MEM GROUP AS A GENERAL PROTECTING GROUP FOR HYDROXYL FUNCTIONS OF CARBOHYDRATES

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A variety of functional groups have been used for the protection of hydroxyls in carbohydrate chemistry[1]. The achiral MEM (β-methyoxyethoxymethyl) was found to react with hydroxyls to form MEM ethers, which were then removed under neutral or very mild acidic conditions[2]. The use of the MEM group in carbohydrate chemistry is not widespread although a few examples have been reported[3]. Here we present the use of the MEM group for blocking and deblocking of primary, secondary and tertiary hydroxyl groups in sugar derivatives. Reaction conditions denoted by a-c were used to introduce the MEM group. Method a, where MEM chloride and diisopropylethylamine in dichloromethane were stirred together with the sugar for 24 hours at room temperature gave the best results. The primary hydroxyl of the D - galacto pyranose (1), the secondary hydroxyl of L- rhamno (3) and D- gluco (4) pyranoside derivatives gave the MEM ethers in yields >90%. The secondary hydroxyls of the furanose derivatives of D- gluco (5), D- xylo (6), D- manno (7) and the tertiary hydroxyl in the 6-deoxy-4- methyl - L- talopyranoside (8) provided MEM ethers in good yields. Use of the neutral quaternary ammonium salt (method c) for the introduction of the MEM group for base sensitive compounds as well as use of MEM chloride with NaH (method b) did not give high yields of MEM ethers. Use of $ZnBr_2$ (method d) gave better deprotected yields than the use of methylthiotritrimethylsilane (method e). It is seen that the MEM group could not only be introduced (1B→1A; 2B→2A etc.) but also removed from carbohydrates (1A→1B; 2A→2B etc.) at room temperature in high yields in the presence of several other functionalities. All compounds had ^1H and 13C n.m.r. spectra in accordance with the assigned structures.

References

McOmie, J.F.W. (1973) Protection groups in organic chemistry., Plenum Press, London.

Corey, E.J. (1976) Teterahedron Lett., 809.

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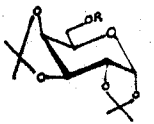
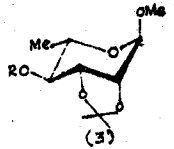
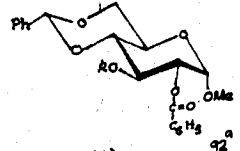
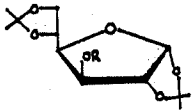
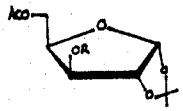
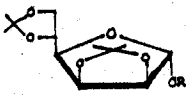
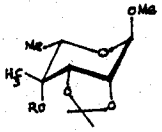
	% Product yield	
	(A) R=MEM	(B) R=H
 (1)	92[a] / 60[b]	85[d] / 60[e]
 (2)	92[a]	80[d]
 (3)	95[a]	90[d]
 (4)	92[a] / 63[c]	85[d]
 (5)	80[a]	65[d]
 (6)	80[a]	75[d]
 (7)	82[a]	80[d] / 60[e]
 (8)	90[a]	70[d]

(a) $CH_3OCH_2CH_2OCH_2Cl$ | $(i\text{-}Pr)_2EtN$ | CH_2Cl_2 | 24h | R.T.

(b) $CH_3OCH_2CH_2OCH_2Cl$ | NaH | THF | 0°C | N_2 | 1h

(c) $CH_3OCH_2CH_2OCH_2N^+Et_3Cl^-$ | CH_3CN | Reflux | N_2 | 12h

(d) $ZnBr_2$ | CH_2Cl_2 | N_2 | 16-24h | R.T.

(e) $MeSSiMe_3$ | ZnI_2 | $n\text{-}Bu_4N^+I^-$ | CH_2Cl_2 | 40°C | 6h