Tetrahedron Letters No. 23, pp 1969 - 1970, 1978. 0040-4039/78/0601-1969$02.00/0
© Pergamon Press Ltd. Printed in Great Britain.

REDUCTION OF SULFOXIDES BY DICHLOROCARBENE UNDER PHASE TRANSFER CATALYSIS CONDITIONS

H.S. Dilanjan Soysa and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

(Received in USA 13 February 1978; received in UK for publication 11 April 1978)

The facile and economical generation of dichlorocarbene from the reaction of chloroform with 50% aqueous sodium or potassium hydroxide under phase transfer catalytic conditions has stimulated study of the reactions of dichlorocarbene with numerous types of non-olefinic substrates.[1] Only one example of the reaction of dichlorocarbene with a sulfoxide has previously been reported. Thus dichlorocarbene generated by reaction of ethyl trichloroacetate with sodium methoxide reacts with dimethylsulfoxide to yield dimethyl sulfide (20%).[2] The considerable interest in reduction of sulfoxides[3] prompts us to report that dichlorocarbene efficiently deoxygenates most sulfoxides to yield the corresponding sulfides and phosgene under basic PTC conditions. The utilization of dichlorocarbene in this reaction is more efficient with diaryl sulfoxides than with dialkyl or alkyl aryl sulfoxides. Thus diphenyl sulfoxide is reduced to diphenyl sulfide (96%) under PTC conditions in the presence of 1.25 equivalents of chloroform. This efficiency is remarkable since even under PTC conditions dichlorocarbene hydrolyzes to some extent.[4] Similar results have been achieved with a variety of diaryl sulfoxides. On the other hand, dibutyl sulfoxide and methyl phenyl sulfoxide require 3.0 equivalents of chloroform to achieve 80% yields of dibutyl sulfide and methyl phenyl sulfide. We believe this lower efficiency may be due to ionization of the hydrogens alpha to the sulfinyl group; the corresponding alpha sulfinyl carbanion is unreactive. To test this idea, the reaction of dichlorocarbene was attempted with dibenzyl sulfoxide, t-butyl phenyl sulfoxide, and di-t-butyl sulfoxide. As expected, the reaction gave poor yields of dibenzyl sulfide. The hydrogens alpha to the sulfinyl group in dibenzyl sulfoxide are expected to be more acidic than those in dibutyl sulfoxide. On the other hand, the reduction of t-butyl phenyl sulfoxide was successful (71%) with 1.0 equivalent of chloroform. Finally, high yields of di-t-butyl sulfide (based on recovered di-t-butyl sulfoxide) are obtained only at low conversion. The reduction of the sterically hindered di-t-butyl sulfoxide is often difficult. We propose that the reaction occurs by initial coordination of the electrophilic dichlorocarbene with the nucleophilic oxygen of the sulfoxide to yield a 1,3-zwitterionic intermediate which decomposes to products.

$$\phi_2\overset{+}{S} \rightarrow \overset{-}{O} + [:CCl_2] \rightarrow [\phi_2\overset{+}{S}\text{-}O\text{-}\overset{-}{C}Cl_2] \rightarrow \phi_2S + COCl_2$$

Experimental

All of the compounds (both starting materials and products) are known. They were obtained commercially[5] or were prepared by literature methods. They all had physical and spectral properties in agreement with lit. values. The following is a typical procedure. The sulfoxide (1 mmol), chloroform (1-3.0 mmol), dichloromethane (5 ml), 50% KOH solution (7.4 g), and benzyltriethylammonium chloride[5] (25 mg) were placed in a 25 ml round bottom flask equipped with a reflux condenser and a teflon covered magnetic stirring bar. The mixture was stirred at rt for 20 h. The organic layer was separated and the aqueous layer was extracted throughly with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and analyzed by glpc on a 1/4" x 18" 20% DCQF-1 on Chromosorb W (treated with hexamethyldisilazane) column (glpc A), on a 1/4" x 7' 20% DCQF-1 on Chromosorb W (treated with hexamethyldisilazane) column (glpc B), or on a 1/4" x 18" 20% polyphenyl ether on Chromosorb P column (glpc C).

REDUCTION OF SULFOXIDES BY DICHLOROCARBENE

Sulfoxide	Sulfide	Yield	mmol $CHCl_3$	glpc
diphenyl sulfoxide[5]	diphenyl sulfide[5]	96%	1.25	A
di-*p*-tolyl sulfoxide[5]	di-*p*-tolyl sulfide[6]	98%	1.20	A
di-*p*-Cl-phenyl sulfoxide[5]	di-*p*-Cl-phenyl sulfide[7]	89%	1.10	A
di-*p*-CH_3O-phenyl sulfoxide[8]	di-*p*-CH_3O-phenyl sulfide[6]	89%	1.3	A
p-NO_2-phenyl phenyl sulfoxide[9]	*p*-NO_2-phenyl phenyl sulfide[9]	78%	1.3	A
dibutyl sulfoxide[5]	dibutyl sulfide[5]	78%	3.0	C
methyl phenyl sulfoxide[12]	methyl phenyl sulfide[5]	80%	3.0	C
t-butyl phenyl sulfoxide[8]	*t*-butyl phenyl sulfide[10]	71%	1.0	B
di-*t*-butyl sulfoxide[11]	di-*t*-butyl sulfide[5]	65%	0.54	B
		49%	1.0	B
		37%	1.3	B
dibenzyl sulfoxide[5]	dibenzyl sulfide[13]	20%	1.3	C

Acknowledgements

This work was supported by the Air Force Office of Scientific Research AFOSR-77-3123.

References

1. For a recent review, see Chapter 3, "Reactions of Dichlorocarbene with Non-Olefinic Substrates" in Phase Transfer Catalysis in Organic Synthesis; W.P. Weber and G.W. Gokel, Springer-Verlag, Berlin 1977.
2. R. Oda, M. Mieno, and Y. Hayashi, Tetrahedron Letters, 2363 (1967).
3. For a recent review, see J. Drabowicz, T. Numata, and S. Oae, Org. Prep. and Procedures Intl., 9, 64 (1977).
4. M. Makosza, M. Wawrzyniewicz, Tetrahedron Letters, 4659 (1969).
5. Aldrich Chemical Company.
6. J.R. Gaylor and C.V. Senoff, Can. J. Chem., 49, 2390 (1971).
7. D.W. Chasar and T.M. Pratt, Synthesis, 262 (1976).
8. G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, J. Chem. Soc., (C), 659 (1968).
9. H.H. Szmant and J.J. McIntosh, J. Am. Chem. Soc., 73, 4357 (1951).
10. V.N. Ipatieff, H. Pines, and B.S. Friedman, J. Am. Chem. Soc., 60, 2731 (1938).
11. D. Barnard, L. Bateman, M.E. Cain, T. Colclough, and J.I. Cunneen, J. Chem. Soc., 5339 (1961).
12. V.J. Traynelis, Y. Yoshikawa, S.M. Tarka, and J.R. Livingston, Jr., J. Org. Chem., 38, 3986 (1973).
13. J. Drabowicz and M. Mikolajczyk, Synthesis, 527 (1976).