Oligomerization of Sulphene in Solution

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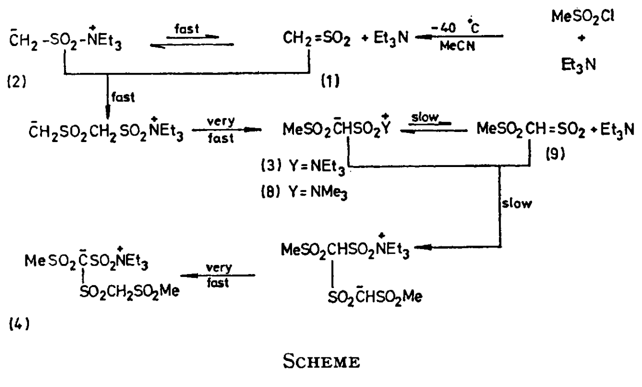
Summary Sulphenes and their amine zwitterions are shown to react in solution with the initial formation of a previously described dimer; this dimer may further dimerize to form a tetramer, which on reaction with water gives the sulphonic acid (**6**).

There are many reports concerning the addition of carbon or oxygen nucleophiles to sulphenes, and these have been thoroughly reviewed.[1] However, considerably less attention has been paid to the fate of sulphenes in solution in the absence of added nucleophiles,[2-4] although it is now clear that the sulphenes exist as zwitterions, complexed to the amines used to generate them.[3,5]

We here report evidence that sulphene (**1**) and its triethylamine complex (**2**) in the first instance dimerize rapidly to form (**3**),[3] and that this in turn dimerizes to form the tetramer (**4**). Experiments were carried out by quenching the reaction with water and then generating an aqueous solution of sulphonic acids by passing the solutions through a cation exchange column. The aqueous solutions were analysed for solid content, by titration with standard alkali, by chromatography on cellulose layers (MeCN–EtOH, 7 : 1), by ^{13}C n.m.r. spectroscopy, and, after replacement of water by deuterium oxide, by ^{1}H n.m.r. spectroscopy. In some cases, recovery of triethylamine was checked and overall mass balances were excellent.

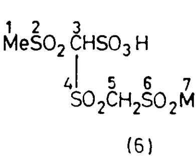
The dimeric acid (**5**) showed two peaks in both the ^{1}H {$\delta(D_2O$; DSS standard) (DSS = $Me_2Si[CH_2]_3SO_3Na$) 4·67 [q 2H, $J(CH_2—CH_3)$ 0·7 Hz) and 3·22 (t, 3H, $J(CH_3—CH_2)$



Scheme

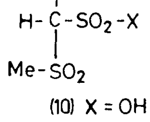
$MeSO_2CH_2SO_3H$

(5)



$MeSO_2CH(SO_3H)SO_2CH_2SO_2Me$

(6)



(10) X = OH

(11) X = CH_2SO_3H

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0·7 Hz)} and the ^{13}C n.m.r. spectra [δ(H_2O; Me_4Si) 68·9 (CH_2) and 41·7 (CH_3)]. Likewise, the n.m.r spectra of tetrameric acid (**6**) showed two proton peaks [δ(D_2O; DSS) 3·47 (s, 3H, Me-1) and 3·37 (s, 3H, Me-7)] and four ^{13}C peaks‡ [δ(H_2O; Me_4Si) 89·8 (methine C), 72·0 (methylene C), and 44·1 + 43·45 (2 × methyl C)]. The acid (**6**) showed no peaks above *m/e* 250 in the mass spectrum, was dibasic, very hygroscopic, and could be characterized as a colourless, stable, crystalline pyridinium salt, m.p. 183—185°, which had satisfactory C, H, N, O, and S analyses, together with expected u.v. and i.r. spectra, and titration curve with alkali. The salt showed no peaks above *m/e* 249·9643 ($C_4H_{10}O_6S_3$) in the mass spectrum, which was appropriately similar to that of the free acid, and gave the following n.m.r. data: δ[$(CD_3)_2SO$; Me_4Si] 10·5 br (1H, s, instantly exchangeable with D_2O), 8·6 (5H, m, pyridinium-H), 6·20 br (1H, s, instantly exchangeable with D_2O), 5·54 (2H, narrow m, D_2O exchangeable), 3·38 (3H, s), and 3·32 (3H, narrow m); δ(H_2O; Me_4Si)‡ 147·6, 141·8, 127·9 (pyridinium-C), 90·3 (methine C), 72·3 (methylene C), and 43·9 + 43·3 (2 × methyl C).

When the reaction of Et_3N (3 mol. equiv.) and $MeSO_2Cl$ (2 mol. equiv.) was quenched after 1 h, methanesulphonic acid (**7**) and compound (**5**) were the only identifiable products, being formed almost quantitatively (93%) in a molar ratio (**7**):(**5**) of *ca.* 1:12. After 4 h reaction time, the products (almost quantitative yield) were in the ratio (**7**):(**5**):(**6**) of *ca.* 1:15:2, and after 48 h§ of *ca.* 1:3:12. Addition of (**1**) + (**2**) to (**3**), and allowing the resultant mixture to stand, produced comparable results. The zwitterion (**8**) has, however, proved much less reactive than (**3**) and we have not yet definitely been able to detect an equilibrium such as (**8**) $\rightleftharpoons$ (**9**) followed by dimerization to a sulphene tetramer. This difference between (**3**) and (**8**) is noteworthy.

These results may be formulated in the series of reactions in the Scheme. The nonsymmetrical tetrameric zwitterion (**4**) must be viewed as the major final product in the oligomerization of sulphene in solution. It is sufficiently weakly nucleophilic (and no doubt sterically hindered) so as to be incapable of further reaction with (**9**). Two minor products, probably the trimer (**10**) (*ca.* 0·3% of the total acids from 4 h reaction) and the symmetrical tetramer (**11**) (*ca.* 1% of the total acids from 4 h reaction) were also detected as methyl peaks in the 100 MHz ^{1}H n.m.r. spectra. These would also be terminal oligomerization products and must arise *via* competitive minor pathways within the equilibria depicted in the Scheme.

Although we have not yet succeeded in isolating (**4**), or a derivative thereof, this species is likely to be the most electronically stabilized sulphene–amine zwitterion thus far prepared. In this connection, we draw attention to the concept of 'stabilized sulphenes'[6] and point out that whereas (**8**) is electronically stablized and is capable of being isolated and stored, there is no evidence to regard (**9**) as being electronically stabilized. It appears to be correct to regard sulphene–amine zwitterions as being stabilized by electron-withdrawing groups,[7] whereas sulphenes themselves may be stabilized by electron-releasing groups.[8]

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‡ Proton-noise decoupled.

§ At −20 °C.

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