

New Synthesis of Dienals†

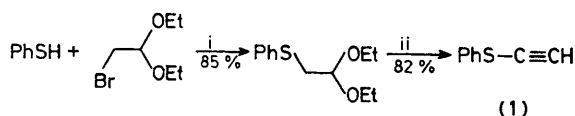
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Summary Addition of sodium derivatives of allyl alcohols (2) to phenylthioacetylene (1) forms adducts (3) which on oxidation and pyrolysis undergo Claisen rearrangement and elimination of benzenesulphenic acid to yield the 2,4-dienals (6).

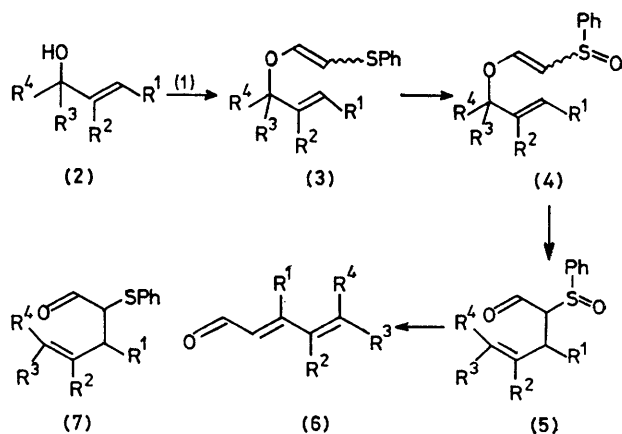
sulphoxides (4) with *m*-chloroperbenzoic acid in dichloromethane at -60°C in almost quantitative yield. Distillation of the sulphoxides (4) from a catalytic amount of zinc carbonate (130°C , bulb to bulb) induced Claisen rearrangement to (5) and elimination to form the 2,4-dienals (6) (Scheme 2).

WE recently described¹ 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 , $-60 \rightarrow 0^{\circ}\text{C}$.

The acetylene (1), prepared as in Scheme 1 (earlier syntheses² 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



SCHEME 2

† 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 ₈ H ₁₁	H	66	63 ^{c,d}
g	Me	H	n-C ₈ H 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**).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.

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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