Sulphonium Ylides with a Phosphinyl Substituent

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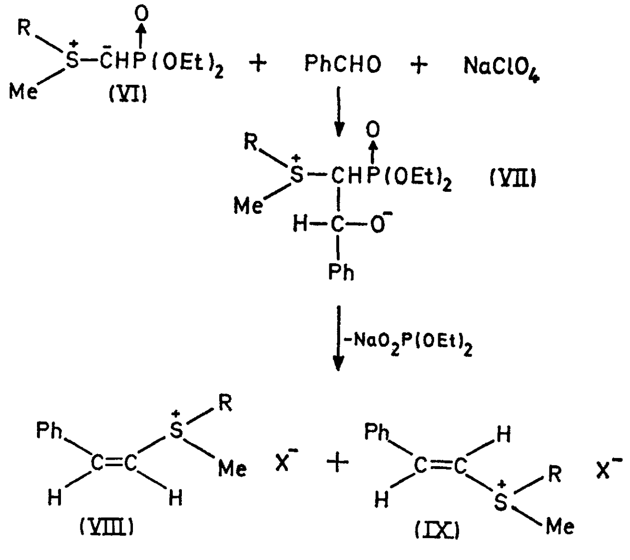
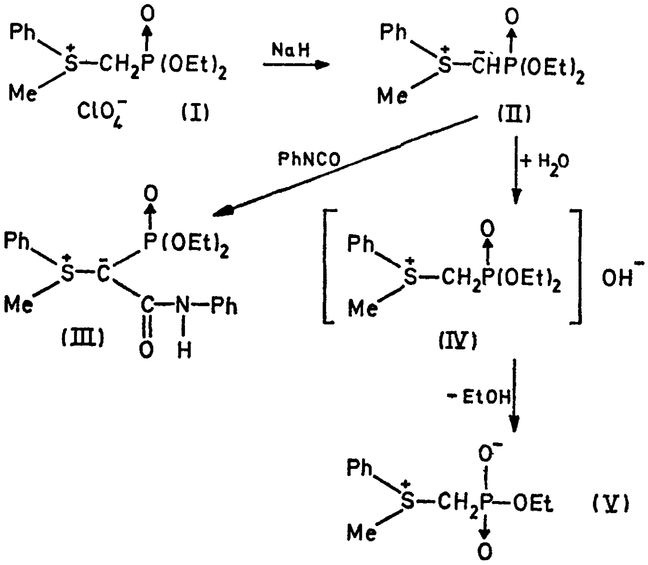
Summary The synthesis and some novel reactions of sulphonium methylides stabilized with a diethoxyphosphinyl group are described.

Sulphur ylides stabilized by an electron-withdrawing substituent have been widely studied.[1] No ylide has, however, been reported in which the negative charge on the carbanion is stabilized by a phosphinyl group. We report here the first synthesis and some reactions of such an ylide.

(Diethoxyphosphinylmethyl)methylphenylsulphonium perchlorate (I) was prepared by the treatment of diethyl phenylthiomethylphosphonate with methyl iodide in the presence of equimolar silver perchlorate. The sulphonium salt was treated with sodium hydride in tetrahydrofuran at $-20°$ and the mixture concentrated under reduced pressure. The resulting syrup was dissolved in methylene chloride. Removal of sodium perchlorate and solvent afforded essentially pure methylphenylsulphonium diethoxyphosphinylmethylide (II) as a relatively unstable oil in quantitative yield. Spectral data are consistent with the structure assigned. Additional evidence for the structure was obtained by the isolation of the stable ylide (III) [73% yield based on (I)], m.p. 89—90°,† by treating (II) with phenyl isocyanate in tetrahydrofuran. This type of stabilization of unstable ylides has many precedents.[2] Attempted purification of the ylide (II) by column chromatography on silica using 99% EtOH as eluant resulted in the formation of the zwitterion (V) (43%), as colourless crystals, m.p. 148—149°. The transformation of (II) to (V) can be explained by assuming the intermediate formation of sulphonium hydroxide (IV) followed by elimination of ethanol.



a; R = Ph, b; R = Me, X = ClO$_4$



When the ylide (II), generated *in situ* in tetrahydrofuran, was treated with benzaldehyde, the sulphonium salt (IXa) was obtained as a viscous oil (66%). The i.r. and n.m.r. spectra of the salt were in good agreement with those of the sulphonium salt prepared from *trans*-phenyl styryl sulphide[3] and methyl iodide in the presence of silver perchlorate. It was, however, impossible to rule out completely the presence of the *cis*-isomer (VIIIa) in the product, because the absorption of the vinylic protons overlapped that of the phenyl protons in the n.m.r. spectrum. A similar reaction with (VIb) gave a mixture of the *cis*- and *trans*-isomers of the sulphonium salt (VIIIb + IXb) (64%) as colourless crystals, m.p. 118—122°. In this case, the ratio of the isomers, *cis* : *trans*, was readily shown to be 33:67 from the n.m.r. spectrum (J_{cis} 10, J_{trans} 16 Hz, vinyl protons[4]). Our results clearly indicate that the leaving power of diethyl sodium phosphate is superior to that of sulphide in the intermediate betaine (VII).

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† All new compounds gave correct elemental analyses and spectra in agreement with the structures assigned.

[1] See for example, A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966.

[2] See for example, H. König and H. Metzger, *Chem. Ber.*, 1965, **98**, 3733.

[3] A. A. Oswald, K. Griesbaum, B. E. Hudson, jun., and J. M. Bregman, *J. Amer. Chem. Soc.*, 1964, **86**, 2877.

[4] M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, 1966, **88**, 5747.