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INTRAMOLECULAR REARRANGEMENT OF THIOOZONIDES: SULFINE FORMATION WITHOUT SULFUR ATOM SCRAMBLING, A DOUBLE ISOTOPE CROSSOVER STUDY

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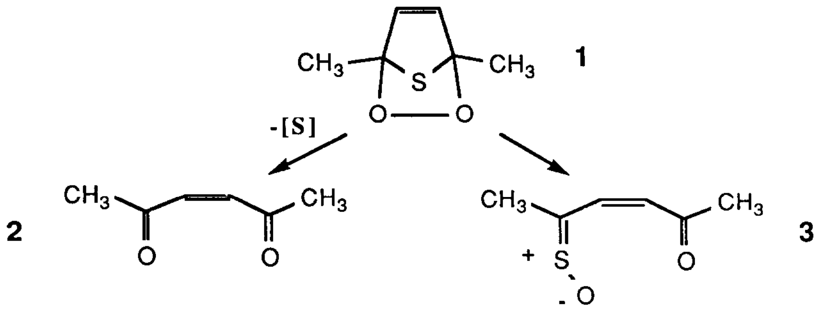
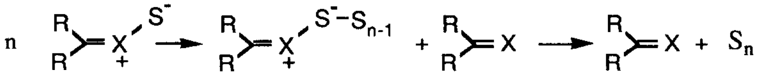
Abstract: Decomposition of a mixture of ^{34}S and deuterium labeled thioozonides prepared by photooxidation of dimethylthiophenes in $CDCl_3$ has shown that intramolecular rearrangement to thioketone S-oxide, a stable 1,3-dipole, proceeds cleanly without sulfur atom scrambling in the presence of sulfur allotropes.

The thermal chemistry of organosulfur compounds is complicated by the facile generation of sulfur allotropes and the secondary reactions that occur, such as sulfur atom transfer and elemental sulfur formation[1]. Detailed mechanistic studies concerning the nature of these fundamental exchange and concatenation processes are generally not available. In the course of our work on heteroatom (S,O) containing bicyclic ozonides we have examined the thermal decomposition of 1,4-dimethyl-2,3-dioxa-7-thiobicyclo[2.2.1]hept-5-ene[2], the endoperoxide of thiophene (**1**). Two apparently separate pathways are observed. One path produces a *cis* -enedione (**2**) with the expulsion of sulfur and a second path involves the formation of a thioketone-S-oxide (**3**), a sulfine, with the same molecular formula as the starting thioozonide.

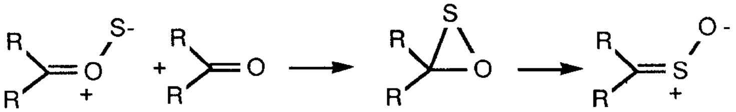


In previous work[3] we have shown that during the decomposition of **1** active sulfur and oxygen transfer agents are present and that heteroatom transfer to form epoxides and thiiranes from olefins occurs with high stereoselectivity . Other trapping experiments demonstrated the formation of sulfur allotropes (trisulfide formation with norbornylene)[4] and S_8. The presence of these allotropes obscures the mechanism of sulfur expulsion. Carbonyl O-sulfides are likely candidates for initial sulfur transfer or loss as proposed for thiocarbonyl-S-sulfides[5] (transfer of terminal sulfur atoms to build sulfur chains which can cyclize and eliminate species such as cyclo-S_6 and -S_8).



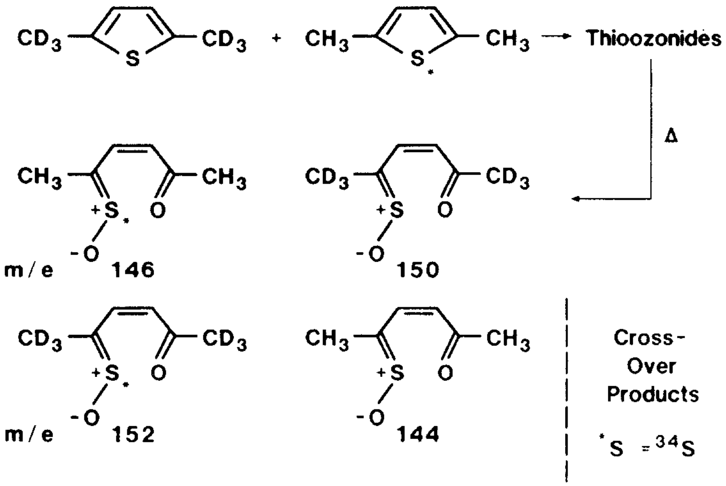
X=S,O

For the monothiozonide **1**, transfer of sulfur from a carbonyl-O-sulfide to the bridging thiozonide sulfur would produce a thiosulfoxide which should have a lower energy path for cheletropic expulsion of S_2 than extrusion of a singlet sulfur atom[6] from **1**. In our system the anticipated sulfur exchange chemistry and the calculated stability of carbonyl O-sulfides relative to sulfines (CH_2SO potential surface)[7] suggests the possibility of sulfur atom exchange during formation of **3** perhaps by attack of an active sulfur transfer species such as a carbonyl O-sulfide on the product enedione. Ring opening[8] would give sulfine **3**.

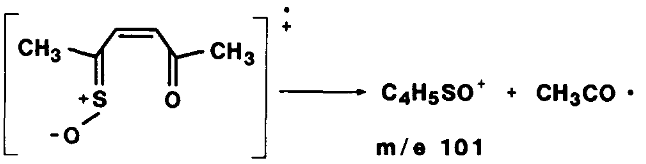


To definitively eliminate the involvement of sulfine in the sulfur expulsion pathway, a double labeling crossover study was conceived (scheme 1). In principle, the decomposition of a 50:50 mixture of thioozonides, one labeled with ^{34}S and the other labeled with deuterium at the bridgehead methyl groups could give rise to a total of 4 possible sulfine products. Clean intramolecular rearrangement would give sulfine-^{34}S(m/e 146) and sulfine-d_6 (m/e 150). Crossover and scrambling of sulfur atoms or other allotropes would give unlabeled sulfine (m/e 144) and the double labeled product, sulfine-$^{34}S,d_6$ (m/e 152).

Scheme 1



Thiophene-^{34}S was prepared by internal condensation and deoxygenation of acetonylacetone with P_2S_5 (93.6% ^{34}S) in CS_2. 2,5-diperdeuteromethylthiophene was prepared by standard alkylation of the parent thiophene with CD_3I. Mixtures of the labeled thiophenes (50:50 mole %) at 0.58 and 0.18 **M** concentration were photooxidized in $CDCl_3$ with methylene blue as a sensitizer at -40°C. The mixture of thioozonides was then purged with nitrogen gas and warmed to room temperature. After 12 hrs the solutions were examined by capillary gc/ms analysis to determine the isotopic composition of the sulfine products. In practice the most abundent ion observed in the sulfine fragmentation pattern is used to calculate the product distribution. For the expected labled products these ions are: $C_4H_5SO^+$, m/e 101; $C_4H_5{}^{34}SO^+$, m/e 103; $C_4D_3H_2SO^+$, m/e 104; $C_4D_3H_2{}^{34}SO^+$, m/e 106.

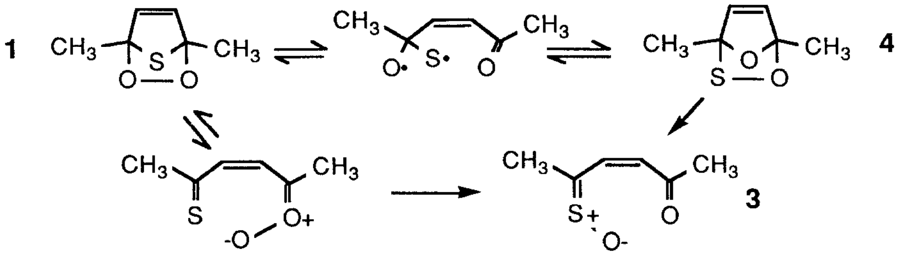


The thermal products derived from the individual labeled thioozonides (d_6 and ^{34}S) were also analyzed to determine the theoretical ion pattern expected for the 50/50 mixed, no exchange case (Table 1, columns 1, 2, and 3 respectively). The total integrated ion intensities for the theoretical 100% scrambled and the mixed experimental cases at 0.18 and 0.58 **M** are also shown.

Table 1: Sulfine Fragment Ion Intensities (Predicted and Measured)

Ion	d_6-Sulfine	S'-Sulfine	50/50	100% Scrambled	Observed (0.18 M)	(0.58 M)
101	-	7	7	53	10	10
103	5	100	105	60	97	99
104	100	21	121	64	120	117
106	15	-	15	57	20	22

By comparing the experimental distributions with the theoretical unscrambled case, no evidence for sulfur atom exchange[9] during sulfine formation was observed and the ion distribution for both concentrations was essentially identical indicating no bimolecular component to the reaction. The lack of scrambling clearly indicates that formation of **3** proceeds by an independent pathway which is not influenced by the sulfur expulsion chemistry. The most likely routes for sulfine formation , a) retro dipolar addition followed by internal oxygen transfer or b) isomerization[10] to the oxygen bridged thioozonide **4** followed by retro dipolar additon, are shown below.



At present no information exists which discriminates between these pathways; it has only been observed that decomposition of **1** in methanol leads to higher yields of sulfine[11], consistent with dipole formation. Currently we are further investigating the sulfur expulsion pathway and seeking synthetic routes to **4**.

References and Notes

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