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AN EFFICIENT SYNTHESIS OF (S)-5-HYDROXYMETHYL-2(5H)-FURANONE

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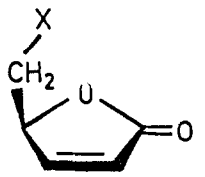
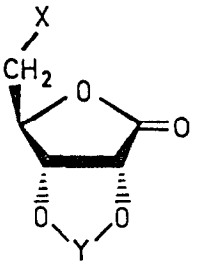
Abstract: A three step synthesis of the title compound 1a from D-ribono-1,4-lactone in 48% yield is described. The concept centers on a novel $NaHSO_3$-induced trans-Br-OAc elimination of the readily prepared bromo-acetate mixture 3a,b to the corresponding butenolides 1e and 1f, the former of which, on hydrolysis and purification, yields pure 1a.

Title compound 1a and its derivatives 1b-d are valuable chiral starting materials for synthesizing natural products such as (+)-trans-burseran[1], (-)-isostegane[1], (+)-steganacin[2], (-)-verrucarinolactone[3] and certain analogues of prostacyclin[4] and chrysanthemic acid[4]. Compounds 1a-c have been obtained[5] from D-ribono-1,4-lactone and its 5-O-substituted derivatives by pyrolysis of the cyclic orthoformate esters 2a-c. Raney nickel desulfurization of 2d and 2e has given 1c[6] and 1d[4] respectively. The intermediacy of 1a during the hydrogenolysis of 2-bromo-2-deoxy-D-arabino-1,4-lactone to 4-(S)-hydroxymethyl-γ-butyrolactone has been demonstrated[7]. Non-carbohydrate-based routes have included a six-step synthesis of 1b,c from L-glutamic acid[8] and of 1b via a route based on the asymmetric epoxidation of (Z)-4-benzyloxy-2-butenol[9]. A straightforward and operationally simple three-step synthesis of 1a from D-ribono-1,4-lactone is reported here.

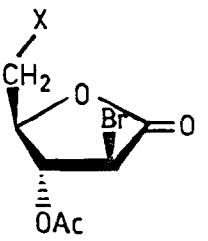
Acetylated bromo-deoxyaldono-1,4-lactones, obtained by treating aldono-1,4-lactones with HBr in acetic acid (HBA), are useful carbohydrate intermediates[10]. Treatment of D-ribono-1,4-lactone (14.8 g, 0.10 mol) with HBA (65 mL of 33% soln)[2 h, room temp; dropwise addn of Ac_2O (65 mL); aq quenching, CH_2Cl_2 extraction and work-up after 2 more h][11] gave an oily 6/1 mixture of 3a/3b (31.9 g): NMR ($CDCl_3$) δ 4.35 (d, $\underline{CH_2}OAc$) / 3.72 (d, $\underline{CH_2}Br$). This material in 2-PrOH (300 mL) produced, on stirring with aq $NaHSO_3$ (41.6 g in 160 mL) [72 h, room temp; aq quenching, CH_2Cl_2 extraction, drying and solvent removal], a syrupy 6/1 mixture of 1e/1f (13,3 g): NMR ($CDCl_3$) δ 4.34 (d, $\underline{CH_2}OAc$) / 3.72 (d, $\underline{CH_2}Br$). Hydrolysis thereof [HCl 0.5M in MeOH, 100 mL; 18 h, 5°C; evaporation and chromatography (silica gel: CH_2Cl_2-EtOAc, 1:2)] then gave essentially pure, oily 1a (5.6 g; 48% overall): NMR ($CDCl_3$-CD_3OD, 3:1) δ 3.75 (dd, J = 12 and 4 Hz, 1H), 3.85 (dd, J = 12 and 4 Hz, 1H), 4.3 (s, 1H), 5.15 (tdd, J = 4, 2 and 1.5 Hz, 1H), 6.13 (dd, J = 5.5 and 2 Hz, 1H), 7.58 (dd, J = 5.5 and 1.5 Hz, 1H). Kugelrohr distillation provided material (bp 135°C/0.2 mm) solidifying at room temp: mp 39-41°C; $[\alpha]_D^{20}$ -140° (c 3.18, H_2O)[12].



1 a-f



2 a-e



3 a,b

1 : a, X = OH; b, X = OCH_2Ph; c, X = $OCPh_3$; d, X = $OSi(t.Bu)Ph_2$; e, X = OAc; f, X = Br.
2 : a, X = OH, Y = CHOEt; b, X = OCH_2Ph, Y = CHOEt; c, X = $OCPh_3$, Y = CHOEt; d, X = $OCPh_3$, Y = C=S; e, X = $OSi(t.Bu)Ph_2$, Y = C=S.
3 : a, X = OAc; b, X = Br.

The $NaHSO_3$-induced elimination of 3a,b to butenolides 1e,f merits comment. Whereas $NaHSO_3$ has been mentioned only briefly as a method for bringing about a related trans-2-H-3-OAc elimination[13], the trans-2-Br-3-OAc elimination described here appears to be unprecedented. Further aspects of the reaction, including its application to other bromo-aldonolactones, are currently under investigation and will be reported shortly.

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12. The authors thank Mr. H. Regeling for assistance with the Kugelrohr distillation.

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