

Deoxygenation of Sulfoxides and Selenoxides with Nickel Boride

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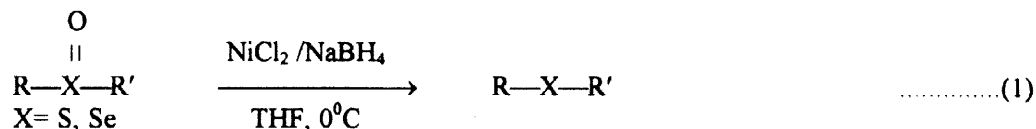
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Abstract : The deoxygenations of a variety of acyclic sulfoxides and selenoxides have been reported with nickel boride in THF at 0–5°C in nearly quantitative yields. The deoxygenations are proposed to proceed by an oxidative-addition and reductive-elimination mechanism. © 1998 Elsevier Science Ltd. All rights reserved.

Nickel boride, first reported by Schlesinger *et al.*¹ in 1949, has since been employed as a reagent and catalyst in a number of processes.² The advantages of nickel boride over other reducing agents include its low cost, ease of handling and preparation and non-pyrophoric nature. Reduction of organosulfur compounds with nickel boride was first reported by Truce and Roberts.³ This as well as all the subsequent work^{3–8} have reported desulfurization of organosulfur compounds with nickel boride. Deselenization of selenides with nickel boride has also been reported.⁹ Only recently, Back *et al.* have reported the formation of small amounts of sulfides along with the predominantly desulfurized product in the case of dibenzothiophene oxide^{8a} and di n-dodecyl sulfoxide^{8c}. This led us to investigate the possibility of selective deoxygenation of sulfoxides and selenoxides using nickel boride thereby widening the scope and selectivity of this reagent.

This is the first report on the exclusive deoxygenation of a variety of sulfoxides and selenoxides with nickel boride formed *in situ*. The reactions have been performed with diaryl, dibenzyl, benzyl aryl, benzyl alkyl, aryl alkyl and dialkyl (including fatty) sulfoxides and selenoxides. The deoxygenations have been achieved successfully with anhydrous nickel chloride and sodium borohydride in tetrahydrofuran at 0–5°C (Eq. 1). The products were isolated in good yields using different work up procedures. Deoxygenation of diphenyl selenone



was also observed and competed strongly with deselenization. All our results have been compiled in Table 1. To achieve our goal, quite a few parameters had to be modified by carrying out reactions under a variety of reaction conditions since the catalytic properties of nickel boride are known to change with the method of catalyst preparation, source of metal used, solvents used in the catalyst preparation, catalyst support and amount

Table I . Deoxygenation of Sulfoxides and Selenoxides with Anhyd $\text{NiCl}_2 \cdot \text{NaBH}_4$ in THF at 0-5° C

Entry	Substrate	Molar Ratio Substrate: NiCl_2 : NaBH_4	Time (hr)	% Isolated yield (Sulfide/Selenide)	Method
1.	Dibenzyl sulfoxide	1:3:9	2	81	A
2.	Benzylphenyl sulfoxide	1:3:9 ^a	1.5	72	A
3.	Benzyl n-Propyl sulfoxide	1:5:15	2	62	A
4.	Benzy n-propyl sulfoxide	1:5:15 ^b	2.5	74	B
5.	Diphenyl sulfoxide	1:5:15	4	75	A
6.	Diphenyl sulfoxide	1:20:60 ^b	1.5	80	B
7.	Phenyl n-propyl sulfoxide	1:3:9	1	65	A
8.	Phenyl n-propyl sulfoxide	1:15:45 ^b	1.5	87	B
9.	Methyl phenyl sulfoxide	1:3:96 ^a	1.5	69	A
10.	Di n-butyl sulfoxide	1:2:6	5	33	A
11.	Di n-butyl sulfoxide	1:5:15 ^b	1	75	B
12.	Di n-propyl sulfoxide	1:2:6	3	83	A
13.	Dimethyl sulfoxide	1:3:9 ^a	1	45 ^d	A
14.	Di n-dodecyl sulfoxide	1:10:30 ^b	1.5	96	B
15.	n-Octadecyl phenyl sulfoxide	1:11:33 ^b	3	96	B
16.	Benzyl n-dodecyl sulfoxide	1:12:36 ^b	1.5	84	B
17.	Dibenzyl selenoxide	1:1:1	5 min	93	B
18.	Di n-dodecyl selenoxide	1:1:1	5 min	93	B
19.	Diphenyl selenoxide	1:1:1	5 min	94	B
20.	Di n-butyl selenoxide	1:1:1	5 min	72	B
21.	Diphenyl selenone	1:2:6	15 min	35 ^d	B

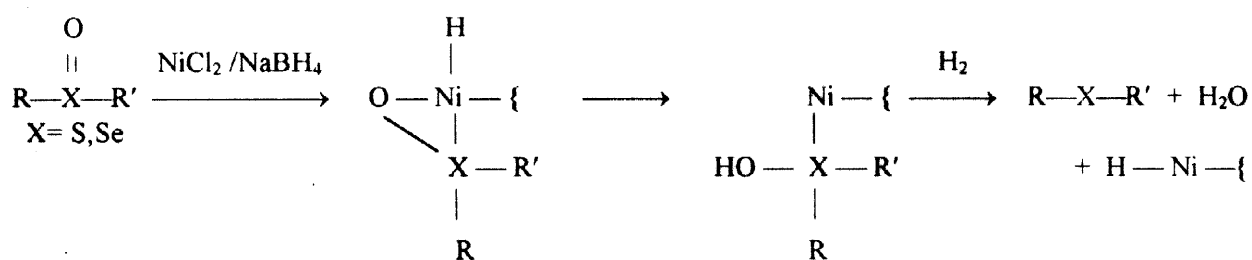
a) The initial molar ratio was 1:2:6. Subsequently small lots of 1:3 molar ratio of anhyd $\text{NiCl}_2 \cdot \text{NaBH}_4$ were added. b) Reactions carried out in dry THF. c) The yield reported corresponds to the mercuric chloride adduct. d) Selenium metal (61%) was also obtained.

of catalyst used etc. THF was found to be the solvent of choice. It is obvious from **Table 1** that deoxygenation of selenoxides is faster than sulfoxides and even requires lower substrate : NiCl_2 : NaBH_4 ratios. In some cases better yields could be obtained by a change in reaction work up. The reactions using methanol or ethanol substituting for THF were very sluggish.

Earlier studies conducted by Okamoto *et al.*¹⁰⁻¹² and Maybury *et al.*¹³ have shown that surface contamination by spectator ions such as Na^+ and Cl^- and the percentage of BO_2^- have a marked effect on the reactivity of this catalyst. The lower the ion solubility in boride forming solvents, the higher is its concentration as a surface contaminant and lower is the reactivity. Thus, while the contamination of Na^+ and Cl^- was high because of the use of THF, anhydrous nickel chloride and THF reduced (if not completely eliminated) the contamination of BO_2^- which is produced separately by reaction of NaBH_4 with water.¹⁴ This presumably rendered the catalyst with ideal selectivity for deoxygenation without desulfurization and deselenization.

The possibility of prior complexation of the substrate and nickel chloride followed by reduction with sodium borohydride was ruled out by the fact that the UV-Vis spectra of an equimolar mixture of NiCl_2 and diphenyl sulfoxide in dry THF was identical to the superimposed spectra of the individual compounds. Since nickel boride catalyzes the formation of dihydrogen from NaBH_4 under the reaction conditions, it appears likely that hydrogen is first produced and then adsorbed and activated on the nickel boride surface i.e. a nickel hydride species is responsible for the reduction. This is consistent with the report by Hawthorne *et al.*¹⁵ that fresh nickel boride has a composition $(\text{Ni}_2\text{B})_2\text{H}_3$ and the hydrogen is gradually lost when heated. These reactions are however less reactive and more selective than the desulfurization and deselenization with nickel boride reported by Back *et al.*⁸ because of the absence of a protic solvent and thus the liberation of lesser quantity of hydrogen.

The rapid loss of reactivity of catalyst upon aging is consistent with our observations since very little deoxygenation of dibenzyl sulfoxide and di n-dodecyl sulfoxide was observed with preformed nickel boride. This suggests that a transient intermediate, nickel hydride - and not merely adsorbed hydrogen - is formed on its surface. The probable mechanism which operates in these reactions is an oxidative addition of sulfoxide/selenoxide followed by hydrogenolysis (Scheme 1). It was observed that when dibenzyl sulfoxide was treated with preformed nickel boride



SCHEME 1

and hydrogen under pressure, 70% of dibenzyl sulfide and 30% of dibenzyl sulfoxide (HPLC ratios) were present even after 4 hr using higher molar ratios of substrate: NiCl_2 : NaBH_4 (compare with entry 1). This is also consistent with the above pathway.

General Procedure of Deoxygenation of Sulfoxides with Anhyd NiCl_2 - NaBH_4 in THF; Method A. The sulfoxide (1 mmol), anhyd nickel chloride (see Table) and THF (20 mL) were placed in a 50 mL RB flask fitted with a condenser. The flask was maintained in an ice-bath and mounted over a magnetic stirrer. Sodium borohydride (see Table) was added while stirring the solution vigorously. The progress of the reaction was monitored by thin layer chromatography (tlc) using benzene : ethyl acetate (95 : 5 v/v) as eluent. After complete disappearance of the sulfoxide, the reaction was quenched with conc nitric acid till the disappearance of the black precipitate of nickel boride. It was diluted with distilled water (150 mL) and the product extracted with ether (3 x 20 mL). The combined extract was dried over anhyd MgSO_4 , filtered and concentrated on a rotary vacuum evaporator. After drying under vacuum, the product was analysed by mp, IR and NMR spectra. In case of dimethyl sulfoxide, the outlet was connected to a gas passing tube dipped deep in mercuric chloride solution and the adduct $\text{Me}_2\text{S} \cdot \text{HgCl}_2$ was obtained.

General Procedure of Deoxygenation of Sulfoxides and Selenoxides with Anhyd $\text{NiCl}_2\text{-NaBH}_4$ in THF;

Method B. The sulfoxide/ selenoxide (1 mmol), anhyd nickel chloride (see Table) and THF (20 mL) were placed in a 50 mL RB flask fitted with a condenser and sealed with a mercury trap. The flask was maintained in an ice-bath and mounted over a magnetic stirrer. Sodium borohydride (see Table) was added while stirring the solution vigorously. The progress of the reaction was monitored by tlc. After complete disappearance of the sulfoxide/selenoxide, the reaction was quenched by filtration through a celite pad. The filtered nickel boride precipitate was washed with dichloromethane (2 x 20 mL) and the combined filtrate was washed with water (2 x 20 mL) and dried over anhyd MgSO_4 . The solvent was distilled off on a rotary vacuum evaporator. After drying under vacuum, the product was analyzed by mp, IR and NMR spectra.

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