Dimethyl-α-styrylsulphonium Bromide as a Reaction Intermediate

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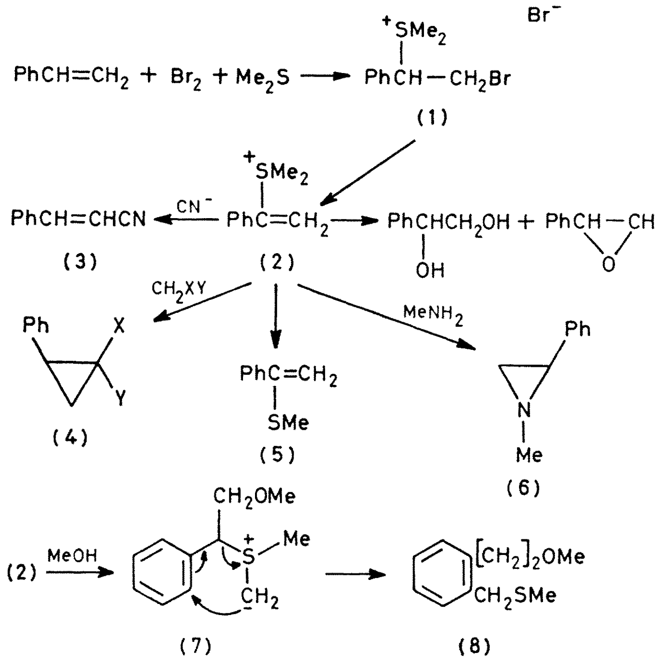
Summary The addition product of styrene, bromine, and dimethyl sulphide was treated with bases to give the dimethyl-α-styrylsulphonium ion which reacted rapidly with various nucleophiles and also underwent slower base-catalysed rearrangement.

VINYLSULPHONIUM salts are versatile electrophilic alkylating agents that can serve in multistep reactions, and are generally prepared by alkylation of the corresponding alkyl vinyl sulphides.[1,2] We report a simple method for the generation of a dimethylvinylsulphonium ion and its reactions.

Styrene reacted with a mixture of bromine and dimethyl sulphide in *ca.* 1 : 5 molar ratio in methylene chloride to give the crystalline bromosulphonium bromide (**1**) in 85% yield; m.p. 145—158 °C. The structure of (**1**) was supported by i.r., ^{1}H n.m.r. (ABX system at δ 4·24 and 5·12, J = 8·5, 6·5, and 14·5 Hz, and singlets at δ 2·69 and 2·98), and ^{13}C n.m.r. (t, δ 29·6; d, 62·05 p.p.m.) spectroscopy and analysis. The compound was obviously formed by the attack of the bromonium ion on the double bond followed by dimethyl sulphide as suggested by extensive skeletal rearrangements in a similar addition to norbornene.



Using ^{1}H n m r spectroscopy to monitor the reaction, treatment of (**1**) with potassium carbonate, triethylamine, or potassium hydroxide in deuteriated solvents, such as D_2O, $(CD_3)_2SO$, or CD_3OD, rapidly gave the dimethyl-α-styrylsulphonium ion (**2**) which was gradually transformed into other compounds when left at room temperature Much slower deuterium exchange of the methyl group was also observed For example, in D_2O a clean spectrum of three singlets at 3 04, 6 40, and 7 55 (6 . 2 · 5 ratio, sodium 3-trimethylsilylpropanesulphonate as the internal standard) was observed for (**2**) Brief heating of an aqueous solution of (**1**) containing 5—10% potassium carbonate gave a 1 : 1 mixture of styrene oxide and styrene glycol without a trace of other products a similar reaction in the two phase carbon tetrachloride–aqueous system gave a nearly quantitative yield of styrene oxide Under similar conditions the vinylsulphonium ion (**2**) reacted with CH_2XY (*e g* X = Y = CN, COMe, or CO_2 Et, X = CN, Y = CO_2Et, X = COMe, Y = CO_2 Et) smoothly at 50 °C in several minutes, to give the corresponding cyclopropane derivatives (**4**)[1] Sodium cyanide also reacted rapidly at room temperature to give *cis*- and *trans*-cinnamonitrile (**3**)[3] in 2 3 ratio The reaction of (**1**) in aqueous methylamine give aziridine (**6**)[4] Most of these compounds are known compounds, in the present syntheses they are obtained cleanly in *ca* 80% yields without tedious separation processes

In methylene chloride, triethylamine reacts with (**1**) instantaneously at room temperature to give α-methylmercaptostyrene (**5**)[5] without a trace of other products In methanol–potassium carbonate, (**2**) reacted slowly to give (**8**) as the major product The structure of (**8**) was supported by its n m r , i r , and mass spectra and analysis, in particular by the proton signals at δ 2 95 and 3 45 (A_2B_2 system) and singlets at δ 1 95, 3 22, and 3 62 While the formations of compounds other than (**5**) and (**8**) involve efficient straightforward attacks of nucleophiles, that of (**8**) follows the Sommelet–Hauser rearrangement[6] *via* the ylide (**7**), the deprotonation step of which rearrangement is shown to be relatively slow As a result, the crude product is contaminated by various by-products arising from nucleophilic substitutions, *e g* , 1,2-dimethoxyphenylethane, 1-methylthio-2-methoxy-1-phenylethane, and other unidentified compounds

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