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Formation of Allyl Sulphides by Phenylthio Migration: Effects of Alkyl Substitution and Control by Silicon

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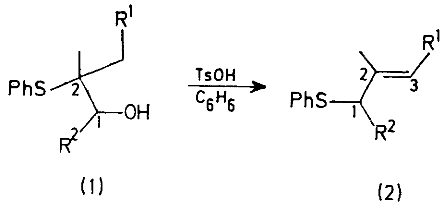
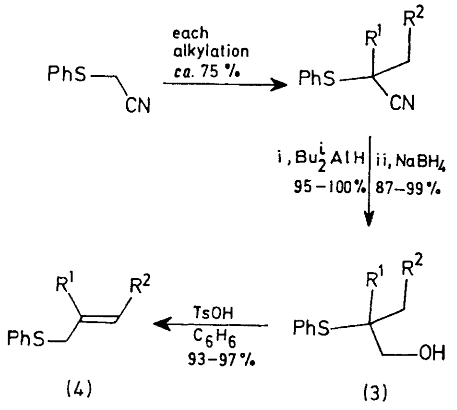
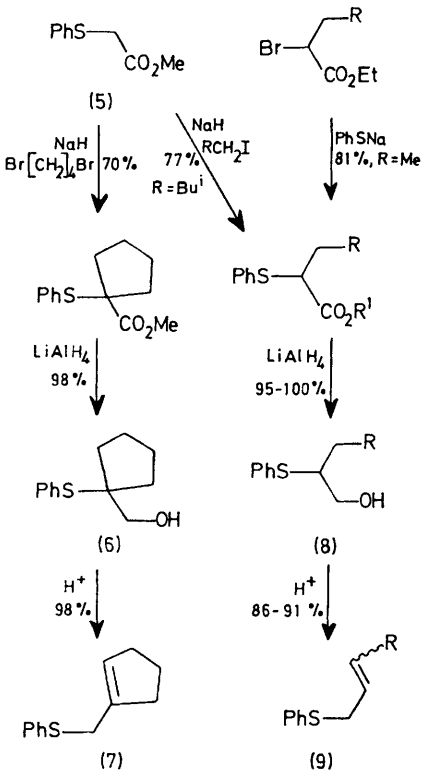
Summary The acid-catalysed rearrangement of β-hydroxyalkyl phenyl sulphides leads to phenylthio migration from a tertiary or secondary centre to a primary centre, and, when assisted by silicon, between two secondary centres or even from a secondary to a tertiary centre.

Allyl sulphides (**2**), whose anions are versatile nucleophilic synthons,[1] can be made by phenylthio (PhS) migration[2] (**1** → **2**). The only structural class we have previously investigated[2] has a tertiary migration origin [C-2 in (**1**)] and a secondary migration terminus [C-1 in (**1**)] and thus inevitably gives allyl sulphides with a substituent on each carbon [C-1, C-2, and C-3 in (**2**)]. We now report that the PhS group migrates naturally within a much wider range of structural classes, giving simpler allyl sulphides of





TsOH = $MeC_6H_4SO_3H$



Scheme 1

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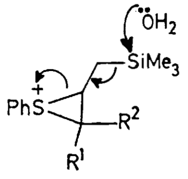
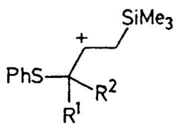
many types, and that a suitably placed trimethylsilyl (Me_3Si) group increases this range still further.

The starting materials (**3**) for PhS migration from an unsymmetrical tertiary migration origin to a primary migration terminus can be made by alkylation and reduction, each in two steps, from phenylthioacetonitrile.[2] Compounds [*e.g.* (**6**)] with a symmetrical migration origin can be made by a shorter route from phenylthioacetic esters (**5**) (Scheme 1). The rearrangements of (**3**) and (**6**) need conditions [toluene-*p*-sulphonic acid (TsOH) in benzene under reflux for 5 min] similar to those used for a secondary migration terminus [*e.g.* (**1**)][2] and again give rearranged allyl sulphides (**4**) and (**7**) in high yield. Similar synthetic routes (Scheme 1), again from the ester (**5**), give the starting materials (**8**) for PhS migration from a secondary migration origin to a primary migration terminus. The conditions for this rearrangement are much more vigorous (TsOH in toluene under reflux for 1 h) but still give very good yields of allyl sulphides (**9**).

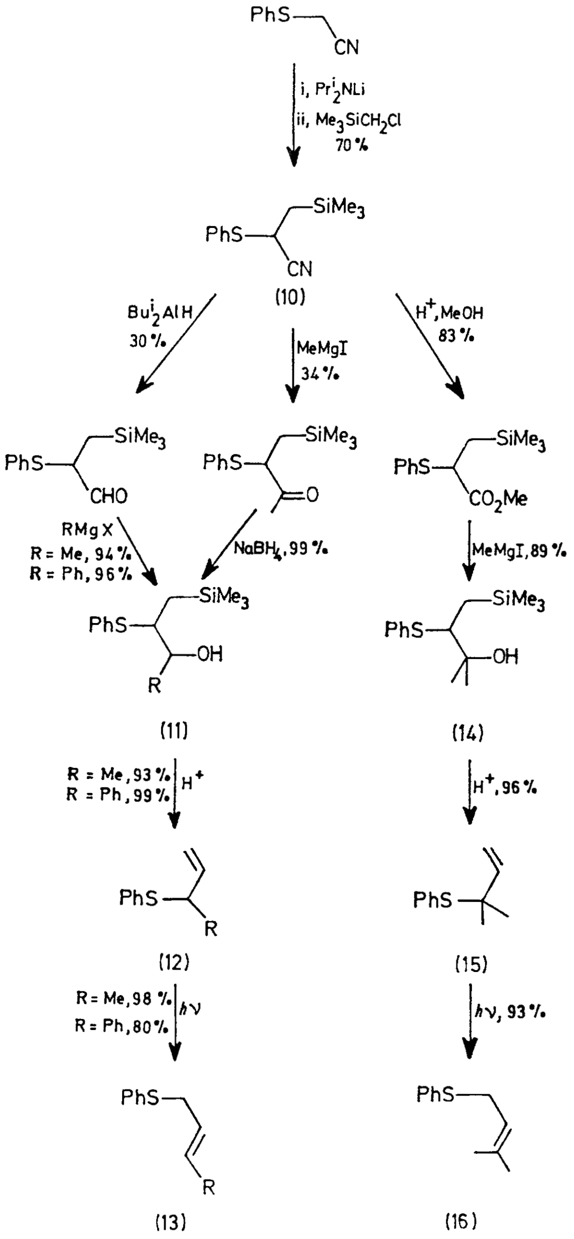


(17)



(18)

No rearrangement was observed when both migration origin and terminus were secondary, nor naturally was there any rearrangement 'uphill' when the migration origin was secondary and the migration terminus tertiary. However, both these rearrangements could be induced by a Me_3Si group. The starting materials (**11**) and (**14**) can readily be made *via* trimethylsilylmethylation of phenylthioacetonitrile (Scheme 2). Rearrangement of these alcohols (**11**) and (**14**) goes by PhS migration and loss of the Me_3Si group to give the allyl sulphides (**12**) and (**15**). The driving force for these reactions is the ease of removal of the Me_3Si group from the intermediate (**17**) and/or the stabilisation given to the rearranged cation (**18**) by the Me_3Si group.[3] Both allyl sulphides (**12**) and (**15**) readily undergo the light induced [1,3] PhS shift to give the allyl sulphides (**13**) and (**16**).



Scheme 2

These reactions considerably increase the scope of the PhS migration as a synthetically useful and general route to allyl sulphides, as allyl sulphides lacking substituents on any one or two of the atoms C-1, C-2, or C-3 in (**2**) can now be made by these methods. The diphenylphosphinoyl group (Ph_2PO) migrates in a similar fashion from tertiary to secondary centres[5,6] and the regioselectivity of the reaction may also be controlled by the Me_3Si group,[3,6] but the Ph_2PO group does not migrate in all the situations described in this communication. PhS is intrinsically a more efficient migrating group.

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