New Synthesis of Conjugated Ketones from 2-Phenylthio-allyl and -allenyl Alcohols†

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Summary 2-Phenylthioallyl alcohols (I) rearrange in acid to α-phenylthioethyl ketones (II) which, on oxidation and elimination, yield vinyl ketones; through a similar reaction sequence 2-phenylthioallenyl alcohols (IX) give the 2,4-dienones (XII).

1-PHENYLTHIOVINYL-LITHIUM‡ reacts with a wide range of electrophiles to form 1-phenylthiovinyl derivatives. We now report that the 2-phenylthioallyl alcohols formed in high yields from aldehydes[1] are convenient precursors to vinyl ketones.

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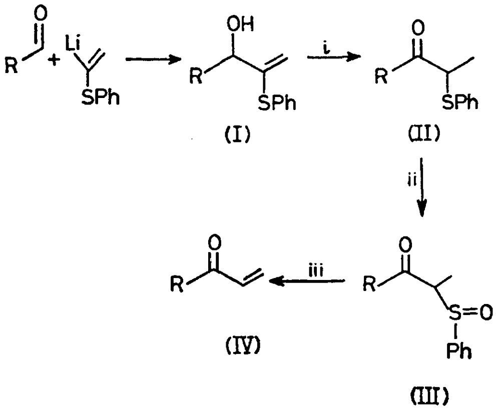
† No reprints available.

‡ Alternative ways of making this reagent have been recommended (ref. 1; B. Harirchian and P. Magnus, *J.C.S. Chem. Comm.*, 1977, 522). We find that the most convenient and efficient method is to add phenyl vinyl sulphide in tetrahydrofuran (THF) to n-butyl-lithium and tetramethylethylenediamine (1 mol each) in THF at −90 °C.

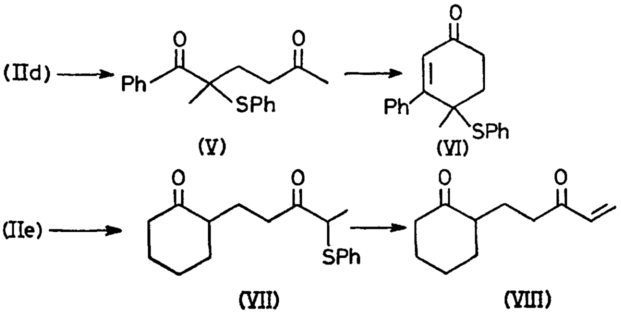
For example, passage of HCl into a solution of the secondary alcohol (Ia) in wet acetonitrile§ for 2 s and immediate neutralisation by pouring into sodium hydrogen carbonate solution gave the isomeric ketone (IIa) in 81% yield after chromatography. Oxidation to the sulphoxide (IIIa) was quantitative and pyrolysis in carbon tetrachloride[2] to the vinyl ketone (IVa) proceeded in 70% yield. The reaction sequence (I) → (IV) was equally satisfactory not only when R was another alkyl group, but also when R was phenyl or vinyl.



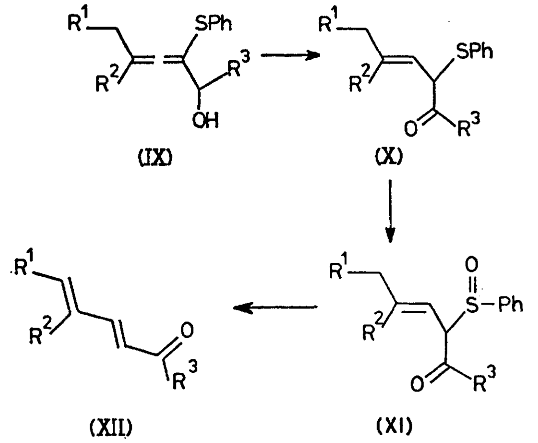
R	R
a; n-C_6H_{13}	**d**; Ph
b; n-C_5H_{11}	**e**; CH=CH_2
c; Bu^n	

i, HCl + H_2O in MeCN; ii, *m*-$ClC_6H_4CO_3H$; iii, boiling CCl_4.

Condensation of the phenyl ketone (IId) with 4-chlorobutan-2-one¶ gave the diketone (V) which cyclised to the cyclohexenone (VI). The vinyl ketone (IIe) is particularly interesting because it makes easily available a protected form of divinyl ketone in which the two double bonds can be separately manipulated. As an illustration, (IIe) added to 1-pyrrolidinocyclohexene to form (VII) after treatment with acid. Oxidation, followed by elimination of benzenesulphenic acid, then gave the unsaturated diketone (VIII).



Allenyl alcohols[3] (IX), on treatment with HCl in wet acetonitrile, afforded the $\beta\gamma$-unsaturated ketones (X), which produced the $\alpha\beta\gamma\delta$-unsaturated ketones (XII) after oxidation to (XI) and pyrolysis in carbon tetrachloride.



a; R^1 = H, R^2 = Me, R^3 = Bu^n
b; R^1R^2 = $[CH_2]_4$, R^3 = Me

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§ Other acids, such as toluenesulphonic acid in benzene, were also satisfactory.

¶ Kindly given by Mr. M. C. Cramp.

[1] R. C. Cookson and P. J. Parsons, *J.C.S. Chem. Comm.*, 1976, 990.

[2] P. A. Grieco, D. Boxler, and C. S. Pogonowski, *J.C.S. Chem. Comm.*, 1974, 497.

[3] P. J. Parsons, Ph.D. Thesis, Southampton, 1978; R. C. Cookson and P. J. Parsons, following communication.