Tetrahedron Letters, Vol. 33, No. 40, pp. 5897-5900, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

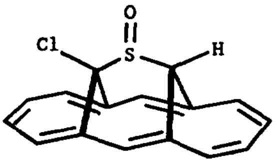
The One-pot Generation and Ring Opening of Alkyl and Aryl Thiirane-S-oxides

Adrian L. Schwan* and David A. Wilson

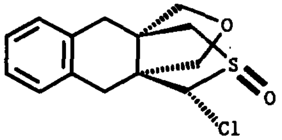
Guelph-Waterloo Centre for Graduate Work in Chemistry. Guelph Campus. Department of Chemistry and Biochemistry,
University of Guelph, Guelph, ON, Canada N1G 2W1.

Abstract: Base induced dehydrochlorination of acyclic α-chlorosulfoxides affords thiirane-S-oxides which react further under the alkaline reaction conditions.

The Ramberg-Bäcklund rearrangement is a valuable synthetic tool for the generation of alkenes.[1] The reaction involves the γ-dehydrohalogenation of an α-halosulfone to afford a thiirane-S,S-dioxide which extrudes SO_2 in the alkaline medium.[1] Although α-halosulfones are the most popular alkene precursors, there are reports of the analogous chemistry occurring with α-chlorosulfoxides.[2,3] Vogel has described a successful synthesis of an alkene from the treatment of 1 with KOtBu (90%).[2] In addition, the Weinges group has studied several substrates (represented here by α-chlorosulfoxide 2) and found in many instances that the α-chlorosulfoxides provided alkene much more efficiently than did the corresponding chlorosulfones.[3]



1 ref. 2

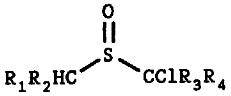
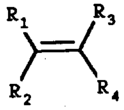


2 ref. 3(a)

If the so called 'W-mechanism' for the dehydrohalogenation of α-halosulfones[1] is operative with compounds 1 and 2, then it is not surprising that the γ-dehydrochlorination of 1 and 2 proceeds efficiently since the hydrogen and chlorine atoms to be eliminated are ideally positioned. Hence α-chlorosulfoxide 1 and those represented by 2 do not offer any sign that the γ-dehydrochlorination of α-chlorosulfoxides is a general process. This communication describes our preliminary results that offer evidence for the γ-dehydrochlorination of a series of acyclic α-chlorosulfoxides.

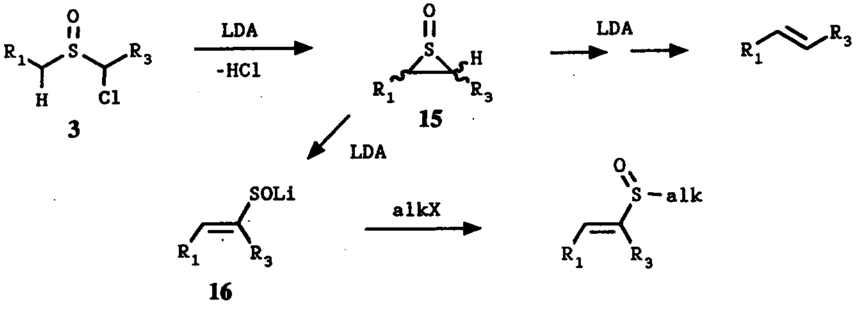
The α-chlorosulfoxides were prepared using established methods.[4] Before starting experiments it was realized that should thiirane-S-oxides form via γ-dehydrohalogenation, rapid ring-opening to ethenesulfenate anions may occur.[5] For this reason reaction mixtures were quenched with an alkyl halide in order to capture any sulfenates. Exposure of the α-chlorosulfoxides to two or more equivalents of LDA followed by quenching afforded the products indicated in the Table.[6] Gas chromatography

Table. Reaction of α-Chlorosulfoxides with LDA[a]

#	α-Chlorosulfoxide[b]	Cond.[c]	Products (yield)[d]	Total[e]
				
1	**3a**	A	**4**, $R_1 = S(O)CH_2Ph$ (35%)	35%
2	**3b**, $R_1 = Ph$	A	**5**, $R_1 = Ph$; $R_4 = S(O)Me$ (60%) styrene (8%)	68%
3	**3c**, $R_1 = R_3 = Ph$, 3:2 isomer ratio	A	**6**, $R_1 = R_3 = Ph$; $R_4 = S(O)Me$ (43%) *trans*-stilbene (21%)	64%
4	**3d**, $R_1 = C_{11}H_{23}$	B	**7**, $R_1 = C_{11}H_{23}$; $R_4 = S(O)Me$ (32%)	32%
5	**3e**, $R_3 = C_{11}H_{23}$, 5.5:1 isomer ratio	B	**7** (49%) **8**, $R_1 = C_{11}H_{23}$; $R_2 = S(O)Me$ (31%)	80%
6	**3f**, $R_1 = R_3 = CH_2Ph$, one isomer	B	**9**, $R_1 = R_3 = CH_2Ph$; $R_4 = S(O)Me$ (56%) **10**, $R_1 = Ph$; $R_3 = CH(S(O)Me)CH_2Ph$ (10%, 3:2 mixture of diastereomers)[f]	66%
7	**3g**, all R's = Me	C	$Me_2C{=}CMe_2$ (ca. 90%)	ca. 90%
8	**3h-A**, $R_1 = Ph$; $R_3 = \underline{n}Pr$, less polar isomer	B	**12**, $R_1 = Ph$; $R_4 = \underline{n}Pr$ (9%) **13**, $R_1 = Ph$; $R_2 = S(O)Me$; R_3 or $R_4 = \underline{n}Pr$ (32%, E:Z = 1:14.5)[f] **14**, $R_1 = Ph$; $R_4 = S(O)Me$; $R_3 = \underline{n}Pr$ (35%)	76%
9	**3h-B**, $R_1 = Ph$; $R_3 = \underline{n}Pr$, more polar isomer	A	**13** (59%, E:Z = >25:1)[f] **14** (18%)	77%

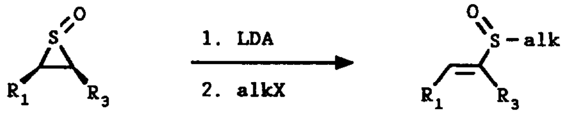
Footnotes. [a]Reactions were quenched with MeI, $PhCH_2Br$ or nothing (Entry #7). [b]$R_1 = R_2 = R_3 = R_4 = H$ unless otherwise noted. [c]Cond. = experimental conditions: Method A: Add **3** to 2 eq. LDA in THF at -78 °C; stir for 1 h (20 min. for **3c**); add RX. Method B: Add **3** to 2 eq. LDA in THF at -78 °C; stir for 1 h at 0 °C, cool to -78 °C; add RX. Method C: Add **3g** to 3 eq. LDA in ether at 78 °C, stir for 1h. [d]Yields reported for sulfoxides are of chromatographed material. Alkene yields were obtained by GC or NMR methods or by isolation. [e]Total yield of all products resulting from initial γ-dehydrochlorination. [f]Isomer ratios were obtained from the ^1H NMR spectra by comparing the intensities of the methyl singlets.

indicated that no alkene formed from **3d**, **3e** or **3f**. Note the exclusive formation of trans vinyl sulfoxides in many instances. The products can be accounted for by the mechanism in Scheme 1. We propose that the products shown in the Table all arise from initial γ-dehydrochlorination. This process consumes one equivalent of base. The second base attack may be at sulfur or at a ring hydrogen. When the thiirane-S-oxide bears a phenyl substituent (benzyl in the starting α-chlorosulfoxide; substrates **3b**, **3c** and **3i**), attack can be at sulfur to eventually afford the alkene.[5]



Scheme 1

The alternative pathway for base attack involves removal of a hydrogen from the thiirane-S-oxide ring. Rapid ring opening ensues[5,7] to give a lithium ethenesulfenate (**16**). The alkyl halide reacts with **16** at sulfur to furnish a vinyl sulfoxide.[8] Bonini et al.[5] have previously demonstrated this reaction mode for phenyl substituted thiirane-S-oxides. To further support the proposed mechanism, we report the first two examples of the corresponding chemistry on non-aryl substituted thiirane-S-oxides. Thus thiirane-S-oxide and *anti*-1-decyl thiirane-S-oxide were treated with one equivalent of LDA and then an alkyl halide (Scheme 2). The subsequent isolation of vinyl sulfoxides **4**(65%) and **7**(55%) and the previous work[5] confirm that the proposed transient aryl and alkyl substituted thiirane-S-oxides (**15**) can be ring opened with LDA. Furthermore, the resulting ethenesulfenates can be alkylated to afford vinyl sulfoxides having the trans configuration only (Scheme 2). The finding that thiirane-S-oxides and α-chlorosulfoxides both produce trans vinyl sulfoxides is particularly important, since geometrically pure vinyl sulfoxides are often difficult to synthesize.[9] Diastereomers **10** (Entry #6 of Table) probably arise from removal of a benzylic proton from 1,2-dibenzyl thiirane-S-oxide. Ring opening affords a substituted prop-2-enesulfenate which is captured by MeI.



5, 22%ref. 5
6, 70%ref. 5
4, 65%
7, 55%

Scheme 2

Only one option is available after ring closure of 2-chloro-2-propyl 2-propyl sulfoxide (**3g**). The expected deprotonation/ring opening is precluded by the absence of ring hydrogens on tetramethyl thiirane-S-oxide. In this instance the lone alternative is attack at sulfur, despite the fact that this process is not observed with other alkyl chloroalkyl sulfoxides. Clearly alkene formation can occur efficiently when there are no competing reactions. The high yield of tetramethylethylene hints at the possibility that α-chlorosulfoxides may be equal to or superior to α-chlorosulfones for the formation of tetra substituted alkenes via dehydrohalogenation chemistry.[1]

Finally, we were able to separate diastereomers **3h-A** and **3h-B** and their relative reactivities are quite striking. The data in the Table indicate that **3h-A** reacts to form predominantly **13E** and **14**, in similar yields. On the other hand, with the more polar isomer **3h-B**, γ-dehydrochlorination and subsequent reactions afford **13Z** as a major product rather than **13E** or **14**. This result implies that the dehydrochlorination/deprotonation sequence possesses noteworthy stereochemical attributes. The stereochemistry of this reaction is the subject of our current investigations.

ACKNOWLEDGEMENTS. The authors are indebted to NSERC of Canada and the University of Guelph for their financial support. We also thank Prof. E. Block (SUNY/Albany) for helpful comments.

REFERENCES AND NOTES

1. (a) Paquette, L.A., *Org. React.* 1977, *25*, 1-71. (b) Block E.; Putman, D.; Schwan, A. In *Sulfur-centered Reactive Intermediates in Chemistry and Biology NATO-ASI Series, Life Sciences*; Chatgilialoglu, C; Asmus K.-D., Eds.; Plenum Press, London, 1990 pp. 257-267.

2. Vogel, E.; Wieland, H.; Schmalstieg, L.; Lex, J. *Angew. Chem. Internat. Ed. Engl.* 1984, *23*, 717-719.

3. (a) Weinges, K.; Kasel, W.; Klein, J.; Hubertus, G.; Irngartner, H.; Huber-Patz,; Rodewald, H. *Chem. Ber.* 1984, *117*, 966-981. (b) Weinges, K.; Kasel, W.; Huber-Patz, U.; Rodewald, H.; Irngartner, H.; *Chem. Ber.* 1984, *117*, 1868-1876. (c) Weinges, K.; Sipos, W.; Klein, J.; Deuter, J.; Irngartner, H.; *Chem. Ber.* 1986, *120*, 5-9.

4. (a) Tin, K.-C.; Durst, T. *Tetrahedron Letters.* 1970, 4643-4644. (b) Dilworth, B.M.; McGilvey, M.A. *Tetrahedron*, 1986, *42*, 3137-3752.

5. Bonini, B.F.; Maccagnani, G.; Mazzanti, G.; Zani, P. *Gazz. Chim. Ital.* 1990, *120*, 115-121.

6. Double bond geometry was established using the H-C=C-H ^{1}H nmr coupling constants or by employing the alkene chemical shift additivity rule which has been shown to be reliable for comparable vinyl sulfoxides. See: Mikołajczyk, M.; Grzejszczak, S.; Zatorski, A. *Tetrahedron.* 1976, *32*, 969-973. Geometry of isomers 13 was assigned by comparison to model compounds.$^{\text{Ref. 5}}$ Satisfactory spectroscopic data was obtained for all new vinyl sulfoxides.

7. Homologous versions of anionic ring-openings of cyclic sulfoxides have been noted previously: (a) Neville-Jones, D; Kogan, T.P.; Newton, R.F.; Smith, S. *J. Chem. Soc., Chem. Commun.* 1982, 589-591. (b) Dodson, R.M.; Hammen, P.D.; Fan, J.Y. *J. Org. Chem.* 1971, *36*, 2703-2708.

8. Substituted lithium ethenesulfenates have been proposed heretofore, but not the parent lithium ethenesulfenate. See: (a) van der Leij, M.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* 1982, *99*, 49-52. (b) Crumbie, R.L.; Ridley, D.D. *Aust. J. Chem.* 1981, *34*, 1017-1026. Potassium ethenesulfenate has been generated: Schank, K.; Wilmes, R.; Ferdinand, G. *Int. J. Sulfur Chem.* 1973, *8*, 397-400.

9. (a) Mikołajczyk, M.; Perlikowska, W.; Omelańczuk, J.; Cristau, H.-J.; Perraud-Darcy, A. *Synlett* 1991, 913-915 and references therein.

(Received in USA 4 May 1992; accepted 22 June 1992)