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CONVERSION OF POLYFUNCTIONAL ALCOHOLS TO ACETALS UNDER NON-ACIDIC CONDITIONS

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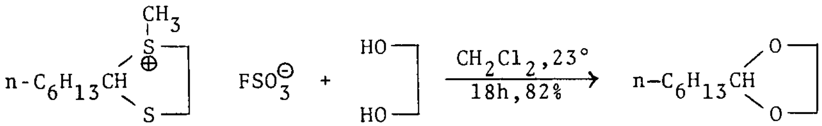
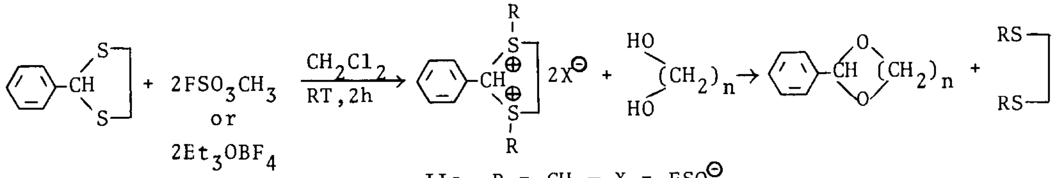
A recent report by Corey and Hase[1] describes the conversion of thioacetals to acetals by means of an exchange reaction with sulfonium salts shown in Scheme I. We wish to report the results of our own studies of a similar procedure involving disulfonium salts of thioketals for the conversion of polyfunctional alcohols to benzal derivatives under non-acidic conditions.

Scheme I



Although benzal derivatives are used extensively as protecting groups in carbohydrate chemistry,[2] their formation under acidic conditions has been a limitation to their usefulness because some carbohydrates (e.g., sucrose) are sensitive to the acidic conditions. A base catalyzed process which uses benzal chloride in pyridine has been reported,[3] but the required experimental conditions are vigorous (~100°,~8h) and the yields are not attractive. We therefore chose to examine the benzaldehyde ethylenedithioacetal (I) as a benzalation reagent *via* its disulfonium salt (II) as shown in Scheme 2.

Scheme 2



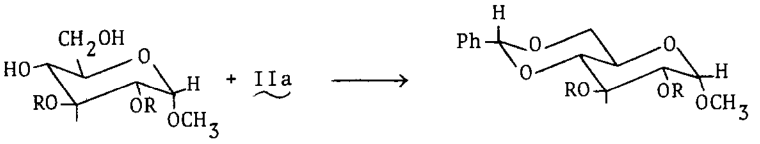
I

IIa R = CH_3-, X = $FSO_3^{\ominus}$

IIb R = CH_3CH_2-, X = $BF_4^{\ominus}$

The treatment of I with two equivalents of methyl fluorosulfonate (Magic Methyl[R], Aldrich) in methylene chloride at 25° for 1-2h gave the disulfonium salt (IIa)[4] as a light yellow solution The addition of 1,2-, 1,3- and 1,4-diols to the solution of IIa in the presence of either solid potassium carbonate, dry triethylamine or dry pyridine gave the corresponding benzal derivatives in fair to good yields (Table I).[5]

The treatment of methyl α-D-glucopyranoside (IIIa) in dry pyridine with II gave the corresponding benzylidene compound (IVa), which was acetylated *in situ* (acetic anhydride) to give the corresponding diacetate (IVc)[6] in 20-25% yield. Methyl 2,3-di-O-methyl-α-D-glucopyranoside (IIIb) was similarly treated in methylene chloride in the presence of solid potassium carbonate and Drierite to give IVb[6] in 35% yield



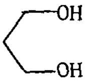
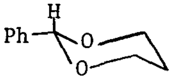
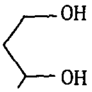
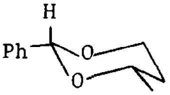
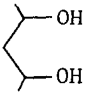
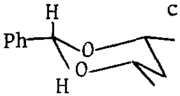
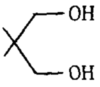
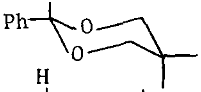
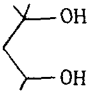
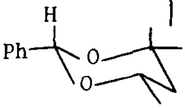
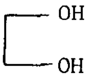
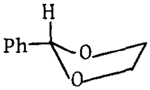
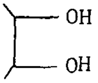
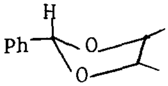
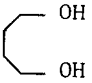
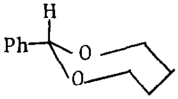
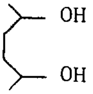
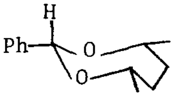
IIIa R = H
IIIb R = CH_3

IVa R = H
IVb R = CH_3
IVc R = CH_3CO-

The use of I without activation by way of the disulfonium salt, but in the presence of mercury(II) chloride and cadmium carbonate or mercuric oxide, also proved successful but the yields were considerably lower in the case of the 1,2-diols and the glucosides.

Table I

Synthesis of benzal derivatives by the reaction of II with diols at room temperature for ~16h.

	Diol	Product	Yield %	m p /b p. (°C)	Refractive Index
1			75	47-49	—
2.			60(55)^a	75/9.15 torr	n_D^{27} 1 5150
3		 c	82(90)	90/0.2 torr	n_D^{26} 1.5076
4			65(65)	82/0.2 torr	n_D^{27} 1 5070
5.			80(65)	83/0 3 torr	n_D^{27} 1 5014
6			60(20)	80/0.4 torr	n_D^{27} 1.5235
7		 c	65(22)	78/0.2 torr	n_D^{27} 1 5016
8			(53)	97/0 2 torr	n_D^{27} 1 5212
9		 c	45	85/0 15 torr	n_D^{27} 1 5025
10	IIIa	IVa	25(~5)	168-171(106-107)^b	
11	IIIb	IVb	35	118-120	

a-The yields in brackets are those of the reaction of the glycol with 1 in the presence of mercury(II) salts.
b-This is the melting point of the 2,3-diacetate derivative (IVc)
c-Mixture of stereoisomers

References

1 E J Corey and T Hase, *Tetrahedron Lett* , 3267 (1975).

2 I Levi and C B. Purves, *Adv Carbohyd Chem* , 4, 1 (1949).

3. P J. Garegg, L Maron, and C. G Swahn, *Acta Chem Scand.*, 26, 518 (1972), P. J Garegg, and C G Swahn, *Acta Chem. Scand* , 26, 3895 (1972).

4 T Oishi, K Kamemoto, and Y Barr, *Tetrahedron Lett.*, 1085 (1972), T L Ho and C. M Wong, *Synthesis*, 561 (1972).

5. The compounds were characterized by means of NMR and all gave satisfactory elemental analyses

6 These products were characterized by comparison with authentic samples and by mixed melting points