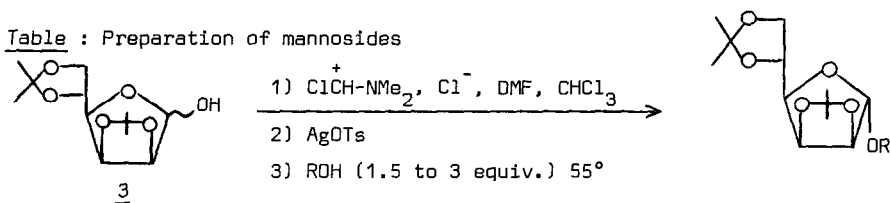


Table : Preparation of mannosides



ROH	Yield ^{a)} %	$[\alpha]_{20}^D$ c in CHCl_3	$^1\text{H NMR}$ (δ , CDCl_3)
CH_3OH	95 (90)	+49.5° 4.65	m, 3.89-4.89, 7 H ; -OCH ₃ , s, 3.31
$(\text{CH}_3)_2\text{CHOH}$	95 (85)	+53° 1.45	H ₁ , s, 5.1 ; m, 3.67-4.83 , 6 H ; CH(CH ₃) ₂ , d, 1.1 (2 Hz)
$(\text{CH}_3)_3\text{COH}$	90 (50)	+50.1° 1.25	H ₁ , s, 5.27 ; m, 3.98-4.90, 6 H ; (CH ₃) ₃ , s, 1.24
	72	+75.3° 1.7	H ₁ , s, 5.1 ; m, 3.90-4.90, 6 H ; CH ₃ , s, 0.85 ; CH ₃ , s, 0.82 ; m, 0.5-2.5, 22 H
	75 ^{b)}	+22° 2.4	H ₁ , s, 5.23 ; H ₂ , d, 4.61 (6 Hz) ; H ₃ , dd, 4.76 (3.5 Hz) ; H ₅ , m, 4.41, H ₆ , H _{6'} , H ₄ , m, 3.92-4.24 ; H' ₁ , d, 5.82 (3.5 Hz) ; H' ₂ , d, 4.57 ; H' ₄ , H' ₅ , H' ₆ , H' _{6'} , m, 3.92-4.24
	80 (40)	-9.5° 1.8	H ₁ , s, 5.05 ; H ₂ , d, 4.63 (6 Hz) ; H ₃ , dd, 4.78 (3.5 Hz) ; H ₄ , dd, 3.97 (7.5Hz) ; H ₅ , m, 4.39 (J ₄ 7.5Hz, J _{6a} 5.75Hz, J _{6b} 4Hz) ; H _{6a} and H _{6b} , 4.13 and 3.93 (J _{6a-6b} 8.5Hz) ; H' ₁ , d, 5.52 (5Hz) ; H' ₂ , dd, 4.31 (2.5Hz) ; H' ₃ , dd, 4.61 (8Hz) ; H' ₄ , dd, 4.21 (2Hz) ; H' ₅ , 3.97 ; H' _{6a} and H' _{6b} , 3.75 and 3.64 (J _{5'-6'a} 6.5Hz, J _{5'-6'b} 7Hz, J _{6'a-6'b} 10 Hz).
	61	-29.9° 0.9 (MeOH)	H ₁ , s, 5.42 ; H ₂ , d, 4.67 (6 Hz) ; H ₃ , dd, 4.78 (3.5 Hz) ; H ₄ , dd, 4.27 (7 Hz) ; H ₅ , 4.39 (J ₄ 7 Hz, J ₆ 6 Hz, J _{6'} 5 Hz) ; H ₆ H _{6'} , 4.07 (J _{6-6'} 8.5 Hz) ; H' ₁ , AB, 3.94, 4.07 (9 Hz) ; H' ₃ , d, 3.71 (7.5 Hz)

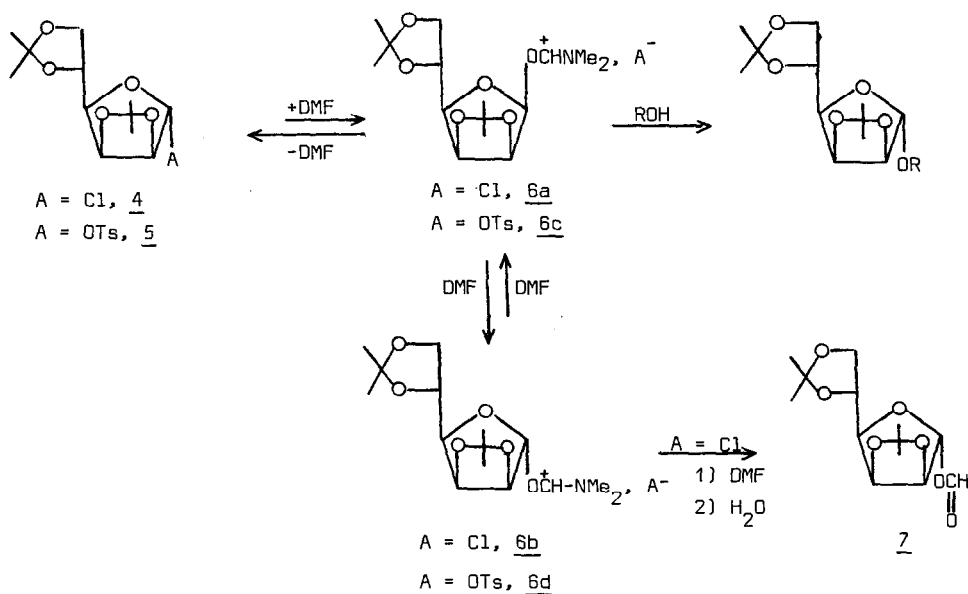
a) As pure isolated products with satisfactory microanalyses ($\text{C} \pm 0.3$; $\text{H} \pm 0.2$ %) ; between brackets : yields without prior treatment by AgOTs.

b) Accompanied by 10 % of the mannoside resulting from the rearrangement of the 1,2;5,6-di-O-isopropylidene- α -D-glucopyranose into the 1,2;3,5-di-O-isopropylidene- α -D-glucopyranose⁴.

By heating at room temperature, all the signals of 6a and 6b disappear without line broadening and are replaced by those of the complex formed between DMF and HCl (HOCH-NMe_2^+ , Cl^- : NMe_2 , s, 3.11 and s, 3.23; $-\text{CH}^+$, s, 8.41 ppm) whereas the intensity of the signals of 4 increases.

After addition of silver tosylate the signals of 4 disappear and are replaced by those of the α -tosyl mannoside 5⁶.

We know⁷ that condensation of an alcohol with either 4 or 5 gives a mixture of α - and β -mannosides, so we believe that DMF plays a specific role to give only α -mannosides. It can exert a very strong solvating effect at C-1 on the reactive species or, possibly, form a small amount of a very reactive β iminium salt at C-1, 6a or 6c, through the equilibrium shown below :



The latter assumption is substantiated by three facts :

- A glycosylation performed with 4, silver tosylate and DMF gives qualitatively the same results, namely the α mannoside.
- The same overall reaction (as in the Table) but run in the presence of a five fold molar excess of hexamethylphosphotriamide gives, as do the oxyphosphonium salts⁷, a mixture of α - and β -mannosides.
- The hydrolysis of the reaction mixture of 3, and 1 gives the α -mannosyl formate 7 (H_1 , s, 6.21; $-\text{CHO}$, s, 8.1; Me, s, 1.35, 6 H, s, 1.45, 3 H, s, 1.49 ppm, 3 H).

We are now investigating the scope of this reaction which is somewhat related to previous results⁸, and explains them.

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- ⁹ *A typical condensations runs as it follows : a solution of 520 mg of 3 and 290 mg (1.15 equiv.) of 1 in CHCl₃ (5 ml) is allowed to stand 0.5 h ; DMF (1.7 equiv.), AgOTs (2.3 equiv.) and 780 mg (3 equiv.) of 1,2;3,4-di-O-isopropylidene- α -D-galactopyranoside are successively added. The solution is refluxed for 3 - 4 h. After cooling, half of the solvent is evaporated, the residue is diluted with ether (100 ml), filtered, washed (H₂O, saturated HNaCO₃ and H₂O) dried and concentrated. By elution (AcOEt/hexane, 2/3 v/v) through a silicagel column, 803 mg of pure mannoside is obtained (80 %).*

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