

Thus, resonance can occur with but one ring at a time, accounting for the very close similarity of the spectra of thioanisole and diphenyl sulfide.

The significance of the infrared data, summarized in Table VII, will be discussed in the following paper.<sup>11</sup> It is, however, appropriate to point out that, although the SO bands of the sulfone are unaffected by whatever conjugation occurs, the C—C bands at 6.2, 10.55 and 11.2  $\mu$  have all been considerably displaced, presumably by resonance of the type indicated by the ultraviolet data.

The general conclusion we draw from this ultraviolet and infrared spectral data is that there can be significant resonance interactions between carbon unsaturation and either sulfide or sulfone groups. In both cases this may involve expansion of the sulfur octet. The data support the conclusion that the geometrical requirements for the sulfide and for the sulfone resonance are quite different, in accord with the postulate that in the sulfone conjugation involves overlap of 2p- and 3d-orbitals, while in the sulfide it involves overlap of 2p- with 3p-orbitals.

The data on copolymerization in Tables I through IV are summarized in Table IX in terms of the copolymerization ratios,  $r_1$  and  $r_2$ ,<sup>12</sup> and the monomer constants,  $Q$  and  $e$ .<sup>13</sup> The values of  $Q$  and  $e$  used for the monomers  $M_1$  were those previously reported.<sup>13b</sup>

In view of the considerable uncertainties in the values for  $r_2$  for the styrene-sulfone and methyl

(11) C. C. Price and R. G. Gillis, *THIS JOURNAL*, **75**, 4750 (1953).

(12) See F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 190 (1950).

(13) (a) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947); (b) C. C. Price, *ibid.*, **3**, 772 (1948).

TABLE IX

$M_1$	$M_2$	$r_1$	$r_2$	$Q_1$	$e_2$
Styrene	Sulfone	3.3	$0.01 \pm 0.01$	0.07	1.0
Vinyl acetate	Sulfone	0.28	.35	.07	1.2
Styrene	Sulfide	4.5	.15	.35	-1.4
Methyl acrylate	Sulfide	0.40	$.05 \pm 0.02$	.29	-1.4

acrylate-sulfide pairs,  $Q$  and  $e$  were also calculated from the equations

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1-e_2)}$$

$$r_1' = (Q_1'/Q_2)e^{-e_1'(e_1'-e_2)}$$

Making suitable substitutions, values of  $Q = 0.07$  and  $e = 1.0$  were obtained for the sulfone and  $Q = 0.30$  and  $e = -1.2$  for the sulfide.

Thus the average values for the resonance ( $Q$ ) and the electrical ( $e$ ) factors for phenyl vinyl sulfone,  $Q = 0.07$  and  $e = 1.1$ , are very nearly the same as those for methyl vinyl sulfone,  $Q = 0.09 \pm 0.02$  and  $e = 1.2$ .<sup>7</sup> In the same way, these factors for phenyl vinyl sulfide,  $Q = 0.32$  and  $e = -1.3$ , are very nearly the same as for methyl vinyl sulfide,  $Q = 0.35$  and  $e = -1.5$ .<sup>8</sup>

The lack of evidence for added resonance stabilization ( $Q$ ) for the phenyl sulfone as compared to the methyl sulfone leads us to suggest that the excitation involved in the intense, short wave length band for aromatic compounds, the one which is so profoundly shifted by flanking a phenyl sulfone with a second unsaturated group (phenyl or vinyl), is due to a transition to an excited state largely ionic in character,<sup>14</sup> rather than one resembling a diradical.<sup>9</sup>

(14) See, e.g., L. Doub and J. M. Vandenberg, *THIS JOURNAL*, **69**, 2714 (1947); **71**, 2414 (1949).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## Spectra and Molecular Refraction for Some Unsaturated Sulfides, Sulfoxides and Sulfones

BY CHARLES C. PRICE AND RICHARD G. GILLIS<sup>1</sup>

RECEIVED APRIL 1, 1953

The molecular refractions of several sulfoxides and sulfones support the recent report by Vogel<sup>2</sup> that the sulfur-oxygen bond in such compounds has an abnormally low contribution to the molecular refraction, confirming the formulation of this bond as a semipolar single covalent bond. Additional evidence for this view is the lack of influence of a vinyl group on the characteristic infrared frequencies for the sulfur-oxygen bond in sulfoxides and sulfones. The sulfide, and to a lesser extent the sulfoxide and sulfone groups, do however influence the characteristic infrared absorption of the carbon-carbon double bond.

The purpose of the present investigation was to obtain additional evidence on the conjugative properties of sulfide, sulfoxide and sulfone groups, seeking confirmation for the earlier conclusions from copolymerization<sup>3-5</sup> and ultraviolet absorption<sup>6</sup> that the sulfur-oxygen bond in such compounds is indeed a semipolar single covalent bond rather than a covalent double bond. For this

purpose we have measured the infrared spectrum and the molecular refraction for methyl vinyl, methyl allyl and methyl propyl sulfide, sulfoxide and sulfone.

### Experimental<sup>7</sup>

Methyl 2-hydroxyethyl sulfide<sup>8</sup> had the following properties: b.p. 62-65° (13-14 mm.),  $n_D^{20}$  1.4900,  $d_4^{20}$  1.0581,  $R_D^{20}$  25.18° (lit.<sup>10</sup> b.p. 80.5-81° (30 mm.),  $n_D^{20}$  1.4867,  $d_4^{20}$  1.0640).

(7) All melting points are uncorrected. Analyses by Micro Tech Laboratories, Skokie, Ill.

(8) W. Windus and P. R. Shildneck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 345.

(9) We will follow Vogel<sup>2</sup> and use  $R_D$  to represent the molecular refraction.

(10) W. R. Kirner, *THIS JOURNAL*, **50**, 2441 (1928).

(1) Abstracted from the Ph.D. dissertation of Richard G. Gillis, January, 1953.

(2) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952).

(3) C. C. Price and J. Zomlefer, *THIS JOURNAL*, **72**, 14 (1950).

(4) C. C. Price and R. D. Gilbert, *ibid.*, **74**, 2078 (1952).

(5) C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

(6) C. C. Price and J. J. Hydock, *ibid.*, **74**, 1943 (1952).

**Methyl vinyl sulfide** was prepared from the alcohol above essentially according to Doumani.<sup>11</sup> Solid potassium hydroxide (10 g.) was placed in a 100-ml. round-bottomed flask which was surmounted by a 20-cm. fractionating column packed with 1/8-in. glass helices. A dropping funnel was introduced at the thermometer inlet. No reflux ratio control was used, but the outer jacket of the column was maintained at 95°.

The flask was heated in an oil-bath to 250° and methyl 2-hydroxyethyl sulfide (46.6 g., 0.5 mole) was slowly added through the column. The temperature of the bath was slowly raised to 300°, during which time a mixture of water and methyl vinyl sulfide distilled. The water was separated from the organic layer which was dried over anhydrous potassium carbonate and fractionated in a similar column. Methyl vinyl sulfide (32.5 g., 0.44 mole, 88%) was collected at 67.0° (745 mm.),  $n_D^{20}$  1.4845,  $d_4^{20}$  0.9026,  $R_D$  23.52 (lit.<sup>3</sup> b.p. 66.4–66.8°,  $n_D^{20}$  1.4835).

**Methyl Vinyl Sulfoxide.**—Methyl vinyl sulfide in methanol was oxidized with commercial sodium hypochlorite solution ("Clorox," 5.25% available chlorine) at 0°. The reaction mixture was extracted with chloroform. After evaporation, the residue was vacuum distilled; methyl vinyl sulfoxide (17% yield) was obtained at 87° (15 mm.). Two consecutive fractions had  $n_D^{20}$  1.4912, 1.4910;  $d_4^{20}$  1.0994, 1.0945;  $R_D$  23.70, 23.85 (lit.<sup>4</sup> b.p. 46–47° (0.8 mm.),  $n_D^{20}$  1.4925). The infrared absorption spectrum showed a small contamination by sulfone.

**Methyl vinyl sulfone** was prepared by oxidation of sulfide with hydrogen peroxide in acetic acid at 90° according to the method of Gilman and Esmay.<sup>12</sup> Methyl vinyl sulfone (16% yield) was obtained at 122–124° (22–24 mm.) (lit.<sup>3</sup> b.p. 115–117° (19 mm.)). Two consecutive fractions had  $n_D^{20}$  1.4640, 1.4636;  $d_4^{20}$  1.2117, 1.2146;  $R_D$  24.17, 24.10 and showed no infrared absorption for sulfoxide.

**Methyl Allyl Sulfide.**—A solution of two moles of sodium methyl sulfide in methanol was heated to reflux on the water-bath with stirring. The bath was then removed and dry, redistilled allyl chloride (153 g., 2 moles) was added at such a rate that refluxing continued. At the end of the addition the bath was replaced and heating continued for a total reaction time of three hours. After cooling, the precipitated sodium chloride was filtered and washed twice with 50 ml. of methanol. The filtrate was distilled from the water-bath and the material boiling up to 64° (an azeotrope of methanol and the product) was collected. This azeotrope was diluted with five times its volume of water, the upper layer which separated was removed, washed with water and dried over anhydrous calcium chloride. The product was fractionated and methyl allyl sulfide (76 g., 0.86 mole, 43%) was collected at 92.2–92.4° (lit.<sup>13</sup> b.p. 90–93°);  $n_D^{20}$  1.4712,  $d_4^{20}$  0.8767,  $R_D$  28.12.

**The Methanol-Methyl Allyl Sulfide Azeotrope.**—By careful fractionation of the crude distillate from the preparation above, the azeotrope was found to have b.p. 61.8° and  $n_D^{20}$  1.3860. A series of mixtures of pure sulfide and pure methanol ( $n_D^{20}$  1.3280) was prepared and refractive indices of these plotted against composition. This gave a smooth curve from which the composition of the azeotrope was read. The mole fraction of methyl allyl sulfide in the azeotrope was found to be 21% and the weight fraction 43.5%.

**Methyl Allyl Sulfone.**—Methyl allyl sulfide (22 g., 0.25 mole) in 50 ml. of glacial acetic acid was chilled in an ice-bath and aqueous hydrogen peroxide (50 ml. of 30%) was added slowly over a period of one hour. The reaction mixture was allowed to stand overnight at room temperature. It was then heated on the water-bath to 85° for one hour, cooled, diluted with an equal volume of water, and extracted with chloroform (200 ml.). The extract was washed with water, dried over anhydrous magnesium sulfate, and the solvent removed on the water-bath. The residue was vacuum distilled and methyl allyl sulfone (9.6 g., 33% yield) collected at 130–131° (16–18 mm.) (lit.<sup>14</sup> b.p. 130° (15 mm.)). This was refractionated and physical constants determined on a middle fraction whose infrared spectrum showed sulfoxide to be absent:  $n_D^{20}$  1.4775,  $d_4^{20}$  1.1752,  $R_D$  28.91.

**Methyl *n*-propyl sulfide** was prepared by the action of *n*-propyl bromide on sodium methyl sulfide in methanol. It

distilled at 94.5–95.6° (lit.<sup>15</sup> b.p. 93–95°). A middle fraction of constant boiling point and refractive index was used for the determination of physical constants:  $n_D^{20}$  1.4436,  $d_4^{20}$  0.8438,  $R_D$  28.38, b.p. 95.0°.

**Methyl *n*-propyl sulfoxide** was prepared by oxidation of the sulfide in glacial acetic acid with aqueous hydrogen peroxide. Three consecutive fractions of constant boiling point and refractive index were obtained, but infrared analysis indicated there was still a little contamination by sulfone: b.p. 102° (15 mm.),  $n_D^{20}$  1.4690,  $d_4^{20}$  1.0122,  $R_D$  29.22.

**Methyl *n*-Propyl Sulfone.**—Methyl *n*-propyl sulfide (22.5 g., 0.25 mole) was mixed with ten volumes of water and oxidized by the addition of powdered potassium permanganate added portionwise until an excess was present. The reaction was kept cold at all times. The precipitate manganese dioxide was filtered and washed well with water. The filtrate was decolorized by sulfur dioxide and extracted with chloroform. The extract was dried over anhydrous sodium sulfate. The chloroform was removed on the water-bath and the residue distilled: yield 7.2 g. (0.06 mole, 24%), b.p. 130–131° (15 mm.),  $n_D^{20}$  1.4458,  $d_4^{20}$  1.1138,  $R_D$  29.24.

**Infrared absorption spectra** were determined with a Baird Associates Model 12B instrument with sodium chloride optics, and our thanks are due to Mr. R. J. Boyle for the actual determinations. Spectra were determined with the pure substances either as capillary films or in 0.05-mm. cells. The data are summarized in Tables II–IV.

TABLE I

MOLECULAR REFRACTIONS FOR SOME SULFIDES, SULFOXIDES AND SULFONES,  $R_2X$ 

$R_2$	$X = S$	$X = S$ (calcd.) <sup>2</sup>	$X = SO$	$X = SO_2$
$Cl_2$	19.87 <sup>a</sup>	...	22.12 <sup>2</sup>	21.43 <sup>2</sup>
$(RO)_2$ ( $-R_2$ ) <sup>b</sup>	...	...	11.34	11.09
$Me_2$	19.13 <sup>c</sup>	19.27	20.06 <sup>d</sup>	20.08 <sup>d</sup>
$Et_2$	28.53 <sup>c</sup>	28.57	29.34 <sup>d</sup>	29.73 <sup>d</sup>
<i>n</i> - $Pr_2$	37.79 <sup>c</sup>	37.87	38.43 <sup>d</sup>	38.73 <sup>d</sup>
$Me, Pr$	28.38	28.57	29.22	29.24
$Me, Allyl$	28.12	28.09	...	28.91
$Me, Vinyl$	23.52	23.45	23.70	24.17
$C_6H_5, Allyl$ <sup>e</sup>	48.46	48.52	49.13	48.72
$C_6H_5, Crotyl$ <sup>d</sup>	53.50	53.17	...	53.54
$C_6H_5, s-Bu$ <sup>e</sup>	53.56	53.65	...	53.63

<sup>a</sup> G. H. Whiting, *J. Applied Chem.*, 2, 381 (1952).  
<sup>b</sup> These values are for the  $SO_3$  and  $SO_4$  groups in many esters (see A. I. Vogel, *J. Chem. Soc.*, 1833 (1948)).  
<sup>c</sup> A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943).  
<sup>d</sup> These values are for the He line (W. Strecker and R. Spitaler, *Ber.*, 59, 1755 (1926)).  
<sup>e</sup>  $R_D^{20}$  from A. C. Cope, D. E. Morrison and L. Field, *THIS JOURNAL*, 72, 64 (1950).

TABLE II

INFRARED ABSORPTION BANDS FOR METHYL PROPYL SULFIDE, SULFOXIDE AND SULFONE (5–15 $\mu$ )

Sulfide		Sulfoxide		Sulfone	
$\lambda, \mu$	Intensity	$\lambda, \mu$	Intensity	$\lambda, \mu$	Intensity
6.8–6.95	V. strong	6.80	Strong	6.77	Med.
7.22	Med.	7.0	Strong	7.02	Med.
7.44	Weak	7.20	Med.	7.20	Weak
7.56	Weak	9.35	V. strong	7.6–7	V. strong
7.68	Med.	9.55	V. strong	7.93	Med.
8.03	Strong	9.70	V. strong	8.20	Weak
9.20	Weak	10.50	Strong	8.78	V. strong
9.30	Weak	14.50	Med.	9.12	Weak
9.45	Weak			9.32	Weak
10.45	Strong			10.35	Strong
11.13	Med.			11.50	Med.
11.27	Weak			12.60	Strong
12.75	Med.			13.05	Strong
14.35	Med.				

(15) C. K. Ingold, J. A. Jessop, K. I. Kuriyan and A. M. M. Mandour, *ibid.*, 533 (1933).

(11) T. F. Doumani, U. S. Patent 2,402,878 (June 25, 1946).

(12) H. Gilman and D. L. Esmay, *THIS JOURNAL*, 74, 2021 (1952).

(13) J. Obermeier, *Ber.*, 20, 2925 (1887).

(14) E. Rothstein, *J. Chem. Soc.*, 684 (1934).

TABLE III  
INFRARED ABSORPTION BANDS FOR METHYL ALLYL SULFIDE AND SULFONE (5-15 $\mu$ )

Sulfide		Sulfone	
$\lambda, \mu$	Intensity	$\lambda, \mu$	Intensity
5.48	Med.	6.10	Weak
6.12	Strong	7.00	Med.
7.00	Strong	7.65	V. strong
7.10	Weak	8.00	Med.
7.57	Weak	8.32	Med.
7.72	Weak	8.80	V. strong
8.12	Strong	9.22	Med.
8.30	Weak	10.05	Med.
9.10	Weak	10.35	Strong
10.10	V. strong	10.65	Strong
10.92	V. strong	11.33	Strong
11.75	Med.	13.02	Med.
13.20	V. strong	14.12	Strong
14.14	Strong		

TABLE IV  
INFRARED ABSORPTION BANDS FOR METHYL VINYL SULFIDE, SULFOXIDE AND SULFONE (5-15 $\mu$ )

Sulfide		Sulfoxide		Sulfone	
$\lambda, \mu$	Intensity	$\lambda, \mu$	Intensity	$\lambda, \mu$	Intensity
5.85	Weak	6.20	Weak	6.15	V. weak
6.30	Strong	7.00	Med.	7.05	Weak
6.97	Strong	7.08	Med.	7.15	Med.
7.20	Med.	7.25	Med.	7.62	V. strong
7.60	Med.	7.57	Weak	8.78	V. strong
7.82	Med.	7.67	Weak	10.40	V. strong
9.63	V. strong	8.00	Weak	12.65	V. strong
10.50	V. strong	8.75	Med.	14.60	Med.
11.70	V. strong	9.35	V. strong		
13.50	Strong	10.42	V. strong		
14.35	Med.	10.70	Med.		
14.80	Strong	14.80	Med.		

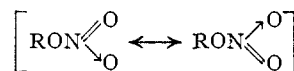
### Discussion

Data on the molecular refraction from our own work and similar studies in the literature are summarized in Table I. The most striking feature of these results is the extremely small contribution of the new oxygen atom and its bond to the sulfur. In some cases, in fact, the molecular refraction actually decreases upon introduction of an oxygen atom bonded to sulfur.

It has been pointed out recently by Vogel<sup>2</sup> that the bond refraction for a single covalent sulfur-oxygen bond is about 4.6 units. In the case of most normal covalent double bonds, the bond refraction for the double bond is more than twice that of the single bond.<sup>2</sup> For example, the sulfur-carbon single bond has a refraction of 4.6 units, the double bond a refraction of 11.9 units. This is readily understood since the  $\pi$ -electrons, being less firmly constrained, are more polarizable. For a genuine sulfur-oxygen covalent double bond one would therefore predict a substantial bond refraction of at least ten units. Actually, the SO bond refraction in sulfoxides is about 0.6 unit or less and the introduction of a second oxygen gives an even smaller increment in molecular refraction.

Vogel gives a value of 1.78 for the bond refraction of the nitrogen-oxygen semipolar bond, appreciably less than the value for the NO covalent single bond (2.43). Actually, the value of 1.78

was derived from the molecular refraction for nitrates. In these substances, the NO bond will certainly have some double bond character due to resonance



For this reason, the value given is probably higher than for a true NO semipolar link.

A better indication of the low value to be expected for the molecular refraction of bonds unquestionably semipolar is the fact that the molecular refraction for boron fluoride etherate ( $R_D$  26.63) is 1.68 units less than the sum of the molecular refraction for boron fluoride ( $R_D$  6.0) and ether ( $R_D$  22.31).<sup>16</sup> Laubengayer and Finlay report the etherate to have a molecular refraction 1.83 units less than the sum of its components.<sup>17</sup>

A similar comparison for the SO bond would require an estimate of the molecular refraction of a single oxygen atom. If this were presumed to be of the order of magnitude of 1.5 to 2 units,<sup>18</sup> then the SO semipolar bond would have about as large a negative contribution to molecular refraction as the boron-oxygen semipolar bond in boron fluoride etherate.

One concludes therefore from these data that the SO bond in sulfoxides and sulfones (and the related bond in sulfites and sulfates) is definitely not a covalent double bond, but a semipolar bond. The fact that the bond refraction for the semipolar bond is actually less than for a covalent single bond may be due to the high charges associated with the atoms. The electric field thus created may place sufficient added constraints upon the electrons in adjacent bonds so as to reduce the over-all polarizability of the molecule to impinging electromagnetic waves.

The infrared data, summarized in Tables II-IV, lends strong support to the view that the SO bond is not a covalent double bond.<sup>19</sup> The characteristic sulfone bands at 7.65 and 8.75  $\mu$ , strong and well defined in the alkyl, allyl and vinyl sulfones, show no displacement as a result of conjugation in

(16) H. Meerwein and W. Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

(17) A. W. Laubengayer and G. R. Finlay, *THIS JOURNAL*, **65**, 884 (1943).

(18) Values for the atomic refraction of oxygen in various compounds vary from 1.5 to 2.2 (see, e.g., R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1948, p. 45).

(19) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, *THIS JOURNAL*, **73**, 1220 (1951), and D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949), have argued that the stronger hydrogen-bonding tendencies of sulfoxides as compared to sulfones favors the covalent double bond structure for the SO bond. The argument of the latter authors, however, unfortunately neglects an important factor which vitiates the conclusion they reach. The weaker hydrogen bonds formed to the sulfone group are not necessarily a measure of the weaker negative charge on the oxygen atom, but of the weaker negative field near the oxygen. In the sulfone, the second SO bond nearly doubles the positive charge on the sulfur atom, thereby increasing the SO bond strength by increasing the electrical attraction between the sulfur and each oxygen atom and, at the same time, decreasing the negative field near each oxygen, thereby weakening the hydrogen bonding capacity of the sulfone group as compared to the sulfoxide. These characteristics are thus predictable on the basis of the semipolar bond picture, even though the polarity of the two SO bonds in a sulfone is less than the polarity of the single SO bond in a sulfoxide.

the latter case. This is equally true in the case of phenyl alkyl and phenyl vinyl sulfones.<sup>5</sup> Thus there is no evidence from infrared data for the popular notation of resonance interaction involving conjugation between carbon-carbon double bonds and the alleged sulfur-oxygen double bond of sulfones. In the case of the alkyl and vinyl sulfide, the intense characteristic SO bond frequency at 9.70  $\mu$  actually shifts to shorter wave length in the vinyl compound (9.35  $\mu$ ).<sup>20</sup>

However, although there is no indication of conjugation with carbon-carbon unsaturation having any of the influence on the SO bond to be expected if the SO bond were double, there is abundant evidence in the infrared spectra for resonance shifts of the absorption for the carbon-carbon double bond itself. The normal behavior for an unconjugated vinyl group is clearly indicated by the bands at 5.48, 6.12 and 10.92  $\mu$  in methyl allyl sulfide. The 6.12 band is the normal unperturbed C=C stretching frequency, the 10.92 band is the C=C normal wagging frequency and the 5.48 band is its first harmonic.

In methyl vinyl sulfide, these three bands have shifted to 5.85, 6.30 and 11.70  $\mu$ , all in accord with the type of resonance interaction previously proposed<sup>3-5</sup> to account for the ultraviolet spectra and copolymerization characteristics of this compound,  $\left[ \begin{array}{c} \text{---}\ddot{\text{S}}\text{---C=C} \leftrightarrow \text{---}\ddot{\text{S}}\text{=C---}\ddot{\text{C}} \end{array} \right]$ . Contributions from the second form would decrease the double

(20) A shift in this direction, which is also observed for thionyl halides as compared to sulfoxides, may be accounted for by the electronegativity of the groups attached to the sulfur. In  $\begin{array}{c} \text{R} \\ \diagup \\ \text{S}^+ \text{---O}^- \\ \diagdown \\ \text{R} \end{array}$ , the more electronegative is R, the more positive will be the sulfur. Increased positive charge on the sulfur will increase the ionic contribution to the SO bond strength and will thus shift the vibration to higher frequency (shorter wave length).

bond character between the carbon atoms, accounting for the decreased resistance to stretching and wagging.

The oxidation of the sulfide group to sulfoxide or sulfone has two pronounced influences on these double bond absorptions of the vinyl group. The first is to reduce markedly the intensity of the C=C absorption relative to the methyl and methylene bands (7.0-7.3  $\mu$ ). As a result, the only band that is positively identifiable is the stretching frequency, which decreases to 6.20  $\mu$  in the sulfoxide and to 6.15  $\mu$  in the sulfone.

These same general effects were observed for the case of phenyl vinyl sulfide, sulfoxide and sulfone.<sup>5</sup> Again these observations are in accord with those from ultraviolet spectra and copolymerization,<sup>3-5</sup> all indicating progressively less resonance interaction as the unshared electrons on the sulfur are utilized in bonds to oxygen atoms.

The one other area where one might look for some evidence for resonance involving the sulfur functions is in the C-S frequency. Using sodium chloride optics, we are not able to obtain good resolution of this band, usually occurring around 14.5  $\mu$ . Almost all of the compounds showed absorption in this region but unfortunately the shifts are all in the direction opposite to that expected. Compared to the alkyl compounds (14.35-14.50  $\mu$ ) the allyl sulfur compounds shift to shorter wave length (14.12-14.14  $\mu$ ), the vinyl to longer (14.60-14.80  $\mu$ ).

Incidentally, it should be pointed out that the strong conjugation in methyl vinyl sulfide, as indicated by copolymerization data and by ultraviolet and infrared spectra, does not produce any appreciable exaltation of the molecular refraction (Table I).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

## A Study of Some Fluorine-containing $\beta$ -Diketones<sup>1</sup>

By J. D. PARK, H. A. BROWN AND J. R. LACHER

RECEIVED DECEMBER 10, 1952

The preparation of seven new  $\beta$ -diketones containing fluorinated groups is reported. The infrared spectra and enolic content of these  $\beta$ -diketones were determined and are noted.<sup>2</sup> Acetylacetone and 1,1,1-trifluoro-2,4-pentanedione were chlorinated and the products identified.

### Introduction

Perfluorinated acetic, propionic, butyric and valeric acids were esterified by treating the acids with an equivalent quantity of ethyl alcohol in the presence of concentrated sulfuric acid<sup>3</sup> (approximately

(1) Abstracted from a thesis submitted by H. A. Brown in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Colorado, June, 1952.

(2) The spectra referred to in the body of this paper have been deposited as Document number 4016 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(3) Private communication, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

1.5 moles per mole of alcohol). Subsequently, these esters were condensed in good yields with various ketones in the presence of sodium methoxide. Ethyl trifluoroacetate was found to react successfully with cyclopentanone, cyclohexanone, 1-indanone and 1-tetralone. The esters of perfluorinated acetic, propionic, butyric and valeric acids were condensed with acetone with equal success. In each case, the yield of the  $\beta$ -diketones was better than 75%.

Copper chelates of all the  $\beta$ -diketones synthesized in this study were prepared. The physical properties of the  $\beta$ -diketones and copper chelates are shown in Table I.

The enolic content of eight  $\beta$ -diketones contain-