

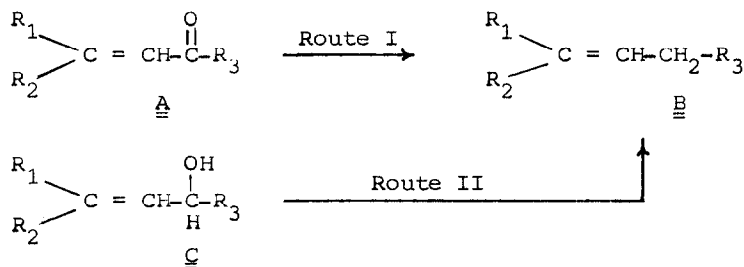
REDUCTIVE REMOVAL OF ALLYLIC FUNCTIONAL GROUPS BY
 NICKEL BORIDE

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Summary: Reductive removal of an allylic functional group proceeds most easily and efficiently with nickel boride as the bond being cleaved becomes a better leaving group (e.g. $\text{OCH}_3 < \text{OH} < \text{OSiMe}_3 < \text{OCOCH}_3 < \text{OCOCF}_3$)

Transformation of an α, β -unsaturated ketone A to an olefin B is generally achieved through thioketal formation followed by Raney nickel desulphurization (Route I). The less attractive procedure is through the allylic alcohol C which on hydrogenolysis or metal hydride reduction furnishes the required olefin B (Route II)¹. Reaction conditions employed in both these procedures may not always be compatible with the sensitive functionalities present in a molecule where this transformation is desired.



Recently reductive removal of various allylic functional groups has been effected using lithium triethylborohydride in the presence of a little tetrakis (triphenylphosphine) palladium (0) and triphenylphosphine in refluxing THF². Our interest in the use of silicon reagents³ led us to discover recently that allylic silyl ethers are reductively cleaved by nickel boride to furnish olefins in moderate to excellent yields⁴. Since some of the allylic silyl ethers were found to hydrolyse quickly under the reaction conditions, it was observed that allylic alcohols are also converted into the corresponding olefins albeit in a lower yield. A study of the reaction of various allylic functional groups with nickel boride then revealed that acetates are most efficiently removed to furnish olefins in excellent yields⁵ (Table I). It is evident from Table I that the rate of reductive removal of an allylic function is increased as the bond being cleaved becomes a better leaving group. Although trifluoroacetate 1c & p-bromobenzoate 1e are most

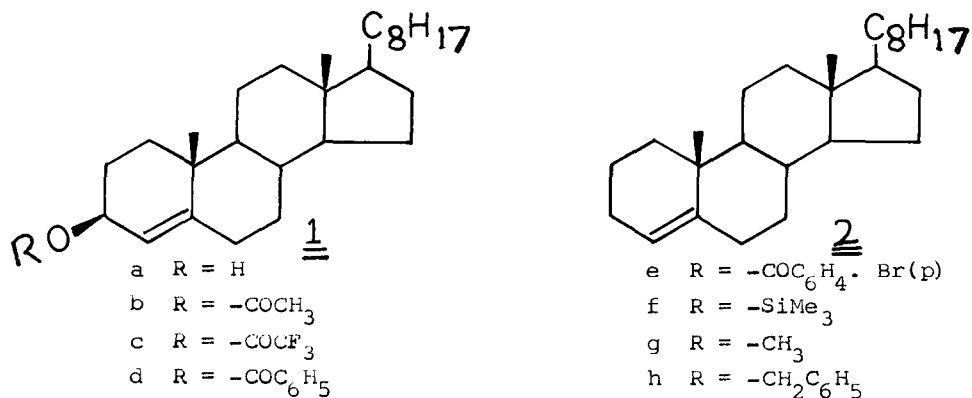


TABLE I

Reductive removal of allylic functional groups with nickel boride and Raney nickel^a.

Substrate	Reagent used	Time/r.t.	% Yield of (2)
1a	Nickel boride	6 hr	80
1b	Nickel boride	10 min	98
	Raney nickel	7 hr	70
1c	Nickel boride	5 min	98
1d	Nickel boride	10 min	98
	Raney nickel	4 hr	90
1e	Nickel boride	5 min	98
	Raney nickel	5 min	60 ^b
1f	Nickel boride	6 hr	80 ^c
	Raney nickel	8 hr	No reaction
1g	Nickel boride	8 hr	No reaction
	Raney nickel	8 hr	No reaction
1h	Nickel boride	8 hr	No reaction
	Raney nickel	6 hr	60

^aAll reactions with nickel boride were carried out in dry diglyme using the procedure mentioned in Ref. 4. Raney nickel was prepared according to the procedure given by I.A. Vogel, "Practical Organic Chemistry" Longman, Green & Co. Ltd. London, 1968. All reactions with Raney nickel were carried out in EtOH. The reaction mixture was continuously stirred till tlc indicated that no further reaction is taking place.

^b30% of 1d was also obtained.

^cAlthough the reaction of 1a and 1f with nickel boride gave identical yields of 2 but with various other substrates it has been observed that allylic silyl ethers give better yields of the olefins than the corresponding alcohols. Reaction of cholest-4-en-3-one with nickel boride and excess sodium borohydride gave only 10% yield of 2.

easily cleaved but preparation of the former from the allylic alcohol 1a is attended with poor yield. Since acetates from primary or secondary allylic alcohols and trimethylsilyl ethers from tert-allylic alcohols can be obtained in almost quantitative yield and the subsequent reductive removal with nickel boride is carried out under extremely mild reaction conditions, it appears that this would prove to be a very useful procedure for achieving transformation of A to B.⁶

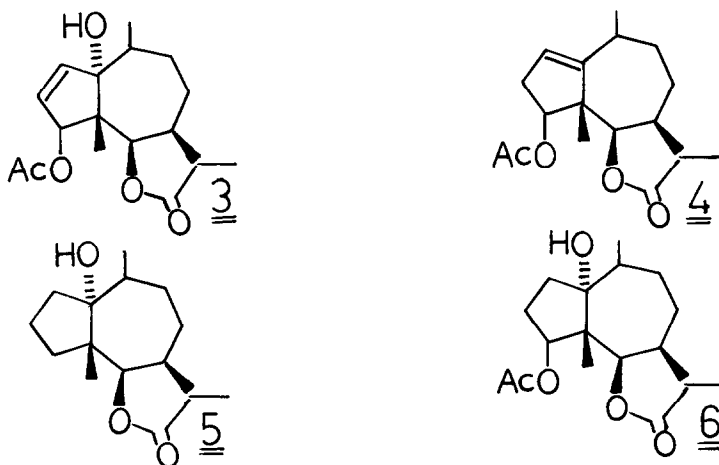
It has been reported that nickel boride acts as a selective hydrogenation catalyst and some reduction also occurs under similar reaction conditions as described by us.⁷ However no reduction of the double bond has been observed during the preparation of cholest-4-ene 2 from the substrates given in the Table I and in several other substrates studied by us except 3. Reaction of 3 with nickel boride furnished a mixture of three products 4, 5 and 6 in 30% yield each; the latter two are clearly the result of reduction of the double bond.

Comparative study of the two catalysts, nickel boride and Raney nickel⁸ (See Table I) reveals that the former is indeed a superior reagent for the reductive removal of an allylic acetate and the latter is superior for the reductive removal of an allylic benzyl ether group.⁹ The above observation could be made use of where selectivity is required.

When the reaction of 1b with nickel boride was conducted in C₂H₅OD under reflux, it resulted in 20% incorporation of deuterium at C-3 in 2.¹⁰

A more detailed study on cis-trans isomerization of the double bond under the reaction conditions, effect of solvent, temperature and that of the presence of a ligand is in progress.

When our manuscript was under preparation, Dr. T.G. Back reported the reductive deselenization of selenides with nickel boride.¹¹



Acknowledgement: The authors thank the Director, Dr. J.N. Barua for providing necessary facilities for this work and one of us (DNS) thanks the CSIR, New Delhi for a fellowship.

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(b) Allylic alcohols can be prepared in almost quantitative yield with $\text{NaBH}_4\text{-CeCl}_3$ e.g. see J.L. Luche, J. Am. Chem. Soc., **100**, 2226(1978) & J.L. Luche, L. Rodriguez-Hahn and P. Crabbe, Chem. Commun., 601(1978). But hydrogenolysis of allylic alcohols, ethers and esters often leads to the mixture of products as the rate of cleavage is similar to the rate of reduction of C-C double bond.
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(Received in UK 21 March 1985)