Mechanism of Sulphur Monoxide Extrusion

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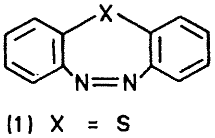
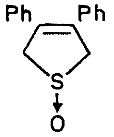
Summary The SO moiety of dibenzo[*b,f*][1,4,6]thiadiazepin 1-oxide is extruded thermally and is trapped by a diene to give a dihydrothiophen 1-oxide.

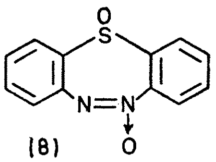
THE elimination of the sulphur bridge during the oxidation of dibenzo[*b,f*][1,4,6]thiadiazepin (**1**) with peracetic acid[1] is puzzling and interesting from the mechanistic point of view.[2] It is now established that the corresponding 1-oxide (**2**) readily decomposes thermally to give benzocinnoline (**3**), whereas both the parent thiadiazepin (**1**) and the corresponding 1,1-dioxide (**4**) are stable up to 210°.

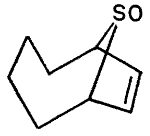


(1) X = S
(4) X = SO_2



(5)

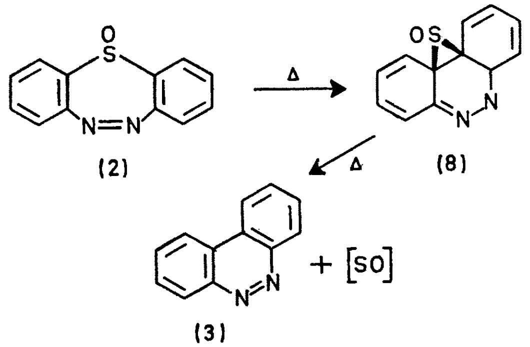




(6)

Heating a solution of (**2**) in benzene or chloroform under reflux causes rapid decomposition of (**2**) to give (**3**) plus sulphur and sulphur dioxide; the formation of the latter two species must result from the disproportionation of a transient sulphur monoxide,[3,4] suggesting that SO is extruded thermally[5] from (**2**). This conclusion is further supported by the trapping[6] of SO with either 2,3-diphenylbutadiene or cyclo-octa-1,3-diene to form 3,4-diphenyl-2,5-dihydrothiophen 1-oxide[6] (**5**), 30%, m.p. 134—136°, and a stereoisomeric mixture of the two 9-thiabicyclo[4,2,1]non-7-ene 9-oxides (**6**), 19%; oil; i.r. 3030, 1620, 1050, and 690 cm^{-1}; n.m.r. τ 4·2 and 6·3 in the ratio of 1 : 1; M^+ 156, respectively. Since elimination of sulphur monoxide from ethylene episulphoxides has been demonstrated,[5-7] (7) is suggested as a logical intermediate and can be reasonably arrived at from (**2**) by thermally initiated disrotatory electrocyclization involving 6π-electrons† according to a conventional application of the Woodward–Hoffmann rules.[8] A conrotatory cyclization of the 6π-electron system would lead to a sterically impossible *trans*-fusion of the episulphoxide ring. No decomposition was observed when a benzene solution of (**2**) was irradiated in a Pyrex apparatus.

The first-order rate constant for the decomposition in toluene, determined by following the disappearance of the u.v. absorption of (**2**) at 430 nm, was found to be $1{\cdot}42 \times 10^{-4}\ \mathrm{s}^{-1}$ at 65°. A plot of the rate constants against reciprocal temperature is shown in the Figure; the activation energy for the decomposition in toluene was computed to be 25·8 ± 1·50 kcal/mole, and that in toluene containing cyclo-octa-1,3-diene (*ca.* 5×10^{-3}M) to be 27·5 ± 1·48 kcal/mole. The activation energy computed by a least-squares method using all the available points is 26·6 ± 0·7 kcal (Figure). The close resemblance of the Arrhenius activation energy in the two cases demonstrates that the generation of transient SO is independent of the presence or



(2) (8) (3)

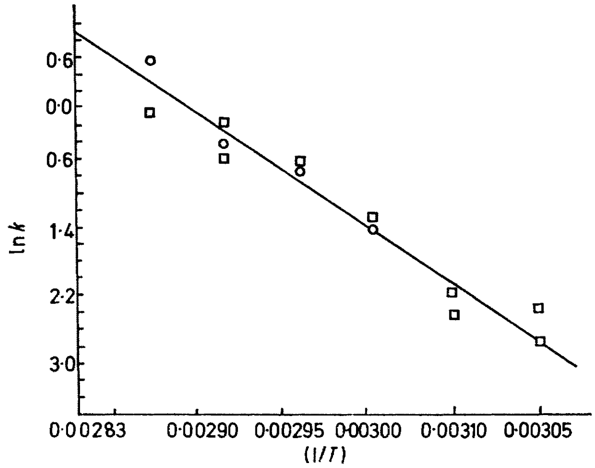


FIGURE. *Arrhenius plot of the decomposition of dibenzo*[b,f]-[1,4,6]*thiadiazepin 1-oxide* (**1**). *The rate constants measured in toluene* ($1{\cdot}05 \times 10^{-3}$M *of* **1**) *are represented by squares and those measured in toluene–cyclo-octa-*1,3-*diene* (ca. 5×10^{-3}M) *by circles. The straight line is computed by least-squares plot.*

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† It has been shown that thiepin 1,1-dioxide has a non-planar boat structure and possesses weak electron delocalization insufficient to acquire a planar conjugated, system [W. L. Mock, *J. Amer. Chem. Soc.*, 1967, **89**, 1281; H. L. Ammon, P. H. Watts, jun., J. M. Stewart and W. L. Mock, *ibid.* 1968, **90**, 4501]. In analogy the thiadiazepin system probably has a non-planar boat conformation. The ring strain of the thiazepin system and the tendency to become a fully conjugated system in (7) may provide a part of the driving force in the electrocyclization (**2**)→(**7**).

the absence of the diene. The transient SO may be in either the ground triplet state ($^3\Sigma^-$), or an excited singlet state ($^1\Sigma^+$ or $^1\Delta$)[3-5], both of which have lifetimes long enough to react with the diene at *ca.* 5×10^{-3}M if a diffusion-controlled bimolecular process is assumed.

Dibenzo[*b,f*][1,4,6]thiadiazepin 1,4-dioxide (**8**), decomposition point 208°, was also shown to decompose at its m.p. to give benzocinnoline (69% yield). In the course of the decomposition of (**8**), the azoxy-bridge was reduced to the azo-group, though the precise mechanism of the reduction is obscure. Other known sulphur monoxide extrusion reactions[9] may proceed by a similar mechanism.

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