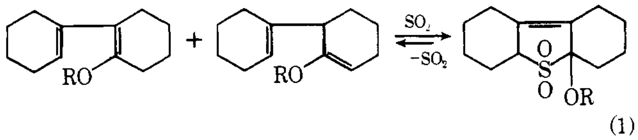
Organic Reactions of Sulfur Dioxide. 3. Ene Reaction: a Facile Regiospecific Isomerization of Olefins

Sir:

Sulfur dioxide readily reacts with nucleophilic double bonds of certain enol ethers[1] and ketenes[2-4] to provide 1,3-dipolar ion intermediates. Depending on the substrate and the reaction conditions these intermediates may react further, or because of the efficient stabilization of charges, they may be stable in solution. Butadiene and various other 1,3-dienes undergo a suprafacial 1,4 cycloaddition reaction with sulfur dioxide to give the corresponding 2,5-dihydrothiophene 1,1-dioxides.[5,6] Although it has been reported that cycloaddition does not occur with 1,4-dienes,[5] we have observed that sulfur dioxide reacts with a 1:1 mixture of isomeric 4-alkoxy-1,3- and -1,4-dienes to give an essentially quantitative yield of the corresponding 1,4 cycloadduct[1] (eq 1). Clearly, the cycloaddition was preceeded by a facile isomerization of the 1,4- to the 1,3-diene, but the mechanism of the isomerization was not known.[1]

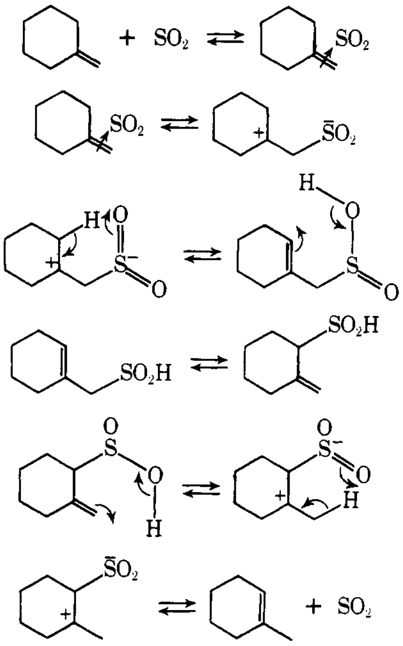


(1)

We would like to report now the sulfur dioxide catalyzed isomerization of various carbon–carbon double bonds which seem to involve a reversible ene reaction with sulfur dioxide. Thus, a solution of β-pinene (0.136 g, 1 mmol) in sulfur dioxide (1 mL) was sealed in an NMR tube at −78 °C and the isomerization to α-pinene was followed at room temperature by the disappearance of the signal at δ 4.54 and appearance of the multiplet at δ 5.19. The reaction exhibited clear pseudo-first-order kinetics with a rate constant of 3.01×10^{-5} min^{-1}. Under similar reaction conditions methylenecyclohexane, methylenecyclopentane, 2-methyl-1-pentene, 2,4,4-trimethyl-2-pentene, and 2,3-diphenyl-1-propene underwent the isomerization to the thermodynamically more stable isomers (Table I). It is noteworthy that the isomerization of 2-methyl-1-pentene afforded only 2-methyl-2-pentene without formation of any 4-methyl-2-pentene(s). Both *cis*- and *trans*-4-methyl-2-pentenes appear quite stable under the same reaction conditions. On the other hand isomeric 4-methyl-1-pentene was stable in sulfur dioxide in the dark, but in the presence of light underwent a known polysulfone formation.[7]

Comparison of the rates of isomerization with the relative thermodynamic stabilities of the olefin pairs (see Table I) and the absence of other possible isomers in the reaction mixtures strongly suggest a kinetically controlled process. Interestingly, the rate of isomerization of β-pinene in sulfur dioxide at 60 °C increased only by a factor of ~5. On the other hand, the same reaction in the presence of a catalytic amount of anhydrous aluminum chloride provided a mixture of *p*-menthadienes and a small quantity of a polymer.

Scheme I



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(7)

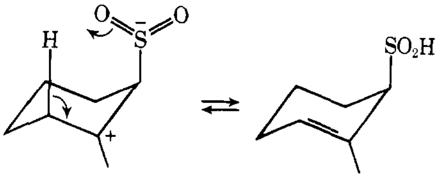
It is known that sulfur dioxide forms π complexes with various nucleophiles[8-11] and therefore it appears reasonable that sulfur dioxide should also form π complexes with carbon–carbon double bonds.[12] However, it seems that such a π complex (e.g., with methylenecyclohexane, Scheme I) would undergo transformation to the corresponding dipolar σ complex (albeit short lived[13]), only if the positive charge in the σ complex could develop on a tertiary carbon atom.[1] The absence of *p*-menthadienes in the reaction with β-pinene strongly argues against free, long-lived carbonium ion intermediates. The fact that the rates of isomerization did not reflect the thermodynamic stabilities of the olefin pairs and that the reaction proceeds with considerable negative entropy of activation suggest that the proton abstraction from the adjacent secondary carbon atom (eq 4) might very well be the rate-determining step. Subsequent 1,3 rearrangement of the allylic sulfinic acid[14,15] (eq 5), followed by intramolecular protonation (a retroene reaction), and reversible dissociation of sulfur dioxide (eq 6, 7) would account for the particular observations in these isomerizations. For example, the extremely slow isomerization

Table I. Regiospecific Isomerization of Olefins in Liquid Sulfur Dioxide[a]

Olefin (OL)	Isomerized Olefin (IOL)	IOL/OL	Relative rate[b]	$\Delta H°$, kcal/mol
β-Pinene	α-Pinene	97/trace[c]	1	−2.4[f]
Methylenecyclohexane	1-Methylcyclohexene	99/trace	~800	−2.1[g]
Methylenecyclopentane	1-Methylcyclopentene	99/trace	Very fast	−3.8[g]
2-Methyl-1-pentene	2-Methyl-2-pentene	91/9[d]	630	−1.46[h]
4-Methyl-2-pentene (*cis*- and *trans*-)	No reaction			
2,4,4-Trimethyl-2-pentene	2,2,4-Trimethyl-1-pentene	81/19[d]		−1.3[i]
2,3-Diphenyl-1-propene	2,3-Diphenyl-2-propene	75/trace[e]	142	

[a] Reactions were carried out in ~1 M solutions in sulfur dioxide in a sealed NMR tube at room temperature. [b] The pseudo-first-order rate constants relative to the value of $3.01 \pm 0.165 \times 10^{-5}$ min^{-1} for the isomerization of β-pinene. More refined kinetic data will be published in a full paper. [c] Accompanied with ~3% *p*-menthadienes. [d] The equilibrium approached from both sides. [e] Both trans (62%), and cis (13%) olefins were formed. In addition about 25% polymer was present. [f] D. V. Banthrope and D. Whittaker, *Chem. Rev.*, **66**, 643 (1966). [g] R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958). [h] "Selective Values of Properties of Hydrocarbons and Related Compounds", American Petroleum Institute, Project 44, April 30, 1975, Table 8p (part 2). [i] R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

of β-pinene may be explained by a poor overlap of the allylic C–H bond with the empty p orbital in the corresponding ene transition state,[16-18] a consequence of the rigid bicyclic structure of this olefin. Furthermore, the observed large negative entropy of activation can be regarded as additional evidence for the well organized ene-type transition state.[16] While the transition state for the formation of the allylic sulfinic acid in the forward reaction would involve an abstraction of the proton from the secondary carbon atom (eq 4), in the reverse reaction the proton abstraction can take place from the primary (eq 6) or secondary carbon atom[19] (eq 8). That both reactions are indeed taking place and that the transition state for the abstraction of a secondary hydrogen (eq 8) is lower in energy than the one for the abstraction of a primary hydrogen (eq 6) are supported by the following transformations. Reaction of 2,2,6,6-tetradeuteriomethylenecyclohexane with sulfur dioxide at room temperature provided 1,2,6,6-tetradeuterio-1-methylcyclohexene in 3 h. Further reaction (24 h) resulted in statistical distribution of four deuteriums and two hydrogens among the six carbon–hydrogen bonds (eq 10). Finally, relatively fast racemization of p-menth-1-ene ([α] + 82.6°) in sulfur dioxide at room temperature (essentially completed in 4 h) provide additional evidence for the 1,3 rearrangement of the secondary allylic sulfinic acids[19] (eq 9).



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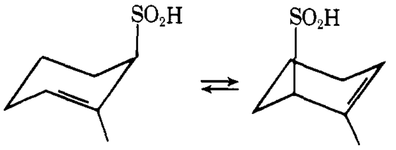

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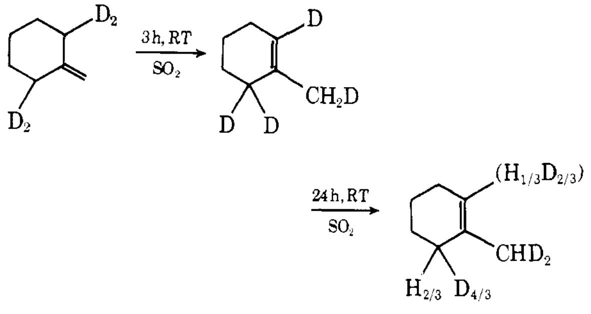

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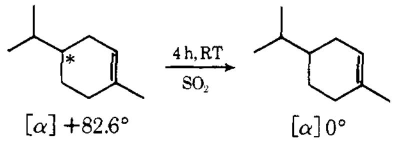

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Evidently, in agreement with the preceeding experiment, the racemization did not involve the alternative higher energy pathway (i.e., eq 7-2 and 2-7).

References and Notes

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(13) It should be noted that none of the sulfur dioxide intermediates in Scheme I was present in significant concentration to be detected by NMR.
(14) Similar migrations have been observed for allylic sulfides, sulfoxides,[15] and sulfones: (a) H. Kwart, N. A. Johnson, T. Eggerichs, and T. J. George, *J. Org. Chem.*, **42**, 172 (1977); (b) H. Kwart and T. C. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976).
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(17) An interesting analogue is found in allylic hydroxylation of olefins by SeO_2: K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972).
(18) P. E. Peterson, R. Brockingham, and M. Dunham, *J. Am. Chem. Soc.*, **97**, 3517 (1975).
(19) The referee pointed out that the direct evidence for the presence of allylic sulfinic acid was not presented and that the racemization of p-menth-1-ene could also be explained if an allylic carbonium ion or free radical were formed in the course of reaction. While we do not have any evidence that the racemization (and hence isomerization) does involve either of the two possibilities, we have no evidence for the involvement of the allylic sulfinic acids either. Consequently, while the experimental facts are explained by the proposed mechanisms, the proposed mechanism should not be construed as a definite explanation of these transformations. Hopefully, further experiments, which will be published in a full paper, will elucidate this point more satisfactorily.

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Catalysis of Superoxide Dismutation by Iron–Ethylenediaminetetraacetic Acid Complexes. Mechanism of the Reaction and Evidence for the Direct Formation of an Iron(III)–Ethylenediaminetetraacetic Acid Peroxo Complex from the Reaction of Superoxide with Iron(II)–Ethylenediaminetetraacetic Acid

Sir:

There are several protein systems which catalyze the dismutation of superoxide ions (reaction 1)

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2 \qquad (1)$$

and these require either Cu, Fe, or Mn ions as cofactors.[1] While the mechanism of the Cu-containing protein has been shown to involve a diffusion controlled cyclic oxidation–reduction process,[2] the Fe- and Mn-containing[3] proteins have not been studied in the same detail and their mechanisms of action remain obscure. Low molecular weight complexes also catalyze superoxide dismutation: thus, a variety of copper(II) complexes,[4] manganese-quinolinol,[5] and iron-ethylenediaminetetraacetic acid (EDTA)[6] have been shown either directly or indirectly to act as catalysts of reaction 1. Since the same metal ions are involved in the protein systems these small complexes may serve as useful models for understanding the protein catalysts. In this communication we present direct confirmation that Fe-EDTA is a catalyst of superoxide dismutation and we proffer a tentative mechanism for this catalysis which involves the formation of a Fe^{III}-EDTA-peroxo complex from the direct reaction of O_2^- with Fe^{II}-EDTA.

The peroxo complex which we observe is the same as that first described by Cheng and Lott[7] in 1956 and subsequently characterized spectrally, thermodynamically, and kinetically by others; in particular, the work of Orhanovic and Wilkins,[8] Walling et al.,[9] and Ringbom et al.[10] can be cited. The color of the peroxo complex derives from an absorption band with a maximum at 520 nm having absorptivity of 530 M^{-1} cm^{-1}.