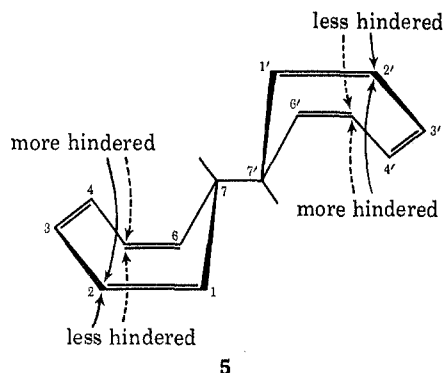


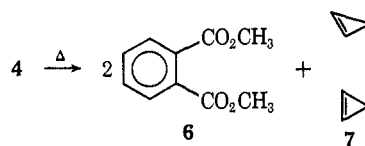
from the top (see 5). It is encouraging to note that this mode of attack also predicts a *trans* orientation of the two types of cyclopropyl hydrogens.



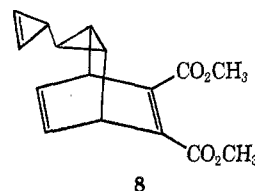
**Pyrolysis of the Adduct 4.**—Cope has demonstrated that cyclobutene may be produced by pyrolysis of the Diels–Alder adduct of 1,3,5-cyclooctatriene and compound 1,<sup>14</sup> and Wiberg<sup>15</sup> has shown that the similar decomposition of compound 2 results in detectable quantities of cyclopropene. Consequently, we felt that pyrolysis of 4 might yield one or more isomers of C<sub>6</sub>H<sub>6</sub>. The *concerted* loss of two molecules of dimethyl phthalate from adduct 4 would produce 3,3'-bicyclopropene which *might* be transformed further into other C<sub>6</sub>H<sub>6</sub> isomers by various intramolecular rearrangements.<sup>16</sup>

(14) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

(15) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).



However, the thermal analysis data are not consistent with such a *concerted* decomposition. Apparently the loss of one molecule of ester 6 produces the reactive cyclopropene derivative 8 which polymerizes before a



second molecule of 6 is lost. This interpretation, which is consistent with the reactivity of cyclopropene observed by Wiberg and Bartley,<sup>15</sup> is supported by the analytical and spectral data for the nonvolatile pyrolysis product and, also, by the further production of ester 6 on pyrolysis of the polymer at a higher temperature.

**Registry No.**—4, 25967-00-4; 5, 25967-01-5; 8, 25967-02-6.

**Acknowledgment.**—We are grateful to Mr. Russell J. Miller for initial nmr measurements.

(16) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *ibid.*, **87**, 5139 (1965). A study of the rearrangement of several polyphenyl derivatives of 7 through the assumed intermediacy of Ladenburg and Dewar benzene structures.

## Stable Carbonium Ions. CV.<sup>1</sup> Protonation of Sulfoxides and Sulfones in Fluorosulfuric Acid–Antimony Pentafluoride–Sulfonyl Chloride Fluoride Solution

GEORGE A. OLAH,\* ALICE T. KU,<sup>2</sup> AND JUDITH A. OLAH

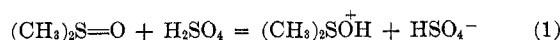
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received April 9, 1970

A series of sulfoxides and sulfones have been studied in HSO<sub>3</sub>F–SbF<sub>5</sub> solution diluted with sulfonyl chloride fluoride. Protonation on sulfur was observed for sulfoxides by nmr spectroscopy. The site of protonation of sulfones is on oxygen. Protonated sulfoxides and sulfones in FSO<sub>3</sub>H–SbF<sub>5</sub>–SO<sub>2</sub>ClF solution are stable up to 65° except protonated benzyl *tert*-butyl sulfone which cleaved to *tert*-butyl cation and phenylmethanesulfinic acid even at a temperature as low as –78°.

The interaction of sulfones and sulfoxides with Lewis acids has been studied by a number of investigations.<sup>3–7</sup> In some cases solid adducts could be obtained.<sup>3,7</sup> Cryoscopic studies of sulfoxides and sulfones in sulfuric acid solution have also been carried out.<sup>8–11</sup> Gillespie<sup>8,10</sup>

showed that aryl sulfoxides are strong bases and aryl sulfones are weak bases in sulfuric acid. However, both cryoscopic and conductometric measurements of Hall and Robinson<sup>11</sup> showed that diphenyl sulfone was a nonelectrolyte in sulfuric acid. These results do not agree with those of Gillespie.<sup>8,10</sup> Alkyl sulfones were found to behave as weak electrolytes in sulfuric acid.<sup>11,12</sup> It was also indicated that dimethyl sulfoxide has a cryoscopic *i* factor of slightly greater than two,<sup>11</sup> in agreement with complete protonation according to eq 1.



\* To whom correspondence should be addressed.

(1) Part CIV: G. A. Olah and P. J. Szilagy, *J. Org. Chem.*, in press.

(2) National Institutes of Health Predoctoral Research Investigator, 1970.

(3) T. Lindquist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959).

(4) F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, **82**, 2986 (1960).

(5) R. G. Laughlin, *J. Org. Chem.*, **25**, 864 (1960).

(6) C. H. Langford and P. O. Langford, *Inorg. Chem.*, **1**, 184 (1962).

(7) R. W. Alder and M. C. Whiting, *J. Chem. Soc.*, 4704 (1964).

(8) R. J. Gillespie, *ibid.*, 2542 (1950).

(9) H. H. Szmant and G. A. Brost, *J. Amer. Chem. Soc.*, **73**, 4175 (1951).

(10) R. J. Gillespie and R. C. Passerin, *J. Chem. Soc.*, 3850 (1956).

(11) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

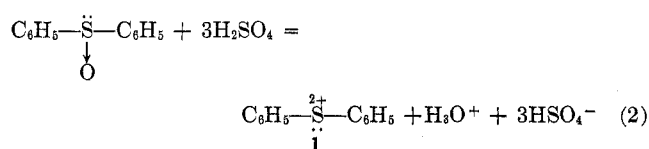
(12) E. M. Arnett and C. F. Douty, *J. Amer. Chem. Soc.*, **86**, 409 (1964).

TABLE I  
 PMR SPECTRAL PARAMETERS<sup>a</sup> OF PARENT AND PROTONATED SULFOXIDES

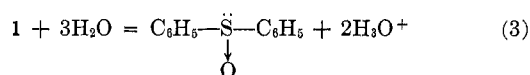
Compd	Registry no.	Temp. °C	Solvent	SH	α-CH <sub>2</sub>	β-CH <sub>2</sub>	γ-CH <sub>2</sub>	CH <sub>3</sub>	Aromatic H
(CH <sub>3</sub> ) <sub>2</sub> S=O	67-68-5	-40	SO <sub>2</sub> ClF					2.66	
(CH <sub>3</sub> ) <sub>2</sub> S <sup>+</sup> =O	26428-06-8	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.83				3.60	
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> S=O	70-29-1	-60	SO <sub>2</sub> ClF		2.97 (q, 7.5)			1.47 (t, 7.5)	
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> S <sup>+</sup> =O	26428-02-4	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.51	3.43 (q, 7.8)			1.53 (t, 7.8)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S=O	4253-91-2	-60	SO <sub>2</sub> ClF		2.61 (t, 7.0)	1.40 (m)		0.80 (t, 7.0)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S <sup>+</sup> =O	26428-07-9	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.49	3.30 (t, 7.0)	1.96 (m)		1.11 (t, 6.0)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S=O	2168-93-6	-20	SO <sub>2</sub> ClF		2.85 (t, 7.5)	1.80 (m)	1.80 (m)	1.11 (t, 6.5)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S <sup>+</sup> =O	26428-08-0	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.53	3.73 (m)	2.13 (m)	2.13 (m)	1.46 (t, 6.5)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S=O	945-51-7	-60	SO <sub>2</sub> ClF						7.53
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S <sup>+</sup> =O	26428-09-1	-80	HF-SbF <sub>5</sub> SO <sub>2</sub> ClF	5.03					8.40- 9.03

<sup>a</sup> Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parentheses following the multiplicities: t = triplet; m = multiplet; q = quartet.

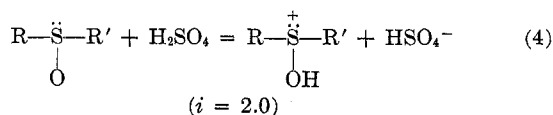
Szmant and Brost<sup>9</sup> postulated that diphenyl sulfoxide ionizes in 100% sulfuric acid according to eq 2. Their



argument was based on their observations that the cryoscopic *i* factor was nearly five and that the original sulfoxide was recovered when the resulting green solution was diluted by water according to eq 3.



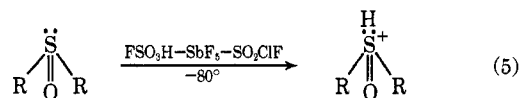
To test the hypothesis of Szmant that the double positively charged ion 1 exists in sulfuric acid solution, Oae<sup>13</sup> and coworkers dissolved diphenyl sulfoxide in 97% sulfuric acid and diluted the solution with an excess of <sup>18</sup>O-enriched water. The original sulfoxide was recovered almost quantitatively but the recovered sulfoxide was found to have no incorporation of excess <sup>18</sup>O, contrary to what one would expect on the basis of Szmant's hypothesis. They extended the cryoscopic study on diphenyl sulfoxide, dimethyl sulfoxide, phenyl methyl sulfoxide, and other similar sulfoxides with 99.5-100% sulfuric acid, and found an *i* factor close to two. They concluded that all the compounds measured ionize according to eq 4.



Nuclear magnetic resonance spectroscopy in highly acidic solvent systems (superacids) offers a good possibility of directly observing protonated heteroorganic compounds. No such studies relating to protonation of sulfoxides and sulfones were so far reported in the literature.

## Results and Discussion

**Sulfoxides.**—In the superacid system, FSO<sub>3</sub>H-SbF<sub>5</sub> ("magic acid") diluted with SO<sub>2</sub>ClF, all the sulfoxides studied were completely protonated. The pmr spectra of protonated sulfoxides in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>ClF solution, recorded at -80°, showed a singlet in the S-H region at δ 5.03-7.10 indicating that sulfoxides are protonated on the sulfur atom (eq 5). These S-H



chemical shifts are in the region observed for that of protonated thiols and sulfides<sup>14</sup> studied previously.

The following sulfoxides were studied: methyl, ethyl, *n*-propyl, *n*-butyl, and phenyl sulfoxide. The chemical shifts and coupling constants of the parent and the protonated sulfoxides studied are summarized in Table I. The proton on the sulfur atom of protonated sulfoxides could be observed only at temperatures below -80°. At higher temperature proton exchange occurred. At -80° all the resonances are broad and

(13) S. Oae, T. Kitao, and Y. Kitaoka, *Chem. Ind. (London)*, 291 (1961).

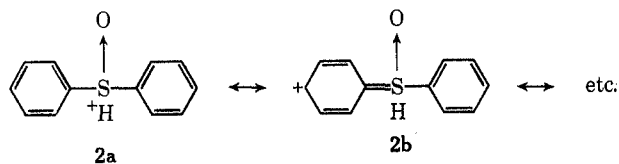
(14) G. A. Olah, D. H. O'Brien, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **89**, 2996 (1967).

the coupling constants were generally evaluated from spectra recorded at  $-20^\circ$ .

The pmr spectrum of protonated **dimethyl sulfoxide** in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  solution, recorded at  $-80^\circ$ , showed the proton on sulfur as a singlet at  $\delta$  6.83 and the methyl singlet at  $\delta$  3.60 which shifted about 1 ppm downfield from that of the parent compound. This S-H resonance, although broad, showed no coupling between the methyl protons. In order to see if dimethyl sulfoxide could be recovered from the protonated species, a quenching of protonated dimethyl sulfoxide in methanol and sodium carbonate was carried out. Indeed, dimethyl sulfoxide was recovered in good yield ( $>85\%$ ).

Protonated **diethyl sulfoxide** in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{-ClF}$  at  $-80^\circ$  showed the proton on the sulfur atom at  $\delta$  6.50 and the ethyl triplet and quartet at  $\delta$  1.90 and 3.75. **Di-*n*-propyl** and **di-*n*-butyl sulfoxide** were also protonated on the sulfur atom.

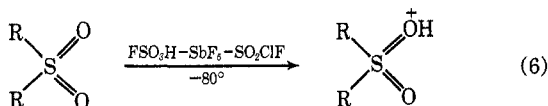
In the case of **diphenyl sulfoxide** in  $\text{FSO}_3\text{-SbF}_5\text{-SO}_2\text{-ClF}$  solution, sulfonation occurred in addition to protonation. However, diphenyl sulfoxide could be protonated in  $\text{HF-SbF}_5$  solution diluted with  $\text{SO}_2\text{ClF}$  without sulfonation. The nmr spectrum of protonated diphenyl sulfoxide in  $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$  solution showed the S-H proton at  $\delta$  5.03 and the phenyl protons at  $\delta$  8.40-9.03, substantially deshielded (about 1.2 ppm) from the parent compound (see Table I). Furthermore, the S-H proton of protonated diphenyl sulfoxide is considerably more shielded than those of protonated alkyl sulfoxides. We believe that this difference is attributed to resonance stabilization of protonated phenyl sulfoxide with contributing structures such as **2a** and **2b**. This also explains the deep green colored solution of protonated diphenyl sulfoxide. Upon quenching of the solution, the sulfoxide is recovered in  $>80\%$  yield. It is, however, possible that some unidentified



decomposition product may contribute to the color of the solution.

In contrast to the observations of Chen and Yan,<sup>15</sup> and Kenney, Walsh, and Davenport,<sup>16</sup> protonated alkyl sulfoxides, investigated in this study in  $\text{FSO}_3\text{H-SbF}_5$  solution diluted with  $\text{SO}_2\text{ClF}$  are very stable. No cleavage reaction occurred even when solutions were heated up to  $+65^\circ$ . Protonated phenyl sulfoxide is stable up to  $-20^\circ$ . At higher temperature the resonances broaden and decrease in intensity. The medium becomes viscous then solidifies to an unidentified dark solid.

**Sulfones.**—All sulfones studied in the extremely strong,  $\text{FSO}_3\text{H-SbF}_5$  acid medium using  $\text{SO}_2\text{ClF}$  as diluent were protonated (eq 6).



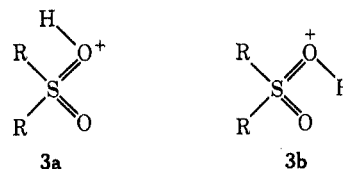
(15) C. T. Chen and S. J. Yan, *Tetrahedron Lett.*, 3855 (1969).

(16) W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Amer. Chem. Soc.*, **83**, 4019 (1961).

No proton on oxygen (or on sulfur) could be observed in the  $\text{FSO}_3\text{H-SbF}_5$  solution but it is assumed that protonation on oxygen occurred. As in the case of protonated sulfonic acids,<sup>17</sup> the  $\text{S}=\overset{+}{\text{O}}\text{H}$  peak could be obscured by, or exchange with the acid solvent peak at  $\delta$  11.9-12.6. The deshielding of the alkyl protons as compared to the parent sulfones clearly indicates that protonation indeed occurred. The alkyl protons of the protonated sulfones all show deshielding, with the methylene protons closest to the sulfur atom deshielded most (see Table II).

The following sulfones were protonated in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  solution at  $-80^\circ$ : dimethyl, diethyl, di-*n*-propyl, di-*n*-butyl, benzyl *tert*-butyl, diphenyl, tetramethylene, sulfone (sulfolane), 3-sulfolene, 3-methyl-3-sulfolane. The chemical shifts and coupling constants of the parent and protonated sulfones are summarized in Table II.

The nmr spectrum of **protonated dimethyl sulfone** at  $-80^\circ$  shows the methyl singlet at  $\delta$  3.96 and a small shoulder at  $\delta$  3.91. When  $\text{SO}_2$  was used as diluent, the nmr spectrum shows two methyl singlets at  $\delta$  3.80 and 3.66, respectively, with a relative area ratio of 70:30. This indicates, as in the case of protonated methanesulfonic acid and protonated methyl methanesulfonate, that two isomeric species (**3a** and **3b**, where  $\text{R} = \text{CH}_3$ ) are present. As the temperature increased to  $-20^\circ$ , only the resonance of the major form is observed.



No coupling was observed between the methyl protons and the proton on oxygen, hence no assignment of the two isomers could be made.

In the protonation of higher homologs, *e.g.*, **diethyl**, **di-*n*-propyl**, and **di-*n*-butyl sulfone**, only one isomer was found. Again, no couplings were observed between the proton on oxygen and the alkyl protons. Hence no structural assignment could be made based on the present pmr data.

Protonated alkyl sulfones in the  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{-ClF}$  solvent system are quite stable. The nmr spectra showed no significant change from  $-80^\circ$  to room temperature.

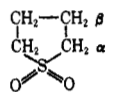
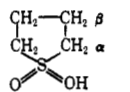
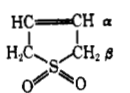
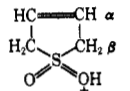
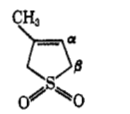
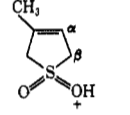
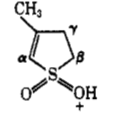
Protonated **benzyl *tert*-butyl sulfone**, however, could not be observed even when sample was prepared and investigated at  $-78^\circ$ . The pmr spectrum of benzyl *tert*-butyl sulfone in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  solution showed only that of the cleavage product, *tert*-butyl cation, at  $\delta$  4.20 and protonated phenyl methanesulfinic acid (aromatic protons centered at  $\delta$  8.10,  $-\text{CH}_2-$  at 5.23, and  $\text{SO}_2\text{H}_2$  at 9.16).

**Phenyl sulfone** in  $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$  was also protonated and stable. The pmr spectrum showed the aromatic protons at  $\delta$  8.43-7.90 and the spectrum again showed no significant change from  $-80^\circ$  to room temperature.

The pmr spectrum of **protonated tetramethylene sulfone** (sulfolane) showed the  $\alpha$ -methylene protons at  $\delta$

(17) G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3908 (1970).

TABLE II

Compd	PMR SPECTRAL PARAMETERS <sup>a</sup> OF PARENT AND PROTONATED SULFONES							Aromatic H
	Registry no.	Temp, °C	Solvent	$\alpha$ -CH <sub>2</sub>	$\beta$ -CH <sub>2</sub>	$\gamma$ -CH <sub>2</sub>	CH <sub>3</sub>	
(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	67-71-0	-60	SO <sub>2</sub> ClF				2.93	
(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub> H <sup>+</sup>	26428-10-4	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF				3.96 3.91	
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub>	597-35-3	-60	SO <sub>2</sub> ClF	2.93 (q, 7.5)			1.40 (t, 7.5)	
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> H <sup>+</sup>	26428-11-5	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	4.17 (q, 7.20)			2.05 (t, 7.2)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub>	598-03-8	-60	SO <sub>2</sub> ClF	3.00 (t, 6.5)	1.96 (m)		1.27 (t, 7.0)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> H <sup>+</sup>	26428-12-6	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	4.20 (m)	2.27 (m)		1.73 (t, 7.0)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub>	598-04-9	-60	SO <sub>2</sub> ClF	3.05 (m)	1.93 (m)		1.25 (t, 7.2)	
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> SO <sub>2</sub> H <sup>+</sup>	26428-13-7	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	4.17 (m)	2.23 (m)	2.23 (m)	1.50 (t, 7.0)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	127-63-9	-30	SO <sub>2</sub>					7.20-7.73
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub> H <sup>+</sup>	26428-14-8	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF					8.43-7.90
	126-33-0	-60	SO <sub>2</sub> ClF	3.26 (t, 7.0)	2.43 (m)			
	26428-15-9	-60	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	4.41 (t, 7.0)	3.10 (m)			
	77-79-2	-60	SO <sub>2</sub> ClF	6.37	3.85			
	26428-03-5	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.77	4.91			
	1193-10-8	-40	SO <sub>2</sub> ClF	5.96	3.80	3.80	2.03	
	26428-04-6	-80	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	6.35	4.86	4.81	2.30	
	26428-05-7	-30	FSO <sub>3</sub> H-SbF <sub>5</sub> SO <sub>2</sub> ClF	7.73 7.50	4.50 (t, 6.2)	3.68 (t, 6.2)	2.70 (90%) 2.83 (10%)	

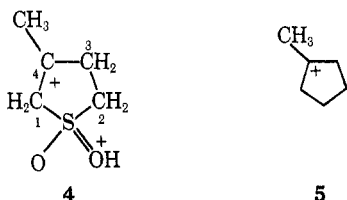
<sup>a</sup> Chemical shifts are in parts per million from external TMS. Coupling constants in hertz are given in parenthesis following the multiplicities: t = triplet; q = quartet; m = multiplet.

4.41 deshielded about 1.15 ppm from that of the parent sulfone in SO<sub>2</sub>ClF at the same temperature. The  $\beta$ -methylene protons have a chemical shift centered at  $\delta$  3.10. Protonated sulfolane is stable and the nmr spectrum showed no significant change from -60° to room temperature.

**3-Sulfolene** (butadiene sulfone, 2,5-dihydrothiophene 1,1-dioxide) in FSO<sub>3</sub>H-SbF<sub>5</sub>-SO<sub>2</sub>ClF is protonated only on the sulfonyl oxygen. No double bond protonation was observed even when the solution was warmed up to room temperature (see Table II).

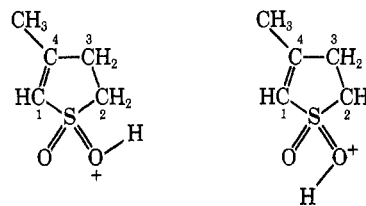
**3-Methyl-3-sulfolene** (isoprene sulfone) in FSO<sub>3</sub>H-SbF<sub>5</sub> solution using SO<sub>2</sub>ClF as diluent, at -80° gave an nmr spectrum similar to that of the parent sulfone in SO<sub>2</sub>ClF except that the resonances are shifted to lower field. This indicates that 3-methyl-3-sulfolene is also protonated on the sulfonyl oxygen without attacking on the double bond. (The pmr chemical shifts are given in Table II.) When the temperature of the solution was increased to -60°, a slow change of the pmr spectrum is observed which can be accelerated by further raising the temperature. The pmr spectrum recorded

at  $-30^\circ$  showed two triplets at  $\delta$  4.50 and 3.68, indicating two adjacent methylene groups formed. In addition to these two methylene groups, the nmr spectrum showed two singlets at  $\delta$  2.70 and 7.30. Diprotonation on the sulfonyl oxygen and the carbon-carbon double bond would presumably lead to the dication **4**. However, upon comparison of the pmr chemical shifts with that of 1-methylcyclopentyl cation **5**<sup>18</sup> ( $\text{CH}_3-\text{C}^+$ ) at  $\delta$  3.98) it appears that the methyl and methylene chem-



ical shifts, except that of the methylene protons between the two positive centers, are at too high field to be considered as species **4**. Noteworthy is also that the long-range coupling ( $J_{\text{HH}} = 4.0$  cps) of the methylene and methyl protons through the  $\text{sp}^2$  hybridized center of ion **5** is absent. Furthermore, integration showed the relative area ratio of the resonances at  $\delta$  2.70, 3.68, 4.50, and 7.30 is 3:2:2:1 indicating that there is only one proton on carbon 1. This indicates that structure **6** is in accord with the nmr data. Thus as soon as ion **4** is

(18) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2692 (1967).



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formed, it undergoes deprotonation to form a double bond conjugated to the protonated sulfonyl group. At  $-60^\circ$  the nmr spectrum shows a small singlet at  $\delta$  2.83, broad multiplets at  $\delta$  3.86, 4.90, and a weak resonance at  $\delta$  7.50 in addition to the major resonances. This probably indicates as in the case of protonated dimethyl sulfone, that two isomeric species of **6** are present.

### Experimental Section

**Materials.**—All sulfoxides and sulfones were commercially available materials.

**Nmr Spectra.**—Varian Associates Model A-56/60A spectrometer with variable-temperature probe was used for all spectra.

**Preparation of Protonated Sulfoxides and Sulfones.**—The procedure used for the preparation of solutions of protonated sulfoxides and sulfones was identical with that described previously.<sup>19</sup>

**Acknowledgment.**—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

(19) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

## Stable Carbonium Ions. CVI.<sup>1</sup> Protonation and Cleavage Reactions of Alkyl- and Arylsulfonic Acids and -sulfinic Acids and Alkyl Sulfonates and Sulfinates in Fluorosulfuric Acid-Antimony Pentafluoride Solution

GEORGE A. OLAH,\* ALICE T. KU,<sup>2</sup> AND JUDITH A. OLAH

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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A series of sulfonic acids, sulfinic acids, and sulfonates were protonated in fluorosulfuric acid-antimony pentafluoride-sulfuryl chloride fluoride solution at low temperature ( $-60^\circ$ ). Two isomers were found for both protonated methanesulfonic acid and methyl methanesulfonate. At higher temperatures, protonated methane-, benzene-, and toluenesulfonic acid underwent dehydration to give the suggested sulfonylium ion which is not observed as it quickly picks up a fluoride ion from the acid system to form the corresponding sulfonyl fluoride. For protonated higher alkyl homologs, carbonium ions are the cleavage products. Protonated methyl methanesulfonate and methyl benzenesulfonate underwent alkoxy-sulfur cleavage whereas alkyl-oxygen cleavage was found for protonated ethyl and propyl methanesulfonate. Protonated sulfinic acids and methyl methanesulfinates are very stable; no cleavage reaction was observed.

Our recent investigations of protonated thiocarboxylic acids, *S*-alkyl esters,<sup>3</sup> dithiocarboxylic acids, thion esters, and dithio esters<sup>4</sup> lead us to study the protonation of a series of sulfonic acids, sulfinic acids, sulfonates, and sulfinates in the strong acid system,  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2\text{ClF}$ . No systematic studies relating to these systems in superacid solutions was previously reported.

Hantzsch<sup>5</sup> in 1908 studied the cryoscopic behavior of the sodium salts of benzene-, *m*-nitrobenzene-, and *p*-toluenesulfonic acids in sulfuric acid, and concluded that benzene- and *p*-nitrobenzenesulfonic acids behave as nonelectrolytes in sulfuric acid while *p*-toluenesulfonic acid behaves as a weak base. Gillespie<sup>6</sup> carried out similar measurements on solutions of sodium benzenesulfonate and sodium *p*-toluenesulfonate in slightly aqueous sulfuric acid and concluded that these acids behave as weak bases. The conductimetric behavior of methanesulfonic acid in sulfuric acid studied by Gillespie and

\* To whom correspondence should be addressed.

(1) Part CV: G. A. Olah, A. T. Ku, and J. A. Olah, *J. Org. Chem.*, **35**, 3904 (1970).

(2) National Institutes of Health Predoctoral Research Investigator, 1970.

(3) G. A. Olah, A. T. Ku, and A. M. White, *J. Org. Chem.*, **34**, 1827 (1969).

(4) G. A. Olah and A. T. Ku, *ibid.*, **35**, 331 (1970).

(5) R. Hantzsch, *Z. Phys. Chem.*, **65**, 41 (1908).

(6) R. J. Gillespie, *J. Chem. Soc.*, 2542 (1950).