

FUNCTIONALIZED DIENES VIA THERMOLYSIS OF ALLYLIC SULFOXIDES

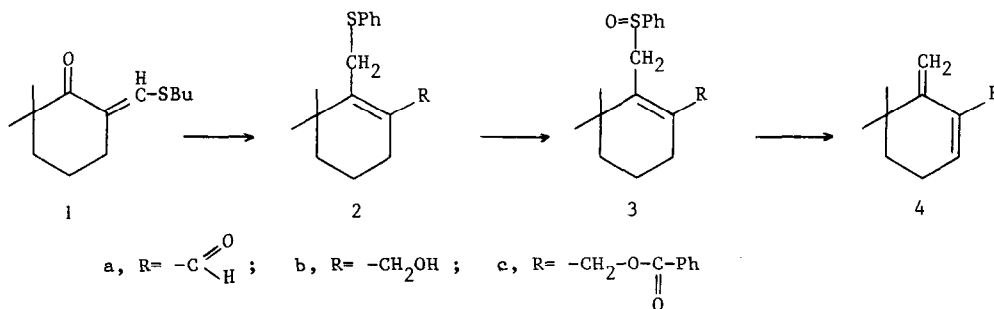
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Summary: Thermolysis of allylic sulfoxides is a useful method for the synthesis of functionalized dienes.

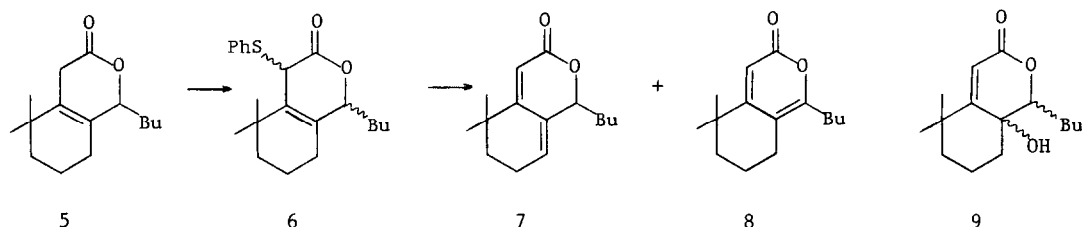
Thermal interconversion of allylic sulfoxides and sulfenates, eventually followed by nucleophilic decomposition of the latter to alcohols, has found wide application in organic synthesis^{1,2}. Elimination of sulfenic acid from allylic sulfoxides or sulfenates to dienes does not seem to have found much synthetic use. An example of this type of elimination is suggested by Ultee and Louw³ as an explanation of the thermolysis of 4-methylsulfinyl-1-butene and Kwart *et al.*⁴ also mention an allylic sulfenate as a possible intermediate in the formation of butadiene from 3-phenylsulfinyl-1-butene. The formation of dienes from allylic sulfoxides via basic elimination of sulfenate is used by Guitet and Julia⁵. We have found that thermolysis of allylic sulfoxides can offer an elegant and useful solution for the synthesis of functionalized dienes. The allylic sulfoxides can be obtained in several ways, which benefits the flexibility of the approach.

For instance, addition of phenylthiomethyl lithium to *n*-butylthiomethylene derivatives of ketones gives allylic sulfides of type 2 after hydrolysis of the adducts⁶. The sulfoxide 3a was obtained by oxidation of 2a with NaIO₄ in methanol/water⁷. Thermolysis of sulfoxide 3a in refluxing toluene gives a 80-90% yield of diene 4a⁸. Addition of 1 equiv. of K₂CO₃ gives



a cleaner reaction mixture but is not essential. Alcohol 3b, obtained by reduction (LiAlH_4) and oxidation (NaIO_4) of 2a had to be refluxed in xylene to assure a reasonable rate of elimination to diene 4b (90% yield). Likewise the benzoate 3c gave the corresponding diene in 87% yield (reflux in xylene, 1 equiv. of K_2CO_3). Functionalized dienes of type 4 are mentioned by Kende *et al.*⁹ and used by Goldsmith *et al.*¹⁰ in their communications on the total synthesis of Warburganal.

Allylic sulfides of type 6 can be obtained by sulfenylation of lactone 5¹¹. Treatment of 6 with excess NaIO_4 at reflux temperature gave 7 (50%) and 8 (30%) directly. The probable intermediate sulfoxide could not be isolated in this case and no base was added during this reaction. When



the oxidation of 6 was performed with *m*-chloroperbenzoic acid, the alcohol 9 was isolated as a minor product. The conversion of alkenes of type 5 to dienes of type 7 or 8 may be of use in the total synthesis of podolactones¹².

The mechanism of these eliminations was not studied but allylic rearrangement of the sulfoxides followed by thermal elimination of sulfenic acid from the sulfenates may have occurred. The isolation of 9 also points in this direction since it may be formed by nucleophilic attack on the sulfenate.

References and Notes

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8. All compounds showed correct IR, NMR and Mass spectra. Compounds 2a,b,c, 3a,b,c, 4a (as DNHP), 5 and 6 showed correct elemental analysis.
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(Received in UK 3 August 1981)