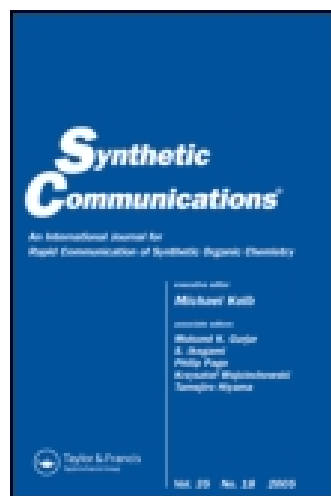


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EFFICIENT DEPROTECTION OF TETRAHYDROPYRANYL ETHERS BY BISMUTH(III) SALTS

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EFFICIENT DEPROTECTION OF TETRAHYDROPYRANYL ETHERS BY BISMUTH(III) SALTS

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ABSTRACT

Treatment of tetrahydropyranyl(THP) ethers with bismuth(III) salts including BiCl_3 , $\text{Bi}(\text{TFA})_3$ and $\text{Bi}(\text{OTf})_3$ in methanol provides a simple and efficient process for deprotection of these ethers and the parent alcohols were obtained in excellent yields.

The protection of alcohols as their tetrahydropyranyl ethers is a useful and representative method in modern synthetic chemistry due to their stability toward basic media, Grignard reagents, lithium alkyls, alkylating and acylating reagents and reactions involving oxidation and reduction by inorganic hydrides.^[1] Deprotection of these ethers to their corresponding alcohols under mild conditions is also of practical importance and many methods and catalysts have already been applied for this conversion.^[2–9]

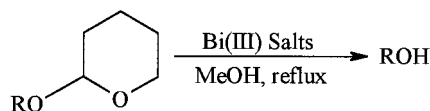
*Corresponding author.



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Although some of these methods are useful, there is still a need for an efficient and excellent yielding alternative catalyst that can work under mild conditions and shorter reaction times.

Over recent years, the catalytic activity of bismuth(III) derivatives as Lewis acids has been demonstrated in organic transformations.^[10] In connection with our ongoing work on catalysis by Bi(II) salts,^[11-14] we herein report a simple and efficient method for the cleavage of tetrahydropyranyl ethers using BiCl₃, Bi(TFA)₃ and Bi(OTf)₃ as catalysts (Scheme 1).



Scheme 1.

As shown in Table 1, when a variety of tetrahydropyranyl ethers were treated with catalytic amounts of BiCl₃, Bi(TFA)₃ and Bi(OTf)₃ in refluxing methanol, the corresponding alcohols were obtained in excellent yields. The experimental results show that Bi(OTf)₃ is more reactive than BiCl₃ and Bi(TFA)₃ for this transformation. It is important to note that *tert*-butyldimethylsilyl (TBDMS) ether and ester remained unchanged in the reaction mixture (Table 2).

In conclusion, the present procedure provides a simple and convenient methodology for the deprotection of THP ethers. In addition, high yields and short reaction times, easy workup, availability, stability and non-toxicity of the catalysts make this procedure a useful and attractive alternative to the currently available methods.

EXPERIMENTAL

General Procedure for Deprotection of THP Ethers

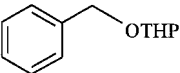
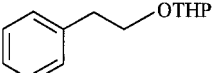
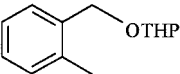
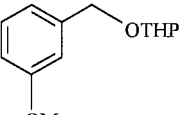
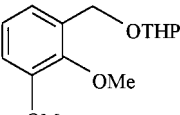
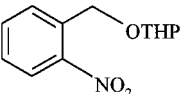
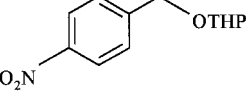
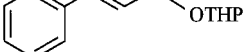
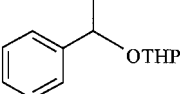
To a solution of THP ether (1 mmol) in methanol (3 ml) was added the catalyst (0.03 mmol of BiCl₃, 0.05 mmol of Bi(TFA)₃ and 0.01 mmol of Bi(OTf)₃). The reaction mixture was stirred under reflux conditions for the length of time indicated in Table 1. The progress of the reaction was followed by TLC. Evaporation of the solvent followed by chromatography



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Table 1. Deprotection of THP Ethers Catalyzed by Bi(III) Salts^a

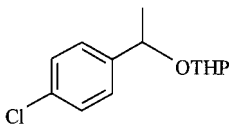
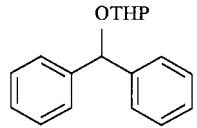
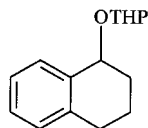
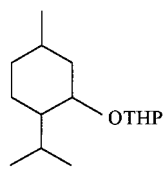
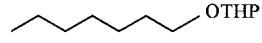
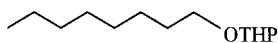
| Run | THP Ether | Yield ^b (%) of Alcohol (Time, min) | | |
|-----|---|---|----------------------|----------------------|
| | | BiCl ₃ | Bi(TFA) ₃ | Bi(OTf) ₃ |
| 1 |  | 96 (20) | 95 (30) | 97 (3) |
| 2 |  | 95 (30) | 93 (45) | 98 (3) |
| 3 |  | 97 (15) | 97 (15) | 98 (3) |
| 4 |  | 97 (15) | 94 (30) | 97 (3) |
| 5 |  | 98 (5) | 97 (10) | 99 (2) |
| 6 |  | 93 (35) | 85 (60) | 97 (5) |
| 7 |  | 94 (35) | 80 (60) | 96 (5) |
| 8 |  | 94 (15) | 92 (40) | 95 (10) |
| 9 |  | 95 (15) | 96 (20) | 98 (3) |

(continued)



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Table 1. Continued

| Run | THP Ether | Yield ^b (%) of Alcohol (Time, min) | | |
|-----|---|---|----------------------|----------------------|
| | | BiCl ₃ | Bi(TFA) ₃ | Bi(OTf) ₃ |
| 10 |  | 98 (15) | 93 (25) | 99 (5) |
| 11 |  | 97 (15) | 97 (15) | 99 (3) |
| 12 |  | 95 (20) | 93 (30) | 97 (7) |
| 13 |  | 97 (25) | 96 (25) | 98 (7) |
| 14 |  | 94 (25) | 94 (25) | 97 (5) |
| 15 |  | 95 (25) | 93 (25) | 98 (5) |

^aThe products were characterized by comparison with known samples.^bYields refer to isolated products.

Table 2. Competitive Deprotection Catalyzed by Bi(III) Salts

| Run | Substrate | Product | Yield % (Time, min) | | |
|-----|--|---|---------------------|----------------------|----------------------|
| | | | BiCl ₃ | Bi(TFA) ₃ | Bi(OTf) ₃ |
| 1 | 2-MeOC ₆ H ₄ CH ₂ OTHP | 2-MeOC ₆ H ₄ CH ₂ OH | 99 (15) | 98 (15) | 100 (3) |
| | PhCH=CHCH ₂ OTBDMS | PhCH=CHCH ₂ OH | 0 | 0 | 0 |
| 2 | Ph ₂ CHOTHP | Ph ₂ CHOH | 98 (15) | 98 (15) | 99 (3) |
| | CH ₃ CO ₂ C ₇ H ₁₅ | CH ₃ CO ₂ H | 0 | 0 | 0 |



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on a silica-gel plate or silica-gel column afforded the pure product in 80–99% yield (Table 1).

ACKNOWLEDGMENT

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