A Sulphene by the "Abnormal" Route

By J. F. KING* and R. P. BEATSON

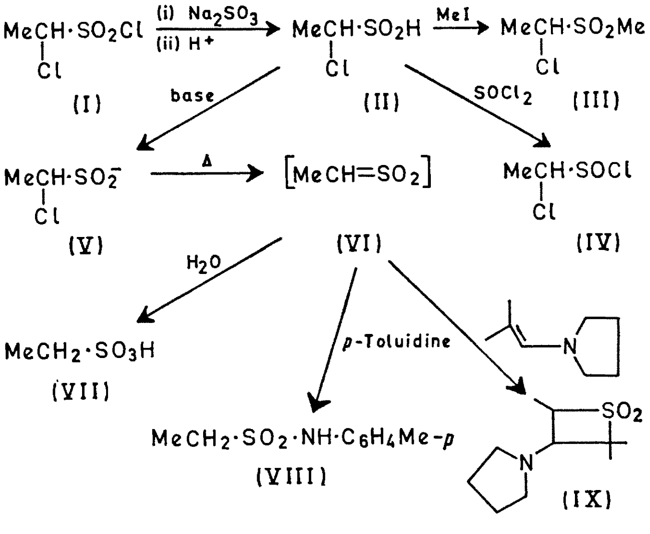
(*Department of Chemistry, University of Western Ontario, London 72, Ontario, Canada*)

Summary Warming 1-chloroethanesulphinic acid (II) with base gives products derived from methylsulphene (VI).

SULPHENES on reacting with nucleophiles give sulphonyl derivatives, formed by attack of the nucleophile on the sulphur atom.[1] We have suggested[2] that in certain circumstances the site of bond formation with a nucleophile might be the carbon or even the oxygen atoms, leading to a sulphinyl derivative, and have called such reaction "abnormal" attack. We now describe a method of forming a sulphene by the hitherto unknown "abnormal" route, *i.e.* a process that is the formal reverse of "abnormal" attack.

In 1931 it was reported[3] that 1-chloroethanesulphonyl chloride (I) with zinc and ethanol gives ethanesulphonic acid (VII), an observation readily explained by assuming that reduction leads to methylsulphene (VI) which then reacts normally with water. We have verified the formation of (VII) though our yield was only 15—20%. With Na_2SO_3 as the reducing agent, however, we obtained a good yield of 1-chloroethanesulphinic acid (II) as a colourless oil which was characterised by (i) spectra [n.m.r. δ 1·76 (d, J 7 Hz), 4·53 (q), 10·5 p.p.m. (s), in the ratio 3 : 1 : 1; i.r. 1075 and 835 cm^{-1}], (ii) $pK_a < 2$, (iii) conversion into two derivatives (III) and (IV) as follows. Reaction with methyl iodide gave methyl 1-chloroethyl sulphone (III) m.p. 56—57° (reported[4] m.p. 62°), bands at 1·85 (d), 2·98 (s), and 4·68 p.p.m. (q, J 8 Hz) in the n.m.r., and 1322 and 1145 cm^{-1} in the i.r. Treatment of (II) with thionyl chloride gave (IV) as a colourless liquid which showed strong i.r. absorption at 1150 cm^{-1}. The n.m.r. spectrum clearly showed the presence of two diastereoisomers† with superimposed quartets at 5·02 and 5·18 (J 6·5 Hz, relative areas 3 : 5) and doublets at 1·92 and 1·91 p.p.m. (resolvable on a Varian HA 100 instrument).

Addition of triethylamine to (II) gives a solution which is moderately stable at room temperature but is completely decomposed after ½ h at 80°. With dilute aqueous NaOH (II) gave a good yield of (VII); with *p*-toluidine and triethylamine in refluxing benzene (II) gave (VIII) in 77% yield. In refluxing benzene (II) in the presence of triethylamine and an excess of 1-(2-methylpropenyl)pyrrolidine gave the cycloaddition product (IX) in 16% yield. Treatment of ethanesulphonyl chloride with triethylamine and the same enamine under the same conditions gave (IX) in 20% yield, though higher yields were obtained at lower temperatures. The structure of (IX) follows from its synthesis from ethanesulphonyl chloride (*via* an undoubted sulphene) and its elemental analysis and spectra; the large coupling (9 Hz) between the two protons on the four-membered ring suggests that the methyl and pyrrolidino-group are *trans*.[6]



The simplest interpretation of these facts is that unimolecular decomposition of (V) gives (VI). In agreement with this, it was found that the rate of release of chloride ion from (II) was sensibly the same at pH 4·0, 5·0, and 5·9. The remote possibility existed that (VI) is formed by the action of base on ethanesulphonyl chloride [which could arise from rearrangement of (II)], rather than directly from (V). To exclude this, (II) was treated as before with [$^2H_2$]toluidine. The product (after work-up) was the monodeuteriated amide ($MeCHD{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4Me$) together with a small amount of the undeuteriated amide (VIII) but with no $MeCD_2{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4Me$ detectable either by n.m.r. or m.s. If any ethanesulphonyl chloride were produced in such an environment, it would have to be

---

† Though isomerism due to asymmetric sulphur is well-known with sulphonium salts, sulphoxides, and sulphinic esters, and has been reported for a crystalline sulphinic acid,[5] this seems to be the first reported occasion of its arising in a sulphinyl chloride.

largely $MeCHD{\cdot}SO_2Cl$ and this we found gives $MeCD_2{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4Me$ as its major product under these conditions. These results exclude ethanesulphonyl chloride or any other species in which the chlorine is replaced by hydrogen as an intermediate in this reaction. These are clearly the only previously authenticated sources of sulphenes conceivably present; the reaction therefore must be a new route to sulphenes.‡

The observation of sulphene formation from the 1-chloroethanesulphinate anion demonstrates that the transition state for the reverse process is, by microscopic reversibility, not of impossibly high energy. It follows that such "abnormal" attack on a sulphene must be seriously considered in accounting for the products derived from a sulphene, especially in those cases in which normal addition leads to starting material or other compounds capable of regenerating the sulphene.

(*Received, April* 20*th*, 1970; *Com.* 551.)

---

‡ The mechanism of reaction is not known, though the simplest, *i.e.* direct loss of Cl^- assisted by the electron pair on sulphur, is the most likely; a number of others are conceivable, *e.g.* displacement of Cl by a sulphinyl oxygen followed by rearrangement.

[1] *Cf.* G. Opitz, *Angew Chem. Internat. Edn.*, 1967, **6**, 107.
[2] J. F. King and T. Durst, *Tetrahedron Letters*, 1963, 585; see also J. F. King and T. Durst, *Canad. J. Chem.*, 1966, **44**, 819, footnote 2; T. Durst and J. F. King, *ibid.*, p. 1859; J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. de Mayo, *Chem. Comm.*, 1969, 31; J. F. King, A. Hawson, D. M. Deaken, and J. Komery, *ibid.*, p. 33.
[3] E. Müller and H. Raudenbusch, *Ber.*, 1931, **64**, 94.
[4] H. Bohme and H. J. Gran, *Annalen*, 1952, **577**, 68.
[5] F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 4099.
[6] *Cf.* L. A. Paquette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, 1969, **34**, 2901.