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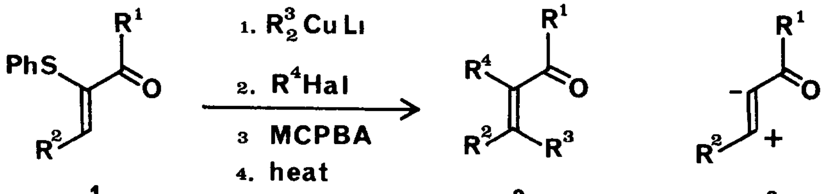
SYNTHESIS WITH MIGRATING PHENYLTHIO GROUPS
CONNECTIVE ROUTES TO 2-PHENYLTHIOALLYL ALCOHOLS AND 2-PHENYLTHIO ENONES

Philip Blatcher and Stuart Warren*

University Chemical Laboratories,
Lensfield Road,
CAMBRIDGE CB2 1EW

Summary The title compounds may be made from bis(phenylthio) acetals and aldehydes by routes involving PhS migration

The introduction of a phenylthio (PhS) group into a molecule often leaves unaltered the chemistry of the other functional groups but may add a latent ketone or masked double bond Thus 2-PhS enones (1) are good Michael acceptors[1] and the double bond can be regenerated by oxidation and elimination of the PhS group (1 → 2) The enone (1) is therefore a reagent for the synthon (3) 2-PhS allyl alcohols (4) undergo normal Claisen or Carroll rearrangements[2] giving 1,4-dicarbonyl derivatives (5) in which the vinyl sulphide is a latent ketone



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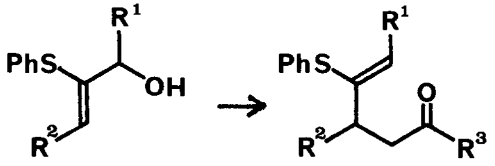

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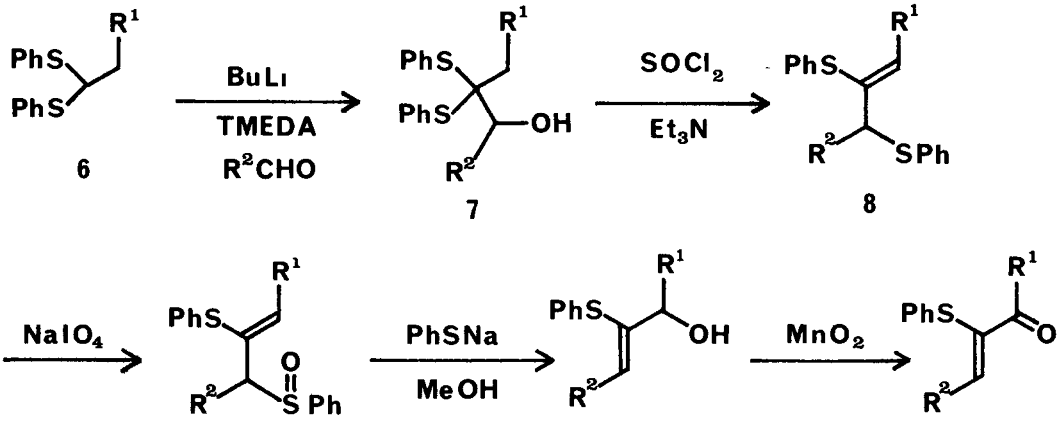
Application of these methods has so far been restricted by the absence of general routes to the enones (1) and the allyl alcohols (4) A few syntheses for specific, usually cyclic, 2-PhS enones (1) are available,[3] and the alcohols (4) can be made[2,4] by adding PhS-vinyl-lithium to carbonyl compounds but this necessarily gives (4, R^2 = H) We now report general, connective syntheses of both classes of compounds by routes involving [1,2] and [1,3] PhS shifts.[5]



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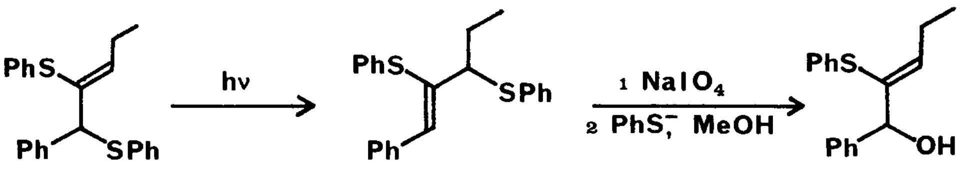
Anions from bis-PhS-acetals (6) react with aldehydes to give the adducts[6] (7) These rearrange with PhS migration to give products[6,7] (8) with allylic and vinylic PhS groups The allylic PhS group can be selectively oxidised to the sulphoxide (9) which undergoes the normal [2,3] sigmatropic rearrangement[8] in the presence of the thiophile PhS^- to give the 2-PhS-allyl alcohols (10) Yields are good, e g for $R^1 = R^2$ = Me, (7) 73%, (8) 83%, (9) 89%, and (10) 81%



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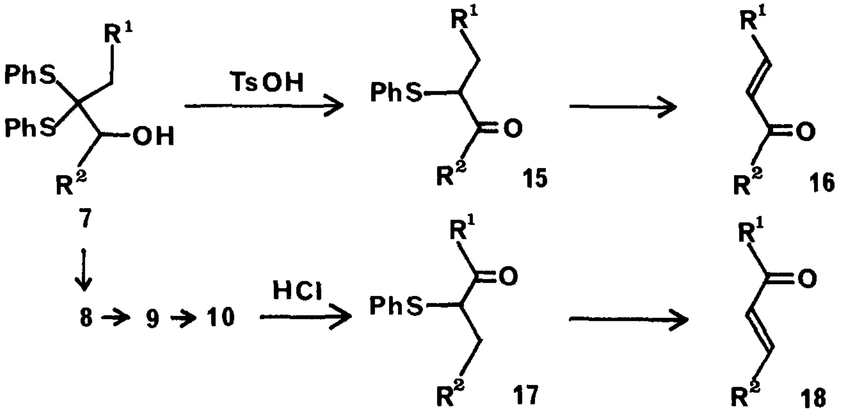
Light initiates a [1,3] PhS shift[9] on the intermediates (8) For symmetrical compounds (8, $R^1 = R^2$) this simply alters the proportion of geometrical isomers* present For unsymmetrical compounds (8, $R^1 \neq R^2$) the [1,3] shift may allow access to a different series Since both the [1,3] PhS shift and the conversion of the sulphoxide to the alcohol are formal [1,3] transpositions, using them one after the other gives a product with the same skeleton as the intermediate (8) Thus (12) gives conjugated (13, 80%) in light, and hence, via the sulphoxide (79%), the alcohol (14, 75%)

We have already used[6] the adducts (7) in a general synthesis of α-PhS-ketones (15) Cookson and Parsons[4] report that the alcohols (10) give α-PhS-ketones (17) on treatment with acid Two alternative series of α-PhS-ketones (15) and (17) and two series of enones (by oxidation and elimination of PhS) are therefore available from the same starting material (7) Again, the two series have a formal [1,3] relationship



Oxidation of the 2-PhS-allyl alcohols (10) with MnO_2 in dry ether gave 2-PhS-enones (11) in moderate yield, e g (11, R^1 = Et, R^2 = Ph, 65%)

The reactions seem to be general except that R^1 in (8) cannot be H as the rearrangement (7 → 8) does not give the exo-methylene compounds The primary alcohols (10, R^1 = H) or enols (11, R^1 = H) are therefore not available by this route

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* Compounds (8-14) are formed as mixtures of geometrical isomers We have drawn only the major isomer in each case In the applications described here (e g to give 2, 3 or 17), both isomers give the same products

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