Preparation and Acetalization of Cyclo-oct-5-ene-1,2-dione

By PETER YATES* and E. G. LEWARS

(*Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada*)

Summary Oxidation of cyclo-oct-5-ene-*trans*-1,2-diol with dimethyl sulphoxide and acetic anhydride gives cyclo-oct-5-ene-1,2-dione, which with ethylene glycol and toluene-*p*-sulphonic acid forms a monoacetal and two diacetals, whose structures have been assigned on the basis of deacetalization experiments and mass and ^{1}H n.m.r. spectroscopy.

Two recent reports on the acetalization of α-diketones by Fuchs[1] and Cohen, Harper, and Levine[2] prompt us to report on an investigation of the preparation and acetalization of cyclo-oct-5-ene-1,2-dione (I).

Treatment of cyclo-octa-1,5-diene with performic acid gave cyclo-oct-5-ene-*trans*-1,2-diol (II)† in 55% yield as a colourless liquid, b.p. 100° (0·5 mmHg). Oxidation of (II) with dimethyl sulphoxide–acetic anhydride[5] gave (I) in 40% yield as a very pale yellow solid, m.p. 35—36°. The dione (I) gave with *o*-phenylenediamine a quinoxaline, m.p. 118—119°.

Treatment of (I) for several days with ethylene glycol and toluene-*p*-sulphonic acid in boiling dichloromethane in a Soxhlet apparatus with calcium hydride or molecular sieves in the thimble gave the monoacetal (III), m.p. 63·5—64·5°, and the isomeric diacetals (IV) (m.p. 67·5—68°) and

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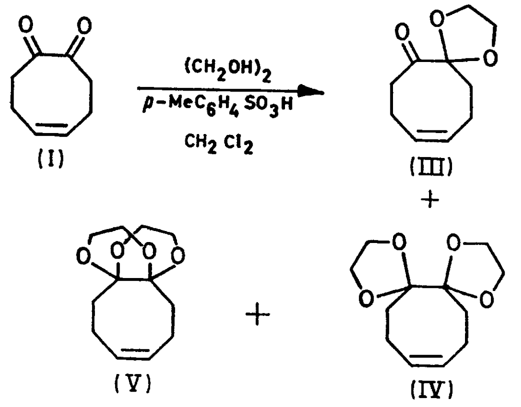
† Reports in the patent literature[3] and in a review[4] refer to the preparation of (II) from the corresponding epoxide. Satisfactory elemental analytical and spectroscopic data have been obtained for all compounds.

(V) (m.p. 121—122°). Diacetal (IV) was obtained in good yield when the reaction was allowed to proceed for 2 weeks, while diacetal (V) was best isolated after 2—3 days, albeit in poor yield. The monoacetal (III) was best obtained by treatment of (I) with acetone ethylene acetal and boron trifluoride etherate for 5 h at 25°; the major product was (III), accompanied by (IV) and unconsumed (I).



The assignment of the diacetal structures is based on deacetalization studies. The product assigned structure (IV) was converted by boron trifluoride etherate in acetone at room temperature into the monoacetal (III). The product assigned structure (V) was converted under these conditions into (I). The monoacetal (III) was stable under these conditions, but could be hydrolysed to (I) by treatment with 6N-hydrochloric acid for an extended period.

The mass spectra of the diacetals and their relationship to the mass spectrum of the monoacetal are in accord with these assignments. In particular, the peak at *m/e* 125 in the spectra of both (III) and (IV) most probably corresponds to an ion that has been observed previously as a distinctive feature of the spectra of ethylene acetals of cyclic ketones;[6] the relative abundance of the peak at *m/e* 125 in the spectrum of (V) is much lower.

The relationship among the ^{1}H n.m.r. spectra of (III)—(V) also corroborates these structural assignments. The multiplets due to the protons of the $-OCH_2{\cdot}CH_2O-$ groups in the spectra of (III) and (IV) are relatively narrow, in contrast to the multiplet due to the protons of the $-OCH_2{\cdot}CH_2O-$ groups in the spectrum of (V), which is much broader. This difference can be attributed to the fact that the $-OCH_2{\cdot}CH_2O-$ groups in both (III) and (IV) are incorporated into 1,3-dioxolan systems, whereas in (V) they form part of more rigid 1,4-dioxan systems.‡

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‡ *Cf.* ref. 1.

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