Tetrahedron Letters,Vol.26,No.52,pp 6453-6456,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

SELECTIVE DEOXYGENATION OF SULFOXIDES WITH THEXYLCHLOROBORANE-METHYL SULFIDE COMPLEX

Jin Soon Cha*, Jin Euog Kim, and Jong Dae Kim

Department of Chemistry, Yeungnam University, Gyongsan 632, Korea

Summary: Thexylchloroborane-methyl sulfide complex selectively deoxygenated both aromatic and aliphatic sulfoxides to the corresponding sulfides in high yield and purity at 0° C without affecting some other reducible structures.

The growing usefulness of organosulfur compounds in organic synthesis has been reviewed extensively[1]. The majority of the successful synthetic application of sulfoxides as important intermediates usually requires the removal of oxygen on sulfur after achieving such a synthetic transformation. For this reason, numerous reagents capable of effecting deoxygenation of sulfoxides to sulfides have been developed. The reagents, for examples, include borane and substituted boranes[2], complex metal hydrides[3], silanes[4], acid chloride[5], titanium compounds[6], sodium hydrogen sulfite[7], hydrogen[8], iron pentacarbonyl[9], and other miscellaneous reagents[10].

However, in most cases, the reaction requires the use of large excess of reagent or an elevated reaction temperature. Among boron reagents, although dichloroborane is the reagent which has been used successfully, it is not very reactive toward aromatic sulfoxides. Some hydride reagents like lithium aluminum hydride are strong reducing agents and therefore do not show any discrimination against most organic functional groups[11].

Very recently, a study on the approximate rate and stoichiometry of the reaction of excess thexylchloroborane-methyl sulfide complex, ThxBHCl·SMe_2, with representative organic compounds under standardized reaction condition (0° C, methylene chloride) has been completed[12]. The systematic study revealed that the reagent possesses an unique reducing characteristics and thus is a mild selective reducing agent. Excess thexylchloroborane at 0° C does not attack esters, epoxides, quinones, etc. Amides and acid chlorides are reduced only slowly. Carboxylic acids and acid anhydrides are reduced partially to form aldehydes[13]. The reagent reduces both aliphatic and aromatic sulfoxides remarkably rapidly, but disulfides and sulfones are inert toward

this reagent. This excellent chemoselectivity suggested the possibility of achieving a selective deoxygenation of sulfoxides under mild conditions, even in the presence of some other readily reducible functional groups.

The reaction of thexylchloroborane with both aliphatic and aromatic sulfoxides was established to be fast and effective. Dimethyl sulfoxide, di-n-butyl sulfoxide, and tetramethylene sulfoxide are reduced almost quantitatively in a matter of minutes with the 20% excess ThxBHCl·SMe_2 at 0°C. Even dibenzyl sulfoxide and alkyl phenyl sulfoxides are also reduced quantitatively within 10 min at 0°C. However, the reaction of diphenyl sulfoxide is much slower, but still much faster than that of dichloroborane. Thus, it was converted almost quantitatively to diphenyl sulfide in 2 hr at 25°C using 100% excess thexychloroborane. The results of the reaction are listed in Table 1.

Table 1. Reduction of Sulfoxides with Thexylchloroborane-Methyl Sulfide in Methylene Chloride at 0°C

Compound	Ratio (ThxBHCl:Sulfoxide)	Reaction time	Yield,% (isolated)
Dimethyl sulfoxide	1.0:1	1 min	84[a], 86[a,b]
	1.2:1	1 min	91[a], 95[a,b]
Di-n-butyl sulfoxide	1.2:1	5 min	87, 98[a]
Tetramethylene sulfoxide	1.2:1	5 min	84.5, 88[b], 97[a]
Dibenzyl sulfoxide	1.5:1	10 min	91[c], 94[b]
Benzyl phenyl sulfoxide	1.5:1	10 min	93[c], 95[b,c]
Methyl phenyl sulfoxide	1.2:1	10 min	92
Ethyl phenyl sulfoxide	1.2:1	10 min	82.5, 85[b]
Diphenyl sulfoxide	2.0:1	24 hr	84
	2.0:1[d]	2 hr	86, 89[b]

a)Yields determined by glc. b)Repeated data. c)Quantitative yield for the crude before recrystallization. d)At 25°C.

Thexylchloroborane-methyl sulfide shows an excellent selectivity. This selectivity can be applied to the selective deoxygenation of sulfoxides in the presence of other reducible compounds. Indeed, the reagent showed an excellent chemoselectivity. Thus, on the reaction of di-n-butyl sulfoxide in the presence of an equimolar amount of caproyl chloride, ethyl caproate, 1,2-butylene oxide, and N,N-dimethylbenzamide, the reagent reduced only the sulfoxide and the added reducible compound was recovered almost quantitatively. The results are summarized in Table 2.

Thexylchloroborane-methyl sulfide can be easily prepared from the hydroboration of monochloroborane-methyl sulfide with 2,3-dimethyl-2-butene. The reagent in methylene chloride is very stable. The reaction with sulfoxides is fast and the byproduct boronic acid can be removed easily. The reagent reacts with sulfoxides in a 1:1 molar ratio to yield the corresponding sulfides without liberation of any hydrogen; however, any excess of the reagent results in

a fast evolution of hydrogen(practically, about 20% excess of the reagent is needed to give a quantitative yield.). Therefore, the reaction mechanism seems to be very similar to the reaction of dichloroborane, with the exception that the hydrogen evolution from the boronic acid derivative 1 and thexylchloroborane is much faster than that from the dichloroborane reaction.

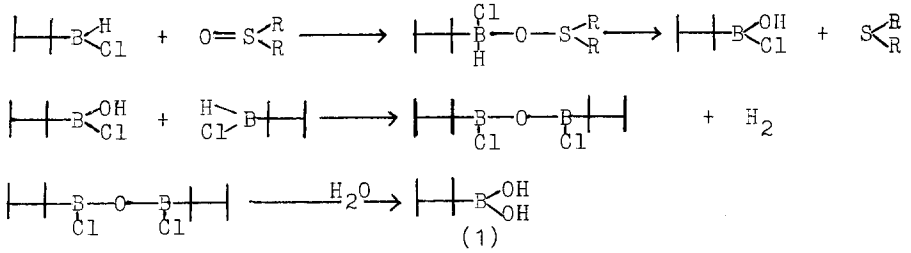

Table 2. Selective Deoxygenation of Di-n-butyl Sulfoxide with Thexylchloroborane-Methyl Sulfide in the Presence of Other Reducible Compounds in Methylene Chloride at 0°C[a]

Reducible compound	Time, min	Yield,% of di-n-butyl sulfide[b]	Recovery,% of reducible compound[b]
Caproyl chloride	5	93	98
Ethyl caproate	5	96	99
	60	97	99
1,2-Butylene oxide	5	95	97
	60	96	97
N,N-dimethylbenzamide	5	90	98
	30	97	98

a)1.0 M of each compound; 1.2 M of the reagent. b)Glc yield.

The following procedure for the deoxygenation of benzyl phenyl sulfoxide is representative. An oven-dried 100-ml flask was flushed with nitrogen, charged with 4.33 g(20 mmol) of benzyl phenyl sulfoxide and 10 ml of methylene chloride, and then immersed in an ice-water bath. To this was added 15 ml of 2.0 M ThxBHCl·SMe_2 in methylene chloride dropwise at 0°C. The reaction mixture was stirred for 10 min at 0°C and quenched with an aqueous 2 N NaOH solution. The organic layer was separated and the aqueous layer was extracted with pentane (10 ml x 3). The combined organic layer was concentrated on a rotary evaporator and passed through an alumina column to give the quantitative yield of product. Recrystallization from alcohol provided 3.73 g(93%) of pure benzyl phenyl sulfide. An alternative work-up procedure is available. After completion of the reaction, the mixture was quenched with aqueous 2 N NaOH and the organic layer was extracted two times with aqueous 2 N NaOH to remove the residual thexylboronic acid. Evaporation of the solvent followed by recrystallization yielded 95% of the pure product.

The procedure for the reaction of di-n-butyl sulfoxide in the presence of ethyl caproate is representative for the selective deoxygenation. An usual

setup was adopted and the flask was charged with methylene chloride, di-n-butyl sulfoxide(10 mmol), ethyl caproate(10 mmol), and an internal standard. The flask was cooled to 0°C and to this was added 12 mmol of thexylchloroborane dropwise at 0°C(1.0 M in each compound, 1.2 M in reagent). After stirring for 5 min, an aliquot was quenched with 2 N NaOH solution and washed two times with additional 2 N NaOH. Glc analysis of the organic layer indicated a 96% yield of di-n-butyl sulfide and a 99% of ethyl caproate unchanged.

Acknowledgement: Ministry of Education of Korea is gratefully acknowledged for financial support. One of author(Cha) is very thankful to Professor Herbert C. Brown for providing him laboratory facilities and helpful discussions, and also thanks Dr. B. Nazer for technical assistance.

References

1.(a)S. Oae, in "Organic Chemistry of Sulfur", Plenum Press, New York, 1977. (b)E. Block, in "Reaction of Organosulfur Compounds", Academic Press, New York, 1978.

2.(a)H.C. Brown and N. Ravindran, Synthesis, 42 (1972). (b)G.W. Kabalka, J.D. Baker, and G.W. Neal, J. Org. Chem., 42, 512 (1977). (c)E. Block, E.R. Corey, R.E. Penn, T.L. Renken, and P.F. Sherwin, J. Am. Chem. Soc., 98, 5715 (1976). (d)B.T. Cho and N.M. Yoon, J. Korean Chem. Soc., 26, 340 (1982). (e)Y. Guindon, J.G. Atkinson, and H.E. Morton, J. Org. Chem., 49, 4538 (1984).

3.(a)J. Drabowicz and M. Mikolajczyk, Synthesis, 527 (1976);A.G. Anastassiou, J.C. Wetzel, and B.Y-H. Chao, J. Am. Chem. Soc., 97, 1124 (1975). (b)D.W. Chasar, J. Org. Chem., 36, 613 (1971). (c)H.D. Durst, J.W. Zubrick, and G.R. Kieczykowski, Tetrahedron Lett., 19, 1977 (1974). (d)S. Kozuka, S. Furumai, T. Akasaka, and S. Oae, Chem. Ind.(L), 496 (1974).

4.(a)K. Naumann, G. Zon, and K. Mislow, J. Am. Chem. Soc., 91, 2788 (1968). (b)M.R. Detty, J. Org. Chem., 44, 4528 (1979). (c)T.H. Chan, A. Melnyk, and D.N. Harpp, Tetrahedron Lett., 201 (1969).

5.T. Numata and S. Oae, Chem. Ind.(L), 277 (1973).

6.(a)J. Drabowicz and M. Mikolajczyk, Synthesis, 138 (1978). (b)V. Baliah and P.V.V. Satyanarayana, Indian J. Chem. 17A, 183 (1979). (c)T-L. Ho and C.M. Wong, Synth. Commun., 3, 37 (1975).

7.C.R. Johnson, C.C. Bacon, and J.J. Rigau, J. Org. Chem., 37, 919 (1972).

8.K.Ogura, M. Yamashita, and G. Tsuchihashi, Synthesis, 385 (1975).

9.H. Alper and C.H. Keung, Tetrahedron Lett., 55 (1970).

10.(a)D.W. Chasar and T.M. Pratt, Synthesis, 262 (1976);M. Dreux, Y. Leroux, and P. Savignac, Synthesis, 506 (1974). (b)For a review, see: L. Field, Synthesis, 713 (1978).

11.(a)H.C. Brown, P.M. Weissman, and N.M. Yoon, J. Am. Chem. Soc., 88, 1458 (1966). (b)H.C. Brown and N.M. Yoon, J. Am. Chem. Soc., 88, 1464 (1966).

12.H.C. Brown, B. Nazer, J.S. Cha, and J.A. Sikorski; manuscript in preparation.

13.H.C. Brown, J.S. Cha, B. Nazer, and N.M. Yoon, J. Am. Chem. Soc., 106, 8001 (1984).

(Received in Japan 8 October 1985)