^{1}H and ^{13}C Nuclear Magnetic Resonance Evidence for a Long-lived Thiirenium Ion

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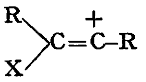
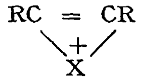
Summary Trimethyl- and 1-methyl-2,3-diethyl-thiirenium ions have been observed by n.m.r. spectroscopy as stable species in liquid SO_2 at low temperature.

VINYL cations (**1**) and the corresponding bridged ions (**2**), have been suggested as reactive intermediates in electrophilic additions to acetylenes as well as in solvolytic reactions of the appropriate vinyl derivatives.[1]



(1)

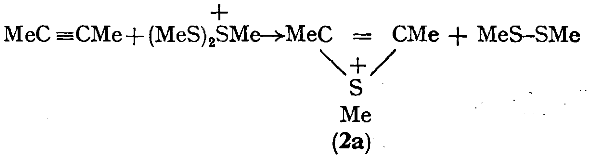


(2)

(**a**); X = SMe, R = Me
(**b**); X = SMe, R = Et

We now report the first observation of thiirenium ions (**2a**) and (**2b**) as stable species at low temperature. Ions of type (**1**) have been recently observed.[2]

The trimethylthiirenium ion (**2a**) is quantitatively formed by reaction of dimethylthio-methylsulphonium hexachloroantimonate (**3**)[3] with excess but-2-yne at about $-80°$ in liquid SO_2 (equation 1).



$$\mathrm{MeC{\equiv}CMe} + \mathrm{(MeS)_2\overset{+}{S}Me} \rightarrow \mathrm{MeC{=}CMe\ (\overset{+}{S}Me\ ring)} + \mathrm{MeS{-}SMe} \quad (1)$$

(2a)

The ^1H n.m.r. spectrum, which is unchanged for hours at low temperatures (-70 to $-50°$), shows, besides a singlet at δ 1·72 due to the excess butyne, three singlets at δ 2·43, 2·51 and 2·77 in the ratio 2 : 1 : 2. The signal at δ 2·43 corresponds to that of dimethyl disulphide in the same medium, and those at δ 2·51 and 2·77 are assigned to the SMe and CMe of the thiirenium ion respectively. This assignment was confirmed by carrying out the reaction in excess of (**3**); the butyne signal is absent, those of the thiirenium ion are unchanged in chemical shift and intensity ratio, but the other absorption, with a relatively higher intensity, now appears at lower field because of the fast exchange[3] between disulphide and excess of (**3**).

Addition of excess *N*-methylpyridinium chloride causes the disappearance of the thiirenium ion absorptions, and the appearance of those of (*E*)-1,2-dimethyl-2-methylthiovinyl chloride (**4**). This product was isolated in 60—80% yields after work up.†

The reaction solution of (**3**) with excess hex-3-yne using the same conditions gave a spectrum consistent with the formation of 1-methyl-2,3-diethylthiirenium ion (**2b**), δ 3·14 (4H, q, *J* 7·4), 1·46 (6H, t), and 2·54 (3H, s), and dimethyldisulphide, δ 2·42 (6H, s). The resonances of the excess hexyne are shown at δ 2·09 (4H, q, *J* 7·3) and 1·09 (6H, t).

The structure (**2a**) was confirmed by ^{13}C n.m.r. spectroscopy. The reaction solution of (**3**) with excess butyne shows signals‡ at δ 9·1 (C*Me*), 25·1 (SMe), and 103·1 (ring carbons) for the thiirenium ion, at δ 3·5 and 80·2 (butyne) and at 20·0 (dimethyl disulphide). The C*Me* and SMe shifts compare well with those reported for the α-methyls and SMe of the pentamethyl thiophenium ion[4] (δ 10·0 and 26·0). The alternative interpretation of the spectral data on the basis of a fast 1-2 sulphur shift in (**1**) seems unlikely since it would have required a lower chemical shift for SMe and a much higher one for the vinylic carbons.[5]

The stability of the thiirenium ions observed is consistent with results from chemical, kinetic and theoretical studies.[1,6] We also observed (**2a**) by ^1H n.m.r. spectroscopy, in the reaction of methanesulphenyl chloride with but-2-yne in SO_2 at low temperature, but only as a transient species.

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† Compound (**4**) was obtained by addition of methane sulphenyl chloride to but-2-yne in methylene chloride at 0° (b.p. 50°, 10 mmHg; ^1H n.m.r. spectrum (SO_2, $-60°$): δ 2·26 (3H, s) 2·18 (3H, q, *J* 1·6) and 2·02 (3H, q).

‡ p.p.m. from external Me_4Si in [$^2H_6$]-acetone.

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