

NICKEL BORIDE REDUCTIVE CLEAVAGE OF ALLYLIC TRIMETHYLSILYL ETHERS

D N Sarma and R P Sharma \*

Natural Products Chemistry Division

Regional Research Laboratory, Jorhat-6, Assam, India

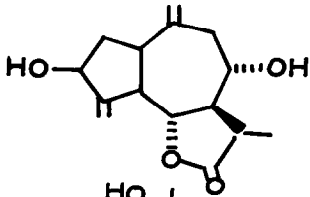
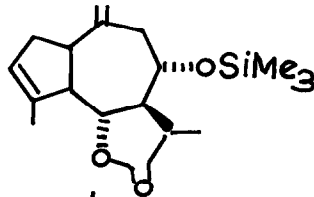
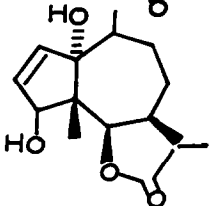
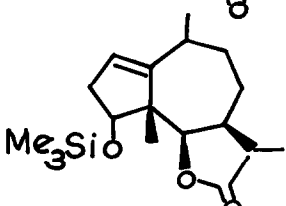
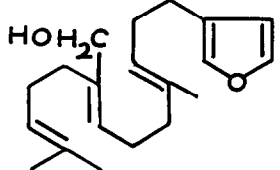
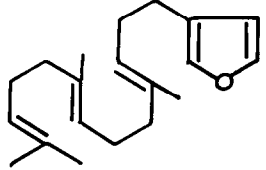
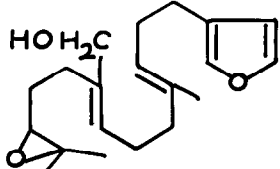
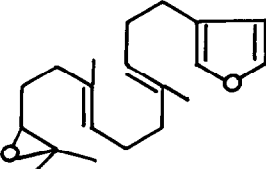
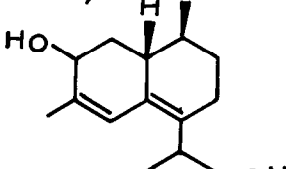
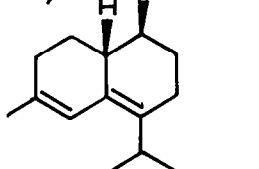
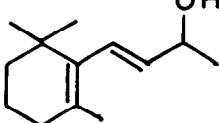
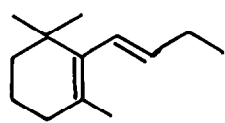
Abstract : Nickel boride reductive cleavage of allylic trimethylsilyl ethers yielding alkenes is described.

Reductive cleavage of carbon sulphur bonds with nickel boride has been studied by Barton et al<sup>1</sup>. We have examined the reaction of various allylic trimethylsilyl ( TMS ) ethers with nickel boride and the results are presented in table 1. Naturally occurring compounds were converted into suitable substrates e.g. 3, 4, 5, 6 & 7 and their reaction with nickel boride demonstrates the utility of this procedure<sup>2</sup>. When a solution of 1 in diglyme was treated with excess sodium borohydride for 9 hr at r.t., no reaction took place and the starting material was recovered unchanged, implying that nickel boride is involved in the reductive removal of TMS ether group. Migration of the double bond in the substrates 3 & 4 is noteworthy.

Since the reductive removal of an allylic hydroxyl group is normally difficult because of its propensity to undergo dehydration under mild reaction conditions, the single pot procedure described below for the reductive removal of the TMS ether group will make an attractive alternative to the existing methods<sup>3</sup>.

General Procedure : Reaction of an alcohol ( 0.25 m mol ) with excess hexamethyldisilazane and chlorotrimethylsilane ( a drop of pyridine was added when the alcohol was not soluble in the reagents ) for 1 hr at r.t. furnished the TMS ether in almost quantitative yield ( t.l.c. ). The excess reagents were completely removed under vacuum and to a solution of the residue in 4 ml of dry diglyme was added nickel chloride ( 3.50 m mol ) followed by sodium borohydride ( 7.00 m mol ) which resulted in an immediate formation of the black precipitate of nickel boride. The reaction mixture was stirred at r.t. monitored by t.l.c. and was worked up by diluting with water and extracting with dichloromethane. The products were purified by preparative t.l.c. and characterized by spectroscopic methods and by direct comparison with the authentic sample in the case of entry 1, 2, 4, 5, 6 & 7. In each case, besides the reaction product, the rest of the material consisted of a mixture of the unreacted TMS ether and the starting alcohol which were recovered.

Table 1 : Nickel boride reduction of TMS ethers of allylic alcohols

Entry	Substrate	Product	Time (hr)	Yield (%)
1	Cholest-4-en-3 $\beta$ -ol	Cholest-4-ene	6	80
2	Cholest-5-en-4 $\beta$ -ol	Cholest-5-ene	6	50
3			3	60
4			3	60
5			1	80
6			1.5	80
7			2	75
8			6	30

## References :

1. R B Boar, D W Hawkins, J F McGhie and D H R Barton, *J. Chem. Soc.*, 1973, 654
2. Compounds given at entry 3, 4, 5, 6 & 7 were prepared from the natural products available in our laboratory<sup>4-7</sup>.
3. a) R O Hutchins and K Learn, *J. Org. Chem.*, 1982, 47, 4380.  
b) H J Williams, *Tetrahedron Lett.*, 1975, 1271.
4. A K Singhal, P K Chowdhury, R P Sharma, J N Barua and W Herz, *Phytochemistry*, 1982, 21, 462.
5. D N Sarma, J C Sarma, N C Barua and R P Sharma, *Chem. Comm.*, 1984, 13, 813.
6. U C Pandey, P Sarman and R P Sharma, *Tetrahedron* (in press).
7. V S Shukla, N C Barua, P K Chowdhury, R P Sharma & J N Barua, *Chem. & Ind.*, 1983, 863.

(Received in UK 13 November 1984)