

A New Route to Mellophanic Dianhydride

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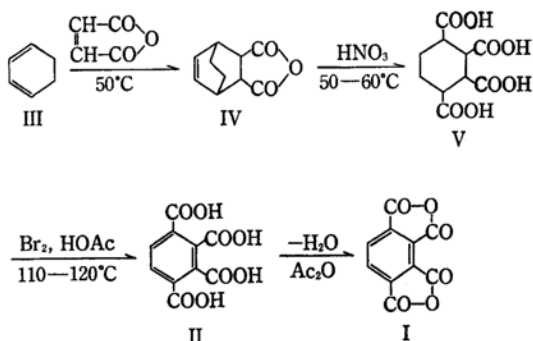
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Mellophanic dianhydride (I), the dianhydride of benzene 1, 2, 3, 4-tetracarboxylic acid (II), is thought to be an interesting raw material for high-temperature-resistant polyimide. Until the present time, however, there has been no satisfactory method for preparing I of a high purity in a large quantity, although convenient methods have been developed for the preparation of pyromellitic dianhydride.^{1,2}

The present author wishes to report a new method of synthesizing I, starting from 1, 3-cyclohexadiene (III) and maleic anhydride.

The reaction sequence is shown below:



Bicyclo[2, 2, 2]-5-octene-2, 3-dicarboxylic anhydride (IV) was easily obtained by the Diels-Alder reaction of III with maleic anhydride.²⁾ The liquid-phase nitric acid oxidation of IV at 50–

60°C, catalyzed by vanadium, afforded cyclohexane-1, 2, 3, 4-tetracarboxylic acid (V), mp 167°C (monohydrate), in a 70–80% yield.

The configurational relationship between the four carboxyl groups has been identified as 1, *cis*-2, *cis*-3, *cis*-4, by the fact that bicyclo[2, 2, 2]-octene-2 gave *cis*-1, 4-dicarboxycyclohexane in the nitric acid oxidation, and by examining the NMR spectrum of the V-tetramethyl ester. The dianhydride, mp 199–199.4°C, was obtained by treating V with excess acetic anhydride. The catalytic dehydrogenation of V using a Pd catalyst has been unsuccessful because of tar formation. II has been smoothly prepared by the oxidative dehydrogenation of V using bromine. The treatment of V with a three-fold equivalent of bromine in acetic acid at 110–120°C afforded II in an excellent yield.

The subsequent dehydration was carried out by treating II with excess acetic anhydride under reflux. The purification of the resultant dianhydride by sublimation, followed by recrystallization from benzene, afforded pure I mp 196–197°C (lit.³⁾ 193–196°C). The structure was further confirmed by elemental analysis and by a study of the IR spectrum.

An interesting high-temperature-resistant polyimide has been obtained by the polycondensation of I with aromatic diamine. The thermal stability of polymellophanimide is similar to that of the corresponding polypyromellitimide.

A detailed discussion will be presented elsewhere.

1) L. I. Smith and G. D. Byrkit, *J. Am. Chem. Soc.*, **55**, 4305 (1933); J. Braun and G. Lemke, *Ber.*, **57**, 681 (1924); French Pat. 1409396 (Aug. 27, 1965).

2) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

3) H. Bamford and J. L. Simonson, *J. Chem. Soc.*, **97**, 1904 (1910).