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Synthetic Studies of Carbohydrate Derivatives with Photochemical Reaction. VIII.[1] Photochemical Desulfurization of Some Sugar Diethyl Dithioacetal Acetates into the Corresponding 1-*S*-Ethyl-1-thioalditol Acetates

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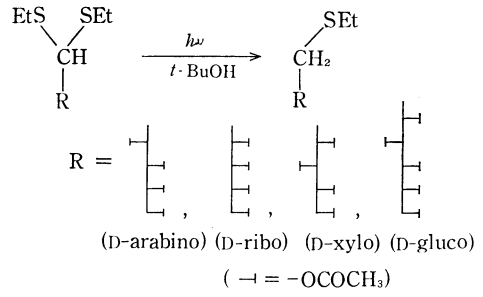
In the series of this investigation, a facile photochemical addition of thiols to enoses has briefly been reported from our laboratory.[1,2] As a part of this investigation, the present authors wish to report successively a photochemical desulfurization of some sugar diethyl dithioacetal acetates into the corresponding 1-*S*-ethyl-1-thioalditol acetates since such a conversion has been known solely with respect to D-galactose diethyl dithioacetal which affords 1-*S*-ethyl-1-thiogalactitol.[3] The photochemical desulfurization of diethyl dithioacetal acetates of D-arabinose, D-ribose, D-xylose, and D-glucose are described herewith.



(D-arabino) (D-ribo) (D-xylo) (D-gluco)

(⊣ = $-OCOCH_3$)

The corresponding 1-*S*-ethyl-1-thioalditol acetates were easily obtained in excellent yields by a chromatography on a column of silica gel (eluting solvent: 1%-acetone–benzene) of each sirup resultant from the concentration of the solution which was obtained by a previous irradiation of a *t*-butyl alcohol solution of the sugar diethyl dithioacetal acetates with a low pressure mercury lamp at room temperature under nitrogen atmosphere for 20 hr; the yields of 1-*S*-ethyl-1-thio-D-arabinitol, -D-ribitol, -D-xylitol, and -D-glucitol acetates were 79.3%, 85.3%, 86.9%, and 84.1%, respectively. The NMR data showed good agreement with their expected structures. According to the result of Horton and Jewell,[3] incidentally, 1-*S*-ethyl-1-thio-D-galactitol was obtained in a 55% yield by irradiation of methanolic solution of D-galactose diethyl dithioacetal with a low pressure mercury lamp (450 W) for 36 hr. The results described here were thus considerably superior to this result with respect to the yields of the photochemical reaction. The superiority may depend on the use of mercaptal acetates and *t*-butyl alcohol as the reaction solvent in place of methanol. *t*-Butyl alcohol may probably facilitate the reaction in comparison with the reaction in methanol; 1-deoxy-D-galactitol (L-fucitol) is already produced in the latter case as a result of concomitant process of further elimination of the ethylthiyl radical, and, in addition, the diethyl dithioacetal is yet remained in the reaction mixture.[3]

Two procedures have generally been known for the preparation of 1-*S*-alkyl-1-thioalditols; 1) Partial reduction of sugar mercaptals by the use of an aged Raney nickel as the catalyst.[4] 2) Reduction of 1-halogeno-1-alkylthioalditol derivatives, which was obtained from sugar mercaptals by halogenation, with lithium aluminum hydride.[5] The yield of the product in problem were, however, not so good in these procedures. Consequently, the procedure described in this article can be concluded to be practically feasible for the general synthetic method of 1-*S*-alkyl-1-thioalditols.

Experimental

Melting points are uncorrected. The irradiations were carried out by the use of a low pressure mercury lamp (6 W) of Ushio Electric Co. Inc. at room temperature under nitrogen atmosphere. NMR spectra were taken with a JEOL JNM-H-100 at 100 MHz in deuterochloroform by the use of tetramethylsilane as the internal standard. The acetates of diethyl dithioacetals of D-arabinose, D-ribose, D-xylose, and D-glucose were prepared according to the usual method.[6]

2,3,4,5-Tetra-O-*acetyl-1*-S-*ethyl-1-thio*-D-*arabinitol*: A solution of 2,3,4,5-tetra-*O*-acetyl-D-arabinose diethyl dithioacetal (1.00 g) in *t*-butyl alcohol (170 ml) was irradiated with the UV lamp under nitrogen atmosphere at room temperature for 20 hr. Resultant solution was evaporated *in vacuo* to afford brown sirup, which was subsequently chromatographed on a silica gel column (3×20 cm) by eluting with benzene containing 1% volume of acetone. The starting material (4 mg, 0.4%) was eluted out as the first portion, and 2,3,4,5-tetra-*O*-acetyl-1-*S*-ethyl-1-thio-D-arabinitol was as the second portion. The eluate was concentrated *in vacuo* to a sirup which was soon crystallized on standing at room temperature and is already pure enough for the elemental analysis. Yield

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3) D. Horton and J. S. Jewell, *J. Org. Chem.*, **31**, 509 (1966).

4) J. K. N. Jones and D. L. Mitchell, *Can. J. Chem.*, **36**, 206 (1958).

5) H. Zinner, R. Kleeschätzky, and P. Neels, *Chem. Ber.*, **98**, 1492 (1965).

6) a) S. M. Olin, "Methods in Carbohydrate Chemistry," Vol. 1, ed. by R. L. Whistler and M. L. Wolfrom, Academc Press, New York and London (1962), p. 148. b) M. L. Wolfrom and A. Thompson, *ibid.*, Vol. 2, (1963), p. 427. c) J. Stanĉk, M. Čérný, J. Kocourek, and J. Pacák, "The Monosaccharides," Academic Press, New York and London, and Publishing House of the Czechoslovak Academy of Science, Prague (1963), p. 589.

0.681 g (79.3%), mp 56—58 °C, $[\alpha]_D^{22}$ +43.3° (*c* 1.0, Me_2CO) {lit,[7] mp 58 °C, $[\alpha]_D$ 38±4° (*c* 1.3, $CHCl_3$)}. NMR: δ 1.25 (3H, t, $J_{CH_3-CH_3}$=7.0 Hz, C–C$\underline{H}_3$), 2.56 (2H, q, –C$\underline{H}_2$–Me), 2.58 (1H, q, $J_{1,1'}$=13.5 Hz, $J_{1,2}$=7.0 Hz, H-1), 2.60 (1H, q, $J_{1',2}$=6.0 Hz, H-1'), 5.23 (1H, oct, $J_{2,3}$=2.5 Hz, H-2), 5.45 (1H, q, $J_{3,4}$=8.5 Hz, H-3), 5.15 (1H, oct, $J_{4,5}$=5.0 Hz, $J_{4,5'}$=3.5 Hz, H-4), 4.15 (1H, q, $J_{5,5'}$=12.5 Hz, H-5), 4.23 (1H, q, H-5'), 2.05, 2.06, 2.08, and 2.14 (4×–OCOC$\underline{H}_3$).

The other mercaptal acetates (1.00 g) were respectively treated in the same way as had been described in the above experiment, and the results thus obtained were summarized as below.

2,3,4,5-Tetra-O-*acetyl-1*-S-*ethyl-1-thio*-D-*ribitol*: Yield 0.733 g (85.3%), mp 59—61 °C, $[\alpha]_D^{22}$ −4.7° (*c* 1.0, Me_2CO). Found: C, 49.69; H, 6.85; S, 8.59%. Calcd for $C_{15}H_{24}O_8S$: C, 49.45; H, 6.64; S, 8.78%. NMR: δ 1.23 (3H, $J_{CH_3-CH_3}$= 7.5 Hz, CH_2–C$\underline{H}_3$), 2.55 (2H, q, –S–C$\underline{H}_2$–Me), 2.70 (1H, $J_{1,1'}$=13.5 Hz, $J_{1,2}$=8.0 Hz, H-1), 2.82 (1H, q, $J_{1',2}$= 5.0 Hz, H-1'), 5.05—5.45 (3H, m, H-2, H-3, and H-4), 4.16 (1H, q, $J_{4,5}$=6.0 Hz, $J_{5,5'}$=12.0 Hz, H-5), 4.37 (1H, q, $J_{4,5'}$=3.0 Hz, H-5'), 2.05, 2.09, and 2.10 (3H, 6H, and 3H, –OCOC$\underline{H}_3$). The starting material was recovered in a 2.5% yield (25 mg) in this case.

2,3,4,5-Tetra-O-*acetyl-1*-S-*ethyl-1-thio*-D-*xylitol*: Yield 0.747 g (86.9%), sirup, $[\alpha]_D^{22}$ −21.7° (*c* 1.1, Me_2CO). Found: C, 49.31; H, 6.49; S, 9.08%. Calcd for $C_{15}H_{24}O_8S$: C, 49.45; H, 6.64; S, 8.78%. NMR: δ 1.24 (3H, t, $J_{CH_3-CH_3}$=7.5 Hz, –CH_2–C$\underline{H}_3$), 2.57 (2H, q, –S–C$\underline{H}_2$–Me), 2.66 (1H, q, $J_{1,1'}$= 13.5 Hz, $J_{1,2}$=6.5 Hz, H-1), 2.68 (1H, q, $J_{1',2}$=6.0 Hz, H-1'), 5.17 (1H, oct, $J_{2,3}$=4.5 Hz, H-2), 5.49 (1H, q, $J_{3,4}$= 6.0 Hz, H-3), 5.27 (1H, sex, $J_{4,5}$=6.0 Hz, $J_{4,5'}$=3.5 Hz, H-4), 4.02 (1H, q, $J_{5,5'}$=12.5 Hz, H-5), 4.33 (1H, q, H-5'), 2.05, 2.08, and 2.11 (3H, 3H, and 6H, –OCOC$\underline{H}_3$).

2,3,4,5,6-Penta-O-*acetyl*-*1*-S-*ethyl*-*1*-*thio*-D-*glucitol*: Yield 0.739 g (84.1%), mp 84—86 °C, $[\alpha]_D^{22}$ +1.3° (*c* 1.0, Me_2CO) {lit,[4] mp 82 °C, $[\alpha]_D^{26}$ 5±1° (*c* 1.1, $CHCl_3$)}. NMR: δ 1.24 (3H, t, $J_{CH_3-CH_3}$=7.5 Hz, –CH_2–C$\underline{H}_3$), 2.57 (2H, q, –S–C$\underline{H}_2$–Me), 2.66 (1H, q, $J_{1,1'}$=14.0 Hz, $J_{1,2}$=6.5 Hz, H-1), 2.74 (1H, q, $J_{1',2}$=5.5 Hz, H-1'), 4.95—5.2 (2H, m, H-2 and H-5), 5.51 (1H, q, $J_{2,3}$=5.0 Hz, $J_{3,4}$=4.0 Hz, H-3), 5.43 (1H, q, $J_{4,5}$=10.5 Hz, H-4), 4.14 (1H, q, $J_{5,6}$=5.5 Hz, $J_{6,6'}$=12.5 Hz, H-6), 4.25 (1H, q, $J_{5,6'}$=3.5 Hz, H-6'), 2.04, 2.06, 2.09, and 2.12 (3H, 6H, 3H, and 3H, –OCOC$\underline{H}_3$). The starting material was recovered in a 1.3% yield (13 mg) in this case.

7) L. Hough, J. K. N. Jones, and D. L. Mitchell, *Can. J. Chem.*, **37**, 725 (1959).