Communications to the Editor

UDC 547.458.2

A Novel Synthesis of Trehalose-Type Thiodisaccharides. An Anomalous Reaction of Potassium Methyl- and Benzyl-xanthates with Halogeno-0-acetyl Sugars in Acetone

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

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-0-acetylsugars in acetone to give acylated diglycosyl sulfides (trehalose-type thiodisaccharides) in good yield different from other potassium xanthates.


On the other hand, the condensation of potassium methyl- and benzyl-xanthates with (I) under the same condition did not afford sugar xanthates but bis(2,2',3',3',4',4',6'-octa-O-acetyl-β,β'-D-glucopyranosyl)sulfide(Ⅵ),¹³ m.p. 175~176°, [α]₀ᵦ −38.0 (c=1.0, CHCl₃), Anal. Calcd. for C₂₅H₄₀O₁₀S₂: 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'-octa-O-acetyl-β,β'-D-galactopyranosyl)sulfide (Ⅷ), m.p. 201~202°, [α]₀ᵦ −21.0 (c=1.0, CHCl₃), Anal. Calcd. for C₂₅H₄₀O₁₀S₂: C, 48.41; H, 5.51. Found: C, 48.22; H, 5.63, in 82% yield. With potassium ethylnxanthate, Ⅶ reacted normally to give 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl ethylxanthate (Ⅸ), m.p. 81~82°, [α]₀ᵦ + 92.0 (c=1.0, CHCl₃), Anal. Calcd. for C₂₅H₄₀O₁₀S₂: C, 45.09; H, 5.35. Found: C, 45.12; H, 5.24.

4) W. Schneider, R. Gille, K. Eiffeld: 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-(2,3',4,4',6,6'-octa-O-acetyl-α,α'-d-glucopyranosyl)sulfide (XI), m.p. 191~192°, [α]D +259.2 (c=2.0, CHCl₃), Anal. Calcd. for C₃₉H₅₀O₁₅S: C, 48.41; H, 5.51. Found: C, 48.49; H 5.48., in good yield.

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Received May 16, 1963

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