An Exceptionally Rapid and Selective Deoxygenation of Aliphatic Sulfoxides to Sulfides under Mild Conditions with a New Reducing Agent, Dichloroborane

Herbert C. Brown and N. Ravindran*

Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907, U.S.A.

Aliphatic sulfoxides are rapidly deoxygenated to the corresponding sulfides in excellent yields by dichloroborane ($BHCl_2$)[1] in tetrahydrofuran at 0°, in a matter of minutes. Under these mild conditions, the sulfoxide is selectively reduced by the reagent without affecting other reducible structures, such as ketones, esters, and amides.

A study of the reaction of chloroboranes[1] with representative organic compounds[2] revealed that dichloroborane ($BHCl_2$) is a very mild reducing agent. Excess $BHCl_2$ in tetrahydrofuran at 0° does not reduce esters, acid chlorides, nitriles, nitro compounds, etc. Aldehydes, ketones, and amides are reduced only slowly. Very surprisingly, dimethyl sulfoxide is reduced remarkably rapidly, but sulfones and amine oxides are found to be inert. Moreover, the reaction of $BHCl_2$ with olefins is very sluggish in tetrahydrofuran[3,4]. These findings suggested the possibility of achieving a highly selective deoxygenation of sulfoxides under mild conditions with $BHCl_2$, even in the presence of other readily reducible groups. The need for such a mild reduction procedure for sulfoxides has recently been pointed out by Chasar[5].

It was observed that dimethyl sulfoxide and tetramethylene sulfoxide (tetrahydrothiophene-1-oxide) are reduced quantitatively in one min at 0° in tetrahydrofuran (1.0 *M* $BHCl_2$, 1.0 *M* sulfoxide). Under these conditions, di-*n*-propyl sulfoxide needed 5 min for nearly quantitative reduction. However, the reaction of diphenyl sulfoxide is much slower. But, it was converted to diphenyl sulfide in 90% yield in 24 hr at 25° using 100% excesss $BHCl_2$. The results of the reduction of sulfoxides are given in Table 1.

In order to explore the selectively of this reaction, the deoxygenation of di-*n*-propyl sulfoxide in the presence of an equivalent amount of 2-heptanone, ethyl hexanoate, and N,N-dimethylhexanamide was studied, employing 1.0 *M* $BHCl_2$ and 1.0 *M* sulfoxide. The sulfoxide was selectively reduced and the added "reducible" compound was recovered almost quantitatively. The results are given in Table 2.

Since $BHCl_2$ in tetrahydrofuran is a very poor hydroborating agent[3,4], C=C double bonds, if present in the sulfoxide, should not be affected by the reagent.

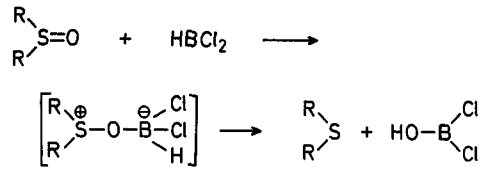
It is reported in the literature that sulfoxides are deoxygenated by hydriodic acid at higher temperatures[6], by excess triphenylphosphine at elevated temperatures[7,8], by considerable excess of trichlorosilane at room temperature[9], by hexachlorodisilane at room temperature[10], by a slight excess of $Fe(CO)_5$ at higher temperature[11], by a large excess of sodium borohydride/cobalt chloride mixture at room temperature[5], and to a very limited extent by aqueous sodium hydrogen sulfite at room temperature[12]. Either excess reagent or elevated temperatures or both are employed in these procedures in order to achieve a moderate yield of the sulfide. Mercaptal is formed as a major side product when trichlorosilane is used[9]. Some of the recommended reagents are very strong deoxygenating agents capable of deoxygenating even phosphine oxides[9,10]. Sodium borohydride/cobalt chloride mixture is a strong reducing system capable of reducing amides, nitriles, and nitro compounds[13]. The new method reported here for the deoxygenation of aliphatic sulfoxides clearly surpasses all the existing methods in the mildness of the reaction conditions, the speed of the reaction, and, above all, its selectivity.

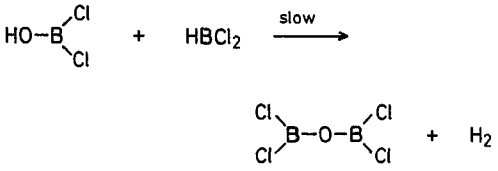
The $BHCl_2$ for these studies was prepared according to the procedure of Brown and Tierney[1] by mixing stoichiometric amounts of BCl_3 in tetrahydropyran with BH_3 in tetrahydrofuran at 0° (Reaction *1*) and stirring overnight.

(1) $2\,BCl_3 + BH_3 \longrightarrow 3\,HBCl_2$

The reagent is stable to loss of hydride over several months at 0°.

Finally, a word about the mechanism of the reaction might be in order. It was observed that dichloroborane reacts with the aliphatic sulfoxides in a 1:1 molar ratio to give the corresponding sulfides without liberation of hydrogen. However, if two moles of dichloroborane were used per mole of sulfoxide, there occurred a subsequent slow liberation of hydrogen. We suggest that the reaction involves the following mechanism (Reactions *2* and *3*).

(2) 

(3) 

The enzyme-like selectivity and the remarkable speed of the reaction under mild conditions make dichloroborane a very unique reagent for achieving the deoxygenation of aliphatic sulfoxides.

Tabe 1. Reduction of Sulfoxides with Dichloroborane in Tetrahydrofuran[a]

Sulfoxide	Reaction Temperature	Reaction Time	Yield of Sulfide (%)
Dimethyl sulfoxide[b]	0	1 min	90[c], 99[d]
Tetramethylene sulfoxide[b]	0	1 min	95[c]
Di-*n*-propyl sulfoxide[b]	0	5 min	94[c], 86[e]
Diphenyl sulfoxide[b]	0	2 hr	10[c]
Diphenyl sulfoxide[f]	25	4 hr	37[c]
Diphenyl sulfoxide[f]	25	24 hr	90[c]

[a] The solution contains 31% tetrahydropyran by volume.
[b] 1.0 *M* in sulfoxide, 1.0 *M* in $BHCl_2$.
[c] G.L.C. yield.
[d] Yield as indicated by stoichiometry of hydride used for reduction.
[e] Isolated yield.
[f] 1.0 *M* sulfoxide, 2.0 *M* in $BHCl_2$. In this case, the solution contains 62% tetrahydropyran by volume.

Preparation of Dichloroborane ($BHCl_2$) Solution:
To a solution of borane (516 mmol) in tetrahydrofuran (170 ml) in a dry 1-l round-bottom flask, a freshly prepared solution of boron trichloride (1032 mmol) in tetrahydropyran (556 ml) was slowly added with stirring at 0°. The solution was stored overnight at 0° before use. The solution was estimated to be 2.13 *M* in dichloroborane.

Reduction of Tetramethylene Sulfoxide:
A 100-ml round-bottom flask was charged with tetrahydrofuran (4 ml), tetramethylene sulfoxide (0.9 ml, 10 mmol), and *n*-octane (0.407 ml, 2.5 mmol; internal standard for G.L.C. analysis) under nitrogen. The flask was immersed in an ice bath and dichloroborane solution (4.7 ml, 10 mmol) was slowly added with stirring. One min after the addition was complete, an aliquot of the reaction mixture was quenchend in ice-cold aqueous sodium hydroxide; G.L.C. analysis of the organic layer indicated a 95% yield of tetrahydrothiophene. Analysis of the reaction mixture after 1 hr gave the same result.

Selective Deoxygenation of Dipropyl Sulfoxide:
A 100-ml round-bottom flask was charged with tetrahydrofuran (1.76 ml), *n*-heptane (0.732 ml, 5 mmol; internal standard for G.L.C. analysis), di-*n*-propyl sulfoxide (1.4 ml, 10 mmol), and 2-heptanone (1.41 ml, 10 mmol) under nitrogen. The flask was cooled in an ice bath and dichloroborane solution (4.7 ml, 10 mmol) was slowly added with stirring. Five min after the addition was complete, an aliquot of the reaction mixture was quenched in ice-cold aqueous sodium hydroxide; G.L.C. analysis of the organic layer indicated a 92% yield of dipropyl sulfide and only traces of 2-heptanol (96% of the 2-heptanone was found unchanged).

The experiment was repeated using ethyl hexanoate and N,N-dimethylhexanamide in place of 2-heptanone. In all cases, the sulfoxide was selectively deoxygenated and the added "reducible" compound was recovered almost quantitatively. The results are presented in Table 2.

Preparative-Scale Reduction of Dipropyl Sulfoxide to Dipropyl Sulfide:
To a solution of di-*n*-propyl sulfoxide (100 mmol) in tetrahydrofuran (53 ml) in a dry flask under nitrogen at 0°, dichloroborane solution (47 ml, 100 mmol) was added very slowly while stirring the reaction mixture. The temperature of the reaction mixture was not allowed to rise above 7°. Stirring was continued for a further 5 min, water (25 ml) and 3 *N* aqueous sodium hydroxide (67 ml, 200 mmol) were then added, and stirring was continued for 30 min at 0°. The mixture was extracted thrice with pentane, the extract washed with water, and dried with sodium sulfate. The solvent was removed and the sulfide purified by distillation under atmospheric pressure; yield: 86%; b.p. 140–142°. The product gave the expected ^{1}H-N.M.R. spectrum.

Table 2. Selective Deoxygenation of Di-*n*-Propyl Sulfoxide[a] by $BHCl_2$[a] in Tetrahydrofuran[b] at 0° in the Presence of Other "Reducible" Compounds[a]

"Reducible" Compound	Time, min	Yield (%) of Di-*n*-propyl sulfide	Recovery (%) of the "Reducible" Compound
2-Heptanone	5	92	96[c]
Ethyl hexanoate	5	96	99.5[d]
N,N-Dimethylhexanamide	5	87	100[e]
	15	87	100[e]
	60	96	100[e]

[a] 1.0 *M*.
[b] The solution contained 31% tetrahydropyran by volume.
[c] Traces of 2-heptanol were detected in the reaction mixture.
[d] 1-Hexanol was not found in the reaction mixture.
[e] No possible reduction product of the amide was detected in the reaction mixture. The slower rate of reduction of the sulfoxide in the presence of the amide might be due to the complexation of $BHCl_2$ by the amide.

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[1] H. C. Brown, P. A. Tierney, *J. Inorg. Nucl. Chem.* **9**, 51 (1959).
[2] H. C. Brown, N. Ravindran, A detailed study of selective reductions using chloroboranes has been completed. These results will be published shortly.
[3] G. Zweifel, *J Organometal. Chem.* **9**, 215 (1967).
[4] D. J. Pasto, P. Balasubramaniyan, *J. Amer. Chem. Soc.* **89**, 295 (1967).
[5] D. W. Chasar, *J. Org. Chem.* **36**, 613 (1971).
[6] E. N. Karaulova, G. D. Galpern, *Zh. Obshch. Khim.* **29**, 3033 (1959); *Engl. Edit.*, p. 2998.
[7] H. H. Szmant, O. Cox, *J. Org. Chem.* **31**, 1595 (1966).
[8] J. P. A. Castrillón, H. H. Szmant, *J. Org. Chem.* **30**, 1338, (1965).
[9] T. H. Chan, A. Melnyk, D. N. Harpp, *Tetrahedron Lett.* **1969**, 201.
[10] K. Naumann, G. Zon, K. Mislow, *J. Amer. Chem. Soc.* **91**, 7012 (1969).
[11] H. Alper, E. C. H. Keung, *Tetrahedron Lett.* **1970**, 53.
[12] C. R. Johnson, C. C. Bacon, J. J. Rigau, *J. Org. Chem.* **37**, 919 (1972).
[13] T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji, Z. Imai, *Tetrahedron Lett.* **1969**, 4555.