

THE EXTRUSION REACTION OF SULFUR DIOXIDE FROM STRAINED SULFOLENE

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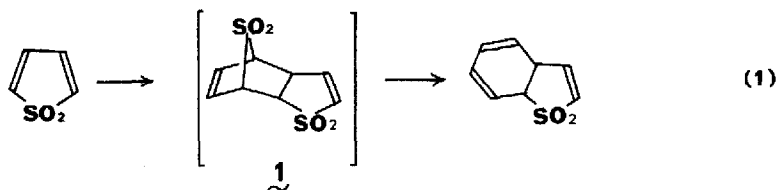
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By many kinetic and mechanistic studies on the SO_2 extrusion reaction of substituted sulfolenes,¹ it has been elucidated that the reaction proceeds via concerted, suprafacial (disrotatory) process, in accord with the orbital symmetry conservation rule.²

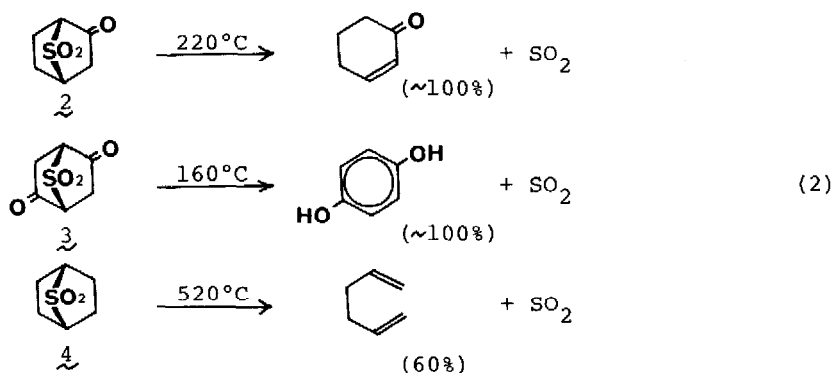
Strained sulfolene, such as thiophene dioxide dimer (1), has been postulated as an intermediate to give dihydrobenzothiophene dioxide by SO_2 extrusion in the dimerization reaction of thiophene dioxide (eq. 1).³



Similar extrusion of sulfur atom⁴ or sulfur monoxide^{4c} has also been reported for 7-thiabicyclo[2.2.1]hepta-2,5-diene or corresponding sulfoxide, respectively.

The facts of the enol form participation in the solvolyses of anti-7-tosyloxybicyclo[2.2.1]heptan-2-one⁵ and 3-(2-tosyloxyethyl)cyclopentanone⁶ and the facile SO_2 extrusion of **1** stimulated us to investigate the behavior of 2-oxo-(2) and 2,5-dioxo-7-thiabicyclo[2.2.1]heptane-7,7-dioxide⁷ (3).

Thermolyses of 2 and 3 giving cyclohexen-3-one and hydroquinone, respectively, in quantitative yields, took place at relatively low temperatures (220°C for 2 and 160°C for 3) compared with the thermolysis of 7-thiabicyclo[2.2.1]heptane dioxide (4), which was reported to occur only at much elevated temperature (520°C).⁸ (eq. 2).



In order to gain further insight into this facile SO_2 extrusion reaction, kinetics of the thermolyses for 2 and 3 were investigated. Rate measurements were carried out on the basis of the decrease of the intensity of the carbonyl absorption in ir (1752 cm^{-1} and 1760 cm^{-1} for 2 and 3, respectively). The rate of thermolysis followed first-order kinetics up to 60% conversion. The activation parameters shown in Table 1 clearly indicate that thermolyses of 2 and 3 proceed mechanistically in a different manner, that is, thermolysis of 2 is governed mainly by enthalpy of activation, while thermolysis of 3 by entropy of activation. The strikingly large entropy of activation (75.7 eu.) for the decomposition of 3 may be reasonably compared with the negatively large entropy of activation (-78.5 eu.) observed for the copolymerization of isobutene and SO_2 .⁹ This seems to suggest the (stepwise) fission of carbon-sulfur bond in 3 to be the rate determining. The activation parameters for 2 may be compatible with the enol participation in the rate determining step¹⁰ followed by the concerted SO_2 expulsion.

One plausible rationale for this drastic mechanistic change going from 2 to 3 may be offered in view of a probably weakened sulfur-carbon bond

Table 1. First order rate constant and activation parameters for the thermolyses of $\overset{2}{\underset{\sim}{\text{C}}}$ and $\overset{3}{\underset{\sim}{\text{C}}}$ in KBr pellet.

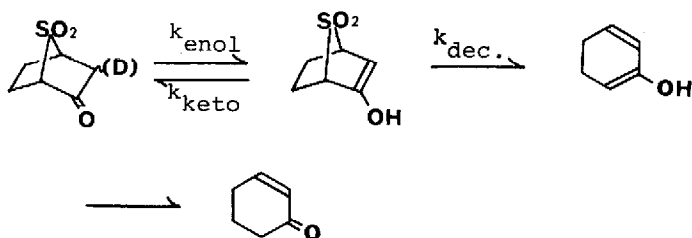
| Temp (°C) | k_{app} (sec ⁻¹) | ΔH^\ddagger (kcal/mole) | ΔS^\ddagger (cal/deg) | ΔF^\ddagger (kcal/mole) |
|--|---------------------------------------|------------------------------------|----------------------------------|------------------------------------|
| 130.0 | $(5.70 \pm 0.08) \times 10^{-5}$ | 23.7 | -17.8 | 30.9 |
| $\overset{2}{\underset{\sim}{\text{C}}}$ 140.0 | $(1.21 \pm 0.09) \times 10^{-4}$ | | | |
| 150.0 | $(2.42 \pm 0.12) \times 10^{-4}$ | | | |
| 88.9 | $(3.99 \pm 0.13) \times 10^{-5}$ | | | |
| $\overset{3}{\underset{\sim}{\text{C}}}$ 98.9 | $(3.09 \pm 0.15) \times 10^{-4}$ | | | |
| 108.0 | $(2.32 \pm 0.11) \times 10^{-3}$ | 55.3 | 75.7 | 26.4 |

caused by introduction of two carbonyl groups in a position where the dipoles of sulfonyl and carbonyl groups are arranged each other in the destabilizing direction.¹¹

References and Note

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10. In order to get the direct evidence for enol form participation, deuterium incorporation reaction for **2** was performed in $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ (50:50 vol. first-order rate constant $3.9 \times 10^{-5} \text{ sec.}^{-1}$ at 100°C), only to find no or less than 4% deuterium incorporation in recovered **2** after 50% reaction. This result may be interpreted assuming $k_{\text{dec.}}$ is much larger than k_{keto} .



Thermolysis of **3** in CD_3OD (first-order rate constant 2.0×10^{-4} at 90°) showed D-incorporation in neither recovered **3** nor hydroquinone.

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