

Effect of Stabilizing Substituents on [2,3] Sigmatropic Rearrangements of Sulphonium Ylides

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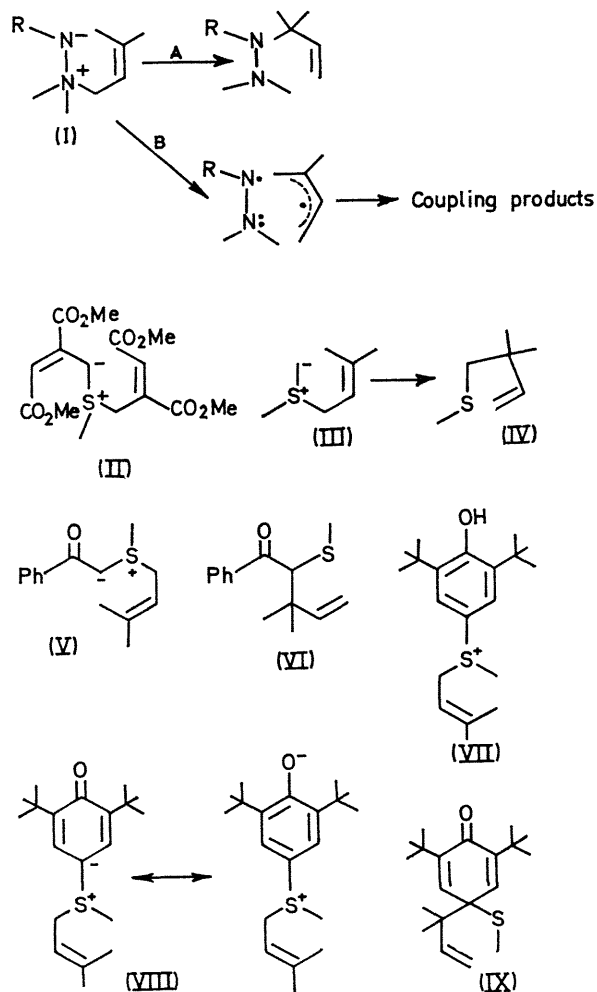
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Summary The sulphonium salt (VII) when exposed to base is cleanly rearranged to the sulphide (IX) even at -40° , indicating that extensive delocalisation of the intermediate ylide is insufficient to prevent the sigmatropic rearrangement.

RECENTLY we reported that the presence of a carbonyl substituent in the nitrogen ylide (I; R = COMe) inhibits the ready [2,3] sigmatropic shift (path A) found in the non-acylated species (I; R = H) and permits at higher temperature the operation of the radical dissociation-recombination route (path B).¹ Prior to these observations it had been reported that the sulphonium ylide (II), like the compounds (I, R = COMe), was a stable, isolable, species.² Since it is now established that ylides of type (III) are not isolable and undergo easy [2,3] sigmatropic rearrangement to the sulphides (IV), with little competition from path (B),³ except where the participating double bond is part of a benzenoid residue,⁴ this report² indicated that the carbonyl group (here as methoxycarbonyl) has a similar stabilizing effect on sulphonium ylides. However, the ylide (V) has been found to rearrange, under mild conditions, solely to the sulphide (VI),⁵ an observation we have confirmed. To verify whether more extensive delocalization of ylides is necessary to provide the stabilization observed in (II) we prepared the sulphonium salt (VII) (fluoroborate counterion)[†]; m.p. $117-119^\circ$ (decomp.); ν_{\max} 3550 cm^{-1} ; n.m.r. (CDCl_3): δ 1.5 (s, 18H), 1.7 (s, 6H), 3.2 (s, 3H), 4.3 (d, 2H), 5.2 (t, 1H), 6.0 (s, exchangeable 1H), and 7.5 p.p.m. (s, 2H), by successive alkylation of 4-mercapto-2,6-di-*t*-butylphenol with dimethylallyl bromide and trimethyloxonium fluoroborate. In the derived ylide (VIII) it was expected that the extensive delocalization into the benzenoid residue would permit isolation, since in this case the anion is part of a 6π electron system and rearrangement interrupts this system. However deprotonation (n-butyl-lithium in tetrahydrofuran, monitored by n.m.r.) at -40° yielded only the rearranged product (IX), as an oil [ν_{\max} 1660 and 1640 cm^{-1} , λ_{\max} (ethanol) 256 nm (ϵ 7500), n.m.r. (CDCl_3): δ 1.2 (s, 6H); 1.3 (s, 18H); 1.6 (s, 3H); 5.1 (m, 2H), 6.2 (q, 1H) and 6.7 p.p.m. (s, 2H)] which was reduced with zinc in acetic acid at room temperature to 4-(1,1-dimethylprop-2-enyl)-2,6-di-*t*-butylphenol, m.p. $68-69^\circ$. Thus even in this extensively delocalized ylide (VIII) the [2,3] sigmatropic rearrangement is extremely rapid and clean.

These results indicate that carbonyl substituents are

inadequate to stabilize sulphonium ylides of type (III) against sigmatropic rearrangements and therefore the existence of ylide (II) is anomalous.⁷



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† All new compounds gave satisfactory analytical data.

¹ J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Comm.*, 1970, 31.

² C. F. Garbers, A. J. H. Labuschagne, and D. F. Schneider, *Chem. Comm.*, 1969, 499.

³ J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 1969, **91**, 3646, and references cited therein.

⁴ J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Comm.*, 1970, 576.

⁵ R. W. C. Cose, A. M. Davies, W. D. Ollis, C. Smith, and I. O. Sutherland, *Chem. Comm.*, 1969, 293.

⁶ E. Mueller, H. Stegmann, and K. Scheffler, *Annalen*, 1969, **645**, 79.

⁷ In a reinvestigation it has been shown that the structural assignment of (II) is incorrect; J. E. Baldwin and J. Walker, unpublished observations.