Synthesis of αβ-Unsaturated Ketones *via* [2,3] Sigmatropic Rearrangement of γ-Chloroallyl Sulphoxides and Amine Oxides

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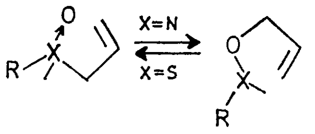
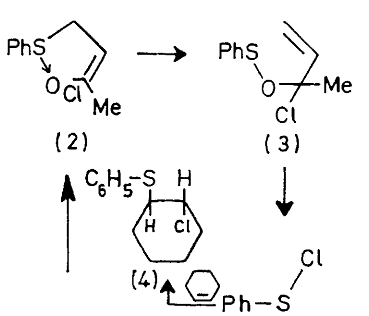
Summary When γ-chloroallyl sulphides and *N*-alkyl anilines are oxidized with *m*-chloroperbenzoic acid, the resultant *S*- and *N*-oxides rapidly undergo [2,3] sigmatropic isomerization to labile products that decompose internally with selective formation of conjugated enones.

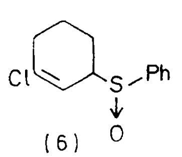
Allyl sulphoxides and amine oxides can undergo sigmatropic reorganizations;[1] in the first case, relatively unstable sulphenates revert mainly to starting material, while the corresponding *O*-allylhydroxylamines are substantially more stable. Recently Evans[2] and Grieco[3] have used the sulphoxide ⇋ 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 ketones[4] 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 αβ-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 expected[5] 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



(2) (3) (4)



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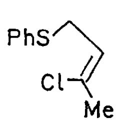
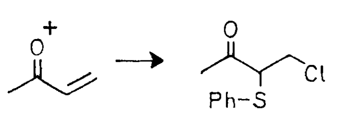


(1)



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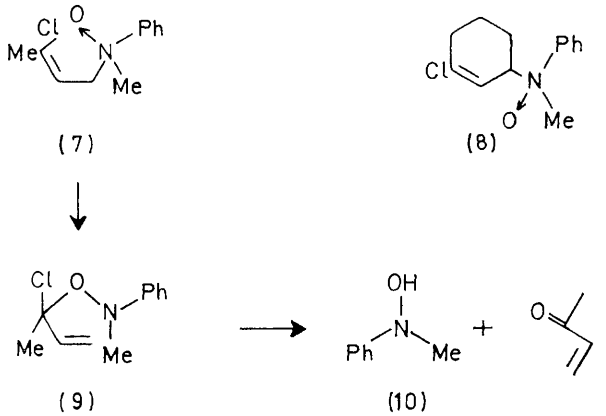

(7) (8) (9) (10)

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.

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