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Note

Bromination of levoglucosenone

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In a program on pyrolytic conversion of cellulosic materials, we have developed a method for the preparation of levoglucosenone (**1**; 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) and have been investigating its potentialities as a synthetic intermediate[1-3]. We now report on the bromination of levoglucosenone, and isolation of the products.

Dropwise addition of molecular bromine to a cooled solution of levoglucosenone in chloroform resulted in a rapid, exothermic reaction. Decolorization occurred, and t.l.c. analysis showed the presence of three compounds [R_F 0.50 (**1**), 0.56, and 0.60] until an excess of two mole-equivalents of bromine (as Br) had been added, whereupon the bromine color remained, and t.l.c. analysis showed the presence of only one compound (R_F 0.60).

Removal of the excess of bromine was accomplished by washing the chloroform solution with dilute, aqueous sodium hydroxide; the solution was dried, and evaporated, to give a waxy solid, from which an analytically pure sample was obtained on crystallization from hexane. Both spectral and micro analyses showed this compound to be the monobromide **2**. The mass spectrum of **2** was similar to that of **1**, in that no parent molecular-ion was observed[4-6]; both compounds appear to lose CO readily. Thus, the highest observed mass for **2** was 176, 178 m.u. The ^{1}H-n.m.r. spectrum of **2** was very similar to that[6] of **1** (see Table I). Loss of the resonance at δ 6.13, and collapse of the doublets at δ 7.40 and of the doublet at δ 5.36 for **1**, all strongly supported the probability that H-3 in **1** had been replaced by a bromine atom. The downfield shift of the H-4 resonance from δ 7.40 to δ 7.71 was strong evidence for an adjacent bromine atom, and its chemical shift indicated the continued presence of the conjugated, alkenic functionality. Proton–proton decoupling of the resonance at δ 7.71 caused a decrease in the width of the multiplet at δ 5.15 by ~5 Hz, indicating the adjacency of the protons assigned as H-4 and H-5. In comparison with the infrared spectrum of **1**, there was a broadening of the carbonyl absorption,

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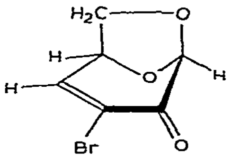
TABLE I

^{1}H-N.M.R. CHEMICAL-SHIFT DATA[a] (p.p.m.) AT 60 MHz FOR LEVOGLUCOSENONE (**1**) AND TWO DERIVATIVES IN $CDCl_3$

Compound	*H-1*	*H-3*	*H-2 + 4*	*H-4*	*H-5*	*H_2-6* (exo, endo)
1	5.36 d	6.13 dd	—	7.40 dd	5.05 m	3.83 m
2	5.60 s	—	—	7.71 d	5.15 m	3.90 m
3	5.66 s	4.26 d	3.83 m	—	4.81 m	4.36 m

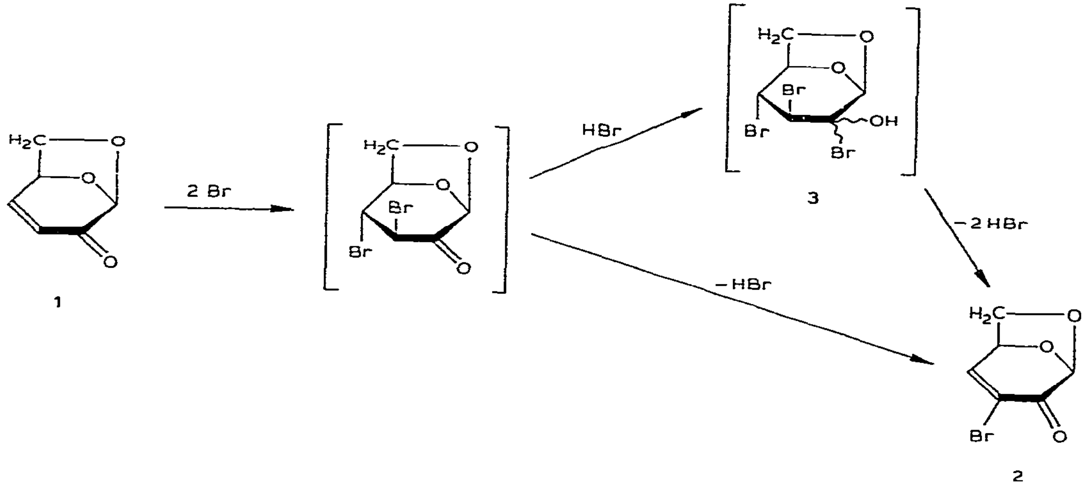
[a] Key: d = doublet, dd = doublet of doublets, m = multiplet, s = singlet. Coupling-constant data: compound **1**, $J_{1,3}$ ~2 Hz, long range; $J_{3,4}$ 10 Hz; H-5 (w/2 12 Hz–poorly resolved); H-6 (w/2 11 Hz); compound **2**, $J_{4,5}$ 5 Hz; H-5 (w/2 12 Hz); H-6 (w/2 5 Hz); compound **3**, $J_{3,4}$ 6 Hz; H-2 + 4 (w/2 14 Hz); H-5 (w/2 10 Hz); H-6 (w/2 5 Hz).

and a shift to higher frequency from 1705, 1687 cm^{-1} to 1730, 1695 cm^{-1}. There was also a decrease in the frequency of the C=C absorbance from 1595, 1370 (**1**) to 1575, 1365 cm^{-1}, which is frequently observed on replacement of a proton in an alkenic group[7] by a bromine atom. These data support the ^{1}H-n.m.r. evidence that the structure of **2** is as follows.



2

Removal of the excess of bromine under vacuum at 20°, instead of by washing the reaction mixture with aqueous sodium hydroxide, gave a brown oil which crystallized from acetone–cyclohexane, to yield long, colorless needle-like crystals of **3** melting sharply at 103–104° (*cf.*, **2**, m.p. 47–48°). The ^{1}H-n.m.r. spectrum of **3** in acetone-d_6 (used because of its insolubility in $CDCl_3$, unlike **2**) showed the presence of 7 protons, and the complete absence of the alkenic functionality. Infrared analysis revealed the complete absence of a carbonyl stretch, expected at ~1700 cm^{-1}, and strong OH stretching was observed at 3400 and 3150 cm^{-1}. Both the mass spectrum and micro-analyses were inconclusive. The mass spectrum showed a molecular ion at 204, 206 m.u., which was not observed with a pure sample of **2**. This can only be interpreted as a monobrominated derivative of **1**, consistent with that expected for **2**. Micro-analytical results were consistently low in bromine, due to dehydrobromination on standing. On dissolution of **3** in warm chloroform, observable evolution of hydrogen bromide resulted in the formation of **2**. A possible explanation for this unusual reaction leading to the formation of **2** is shown in Scheme 1.



We have found only one example of bromination of an α,β-unsaturated ketone to a bromo compound that is similarly dehydrobrominated. Nazarov and Zav'yalov[8] conducted a reaction of this kind with 2-cyclohexen-1-one, to produce 2-bromo-2-cyclohexen-1-one.

DISCUSSION

Generally, reactions of this nature may be conducted in chloroform or carbon tetrachloride, but, in this case, boiling under reflux with a three-fold excess of bromine in carbon tetrachloride for 48 h caused no reaction.

It is possible that **3** may be formed in the presence of hydrogen bromide, which could either be produced because of moisture in the bromine sample, or by a radical reaction between bromine and chloroform to afford bromotrichloromethane plus hydrogen bromide. The presence of four strongly electron-withdrawing groups in the ring could conceptually make compound **3** stable enough to be isolated, but rapid decomposition caused unsatisfactory microanalyses.

EXPERIMENTAL

All ^{1}H-n.m.r. spectra were recorded with a Varian E.M. 360 spectrometer. Mass-spectral analysis was conducted with a Varian M.A.T. III instrument. T.l.c. analysis was performed on Baker-flex Silica Gel IB2-F (J. T. Baker Chemical Co.). Microanalyses were conducted by Galbraith Laboratories, Inc.

Preparation of 3-bromolevoglucosenone (**2**). — To a solution of levoglucosenone (**1**; 1.02 g, 8.1 mmol) in chloroform (10 mL), cooled in an ice bath, was added bromine (0.4 mL, 2 equiv.), dropwise, at such a rate as to keep the temperature at 25°, bromine decolorization being rapid until the two equivalents had been used up. The solution was washed with 1% aqueous sodium hydroxide solution, to remove the slight excess of bromine, and with water, and dried (anhydrous sodium sulfate). T.l.c. then showed one spot, R_F 0.51 in 1:1 hexane–ethyl acetate, and evaporation afforded a reddish-brown oil that readily crystallized from diethyl ether–hexane; yield (1.6 g, 97%), m.p. 47–48°; ν_{max}^{NaCl} 2970, 2920 (C–H stretch) and 1730, 1695 cm^{-1} (conjugated CO stretch, vs); mass spectrum: parent *m/z* 204, 206 (not observed); 176, 178 ($M^{+\cdot}$ — CO or C_2H_4, 75%); 159, 161, (176, $178^{+\cdot}$ — $OH^{\cdot}$, 4.5%); 149, 151 (176, $178^{+\cdot}$ — $C_2H_3^{\cdot}$, 12%); 131, 133 (12%); 117, 119 (15%); and 97 (176, $178^{+\cdot}$ — Br, 100%).

Anal. Calc. for $C_6H_5BrO_3$: C, 35.12; H, 2.44; Br, 39.02. Found: C, 35.10; H, 2.50; Br, 38.86.

Bromination of levoglucosenone. — To a solution of levoglucosenone (0.37 g, 2.9 mmol) in chloroform (10 mL) was added an excess of bromine, as already described. Evaporation of the excess of bromine and the chloroform under vacuum at room temperature gave a brown oil that crystallized from diethyl ether, and was recrystallized from acetone–cyclohexane; yield 0.41 g, m.p. 103–104°; ν_{max}^{KBr} 3400, 3150 (OH), 2950, and 2900 cm^{-1} (CH); no C=O or C=C absorptions were observed: *m/z* 204, 206 (1.7%); 176, 178 ($M^{+\cdot}$ — CO, 30%); 159, 161 (176, $178^{+\cdot}$ — $OH^{\cdot}$; 7%); 149, 151 (5%); 143 (14%); 131, 133, 139 (9%); 119, 111, 113 (9%); 105, 107 (5%); 97 (32%); 69 (35%); 53 (60%); and 41 (100%). The microanalytical results were consistently low in bromine, due to dehydrobromination.

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