

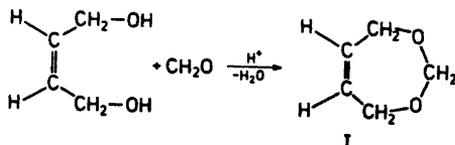
Reactions between Formaldehyde and Polyhydric Alcohols. II.*

A Fourteen-membered Cyclic Acetal from (Z)-2-Butene-1,4-diol and Paraformaldehyde

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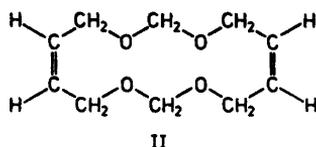
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It was previously described that the reaction between (Z)-2-butene-1,4-diol and paraformaldehyde led to 2*H*-4,7-dihydro-1,3-dioxepin (I) and a viscous residue.³



We have reinvestigated this reaction and isolated a novel fourteen-membered cyclic acetal (II) from the residue.

Elemental analysis and mass spectrometry of the new compound corresponded to the molecular composition $C_{10}H_{18}O_4$. The signals of the proton magnetic resonance spectrum of compound II have almost the same chemical shifts as those found in the spectrum of compound I.³ However, compound II shows larger splittings of the signals from the vinylic and allylic protons, thus allowing the identification of these protons as an AA'M₂M₂' system. From these findings compound II was assigned the structure (5*Z*,12*Z*)-1,3,8,10-tetraoxacyclotetradeca-5,12-diene.



The conformation of saturated cyclic compounds containing the 1,3-dioxa-grouping has been studied extensively,⁴ and the conformation of

1,3,8,10-tetraoxacyclotetradecane (the saturated analogue of II) was recently established by X-ray crystallography.⁵ To our knowledge, no conformational analysis has been carried out on unsaturated compounds containing the 1,3-dioxa-grouping, and we are now investigating the conformation of II.

Experimental. (5*Z*,12*Z*)-1,3,8,10-Tetraoxacyclotetradeca-5,12-diene (II). (Z)-2-Butene-1,4-diol (176 g, 2 mol), paraformaldehyde (60 g, 2 mol of CH_2O), benzene (25 ml) and *p*-toluenesulfonic acid (0.1 g) was heated on an oil bath kept at 86 °C for 24 h. The water formed by the reaction was removed by means of a Dean-Stark-separator. The reaction mixture was cooled to room temperature and stirred for 24 h with solid sodium hydroxide (5 g). The sodium hydroxide was removed and the reaction mixture dissolved in dichloromethane and filtered through silica gel. Distillation through a 20 cm column packed with Fenske rings gave 115 g (57 %) of pure 2*H*-4,7-dihydro-1,3-dioxepin (b.p. 127–129 °C) leaving a viscous residue (41 g). The distillation was continued at diminished pressure (0.3 Torr) with the residue heated to 170–180 °C on an oil bath. During 24 h a product solidified in the condenser. Recrystallization from abs. ethanol gave 1.0 g of analytically pure II, m.p. 114.5–115.0 °C. (Found: C 60.03; H 8.06. Calc. for $C_{10}H_{18}O_4$: C 59.98; H 8.05). Mass spectra were recorded on an AEI MS902 instrument at 70 eV. Compound I: *m/e* 100 (M^+ 5 %), 70 (56), 69 (19), 43 (19), 42 (100), 41 (56). Compound II: *m/e* 200 (M^+ 0.3 %), 100 (12), 70 (40), 69 (100), 68 (24), 53 (32), 42 (25), 41 (21), 40 (25). NMR spectra were recorded on a Bruker HX 90 E instrument. Compound II ($CDCl_3$, ca. 30 °C): δ 5.87 [=C–H (A/A')], 4.13 [=C–CH₂ (M_2/M_2')], 4.72 (s, O–CH₂–O). $^3J_{AA'}$ = 11.0 Hz, $^5J_{MM'}$ = 0 Hz, $^3J_{AM}$ = \pm 7.5 Hz, $^4J_{AM'}$ = \mp 1.1 Hz.

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