Unusually Ready Cleavage of an S–C$_\alpha$ Bond in Sterically Crowded Sulphoxides

Renji Okazaki,* Takayuki Ishida, and Naoki Inamoto

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

Oxidation of sterically crowded sulphides containing a 2,4,6-tri-t-butylphenyl group or its Dewar benzene analogue affords unusually unstable sulphoxides which undergo ready heterolytic S–C$_\alpha$ cleavage to give indan derivatives and sulphenic acids.

During the course of our study on sterically crowded organosulphur compounds,[1] we have found an unusually ready cleavage of the S–C$_\alpha$ bond in sulphoxides leading to the formation of a carbenium ion and a sulphenate anion.

When sulphide (**1**)† was oxidized in dichloromethane with *m*-chloroperbenzoic acid (MCPBA; at room temperature) or ozone (introduced at −78 °C and then gradually warmed to room temperature), indan (**2**)‡ was obtained in high yield instead of the expected sulphoxide (**3**) [Scheme 1; yields of (**2**): (**1a**) + MCPBA, 72%; (**1a**) + O_3, 88%; (**1b**) + MCPBA, 65%; (**1b**) + O_3, 83%]. Monitoring the reaction of (**1a**) with MCPBA by ^{1}H n.m.r. spectroscopy showed that sulphoxide (**3a**) was formed at low temperatures but decomposed around 0 °C to give (**2a**), indicating the instability of (**3a**). Sulphoxide (**3b**) was found to be slightly more stable than (**3a**) and almost pure (**3b**)‡ could be isolated by a rapid work up. However (**3b**) decomposed in solution (the half life in $CDCl_3$ at 25 °C was 4.3 h) to give (**2b**) in high yield.

Since the oxidation of (**1a**) or (**1b**) with ozone in methanol gave (**2a**) (76%) plus methyl ether (**4a**)‡ (11%) or (**2b**) (16%) plus (**4b**)‡ (60%) respectively [oxidation with MCPBA in methanol; (**2a**) (17%) + (**4a**) (62%) or (**2b**) (6%) + (**4b**) (60%)], the direct precursor of (**2**) is considered to be the carbenium ion (**5**) (Ar = 2,4,6-tri-t-butylphenyl). There are some precedents for similar intramolecular cyclizations of carbenium ions on unactivated methyl groups.[3]

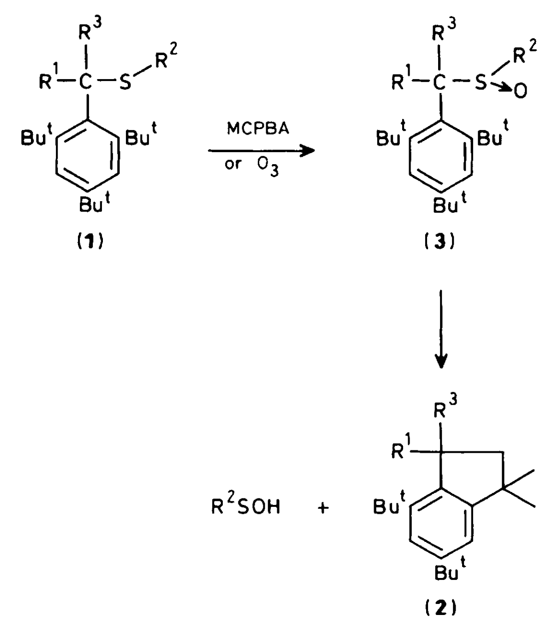
ArCHR^1(OMe)	Ar$\overset{+}{C}$HR^1	Ar–$\ddot{C}$–R
(**4**)	(**5**)	(**6**)

Although the formation of indan (**2**) and ether (**4**) can be accounted for also in terms of the intermediacy of carbene (**6**) which might be formed by α-elimination of sulphenic acid R^{2}SOH from (**3**), this possibility was discounted since the oxidation of deuteriated (**1c**)† with MCPBA gave (**2c**) with complete retention of the deuterium.

The formation of sulphenic acids in these oxidation reactions was confirmed by a trapping experiment.[4] Thus the reaction of (**1b**) with MCPBA in dichloromethane in the presence of excess of methyl propiolate gave a trapped product [$PhCH_2S(O)CH=CHCO_2Me$] (24%) and thiosulphinate [$PhCH_2S$–$S(O)CH_2Ph$] (**7**)[5] (11%) along with (**2b**) (91%). In the absence of methyl propiolate (**7**) (60%) was obtained together with 65% of (**2b**).§ Thiosulphinates are known to be formed from sulphenic acids by dimerization followed by loss of water.[4]

The present reaction represents the first example of the S–C$_\alpha$ heterolytic cleavage of sulphoxides,[6] although it is well known that sulphoxides with β-hydrogens undergo thermal pericyclic reactions involving S–C$_\alpha$ bond cleavage.[7,8] This unusually facile cleavage obviously results from the extremely high steric congestion around the sulphoxide group and the weakening of the S–C$_\alpha$ bond[9] by the introduction of the sulphoxide oxygen, [C–S(O) bonds are 20 kcal/mol weaker than C–S bonds].

The ready bond cleavage observed in highly crowded sulphoxides is not restricted to benzyl type compounds. Interestingly, sulphide (**8**)[1c] containing a Dewar benzene skeleton was oxidized with MCPBA at room temperature to give indan (**2a**) (79%) with concomitant aromatization. The



a; R^1 = R^2 = Bu^t, R^3 = H
b; R^1 = Ph, R^2 = CH_2Ph, R^3 = H
c; R^1 = R^2 = Bu^t, R^3 = D

Scheme 1

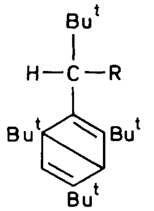
† Sulphide (**1b**) was prepared by the reaction of PhMgBr with ArCHS (Ar = 2,4,6-tri-t-butylphenyl)[1a] followed by benzylation with benzyl chloride. Sulphide (**1c**) was obtained by the reaction of $ArCDS^2$ with Bu^{t}MgCl. For (**1a**), see ref. 1b.

‡ All new compounds gave satisfactory spectral and analytical data. *Spectroscopic data* for (**2a**): m.p. 79—80 °C; ^{1}H n.m.r. ($CDCl_3$) 0.76 (s, 9H), 1.04 (s, 3H), 1.30 (s, 9H), 1.40 (s, 9H), 1.46 (s, 3H), 1.94 (d, *J* 5.4 Hz, 2H), 3.60 (t, *J* 5.4 Hz, 1H), 6.82 (d, *J* 2.0 Hz, 1H), 7.25 (d, *J* 2.0 Hz, 1H); ^{13}C n.m.r. ($CDCl_3$) 27.8, 29.3, 31.6, 33.7, 34.5, 35.3, 38.0, 38.8, 41.31, 41.36, 52.7, 115.0, 123.7, 136.4, 147.3, 148.7, 153.5; mass spectrum *m/z* 314 (M^+, 20%), 257 (100).

(**3b**): m.p. 93—94 °C (decomp.); ^{1}H n.m.r. ($CDCl_3$) 1.23 (br. s, 9H), 1.37 (s, 9H), 1.53 (br. s, 9H), 3.10 (d, *J* 13 Hz, 1H), 3.63 (d, *J* 13 Hz, 1H), 6.39 (s, 1H), 7.2—7.4 (m, 10H), 7.62 (br. s, 2H); mass spectrum *m/z* 334 (M^+ − $PhCH_2SOH$, 16%), 57 (100); i.r. (KBr) 1040 cm^{-1} (S–O).

(**4a**): ^{1}H n.m.r. ($CDCl_3$) 0.52 (s, 9H), 1.27 (s, 9H), 1.50 (s, 9H), 3.68 (s, 3H), 4.87 (s, 1H), 7.14 (d, *J* 2.4 Hz, 1H), 7.23 (d, *J* 2.4 Hz, 1H); ^{13}C n.m.r. ($CDCl_3$) 22.8, 31.4, 34.39, 34.42, 35.4, 38.1, 39.5, 40.5, 60.3, 89.0, 120.9, 122.3, 137.0, 145.6, 149.5, 150.7; mass spectrum *m/z* 347 (M^+ + 1, 8%), 289 (100).

§ Oxidation of (**1b**) with ozone in dichloromethane afforded (**2b**) (83%), $(PhCH_2S)_2$ (59%), and $PhCH_2SSO_2CH_2Ph$ (24%).



(**8**), R = S-Bu^t
(**9**), R = +

Dewar benzene (**8**) itself is so stable towards aromatization that it only isomerizes into (**1a**) at 200 °C for 4 h. This unusually ready aromatization most likely proceeds *via* valence isomerization of (**9**) into (**5a**) and represents, to our knowledge, the first example of isomerization of 'Dewar benzyl cation' to 'Kekulé benzyl cation.' The reaction is reminiscent of the marked acceleration by electron acceptor catalysts of isomerization of hexamethyl(Dewar benzene) to hexamethylbenzene.[10]

Received, 14th September 1987; Com. 1341

References

1 (a) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1982, 1187; (b) R. Okazaki, N. Fukuda, H. Oyama, and N. Inamoto, *Chem. Lett.*, 1984, 101; (c) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *Tetrahedron Lett.*, 1984, **25**, 849; (d) R. Okazaki, T. Fujii, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, 1984, 1010; (e) R. Okazaki, A. Ishii, and N. Inamoto, *J. Am. Chem. Soc.*, 1987, **109**, 279.

2 A. Ishii, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1037.

3 S. E. Biali and Z. Rappoport, *J. Org. Chem.*, 1986, **51**, 964 and references cited therein; G. Yamamoto and M. Ōki, *Chem. Lett.*, 1987, 1163.

4 D. R. Hogg, in 'Comprehensive Organic Chemistry,' ed. D. H. R. Barton and W. D. Ollis, Pergamon Press, New York, 1978, vol. 3, p. 265.

5 L. E. Legler, S. L. Jindal, and R. W. Murray, *Tetrahedron Lett.*, 1972, 3907.

6 It has been reported (G. Modena, U. Quintily, and G. Scorrano, *J. Am. Chem. Soc.*, 1972, **94**, 202) that the racemization of t-butyl phenyl sulphoxide in a strongly acidic medium can be explained by a S–C_α bond cleavage in a protonated sulphoxide. Although an acid catalyzed cleavage due to *m*-chlorobenzoic acid formed during the reaction is possible in the reactions with MCPBA, this possibility can be eliminated since: (i) the results for reactions with (**1b**) are essentially the same as those obtained for reactions using isolated sulphoxide (**3b**); (ii) reactions with ozone as an oxidizing agent gave almost similar results to those with MCPBA.

7 T. Durst, in 'Comprehensive Organic Chemstry,' ed. D. H. R. Barton and W. D. Ollis, Pergamon Press, New York, 1978, vol. 3, p. 140.

8 E. Block, 'Reactions of Organosulfur Compounds,' Academic Press, New York, 1978, p. 280.

9 S. W. Benson, *Chem. Rev.*, 1978, **78**, 23.

10 N. J. Peacock and G. B. Schuster, *J. Am. Chem. Soc.*, 1983, **105**, 3632; H. Iwamura, Y. Tanabe, and H. Kobayashi, *Tetrahedron Lett.*, 1976, 1987.