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[3,2] SIGMATROPIC REARRANGEMENTS OF ALLYLIC OXOSULPHONIUM YLIDES

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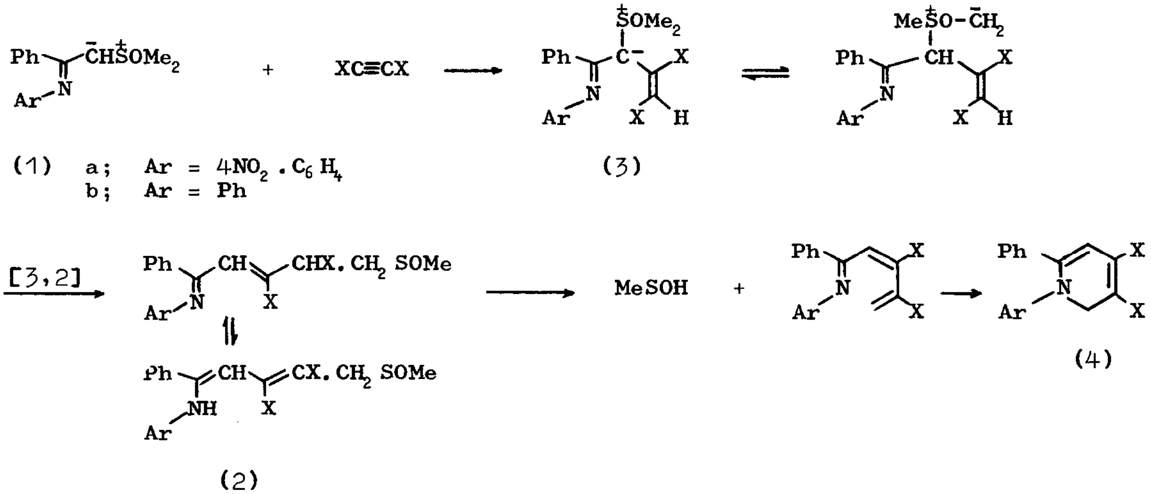
The oxosulphonium ylides (1) and (5) react with electrophilic acetylenes to give allylic ylides, which undergo successive [3,2] rearrangement, elimination of methanesulphinic acid, and cyclisation on heating.

The thermal [3,2] sigmatropic rearrangement of allylic sulphonium ylides is established as a useful method of forming carbon–carbon bonds,[1] but there are few examples of the [3,2] rearrangement of allylic oxosulphonium ylides.[2] We have found that such rearrangements can take place under very mild conditions, and that the reaction has some potentially useful features as a procedure for the construction of six-membered rings.

The imidoyloxosulphonium ylides (1)[3] reacted with dimethyl acetylenedicarboxylate (CH_2Cl_2, 20° C, 1h) to give, in good yields, 1:1 adducts which were identified as the sulphoxides (2). Thus, compound (2a) showed signals in the ^1H n.m.r. spectrum at δ2.64 (3H, s), 3.50 (3H, s), 3.77 (3H, s), 3.94 (2H, s), 6.31 (1H, s), 6.51 (2H, d), 7.16–7.56 (6H, m), and 7.97 (2H, d), and in the i.r. ($CHCl_3$) at 3400 cm^{-1}, compatible with the enamino tautomeric structure shown in Scheme 1. These are the products to be expected from [3,2] rearrangement of initially formed Michael adducts (3): such a rearrangement must take place at, or below, room temperature. When the sulphoxides were heated in solution (80° C, 1–3 h) the dihydropyridines (4a) and (4b) were isolated.[4] The orange crystalline compounds were assigned the dihydropyridine structures mainly on the basis of their ^1H n.m.r. spectra. For example, the spectrum of compound (4a) showed signals at δ 4.80 (2H, s) and 6.17 (1H, s) for the hydrogen atoms at C-2 and at C-5, these being incompatible with alternative dihydropyridine or open (azatriene) structures. When dibenzoylacetylene was reacted with the ylides (1) an analogous series of reactions was observed, and the dihydropyridines (4c) and (4d) were isolated.

SCHEME 1



(1) a; Ar = $4NO_2.C_6H_4$
b; Ar = Ph

(3)

(2)

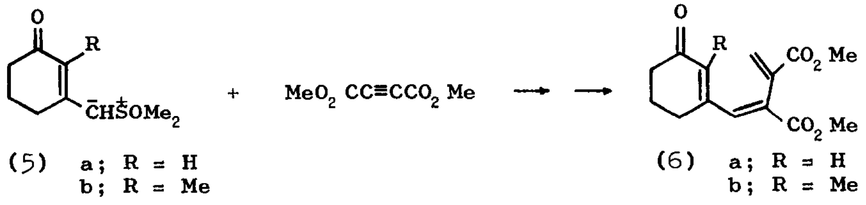
(4)

		Ar	X	Yield/%	m.p./°C
(4)	a;	$4NO_2.C_6H_4$	CO_2Me	62	112
	b;	Ph	CO_2Me	54	110
	c;	$4NO_2.C_6H_4$	COPh	57	149 dec.
	d;	Ph	COPh	59	106 dec.

The later steps of this sequence illustrate two useful features of the reactions: (i) the sulphoxides formed by rearrangement can readily undergo thermal elimination of methanesulphinic acid, and (ii) the resulting azatrienes cyclise on heating.

In order to discover whether these features would also apply to other types of oxosulphonium ylides with extended conjugation, we carried out a similar sequence with the ylides (5a)[5] and (5b)[6] (Scheme 2). Both ylides reacted readily with dimethyl acetylenedicarboxylate at room temperature to give 1:1 Michael adducts. These adducts then gave the trienones (6a) (41%) and (6b) (46%) when heated in solution at 80° C.

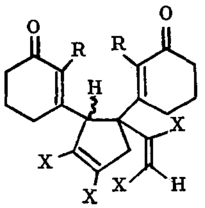
SCHEME 2



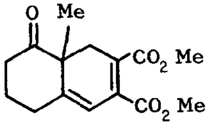
(5) a; R = H
b; R = Me

(6) a; R = H
b; R = Me

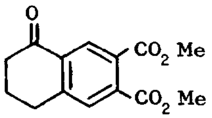
In addition to the trienones (6), a significant minor product was isolated from each of these reactions. The minor products were assigned the cyclopentene structures (7) on the basis of their n.m.r. spectra. The spectrum of (7b) showed signals for two C-methyl groups at δ 1.63 and 1.84, and for four O-methyl groups at δ 3.51, 3.65, 3.70, and 3.74. There were also two 1H singlets at δ 4.46 and 6.71 which were assigned to the methine hydrogen atom on the cyclopentene ring and to the vinylic hydrogen atom, respectively. Compound (7a) had a similar spectrum which included a 1H singlet for the methine hydrogen atom at δ 4.27. The ylides formed from compounds (5) and dimethyl acetylenedicarboxylate are apparently sufficiently nucleophilic to react with the trienones (6) as they are formed. Conjugate addition of oxosulphonium ylides to α,β-unsaturated ketones usually results in the formation of cyclopropanes,[1] but cyclopropane structures are ruled out in this case by the n.m.r. spectra of the compounds.[7]



(7) a; R = H, X = CO_2Me
b; R = Me, X = CO_2Me



(8)



(9)

The trienone (6b) was cyclised by heating in xylene (138° C, 24 h) to give the ketone (8) (64%) as an oil (2,4-dinitrophenylhydrazone, m.p. 272° C). This bicyclic ketone was obtained in better overall yield [63% based on the ylide (5b)] by slowly adding a solution containing the 1:1 adduct of (5b) and dimethyl acetylenedicarboxylate to boiling xylene; this procedure reduced the bimolecular side reaction leading to (7b). The trienone (6a) gave a mixture of several bicyclic ketones when it was heated in xylene under nitrogen: this mixture probably results from the disproportionation of the initial product of cyclisation, a dihydroaromatic species. When the reaction was repeated in the presence of sulphur, the aromatic ketone (9) was isolated as the major product (44%).

The experiments show that oxosulphonium ylides bearing a conjugative C=N or C=C functional group can give cyclic products in useful yields by this reaction sequence. The ring synthesis has the advantage of providing systems with a pattern of substitution which is not readily available by other methods. We are currently attempting to further extend the scope of the reaction.

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

[2] J. Ide and Y. Kishida, Chem. Pharm. Bull., 1968, **16**, 793; Y. Tamura, T. Miyamoto, T. Nishimura, and Y. Kita, Tetrahedron Letters, 1973, 2351.

[3] R. Faragher and T. L. Gilchrist, J.C.S. Perkin I, 1977, 1196.

[4] New compounds were isolated by preparative layer chromatography, and were fully characterised. Yields of dihydropyridines are based on the starting ylides (1) and have not been optimised.

[5] Y. Tamura, T. Miyamoto, T. Nishimura, J. Eiho, and Y. Kita, J.C.S. Perkin I, 1974, 102.

[6] R. H. Bradbury, T. L. Gilchrist, and C. W. Rees, J.C.S. Chem. Comm., 1979, 528.

[7] Reaction of the trienone (6a) with dimethyloxosulphonium methylide gave a cyclopropane, by addition to the terminal double bond. The formation of cyclopropanes by the more highly substituted ylides may be disfavoured for steric reasons.

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