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REDUCTIVE CLEAVAGE OF *tert* -BUTYLDIMETHYLSILYL ETHER VIA INTRAMOLECULAR TRANSFER OF HYDRIDE

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Abstract: The cleavage of α -hydroxy tert-butyldimethylsilyl ether to diol takes place efficiently with LAH. It has been proposed that the reaction proceeds via intramolecular hydride transfer from the alkoxy aluminium hydride. In order to substantiate this, reduction of TBDMS ether with LAH in a variety of substrates was studied.

Protection of alcohols as *tert*-butyldimethylsilyl (TBDMS) ether is very well utilized in organic synthesis because of its easy installation and general stability to basic and mild acidic reagents.¹ There is a variety of methods available for the cleavage of TBDMS ethers.² Although TBDMS ethers in general are stable to reducing agents, there are a few reports where these have been cleaved under reductive conditions. For example, NaH in HMPA at rt cleaves TBDMS ethers in a very clean fashion.³ DIBAL-H in CH₂Cl₂ has recently been used for reductive cleavage of TBDMS ethers under mild conditions.⁴ However, under the normal

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conditions (0 °C or rt) for LAH reduction, the TBDMS ethers are very stable. While working on the synthesis of suitable substrates for studying chelation effect of TBDMS ethers so as to get insight about the enantioselective deprotonation of epoxides,⁵ we noticed smooth cleavage of TBDMS ether of α -hydroxy ester 1 with LAH, alongwith reduction of the ester group. There are few reports in the literature where similar cleavage of TBDMS ether is known.⁶ In this paper we extend the work further and report the effect of oxygen atom, present at different postions, on the cleavage of TBDMS ethers.

The substrate 1 on reaction with one equivalent of LAH in ether at 0 °C for 2 h gave a diol 2 in more than 70% yield. In order to see the role of COOMe in 1 in the cleavage of TBDMS group, a compound 3 was treated with LAH and it was observed that the TBDMS ether in 3 remained intact even on reflux with LAH in ether for 4 h. This indicated that the COOMe or its reduced product was responsible for the facile cleavage of the vicinal TBDMS ether. In order to see the uniformity in the reaction, we synthesized a series of related substrates in which COOMe was α , β , and γ to the TBDMS ether. In the cases of α - and β -COOMe, TBDMS ether was cleaved in a very facile manner (entries 1, 3 - 6) but in case of γ -COOMe, only partial cleavage of TBDMS ether was observed (entry 11). However, in the case of remote COOMe, the cleavage of TBDMS ether did not take place at all (entry 12). Based on these facts, we propose that the reaction proceeds via intramolecular delivery of hydride as shown in 1a. As per the mechanism, chelation of Al-complex to the nearby heteratom is prerequisite for the desilylation reaction. This was further substatantited by doing the desilvation reaction on related substartes as shown in the table (entries 7-9). Partial cleavage of TBDMS ether in the case of α -methoxy TBDMS ether 15 indicates some chelation with lone pair of oxygen atom of the methoxy group.

In conclusion we report a facile reductive cleavage of TBDMS ethers using LAH. This report is important in view of the literature report⁷ where this cleavage has been confused with dilute acidic work-up in a LAH reduction.



Table: Reduction of TBDMS protected hydroxy-carbonyls with LAH^a

Entry	Substrate	Product	Yield (%)
1.	OTBDMS Ph COOMe 1 OTBDMS		70
2.	Ph Me	Nil	No reaction ^b
3.		ОН Me 5 ОН	74
4.		он он 7	30°
5.		он	65
6.		он Он Он Он	66

(continued)



Table Continued

^aThe reaction was done in ether at 0 °C for 2 h unless stated otherwise and the work-up was done using aq. NaOH. ^bEven on reflux for 4 h, the TBDMS ether was intact. ^cThe tlc is very clean and the low yield is due to poor recovery. ^dThe remaining material is the substrate itself. ^e10% of the diol was also obtained.

Experimental Section

General Procedure for Reductive Cleavage of TBDMS Ether: A solution of TBDMS ether (0.5 mmol) in diethyl ether (1 mL) was treated with a suspension of LAH (1 mmol) in diethyl ether (3 mL) at 0 °C and the reaction mixture was stirred for 2 h (0 ° C). Excess LAH was destroyed by addition of 250 μ L of EtOAc. Water (150 μ L) was added followed by the same amount of 4N NaOH. After 5 min, 250 μ L of water was added and the mixture stirred for 15 min. A white precipitate was filtered off, the filtrate was dried, and solvent evaporated. The crude mixture was purified by silica gel column chromatography. Acknowledgement: We thank Department of Atomic Energy for financial support.

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