Note

Two carbohydrate chloralides

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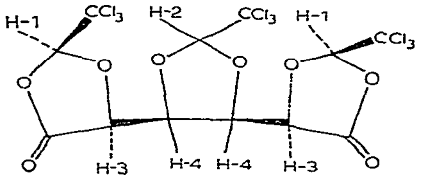
Meldrum and Bhatt[1] reported that the condensation of galactaric acid with chloral in sulphuric acid gave a 1:3 adduct, m.p. 200–201°. Soon afterwards, Shah and Alimchandani[2] reported that the product had m.p. 198° (from ether), but that crystallization from ethanol gave a product having m.p. 174–175°. A re-investigation of this reaction has now given a crude product, m.p. 148–152°, which, on crystallization from ether and then ethanol, gave a product $C_{12}H_7Cl_9O_8$, m.p. 172°. The molecular formula and an interpretation of the p.m.r. spectrum show that this product is the bischloralide monotrichloroethylidene derivative **1**.



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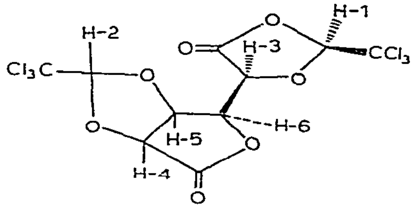

2

A solution of compound **1** in perdeuterioacetone gave a relatively simple p.m.r. spectrum consisting of a 2-proton doublet at δ 6.22 (*J* 1.5 Hz), a 1-proton singlet at δ 5.59, and two more-complex, but narrow, groups of signals near δ 5.5 and 5.1, each accounting for two protons. The chemical shift of the low-field doublet, attributable to the two H-1 protons, is characteristic of the protons at C-2 in a trichloromethyl-1,3-dioxolan-4-one (chloralide) ring[3], and the long-range coupling (*J* 1.5 Hz) between the protons at C-2 and C-5 in such a system may be characteristic of a *cis*-arrangement of these protons[4]. The singlet at δ 5.59 can be assigned to H-2 at C-2 in the central 1,3-dioxolane ring, as long-range splitting has only been observed in the 1,3-dioxolan-4-one system; the protons at C-2 in the 2-trichloromethyl-1,3-dioxolane rings in the chloral acetals of D-glucose and their derivatives occur as sharp singlets[5]. A different spectrum of **1** was obtained for a solution in perdeuteriobenzene. The low-field doublet due to the H-1 protons was shifted upfield to δ 5.64 and the singlet due to H-2 to 4.77. Lack of sufficient analogies precludes the deduction (from the chemical shifts of H-2) of the stereochemistry of H-2 relative to the two equivalent H-4 protons. The remaining signals in perdeuteriobenzene occurred as two groups at δ 4.83 (six lines) and 3.92 (four lines of equal intensity). Simplification of the spectrum was achieved by spin-decoupling experiments. When the signals due to H-1 were irradiated, the signals due to the four protons other than H-2 were revealed as an AA'XX' system[6] (J_{AX} 2.3, $J_{AX'}$ 1.3 Hz), and the group of signals near δ 4.83 became identical in appearance with the group of signals near δ 3.92, which remained unchanged. The signals near δ 4.83 can thus be assigned to the H-3 protons and those near 3.92 to the central protons H-4, and these assignments were confirmed by further decoupling experiments.

Condensation of potassium hydrogen D-glucarate[7] with chloral in sulphuric acid gave a compound $C_{10}H_6Cl_6O_7$, m.p. 279–280°. The molecular formula and an interpretation of the p.m.r. spectrum show that this product is the monotrichloroethylidenelactone chloralide 2. Molecular models show that, in order to accommodate the three groups, lactone, acetal, and chloralide, the product must be a derivative of D-glucaro-6,3-lactone. The p.m.r. spectrum (perdeuterioacetone, 60 MHz) could be completely assigned on the basis of a first-order analysis. The signal for H-1 attached to C-2 of the dioxolanone ring occurs as a doublet at δ 6.42 (J 1.6 Hz) showing the characteristic, small, long-range coupling with H-3 at C-5 in the dioxolanone ring which may indicate that H-1 and H-3 are in a *cis*-relationship[4]. Proton H-3 is also coupled (J 4.4 Hz) to H-6 (δ 5.33) which, in turn, is coupled (J 3.7 Hz) to H-5. Protons H-4 and H-5 form an AB system (J_{AB} 6.0 Hz), δ_A 5.54, δ_B 5.58. Proton H-2 occurs as a singlet at δ 5.88. The formation of 2 in this reaction is reminiscent of the formation of ethyl 2,4-*O*-methylene-D-glucaro-6,3-lactone in the reaction of formaldehyde with diethyl D-glucarate[8].

EXPERIMENTAL

P.m.r. spectra were determined on Varian A-60 and HA-100 instruments. Chemical shifts are reported relative to tetramethylsilane as internal standard.

Reaction of galactaric acid with chloral. — Galactaric acid (14.3 g) and chloral hydrate (33.8 g) were kept for 3.5 days in 18M sulphuric acid (100 ml) at room temperature. The mixture was then poured onto ice, yielding a crude product (32 g), m.p. 148–152°. Crystallization from ether gave material having m.p. 168°, and recrystallization from ether and then ethanol gave 3,4-*O*-(trichloroethylidene)galactaric acid bischloralide (1), m.p. 172° (Found: C, 23.9; H, 1.2; Cl, 53.6. $C_{12}H_7Cl_9O_8$ calc.: C, 24.1; H, 1.2; Cl, 53.4%).

Reaction of potassium hydrogen D-*glucarate with chloral.* — A mixture of potassium hydrogen D-glucarate[7] (10.5 g) and chloral hydrate (21.0 g) in 18M sulphuric acid (80 ml) was kept at room temperature overnight and then poured onto ice. The solid product (11 g, air dried) was collected on a filter and then extracted with cold chloroform (2×3 l). The combined extracts were evaporated to 1.5 l, and the resulting crystals were recrystallized from chloroform and then twice from benzene to give 4,5-*O*-(trichloroethylidene)-D-glucaro-6,3-lactone chloralide (**2**) (5.8 g), $[\alpha]_D^{26}$ +39.8° (*c* 0.51, tetrahydrofuran) (Found: C, 26.8; H, 1.2; Cl, 47.0. $C_{10}H_6Cl_6O_7$ calc.: C, 26.6; H, 1.3; Cl, 47.2%).

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