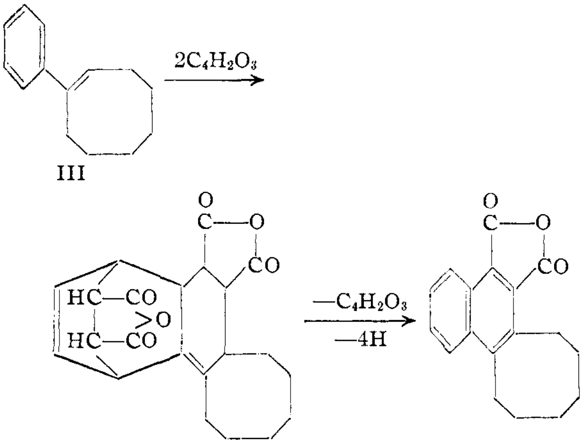
Additions to diene systems in which one double bond is in a benzene ring and the second in an alicyclic ring have not hitherto been reported.[2] The 1,2-double bond in naphthalene in conjugation with the double bond of an olefinic system,[3] with that in cyclopentene[4] or in cyclohexene,[5] is sufficiently reactive to participate in the Diels–Alder condensation. Styrene itself forms copolymers with dienophiles, but some derivatives of styrene form normal adducts.[6,7]

We now have found that 1-phenylcyclohexene-1 (I) adds maleic anhydride at 220° with formation of an amorphous adduct, which can be dehydrogenated to phenanthrene-9,10-dicarboxylic acid anhydride (II); the over-all yield is 25%. Other investigators have prepared this aromatic anhydride from bicyclohexenyl (17% yield)[8]; from phenanthrene, sodium, and carbon dioxide (25.7% yield)[9]; and from diphenyl-2-carboxylic acid (42% yield).[10]



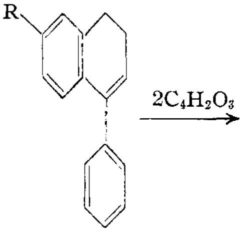
I II

1-Phenylcyclooöctene-1 (III) reacts with maleic anhydride at steam-bath temperature. The product, obtained in quantitative yield, is the bis-adduct (IV), which upon dehydrogenation with sulfur yields 1,2-cyclooöctanonaphthalene-3,4-dicarboxylic acid anhydride (V).

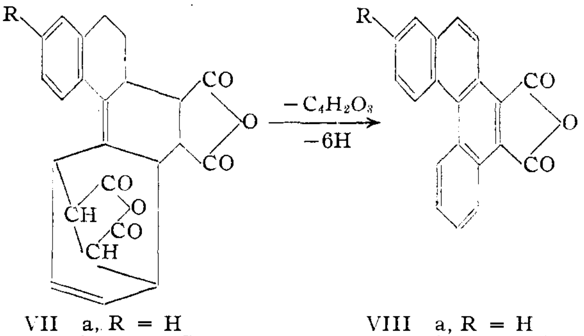


III IV V

1-Phenyl-3,4-dihydronaphthalene (VIa) and 1-phenyl-6-methoxy-3,4-dihydronaphthalene (VIb) react with maleic anhydride; the bis-adducts VIIa and VIIb are formed. The yields vary with the reaction temperature employed, from moderate at 95° to quantitative at 160°.



VI a, R = H
b, R = OCH$_3$



VII a, R = H
b, R = OCH$_3$

VIII a, R = H
b, R = OCH$_3$

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(1) On leave of absence from the Weizmann Institute of Science, Rehovoth, Palestine.

(2) Kloetzel, "Organic Reactions," Vol. IV, John Wiley and Sons, New York, N. Y., in press.

(3) Cohen and Warren, *J. Chem. Soc.*, 1315 (1937).

(4) Bachmann and Kloetzel, THIS JOURNAL, **60**, 2204 (1938).

(5) F. Bergmann and Szmuszkovicz, *ibid.*, **69**, 1367 (1947).

(6) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941).

(7) Wagner-Jauregg, *Ann.*, **491**, 1 (1931).

(8) C. Weizmann, E. Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

(9) Jeanes and Adams, *ibid.*, **59**, 2608 (1937); U. S. Patent 2,231,787 [*C. A.*, **35**, 3268 (1941)].

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Upon treatment with sulfur VIIa and VIIb are aromatized to the anhydrides VIIIa and VIIIb in 100 and 68.5% yields, respectively.

Decarboxylation of VIIIa with barium hydroxide and copper bronze affords 3,4-benzphenanthrene in 70% yield (compare ref. 5). Decarboxylation of VIIIb gives the hitherto unknown 7-methoxy-3,4-benzphenanthrene (63.7% yield).

These reactions thus constitute an efficient synthesis of 3,4-benzphenanthrene in three steps and provide a route to various substituted benzphenanthrenes. Comparable additions to systems containing the thiophene ring will be reported shortly.

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Experimental[11]

Phenanthrene-9,10-dicarboxylic Acid Anhydride, II.—1-Phenylcyclohexene-1[12] (1 g.) was heated with maleic anhydride (2 g.) at 220° for three hours. The brown viscous mass was cooled, dissolved in warm acetic acid, and precipitated with water. The light brown substance, obtained in quantitative yield, softens at 105° and melts completely at 160°. This crude material (1.7 g.) was heated with 850 mg. of sulfur for twenty minutes at 230–250°. The anhydride II was sublimed at 240–270° (0.005 mm.), 390 mg., 25%. On crystallization from acetic anhydride it forms yellow rods melting at 316–317°.

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.42; H, 3.25. Found: C, 77.00; H, 3.25.

1,2-Cycloöctanonaphthalene-3,4-dicarboxylic Acid Anhydride, V.—1-Phenylcycloöctene-1[13] (1 g.) was heated with maleic anhydride (2 g.) on the steam-bath for twenty-four hours. The brown oil was decanted from the well-formed prisms, which were washed with acetic acid and methanol; m. p. 249–250°.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.09; H, 5.80. Found: C, 68.74; H, 5.43.

The oil was dissolved in acetic acid and precipitated with water. This crude material could be purified by crystallization from dilute dioxane. The over-all yield was quantitative.

Dehydrogenation of the adduct (284 mg.) was carried out with sulfur (70 mg.) at 220–240° for fifteen minutes. The crude product sublimed at 220–240° (0.001 mm.); the yellow sublimate (150 mg., 53.5%), after crystallization from acetic acid, was obtained as yellow plates, m. p. 175–176°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.08; H, 5.63.

3,4-Benzphenanthrene.—A mixture of 1-phenyl-3,4-dihydronaphthalene[14] (1 g.) and maleic anhydride (2.5 g.) was heated on the steam-bath for twenty hours. The brown oil was dissolved in acetic acid; scratching induced crystallization. The white precipitate was filtered and washed with methanol (300 mg., 14.8%), m. p. 315–316°. Crystallized from acetic acid, it forms clusters of leaflets, m. p. 315–316° (dec.). The analysis conforms to that of the tetracarboxylic acid monoanhydride of VIIa.

Anal. Calcd. for $C_{24}H_{20}O_7$: C, 68.56; H, 4.80. Found: C, 68.43; H, 5.05.

If the mixture of starting materials was heated for twenty hours at 150–160°, 1.5 g. of the bis-adduct was obtained, m. p. 315–316°. An additional 500 mg. of white material melting at 160–170° (probably the tetracarboxylic acid) resulted from addition of water to the filtrate. The yield was quantitative.

Dehydrogenation of the adduct (200 mg.) was conducted with large excess of sulfur (75 mg.) at 270–290° for nine minutes. The excess sulfur is necessary in this case to lower the initial temperature and to prevent carbonization; The product (VIIIa) sublimed at 230–245° (0.001 mm.). m. p. 249–251°. It crystallized from acetic anhydride in the form of elongated yellow needles melting at 257–258°.[5] The yield was quantitative.

Anal. Calcd. for $C_{20}H_{10}O_3$: C, 80.53; H, 3.38. Found: C, 80.53; H, 3.38.

The same aromatic anhydride resulted from the dehydrogenation of the tetracarboxylic acid mentioned above.

The aromatic anhydride (VIIIa) (0.7 g.) was finely ground with 4 g. of crystalline barium hydroxide and 1.4 g. of copper bronze and the mixture was heated in a tube. The reaction started at 300°; water-pump suction was applied and heating was continued to 350°. The oily distillate solidified on treatment with methanol (375 mg., 70%). This material, crystallized from ethanol, m. p. 68°, was identical with 3,4-benzphenanthrene (mixed m. p. determination).

7-Methoxy-3,4-benzphenanthrene.—The addition of maleic anhydride to 1-phenyl-6-methoxy-3,4-dihydronaphthalene[15] was carried out as in the preceding case. The bis-adduct (VIIb) was obtained in 49% yield at 95° and in quantitative yield at 150–160°. It crystallized from the reaction mixture in the form of white prisms, m. p. 348–349° (dec.).

Anal. Calcd. for $C_{25}H_{20}O_7$: C, 69.44; H, 4.66. Found: C, 69.39; H, 4.81.

A mixture of VIIb (1.75 g.) and sulfur (0.49 g.) was heated to 307°. A violent reaction ensued and heating was continued at 270–280° for twenty minutes. Sublimation at 230–300° (0.001 mm.) yielded 0.91 g. (68.5%) of yellow material VIIIb, m. p. 220–225°, which crystallized from acetic anhydride as yellow needles, m. p. 233–234°.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.82; H, 3.69. Found: C, 76.90; H, 3.50.

Decarboxylation, carried out as before, led to a yellow oil (63.7% yield), which solidified on treatment with methanol and which crystallized from the same solvent in the form of colorless plates, m. p. 90–91°. The analysis conforms to that of 7-methoxy-3,4-benzphenanthrene.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.28; H, 5.59.

The picrate formed in ethanol and crystallized from the same solvent as elongated red needles, m. p. 120–121°.

Anal. Calcd. for $C_{25}H_{17}O_8N_3$: C, 61.60; H, 3.52. Found: C, 61.39; H, 3.27.

Summary

1. Four compounds of the phenylcycloalkene series have been successfully condensed with maleic anhydride.

2. An efficient synthesis of 3,4-benzphenanthrene has been developed.

3. Preparation of 7-methoxy-3,4-benzphenanthrene is described.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 9, 1948

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[11] All melting points are corrected.

[12] Auwers and Trepmann, *Ber.*, **48**, 1216 (1915).

[13] Fieser and Szmuszkovicz, THIS JOURNAL, submitted for publication.

[14] Weiss and Woidich, *Monatsh.*, **46**, 453 (1925).

[15] F. Bergmann and Szmuszkovicz, THIS JOURNAL, **69**, 1773 (1947).