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Organic Reactions of Sulfur Dioxide. Reactions with Nucleophilic Double Bonds Leading to the Isomerization, Aromatization, Selective Hydrogen–Deuterium Exchange, and Electron-Transfer Processes

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Sulfur dioxide reacts readily with 1-alkoxycyclohexenes to give unstable 1,2,3,4,5a,6,7,8,9,9b-decahydro-4a,9a-dialkoxydibenzothiophene 5,5-dioxides, which, after elimination of alcohol, afford crystalline 1,2,3,4,5a,6,7,8,9-nonahydro-4a-alkoxydibenzothiophene 5,5-dioxides. These tricyclic sulfones undergo sulfur dioxide extrusion to give a 1:1 mixture of 2- and 6-cyclohex-1-enyl-1-alkoxy-1-cyclohexenes. This mixture of the 1,3- and 1,4-dienes reacts quantitatively with sulfur dioxide to give back the starting tricyclic sulfones. The apparent isomerization of the 1,4-diene to 1,3-isomer is an example of a quite general isomerization of a wide variety of olefins in sulfur dioxide. It appears that these reactions involve the allylic sulfinic acids as transient intermediates, which are capable of a very facile 1,3-thiaallylic rearrangement. When the reactions of those olefins that do undergo isomerization in liquid sulfur dioxide are carried out in the presence of deuterium oxide, a highly stereospecific hydrogen–deuterium exchange is observed. For example, optically active 1-methyl-4-isopropylcyclohexene affords 6,6-dideuterio-1-(trideuteriomethyl)-4-isopropylcyclohexene without appreciable racemization. 1,4-Cyclohexadienes react with liquid sulfur dioxide at room temperature to give quantitatively the aromatic hydrocarbon, elemental sulfur, and water. 1,4-Disubstituted 1,3-cyclohexadienes, on the other hand, under similar conditions provide only a small amount of the aromatic hydrocarbon, the main product being a polymeric hydrocarbon(s). Surprisingly, 1-methyl-4-isopropyl-1,3-cyclohexadiene in the presence of oxygen provided 1-methyl-4-isopropylbenzene exclusively. This reaction involves ascaridole as the intermediate, which then reacts with sulfur dioxide to give the aromatic hydrocarbon and sulfuric acid. When the reaction with oxygen is conducted at a low temperature, the ascaridole can be obtained in a quantitative yield. The mechanisms of olefin isomerization, hydrogen–deuterium exchange, and aromatization of cyclohexadienes are discussed.

In the ground-state reactions of sulfur dioxide with organic substrates, the anti-bonding π-orbital localized largely on sulfur[1] plays a dominating role. Interaction of this orbital with the unshared electron pair of various Lewis bases[2] leads to the 1:1 charge-transfer complexes, which are sometimes, as in the case of strongly basic trimethylamine,[3] stable crystalline compounds. With weaker Lewis bases, such as ethers,[4] ketones,[5] etc., the charge-transfer complexes are less stable and cannot be isolated. The intermediates resulting from the reaction of sulfur dioxide with ortho esters[6] and acetals[6] undergo carbon–oxygen bond cleavage to provide alkyl sulfite anions. In the case of ortho esters,[6] the alkyl sulfite anions react with the carbonium ion fragment as an oxygen rather than as a sulfur nucleophile, yielding dialkyl sulfites and esters. Sulfur dioxide also forms charge-transfer complexes with many aromatic compounds[7] and olefins,[8] and the complex with 2,3-dimethyl-2-butene is a first example of such a 1:1 π-complex that exists as a solid compound.[8] In the presence of radical initiators, sulfur dioxide reacts with olefins to give polysulfones;[9] it also reacts with a number of saturated hydrocarbons to give alkane sulfinic acids.[10]

On the other hand, sulfur dioxide readily undergoes suprafacial 1,4-cycloaddition reactions with a variety of conjugated dienes to give 2,5-dihydrothiophene 1,1-dioxides.[11]

It was of interest to establish whether reaction of sulfur dioxide with more nucleophilic carbon–carbon double bonds, such as those of enol ethers and ketenes,[12] would yield either typical charge-transfer π-complexes or the corresponding σ 1,3-dipolar ion intermediates. In this paper we will first describe such a reaction with cyclohexanone enol ethers,[13] which led to the development of a method for a stereospecific isomerization of substituted olefins;[14] then we will describe a method for selective hydrogen/deuterium exchange in substituted olefins[15] and the aromatization of cyclohexadienes with sulfur dioxide,[16] finally, we will discuss sulfur dioxide's role in electron-transfer processes from certain unsaturated systems to molecular oxygen.[16]

Results and Discussion

Reaction of Sulfur Dioxide with Cyclohexanone Enol Ethers. A New 1,3-Dipolar Cycloaddition Reaction. In the case of internally stabilized 1,3-dipolar ions, the cycloadditions are symmetry-allowed, concerted, suprafacial ($\pi 4s + \pi 2s$) processes.[17] In the 1,3-dipolar ion

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(1) For the discussion and description of sulfur dioxide's electronic orbitals, see Walsh, A. D. *J. Chem. Soc.* **1953**, 2266, and references therein.

(2) See, for example: Hoffman, K. R.; WonderWerf, C. A. *J. Am. Chem. Soc.* **1946**, *68*, 997. Bright, J. R.; Fernelius, W. C. *Ibid.* **1943**, *65*, 637.

(3) Grundnes, J.; Christian, S. D. *J. Am. Chem. Soc.* **1968**, *90*, 2239. Van Der Helm, D.; Childs, J. D.; Christian, S. D. *Chem. Commun.* **1969**, 887.

(4) Baume, G. *C. R. Hebd. Seances Acad. Sci.* **1914**, *152*, 1322. *J. Chim. Phys.* **1914**, *12*, 215.

(5) Bellucci, I.; Grassi, L. *Gazz. Chim. Ital.* **1914**, *44*, 559.

(6) Rogić, M. M.; Klein, K. P.; Balquist, J. M.; Oxenrider, B. C. *J. Org. Chem.* **1976**, *41*, 482.

(7) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 4169. Smith, B. C.; Smith, G. H. *J. Am. Chem. Soc.* **1965**, 5514.

(8) Booth, D.; Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1959**, *55*, 1293. Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1950**, *46*, 382.

(9) Dainton, F. S.; Ivin, K. J. *Proc. R. Soc. London, Ser. A* **1952**, *A212*, *96*, 207. Marvel, C. S.; Audrieth. L. E.; Sharkey, W. H. *J. Am. Chem. Soc.* **1942**, *64*, 1229. Marvel, C. S.; Sharkey, W. H. *Ibid.* **1939**, *61*, 1603. Marvel, C. S.; Glavis, F. J. *Ibid.* **1938**, *60*, 2622.

(10) Dainton, F. S.; Ivin, K. J. *Trans. Faraday Soc.* **1950**, *46*, 374, 383. Cundall, R. B.; Palmer, F. F. *Ibid.* **1960**, *56*, 1211. Bjellquist, B. *Acta Chim. Scand.* **1973**, *27*, 3180.

(11) Turk, S. D.; Cobb, R. L. "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; p 13, and references therein. Isaacs, N. S.; Laila, A. A. R. *Tetrahedron Lett.* **1976**, 715. Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. Grummitt, O.; Eudrey, A. L. *Ibid.* **1960**, *82*, 3614.

(12) Tempesti, E.; Giuffre, Z.; Fornaroli, M.; Airoldi, G. *Chem. Ind. (London)* **1973**, 183. Bohen, J. M.; Joullié, M. M. *J. Org. Chem.* **1973**, *38*, 2652. Lysenko, Z.; Joullié, M. M. *Ibid.* **1976**, *41*, 3925.

(13) For the preliminary communication, see Rogić, M. M.; Vitrone, J. *J. Am. Chem. Soc.* **1972**, *94*, 8642.

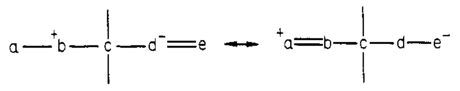
(14) Rogić, M. M.; Masilamani, D. *J. Am. Chem. Soc.* **1977**, *99*, 5219.

(15) Masilamani, D.; Rogić, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 4634.

(16) Masilamani, D.; Rogić, M. M. *Tetrahedron Let.* **1978**, 3785.

0022-3263/83/1948-4918$01.50/0

I, in which c represents an sp^3-hybridized carbon atom, the



$$a-\overset{+}{b}-\underset{|}{\overset{|}{c}}-d^-{=}e \longleftrightarrow \overset{+}{a}{=}b-\underset{|}{\overset{|}{c}}-d-e^-$$

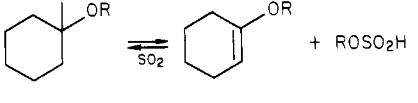
I

internal stabilization of the charges in ^+b–c(d^-) is not possible,[18] but the necessary stabilization could be achieved if the charges could be delocalized over the substituents a and e. Contrary to a generally recognized contention that it is meaningless to assign an electrophilic and nucleophilic end to an internally stabilized 1,3-dipole,[19] dipolar ions such as I possess nucleophilic and electrophilic ends; consequently, they should react with appropriate dipolarophiles with predictable orientation.

A 60-MHz NMR spectrum of a solution of 1-methoxycyclohexene (**1a**) in an excess of sulfur dioxide taken immediately after the mixing showed that the vinylic proton at C_2 was absent. The isolated oily product 1,2,3,4,5a,6,7,8,9,9b-decahydro-4a,9a-dimethoxydibenzothiophene 5,5-dioxide (**3a**) had essentially the same NMR spectrum as the original reaction mixture. After **3a** was stirred in pentane overnight at 0 °C, white crystals of 1,2,3,4,5a,6,7,8,9-nonahydro-4a-methoxydibenzothiophene 5,5-dioxide (**4a**), mp 72–73 °C, separated out. Under similar conditions, 1-ethoxycyclohexene (**1b**) gave **4b**, mp 63–64 °C. Both solids on standing at room temperature overnight decompose to give a slightly colored liquid and sulfur dioxide. In the case of ethoxy derivative **4b**, mild heating under reduced pressure, followed by distillation of the resulting liquid, gave 1:1 mixture of 2- and 6-cyclohex-1-enyl-1-ethoxy-1-cyclohexenes (**5b** and **6b**).[20] Addition of this mixture to an excess of sulfur dioxide at −10 °C produced a colored solution whose NMR spectrum was identical with the spectrum of **4b**. Evaporation of sulfur dioxide gave a 95% yield of **4b**, mp 63–64 °C. Similarly, a 1:1 mixture of **5a** and **6a**, obtained from **4a**, reacted with sulfur dioxide to give back **4a**.

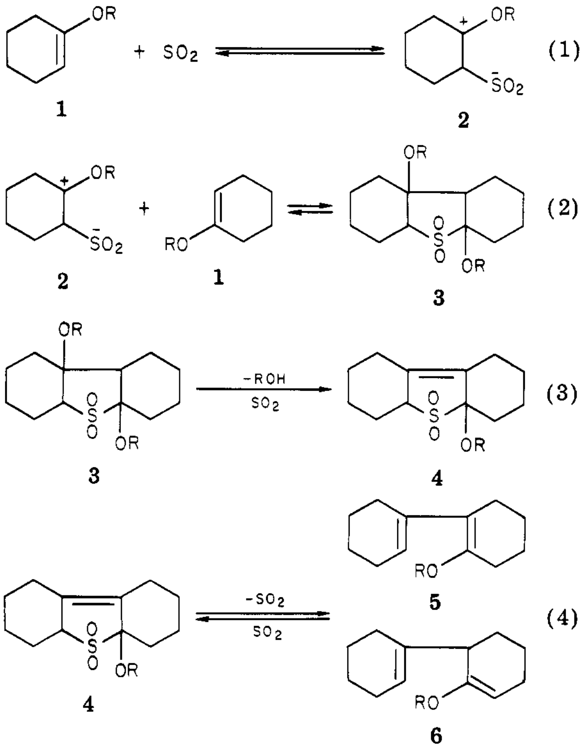
These transformations suggest that reaction of sulfur dioxide with enol ethers **1a** and **1b** does produce a 1,3-dipolar ion intermediate (**2**), whose properties were, indeed, as expected for the 1,3-dipolar ion intermediate of the type I above (Scheme I). Reaction of this intermediate with the second molecule of the enol ether as a dipolarophile gives **3** (eq 2). The elimination of alcohol from **3** provides the final product 4 (eq 3).

Additional support for the involvement of the 1,3-dipolar ion in the above reactions comes from the following observations. The 60-Mz NMR spectra of solutions of either a 1:1 mixture of 1-ethoxycyclohexene and ethanol or cyclohexanone diethyl acetal in sulfur dioxide were the same and showed the presence of a "free" hydroxyl proton at δ 2.73 (1 H). At 0 °C, this proton appeared at δ 3.15 and integrated for only 0.4 H. Clearly, sulfur dioxide cleaves ethanol from the diethyl acetal (eq 5). Since in both cases



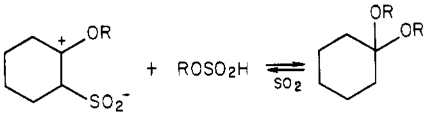
(5)

Scheme I[a]



[a] a = R = Me; b = R = Et.

no signal for the vinyl proton was observed, it would appear that the generated enol ether reacts with sulfur dioxide to form the 1,3-dipolar ion **2** (eq 1), which is, thus, in equilibrium with the acetal (eq 6). Although the charges



(6)

in **2** are separated by an sp^3-hybridized carbon, the necessary stabilization is apparently achieved efficiently through appropriate delocalization of charges over the oxygen atoms attached to positively charged carbon and negative sulfur, as suggested above.

Both isomeric 4-alkoxy-1,3- and -1,4-dienes **5** and **6** react with sulfur dioxide to give the same product 4 (eq 4). This suggests that under the reaction conditions the 1,4-isomer **6** isomerizes first to the 1,3-diene (vide infra), which then undergoes a cycloaddition reaction with sulfur dioxide in the usual manner to give 4 (eq 4). Since it has been shown that sulfur dioxide/1,3-diene adducts lose sulfur dioxide in a concerted suprafacial mode,[21] it seems logical that the cycloaddition reaction itself is also a concerted suprafacial process. On this basis one would assume that in 4, the hydrogen and alkoxy group α to the sulfone group are cis with respect to each other. Since the same product **4** is also obtained by the reaction with enol ethers (eq 1–3), formation of the precursor **3**, albeit as a relatively unstable product, must also be highly stereospecific. However, since the flow of four π electrons between the charges, which is possible in "regular" 1,3-dipoles of the heteroallyl type, is not possible in **2**, the reaction of **2** with the enol ether (eq 2) obviously cannot be a symmetry-allowed, concerted, suprafacial (π4s + π2s) process. The observed stereospecificity may simply reflect the favored stereochemical arrangement in the transition state leading to **3**.

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(17) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. Eckell, A.; Huisgen, R.; Sustmann, R.; Wellbillich, G.; Grashey, D.; Spindler, E. *Chem. Ber.* **1967**, *100*, 2192, 2212.

(18) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. *Ibid.* **1968**, *7*, 321.

(19) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291.

(20) The same mixture of 3-alkoxy-1,3- and -1,4-dienes was also obtained by slow distillation of the required amount of alcohol from the corresponding 1-alkoxycyclohexene in the presence of a catalytic amount of *p*-toluenesulfonic acid, *followed by neutralization* and distillation.

(21) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. McGregor, S. D.; Lemal, D. M. *Ibid.* **1966**, *88*, 2858.

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

olefin (OL)	isomerized olefin (IOL)	IOL/OL	rel rate[b]	$\Delta H°$, kcal/mol
β-pinene	α-pinene	97/trace[c]	1	−2.4[f]
methylenecyclohexane	1-methylcyclohexene	99/trace	ca. 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)		NR		
2,4,4-trimethyl-2-pentene	2,4,4-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 ca. 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. [c] Accompanied with ca. 3% *p*-methadienes. [d] The equilibrium approached from both sides. [e] Both trans (62%), and cis (13%) olefins were formed. In addition, about 25% of a 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] Reference 22. [i] R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

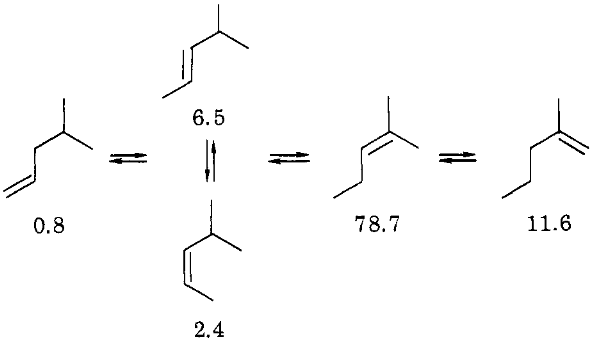
Since it has been reported that sulfur dioxide does not undergo cycloaddition reaction with 1,4-dienes,[11] the above reaction with a 1:1 mixture of 4-alkoxy-1,3- and -1,4-dienes **5** and **6** clearly indicates that the cycloaddition had to be preceded by a facile isomerization of the 1,4-isomer **6** to the 1,3-diene **5**. This particular isomerization and other regiospecific isomerizations of carbon–carbon double bonds of various olefins in liquid sulfur dioxide will be discussed in the following section.

1,3-Dipolar Ions as Intermediates in a Facile Regiospecific Isomerization of Olefins in Liquid Sulfur Dioxide. Neither *cis*- nor *trans*-2-butenes undergo the isomerization reaction in liquid sulfur dioxide under usual reaction conditions. While it is known that many olefins do form π-complexes with sulfur dioxide,[8] it would appear that only more nucleophilic double bonds, such as those in 1-alkoxycyclohexenes[13] or ketenes,[12] could react with sulfur dioxide to give the corresponding dipolar σ-complexes (eq 1). In considering the implied isomerization of **6** to **5** above, it is reasonable to expect that the 4-alkoxy 1,4-diene system of **6** will react with sulfur dioxide to give a dipolar ion intermediate with the positive charge on the C_4 and the negative charge on sulfur attached to C_5 of the diene system. The isomerization of the double bond could then be explained by assuming (a) that the negatively charged SO_2 group at C_5 abstracts the C_3 proton to give the corresponding allylic sulfinic acid and (b) that this generated allylic sulfinic acid loses sulfur dioxide (mechanism unspecified) and provides the isomeric diene **5**, which then undergoes a cycloaddition reaction with sulfur dioxide to give the observed **4**.

In order to test whether the above "mechanism" is more general and to determine whether less nucleophilic double bonds could also undergo similar isomerizations, a behavior of a series of representative olefins in reaction with liquid sulfur dioxide was investigated.

(a) Scope. The following olefins, chosen to represent various types of the double bond, were used: 4-methyl-1-pentene (terminal, monosubstituted), 2-methyl-1-pentene (terminal, disubstituted), *cis*- and *trans*-4-methyl-2-pentenes (internal, disubstituted), and 2-methyl-2-pentene (internal, trisubstituted). The thermochemical data for this set of olefins are available,[22] and their equilibrium concentrations are easily calculated (Scheme II).

Scheme II



The following pairs of olefins were also included in order to evaluate how other structural features of the olefin affect the reaction: β-pinene and α-pinene, methylenecyclohexane and 1-methylcyclohexene, methylenecyclopentane and 1-methylcyclopentene, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, 2,3-diphenyl-1-propene, 2,3-diphenyl-2-propene, and 3-phenyl-2-pentenes.

The extent of isomerization was generally followed by NMR spectroscopy, as illustrated with β-pinene. 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 monitoring the disappearance of the signal at δ 5.19. 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. These results are summarized in 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, 4-methyl-1-pentene was stable in sulfur dioxide in the dark but in the presence of light underwent a known polysulfone formation.[9] 2,3-Diphenyl-1-propene provided a mixture of 62% of *trans*-diphenyl-2-propene, 13% of *cis*-2,3-diphenyl-2-propene, and about 25% of a polymer (vide infra).

The isomerization of β-pinene to α-pinene without the ring opening is remarkable. A sample of (−)-β-pinene of 89.8% optical purity ($[\alpha]^{rt}_D$ −20.3°) gave 97% of (−)-α-pinene of 89.7% optical purity ($[\alpha]^{rt}_D$ 45.9°) and only 3% of dipentene. The same reaction in the presence of a catalytic quantity of anhydrous aluminum chloride was vigorous even at −10 °C and produced only ring-opened products. Clearly, unlike the acid-catalyzed reaction of β-pinene that is known[23] to involve the carbonium ion as intermediate, followed by a rearrangement, isomerization, etc., the reaction of β-pinene with sulfur dioxide either does not proceed through a carbonium ion or, even if it does, the lifetime of the carbonium ion must be very short, since

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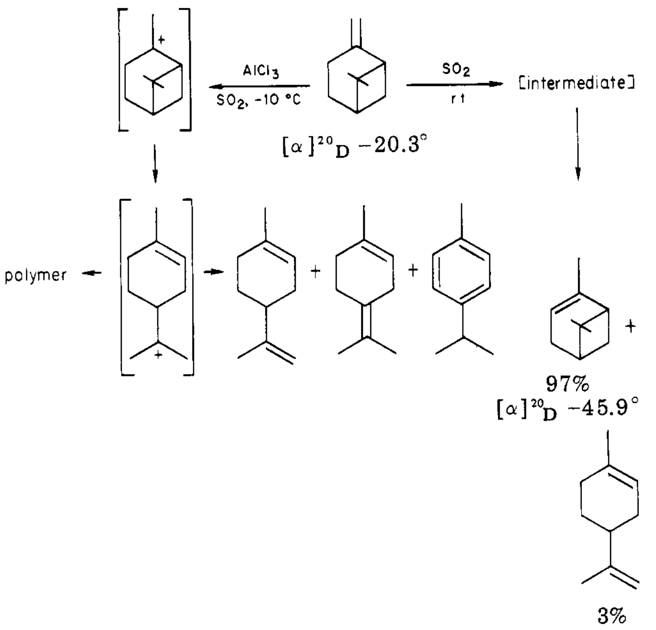
(22) "Selected Values of Properties of Hydrocarbons and Related Compounds"; American Petroleum Institute Project 44, April 20, 1975; Table 8p (Part 2).

(23) Williams, C. M.; Whittaker, D. *J. Chem. Soc. B* 1971, 668.

Scheme III



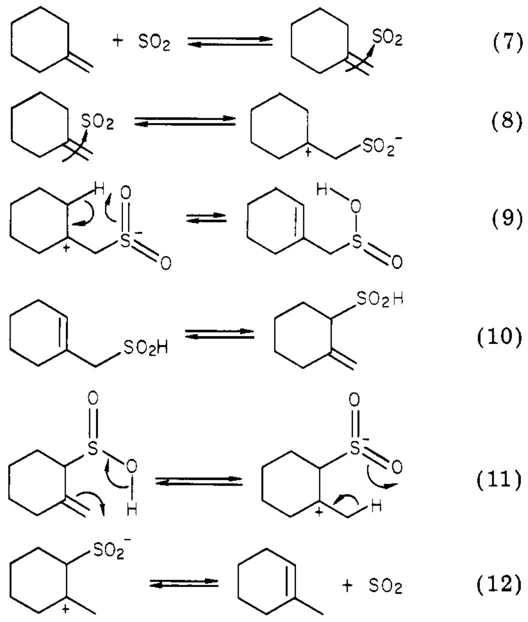
the typical reaction products accompanying the carbonium ion were virtually absent (Scheme III).

A kinetic experiment indicated that the isomerization reaction was first order in β-pinene and first order in sulfur dioxide. The pseudo-first-order rate constant for a 1 M solution of β-pinene in liquid sulfur dioxide was $3.0 \pm 0.17 \times 10^{-5}$ min^{-1}. Interestingly, the rate of isomerization at 60 °C increased only by a factor of ~5.

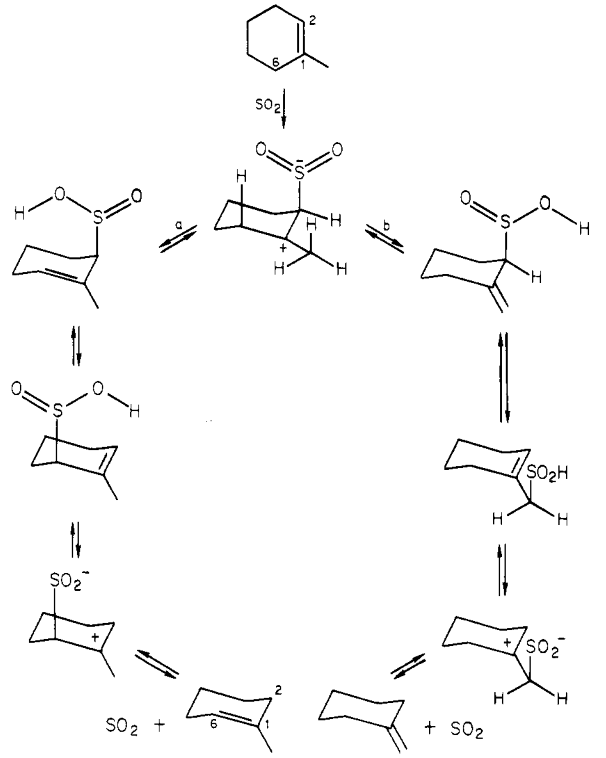
Inspection of the data in Table I reveals that only olefins with double bonds that could give tertiary carbonium ions did undergo the isomerization in sulfur dioxide. While in general the olefins with terminal double bonds (β-pinene, methylenecyclohexane, methylenecyclopentane, etc.) are thermodynamically less stable than their isomers with the internal double bond (Table I), the rates of isomerization of olefin pairs did not parallel these thermodynamic stabilities. Furthermore, even in the case of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene, in which the thermodynamic stability is reversed, the isomerization in sulfur dioxide remains a thermodynamic process.

In the following section we will briefly outline a possible mechanism of this isomerization reaction.

Scheme IV



Scheme V



(b) Possible Mechanistic Pathways for the Regiospecific Isomerization of Olefins in Sulfur Dioxide. While sulfur dioxide forms π-complexes with many olefins, it appears that the corresponding 1,3-dipolar σ-complexes (albeit short lived)[24] could be formed only if the positive charge in the σ-complex could develop on a tertiary carbon atom (e.g., with methylenecyclohexane, Scheme IV). 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 a considerable negative entropy of activation suggests geometrically constrained arrangement of the olefin and sulfur dioxide in the transition state. For these reasons, it is plausible to assume that the rate-determining step for the overall transformation is the abstraction of a proton from the secondary carbon by the negatively charged SO$_2$ group attached to the primary carbon atom ("ene-like" transition state)[25-27] (eq 9). Subsequent 1,3-thiaalylic rearrangement of the thus generated allylic sulfinic acid[28,29] (eq 10), followed by intramolecular protonation of the double bond (eq 11), and reversible dissociation of sulfur dioxide (eq 12) would account for the particular observations in these isomerizations. For example, the extremely slow isomer-

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[24] It should be noted that none of the sulfur dioxide intermediates in Scheme IV was present in significant concentration to be detected by NMR.

[25] Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

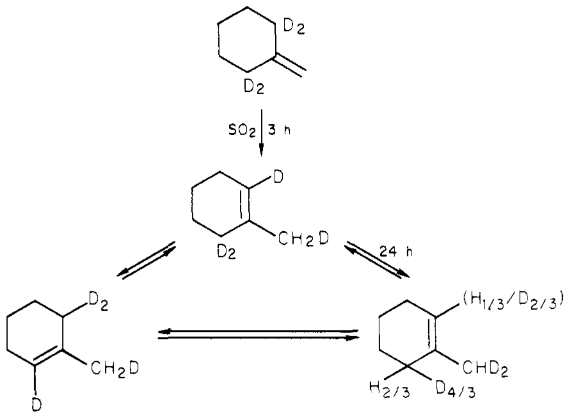
[26] An interesting analogue is found in allylic hydroxylation of olefins by SeO$_2$: Sharpless K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154.

[27] Peterson, P. E.; Brockingham, R.; Dunham, M. *J. Am. Chem. Soc.* **1975**, *97*, 3517.

[28] Similar migrations were observed for allylic sulfides, sulfoxides,[29] and sulfones: Kwart, H.; Johnson, N. A.; Eggerichs, T.; George, T. J. *J. Org. Chem.* **1977**, *42*, 172. Kwart, H.; Stanulonis, T. C. *J. Am. Chem. Soc.* **1976**, *98*, 4009.

[29] Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

Scheme VI

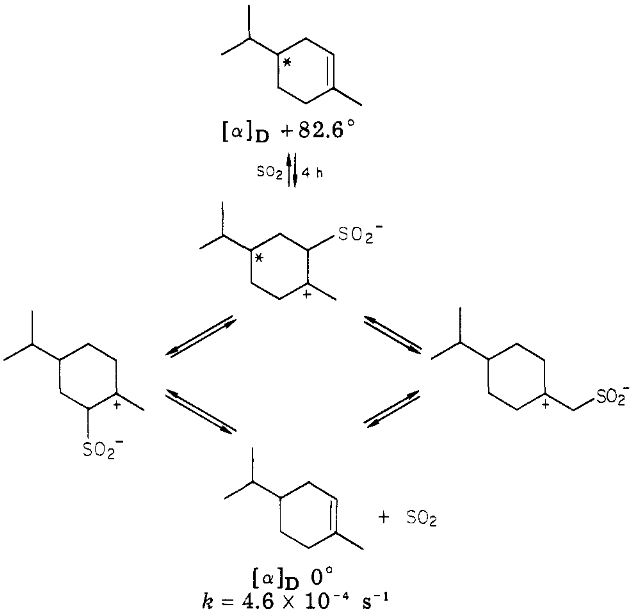


ization of β-pinene may be explained by a poor overlap of the allylic C–H bond with the empty p orbital in the corresponding ene-like transition state, a consequence of the rigid bicyclic structure of the olefin.

The proton abstraction by the negatively charged SO_2 group in the 1,3-dipolar ion intermediate in the forward reaction (eq 9) would involve a proton(s) on the secondary carbon atom(s); in the reverse reaction (Scheme V), the proton abstraction can take place from the secondary (path a) or from the primary carbon atom (path b). Since the transformations in path a are degenerate, the regenerated olefin should be a 1:1 "mixture" of the equivalent 1,2 and 1,6 double bond "isomers". On the other hand, the transformations in path b should provide the isomer with the exocyclic double bond. However, because of the preponderance of the more stable isomer at equilibrium, the less stable isomer will be present in a rather low concentration whose accurate determination under our conditions may be difficult. In order to show that both of these reaction pathways are indeed taking place, the following transformations were carried out.

A complete isomerization of 2,2,6,6-tetradeuterio-1-methylenecyclohexane to 2,6,6-trideuterio-1-(deuteriomethyl)cyclohexene in liquid sulfur dioxide at room temperature (see Experimental Section) required 3 h. Further reaction, leading to a statistical distribution of four deuteriums and two hydrogens among the six carbon–hydrogen bonds, was completed after 24 h (Scheme VI). This clearly shows that the first reaction step in Scheme VI, which involves the abstraction of the hydrogen (deuterium) from the secondary carbon, is a significantly faster process than the second reaction step, which involves abstraction of the hydrogen (deuterium) from the primary carbon.

Scheme VII



The free energy of activation for the isomerization of methylenecyclohexane into 1-methylcyclohexene, based on the pseudo-first-order rate constant of 5.5×10^{-5} s^{-1} (Table I), is 23.25 kcal/mol. Since 1-methylcyclohexene is more stable than methylenecyclohexane by 2.5 kcal/mol, the free energy of activation of the reverse process (Scheme V, path b) would be 2.5 kcal/mol higher, i.e., 25.75 kcal/mol. The free energy of activation for the isomerization of the 1,2 double bond to the 1,6-position in 1-methylcyclohexene (Scheme V, path a) can be ascertained by measuring the rate of racemization of some optically active derivative of 1-methylcyclohexene. A 1-M solution of (+)-*p*-menthene, $[\alpha]^{rt}$ +82.6°, in liquid sulfur dioxide underwent a complete racemization in about 4 h at room temperature with a pseudo-first-order constant of 4.6×10^{-4} s^{-1}. Since the rate of isomerization is half the racemization rate[30] (Scheme VII), it follows that the free energy of activation for the isomerization of the 1,2 double bond to the 1,6-position in path a, Scheme V, is 22.4 kcal/mol. This is of the same order as the activation energy required for the isomerization of methylenecyclohexane into 1-methylcyclohexene, suggesting that in both processes the rate-determining step may indeed be the abstraction of the hydrogen from the secondary carbon atom as suggested above. The energy profile for the isomerization of methylenecyclohexane is summarized in Figure 1.

It should be emphasized that the values of the free energies of activation in the above transformations are composite values of several individual reaction steps. While the assumption that the abstraction of the hydrogen(s) from the secondary and primary carbon atoms are the respective rate-determining steps of the forward and reverse reactions may be reasonable, no deuterium isotope effects were measured to establish this point with certainty.

It should be noted that none of the sulfur dioxide intermediates in Scheme IV was present in significant concentration to be detected by NMR. In order to establish whether implicated allylic sulfinic acids intermediates are indeed as unstable as the outlined mechanism suggests, a synthesis of a number of representative allylic sulfinic acids was attempted.

(c) Allylic Sulfinic Acids from the Corresponding Magnesium Salts. Treatment of the Grignard reagents (prepared from the respective allylic chlorides) with sulfur dioxide in ether produced the magnesium salts of the corresponding allylic sulfinic acids. These salts were insoluble in organic solvents; IR analysis showed the presence of sulfinate and olefinic functions, and the ^1H NMR

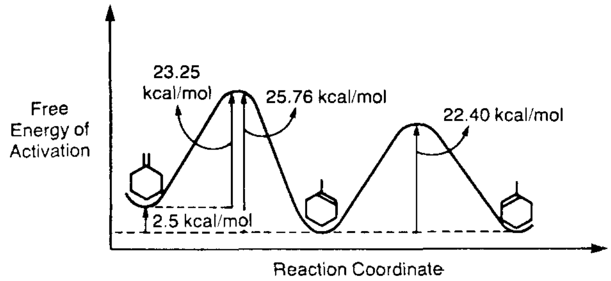


Figure 1. Energy profile for the isomerization of methylenecyclohexane.

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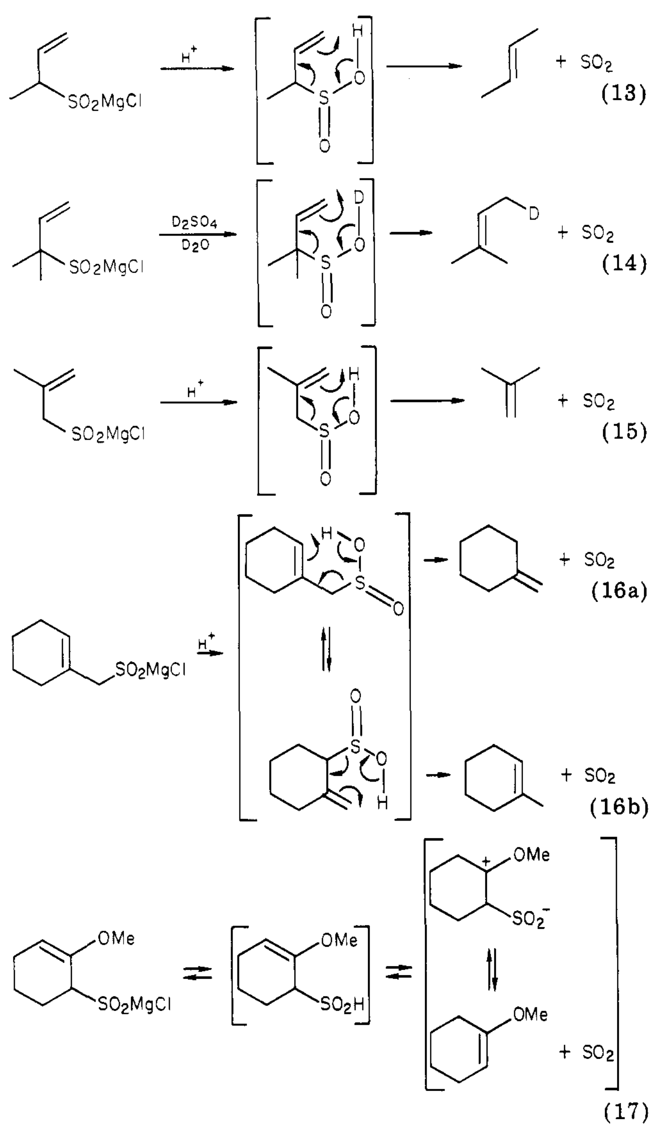
[30] See, for example: Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 34.

Scheme VIII



spectra in D_2O confirmed their structures. Unfortunately, these solutions were not sufficiently stable for recording ^{13}C NMR spectra.

Treatment of the magnesium salts, suspended in an inert solvent, with diluted acids led to the rapid liberation of sulfur dioxide and formation of the olefin. The results are summarized in Scheme VIII. Presumably, the acidification generates the corresponding allylic sulfinic acid, which then loses sulfur dioxide. It is of interest that the extrusion of sulfur dioxide from the 1-methyl- and 1,1-dimethyl-2-propenesulfinic acids (eq 13 and 14), were almost instantaneous. Moreover, the former led exclusively to *trans*-2-butene, indicating that the transition state that would produce the *cis*-2-butene was considerably higher in energy. If the decomposition of allylic sulfinic acids proceeds in a stepwise manner, one would expect that the rotation about the C_1–C_2 bond in the 1,3-dipolar ion intermediate, before sulfur dioxide extrusion, would lead to both the *trans*- and *cis*-2-butenes. Since only *trans*-olefin was formed, either this rotation is slower than the sulfur dioxide extrusion or sulfur dioxide elimination takes place directly from the allylic sulfinic acid through a retro-ene-like transition state, which, again, must be considerably lower in energy than the isomeric one. When the 1,1-dimethyl-2-propenesulfinate was treated with a deuterated acid in D_2O, the isolated 2-methyl-2-butene contained the deuterium exclusively at C_4 (eq 14). In both of these experiments the positive charge on the 1,3-dipolar ion intermediate would have to be on a secondary carbon atom; consequently, it is not unreasonable that, because of the instability of the secondary carbonium ion, the extrusion of sulfur dioxide did occur faster than the rotation about the C_1–C_2 bond.

In the next two examples (eq 15 and 16), the incipient positive charge on the 1,3-dipolar ion intermediate would develop on a tertiary rather than on a secondary carbon atom. This would increase the relative stabilities of the intermediates, and the extrusion of sulfur dioxide should become slower than in the preceding two cases. Indeed, 2-methyl-2-propenesulfinic acid gave off sulfur dioxide rather slowly and produced the expected isobutylene (eq 15). 1-Cyclohexenylmethanesulfinic acid (eq 16) was also proposed as the intermediate in the isomerization of the methylenecyclohexane to 1-methylcyclohexene (Scheme IV, eq 9). The reaction of the magnesium salt with aqueous acid produced both methylenecyclohexane (eq 16a) and 1-methylcyclohexene (eq 16b) in approximately equal amounts. The liberation of sulfur dioxide was slow and continued up to 3 min. Clearly, the result suggests (a) that, because of the increased relative stability of the allylic sulfinic acid, the 1,3-thiaallylic rearrangement of the sulfinic acid group begins to compete with the extrusion of sulfur dioxide and (b) that, because of the greater stability of positive charge in the 1,3-dipolar ion intermediate, the extrusion of sulfur dioxide is indeed significantly slower.[31]

In the reaction of 1-methoxycyclohexene with sulfur dioxide, the intermediate 1,3-dipolar ion **2** (eq 1) was sufficiently stable to undergo a bimolecular reaction with another molecule of the enol ether (eq 2), providing a product that eventually lost sulfur dioxide and gave a 1:1 mixture of the 1,3- and 1,4-diene enol ethers **5** and **6**. Reaction of 2-methoxy-2-cyclohexenesulfinic acid, generated from the corresponding magnesium salt in methylene chloride with dry hydrogen chloride, also provided a 1:1 mixture of **5** and **6** (eq 17). This suggests that the generated allylic sulfinic acid afforded the 1,3-dipolar ion **2**, which even in methylene chloride gave the same final products as in eq 1–4.

These results show that the allylic sulfinic acids, which could give 1,3-dipolar ion intermediates with the positive charge on a secondary carbon, undergo a rapid extrusion of sulfur dioxide, a reaction resembling a retro-ene process (eq 13 and 14). When the developing positive charge on the 1,3-dipolar intermediate is stabilized by a substituent, the relative stabilities of both the 1,3-dipolar ion intermediates and the allylic sulfinic acids are increased, resulting not only in slower elimination of sulfur dioxide but also in competing 1,3-thiaallylic rearrangements (eq 15 and 16). The corresponding 1,3-dipolar ion intermediates in eq 15 and 16 were not sufficiently stable to exist in significant concentration at equilibrium in order that a bimolecular trapping by another molecule of olefin became discernible. In 2,3-diphenyl-1- and -2-propenes, the positive charge generated by the reaction with sulfur dioxide is stabilized by a phenyl group, and, not surprisingly, a bimolecular process leading to significant polymer formation does become important (Table I). However, still more efficient stabilization of the positive charge by the alkoxy group does lead to 1,3-dipolar ion intermediates, which do undergo the 1,3-dipolar cycloaddition reaction with another molecule of enol ether as a dipolarofile, regardless of whether the intermediate was generated by the

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[31] In a control experiment, no isomerization of methylenecyclohexane was observed, even after 30 min.

Table II. Regiospecific Hydrogen–Deuterium Exchange in Representative Olefins in Liquid SO_2/D_2O[a]

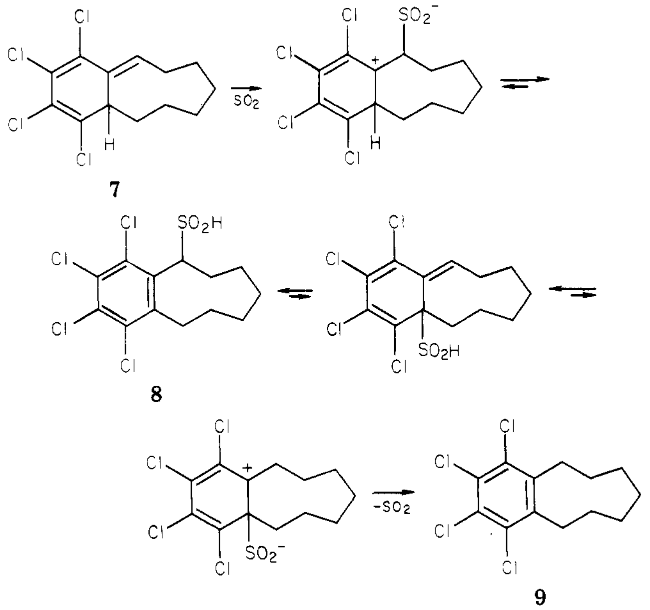
olefin (R)	deuterated olefin	$(R/D_2O/SO_2)$[b]	time,[c] h	% deuteration (expected/obsd)[d]
methylenecyclohexane	2,2,6,6-D_4-R	9:10:60	4	72/70
1-methylcyclohexene	6,6-D_2-1-CD_3-R	0.44:0.72:1.15	121.5	75.7/27
1-methyl-4-isopropylcyclohexene[e]	6,6-D_2-1-CD_3-R[f]	2:4:60	118	84.6/10
2,4,4-trimethyl-1-pentene	3,3-D_2-2-CD_3-R	3.6:4:60	96	72.7/63.3
2,4,4-trimethyl-2-pentene	1,1,1-D_3-CD_3-R	3.6:4:60	144	72.7/50
2-phenylpropene	3,3,3-D_3-R	5:5:60	141	79.8/50
1-phenylcyclohexene	6,6-D_2-R	1.39:1.1:15	168	86.1/20
		1.39:1.1:15	(45 °C, 72)	86.0/30.6
		1.39:1.1:15	(70 °C, 72)	86.0/83.3

[a] Reaction generally carried out in a pressure bottle at room temperature (see typical example procedure). [b] Ratio of the olefin substrate (grams), deuterium oxide (grams), sulfur dioxide (milliliters). [c] If not otherwise indicated, the time for a single equilibration at room temperature. Numbers in parentheses indicate the temperature and time required for a single equilibration at that temperature. [d] Extent of deuteration based on the available D_2O after a single equilibration. [e] [α] 82.6°. [f] [α] 79.5°.

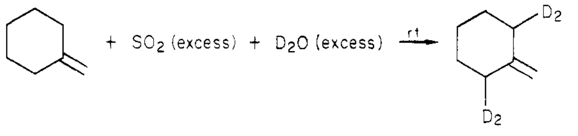
reaction of sulfur dioxide with the nucleophilic double bond (Scheme I) or by the rearrangement of the corresponding allylic sulfinic acid generated from the magnesium salt (eq 17). A similar substituent effect in the decarboxylation of allylic acids to the corresponding olefin and carbon dioxide is well knonw.[32]

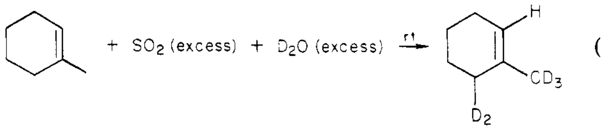
Raash and Smart[33] described a special system, **7**, in which the intermediate allylic sulfinic acid **8** was sufficiently stable to be isolated as such. The reaction of sulfur dioxide with a special methylenecyclohexadiene, **7**, provides an allylic (benzylic) sulfinic acid **8**, in which the reverse formation of the 1,3-dipolar ion intermediate and the corresponding 1,3-thiaallylic rearrangement are suppressed because both processes involve an interim destruction of the aromatic structure. Nevertheless, at higher temperatures, the reaction did provide the isomerized aromatic hydrocarbon **9**, suggesting that under more vigorous conditions, the allylic sulfinic acid did undergo the 1,3-thiaallylic rearrangement and formation of the isomeric 1,3-dipolar ion intermediate, followed by the irreversible extrusion of sulfur dioxide (Scheme IX).

Scheme IX



A Facile Regiospecific Hydrogen–Deuterium Exchange in Olefins. The isomerization of methylenecyclohexane to 1-methylcyclohexene in liquid sulfur dioxide (Scheme IV) is completely suppressed in the presence of water. Surprisingly, the reactions of sulfur dioxide with the double bond leading to the generation of the 1,3-dipolar ion intermediate (eq 7, 8, or 12) and the corresponding allylic sulfinic acid intermediates (eq 9 or 11) are apparently not affected. As a consequence, in the presence of deuterium oxide a very facile exchange of the allylic hydrogens and deuterium takes place (eq 18 and 19).

 (18)

 (19)

For example, a simple stirring of a solution of methylenecyclohexane in sulfur dioxide in the presence of an excess of deuterium oxide (see Experimental Section) provided 2,2,6,6-tetradeuteriomethylenecyclohexane. Mass spectrum and NMR analysis indicated that 87.5% of the expected 92.5% deuterium incorporation occurred (100% yield). Similarly, 1-methylcyclohexene, 1-methyl-4-isopropylcyclohexene, 2,4,4-trimethylpent-1-ene, 2,4,4-trimethylpent-2-ene, α-methylstyrene, and 1-phenylcyclohexene all afforded the corresponding regiospecifically deuterated olefins. Importantly, optically active 1-methyl-4-isopropylcyclohexene underwent hydrogen–deuterium exchange without significant racemization. The results of these experiments are summarized in Table II. It is noteworthy that the reaction times can be reduced significantly by carrying out the exchange at elevated temperatures. In some instances, a very long reaction time led to formation of side products resulting from trapping of the tertiary carbonium ion with water.[34] For example, the deuterium-exchange reaction with methylenecyclohexane was accompanied by formation of a small amount of the tertiary alcohol.

The lack of the isomerization of the double bond in sulfur dioxide containing water suggests that the 1,3-thiaallylic rearrangement of the allylic sulfinic acid intermediates (eq 10, Scheme IV) is being suppressed. Presumably, the generated allylic sulfinic acid under these conditions undergoes a rapid proton exchange with water and exists predominantly in the ionized form (eq 20). However, the observed proton–deuterium exchange at the

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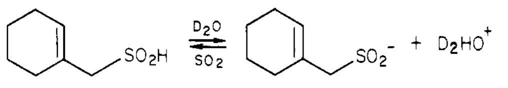
(32) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 8344.

(33) Raasch, M. S.; Smart, B. E. *J. Am. Chem. Soc.* **1979**, *101*, 7733.

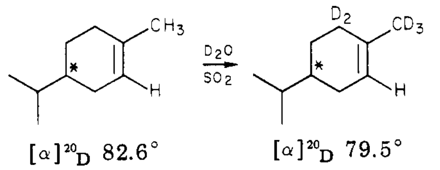
(34) Presumably, by the protonation of the olefin, followed by reaction of the produced carbonium ion with water.



(20)

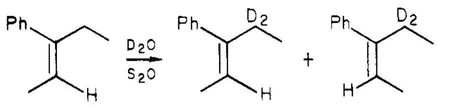
allylic carbons (eq 18 and 19) clearly implies that the sulfur dioxide reaction with the double bond leading to the formation of the 1,3-dipolar intermediate (Scheme IV, eq 7, 8, or 12) and the subsequent formation of allylic sulfinic acids (eq 9 or 11) are proceeding as effectively as in the absence of water. The absence of the 1,3-thiaallylic rearrangement *in the presence of water* is probably due to the fact that the negatively charged sulfinate anion is a less efficient migrating group than a free, un-ionized sulfinic acid.[35]

In accord with the mechanism outlined in Scheme IV, the regioselective hydrogen–deuterium exchange in optically active 1-methyl-4-isopropylcyclohexene ($[\alpha]^{20}{}_D$ 82.6°)



occurs readily, providing 3,3-dideuterio-1-(trideuteriomethyl)-4-isopropylcyclohexene ($[\alpha]^{20}{}_D$ 79.5°) without significant loss of optical purity. It is of interest that those olefins that underwent isomerization readily also underwent a fast hydrogen–deuterium exchange (methylenecyclohexane), and those that were slow in the isomerization were also slow in the deuterium exchange (1-methylcyclohexene).

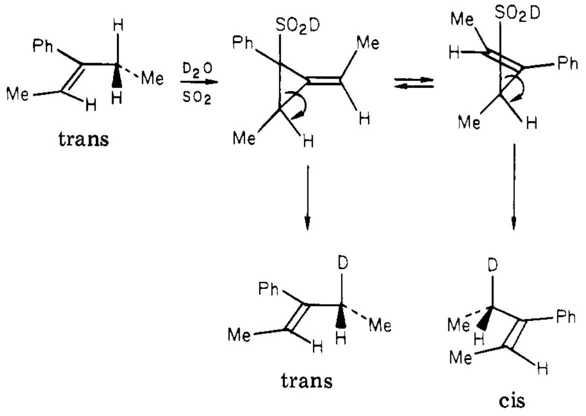
The isomerization of *trans*-3-phenyl-2-pentene in liquid sulfur dioxide affords a 74:26 mixture of the cis and trans isomers (Table I). In principle, this isomerization could result from the rotation about the C_2–C_3 bond either in the dipolar ion intermediate or in the allylic sulfinic acid without involvement of the degenerate 1,3-thiaallylic rearrangement(s). Indeed, in the presence of D_2O, the H/D exchange occurred, as expected, only at the C_4 and was accompanied by the isomerization of the C_2–C_3 double bond (eq 21). When this mixture of the *cis*- and *trans*-



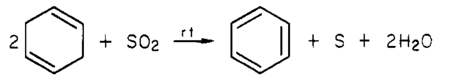
(21)

3-phenyl-4,4-dideuterio-2-pentenes was reequilibrated in liquid sulfur dioxide *without* D_2O, the intramolecular C_2 H–C_4 D exchange (and hence the 1,3-thiaallylic rearrangements) did take place as expected. It is interesting that in a kinetic experiment the H–D exchange was about twice as fast as the trans–cis isomerization of the C_2–C_3 double bond, reflecting the fact that the C_4 H–D exchange occurs from two conformations of the allylic sulfinic acid, only one of which would provide the C_4-deuterated isomerized olefin (Scheme X). This experimental observation implies that the rates of the deuterium transfer from the SO_2D group to the C_4 carbons are comparable to the rate of the C_2–C_3 bond rotation between two conformers.

Scheme X



Aromatization of Cyclohexadienes in Liquid Sulfur Dioxide. (a) 1,4-Cyclohexadienes. A 1 M solution of 1,4-cyclohexadiene in liquid sulfur dioxide undergoes a slow reaction at room temperature (half-life of 2 weeks) to give benzene quantitatively, elemental sulfur, and water (eq 22). No other products were observed. The presence

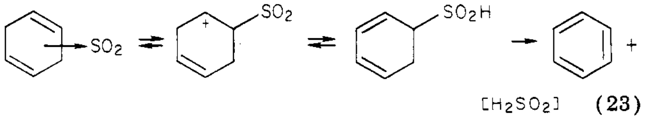


(22)

of an alkyl group on the double bond of 1,4-cyclohexadiene significantly increased the rate of aromatization. Thus, the 1-ethyl-1,4-cyclohexadiene aromatized at room temperature in ca. 24 h, and 1-methyl-4-isopropyl-1,4-cyclohexadiene was completely converted to 1-methyl-4-isopropylbenzene in about 12 h.

Unlike in other reactions of sulfur dioxide with olefins discussed thus far, no hydrogen–deuterium exchange in the presence of D_2O was observed with the 1,4-cyclohexadienes.

The aromatization of 1,4-cyclohexadienes in liquid sulfur dioxide can be rationalized by invoking the mechanism for the isomerization of olefins with sulfur dioxide. Presumably, the reaction involves a reversible attack of sulfur dioxide at the double bond of the 1,4-diene to give the corresponding dipolar ion with the positive charge on a secondary carbon atom (homoallylic carbonium ion), followed by an intramolecular hydrogen abstraction (ene-like reaction) to give the 2,4-cyclohexadienesulfinic acid, and the 1,2-elimination to benzene and sulfoxylic acid,[37] which undergoes further disproportionation to sulfur, sulfur dioxide, and water (eq 23 and 24).



(23)

$$2[H_2SO_2] \longrightarrow S + SO_2 + 2H_2O \quad (24)$$

Presumably, as in the isomerization of olefins, the rate-determining step is formation of the 2,4-cyclohexadienesulfinic acid. The observed faster rates of aro-

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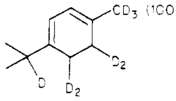
[35] Mechanism(s) of the 1,3-sulfur migrations[36] is not well understood. One possibility may involve a four-membered cyclic dipolar intermediate with the negative charge localized on the sulfur's oxygen and the positive charge on the tertiary carbon atom. The effectiveness with which various allylic sulfur compounds (sulfides, sulfoxides, sulfones, sulfinic acids) undergo the 1,3-rearrangement may depend on the ability of the corresponding sulfur centers to open up a new coordination site. Kwart and co-workers (Kwart, H.; Johnson, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 3441. Kwart, H.; George, T. J. *Ibid.* **1977**, *99*, 5214. Kwart, H.; Johnson, N. A. *J. Org. Chem.* **1977**, *42*, 2855. Kwart, H.; King, K. "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur"; Springer Verlag: New York, 1977. Also ref 28) have discussed the thiaallylic rearrangements as a well-characterized process involving a dipolar trigonal bipyramid intermediate as mentioned above. A referee also made the following suggestion. The finding that water completely shuts off the apparent thiallylic rearrangement occurring in liquid SO_2 suggests yet another possibility, however. Perhaps in that polar, acidic solvent sulfinic acid ionizes slightly to $R\text{-}SO^+$, which one might expect to be capable of very rapid thiaallylic rearrangement.

[36] Brounbridge, P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 1131. ref 29.

[37] Moeller, T. "Inorganic Chemistry"; Wiley: New York, 1952; p 527.

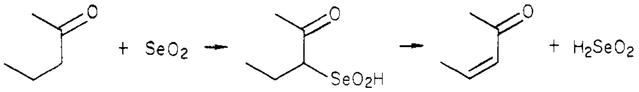
Table III. Reactions of 1-Methyl-4-isopropyl-1,3-cyclohexadiene in the Presence of Sulfur Dioxide[a]

						products yield, %	
no.	solvent	t, °C	time	H_2O[b]	O_2[c]	*p*-cymene	polymer
1	SO_2	25	2 weeks	–	–	5	95
2	SO_2	25	5 days	+	–	NR[d]	
3	SO_2	25	2 days	D_2O	–		
4	SO_2	25	16 h	–	+	15	85
5	SO_2	25	4 days	+	+	90[e]	10
6	$(CH_2Cl_2 + SO_2)$[f]	25	1 h	–	+	95[e]	5
7	$(CH_2Cl_3 + SO_2)$[f]	25	4 h	+	+	90[e]	10
8	$(CH_2Cl_2 + SO_2)$[g]	25	16 h	–	+	96[e]	4
9	$(CH_2Cl_2 + SO_2)$[f]	–30	4 h	–	+	50[e]	ascaridole (50)
10	SO_2	–49	2.25 h	–	+	1	ascaridole (99)
11	SO_2	–70	3.5 h	–	+	2	ascaridole (98)
12	SO_2[g]	–72	4.25 h	–	+	1	ascaridole (99)

[a] For a more detailed procedure, see Experimental Section. [b] A 60:40 (v/v) ratio of SO_2/H_2O was used. [c] Generally, a molar equivalent of oxygen was taken up for each mole of the diene consumed. [d] NR = no reaction. The starting diene was isolated unchanged; however, see next entry. [e] Approximately a molar equivalent of sulfuric acid was also produced for each mole of *p*-cymene formed. [f] Approximately 3% solution of SO_2 in methylene chloride. [g] Reaction carried out protected from light.

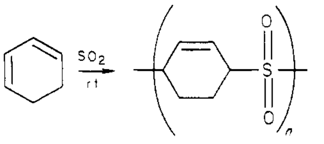
matization of the substituted cyclohexadienes can then be explained by a better stabilization of the developing positive charge in the rate-determining step by the substituent on the tertiary carbon atom. Evidently, once formed, the dienyl sulfinic acid intermediate undergoes a rapid and irreversible 1,2-elimination to benzene accompanied by a large release of free energy due to aromatization.

Clearly, the aromatization of 1,4-cyclohexadienes by sulfur dioxide rests on the ability of sulfur dioxide to accept electrons from the organic substrate. In this process, sulfur becomes reduced from S(IV) to an unstable S(II) state, which rapidly disproportionates to elemental sulfur and sulfur dioxide. This reaction has an analogy in the oxidative dehydrogenation of ketones by selenium dioxide,[38] where, similarly, selenium becomes reduced from the Se(IV) to Se(II) state (eq 25).



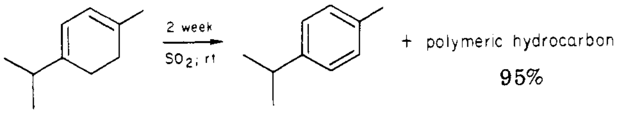
(25)

(b) 1,3-Cyclohexadienes. Unlike the 1,4-isomer(s), the 1,3-cyclohexadiene itself does not undergo the aromatization with sulfur dioxide under comparable conditions to an appreciable extent. Instead, the 1,3-cyclohexadiene reacts with sulfur dioxide to give a high-molecular-weight polysulfone and only about 5% of benzene. The reaction is very fast, and even at –10 °C, addition of the diene to sulfur dioxide leads to an instantaneous precipitation of the white polymer (eq 26).



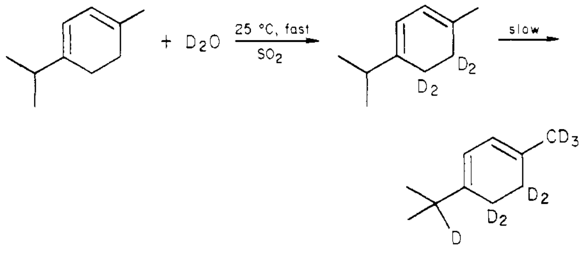
(26)

The presence of alkyl groups at the termini of the 1,3-diene (1-methyl-4-isopropyl-1,3-cyclohexadiene) suppresses formation of the polysulfone but does not lead to aromatization. Instead, a polymeric *hydrocarbon* becomes the principal reaction product, which is accompanied by small amounts (~5%) of the *p*-cymene. This reaction is very slow and at room temperature requires 2 weeks for completion (eq 27, Table III, entry no. 1). When the reaction



(27)

was carried out with added water or D_2O (Table III), both the polymerization and aromatization were effectively suppressed, and the diene could be isolated unchanged. However, as in the case of trisubstituted olefins (vide supra), a rapid hydrogen–deuterium exchange occcurs at all allylic carbon atoms (eq 28). When the reaction in sulfur dioxide was carried out in the absence of water but in the presence of atmospheric oxygen (Table III, entry 4), the starting diene was consumed in 16 h (compare with entry 1), and the amount of *p*-cymene was somewhat increased. Evidently, the presence of oxygen catalyzed the rate of polymerization processes. On the other hand, when both water and oxygen were present (Table III, entry 5), the polymerization reaction was almost suppressed (about 10% of the polymer formed), but the aromatization reaction became almost exclusive (90% *p*-cymene). When methylene chloride as a solvent (containing about 6–7 M excess of sulfur dioxide relative to the diene) was used in the presence of oxygen, a significantly faster formation of *p*-cymene (95%) accompanied with a small amount of the polymer resulted (Table III, entry 6). When the same experiment was repeated in the presence of water, the reaction rate became somewhat slower, and the yield of



(28)

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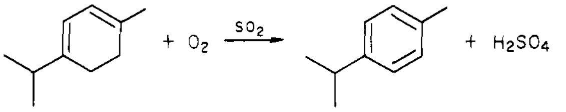
(38) Hori, T.; Singer, S. P.; Shapriess, K. B. *J. Org. Chem.* **1978**, *43*, 1456.

(39) The divalent sulfur intermediate subsequently disproportionates to elemental sulfur and an S(IV) product.

the aromatic hydrocarbon was slightly lower (Table III, entry 7). Furthermore, when the experiment was performed in the absence of water but protected from light (Table III, entry 8), the yields of the *p*-cymene and polymer were about the same as for entry 6 of Table III; however, the reaction rate was significantly slower.

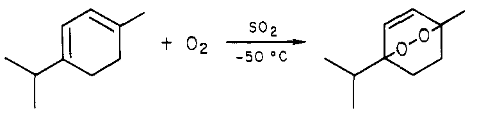
Unlike in the aromatization of 1,4-cyclohexadiene in which sulfur dioxide acted as a dehydrogenating agent and was reduced to a divalent sulfur state (vide supra), in the aromatization experiments with the 1,3-cyclohexadiene in the presence of oxygen (Table III, entries 5–8) no elemental sulfur was formed. Instead, for each molar equivalent of diene and oxygen used in the reaction, 1 molar equiv of sulfuric acid was formed (eq 29).



(29)

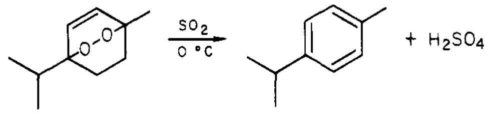
Since the overall reaction is a four-electron reduction of oxygen, two electrons being provided by the substrate and two by the sulfur dioxide, which by themselves do not react with molecular oxygen, it was of interest to learn more about this transformation.

In methylene chloride containing sulfur dioxide at −30 °C (Table III, entry 9, compare with entry 6), the reaction was slower and afforded only 50% of *p*-cymene but also provided 50% of a new product—ascaridole.[40] In neat sulfur dioxide at −49 and −70 °C (eq 30), clean conversion



(30)

of the diene to ascaridole was observed (entriens 10 and 11). In the absence of light the reaction was somewhat slower, but ascaridole was again produced quantitatively (entry 12). Evidently, ascaridol is stable in sulfur dioxide at temperatures below ca −50 °C. At 0 °C, however, an exothermic reaction takes place, and *p*-cymene and a molar equivalent of sulfuric acid are produced in a quantitative yield (eq 31).

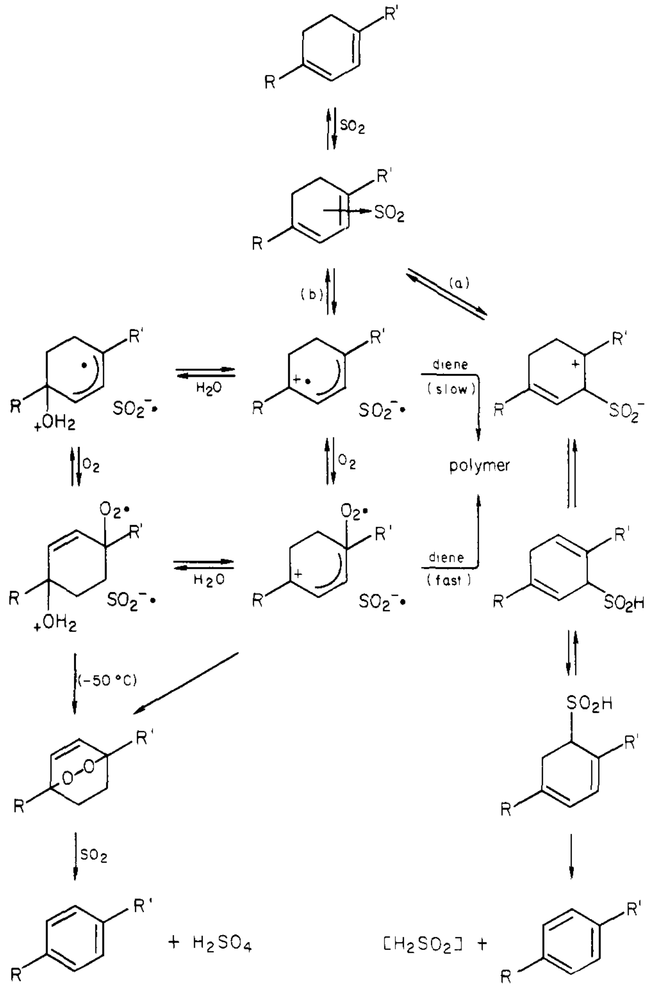


(31)

While it is known that the same diene reacts with singlet oxygen to give ascaridole, formation of this peroxide in the presence of sulfur dioxide does not involve singlet oxygen.[41] It is more likely that the reaction involves cation radicals generated by an electron transfer from the diene to sulfur dioxide, which by a known reaction with oxygen provide the peroxide.[42]

Exceedingly rapid polysulfone formation in the reaction of the 1,3-cyclohexadiene itself with sulfur dioxide suggests a radical polymerization. Probably, a reversible electron transfer to sulfur dioxide, from one of the carbon termini in the initially formed complex between the diene and sulfur dioxide, provides a high-energy diradical intermediate, possibly in equilibrium with the corresponding tight ion radical pair. Intramolecular cyclization to the possible bicyclic sulfone (analogous to "cycloadducts" from larger-ring 1,3-cyclodienes) does not take place because of steric reasons,[11] and instead an intermolecular reaction affords the observed polysulfone polymer.[43] Scheme XI summarizes the transformations of 1,4-disubstituted 1,3-cyclohexadienes (R = *i*-propyl, R′ = methyl). The significantly slower polymerization in this case is very likely a consequence of the presence of the substituents at the terminal carbons of the diene; the attack of sulfur dioxide on these carbon atoms is now less likely, and the subsequent polymerization of the resulting intermediates is accordingly suppressed. The small amount of *p*-cymene that is being formed in this reaction could then be a result of a competing transformation of the initially formed diene–sulfur dioxide complex to give a dipolar ion with a positive charge on a *tertiary* carbon atom (path a). Further

Scheme XI



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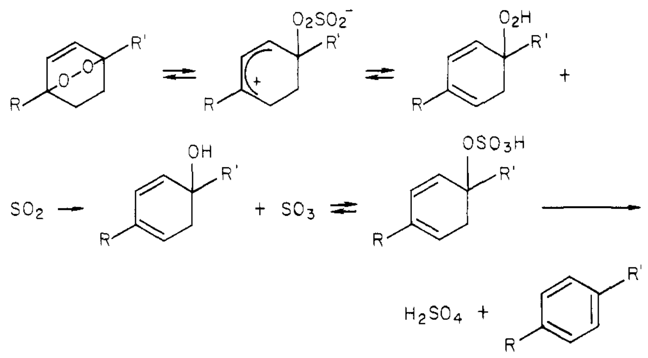
(40) Approximately at the same time, Haynes made an almost identical observation independently: Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121 and 131.

(41) For a more elaborate discussion of the possible mechanisms for similar, apparently "facile spin inversion in oxygen", see: Barton, D. H. R.; Haynes, R. K.; Leclerg, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc. Perkin Trans. 1* **1975**, 2055. Barton, D. H. R.; Haynes, R. K. *Ibid.* **1975**, 2064. Ericksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455.

(42) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248.

(43) Cation radical initiated polymerizations have been studied by Tokura and his co-workers: Tokura, N.; Nagai, T.; Somoyama, Y. *Tetrahedron Lett.* **1965**, 1145. Nagai, T.; Miyazaki, T.; Tokura, N. *Polym. Lett.* **1968**, *6*, 345. Nagai, T.; Miyazaki, T.; Sonoyama, Y.; Tokura, N. *J. Polym. Sci., Part A-1* **1968**, *6*, 3087. Tokura proposed that the sulfur dioxide anion radical transfers an electron to oxygen to form the superoxide ion. One may visualize the trapping of the superoxide ion by the cation radical of the diene to form endoperoxide. However, Swayer has shown conclusively that formation of the superoxide ion from the sulfur dioxide anion radical is not a thermodynamically favored process. The reverse process occurs more readily: Wilshire, J.; Sawyer, D. T. *Acc. Chem. Res.* **1979**, *12*, 105. Stallings, M. D.; Sawyer, D. T. *J. Chem. Soc., Chem. Commun.* **1979**, 340.

Scheme XII

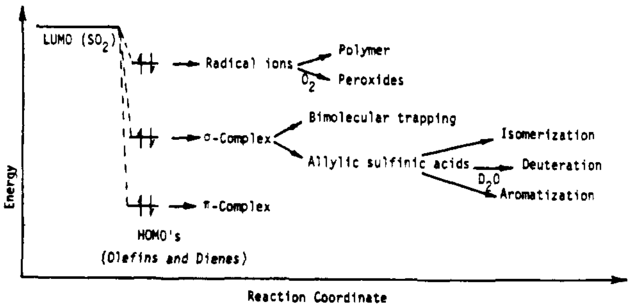


transformation of the dipolar ion, as outlined, could afford *p*-cymene and sulfoxylic acid. In the presence of water, both the polymerization and isomerization of the 1,3- to 1,4-diene (and hence aromatization) were prevented. However, the fact that the hydrogen–deuterium exchange at the allylic carbons (vide supra) were not suppressed shows that the attack of sulfur dioxide at the middle carbon atoms of the diene system (with a subsequent formation of the corresponding allylic sulfinic acids) was still very efficient. Presumably, water reacts with the positive charge in the radical cation, providing hydrated radical that is inefficient as a polymerization initiator. On the other hand, if molecular oxygen is also present, the hydrated radical can react with oxygen to give a peroxy radical and, following a back-donation of electron from sulfur dioxide and an intramolecular nucleophilic replacement of water, the ascaridole itself (path b). However, if water is not present, the rate of polymer formation is increased due to a known ability of oxygen to catalyze cation radical initiated polymerizations.[43] Nevertheless, at low temperatures (<–50 °C), polymerization processes are efficiently suppressed, and the peroxy cation-radical intermediate, after an electron back-donation from sulfur dioxide, undergoes the intramolecular cyclization to give the bicyclic peroxide almost quantitatively.

In methylene chloride solution the polymerization processes at room temperature were significantly slower (compare entries 4 and 6). Presumably, the equilibrium concentration of cation radicals generated by the interaction of the diene with the sulfur dioxide present is not as high as in the neat sulfur dioxide because of inefficient solvation. Since the aromatization reaction in methylene chloride in the absence of light was significantly slower, it appears that light was not essential for the reaction. However, when present, light can catalyze the electron transfer from the diene to sulfur dioxide, thus assuring a faster production of cation radicals and, hence, faster overall reaction with oxygen. A similar effect of light on the rate of a different reaction has been reported previously.[44]

The final step in path b in the scheme is an overall two-electron oxidation of sulfur dioxide by the peroxide, followed by the dehydration of the reduced peroxide products. It is of interest that the dihydroascaridole does not react with sulfur dioxide even at 70 °C. This clearly indicates that the double bond in ascaridole is essential for the subsequent reaction with sulfur dioxide leading to *p*-cymene and sulfuric acid. Unfortunately, the precise mechanism of this particular transformation and the role of the peroxide's double bond are not known. The mechanism outlined in Scheme XII is a reasonable rationale for the observed experiment facts and is based on observations made by a number of workers.[45]

Scheme XIII



Summary

If Walsh's notation is used,[1] the lowest unoccupied orbital on sulfur in sulfur dioxide is an anti-bonding b_1''-π_u orbital, localized mainly on the sulfur atom. It is believed that this orbital is not entirely pπ in character and that it is hybridized to a considerable extent with the available dπ orbital. According to the accepted molecular orbital picture of sulfur dioxide, this orbital occupies a plane bisecting the sulfur dioxide molecule and passing through the sulfur atom and between two oxygens. However, because of the above-mentioned hybridization, the two opposite lobes of this orbital are not perpendicular to the plane of the molecule but instead form an angle of about 105° between each other. In the formation of π-complexes with typical symmetrical olefins, a symmetry allowed, more or less synchronous interaction between occupied bonding orbitals (HOMO's) with the empty anti-bonding orbitals (LUMO's) can take place.[8] The stabilities of the resulting complexes depend on the extent of these allowed interactions. Similar representation of the interaction of sulfur dioxide with the more nucleophilic double bonds is not satisfactory. In the more nucleophilic carbon–carbon double bonds, the electron density is shifted more toward the less substituted carbon of the double bond. Since the lowest unoccupied orbital in sulfur dioxide is predominantly localized on sulfur, it appears likely that the overall extent of the interaction will be controlled not by the orbital symmetry but rather by the charge-transfer interactions between the carbon atom of the double bond carrying the highest electron density and sulfur atom with the lowest electron density.

Generally, the closer the energy between the interacting molecular orbitals is, the better overlap and greater stability (lower energy) of the resulting new bond will be. An increase in nucleophilicity of the olefins raises the energy level in their HOMO's and thus narrows the energy gap relative to sulfur dioxide's LUMO. As the energy gap between interacting molecular orbitals decreases, the intermediates in the reactions of sulfur dioxide with olefins and dienes change from π-complexes to σ-complexes and to radical ions. Depending on the lifetimes of the σ-complexes or their relative stabilities, they can undergo isomerization, aromatization, or bimolecular trapping. Radical ions can initiate polymerizations or enter in reaction with oxygen to form peroxides. This dependence of the reaction pathway on the difference in energies between the inter-

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[44] Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961. Klinger, R. J.; Mochida, K.; Kochi, J. K. *Ibid.* **1979**, *101*, 6626.

[45] Mazzolini, C.; Patron, K.; Moretti, A.; Campane, M. *Ind. Eng. Chem., Prod. Res. Dev.* **1970**, *9*, 504. DeJang, W. A. U.S. Patent 2853532, 1958. Oldham, W. J.; Wirth, M. M. U.S. Patent 2645656, 1953.

[46] (a) Fieser, L. F.; Fieser, M. "Reagents in Organic Chemistry", Wiley: New York; 1967; p 1238. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Melno Park, CA, 1972; p 682.

acting orbitals in the reactions of sulfur dioxide with various types of double bonds is summarized in Scheme XIII.

Despite the fact that sulfur dioxide is readily available and quite inexpensive, its chemistry with organic substrates was for a long time almost completely neglected. Particular solvent properties of sulfur dioxide are well understood; however, except for its use in the industry for hydrocarbon separations, sulfur dioxide is not widely used in a laboratory either as a solvent or as a reagent. It appears that the main reason for this situation is that a majority of practicing chemists are not aware that in spite of its gaseous nature, sulfur dioxide can be handled safely and conveniently in almost any laboratory with extreme ease.

It should be clear that sulfur dioxide is good not only as a solvent for a variety of electrophilic reactions but also that it can react with various organic substrates. In some instances this provides unique methods for selective transformations that either were not previously available or were more difficult to perform.

Experimental Section

The ^{1}H NMR spectra and the infrared spectra were recorded on Varian T-60 and a Perkin-Elmer 128 spectrometers, respectively. Matheson's high-purity sulfur dioxide was dried over molecular sieve prior to use. β-Pinene and *p*-mentha-1,3-diene (α-terpinene or 1-methyl-4-isopropyl-1,3-cyclohexadiene) were from Chemical Samples Co. 2,4,4-Trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene were purchased from Phillips Petroleum Co. Methylenecyclohexane, 1-methylcyclohexene, (+)-*p*-menth-1-ene, *cis*- and *trans*-3-phenyl-2-pentenes, 1,3- and 1,4-cyclohexadienes, α-methylstyrene, crotyl chloride, 3-chloro-2-methylpropene, and all the five isomers of 2-methylpentenes were commercial samples from Aldrich Chemical Co. Methylenecyclopentane, 2-chloro-1-methylenecyclohexane, and 2,3-diphenylpropene were prepared from cyclopentanone, 2-chlorocyclohexanone, and deoxybenzoin, respectively, using the Wittig reagent.[6] 4-Chloro-2-methyl-2-butene was prepared by the addition of hydrogen chloride gas to isoprene by a known procedure.[47] Ascaridole was prepared by a procedure described by Boden.[48] 1-Ethyl-1,4-cyclohexadiene and 1-methyl-4-isopropyl-1,4-cyclohexadiene (γ-terpinene) were prepared, respectively, from ethylbenzene and *p*-cymene by Birch reduction[49] using sodium and liquid ammonia. Dihydroascaridole[50] was prepared by the reduction of ascaridole with diimide.[51]

1,2,3,4,5a,6,7,8,9,9b-Decahydro-4a,9a-dimethoxydibenzothiophene 5,5-Dioxide (3a). A 250-mL reaction flask equipped with a dry ice condenser and a magnetic stirrer was charged with 50 mL of sulfur dioxide. 1-Methoxycyclohexene (**1a**) was added to sulfur dioxide with stirring at −10 °C (reflux). An intense orange color was formed immediately. A small sample of the reaction solution was sealed in an NMR tube, and the NMR spectrum was recorded at room temperature. The vinylic proton was absent; two methoxy signals at δ 3.35 and 3.08 were present. After the solution was stirred for 1 h under reflux, about 100 mL of dry ether was added, and the solution stirred for an additional 30 min. Both solvents were then removed under vacuum, and the NMR spectrum of the resulting oil in carbon tetrachloride was essentially the same as that of the original reaction mixture. The oil was suspended in pentane and stirred at 0 °C overnight. During this time, white crystals of 1,2,3,4,5a,6,7,8,9-nonahydro-4a-methoxydibenzothiophene 5,5-dioxide (**4a**), mp 72–73 °C, separated out (85% yield): NMR (CCl_4) δ 3.35 (s, OCH_3), 3.20–1.50 (br m, 17 H); IR (CCl_4) 1305 and 1120 (SO_2), 1150, 1050 cm^{-1}; mass spectrum (70 eV), *m/e* 192 and 64. Anal. ($C_{13}H_{20}SO_3$) C, H, S.

1,2,3,4,5a,6,7,8,9,9b-Decahydro-4a,9a-diethoxydibenzothiophene 5,5-Dioxide (3b) and 1,2,3,4,5a,6,7,8,9-Nonahydro-4a-ethoxydibenzothiophene 5,5-Dioxide (4b). Under conditions similar to those used for **3a**, 1-ethoxycyclohexene (**1b**) gave **4b**, mp 63–64 °C. Anal. ($C_{14}H_{22}SO_3$), C, H, S.

2- and 6-Cyclohex-1-enyl-1-ethoxy-1-cyclohexenes (5b and 6b). Heating **4b** at 60–70 °C (200–300 mm) produced a yellow liquid, which distilled at 89 °C (3 mm) to give colorless **5b** and **6b**: ^{1}H NMR (CCl_4) δ 5.6, 5.5, and 4.7 (CH=C, 3 H); GLPC analysis suggested an 1:1 mixture of isomers; mass spectrum (70 eV), *m/e*, 206. Anal. ($C_{14}H_{22}O$) C, H.

Acid-catalyzed hydrolysis of a mixture of **5b** and **6b** afforded the known 2-cyclohex-1-enylcyclohexanone.

Similarly, heating **4a** provided a ~1:1 mixture of analogous **5a** and **6a**.

Reaction of Cyclohex-1-enyl-1-alkoxy-1-cyclohexenes (5a and 6a or 5b and 6b) with Sulfur Dioxide. Addition of either of the two diene mixtures to liquid sulfur dioxide, followed by a workup procedure similar to the one described above, afforded either **4a** or **4b** almost quantitatively.

6-Chloro-1-methoxycyclohexene. 2-Chlorocyclohexanone (53 g, 0.4 mol) was dissolved in 32 g (1 mol) of anhydrous methanol. Trimethylorthoformate (50.8 g, 0.48 mol) was added and stirred under nitrogen at 18 °C. Four drops of concentrated sulfuric acid were added to initiate the reaction. The temperature rose to 28 °C in 30 min. Stirring was continued overnight at room temperature. Low-boiling liquids (methanol, methyl formate, and trimethyl orthoformate) were removed under vacuum. The residue was distilled [67–70 °C (5 mm)]. Sixty-one grams of the ketal (1,1-dimethoxy-2-chlorocyclohexane) was obtained: ^{1}H NMR ($CDCl_3$) δ 4.20 (br, 1 H), 3.23 (s, 3 H), 3.20 (s, 3 H), 1.27–2.30 (br, 8 H).

The ketal (17.9 g, 0.1 mol) and a catalytic amount of *p*-toluenesulfonic acid were heated in a RB flask provided with a Dean–Stark condenser and receiver. When the theoretical amount of methanol (3.2 g or 4.1 mL) had collected in the receiver, the reaction was stopped, and the residue was distilled [69–70 °C (4 mm)] to yield 12.5 g (85% yield) of 6-chloro-1-methoxycyclohexene as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 4.81 (t, 1 H), 4.43 (t, 1 H), 3.53 (s, 3 H), 1.24–2.50 (m, 6 H); IR 1650 (C=C) cm^{-1}.

General Procedure for the Isomerization of Olefins in Liquid Sulfur Dioxide. (a) Small Scale. One millimole of the given olefin was weighed in a thick-wall NMR tube. A drop of Me_4Si was added as an internal standard. Sulfur dioxide (1 mL) was condensed into the tube at −78 °C, and the tube was sealed under vacuum. The solution developed a pale yellow color. After warming to room temperature, the isomerization was followed by recording the NMR spectra at different time intervals.

(b) Large Scale. The olefin to be isomerized (0.05 to 0.5 mol) was placed in a 100-mL Fisher pressure bottle provided with a magnetic stirrer, a pressure gauge, a sampling device, and a gas-escape nozzle. The bottle was cooled to −20 °C, and sulfur dioxide (60 mL) was distilled in. The closed bottle was stirred at room temperature, and the progress of the reaction was followed by a periodic analyses. After completion, sulfur dioxide was allowed to escape through the outlet nozzle into a 50% sodium hydroxide solution. The residue was treated with 50 mL of methylene chloride or ether and washed with a saturated sodium bicarbonate solution, dried (Na_2SO_4), and concentrated. The final product was distilled if necessary. The results are summarized in Table I.

Kinetic Measurements. Pseudo-first-order rate constants for the isomerization of olefins were measured by NMR spectroscopy. A 1-M solution of a given olefin in sulfur dioxide was sealed in a thick-wall NMR tube as described earlier. The tube was maintained at the desired temperature in a thermostated bath. The NMR spectra were recorded periodically.

The rate of racemization of (+)-*p*-menth-1-ene was measured by using a Fisher pressure bottle as described earlier. Samples withdrawn at different time intervals were quenched with aqueous sodium hydroxide, and *p*-menth-1-ene was extracted with methylene chloride. After drying, the solution was concentrated and distilled. The specific rotations were measured in methanol.

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(47) Johnes, W. J.; Chorley, H. W. T. *J. Chem. Soc.* **1946**, 832.

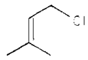
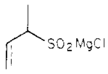
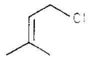
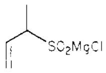
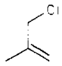
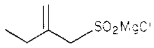
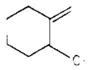
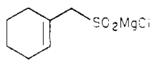
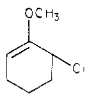
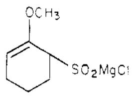
(48) Boden, R. M. *Synthesis* **1974**, 783.

(49) Birch, A. J. *J. Chem. Soc.* **1944**, 430. *Ibid.* **1946**, 583. *Ibid.* **1947**, 102, 1642.

(50) (a) Adam, W.; Eggelety, H. J. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 713. (b) Paget, H. J. *J. Chem. Soc.* **1938**, 829.

(51) Coughlin, D. J.; Solomon, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 655. The diamide was prepared in situ in methanol solution by the addition of acetic acid to a suspension of potassium azodicarboxylate. See also ref 50a.

Table IV. Magnesium Salts of Allylic Sulfinic Acid in D_2O

starting allylic chloride	magnesium salt of allylic sulfinic acid	NMR (D_2O), δ
		6.23–4.93 (m, 3 H, $CH{=}CH_2$), 2.87 (m, 1 H, $={CHC}\mathit{H}CH_3$), 1.23 (d, 3 H, $CHC\mathit{H}_3$)
		6.2–5.63 (m, 1 H, $CH{=}C$), 5.50–5.10 (m, 2 H, $C{=}CH_2$), 1.13 [s, 6 H, $C(CH_3)_2$]
		4.93 (s, 2 H, $C{=}CH_2$), 3.10 (s, 2 H, CH_2), 1.80 (s, 3 H, CH_3)
		5.67 (br, 1 H, $C{=}CH$), 3.00 (s, 2 H, CH_2SO_2)
		5.50 (br, 1 H, $CH{=}C$), 3.40 (s, 3 H, OCH_3)

General Procedure for Regioselective Deuteration of Olefins. On a small scale, deuterations of olefins were carried out in NMR tubes. The olefin to be deuterated (5 mmol) and D_2O (25 mmol) were placed in a thick-wall NMR tube. A drop of Me_4Si was added as an internal standard. Sulfur dioxide (1.5 to 2.0 mL) was condensed into the tube at −20 °C, and the tube was sealed under vacuum at −78 °C. On warming to room temperature, D_2O separated as the top layer, while the olefin dissolved in the sulfur dioxide layer below. In order to mix the two layers, the tube was spun at 20 rpm using a stirrer motor. Deuteration of the olefin was followed by recording the NMR spectra of the lower sulfur dioxide layer at different time intervals.

Large-scale deuterations were carried out in a Fisher pressure bottle (100 mL) equipped with a pressure gauge and a magnetic stirrer. Olefin (0.1 mol) and D_2O (10 g, 0.5 mol) were stirred with 60 mL of liquid sulfur dioxide at room temperature. The pressure ranged from 30 to 35 psi. If the olefin was to be equilibrated more than once, the pressure bottle was cooled to −20 °C and the water was quickly removed by means of a syringe. A fresh quantity of D_2O (10 g) was then added, and the equilibration continued until satisfactory D exchange was attained. For deuterations at higher temperatures, a stainless-steel bomb was used instead of the Fisher bottle. The results are summarized in Table II.

General Procedure for Making Allylic Sulfinic Acids. (a) Preparation of Allylic Grignard Reagents. Magnesium turnings (0.2 mol) were suspended in 40 mL of dry THF in a four-neck flask provided with a mechanical stirrer, condenser, and pressure-equilibrated addition funnel. A small crystal of iodine was added, and the magnesium turnings were stirred under nitrogen. Allylic chloride (0.04 mol) dissolved in 10 mL of dry THF was added dropwise. After commencing, the reaction was exothermic, and the allylic chloride was added at a rate to maintain a steady reflux. Refluxing was continued for another hour. After the solution cooled, the excess magnesium was filtered through glass–wool and weighed. Conversions were usually of the order of 90–95% based on allylic chloride. The filtrate (0.8 M Grignard reagent) was stored in an air-tight bottle under nitrogen.

(b) Preparation of Magnesium Salts of Allylic Sulfinic Acids. Allylic Grignard reagent in THF (40 mL of 0.8-M solution) was transferred into a three-neck flask provided with a magnetic stirrer and a graduated dropping funnel. Sulfur dioxide (1.5 mL) was condensed into the dropping funnel using a dry ice condenser and then added slowly to the stirred Grignard solution maintained at 0 °C. After the solution was stirred for an hour at 0 °C, the solvent was removed on a rotary evaporator, and the residue was kept under vacuum overnight. The resulting yellow solid was stored in a refrigerator in an air-tight bottle. The infrared spectrum (KBr) showed a broad and strong doublet between 900 and 1100 cm^{-1} centered at 950 cm^{-1} for sulfinate ion. The NMR data for the sulfinates in D_2O are summarized in Table IV.

(c) Generation of Allylic Sulfinic Acids and Their Conversion to Olefins. The allylic sulfinic acids were generated from the magnesium salts by suspending them in water, D_2O, or methylene chloride and adding an acid. The allylic sulfinic acids were too unstable to be isolated. Allylic sulfinites with α-substituents were converted to olefins and sulfur dioxide instantaneously, while those with β-substituents reacted slowly. The results are summarized in Scheme VIII.

Aromatization of 1,4-Cyclohexadienes in Liquid Sulfur Dioxide. Sulfur dioxide (60 mL) was condensed at −15 to −20 °C into a 100-mL Fisher bottle provided with a magnetic stirrer and a pressure gauge. Twenty-five millimoles of 1,4-cyclohexadiene, 1-ethyl-1,4-cyclohexadiene, or 1-methyl-4-isopropyl-1,4-cyclohexadiene (γ-terpinene) was added to the bottle and stirred at room temperature (pressure 30–35 psi) for 15 days, 24 h, and 12 h, respectively. Yellow sulfur was deposited on the sides of the bottle.

Sulfur dioxide was allowed to escape into a 50% sodium hydroxide solution, and the residue was dissolved in methylene chloride and filtered to remove insoluble sulfur. The filtrate was dried (Na_2SO_4) and concentrated to yield benzene, ethylbenzene, or *p*-cymene in 85–90% yield.

When the above reactions were carried out in the presence of D_2O, NMR and IR analyses showed no deuterium incorporation either in the products or in the unreacted starting compounds.

Sulfur Dioxide Catalyzed Reactions of *p*-Mentha-1,3-diene at Room Temperature. (a) Sulfur Dioxide as the Solvent. *p*-Mentha-1,3-diene (α-terpenine or 1-methyl-4-isopropyl-1,3-cyclohexadiene; 0.83 g, 0.006 mol) was dissolved in 60 mL of sulfur dioxide in a 100-mL Fisher bottle and stirred at room temperature under the following conditions: (a) in the absence of other reagents; (b) with H_2O or D_2O (4 mL); (c) with oxygen at 50 psi; and (e) with water (4 mL) and oxygen at 50 psi. The results are summarized in Table III.

(b) Methylene Chloride as the Solvent. *p*-Mentha-1,3-diene (0.83 g, 0.006 mol) was dissolved in 60 mL of methylene chloride containing 2.25 g of sulfur dioxide and stirred at room temperature under oxygen from a burette until 0.006 mol (134 mL) of oxygen was absorbed. The reaction was carried out under the following conditions: (a) with no other added reagents under normal laboratory light; (b) with 1 g of water under normal laboratory light; and (c) with no other reagents but in the dark. The results are summarized in Table III.

Sulfur Dioxide Catalyzed Conversion of *p*-Mentha-1,3-diene to Ascaridole. A four-neck, 250-mL flask equipped with a dry ice condenser, magnetic stirrer, and a gas inlet was placed in a low-temperature bath (−30 to −70 °C), and dry sulfur dioxide was then distilled in (60 mL). After purging with oxygen, the system was connected to an oxygen gas burette. *p*-Mentha-1,3-diene (0.83 g, 6 mmol) was introduced with a syringe, and the reaction mixture was stirred until 1 mol equivalent of oxygen (135 mL) was absorbed. The resulting pale yellow solution was poured into 250 mL of pentane and then cooled at −50 °C, and sulfur dioxide was removed on a rotary evaporator at −30 to −40 °C. The pentane solution was then washed with 2 × 100 mL of saturated sodium bicarbonate solution and 2 × 100 mL of water. After drying over sodium sulfate and concentration, the product was analyzed by GLC (OV-1 10% on Chromosorb W 6-ft column) and ^1H NMR. The results are summarized in Table III.

Registry No. **1a**, 931-57-7; **1b**, 1122-84-5; **3a**, 87555-83-7; **3b**, 87555-84-8; **4a**, 39190-58-4; **4b**, 39190-59-5; **5a**, 39190-60-8; **5b**, 39190-62-0; **6a**, 39190-61-9; **6b**, 39487-03-1; $H_3CCH{=}CHCH_2Cl$, 591-97-9; $H_2C{=}CHCH(CH_3)SO_2MgCl$, 87555-86-0; $H_2C{=}CHC(CH_3)_2SO_2MgCl$, 87555-87-1; $H_2C{=}C(CH_3)CH_2SO_2MgCl$, 87555-88-2; $H_3CC(CH_3){=}CHCH_2Cl$, 503-60-6; $H_2C{=}C(CH_3)CH_2Cl$, 563-47-3; sulfur dioxide, 7446-09-5; 6-chloro-1-methoxycyclohexene, 59892-15-8; 2-chlorocyclohexanone, 822-87-7; 1,1-dimethoxy-2-chlorocyclohexane, 65933-44-0; β-pinene, 127-91-3; methylenecyclohexane, 1192-37-6; methylenecyclopentane, 1528-30-9; 2-methyl-1-pentene, 763-29-1; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; 2,4,4-trimethyl-2-pentene, 107-40-4; 2,3-diphenyl-1-propene, 948-97-0; α-pinene, 80-56-8; 1-methylcyclohexene, 591-49-1; 1-methylcyclopentene, 693-89-0; 2-methyl-2-pentene, 625-27-4; 2,4,4-trimethyl-1-pentene, 107-39-1; *trans*-2,3-diphenyl-2-propene, 833-81-8; *cis*-2,3-diphenyl-2-propene, 1017-22-7; (+)-*p*-menth-1-ene, 1195-31-9; 1-methyl-4-isopropylcyclohexene, 5502-88-5; 2-phenylpropene, 98-

83-9; 1-phenylcyclohexene, 771-98-2; 1-methyl-4-isopropyl-1,3-cyclohexadiene, 99-86-5; 1-(methyl-d_3)-4-(1-methylethyl-*1-d*)-1,3-cyclohexadiene-*5,5,6,6*-d_4, 87555-85-9; magnesium chloride (1-cyclohexenyl)methylsulfinate, 87555-89-3; magnesium chloride (2-methoxy-1-cyclohexen-3-yl)sulfinate, 87555-90-6; magnesium, 7439-95-4; 1,4-cyclohexadiene, 628-41-1; 1-ethyl-1,4-cyclohexidiene, 19841-74-8; γ-terpinene, 99-85-4; benzene, 71-43-2; ethylbenzene, 100-41-4; *p*-cymene, 99-87-6; ascaridole, 512-85-6; 1-chloro-2-methylenecyclohexane, 71518-98-4; 3-chloro-2-methoxy-1-cyclohexene, 59892-15-8.

Electrogenerated Bases. 8.[1] Epoxidations by Electrogenerated Superoxide with/without Auxiliary Carbon Acids. α,β-Unsaturated Ketones

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Excellent yields of the epoxides of cyclohexenone (**14**), 4,4-dimethylcyclohexenone (**15**), mesityl oxide (**17**), and benzalacetophenone (**18**) were obtained by treating the enones contained in the cathode chamber of an electrochemical cell with in situ electrogenerated superoxide in the presence of an auxiliary carbon acid such as diphenylacetonitrile (**6**) or, better, diethyl methylmalonate (**1**). Poor or no yields were obtained in the absence of the carbon acid. Products previously prepared by the reaction of electrogenerated superoxide with these carbon acids alone were formed here as coproducts. A rationalization is offered for the effectiveness of this methodology and an explanation of the difference between these results and those that had been reported by others using potassium superoxide/18-crown-6 as an epoxidant.

The development of new methods and new features of epoxidation continues to be a very active area of research.[3] Of the variety of epoxidizing systems that have been employed, those using dioxygen or its derivatives are most relevant to the work reported here: (a) O_2 + Ag ± dopant ± a support;[4a] (b) O_2 and a transition metal ion, often with AIBN;[4b] (c) singlet oxygen produced photochemically in the presence of a sensitizer;[4c] (d) derivatives of H_2O_2 such as HO_2^-, peracids, *t*-BuOO$^-$, and peroxyamidic acids;[5] (e) superoxide[6] with/without an "adjunct reagent"; (f) α-hydroperoxy carbonyl compounds.[7]

We report here a new methodology for epoxidizing olefins. The scope and limitations of this method are to be determined. We have chosen to use first α,β-unsaturated ketones as substrates because the results are novel, are synthetically useful, and may also serve to clarify some of the discrepancies in the literature concerning attempted epoxidations of this subgroup of olefins (vide infra).

Superoxides with R_4N^+ counterions are most conveniently prepared by electrochemical one-electron reduction of oxygen (O_2) in aprotic media containing R_4NX electrolytes. They are readily soluble in organic solvents. *Since only part of the oxygen (O_2) supplied to the cathode compartment of a cell is reduced, the intermediates, if formed by reaction of superoxide with substrates, have the opportunity directly upon their generation to react with excess dissolved oxygen.* This is different from the situation that obtains when KO_2/18-crown-6 is the reagent: the latter makes oxygen available only in semimolar quantity when it is functioning as an electron-transfer agent.[8] The special features of the electrochemical method have led to the development of a number of useful syntheses which involve oxygenation of appropriate[9] carbon acids *under reducing conditions*.[1,10]

The selected examples shown in eq 1–3 illustrate oxygenation of the starting material at the α-position and three types of concomitant consequences for the electron-withdrawing groups (EWGs): (1) the EWGs remain intact (eq 1); (2) they are partially cleaved (displaced) (eq 2); (3) they are totally displaced (eq 3). It has been suggested[10a] that these transformations occur by the following steps: (1) superoxide, as an electrogenerated base (EGB) deprotonates the carbon acid; (2) the resulting carbanion reacts with oxygen (in several electron-transfer steps)[11] to yield the hydroperoxy anion; (3) the latter evolves into the

$$\underset{\mathbf{1}}{\mathrm{MeCH(COOEt)_2}} \xrightarrow[\substack{\mathrm{DMF}\\ \mathrm{Et_4NBr}\\ \mathrm{Hg}\\ -1.0\ \mathrm{V\ vs.\ SCE}}]{\mathrm{O_2}} \underset{\mathbf{2}\ (95\%)}{\mathrm{MeC(OH)(COOEt)_2}} \qquad (1)$$

$$\underset{\mathbf{3}}{\mathrm{PhCH(COOEt)_2}} \xrightarrow[\text{conditions}]{\text{same}} \underset{\mathbf{4}\ (74\%)}{\mathrm{PhCOCOOEt}} + \underset{\mathbf{5}\ (7\%)}{\mathrm{PhC(OH)(COOEt)_2}} \qquad (2)$$

$$\underset{\mathbf{6}}{\mathrm{Ph_2CHCN}} \xrightarrow[\text{conditions}]{\text{same}} \underset{\mathbf{7}\ (95\%)}{\mathrm{Ph_2CO}} + \mathrm{CN^-} \qquad (3)$$

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(1) Paper 7: Sugawara, M.; Baizer, M. M. *Tetrahedron Lett.* **1983**, *24*, 2223.

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(3) (a) A review of the *synthetic* work published between July 1980 and June 1981 has 93 references: Mason T. J. In "Heterocyclic Chemistry"; The Royal Society of Chemistry: London, 1982; Vol. 3, pp 1–47. (b) An excellent discussion of earlier work is given by: House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1972; pp 296–319. (c) After this work was completed, we gained access to Frimer's superb review: Frimer, A. A. "The Organic Chemistry of Superoxide Anion Radical in Superoxide Dismutase"; Oberley, L. W., Ed.; CRC Press: Boca Raton, FL, 1982; Vol. II, pp 83–125.

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(5) Sawaki, Y.; Ozatu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 793 and references therein.

(6) (a) In all but one case, discussed later, it was supplied by KO_2 or, for better solubility in organic media, KO_2/18-crown-6. (b) Valentine, J. S.; Curtis, A. B. *J. Am. Chem. Soc.* **1975**, *97*, 224.

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(8) It is well-known that superoxide is a multipotent reagent.[3c] Depending upon the demands of the substrate, it may serve as a nucleophile, as a base, as an electron-transfer reagent, or as a radical. Of course, additional oxygen could be supplied from an external source.

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