2-Phenylthioallyl Alcohols and Their Use in the Synthesis of 1,4-Diketones and Cyclopentenones†

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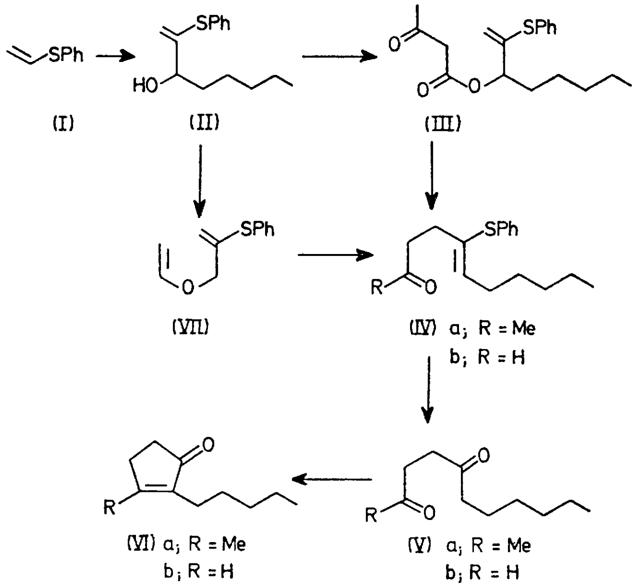
Summary 1-Phenylthiovinyl-lithium adds to n-hexanal to give the allylic alcohol (II) that undergoes the Carroll and Claisen rearrangement with formation of the carbonyl compounds (IV) which can be converted into dihydrojasmone (VIa) and 2-n-pentylcyclopent-2-enone (VIb) by hydrolysis and cyclisation.

Alkyl vinyl sulphides have been reported[1] to require the very strongly basic system 2-butyl-lithium in tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA) for complete conversion into the 1-lithio-derivatives, which are useful for the synthesis of 1-substituted vinyl sulphides and thence of ketones. We find that phenyl vinyl sulphides are efficiently lithiated by lithium di-isopropylamide in THF containing HMPA and then add to carbonyl compounds to form 2-phenylthioallyl alcohols in high yield. Thus phenyl vinyl sulphide (I) was added to lithium di-isopropylamide in THF containing HMPA at −60 °C and after 30 min n-hexanal was added to the solution. The adduct (II) was isolated in 76% yield after distillation.

In spite of some success with mercuric chloride[1,2] or titanium tetrachloride[3] in aqueous acetonitrile, hydrolysis of vinyl sulphides is often difficult. Although it limits their application as precursors of carbonyl compounds,[4] the relative stability of vinyl sulphides to heavy metal ions and Lewis and proton acids (as well as to strong bases) can be turned to advantage. For example, the acetoacetate (III), obtained from the allylic alcohol (II) and diketen, when heated to 160 °C with a catalytic amount of aluminium isopropoxide, underwent the Carroll reaction to produce the ketone (IVa) (88%). Treatment of (IVa) with titanium tetrachloride in aqueous acetonitrile or with trifluoroacetic acid, followed by hot 2% NaOH in aqueous ethanol, gave dihydrojasmone (VIa) (60% overall).



Mercuric acetate-catalysed acetal exchange[5] of the allylic alcohol (II) with ethyl vinyl ether produced the ether (VII), which rearranged at 120 °C to the aldehyde (IVb) (75% overall). Treatment of (IVb) with trifluoroacetic acid for 2 min formed the keto-aldehyde (Vb), cyclised by dilute alkali to 2-pentylcyclopent-2-enone (VIb) (60%).

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