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CLEAVAGE OF METHYLTHIOMETHYL ETHERS BY ELECTROLYTIC PROCEDURE

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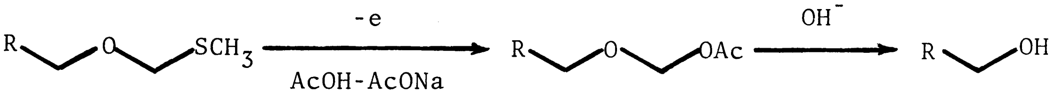
An electrolytic method for deblocking a methylthiomethyl group is newly developed.

The methylthiomethyl (MTM) group is a well known protecting group of hydroxy functions which has been widely used in natural product syntheses.$^{1-4)}$ As for the removal of the protection, three practical methods have been proposed thus far; that is, i) $HgCl_2$-CH_3CN-H_2O,$^{1,5)}$ ii) $AgNO_3$-THF-H_2O-2,6-lutidine,$^{1)}$ and iii) MeI-acetone-H_2O-$NaHCO_3$.$^{6)}$

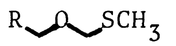
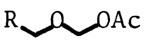
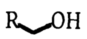
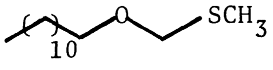
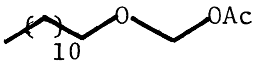
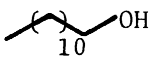
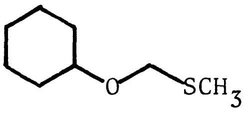
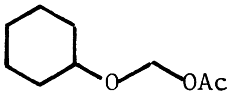
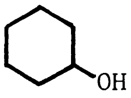
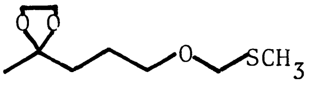
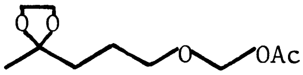
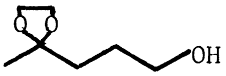
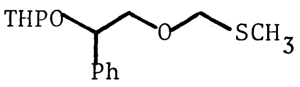
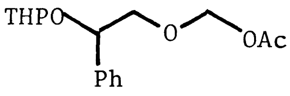
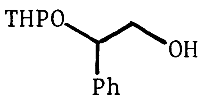
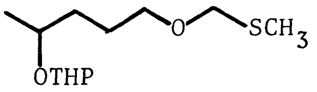
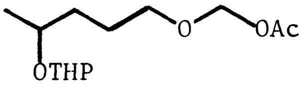
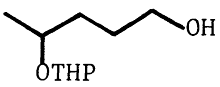
In this communication, we wish to report that a facile deprotection of the MTM group can be achieved through an electrolytic procedure. Namely, MTM ethers 1 are converted into acetoxymethyl ethers 2 in high yields by electrolysis in an AcOH-AcONa medium. And then, weak alkaline hydrolysis (K_2CO_3-MeOH-H_2O) of 2 results in recovery of original alcohols 3.



1 2 3

Electrolysis of 1 was carried out in an undivided cell equipped with platinum electrodes (4 cm x 2 cm). A mixture of 1 (0.46-1.0 mmol) and AcONa (20 mmol) in AcOH (20 ml) was electrolyzed under a constant current (0.06 A) at applied voltage of 10 V at 18-20 °C for 1-5 h. The reaction mixture was diluted with benzene (100 ml) and neutralized with $NaHCO_3$ solution. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The resultant oil was purified by column chromatography on silica gel to give 2. Then, the alcohols 3 were recovered in excellent yields by treatment of 2 with K_2CO_3-MeOH-H_2O. The results are summarized in Table 1. It should be further noted that isolation of 2 is not always unavoidable since the crude products of 2 are pure enough for the next use. Thus, alkaline hydrolysis of crude oils obtained by evaporating benzene gave rise to quite analgous results in Table 1.

Table 1. Electrochemical Deblocking of a MTM Group

Entry	 1	Current F mol^{-1}	 2	Yield/%$^{a)}$	 3	Yield/%$^{a)}$
1		12.1		91		98
2		4.5		83		93
3		5.3		86		88
4		13.4		96		95
5		11.9		90		95

a) Isolated yields after column chromatography.

Apparently, the reaction conditions are very mild and accordingly acid labile functions such as ketal and OTHP groups remain intact during the reaction course. Since the reagent employed is only K_2CO_3 throughout these pocedures, the present method provides a highly clean and efficient deblocking process of a synthetically useful MTM group.

References

1) E. J. Corey and M. G. Bock, Tetrahedron Lett., 1975, 2463.
2) E. J. Corey, D. H. Hua, and S. P. Seitz, Tetrahedron Lett., 25, 3 (1984).
3) R. A. Holton and R. G. Davis, Tetrahedron Lett., 1977, 533.
4) K. Suzuki, J. Inanaga, and M. Yamaguchi, Chem. Lett., 1979, 1277.
5) K. Yamada, K. Kato, H. Nagase, and Y. Hirata, Tetrahedron Lett., 1976, 65.
6) P. M. Pojer and S. J. Angyal, Tetrahedron Lett., 1976, 3067.

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