New Synthesis of Dienals†

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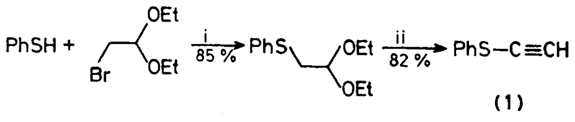
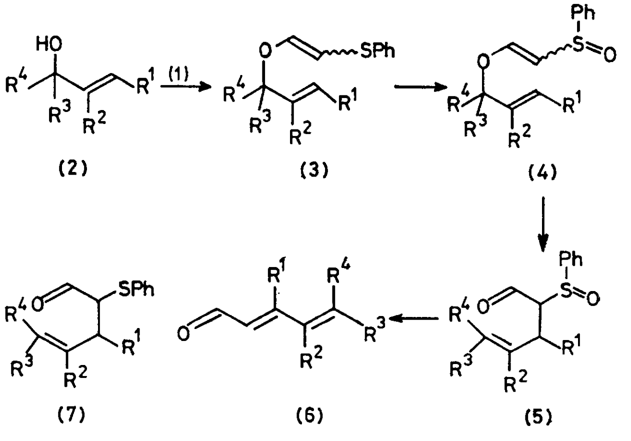
Summary Addition of sodium derivatives of allyl alcohols (**2**) to phenylthioacetylene (**1**) forms adducts (**3**) which on oxidation and pyrolysis undergo Claisen rearrangement and elimination of benzenesulphenic acid to yield the 2,4-dienals (**6**).

We recently described[1] a synthesis of 2,4-dienones from allyl alcohols and allenyl phenyl sulphoxides; we now report a synthesis of 2,4-dienals from allyl alcohols and phenylthioacetylene (**1**).



Scheme 1 i, EtONa in boiling EtOH. ii, 2 mol lithium diisopropylamide in Et_2O, −60→0 °C.

The acetylene (**1**), prepared as in Scheme 1 (earlier syntheses[2] proving inconvenient), in tetrahydrofuran (THF) was added to the sodium derivative of the primary or secondary allyl alcohol (**2**) made by treatment with sodium hydride in THF.‡ After 8 h at 50 °C the resulting adducts (**3**) were isolated by chromatography on silica gel as a mixture of *cis* and *trans* isomers, which were oxidised to the sulphoxides (**4**) with *m*-chloroperbenzoic acid in dichloromethane at −60 °C in almost quantitative yield. Distillation of the sulphoxides (**4**) from a catalytic amount of zinc carbonate (130 °C, bulb to bulb) induced Claisen rearrangement to (**5**) and elimination to form the 2,4-dienals (**6**) (Scheme 2).



Scheme 2

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† No reprints available.

‡ A cheap and effective alternative is to use benzene and aqueous alkali with benzyltrimethylammonium chloride as phase-transfer catalyst.

TABLE. Addition of allyl alcohols (**2**) to phenylthioacetylene followed by oxidation and pyrolysis of the sulphoxides (**4**).

	R^1	R^2	R^3	R^4	% Yield of (**3**)	% Yield of (**6**)
a	H	H	H	H	73	76[a]
b	H	Me	H	H	75	84[b]
c	Me	H	H	H	63	69[b]
d	H	Cl	H	H	78	72
e	H	H	Et	H	69	68[c,d]
f	H	H	n-C_5H_{11}	H	66	63[c,d]
g	Me	H	n-C_5H_{11}	H	58	60
h	H	H	Me	Me	57[e]	63

[a] E. L. Pippen and M. Nonaka, *J. Org. Chem.*, 1958, **23**, 1580. [b] E. E. Boehm and M. C. Whiting, *J. Chem. Soc.*, 1963, 2541. [c] K. Markav and W. Maier, *Chem. Ber.*, 1962, **95**, 889. [d] 'The Aldrich Library of N.M.R. Spectra,' Aldrich Chemical Co., Milwaukee, 1974–5. [e] Yield of (**7**).

The yields of products in some representative cases are given in the Table. Under the conditions described above tertiary alcohols gave very poor yields of adducts (**3**). Only polymer was formed by reaction of the potassium derivatives in the solvating media THF, hexamethylphosphoric triamide, or trimethyl phosphate. However, reaction of compound (**2h**) (1·2 mol) with potassium (1 atom) in benzene followed by the acetylene (**1**) (1 mol) gave, after 6 h boiling, the Claisen product (**7h**). Oxidation to the sulphoxide (**5h**) and distillation then produced the dienal (**6h**).

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[1] R. C. Cookson and R. Gopalan, *J.C.S. Chem. Comm.*, 1978, 608.

[2] W. E. Parham and P. L. Stright, *J. Amer. Chem. Soc.*, 1956, **78**, 4783; W. E. Parham, R. F. Motter, and G. L. O. Mayo, *ibid.*, 1959, **81**, 3386; J. F. Arens and T. Doombos, *Rec. Trav. chim.*, 1956, **75**, 481.