The α-benzyldesoxybenzoin required in the above synthesis was prepared by alkylation of desoxybenzoin with benzyl chloride in the presence of sodamide in liquid ammonia using the general procedure developed by Hauser[9] for such alkylations.

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(9) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1161 (1959).

Diels-Alder Reactions with Dihydronaphthalenes[1]

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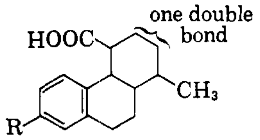
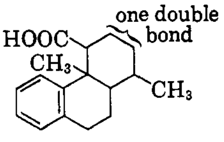
It had been shown that 1,2-dihydronaphthalene reacts with 2,4-hexadienoic acid (sorbic acid) to give a phenanthrene derivative I in 18% yield.[2] This reaction has now been extended to 7-methoxy-1,2-dihydronaphthalene and 1-methyl-3,4-dihydronaphthalene. In both cases the Diels-Alder reaction with 2,4-hexadienoic acid gave low yields of noncrystalline gums. These two products were shown to be primarily structures II and III respectively by degradation of II to 1-methyl-7-methoxyphenanthrene and III to 1-methylphenanthrene. The crude products may have been mixtures of isomers. The position of the double bond was not determined.



I. R = H
II. R = CH_3O



III

The structural isomer formed in these reactions is analogous to that formed when 2,4-hexadienoic acid reacts with styrene and its derivatives.[2] In all of these reactions, the number two carbon atom of 2,4-hexadienoic acid bonds to the α-carbon of the phenylolefin system and the number five carbon atom bonds to the β-carbon of the phenylolefin.

EXPERIMENTAL

7-Methoxy-1,2-dihydronaphthalene plus 2,4-hexadienoic acid. 7-Methoxy-1,2-dihydronaphthalene was prepared by the following sequence: β-Naphthol was hydrogenated to 1,2,3,4-tetrahydro-6-hydroxynaphthalene by the method of Stork.[3] The conversion to the methyl ether was effected with methyl sulfate.[4] Oxidation with lead tetraacetate and thermal removal of acetic acid gave 7-methoxy-1,2-dihydronaphthalene.[5]

7-Methoxy-1,2-dihydronaphthalene was treated with 2,4-hexadienoic acid in a manner similar to that used with 1,2-dihydronaphthalene.[2] Dimethylaniline was added to the extent of one-fourth the total weight of the reactants and 2% by weight of hydroquinone was also added. An atmosphere of carbon dioxide was employed. Variation in the ratio of reactants from equimolar to 1:2 and 2:1 seemed to have little effect. Raising the temperature of the reaction from 140° to 190° increased the yield of distillable product from 6 to 12.5% and lowered the yield of acidic copolymer from 35 to 12%. The runs were held at these temperatures for 100 to 150 hr.

The product II was collected as a hard, yellow gum, b.p. 150–200° (1 mm.). The neutral equivalent was 274, which agrees with 272 which is that calculated for $C_{17}H_{20}O_3$.

The carbon skeleton of the adduct was indicated by its degradation to 1-methyl-7-methoxyphenanthrene. A mixture of 0.95 g. of adduct and 0.4 g. of 10% palladium-carbon catalyst was heated for 20 min. at 300–315° in a carbon dioxide atmosphere. The crude product was dissolved in acetone and the catalyst was removed by filtration. The acetone was replaced by benzene and the solution washed with aqueous alkali. After evaporative distillation and recrystallization of the distillate from methanol, 40 mg. (5%) of white plates, m.p. 134–135°, were isolated. The melting point was not depressed when mixed with an authentic sample of 1-methyl-7-methoxyphenanthrene.[6]

1-Methyl-3,4-dihydronaphthalene plus 2,4-hexadienoic acid. 1-Methyl-3,4-dihydronaphthalene was prepared by the method of English and Cavaglieri.[7]

A mixture of 35 g. of this compound, 22.4 g. of 2,4-hexandienoic acid, 5 ml. of dimethylaniline, and 1.5 g. of hydroquinone was heated at 190° for 100 hr. in a carbon dioxide atmosphere. An ether solution of the reaction mixture was extracted with 5% potassium hydroxide solution and the aqueous extract precipitated with dilute hydrochloric acid. Evaporative distillation of the precipitated acid at 170–210° (1 mm.) gave 6.2 g. (12%) of distillate and 6.4 g. (12.5%) of acidic copolymer. The distillate was a hard yellow, acidic gum and is believed to possess structure III. The position of the double bond is uncertain.

The carbon skeleton of III was indicated by its degradation to 1-methylphenanthrene. The experimental conditions were identical with those used in the degradation of II to 1-methyl-7-methoxyphenanthrene. The yield of 1-methylphenanthrene, m.p. 117–119°, was 30%. The melting point was not depressed when mixed with an authentic sample of 1-methylphenanthrene and the identity was further checked by preparation of the picrate, m.p. 134–137°.

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(1) Grateful acknowledgment is made for the support of this research by the Bristol Laboratories Inc., Syracuse, N. Y.

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(3) G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).

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(6) This sample was kindly supplied by Dr. Andre S. Dreiding of the Detroit Institute for Cancer Research.

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Preparation of Some Bicyclic Nitriles by the Diels-Alder Reaction

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As part of a program to relate the dielectric properties of some nitriles to their structures it