Communications to the Editor

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A Novel Synthesis of Trehalose-Type Thiodisaccharides. An Anomalous Reaction of Potassium Methyl- and Benzyl-xanthates with Halogeno-O-acetyl Sugars in Acetone

Up to the present time, several sugar xanthates (acylated glycosyl xanthates) have been studied[1] as an important intermediate for the preparation of thiosugars.[2] Recently the increasing interests are directed to the sugar xanthates from the view point of optical rotatory dispersion.[3]

Usually the sugar xanthates are prepared by the condensation of acetohalogeno-sugars with potassium xanthates in proper solvents such as ethanol or acetone.

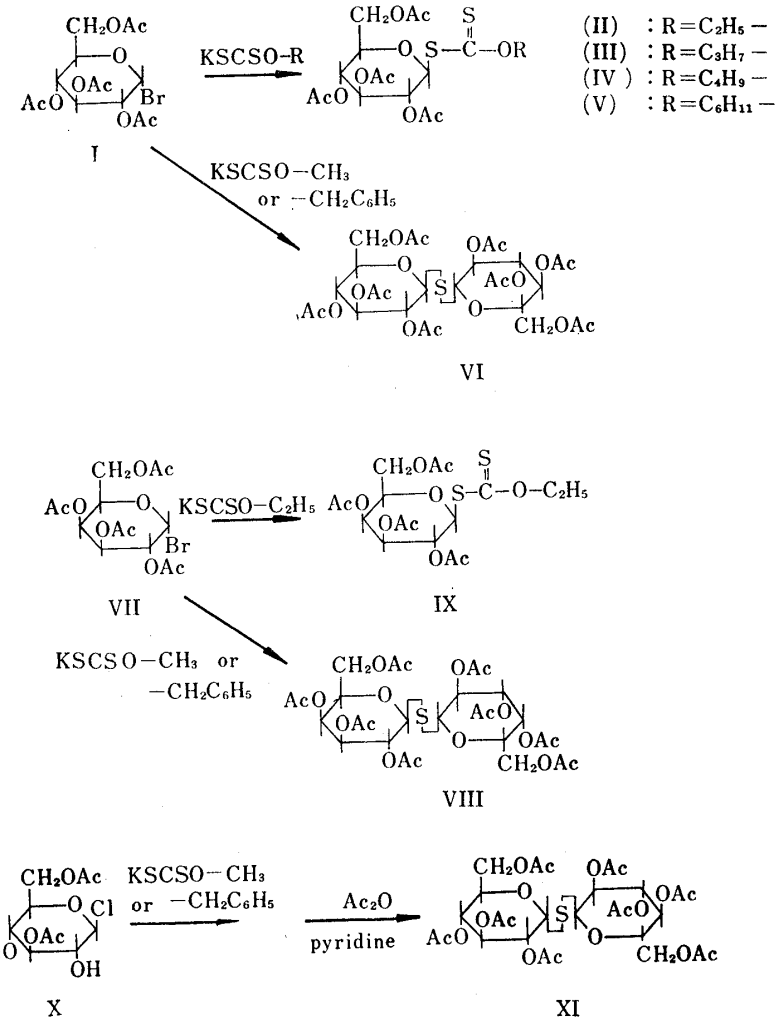
In this communication the authors wish to describe that potassium methyl- and benzylxanthates reacted abnormally with halogeno-O-acetylsugars in acetone to give acylated diglycosyl sulfides (trehalose-type thiodisaccharides) in good yield different from other potassium xanthates.

The condensation of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (I) with potassium ethyl-, propyl-, butyl-, and cyclohexyl-xanthates in hot acetone gave the corresponding sugar xanthates in good yield, respectively. That is, 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl ethylxanthate (II), m.p. 75~76°, $[\alpha]_D^{18}$ +30.0 (c=1.2, $CHCl_3$),[4] *Anal.* Calcd. for $C_{17}H_{24}O_{10}S_2$: C, 45.09; H, 5.35. Found: C, 45.26; H, 5.32. 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl propylxanthate (III), m.p. 90~91°, $[\alpha]_D^{18}$ + 31.0 (c=2.0, $CHCl_3$), *Anal.* Calcd. for $C_{18}H_{26}O_{10}S_2$: C, 46.34; H, 5.62. Found: C, 46.17; H, 5.63. 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl butyl xanthate (IV), m.p. 114~115°, $[\alpha]_{1D}^{\infty}$ + 28.8 (c= 1.0, $CHCl_3$), *Anal.* Calcd. for $C_{19}H_{28}O_{10}S_2$: C, 48.32; H, 5.87. Found: C, 48.39; H, 5.59. 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl cyclohexyl xanthate (V), m.p. 111~112°, $[\alpha]_D^{18}$ +97.0 (c=2.0, $CHCl_3$), *Anal.* Calcd. for $C_{21}H_{30}O_{10}S_2$: C, 49.19; H, 5.97. Found: C, 49.43; H, 5.76.

On the other hand, the condensation of potassium methyl- and benzyl-xanthates with (I) under the same condition did not afford sugar xanthtes but bis(2,2',3,3',4,4',6,6'-octa-O-acetyl-β,β'-D-glucopyranosyl)sulfide(VI),[5] m.p. 175~176°, $[\alpha]_D^{18}$ −38.0(c=1.0, $CHCl_3$), *Anal.* Calcd. for $C_{28}H_{38}O_{18}S$: C, 48.41; H, 5.51 .Found: C, 48.24; H, 5.56., was obtained in 93% yield.

Similarly, 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide (VII) reacted with potassium methyl and benzyl-xanthates under the same condition to give bis(2,2',3,3',4,4',6,6'-octa-O-acetyl-β,β'-D-galactopyranosyl)sulfide (VIII), m.p. 201~202°, $[\alpha]_D^{18}$ −21.0 (c= 1.0, $CHCl_3$), *Anal.* Calcd. for $C_{28}H_{38}O_{18}S$: C, 48.41; H, 5.51. Found: C, 48.22; H, 5.63., in 82% yield. With potassium ethylxanthate, VII reacted normally to give 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl ethylxanthate (IX), m.p. 81~82°, $[\alpha]_D^{18}$ +92.0 (c=1.0, $CHCl_3$), *Anal.* Calcd. for $C_{17}H_{24}O_{10}S_2$: C, 45.09; H, 5.35. Found: C, 45.12; H, 5.24.

1) M. Akagi, S. Tejima, M. Haga: This Bulletin, **9**, 360 (1961).
2) A. L. Raymond: "Advances in Carbohydrate Chemistry," **1**, 129 (1945) Academic Press Inc., New York, N. Y.
3) C. Djerassi: "Optical Rotatory Dispersion, Application to Organic Chemistry," Chap. 14 (1960) McGraw-Hill Inc., New York, N. Y.
4) W. Schneider, R. Gille, K. Eisfeld: Ber., **61**, 1244 (1928).
5) W. Schneider, F. Wrede; *Ibid.*, **50**, 793 (1917).



The condensation of 3,4,6-tri-O-acetyl-β-D-glucopyranosyl chloride (X)[6] with potassium methyl- and benzyl-xanthates in hot acetone and successive acetylation gave bis-(2 2′ 3,3′,4,4′,6,6′-octa-O-acetyl-α,α'-D-glucopyranosyl)sulfide (XI), m.p. 191~192°, $[\alpha]_D^{18}$ +259.2 (c=2.0, $CHCl_3$), *Anal.* Calcd. for $C_{28}H_{38}O_{18}S$: C, 48.41; H, 5.51. Found : C, 48.49; H 5.48., in good yield.

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6) P. Brigl : Z. physiol. Chem., **116**, 1 (1921).