First Preparation of an Acetal of Buta-2,3-dienal, the Simplest, so far Unknown, Allenic Aldehyde

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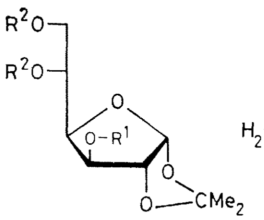
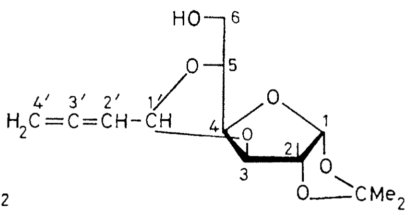
Summary A crystalline, six-membered, cyclic acetal of buta-2,3-dienal was obtained in 83% yield by the treatment of 3-*O*-(*Z*-but-1-en-3-ynyl)-1,2-*O*-isopropylidene-α-D-glucofuranose with potassium hydroxide, and in 31% yield by the mild, acidic hydrolysis of 3-*O*-(*E*-but-1-en-3-ynyl)-1,2, 5,6-di-*O*-isopropylidene-α-D-glucofuranose.



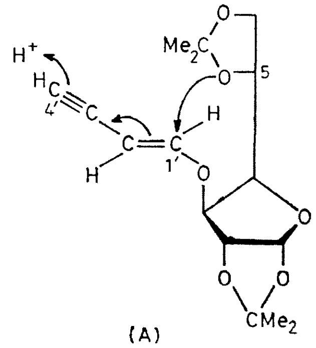
(1) R^1 = (*E*)-CH≡CCH=CH, R^2, R^2 = $Me_2C<$

(2) R^1 = (*Z*)-CH≡CCH=CH R^2, R^2 = $Me_2C<$

(3) R = (*Z*)-CH≡CCH=CH, R^2 = H



(4)



(A)

No acetal of buta-2,3-dienal has been described and very few acetals of α-allenic aldehydes are known[1] Several syntheses of the α-allenic aldehydes themselves have been reported,[2,3] but it seems that there is only one detailed report on the preparation of gram quantities of crude samples[2] The preparation of buta-2,3-dienal by any of these methods[2,3] was either not considered or reported to fail We report here the synthesis of a crystalline, cyclic acetal (**4**) of buta-2,3-dienal in two or three steps from commercially available starting materials by a route which involves only cheap reagents

A 45:55 mixture of the *trans*-(**1**) and *cis*-(**2**) enynyl ethers may be prepared in 96% yield from 'diacetone-glucose' and 2,7-dimethylocta-3,5-diyne-2,7-diol[4] A 0·5 M solution of the *trans*-ether (**1**) in 60% aqueous acetic acid was heated for 30 min at 45 °C, neutralized with KOH, and extracted with ether Silica gel column chromatography (ether–light petroleum, 3:1) of the extract gave, as almost the only mobile component, the allenic acetal (**4**) (31%), m p 147—148 °C after one recrystallization (ether–light petroleum) This may result from protonation of C-4′ followed by, or concerted with, attack of the incipient carbenium ion at C-1′ by the dioxolan oxygen 5-O [see (A)]. The first steps thus would be the same as those of the hydrolysis of enynyl ethers to allenic ketones in D_2O[5]

A similar treatment (extended to 75 min) of the *cis*-ether (**2**) gave two products Elution from a silica gel column, first with 2-isopropoxypropane and then with ether, gave the allenic acetal (**4**) (6 6%) followed by the 5,6-diol (**3**) (60%) A 0·25 M solution of this diol in oxolan was heated for 2 h at 60 °C in the presence of KOH (0 66 equiv) and hydroquinone (0 2 equiv) T l c (ether–light petroleum, 3:1) then indicated the presence of only one component, the acetal (**4**), which was extracted with ether and obtained crystalline on evaporation of solvent (m p 108—140 °C; 83%).

Preparations of acetal (**4**) by these two methods gave samples which, but for their melting behaviour, were found to be identical in every respect. Three recrystallizations of the sample with m.p. 108—140 °C gave a derivative with m.p. 148 °C which, however, exhibited the same optical rotation and i.r. and ^1H n.m.r. spectra as the combined mother-liquors. Such behaviour is indicative of a mixture of dimorphic forms in the solid state,[†] with the following common properties: $[\alpha]_D^{20}$ 13·4° (*c* 1 in CH_2Cl_2); ν_{max} (KBr) 1960, 1985 (C=C=C), and 3470 cm^{-1} (OH); ^1H n.m.r. (250 MHz, $CDCl_3$, Me_4Si) δ 1·33, 1·50 (2s, 6H, CMe_2), 2·06 (1H, OH), 3·87 (dd, 1H, $J_{5,6a}$ 4·5 Hz, $J_{6a,6b}$ 12 Hz, 6a-H), 3·98 (dd, 1H, $J_{5,6b}$ 7 Hz, 6b-H), 4·05 (dd, 1H, $J_{3,4}$ 2Hz, $J_{4,5}$ 1·7 Hz, 4-H), 4·24 (m, 1H, 5-H), 4·33 (d, 1H, 3-H), 4·60 (d, 1H, $J_{1,2}$ 3·7 Hz, 2-H), 4·97 (dd, 2H, $J_{2',4'}$ 6 Hz, $J_{1',4'}$, 1Hz, 2 × 4′-H, 5·26 (q, 1H, $J_{1',2'}$ 6 Hz, 2′-H), 5·41 (ddd, 1H, 1′-H), and 6·01 (d, 1H, 1-H); ^{13}C n.m.r. (15·08 MHz, CD_3COCD_3, Me_4Si) 26·8, 27·3 (2 × CH_3), 62·8 (t, C-6), 73·6, 75·0, 78·2, 84·7 (4 × d, C-2 to C-5), 77·8 (t, C-4′), 91·2 (d, C-2′), 93·9 (d, C-1) 105·6 (d, C-1′), 111·9 (s, CMe_2), and 209·8 (s, C-3′) p.p.m. Analyses (C, H) were satisfactory for the formula $C_{13}H_{18}O_6$. The ether function in (**1**) is too labile to allow the preparation of the *trans*-analogue of the diol (**3**). Separate treatment of (**1**) by the first method and (**2**) by the second gave the acetal (**4**) in 38% overall yield from 'diacetone-glucose.' There is no obvious limit to the scaling up of these preparations other than the potential hazards of handling conjugated acetylenes. However, we have repeatedly prepared the ethers (**1**), (**2**), and some analogues without accident on the 100 g scale.

Preliminary investigations[‡] indicated that the acetal (**4**) could be hydrolysed by stirring a 10% solution in CH_2Cl_2 for 6 h at room temperature, in the presence of the silica gel–sulphuric acid reagent of Huet *et al.*[6] Preparative g.l.c. gave a crude sample with a pungent smell, the properties of which were compatible with the presence of buta-2,3-dienal [*m/e* 68; ν_{max} 1695 (CO), 1930, and 1955 cm^{-1} (C=C=C), ^1H n.m.r. δ 5·36 (d, 2H, $J_{2,4}$ 6·3 Hz, CH_2), 5·86 (sex. 1H, $J_{1,2}$ 7 Hz, 2-H), and 9·55 (d, 1H, CHO)].

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[†] This interpretation was suggested as the more plausible one by one referee.

[‡] Monitored by g.l.c. on a 10% Carbowax, 20 M, Gas Chrom Q, 150 cm column, at 50 °C.

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