

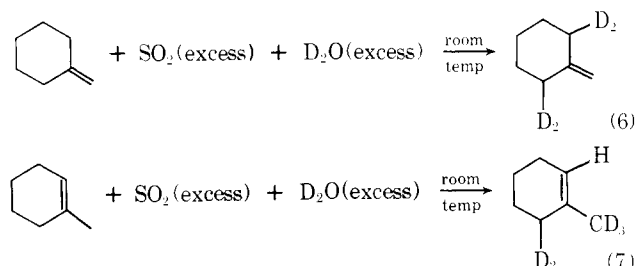
### Organic Reactions of Sulfur Dioxide. 4. A Facile Regiospecific Hydrogen–Deuterium Exchange in Olefins. Consequence of the Intermediacy of Allylic Sulfinic Acids in the Ene Reaction of Sulfur Dioxide with Double Bonds

Sir:

Recently we described a facile and regiospecific isomerization of olefinic double bonds in liquid sulfur dioxide.<sup>1</sup> In the discussion of the possible mechanism we suggested that the isomerization proceeds by a sequence of reversible reactions (Scheme I) that involves formation of a dipolar olefin–sulfur dioxide adduct which in an ene reaction provides the corresponding allylic sulfinic acid as a reactive intermediate. The 1,3 rearrangement of the allylic sulfinic acid, followed by retro-ene reaction and elimination of sulfur dioxide, provides the isomerized olefin.

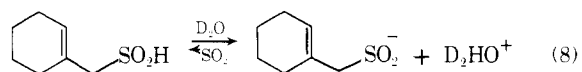
We would like to report now that the isomerization of the double bond, and presumably the rearrangement of the allylic sulfinic acid intermediates (eq 3), is completely suppressed in the presence of water. Surprisingly, the reaction of sulfur dioxide with the double bond and the ene reaction in the resulting dipolar ions (i.e., eq 1 and 2 or eq 5 and 4) are apparently not affected. As a consequence, in the presence of deuterium oxide a very facile exchange of the allylic hydrogens<sup>2</sup> and deuterium takes place (eq 6 and 7).

A typical reaction procedure follows. A 100-mL Fisher pressure bottle, equipped with a pressure gauge and a magnetic stirring bar was charged with 9.0 g (94 mmol) of methylenecyclohexane and 10 g (500 mmol) of deuterium oxide. Sulfur



dioxide (60 mL) was distilled into the precooled mixture and the resulting two-phase system<sup>3</sup> was stirred at room temperature for 4 h (sulfur dioxide generates ~35–45-psi pressure at room temperature). The system was cooled to about –20 °C, and the deuterium oxide layer was removed by a syringe and replaced by a fresh quantity of deuterium oxide. After the mixture was stirred overnight at room temperature, the flask was opened and the excess of sulfur dioxide removed by evaporation. The organic layer was separated and the water layer was washed with a small amount of ether. The organic solutions were combined, dried over sodium sulfate, and distilled to give 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,  $\alpha$ -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 in accordance with the proposed mechanism. The results of these experiments are summarized in Table I. It is noteworthy that the reaction times can be reduced significantly by carrying out the exchange at elevated temperatures (Table I). In some instances a very long reaction time led to formation of side products resulting from trapping of the tertiary carbonium ion with water.<sup>5</sup> 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 rearrangement of the allylic sulfinic acid intermediate (eq 3) is being suppressed. Presumably, the allylic sulfinic acid intermediate under these conditions undergoes a rapid proton exchange with water and exists predominantly in the ionized form (eq 8).



However, the observed proton–deuterium exchange at the allylic carbons (eq 6 and 7) clearly implies that the sulfur

Scheme I

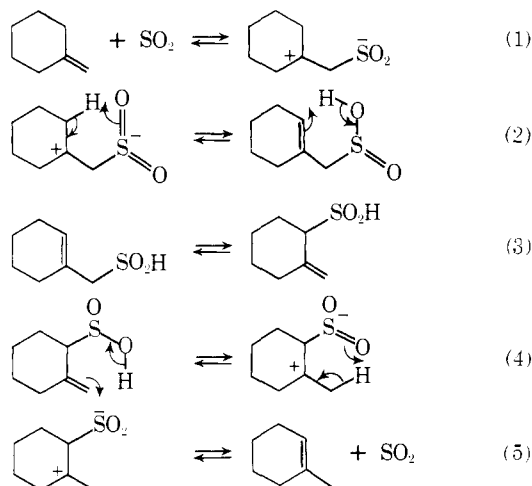


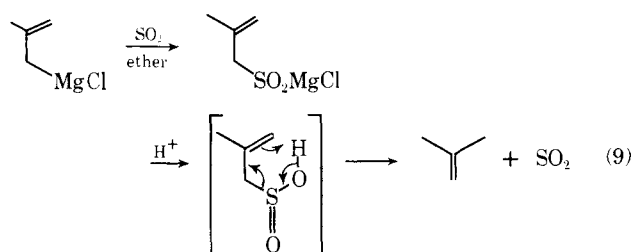
Table I. Regiospecific Hydrogen–Deuterium Exchange in Representative Olefins in Liquid  $\text{SO}_2/\text{D}_2\text{O}^a$

olefin, R	deuterated olefin	R:D <sub>2</sub> O:SO <sub>2</sub> <sup>b</sup>	Time, <sup>c</sup> h	% deuteration, expected/obsd <sup>d</sup>
methylenecyclohexane	2,2,6,6-tetradeuterio-R	9:10:60	4	72/70
1-methylcyclohexene	1',1',1',6,6-pentadeuterio-R	0.44:0.072:1.15	121.5	75.7/27
1-methyl-4-isopropylcyclohexene <sup>e</sup>	1',1',1',6,6-pentadeuterio-R <sup>f</sup>	2:4:60	118	84.6/10
2,4,4-trimethylpent-1-ene	2',2',2',3,3-pentadeuterio-R	3.6:4:60	96	72.7/63.3
2,4,4-trimethylpent-2-ene	1,1,1,2',2',2'-hexadeuterio-R	3.6:4:60	144	72.7/50
2-phenylpropene	3,3,3-trideuterio-R	5:5:60	141	79.8/50
1-phenylcyclohexene	6,6-dideuterio-R	1.39:1.1:15	168	86.1/20
1-phenylcyclohexene	6,6-dideuterio-R	1.39:1.1:15	(72, 45 °C)	86.0/30.6
1-phenylcyclohexene	6,6-dideuterio-R	1.39:1.1:15	(72, 70 °C)	86.0/83.3

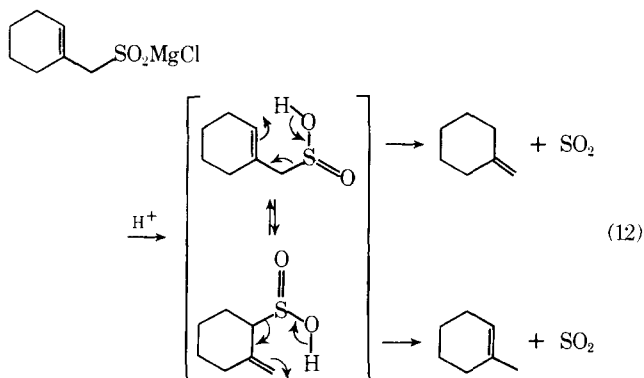
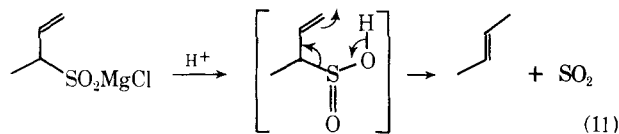
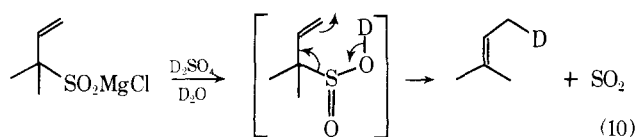
<sup>a</sup> Reaction was generally carried out in a pressure bottle at room temperature (see typical example procedure). <sup>b</sup> Ratio of the olefin substrate (g), deuterium oxide (g), sulfur dioxide (mL). <sup>c</sup> If not otherwise indicated, the time for a single equilibration at room temperature. Numbers in parenthesis indicate the time and temperature required for a single equilibration at that temperature. <sup>d</sup> Extent of deuteration based on the available D<sub>2</sub>O after a single equilibration. <sup>e</sup>  $[\alpha] +82.6^\circ$ . <sup>f</sup>  $[\alpha] +79.5^\circ$ .

dioxide reaction with the double bond (eq 1) and the subsequent ene reaction (eq 2) are proceeding effectively as in the absence of water. The absence of the 1,3 rearrangement *in the presence of water* (eq 8) 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.<sup>6</sup>

We have now obtained evidence that allylic sulfinic acids are indeed very unstable species which in situ undergo smooth decomposition to sulfur dioxide and the olefin, as we suggested earlier.<sup>1</sup> Thus, treatment of the Grignard reagent prepared from 3-chloro-2-methylpropene<sup>8</sup> with liquid sulfur dioxide in ether produced a white precipitate which was filtered, washed with pentane,<sup>9</sup> and characterized by NMR and IR analyses as the magnesium salt of the corresponding allylic sulfinic acid.<sup>10</sup> Addition of dilute hydrochloric acid to an ether suspension of the salt in a reaction flask protected with a dry ice condenser led to the instantaneous liberation of sulfur dioxide and formation of isobutylene which was identified by NMR analysis (eq 9). In addition to the olefin, the ether solution contained a small amount of *tert*-butyl chloride resulting from the addition of hydrogen chloride to isobutylene.



Similarly, magnesium salts of the allylic sulfinic acids, prepared by reaction of sulfur dioxide with the Grignard reagents derived from 1-chloro-3-methylbut-2-ene,<sup>11</sup> *trans*-1-chloro-2-butene,<sup>13</sup> and 2-chloromethylenecyclohexane,<sup>14</sup> on acid hydrolysis gave the olefin and sulfur dioxide. The following observations are noteworthy. The deuterolysis of the magnesium salt of  $\alpha,\alpha$ -dimethylallylsulfinic acid in the presence of deuteriosulfuric acid gave 4-deuterio-2-methylbut-2-ene (eq 10). Hydrolysis of the magnesium salt of  $\alpha$ -meth-



allylsulfinic acid gave predominantly *trans*-2-butene (eq 11). Hydrolysis of the magnesium salt of the allylic sulfinic acid derived from 2-chloromethylenecyclohexane afforded ap-

proximately a 1:1 mixture of 1-methylcyclohexene and methylenecyclohexane and sulfur dioxide (eq 12).

The formation of 1-methylcyclohexene and methylenecyclohexane, in approximately equal amounts in the last reaction, suggests that in this case the generated amounts in the last reaction, suggests that in this case the generated allylic sulfinic acid had a sufficiently long lifetime to undergo the 1,3 rearrangement before the retro-ene reaction occurred.<sup>15,16</sup>

## References and Notes

- (1) M. M. Rogić and D. Masilamani, *J. Am. Chem. Soc.*, **99**, 5219, (1977). For earlier papers in this series, see M. M. Rogić and J. Vitrone, *ibid.*, **94**, 8642 (1972); M. M. Rogić, K. P. Klein, J. M. Balquist, and B. C. Oxenrider, *J. Org. Chem.*, **41**, 482 (1976).
- (2) Note that not all allylic hydrogens exchange. Only allylic hydrogens on the carbon atoms adjacent to the generated tertiary carbonium ion carbon are undergoing the exchange.
- (3) For a summary of general and solvent properties of liquid sulfur dioxide, see P. J. Elving and J. M. Markovitz, *J. Chem. Educ.*, **37**, 75 (1960). Water dissolves in sulfur dioxide, but the extent of its solubility is not very accurately determined. Wickert<sup>4</sup> reported that the equilibrium solubility of water in liquid sulfur dioxide at 22 °C is  $2.3 \pm 0.1$  g/100 g of solvent.
- (4) K. Wickert, *Z. Anorg. Chem.*, **239**, 89 (1938).
- (5) Presumably, by protonation of the olefin, followed by reaction of the generated carbonium ion with water.
- (6) Mechanism of the 1,3-sulfur migrations<sup>7</sup> is not well understood. One possibility may involve a four-membered cyclic dipolar intermediate with the negative charge localized on the sulfur 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. The referee pointed out that H. Kwart and co-workers (H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, **99**, 3441 (1977); H. Kwart and T. J. George, *ibid.*, **99**, 5214 (1977); H. Kwart and N. A. Johnson, *J. Org. Chem.*, **42**, 2855 (1977); H. Kwart and K. King, "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur", Springer Verlag, New York, N.Y., 1977) have discussed the thiaallylic rearrangement as a well-characterized process involving a dipolar trigonal bipyramid intermediate as mentioned above.
- (7) See, for example, (a) H. Kwart, N. A. Johnson, T. Eggericks, and T. J. George, *J. Org. Chem.*, **42**, 172 (1977); (b) H. Kwart and T. C. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976); (c) P. Brownbridge and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1131 (1977); (d) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
- (8) R. B. Wagner, *J. Am. Chem. Soc.*, **71**, 3214 (1949).
- (9) At this point, any hydrocarbon dimers formed during the preparation of the Grignard reagent are removed.
- (10) NMR ( $D_2O$ )  $\delta$  1.81 (s, 3 H), 3.0 (s, 2 H), 4.95 (s, 2 H); IR (KBr) 1640 (C=C), 880, 1020 ( $SO_2^-$ )  $cm^{-1}$ .
- (11) It is known that the Grignard reagent from this chloro olefin reacts with carbon dioxide to give 2,2-dimethyl-3-butenic acid.<sup>12</sup> The reaction with sulfur dioxide, however, provided the magnesium salt of  $\alpha,\alpha$ -dimethylallylsulfinic acid: NMR ( $D_2O$ )  $\delta$  1.1 (s, 6 H), 4.6–6.4 (ABX, 3 H); IR (THF) 1630 (C=C), 880, 1010 ( $SO_2^-$ )  $cm^{-1}$ .
- (12) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **76**, 5403 (1954).
- (13) Reaction of the corresponding Grignard reagent with sulfur dioxide gave the magnesium salt of  $\alpha$ -methylallylsulfinic acid: NMR ( $D_2O$ )  $\delta$  1.22 (d, 3 H), 2.84 (m, 1 H), 4.8–6.2 (ABX, 3 H); IR (THF) 1635 (C=C), 880, 1020 ( $SO_2^-$ )  $cm^{-1}$ .
- (14) Reaction of 2-chloromethylenecyclohexane with magnesium apparently provides the isomerized Grignard reagent with the magnesium on the primary carbon atom and the double bond in the ring. Reaction of this Grignard reagent with carbon dioxide in tetrahydrofuran gave 2-methylenecyclohexanecarboxylic acid quantitatively. On the other hand, reaction with sulfur dioxide provided the magnesium salt of the primary sulfinic acid.
- (15) The hydrolysis of the magnesium salt of this allylic sulfinic acid is not very clean. Several other as yet unidentified by-products are also formed.
- (16) We are thankful to a referee who called our attention to another hydrogen-deuterium exchange published after we submitted our manuscript: T. Horii, S. P. Singer, and K. B. Sharpless, *J. Org. Chem.*, **43**, 1456 (1978).

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## Photochemical Upconversion in the Chlorophyll a Water Splitting Light Reaction: Causative Factors Underlying the Two-Quanta/Electron Requirement in Plant Photosynthesis

Sir:

The minimum quantum requirement in plant photosynthesis is 8 quanta/ $O_2$  molecule evolved or 2 quanta/electron trans-