A New Synthesis of Conjugated Dienones†

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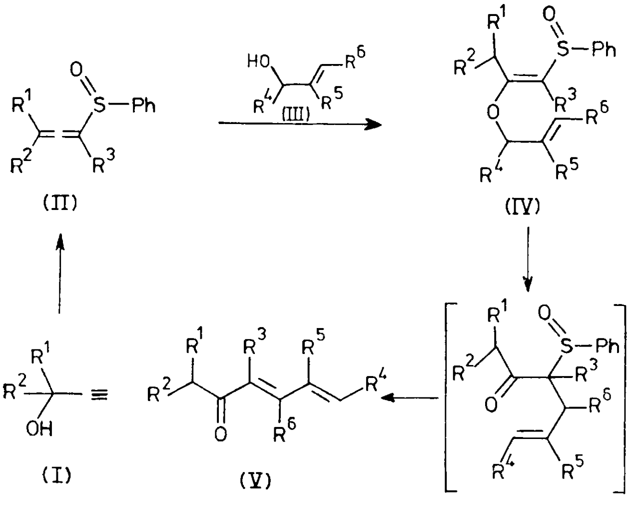
Summary Primary and secondary allyl alcohols add to allenyl phenyl sulphoxides to form enol ethers that undergo Claisen rearrangement and elimination of benzenesulphenic acid, producing 2,4-dienones.

WE describe a new synthesis of 2,4-dienones in which a primary or secondary allyl alcohol is added to an allenyl sulphoxide with subsequent elimination of a sulphenic acid.



SCHEME 1

TABLE. Reaction of allenyl phenyl sulphoxides (II) with allyl alcohols (III) and sodium hydride in benzene followed by distillation from zinc carbonate.

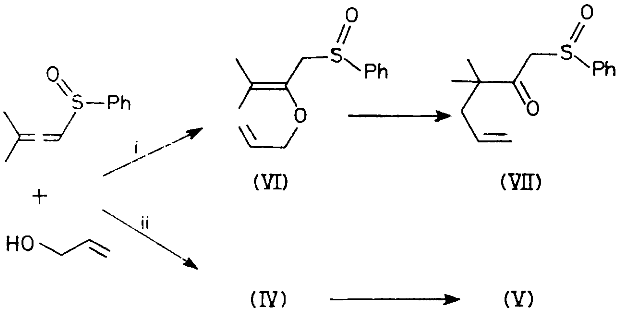
No.	R^1	R^2	R^3	R^4	R^5	R^6	Yield[a] of (IV)	Yield[a] of (V)
1	H	H	H	H	H	H	62	82[b]
2	H	H	H	H	Me	H	67	85[b,c]
3	H	H	H	H	H	Me	64	78[b]
4	H	H	H	Et	H	H	52	68[b,d]
5	H	H	H	n-C_5H_{11}	H	H	48	62
6	H	H	H	Ph	H	H	55	58[e]
7	Me	Me	H	H	H	H	63[f]	58
8	Me	H	H	H	H	H	—	—
9	H	H	Me	H	H	H	—	—

[a] After chromatography on silica gel. [b] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 3383. [c] ^{1}H N.m.r. spectrum shows presence of *trans* isomer only. [d] Y. Tei, N. Michiko, and N. Yoichi, *Agric. and Biol. Chem.* (*Japan*), 1970, **34**, 599. [e] Y. Leraux, *Ann. Chim.* (*France*), 1968, **14**, 133. [f] THF solvent.

The allyl alcohol (III) was converted into its sodium derivative with sodium hydride in benzene under nitrogen and then treated with the allenyl sulphoxide‡ (II) in benzene with cooling in an ice-bath (Scheme 1). After 1 h at 20 °C the adduct (IV) was isolated. Distillation of the enol ether (IV) from zinc carbonate induced Claisen rearrangement and elimination of benzenesulphenic acid to produce the dienone (V). The yields in some representative examples are shown in the Table.

Treatment of buta-1,2-dienyl phenyl sulphoxide with sodium allyl oxide in benzene in the usual way (Table, example 8) led not to addition but to isomerisation of the allene to but-2-ynyl phenyl sulphoxide (84%). The isomer with the methyl group at the other end of the allene, 1-methylpropadienyl phenyl sulphoxide (no. 9) did not react (92% recovered). Nor did allenyl phenyl sulphoxide react with the tertiary alcohols, 2-methylbut-3-en-2-ol or linalo-ol [either as the sodium salts in benzene or the presumably more reactive potassium salts in tetrahydrofuran (THF)].

Under the standard conditions in benzene, 3-methylbuta-1,2-dienyl phenyl sulphoxide and allyl alcohol gave the adduct (VI), which formed the phenylsulphoxy-ketone (VII) on distillation from zinc carbonate. Changing the solvent to THF (no. 7), however, produced the other tautomer (IV) which then gave the dienone (V) (Scheme 2).



SCHEME 2. i, C_6H_6; ii, THF (no. 7 in Table).

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† No reprints available.

‡ The unsubstituted and 3-mono- or 3,3-di-substituted allenyl phenyl sulphoxides are most easily made by reaction [(a) L. Horner and V. Binder, *Annalen*, 1972, **757**, 33; (b) P. J. Parsons, Ph.D. Thesis, Southampton University, 1978] of the prop-2-ynyl alcohol with benzenesulphenyl chloride and triethylamine in ether at −60 °C. The 1-substituted compounds can be made by alkylation of the 1-lithio-derivatives (ref. b above).