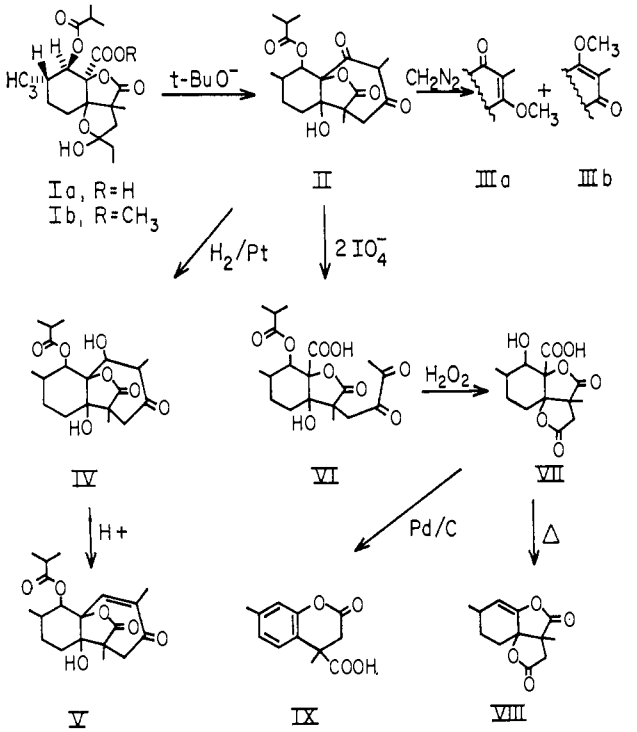
periodate (the first mole hydroxylates the α carbon, the second mole cleaves the α-hydroxy ketone), yielding the acid $C_{19}H_{26}O_9$ (VI) (mp 212°; ν 3500, 1770, 1755, 1720). Structure VI has been assigned arbitrarily; the data do not differentiate between the two possible modes of cleavage. VI is a 1,2-diketone as shown by quinoxaline formation with *o*-phenylenediamine; the presence of the acetyl group was clear from the nmr. VI, with alkaline hydrogen peroxide, gave acetic acid, isobutyric acid by accompanying hydrolysis, and the acid VII.

Pyrolysis of VII to produce VIII, analogous to the previous conversion VIa*[5] to VIII, gave a much poorer yield, ascribed to the hydroxyl and carboxyl in VII being *trans*. A *trans* relationship between the secondary hydroxyl and adjacent carbonyl is assigned as the original configuration in both I and I*. In I, the facile and parallel decarboxylation and elimination of isobutyric acid on treatment with alkali supports this stereochemistry. It remains unchanged throughout the degradation as witnessed by the coupling constant between the protons on the hydroxyl-bearing carbon and the adjacent methyl-bearing carbon (J = 9–11 Hz, *trans* diaxial protons).

In I* the same relationship holds initially (J = 11 Hz). However, acid-catalyzed formation of the internal enol ether II* causes an inversion at the secondary alcohol carbon, and the coupling constant between these two protons becomes, and remains, 2 Hz. Thus in VIa* the hydroxyl and carboxyl are now *cis* and consistent with a ready thermal decarboxylation–dehydration, giving VIII in excellent yield.



Treatment of hydroxy acid VII with palladium on carbon (di-*n*-hexyl ether, 200°) caused decarboxylation and aromatization to dihydrocoumarin IX, identical with the compound previously reported.[3] Thus dihydrocoumarin IX is the end product of this sequence (I → II → VI → VII → IX) as it was in the degradation of the C_{19} 1,3-diketone.[3] The nature of the reactions employed and the properties of the intermediates establish the structures as shown, with stereochemistry in the cyclohexane as given for I. The recent[6] structure presented for ryanodol must also accommodate the C_{19} acid and the C_{19} 1,3-diketone,[3] both now of established structure, which along with formic acid are the products of the action of 3 mol of periodate.

(5) Starred numerals refer to compounds obtained in another degradation sequence, as presented in ref 3.

(6) S. N. Srivastava and M. Przybylska, *Can. J. Chem.*, **46**, 795 (1968), have presented a structure for ryanodol *p*-bromobenzyl ether based on X-ray diffraction studies.

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The Thermal Racemization of Aryl Arenethiolsulfinates. An Extraordinary Rate Acceleration of the Inversion of Sulfoxide Sulfur

Sir:

Unsymmetrically substituted sulfoxides, $R_1S(O)R_2$, are known to be optically stable substances which may undergo thermal racemization *via* pyramidal inversion only under forcing conditions. Recent data[1] indicate typical activation parameters for such inversion to be $\Delta H^{\ddagger}$ = 40 kcal/mol, $\Delta S^{\ddagger}$ = 0 eu, yielding conveniently measurable racemization rates in the neighborhood of 200°.

Although no quantitative information is available on other sulfoxidic substances such as sulfinate or sulfite esters, these also appear to be optically stable under normal conditions and in the absence of acid and nucleophilic catalysis.[2]

In contrast to this behavior, another class of sulfoxidic substances, the aryl arenethiolsulfinates, ArS(O)SAr, which have been recently prepared in an optically active form[3] exhibit exceptionally high optical lability.[3] Mechanistic studies in our laboratory and in that of Kice have revealed that racemization of thiolsulfinates can be achieved by several mechanisms, including a nucleophile-catalyzed route[4] and a concerted nucleophile- and electrophile-catalyzed route.[5] In this communication we wish to report that racemization of thiolsulfinates may also occur in an uncatalyzed path which appears to involve pyramidal inversion at the sulfoxide sulfur. The evidence follows.

Optically active thiolsulfinates, in solution and in the absence of nucleophilic and/or electrophilic substances, lose optical activity without undergoing any appreciable chemical change. The uv absorption spectrum remains unchanged during racemization and the product recovered after 10 half-lives is identical with the starting material except for optical activity. Racemization rates for two substrates under a variety of conditions are reported in Table I.

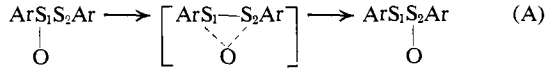
(1) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966).
(2) H. F. Herbrandson and R. T. Dickerson, Jr., *ibid.*, **81**, 4102 (1959).
(3) (a) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (b) J. L. Kice and G. B. Large, *Tetrahedron Letters*, 3537 (1965).
(4) P. Koch, unpublished.
(5) J. L. Kice and G. B. Large, *J. Am. Chem. Soc.*, in press. We are indebted to Dr. Kice for letting us know their results in advance of publication.

Table I. Rates of Racemization of Aryl Arenethiolsulfinates, ArS(O)SAr

Ar	Concn, 10^2 M	Solvent	Temp, °C	Rate 10^4k sec^{-1}
p-$CH_3C_6H_4$	0.95	Benzene	50	3.50
	1.9		50	3.66
	3.8		50	3.85
	7.6		50	4.27
	9.5		50	3.61
	3.8		35	0.53
	3.8		60	9.25
	3.8	Acetonitrile	75	5.25
p-ClC_6H_4	3.3	Benzene	50	4.62

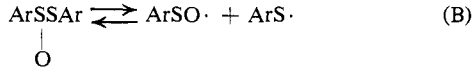
The data, first five entries in Table I, show that the racemization rate does not change appreciably on changing the concentration by a factor of ten. Thus the racemization reaction is first order. Molecular weight determinations in benzene showed the thiolsulfinate to be monomeric. Thus the slow step involves one thiolsulfinate molecule. The activation parameters are $\Delta H^{\ddagger} = 23$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu.

Three mechanistic pathways have been considered: (A) an intramolecular oxygen transfer between the two sulfur atoms; (B) a slow homolytic splitting of the



(A)

S–S bond followed by recombination (a variant of this



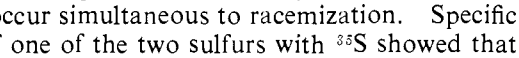
(B)

mechanism (B′) would assume recombination to occur without the radicals ever diffusing out of the solvent cage); (C) pyramidal inversion of the sulfoxide sulfur.

Mechanism A predicts scrambling of the two sulfur atoms to occur simultaneous to racemization. Specific labeling of one of the two sulfurs with ^{35}S showed that after 10 half-lives for racemization the two sulfur atoms had maintained their identity. Thus scrambling does not occur, and mechanism A has to be ruled out.

Mechanism B can also be ruled out: experiments run in the presence of the radical scavenger diphenylpicrylhydrazyl showed that the latter is not appreciably consumed during racemization.

The variant, B′, of this mechanism seems also highly unlikely on the following grounds. The homolytic splitting of the S–S bond can be effected either photochemically or thermally, and its occurrence leads to the irreversible disproportionation of the thiolsulfinate to thiolsulfonate and disulfide.[6] The thermal process



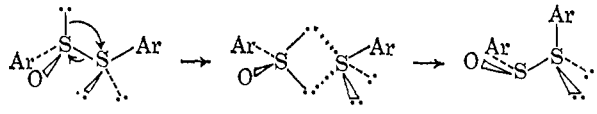
appears to be a chain reaction initiated by the homolytic splitting of the S–S bond. The activation parameters for the initiation step are $\Delta H^{\ddagger} = 34$ kcal/mol, $\Delta S^{\ddagger} = 12$ eu.[4] Comparison of these values with those for racemization, $\Delta H^{\ddagger} = 23$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu, stresses the incompatibility of the two processes. For the two processes to be compatible it would be necessary to assume that diffusion out of the solvent cage requires some 6 kcal/mol of free energy, which is completely unreasonable.[7]

The third mechanism, pyramidal inversion of the sulfoxide sulfur atom, is consistent with the experimental observations: the entropy of activation, −4 eu, is in the range of values known for sulfoxides,[1] and the structural effect is very small, in the direction of greater rates for electron-attracting substituents, as observed also for sulfoxides.[1]

The striking feature of this racemization is the small activation enthalpy, 23 against 40 kcal/mol for sulfoxides, which is responsible for the rate factor of 10^{11}.

This huge acceleration may perhaps be explained by assuming that inversion of the sulfinyl sulfur of thiolsulfinates does not entail a trigonal planar species but occurs by way of a mechanism such as that proposed by Haake[8] for inversion of bis(dialkyl sulfide)dichloroplatinum(II) complexes.[8] Here the rate factor, with respect to sulfoxides, is of the order of 10^{18}.[8]

Following Haake's ideas, inversion of thiolsulfinates can be envisioned to occur by way of a transition state where both electron pairs of sulfinyl sulfur are engaged in weak bonding with sulfenyl sulfur so that the former maintains a distorted tetrahedral configuration and the latter acquires a distorted trigonal-bipyramidal configuration.



Actually this process is better considered as an internal displacement at sulfenyl sulfur rather than a pyramidal inversion at sulfinyl sulfur.

If this view is correct, one should expect relatively rapid stereomutation at sulfur whenever one of the ligand atoms is such as to have d orbitals easily available for bonding. This should be true for sulfur as well as for other pyramidal species. We are currently verifying this expectation.

It is interesting to note that in the inversion at nitrogen a heavy ligand seems to cause acceleration in some cases and deceleration in other ones. Thus, 1-benzenesulfenylaziridine[9] inverts about 10^5 times more rapidly than 1-ethylaziridine.[10] On the other hand, according to a very recent report[11] which contrasts a previous one,[12] 1-chloroaziridines invert very slowly, to the point of actually allowing for the isolation of enantiomers.[13,14]

Acknowledgment. We are greatly indebted to Professor Haake for a very stimulating discussion.

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