TRIPHENYLMETHANETHIOL.

AN USEFUL REAGENT IN THE SYNTHESIS OF 1,2-CIS-1-THIOGLYCOSES

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Summary. - Triphenylmethyl-1-thio- α -<u>D</u>-galactoside was obtained in good yield by treatment of β -acetochlorogalactose with the tetrabutylammonium salt of triphenylmethanethiol. This protecting group of the thiol function is stable under both basic and acidic conditions and may be selectively removed by reaction with phenylmercury(II) acetate, followed by hydrogen sulfide.

In carbohydrate chemistry, most of the thiol at the anomeric position are protected by acyl and alkyl groups or by formation of symmetrical disulfides.¹⁻³ In a search of a temporary protecting group, stable under basic and mild acidic conditions, the trityl ether has emerged as one of the most useful for this purpose. Furthermore, interest in a regenerable thiol function for syntheses in peptide and penicillin-cephalosporin series,^{4,5} prompted us to introduce a thiol with this protective group at the anomeric position of sugars.



i (Bu)4 N+TrS⁻ (1.3 eq) ; toluene ; R.T. ; 12 h ; 60%. *ii* MeO-Na+-MeOH ; quant. *iii* 2,2-dimethoxytoluene (1.3 eq.) ; HBF4 in ether ; DMF. *iv* AC₂O pyr. ; 40%. *v* CH₃CN-CH₂Cl₂ (1:3 v/v) ; HBF4 in water ; 75%. *vi* Ph HgOAc (1.2 eq) ; MeOH-CH₂Cl₂ (4:1 v/v) 96 %. vii H₂S ; CH₂Cl₂-pyr-Ac₂O-(10:1:0.5 v/v) ; 98%.

Typical experiments are shown on the scheme. The tetrabutylammonium salt of triphenylmethanethiol was obtained as described for the salt of thioacetic acid.⁶ On treatment of this salt (1.3 eq) with β -acetochlorogalactose 1⁷ in toluene, the derivative 2 was obtained. Catalytic *O*-deacetylation with sodium methoxide in methanol gave 3. By reaction with benzaldehyde dimethylacetal in *N*,*N*dimethylformamide in the presence of tetrafluoroboric acid,⁸ followed by acetylation with acetic anhydride-pyridine mixture, the 4,6-*O*-Benzylidene derivative 4 was isolated. Acetal cleavage was achieved as described⁸ but in dichloromethane. Treatment of 2 with phenylmercury(II) acetate in methanol-dichloromethane quantitatively gave the phenylmercury(II) tetra-*O*-acetyl-1-thio- α -<u>D</u>-galactopyranose (6). This compound, in dichloromethane, was transformed into 7 by treatment with hydrogen sulfide in the presence of pyridine and acetic anhydride.⁹

In conclusion, the versatility of the trityl group as a temporary protecting group of the thiol functions is demonstrated by its stability towards several reagents used either under basic or acidic conditions. We also report an efficient procedure for introducing a thiol at the anomenic position of a sugar residue. After classical reactions in carbohydrate chemistry, its quantitative transformation into an acetyl group leads to a *S*-acetylglycose which may be selectively activated for the synthesis of thiooligosaccharides.10

References and Notes

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- 9. The structures of all compounds were assigned by 1³C-nmr spectroscopy and elemental analysis. 2 : m.p. 163-168°C (ether), $[\alpha]_D$ +130° (*c* 1.3, chloroform) ; 4 : m.p. 220-226°C (ether), $[\alpha]_D$ +51° (*c* 0.8, chloroform) ; 5 : m.p. 96°C (ether-hexane), $[\alpha]_D$ +82° (*c* 1, chloroform) ; 7 : m.p. 119°C (ether), $[\alpha]_D$ +48° (*c* 0.8, chloroform).
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