Tetrahedron Letters No. 52, pp 5171 - 5174. 0040-4039/78/1222-5171$02.00/0

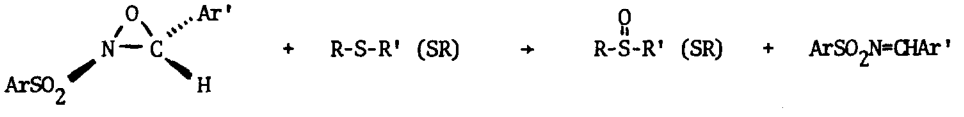
2-ARENESULFONYL-3-ARYLOXAZIRIDINES: A NEW CLASS OF APROTIC OXIDIZING AGENTS (OXIDATION OF ORGANIC SULFUR COMPOUNDS)

By: Franklin A. Davis*, Robert Jenkins Jr. and Steven G. Yocklovich
(Department of Chemistry, Drexel University, Philadelphia
Pennsylvania 19104)

Oxaziridines are an important class of three membered heterocyclic compounds that are unusually reactive and display novel chemistry.[1] At present there is not a clear understanding of the reactions and properties of these molecules. Although oxaziridines are active oxygen compounds capable of oxidizing triphenylphosphine to triphenylphosphine oxide[2] and hydrogen iodide to iodine[3], they have not been reported to oxidize organic sulfur compounds. In fact E-2-t-butyl-3-phenyloxaziridine failed to undergo any detectable reaction with thioanisole even on heating for more than 48 hr. at 60° C.

Recently we reported the synthesis and thermal[4] and photochemical[5] transformations of a new class of oxaziridines, E-2-arenesulfonyl-3-aryloxaziridines (**1**)[6]. These compounds are the first stable examples of this heterocyclic system to have an atom other than carbon attached to nitrogen and are characterized by a highly electrophilic oxygen atom. We wish to report that **1** selectively oxidizes sulfides and disulfides to the corresponding sulfoxides and thiolsulfinates.

The oxidation, which takes place according to eq 1, is carried out by adding an equivalent amount of the oxaziridine in chloroform to the organic sulfur compound[7] at room temperature (Table). The oxidation of sulfides by **1** is virtually instantaneous as determined by NMR with no detectable amount of sulfone formation.[8] Only a few reagents are capable of the selective oxidation of sulfides to sulfoxides without contamination by the corresponding sulfones.[9] Oxidation of sterically hindered disulfides to thiolsulfinates (Table, entries 8 and 9) by **1**



(1)

1a, Ar=Ar'=Ph
b, Ar=4-MeOC$_6$H$_4$, Ar'=Ph

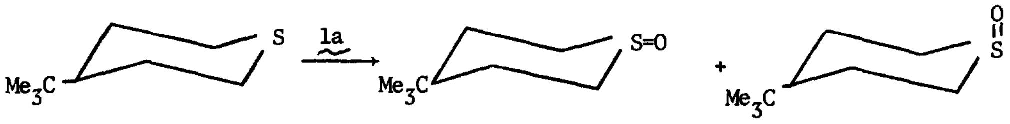
2

took considerably longer.

The yields of sulfoxides, determined by nmr were in excess of 90 percent. Yields by glc were somewhat lower (Table). The sulfoxides and thiolsulfinates may be separated from the sulfonimine, **2**, by preparative TLC and/or vacuum distillation.

Oxidation of sulfides to sulfones by excess **1** is quite slow. For example thioanisole with 2.5 equivalents of **1a** gave after 20 hr. an 80:20 mixture of the sulfone and sulfoxide (Table, entry 3). The less reactive diphenyl sulfide, under similar conditions, gave a 39:55 mixture of the sulfone-sulfoxide (Table, entry 5).

The unprecedented oxidation of organic sulfur compounds by **1** is a consequence of the 2-arenesulfonyl group which apparently increases the electrophilicity of the oxaziridine oxygen atom. We envision the first step in the oxidation (eq 1) to be similar to that proposed for the oxidation of sulfides by peroxy compounds,[10] namely a nucleophilic attack by the sulfur atom on the oxaziridine oxygen atom. The fact that **1a** oxidizes 4-t-butylthian (**3**) to give a 64 percent yield of the thermodynamically less stable, but sterically favored, trans sulfoxide provides additional support for this mechanism.[11] Most peroxy compounds give a similar predominance of the trans sulfoxide.[12] We have proposed an analogous mechanism for the hydroxylation of organometallic reagents by **1a**.[13] Whether the oxidation of organosulfur compounds by **1** is concerted or stepwise is unclear. However, the fact that **1b** oxidizes thioanisole to the sulfone about three times slower than **1a** (Table, entry 3) suggests that there may be a slight negative charge developing on the oxaziridine nitrogen atom in the transition state.[14]

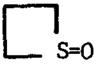
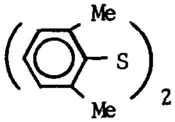
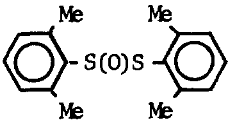
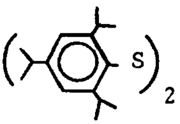
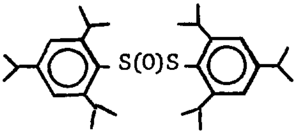


3 64 % 16 %

The east of preparation and lack of reactivity towards alcohols, aldehydes, alkenes and alkynes recommends 2-arenesulfonyl-3-aryloxaziridines (**1**) for the selective oxidation of organic sulfur compounds under aprotic conditions.

Acknowledgement: This investigation was supported by Public Health Service Grant No. CA-14341 from the National Cancer Institute DHEW. We thank Joseph P. Sabatucci for carrying out some preliminary experiments.

Table: Oxidation of Organic Sulfur Compounds by 2-Arenesulfonyl-3-aryloxaziridines (**1**) at 25° C in chloroform.

entry	Sulfur Compound	Oxaziridine (equivalents)	Time (Hr.)	Products (% yield)
1	Ph-S-Me	**1a** (1)	a	$\mathrm{Ph\text{-}\overset{\overset{O}{\|}}{S}\text{-}Me}$ (52)[b](80)[c]
2		**1a** (2.5)	20	$PhSO_2Me$ (80)[d], PhS(O)Me (20)[d]
3		**1b** (2.5)	60	$PhSO_2Me$ (80)[d], PhS(O)Me (20)[d]
4	Ph-S-Ph	**1a** (1)	a	PhS(O)Ph (93-7)[c]
5		**1a** (2.5)	20	$PhSO_2Ph$ (38)[c], PhS(O)Ph (55)[c]
6	$(CH_3CH_2CH_2CH_2)_2S$	**1a** (1)	a	$(CH_3CH_2CH_2CH_2)_2S{=}O$ (85-92)[c]
7		**1a** (1)	a	 (60-63)[b]
8		**1a** (1)	24	 (43-52)[b,e,f]
9		**1a** (1)	24	 (65-70)[b,e,g]

---

a) Oxidation too fast to measure. b) Isolated by preparative TLC on silica Gel (G). c) Glc analysis using a 6 ft. 3% OV-17 on 60/80 mesh Chromasorb W(Regular) column or a 6 ft. 10% GE XF 1150, 80/100 mesh Chromasorb W (Regular) column by comparision of peak areas with standard solutions. d) Determined by nmr. e) The corresponding disulfide was also detected. f) See ref. 16. g) See ref. 17.

References

1. For reviews on the chemistry of oxaziridines see: E. Schmitz, Advn. Heterocycl. Chem., 2, 83 (1963); W. D. Emmons, Heterocyclic Compounds, 19, 624 (1964); M. Lamchen, "Mechanisms of Molecular Migrations," Ed., B. S. Thyagarajan, Vol. 1, John Wiley, N.Y., 1968, p. 1.
2. L. Horner and E. Jurgens, Ber., 90, 2184 (1957).
3. W. D. Emmons, J. Am. Chem. Soc., 79, 5739 (1956).
4. F. A. Davis, U. K. Nadir and E. W. Kluger, JCS Chem. Commun., 25 (1977).
5. F. A. Davis and U. K. Nadir, Tetrahedron Lett., 1721 (1977).
6. J. S. Chen, W. H. Watson, F. A. Davis, J. F. Lamendola, Jr. and U. K. Nadir, Acta. Cryst., In Press
7. Addition of the oxaziridine dropwise or all at once to the sulfide had no effect on the product distribution.
8. Determined by nmr and glc.
9. For a discussion see: G. Barbieri, M. Cinquini, S. Colonna and F. Montanari, J. Chem. Soc. (C), 659 (1968).
10. For a review see: D. Barnard, L. Bateman and J. I. Cunnen, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, 1961, p. 229.
11. Yields were determined by glc using a 6 ft. 10% GE XF 1150, 80/100 mesh Chromasorb W (regular) column by comparision of peak areas with standard solutions.
12. C. R. Johnson and D. McCants Jr., J. Am. Chem. Soc., 87, 1109 (1965).
13. F. A. Davis, K. Balasubramanian, P. A. Mancinelli and U. K. Nadir, Manuscript submitted.
14. A detailed kinetic study of the oxidation is currently in progress.
15. K. A. Hooton and A. L. Allred, Inorg. Chem., 4, 671 (1965).
16. F. A. Davis, S. G. Yocklovich and G. S. Baker, Tetrahedron Lett., 97 (1978).
17. 2,4,6-Triisopropylphenyl 2,4,6-triisopropylbenzenethiolsulfinate has the following properties: mp, 123-124°; Anal. Calcd. for $C_{30}H_{46}OS_2$: C, 74.02; H, 9.52. Found: C, 74.26; H, 9.45; ir (KBr) 1100 cm.$^{-1}$ (S=O); nmr ($CDCl_3$) δ 1.3(m, 36H), 2.8(m,2H), 4.0(m, 2H), and 7.12(s, 4H).

(Received in USA 3 October 1978)