Ylide Rearrangement in Adducts from Allenic Sulphonium Salts and Malonic Esters

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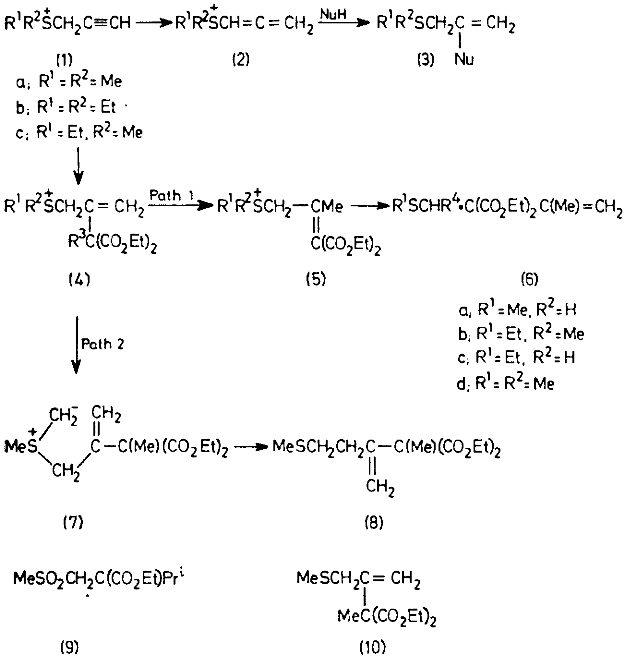
Summary Addition of malonic esters to allenic sulphonium salts gives products derived from subsequent reactions of the initial adducts by two pathways which involve ylide rearrangement; structural factors which determine the pathways are defined.

Much recent work on unsaturated sulphonium salts has been concerned with ylide rearrangements[1] and with synthetic application of addition reactions.[1,2] We now report the diverse rearrangement pathways which follow nucleophilic addition of malonates to allenic sulphonium salts.



SCHEME. Br^- counterion throughout.

Nucleophilic addition to the allenic sulphonium salts (**2**) generated by base-catalysed isomerisation[3] of prop-2-ynylic sulphonium salts (**1**) leads to adducts of type (**3**). Treatment of the salts (**1a**) and (**1b**) with diethyl malonate in ethanolic sodium ethoxide gives the sulphide esters (**6a**) and (**6b**) respectively (75%). The product (**6a**) from the dimethylsulphonium salt (**1a**) was distinguished from a possible alternative product (**10**) by hydrogenation of the derived sulphone to the sulphone (**9**). When the ethyl methyl salt (**1c**) was used, the sulphide (**6c**) and not (**6d**) was obtained. These products result from 2,3-sigmatropic rearrangement in the salts (**5**) (path 1) produced by isomerisation of the acidic [$pK_a(H_2O)$ 10·5] initial adducts (**4**; R^3 = H) isolable from reactions with catalytic quantities of base.

In the reaction of the salt (**1a**) with diethyl methylmalonate, the product was the sulphide (**8**) derived from deprotonation of the initial adduct (**4a**; R^3 = Me) and subsequent 2,3-sigmatropic rearrangement of the ylide (**7**) (path 2) (Scheme). The alternative possibility is a Stevens rearrangement of this ylide which is regarded as less likely as it does not occur in path 1.

The results show that path 1 is dominant unless prototropy is blocked as in (**4**; R^3 = Me). Path 1 also occurs to the exclusion of an intermolecular reaction of the malonyl carbanion derived from (**4**; R^3 = H) which would lead to sulphides such as (**10**). Formation of the sulphide (**6c**) rather than (**6d**) arises by deprotonation of a methyl rather than of an ethyl group.

It is notable that nucleophilic addition to the allenic sulphonium salts is much more rapid than their ylide rearrangement which has recently been shown to occur with aqueous bases.[4]

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[1] B. M. Trost and L. S. Melvin, 'Sulfur Ylids', Academic Press, New York, 1975.

[2] J. W. Batty, P. D. Howes, and C. J. M. Stirling, *J.C.S. Perkin I*, 1973, 59, 65 and references cited.

[3] G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc.* (*C*), 1969, 1904.

[4] G. Pourcelot, L. Veniard, and P. Cadiot, *Bull. Soc. chim. France*, 1975, 1275.