Formation of Allyl Sulphide Synthons by [1,2] and [1,3] Shifts of the Phenylthio Group

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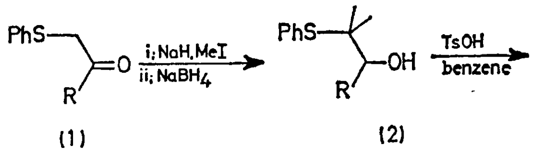
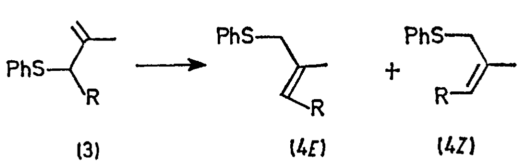
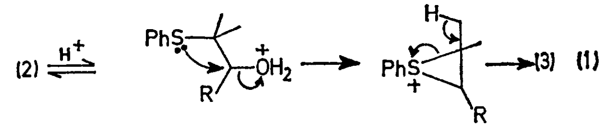
Summary Allyl phenyl sulphides, made from 2-hydroxyalkyl phenyl sulphides by acid-catalysed rearrangement of the phenylthio group, may be isomerised by the [1,3] allylic shift of the same group, and converted into 4-hydroxy carbonyl compounds or allyl alcohols.

MIGRATION of anion-stabilising functional groups (*e.g.* Ph_2PO) during an organic synthesis allows the formation of new carbon–carbon bonds from several atoms in turn using the same group.[1] The phenylthio group (PhS) is an attractive candidate for this role as it is an effective neighbouring group[2] and the expected allyl sulphide products,[3] and the sulphoxides[4] derived from them, are useful nucleophilic synthons. We report that successive [1,2] and [1,3] phenylthio shifts may be used to make allyl sulphides.

The phenylthioketones[5] (**1**, R = Me or Ph) were alkylated and reduced to give the alcohols (**2**). Brief treatment with acid (TsOH in refluxing benzene; half-life of the reaction *ca.* 2 min) brought about a [1,2] shift giving the rearranged allyl sulphides (**3**). The reaction is much faster than Ph_2PO migration, presumably sulphur participation (equation 1) is responsible. The sulphide products are susceptible to the [1,3] allylic shift[6] of the phenylthio group giving the isomeric sulphides (**4**).







The [1,3] shift has been described previously as a thermal reaction[6] but with our compounds it is initiated at room temperature even by daylight filtered through two layers of glass. Since it is evidently very efficient, this photochemical reaction may well be a radical chain process (equation 2). Heat also causes the [1,3] shift, but only at 100 °C without solvent. Thermal and photochemical reactions give the same mixture of (**4***E*) and (**4***Z*).

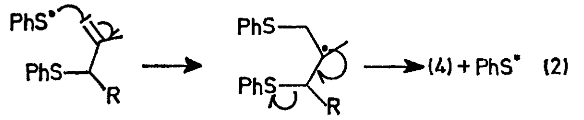
TABLE

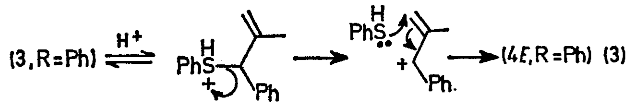
Composition of equilibrium mixtures from [1,3] allyl shifts

	R=Ph			R=Me		
	(**3**)	(**4***E*)	(**4***Z*)	(**3**)	(**4***E*)	(**4***Z*)
Photochemical (daylight)	0	66[a]	34[a]	5	60[b]	35[b]
Thermal (100 °C, neat)	0	66[a]	34[a]	5	60[b]	35[b]
Acid-catalysed (TsOH, benzene, reflux)	0	100[a]	0	c	c	c

[a] Structure elucidated by n.m.r. using the Nuclear Overhauser Effect (N.O.E.). [b] Structure not confirmed by N.O.E. [c] No [1,3] shift occurs under these conditions. Instead $PhSC(Me){=}CMe_2$ is slowly formed.

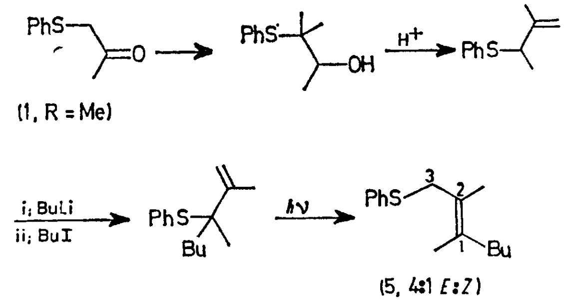
If the product (**3**) of the [1,2] shift is required, the acid treatment must be carried out in a foil-wrapped flask.





This gives (**3**, R = Me) in very high yield uncontaminated by (**4**, R = Me), but for (**3**, R = Ph) an acid-catalysed [1,3] shift does occur slowly with a half-life some two orders of magnitude greater than that of the [1,2] shift (equation 3). This is a useful reaction as, in contrast to the photochemical or thermal processes, it gives only one isomer (**4***E*, R = Ph) of the allyl sulphide, (see Table).†

The [1,2] and [1,3] shifts can therefore be controlled so that the phenylthio group moves *one atom in either direction* along the carbon chain from its original position, and hence any of these three atoms may be made nucleophilic. The sequence (**1**, R = Me) to (**5**) employs one of the nucleophilic atoms [(C-2) in (**5**)] to add the methyl groups, another (C-1) to add the butyl group, and produces a molecule (**5**) whose anion is nucleophilic at the third (C-3)



The phenylthio group may be removed in a number of ways to give for example allyl alcohols[4] and 4-hydroxycarbonyl compounds.[7] Each sequence may be carried out before or after the [1,3] shift so that regioselectivity is complete.

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† Structure elucidated by n.m.r. using the nuclear Overhauser effect.

[1] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

[2] A. Streitwieser, 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, p. 108.

[3] J. F. Biellmann and J. B. Ducep, *Tetrahedron*, 1971, **27**, 5861; K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, 1973, **95**, 7926.

[4] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

[5] A. Delisle, *Annalen*, 1890, **260**, 250.

[6] H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, 1970, **92**, 6064.

[7] P. M. Atlanti, J. F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Letters*, 1974, 2665; see also B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438.