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THERMAL DECOMPOSITION OF CYCLIC SULPHOXIDES

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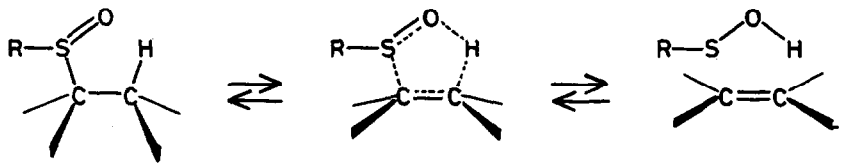
The thermolysis of sulphoxides to olefins and sulphenic acids is well documented,[1] but information about the thermal decomposition of cyclic sulphoxides is scant.[2] We have now augmented this information in connection with our study of the potential synthetic utility of intramolecular additions of sulphenic acids to olefins.[3] The pyrolysis of sulphoxides, and the addition of sulphenic acids to olefins (Scheme 1) involves a cyclic transition state (A) in which the five participating atoms tend to coplanarity.[1,3] Models reveal that the relevant five atoms cannot approach coplanarity in thian 1-oxide (1a), but they can in thiepan 1-oxide (2a) and thiocan 1-oxide (3), albeit with a significant increase in torsional strain and non-bonded interactions. Therefore (2a) and (3) were expected to undergo thermal decomposition more readily than (1a).

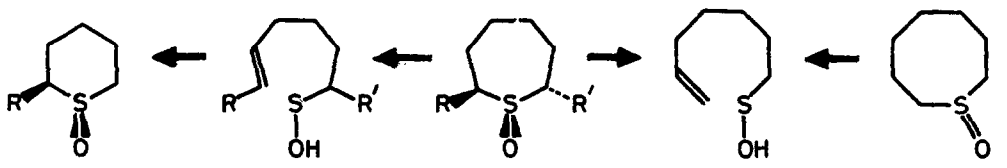
At 140° in xylene, conditions under which acyclic sulphoxides readily decompose,[1] thian-1-oxide (1a) was inert after 6 days, whereas thiepan 1-oxide (2a) decomposed with a half-life of ca. 28 h to give cis-2-methylthian 1-oxide (1b) (40%). Evidently (2a) gave the sulphenic acid (4a) which cyclized to (1b). Under the same conditions cis-2-methylthiepan 1-oxide (2b) decomposed even more readily (half-life 6 h) to give cis-2-ethylthian 1-oxide (1c) (35%) isolated by chromatography on silica; it was identical with the chromatographically more mobile of the two sulphoxides obtained by oxidation of 2-ethylthian with peroxydodecanoic acid. Other products, separated by preparative g.l.c., were 3-thiocen (9) (32%) [$\tau(CDCl_3)$ 4.22 (H-3), 4.49 (H-4), 6.77 (H-2), J_{23} 7.5 Hz, J_{34} 10 Hz, J_{45} 8 Hz] and the disulphide (7a) (8%) [$\tau(CDCl_3)$ 4.22 (H-6), 5.03 and 5.08 (H-7 protons), 7.32 (H-1), J_{12} 7 Hz, J_{56} 6 Hz, J_{67} (trans) 17 Hz, J_{67} (cis) 9 Hz, J_{77} ≃ 1 Hz; m/e (%) 41 (35), 55 (100), 101 (24), 129 (32), 258 (M, 9], whilst the presence of two other disulphides (7b) [m/e (%) 41 (48), 55 (100), 101 (33), 129 (30),

Scheme I



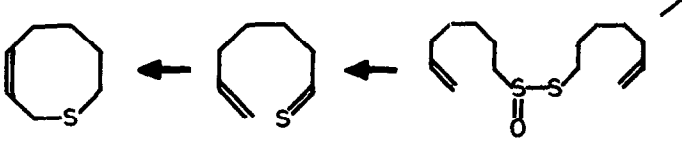
(A)

Scheme II

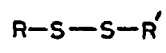


(1) (4) (2) (5) (3)

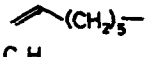
	R		R	R′		R	R′
(a)	H	(a)	H	H	(a)	H	H
(b)	Me	(b)	Me	H	(b)	Me	H
(c)	Et	(c)	H	Me	(c)	H	Me



(9) (8) (6)



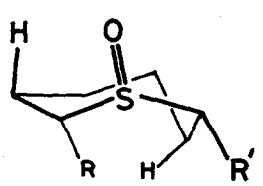
(7)

(a) R = R′ = 

(b) R, R′ = C_7H_{13}

(c) R, R′ = C_7H_{13}

isomeric disulphides



	R	R′
(B)	Me	H
(C)	H	Me
(D)	H	H

258 (M, 6)] and (7c) [m/e (%) 41 (32), 55 (60), 101 (100), 105 (65), 129 (45)] was detected by g.l.c./m.s.; the ratio (7a): (7b); (7c): (9) was 8:25:1:32. In contrast to the behaviour of the cis-isomer (2b), trans-2-methylthiepan 1-oxide (2c) decomposed more slowly than thiepan 1-oxide (2a), 60% remaining unchanged after 6 days at 140° in xylene. The only significant products were (7a), (7b), (7c), and (9) in the ratio 9:7:2:2 according to g.l.c.

The thermal decomposition of (2b) and (2c) may be rationalized in terms of the reactions outlined in Scheme II. Three sulphenic acids, (4b), (4c), and (5) may be formed by concerted elimination of (2b), but (5) should be favoured because models show that a strain-free planar transition state (as A) is readily attainable for exocyclic thermolysis of (2b) to (5), whereas the transition states for endocyclic thermolysis of (2b) to (4b) and (4c) are strained because the relevant five atoms can only approach, and not attain, coplanarity. The sulphenic acid (5) can then revert to (2b) or participate in the transformations (5)→(6), (6)→(7a), and (6)→(5) + (8) for which there are analogies.[4] We propose that the thioaldehyde (8) cyclizes to 3-thiocen (9).[5] Intramolecular cis-addition of the sulphenic acid to the double bond in (4b) accounts for the formation of (1c). The sulphenic acid (4c), if formed, should cyclize to two diastereoisomeric 2,6-dimethylthian 1-oxides (cf. ref 3), and the absence of such products suggests that the transformation (2b)→(4c) is appreciably slower than (2b)→(5) and (2b)→(4b). This is reasonable, because thermolytic cleavage of the C-S bond in sulphoxides is facilitated by increasing alkyl substitution at carbon;[1,6] the slower rate of thermolysis of thiepan 1-oxide (2a) to (4a) than that of cis-2-methylthiepan 1-oxide (2b) to (4b) may be explained similarly. The isomeric disulphides (7) are formed by deoxygenation of the thiolsulphinates (as 6) which arise by combination of the various sulphenic acids present in solution (cf. ref. 4).

The slower endocyclic thermolysis of trans-2-methylthiepan 1-oxide (2c) than thiepan 1-oxide (2a) may be attributed to steric effects, the transition states (B) and (C) connecting (2c) with the sulphenic acids (4b) and (4c) respectively being of higher energy than that (D) derived from thiepan by virtue of marked steric compressions of the pseudo-axially orientated methyl group; the transannular compression is severe in (B), and its consequences clearly outweigh the normally enhancing effect of alkyl substitution upon rate of thermolysis. The formation of disulphides from (2c) may be rationalized in the manner described above, but the production of (7a) deserves comment because exocyclic thermolysis of (2c) to the precursor (5) cannot occur by the concerted mechanism since a cyclic transition state (as A) is geometrically

impossible. Steric retardation of the concerted elimination may allow the incursion of a non-concerted, non-stereospecific homolytic mechanism,[7] and so account for the formation of (5), and subsequently (7a).

Thiocan 1-oxide (3) had a half-life of ca. 24 h at 140° in xylene, the main products of complete decomposition, according to g.l.c., being (7a), (7b), and (9) in the ratio 4:1:2. No cis-2-methylthiepan 1-oxide (2b) or cis-2-ethylthian 1-oxide (1c) were detected during the course of reaction, which was monitored by g.l.c. Evidently the rate of decomposition of (3) to (5) was much slower than any of the reactions in the equilibria involving cis-2-methylthiepan 1-oxide (2b), so that the only significant products were (7a), (7b), and (9), which are formed irreversibly.

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References and Footnotes

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