Temperature-dependent Behaviour of Sulphenic Acids

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Summary The sulphenic acid (**7**) interconverts with the thiazine sulphoxide (**4**) at 20 °C; at 111 °C it equilibrates with both the thiazine sulphoxide (**4**) and the thiazoline sulphoxide (**13**) and then slowly decomposes probably by way of the ion pair (**16**).

It is well established that sulphoxides bearing a hydrogen substituent at a β-carbon atom are thermolysed to olefins and sulphenic acids.[1] The reaction, which involves a sigmatropic hydrogen shift, is believed to require the coplanar transition state (**1**).[1,2] The attainment of such a cyclic arrangement is, in principle, precluded when the functional groups are incorporated into a six-membered ring.[3] Recently, however, we have shown that such a process can be realized when the migrating hydrogen atom is made more acidic by an activating group. For example, the thiazine sulphoxides (**2**) and (**4**) readily racemised in chloroform solution at room temperature; the isomerizations, which involve species (**5**) and (**7**), are considered[4] to proceed *via* the transition states (**8**) and (**9**).

The availability of Δ^4-thiazolines, *e.g.* (**10**), by the base-induced rearrangements of methyl 7-oxo-8-oxa-4-thia-1-azabicyclo[4.3.0]non-2-ene-3-carboxylates,[5] prompted us to examine the thermal behaviour of their sulphoxides. When heated, the derivative (**11**) would be expected to equilibrate with the sulphenic acid (**6**) which, in principle, may return to the starting material, afford the racemate of the thiazoline sulphoxide (**12**), or yield the racemate of the thiazine sulphoxide (**3**). By analogy with the behaviour of the sulphenic acid (**7**), which undergoes[4] exclusive conjugate *syn*-addition at room temperature, derivative (**3**) was the expected product.

However, the sulphoxide (**11**),† obtained (72% after silica gel chromatography) by oxidation of the thiazolinyl

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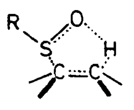
† The composition of new compounds was confirmed by elemental analysis and/or by mass spectroscopy. Structural assignments were supported by i.r., u.v., and n.m.r. spectroscopy.



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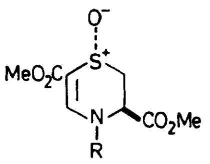
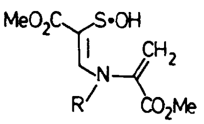
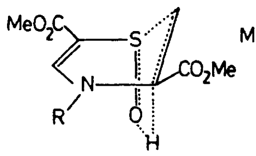


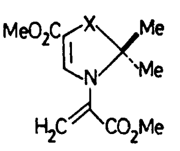
(2) $R = H$
(3) $R = CMe{:}CH_2$
(4) $R = CH_2{\cdot}OEt$



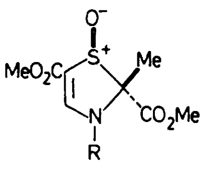
(5) $R = H$
(6) $R = CMe{:}CH_2$
(7) $R = CH_2{\cdot}OEt$



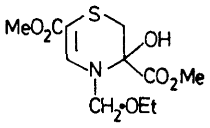
(8) $R = H$
(9) $R = CH_2{\cdot}OEt$



(10) $X = S$
(11) $X = SO$



(12) $R = CMe{:}CH_2$
(13) $R = CH_2{\cdot}OEt$



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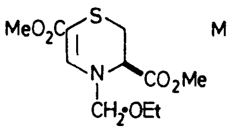

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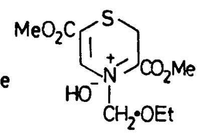

(16)

acrylate (**10**) with *m*-chloroperbenzoic acid, equilibrated (1·2 : 1) with the racemate of the isomeric thiazoline sulphoxide (**12**),† m.p. 128—130 °C, when heated in boiling toluene (under N_2; 4 h). The derivative (**12**), which was isolated in 33% yield after silica gel chromatography, gave an identical mixture of sulphoxides under similar conditions. Furthermore, the racemate of the thiazine sulphoxide (**4**) afforded a 1 : 1·2 mixture of the starting material and the racemate of the thiazoline sulphoxide (**13**),† m.p. 64—66 °C, in refluxing toluene (under N_2; 3·75 h). A similar mixture was obtained when the thiazoline sulphoxide (**13**), isolated in 36% yield after silica gel chromatography, was resubjected to the reaction conditions.

Prolonged heating of the mixture of sulphoxides (**4**) and (**13**) in boiling toluene (under N_2; 10 days) gave an array of products. A similar array of materials was formed (g.l.c. and n.m.r. spectroscopy) when the thiazine (**14**),† prepared (81%) by oxidation of the derivative (**15**)[4] with lead tetra-acetate in benzene, was heated under corresponding conditions.

The foregoing results emphasize that the fate of the sulphenic acids can be temperature dependent. Thus, at 20 °C, the species (**7**) equilibrates with the racemate of the thiazine sulphoxide (**4**); evidently at this temperature only the activation barrier involving the conjugate *syn*-addition can be surmounted. At 111 °C the sulphenic acid (**7**) rapidly interconverts with both the thiazine sulphoxide (**4**) and the thiazoline sulphoxide (**13**); at this temperature the higher-energy transition state, involving the ante-conjugate *syn*-addition, is also accessible and the outcome of the reaction is determined by the thermodynamic stabilities of the products (**4**) and (**13**). A third reaction, possessing an even higher activation energy, is also available at 111 °C. This process, which probably leads to the irreversible formation of the ion pair (**16**) and thence to the thiazine (**14**), reflects the electrophilic character of the sulphenic acid portion of the intermediate (**7**); there is ample precedent for this behaviour in the chemistry of the sulphenic acids.[6]

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