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AN UNUSUAL RING CLEAVAGE: FORMATION OF OCTA-2,4,6-TRIEN-1,8-DIAL FROM *TRANS*-7,8-DIACETOXYBICYCLO[4,2,0]OCTA-2,4-DIENE

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COPE *et al.*[1] prepared *trans*-7,8-diacetoxybicyclo[4,2,0]octa-2,4-diene (I), m.p. 62°, by mercuric acetate oxidation of cycloöctatetraene. The structure of I was proven by hydrogenation to a tetrahydro derivative, followed by hydrolysis to a saturated glycol identical with an authentic specimen of *trans*-7,8-dihydroxybicyclo[4,2,0]octane synthesized from *cis*-hexahydrophthalic acid. We have found that the NMR spectrum[2] of I (60 Mc/s) has two methyl bands (τ, 8.00, 7.95) thus confirming the *trans* disposition of the acetoxy groups. No detectable amount of the isomeric 1,2-diacetoxycycloocta-3,5,7-triene was present even after refluxing I in benzene for 1 hr.

In connection with other work, we were interested in obtaining the unsaturated glycol (II) itself, the preparation of which has not been reported. Alkaline hydrolysis of I gave only intractable material, which, however, was observed to give an immediate crimson precipitate with 2,4-dinitrophenylhydrazine reagent. As it was suspected that the carbonyl compound formed was undergoing further condensation under the reaction conditions, a lithium aluminium hydride cleavage of I was tried. Reaction

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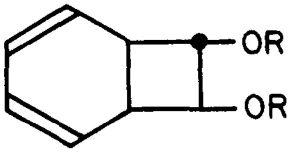
[1] A.C. Cope, N.A. Nelson and D.S. Smith, *J.Amer.Chem.Soc.* **76**, 1100 (1954).

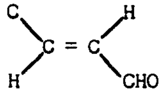
[2] L.M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry.* Pergamon Press, London, New York (1959).



I, R = $COCH_3$

II, R = H

III

at 25° for 2 min in ether gave, on normal working up, not II, but variable quantities of a crystalline compound III. This was found to be an α:β-unsaturated carbonyl compound from its infra-red spectrum (C=O at 1680 cm^{-1}, C=C at 1624, 1610 cm^{-1}, no OH absorption), and from the NMR spectrum ($CDCl_3$ soln.) the carbonyl function was found to be aldehydic (doublet, 0.27τ, J, 7.2 cps). All the other protons were olefinic (2.6-3.8τ), a quartet centred on 3.8τ was due to the proton coupled with the aledhyde proton. In addition to the 7.2 cps spacing, it showed a spacing of 14.1 cps, which must be due to coupling with a proton situated <u>trans</u> on the double bond. This is similar to the coupling present in <u>trans</u>-croton-aldehyde.[3] The partial structure  was therefore indicated. The olefinic protons at lower field could not be analysed satisfactorily by first order treatment, but intensity measurements showed that the ratio of the olefinic protons: aldehyde proton was 3:1. Clearly, III was formed by a facile oxidation of some intermediate produced during the lithium aluminium hydride cleavage.

By suitably modifying the working up conditions, viz. addition of excess ethyl acetate to the ether slurry, followed by washing the organic layer with dilute phosphoric acid and then with 2% sodium hydroxide, the

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[3] J.A. Pople and T. Schaefer, <u>Molec.Phys.</u> **3**, 547 (1960).

yield could be improved to 50-60%. Rapid crystallisation from methylene chloride-petroleum ether at -70°C gave an analytical sample of III, as pale yellow needles, m.p. 140° (d) (Found C, 70.02, H, 6.03; $C_8H_8O_2$ requires C, 70.57, H, 5.88%). The compound was not very stable in air and was detectably altered to less soluble material in a few hours. On hydrogenation (ethyl acetate/Pd black) 3 moles of hydrogen were taken up smoothly in 15 min. The product (C=O at 1720 cm^{-1}) was oxidized by bromine water in presence of sodium bicarbonate to an acid, m.p. 140°, in good yield. The latter was identical (mixed m.p., infra-red spectrum) with an authentic sample of suberic acid, $COCH(CH_2)_6COOH$.

The above evidence defined the structure of III as octa-2,4,6-trien-1,8-dial, with the 2- and 6- double bonds in the <u>trans</u> configuration. It only remained to determine the geometry of the central double bond. This was found to be also <u>trans</u> by the close similarity of the ultra-violet spectrum of III, (λ_{max}^{MeOH} 313 mμ log ε, 4.59, shoulder at 319 mμ, log ε, 4.56) with that of all-<u>trans</u>-2,4,6-octa-trienal[4] (λ_{max}^{EtOH} 315 mμ, log ε, 4.57). It has been pointed out by Braude[5], that in conjugated systems terminated by two oxygen atoms, only one of the carbonyl functions takes part in spectral conjugation. Furthermore, III failed to isomerize in presence of iodine.

The formation of the unsaturated dialdehyde from I can be rationalised as follows. Cleavage with lithium aluminium hydride would be expected to give dianion A. Increase in resonance in going from A to B, and charge repulsion in A may provide sufficient driving force for the ring cleavage to dianion B. This change can be considered as the reverse of ring formation

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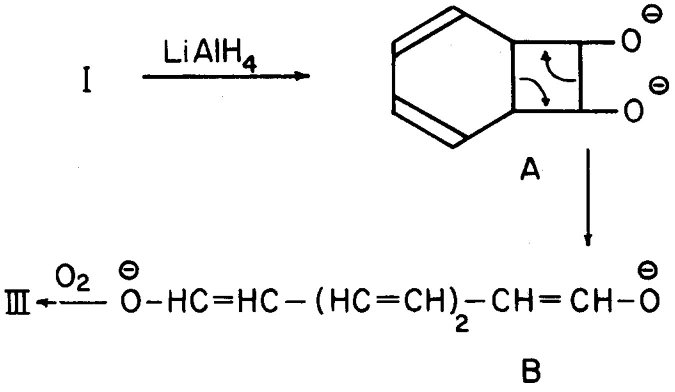
[4] E.R. Blout and M. Fields, <u>J.Amer.Chem.Soc.</u> <u>70</u>, 189 (1948).

[5] E.A. Braude in <u>Determination of Organic Structures by Physical Methods</u> (Edited by Braude and Nachod) p. 148. Academic Press, New York (1955).

by a "four-centre-type" reaction.[6] Protonation of B might take place at



various sites to give a vinylogous ene-diol, a diene aldehyde or a triene-aldehyde-alcohol, all of which should be readily oxidizable to III. Indeed, the ethyl acetate solution (prior to shaking with alkali in air), from the lithium aluminium hydride reaction, contained a strongly reducing species as indicated by a positive test (red colour) with 2,3,5-triphenyltetrazolium chloride.[7] This test was negative for III itself.

It seems unlikely that the cleavage takes place through a cycloöctatriene intermediate, as the conversion of bicycloöcta[4,2,0]-2,4-diene to cycloöcta-1,3,5-triene does not proceed below 30°.[8] Furthermore, there is no particular driving force for this change in the present case.

It is of interest that irradiation of I is reported[9] to give all-*trans*-1,8-diacetoxyocta-1,3,5,7-tetraene; the compound does not seem to have been characterized beyond its ultra-violet spectrum.

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[6] J. Hine, *Physical Organic Chemistry.* McGraw-Hill, Book Co. Inc., New York (1956).

[7] W.J. Mador and R.R. Buck, *Analyt.Chem.* **24**, 666 (1952).

[8] A.C. Cope, A.C. Haven, F.L. Ramp and E.R. Trumbull, *J.Amer.Chem.Soc.* **74**, 4867 (1952).

[9] D.H.R. Barton, *Helv.Chim.Acta* **42**, 2604 (1959).