

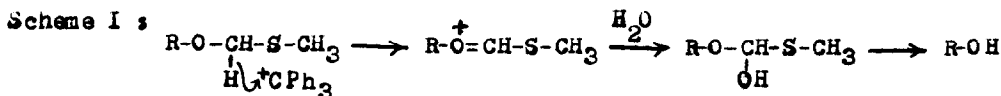
A NEW METHOD FOR DEPROTECTION OF METHYLTHIOMETHYL ETHERS

P K Chowdhury, R P Sharma\* and J N Baruah  
 Division of Natural Products Chemistry, Regional Research Laboratory (CSIR)  
 Jorhat-6, Assam, INDIA

**Summary:** Methylthiomethyl ethers of primary, secondary and tertiary alcohols are efficiently cleaved by trityl tetrafluoroborate whereas that of phenols remain unaffected under the reaction conditions.

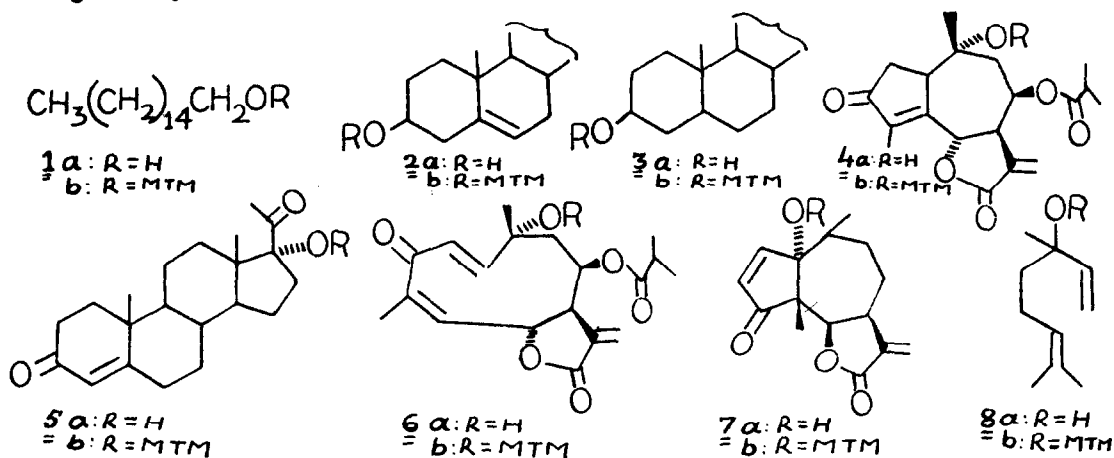
Recently, methylthiomethyl (MTM) ether has come to known as an excellent protecting group for primary, sec, and tert-alcohols as well as for phenols because of its easy method of preparation, stability under stringent reaction conditions and the eventual removal<sup>1-4</sup>. In connection with some other work we required regeneration of alcohol<sup>5</sup> 4a from its MTM ether 4b. Usual methods of deprotection<sup>1-4</sup> using HgCl<sub>2</sub> or AgNO<sub>3</sub> or CH<sub>3</sub>I led largely to the formation of other products and extensive decomposition, only 20% of the required 4a was obtained. However, when a solution of 1.0 mmol of 4b in 4 ml dry dichloromethane was stirred under nitrogen with 1.25 mmol of trityl tetrafluoroborate and followed by aqueous work up, 4a was obtained in 95% yield. The validity of this method was further examined by taking a variety of substrates as shown in Figure I. It is evident from Table I that the cleavage of MTM ethers with trityl tetrafluoroborate is extremely facile. As the reaction conditions are mild and almost neutral, this method may find wide application for deprotection of MTM ethers especially that of tert-alcohols. MTM ethers of phenols were not cleaved under the reaction conditions - a situation which could be exploited for selectivity purpose<sup>6</sup>.

Evidently the mechanism of reaction is the same as proposed by Barton<sup>7</sup> for oxidation of ketone acetals and ethers by hydride transfer to triphenyl-carbonium ion as shown in Scheme I. Ordinary ethers are not cleaved by trityl



tetrafluoroborate as the hydrogens involved for extraction by triphenyl carbonium ion are not sufficiently basic<sup>7,8</sup>.

Figure 1 :

Table I : Cleavage of MTM ethers<sup>a, b</sup>

MTM ether	Time in min/r. t.	% Yield of alcohol	MTM ether	Time in min/r. t.	% Yield of alcohol
1b	10	95	5b	5	95
2b <sup>c</sup>	10	95	6b <sup>d</sup>	4	90
3b <sup>c</sup>	10	95	7b	30	80
4b	5	95	8b	15	80

<sup>a</sup> All the MTM ethers were prepared according to the procedure described in Ref.3 and cleavage reactions carried out as mentioned for compound 4b.

<sup>b</sup> All yields refer to the isolated products which were fully characterised by comparison with authentic samples.

<sup>c</sup> Compounds 2b and 3b belong to normal cholestane series.

<sup>d</sup> Continuation of the reaction for more than four min. led to the formation of other products.

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