

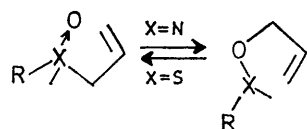
Synthesis of $\alpha\beta$ -Unsaturated Ketones via [2,3] Sigmatropic Rearrangement of γ -Chloroallyl Sulphoxides and Amine Oxides

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Summary When γ -chloroallyl sulphides and *N*-alkyl anilines are oxidized with *m*-chloroperbenzoic acid, the resultant *S*- and *N*-oxides rapidly undergo [2,3] sigmatropic isomerization to labile products that decompose internally with selective formation of conjugated enones.

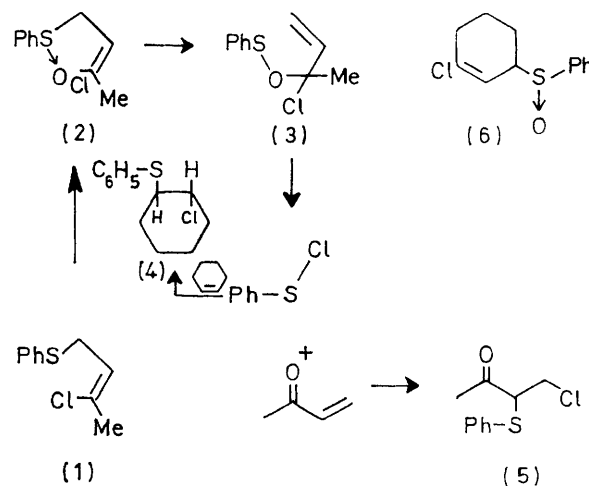
ALLYL sulphoxides and amine oxides can undergo sigmatropic reorganizations;¹ in the first case, relatively unstable sulphenates revert mainly to starting material, while the corresponding *O*-allylhydroxylamines are substantially more stable. Recently Evans² and Grieco³ have used the sulphoxide \rightleftharpoons sulphenate equilibrium by trapping the latter with added thiophilic reagents and developing a new



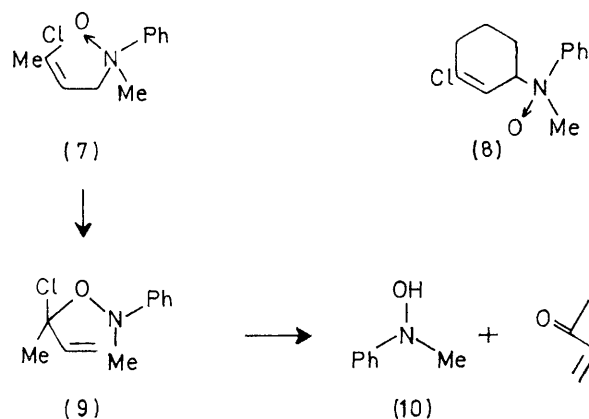
allyl alcohol synthesis including an allylic transfer of functionality. Chloroalkene groupings have been used in various intramolecular carbonium ion closures leading to ketones⁴ and during thermal [3,3] sigmatropic alkylation of sterically hindered ketones.⁴ We now report how these latent carbonyl units can give ketones without strong acid hydrolysis, and with the advantage of site-selective generation of $\alpha\beta$ -unsaturation.

When the sulphide (1) is oxidized with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane, the resulting sulphoxide (2), rearranges within 30 min at ambient temperature in ether once acids are removed by bicarbonate extraction. This is substantially faster than rearrangement (with racemization) of the chiral allyl *p*-tolyl sulphoxide ($t_{1/2}$ ca. 4.5 h at 40° in benzene).¹ The intermediate α -chlorosulphenate (3) resulting from (2) has not been

detected but rather loses phenylsulphenyl chloride a expected with concomitant production of methyl vinyl ketone (MVK). With cyclohexene present (but not required), the relatively slow recombination of sulphenyl chloride and enone is completely prevented; distillation



then affords ca. 65% of MVK and (4) can be isolated in ca. 80% yield. Cyclo-octene is preferred as ArSCL acceptor for use *in situ*; its labile adduct is expected⁵ to serve as a donor of ArSCL to more reactive olefins and other nucleophiles. The cyclohexenyl sulphoxide (6) rearranges in cyclohexene during 2 h at 50°, producing cyclohex-2-en-1-one and compound (4), both in 80% yield. Compound (6) is obtainable by selective *N*-bromosuccinimide bromination of 1-chlorocyclohexene, followed by thiophenolate displacement and MCPBA oxidation. Thus regioselective enone



generation from stable acyclic and cyclic precursors can take place at the desired stage of a synthetic sequence.

The tertiary amine oxide **(7)** rearranges within minutes in wet ether at room temperature (after acid is extracted), followed by hydrolysis of **(9)** to liberate *ca.* 80% each of MVK and hydroxylamine **(10)**. With the amine oxide **(8)** (6 h reflux in aq. tetrahydrofuran), 25–30% each of cyclohexenone and **(10)** are obtained, in addition to tar.

All compounds were characterized spectroscopically (i.r., u.v., n.m.r., mass) by comparison with authentic samples and/or elemental analyses.

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the CIBA-GEIGY Corporation for support of this research.

(Received, 26th September 1973; Com. 1345.)

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