

identical with an authentic sample prepared by methylation of the corresponding  $\alpha$ -hydroperoxy acid with diazomethane.

Our results show that a variety of  $\alpha$ -hydroperoxy esters 1 can be prepared in good to excellent yields via the synthetic sequence outlined in eq 2. We are extending this method to  $\alpha$ -hydroperoxy esters with activated leaving groups as synthons for the labile  $\alpha$ -peroxylactones 2.

### Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were taken on a Hitachi Perkin-Elmer R-24B instrument and IR spectra on a Perkin-Elmer Infracord 237B. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Reagents, solvents, and starting materials were purchased from standard sources and purified according to literature procedures. Esters 5 were prepared following published methods and purified rigorously to match literature physical constants and spectral data.<sup>11</sup>

**Ketene Trimethylsilyl Methyl Acetals 4 (General Preparation).  $\alpha$ -Lithiation.** A 250-mL, two-necked, round-bottomed flask, provided with a magnetic spinbar and a rubber septum, was connected to a nitrogen manifold and flame-dried while flushing with dry nitrogen. While under a  $N_2$  atmosphere, a solution of 283 mmol of dry diisopropylamine (freshly distilled from  $CaH_2$ ) in 50 mL of dry THF (freshly distilled from benzophenone ketyl radical) was syringed into the flask and dry ice cooled to  $-78^\circ C$ . While being stirred magnetically 10 mL of *n*-Buli (2.55 N in hexane) was syringed dropwise into the flask. The solution was stirred 10 min at  $-78^\circ C$ , warmed up to room temperature (ca.  $30^\circ C$ ), and kept at room temperature for 10 min. The lithium diisopropylamide (LDA) solution was again dry ice cooled to  $-78^\circ C$  and 23 mmol of the ester 5 in 10 mL of dry THF was syringed dropwise into the LDA solution while the solution was stirred. The  $\alpha$ -lithiocarboxylate solution was kept at  $-78^\circ C$  for 45 min and used for the silylation as described below.

**Silylation:** Into the freshly prepared (as described above)  $\alpha$ -lithiocarboxylate solution was syringed 25.3 mmol of chlorotrimethylsilane (purged rigorously with dry  $N_2$  to displace adventitious HCl) within 45 min while the solution was being stirred at  $-78^\circ C$ . The reaction mixture was allowed to warm up to room temperature (ca.  $30^\circ C$ ) and the THF was rotoevaporated ( $25^\circ C$  (20–30 mm)). The residue was triturated with  $2 \times 30$  mL of dry benzene (freshly distilled from benzophenone ketyl radical) and filtered under a nitrogen atmosphere. The combined benzene triturates were rotoevaporated ( $25^\circ C$  (20–30 mm)) and the crude oil was fractionally distilled at reduced pressure. The yields and physical and spectral data for the ketene acetals 4 are collected in Table I.

**Methyl Trimethylsilyl Peroxyacetates 3 (General Photooxygenation).** A 100-mL, pear-shaped flask with a side arm which was capped with a rubber septum was connected to a nitrogen manifold. The flask was flame dried under reduced pressure while flushing with

nitrogen and charged with a solution of 20 mmol of the acetal 4 in 20 mL of  $CCl_4$ , containing 2 mg of tetraphenylporphyrin (TPP). The solution was cooled to  $0^\circ C$  with an ice bath and while passing a vivid stream of dry oxygen gas by means of a 15G stainless steel capillary, introduced through the rubber septum-capped side arm to the bottom of the flask, the contents were irradiated directly with a 400 W sodium lamp (General Electric). The reaction progress was monitored periodically by IR, following the disappearance of the  $1660\text{ cm}^{-1}$  ketene acetal band. Usually within 60–90 min photooxygenation was completed, the solvent rotoevaporated ( $25^\circ C$  (80 mm)) and the residue worked up by fractional distillation at reduced pressure in the case of volatile silylperoxy esters or directly methanolized to the hydroperoxy esters in the case of unstable, involatile products. The results are summarized in Table II.

**Methyl  $\alpha$ -Hydroperoxyacetates 1 (General Methanolysis).** A 50-mL, stoppered Erlenmeyer flask, provided with magnetic spinbar, was charged with 20 mL of methanol and cooled to  $0^\circ C$  by means of an ice bath. While being stirred and cooled 4.64 mmol of silylperoxy ester 3 was syringed into the methanol and allowed to stir overnight. The methanol was rotoevaporated ( $10^\circ C$  (10 mm)) and the crude product was fractionally distilled or recrystallized. The results are summarized in Table III.

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**Registry No.**—5a, 10250-48-3; 5b, 27174-71-6; 5c, 547-63-7; 5d, 3469-00-9; chlorotrimethylsilane, 75-77-4.

### References and Notes

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## Steric Effects. 11. Substituents at Sulfur

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SX groups, where X is alkyl, were shown to have constant electrical effects. Steric parameters,  $v_{SX}$ , for eight SR groups were calculated from rates of alkaline hydrolysis of alkyl thiolacetates in 40% v/v dioxane–water at  $35^\circ C$  by the equation:  $v_{SX} = 1.14 \log k_{SX} + 2.06$ . The  $v_{SX}$  parameters were used to correlate rate data for the acid- and base-catalyzed hydrolyses of alkyl thiolacetates with the modified Taft equation. The magnitude of the  $\psi$  values obtained is discussed. Rate and equilibrium data for an additional 17 sets of reactions involving alkyl groups attached to sulfur have been correlated with the  $v_{SX}$ ,  $v_X$ , and  $v_X'$  constants by means of the modified Taft equation. Of the 24 sets studied, 23 gave significant correlations, leading to the conclusion that the effect of alkyl group substitution on sulfur is largely or wholly steric in nature.

In our last two papers in this series, we have developed steric substituent constants for alkoxy groups<sup>1</sup> and for alkylamino and dialkylamino groups.<sup>2</sup> In this paper, we extend our investigation to the problem of the definition of steric

substituent constants for alkylthio groups. For this purpose, let us consider the effect of alkyl groups upon the rates of acid-catalyzed and base-catalyzed hydrolysis of alkyl thiolacetates. In addition to the steric effects of interest to us, we

Table I. Values of Electrical and Steric Constants

X	$\sigma_{1,SX}$	$\sigma_{R,SX}$	$\sigma_{L,X}$	$\sigma_{R,X}$	$\nu_{CH_2X}$	$\nu_{OX}$	$\nu_{SX}$	$\nu_X$	$\nu_{X'}$
Me	0.30	-0.35	-0.01	-0.16	0.56	0.36	0.64	0.52	0.35
Et	0.26	-0.25	-0.01	-0.14	0.68	0.48	0.94	0.56	0.38
Pr	0.25		-0.01		0.68	0.56	1.07	0.68	0.42
<i>i</i> -Pr	0.26	-0.22	0.01	-0.16	0.98	0.75	1.19	0.76	0.62
Bu	0.26		-0.01		0.68	0.58	1.15	0.68	0.42
<i>i</i> -Bu			-0.01		0.68	0.62	1.15	0.98	0.55
<i>s</i> -Bu	0.25		-0.01		1.00	0.86	1.36	1.02	0.66
<i>t</i> -Bu			-0.01	-0.16	1.34	1.22	1.60	1.24	1.23
Am	0.26				0.73	0.58		0.68	
<i>c</i> -Hex	0.32		0.00	-0.15	0.97	0.81		0.87	
Hex	0.25				0.73	0.61		0.73	
<i>t</i> -BuCH <sub>2</sub>			0.00	-0.16				1.34	

must also consider the possibility of electrical effects. The localized (field and/or inductive) electrical effect can be described by the  $\sigma_I$  constants of alkylthio groups. Values for a number of these groups are listed in Table I.<sup>4</sup> Inspection of these values shows that they are fairly constant ( $0.27 \pm 0.025$ ), particularly when the error in the values is considered. Unfortunately, the delocalized (resonance) effect cannot be examined as effectively in this manner as  $\sigma_R$  values are available only for the MeS, EtS, and *i*-PrS groups. We can, however, make use of the method of ascertaining the delocalized effect which we have previously used<sup>2</sup> in our study of alkylamino groups. We have previously shown that the  $\sigma_p$  constants of the SX groups can be calculated from the equation<sup>3</sup>

$$\sigma_{p,SX} = m\sigma_{pX} + c \quad (1)$$

and that any composite substituent constant  $\sigma_X$  can be written as

$$\sigma_X = \lambda\sigma_{LX} + \delta\sigma_{DX} \quad (2)$$

where  $\sigma_{LX}$  is the localized effect parameter and  $\sigma_{DX}$  is the delocalized parameter characteristic of the X group, and  $\lambda$  and  $\delta$  are coefficients. For the localized parameter,  $\sigma_L$ , we will use the  $\sigma_I$  constants<sup>4</sup> and for the delocalized parameter the  $\sigma_R$  constants.<sup>4</sup> Let us apply eq 2 to the case in which  $\sigma_X$  represent the  $\sigma_p$  value of alkyl substituent. For  $\sigma_p$  constants,  $\lambda \equiv \delta \equiv 1$ . The  $\sigma_I$  and  $\sigma_R$  values for alkyl groups are indeed constant with values  $-0.01 \pm 0.01$  for 12 groups and  $-0.16$  for nine groups, respectively. Then  $\sigma_{pX}$  where X is alkyl must be constant, as all of the terms on the right side of eq 2 are constant.

Then, from eq 1, as  $m$  and  $c$  are constants,  $\sigma_{p,SX}$  must be constant. Writing eq 2 for the  $\sigma_{p,SX}$  values and rearranging gives

$$\sigma_{R,SX} = \sigma_{p,SX} - \sigma_{L,SX} \quad (3)$$

Then as  $\sigma_{p,SX}$  and  $\sigma_{L,SX}$  have been shown to be constant,  $\sigma_{R,SX}$  must also be constant. It follows, then, that the electrical effect of alkylthio groups is independent of the nature of the alkyl group and will remain constant throughout the sets studied. We need, therefore, only to concern ourselves with the steric effect of the alkylthio group. In our work on alkoxy and alkylamino groups, we have demonstrated the validity of the equation

$$\nu_{Z'X} = \nu_{ZX} + d \quad (4)$$

where  $\nu$  is the steric parameter we have defined elsewhere<sup>5,6</sup> and Z and Z' refer to constant groups to which the variable fragment, X, and the rest of the molecule are attached. Thus, we have been able to successfully correlate rates of acid- and base-catalyzed hydrolysis of alkyl carboxylates and of *N*-alkyl amides with  $\nu_{CH_2X}$  values by means of the modified Taft equation

$$\log k_{Z'X} = \psi\nu_{CH_2X} + h \quad (5)$$

In these cases, Z is the CH<sub>2</sub> group and Z' is oxygen in the case of alkyl carboxylates or nitrogen in the case of *N*-alkyl amides. Using the  $\nu_{CH_2X}$  values<sup>5,6</sup> we have attempted such correlations here. For the data and the results of the correlations with eq 5, see the paragraph at the end of this paper concerning supplementary material. The results obtained for the correlation of the three sets of base-catalyzed hydrolyses (sets 1-3) and four sets of acid-catalyzed hydrolyses (sets 4-7) of alkyl thiolacetates with eq 5 are not good enough to permit the definition of  $\nu$  values for alkylthio groups. The data were therefore correlated with eq 5 using the  $\nu_{OX}$  values. For the results, see Table II and the discussion of the supplementary material. The alkaline hydrolysis of alkyl thiolacetates in 40% aqueous dioxane at 35 °C (set 1B) gave results which are significant at the 99.9% confidence level (CL). We have therefore utilized this set of data to define  $\nu_{SX}$  values. We have already shown that the  $\psi$  value obtained from correlation of a data set with the modified Taft equation (eq 5) by means of  $\nu_{ZX}$  values is the same as that obtained from correlation by means of  $\nu_{Z'X}$  values. Thus, the value of  $\psi$  obtained from correlation of set 1 with the  $\nu_{OX}$  constants should be equal to the value of  $\psi$  which would result from the correlation of this data with  $\nu_{SX}$  values.

We therefore used the data of set 1 together with the  $\psi$  value obtained for set 1B in defining  $\nu_{SX}$  values. The only other requirement for the definition of  $\nu_{SX}$  values is a value of  $\nu_{SX}$  for some substituent. For this purpose, we again use our previous approach and take the difference between  $\nu_{Me}$  and  $\nu_{Et}$  to represent the effect of replacing a hydrogen in the methyl group by a methyl group. Then by the same type of argument as that previously used<sup>1</sup>

$$\nu_{SMe} = \nu_{SH} + \nu_{Et} - \nu_{Me} = 0.64 \quad (6)$$

In this manner we have obtained the relationship

$$\nu_{SX} = -1.14 \log k_{SX} + 2.06 \quad (7)$$

Values of  $\nu_{SX}$  calculated from eq 7 and the data of set 1 are presented in Table I. Sets 2-7 were correlated with eq 5 by means of the  $\nu_{SX}$  constants defined above (sets 2C-7C). The results obtained are very much better than those which were obtained by correlation with  $\nu_{CH_2X}$  and  $\nu_{OX}$  values. Whereas with the  $\nu_{CH_2X}$  constants, all six sets did not give significant results, with the  $\nu_{SX}$  values all six sets gave significant results. Had the sets contained more than four points each, the results would probably have been much better.

The  $\nu_{SX}$  values were correlated with the  $\nu_{OX}$  values by means of the equation

$$\nu_{SX} = m\nu_{OX} + d \quad (8)$$

The results obtained were:  $m$ , 0.998;  $d$ , 0.460;  $r$ , 0.944;  $F$ , 49.49 (CL = 99.9%);  $s_{est}$ , 0.100;  $s_m$ , 0.142 (CL = 99.9%);  $s_d$ , 0.103 (CL = 99.0%);  $n$ , 8. The value of  $m$  obtained is in excellent agreement with the value of 1.00 predicted by eq 4. The use of eq

Table II. Results of Correlations with Equations 5 and 9

Set <sup>k</sup>	$\psi$	$h$	$r^a$	$F^b$	$s_{est}$	$n^d$
1B	-0.874	1.40	0.946	51.35 <sup>e</sup>	0.0862	8
2C	-1.22	0.487	0.972	33.90 <sup>i</sup>	0.143	4
3C	-1.07	1.10	0.990	101.2 <sup>g</sup>	0.0722	4
4C	-0.455	0.789	0.919	10.88 <sup>j</sup>	0.0940	4
5C	-0.394	1.17	0.935	14.01 <sup>j</sup>	0.0717	4
6C	-0.392	0.509	0.963	25.46 <sup>i</sup>	0.0530	4
7C	-0.276	0.843	0.979	46.67 <sup>h</sup>	0.0276	4
8C	-2.03	2.45	0.978	88.97 <sup>e</sup>	0.152	6
9D	-7.23	5.65	0.996	271.1 <sup>f</sup>	0.251	4
10C	-1.07	2.25	0.857	13.88 <sup>h</sup>	0.138	7
11C	0.510	-0.612	0.997	361.0 <sup>f</sup>	0.0189	4
12C	0.488	-0.445	0.986	71.34 <sup>h</sup>	0.0406	4
13C	0.533	-0.161	0.998	507.3 <sup>f</sup>	0.0166	4
14C	0.555	-0.124	0.996	270.6 <sup>f</sup>	0.0237	4
15D	0.977	-2.18	0.948	17.81 <sup>j</sup>	0.133	4
16D	-6.67	5.86	0.996	260.1 <sup>f</sup>	0.237	4
17D	-7.34	8.28	0.985	67.47 <sup>h</sup>	0.511	4
18E	-4.72	2.80	0.951	37.74 <sup>f</sup>	0.181	6
19E	-5.45	3.91	0.932	26.35 <sup>g</sup>	0.250	6
20D	-1.03	1.66	0.975	116.9 <sup>e</sup>	0.122	8
21D	-1.30	3.24	0.901	95.33 <sup>e</sup>	0.207	24
22D	-5.36	14.4	0.808	9.422 <sup>i</sup>	0.451	7
23D	-7.52	7.30	0.998	621.7 <sup>f</sup>	0.173	4
24D	-4.50	3.52	0.981	50.94 <sup>h</sup>	0.361	4

<sup>a</sup> Correlation coefficient. <sup>b</sup>  $F$  test for significance of regression. Superscript indicates confidence level (CL). <sup>c</sup> Standard errors of the estimate,  $\psi$ , and  $h$ . Superscript indicates CL of the "Student's  $t$ " test. <sup>d</sup> Number of points in the set. <sup>e</sup> 99.9% CL. <sup>f</sup> 99.5% CL. <sup>g</sup> 99.0% CL. <sup>h</sup> 97.5% CL. <sup>i</sup> 95.0% CL. <sup>j</sup> 90.0% CL. <sup>k</sup> The reactions studied are: (1) AcSR + OH<sup>-</sup>, 40% aqueous dioxane, 35 °C; (2) AcSR + OH<sup>-</sup>, 43% w/w aqueous MeOAc, 0 °C; (3) AcSR + OH<sup>-</sup>, 62% aqueous MeOAc, 20 °C; (4,5) AcSR + H<sub>3</sub>O<sup>+</sup>, 43% w/w aqueous MeOAc, 30 °C, 40 °C; (6, 7) AcSR + H<sub>3</sub>O<sup>+</sup>, 62% w/w aqueous MeOAc, 30 °C, 40 °C; (8) AcSR + Ac<sub>2</sub>O, MeNO<sub>2</sub>, AlCl<sub>3</sub>, 45 °C; (9) RSSO<sub>3</sub><sup>-</sup> + SO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>O, pH 7.9,  $\mu = 0.5$ , 25 °C; (10) RSCl + H<sub>2</sub>O, CHCl<sub>3</sub>, 25 °C; (11-14) RS<sup>-</sup> + 4-XC<sub>6</sub>H<sub>4</sub>C<sub>2</sub>Br, MeOH, 25.65 °C (X = Me, H, Cl, Br); (15) Cl<sub>3</sub>CSR + MeOH, 60% MeOH-Et<sub>2</sub>O, 20 °C; (16, 17) Cl<sub>3</sub>CSR + Nu, 60% aqueous MeOH, 20 °C (Nu = OMe<sup>-</sup> benzthiazole, 2-thiolate); (18, 19) RSCl + BuC<sub>2</sub>H, EtOAc, Cl<sub>3</sub>CH, 25 °C; (20) R<sup>1</sup>SR<sup>2</sup> + O<sub>2</sub>(g), V<sub>2</sub>O<sub>5</sub>, 200 °C; (21) R<sup>1</sup>SR<sup>2</sup> + N<sub>2</sub>O<sub>4</sub>, CCl<sub>4</sub>, 10 °C; (22) pK<sub>a</sub> (R<sup>1</sup>R<sup>2</sup>SCH<sub>2</sub>SR<sup>1</sup>R<sup>2</sup>)<sup>2+</sup>, H<sub>2</sub>O; (23) 4-MeC<sub>6</sub>H<sub>4</sub>S(O)R + HCl, 2:1 v/v dioxane-12 M aqueous HCl, 25 °C; (24) PhS(O)R + I<sup>-</sup>, aqueous 4.0 M HClO<sub>4</sub>, 35 °C.

Table III. Values of  $\psi$  as a Function of Intermediate Structure, Solvent, and Temperature

Intermediate	X	Y	Solvent	$T$ °C	$\psi$	Ref	Set in ref
I	SR	Me	40% v/v dioxane-H <sub>2</sub> O	35	-0.874	<i>a</i>	1B
I	OR	Me	40% v/v dioxane-H <sub>2</sub> O	35	-2.65	<i>b</i>	3
I	R	OMe	40% v/v dioxane-H <sub>2</sub> O	35	-1.98	<i>c</i>	5
I	SR	Me	43% w/w MeOAc-H <sub>2</sub> O	0	-1.22	<i>a</i>	2C
I	SR	Me	62% w/w MeOAc-H <sub>2</sub> O	20	-1.07	<i>a</i>	3C
I	OR	Me	62% w/w MeOAc-H <sub>2</sub> O	20	-2.92	<i>b</i>	6
I	R	OEt	70% v/v MeOAc-H <sub>2</sub> O	24.8	-2.65	<i>c</i>	1
II	SR	Me	43% w/w MeOAc-H <sub>2</sub> O	30	-0.455	<i>a</i>	4C
II	SR	Me	43% w/w MeOAc-H <sub>2</sub> O	40	-0.394	<i>a</i>	5C
II	SR	Me	62% w/w MeOAc-H <sub>2</sub> O	30	-0.392	<i>a</i>	6C
II	SR	Me	62% w/w MeOAc-H <sub>2</sub> O	40	-0.276	<i>a</i>	7C
II	OR	Me	62% w/w MeOAc-H <sub>2</sub> O	30.1	-0.967	<i>b</i>	7
II	OR	Me	62% w/w MeOAc-H <sub>2</sub> O	40	-0.767	<i>b</i>	8
II	R	OEt	70% v/v MeOAc-H <sub>2</sub> O	0	-1.80	<i>d</i>	12
II	R	OEt	70% v/v MeOAc-H <sub>2</sub> O	40	-1.78	<i>d</i>	13

<sup>a</sup> This work. <sup>b</sup> Reference 1. <sup>c</sup> M. Charton, *J. Am. Chem. Soc.*, 97, 3691 (1975). <sup>d</sup> Reference 5

8 permits the estimation of many additional  $\psi_{SX}$  values.

It is useful at this point to consider the variation of  $\psi$  with the structure of the intermediates I and II through which the



reaction proceeds. Values of  $\psi$  for acid-catalyzed and for base-catalyzed hydrolysis of various types of ester are given in Table III.

Inspection of the  $\psi$  values in Table III shows that the values obtained for base-catalyzed hydrolysis of alkyl acetates and methyl or ethyl carboxylates are two to three times greater than are the values for alkyl thiolacetates. There are two possible explanations for this observation: (1) the SR and OR groups exert different electrical effects on the reaction; (2) the transition states for the reaction of the alkyl acetates and methyl or ethyl carboxylates resemble the intermediate I to a much greater extent than the transition state for the reaction of the alkyl thiolacetates; as the degree of steric hindrance increases as the resemblance to I increases, this accounts for the magnitude of the  $\psi$  values.

From the structure of I, we expect X and Y to exert only a

Table IV. Results of Correlations with Equation 10

Set	$\psi_{(1)}$	$\psi_{(2)}$	$h$	$R^a$	$F^b$	$r^c$	$s_{est}^d$	$s\psi_{(1)}^d$	$s\psi_{(2)}^d$	$s_h^d$	$n^e$
20F	-0.733	-1.28	1.65	0.975	49.11 <sup>f</sup>	0.985 <sup>f</sup>	0.133	1.24 <sup>g</sup>	1.20 <sup>h</sup>	0.173 <sup>f</sup>	8
21F	-1.69	-0.753	3.21	0.924	61.28 <sup>f</sup>	0.419	0.187	0.200 <sup>f</sup>	0.255 <sup>i</sup>	0.182 <sup>f</sup>	24
22F	-3.99	-21.4	22.1	0.945	16.77 <sup>j</sup>	0.198	0.280	1.17 <sup>k</sup>	5.45 <sup>l</sup>	2.88 <sup>i</sup>	7

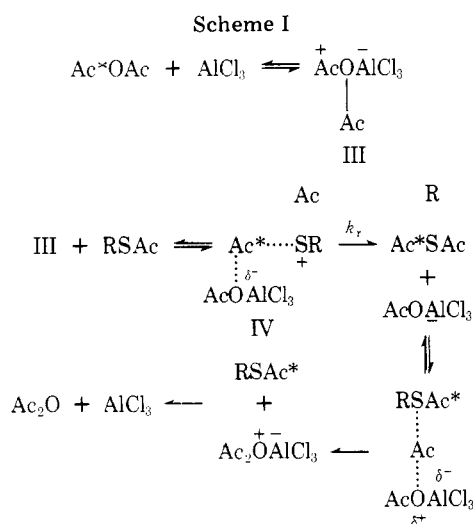
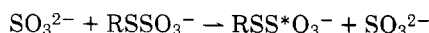
<sup>a</sup> Multiple correlation coefficient. <sup>b</sup>  $F$  test for significance of correlation. Superscript indicates confidence level. <sup>c</sup> Partial correlation coefficient of  $v_{(1)}$  on  $v_{(2)}$ . Superscript indicates CL if  $\geq 90.0\%$ . <sup>d</sup> Standard errors of the estimate,  $\psi_{(1)}$ ,  $\psi_{(2)}$ , and  $h$ . Superscripts indicate CL of the "Student's  $t$ " test. <sup>e</sup> Number of points in the set. <sup>f</sup> 99.9% CL. <sup>g</sup> 20% CL. <sup>h</sup> 50.0% CL. <sup>i</sup> 99.0% CL. <sup>j</sup> 97.5% CL. <sup>k</sup> 95.0% CL. <sup>l</sup> 98.0% CL.

localized effect. The  $\sigma_1$  values for SR groups in Table I give an average value of 0.27. Thus, the localized electrical effect of the OR and SR groups is the same. We may therefore reject the first explanation of the difference in the sensitivity of the base-catalyzed hydrolysis reaction to steric effects.

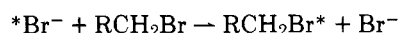
In the acid-catalyzed hydrolysis of the above compounds, the alkyl acetates have  $\psi$  values two to three times greater and the ethyl carboxylates 4.5 to 6 times greater than those of the alkyl thiolacetates. We may account for this situation in terms of the extent to which the transition state resembles the intermediate II. We note that for all three types of substrate, the acid-catalyzed reaction is less susceptible to steric effects than is the base-catalyzed reaction.

The limited results available in Table IV suggest that the temperature effect on the susceptibility of acid-catalyzed hydrolysis to steric effects is generally small, but the solvent effect on the susceptibility of both acid- and base-catalyzed hydrolysis to steric effects is significant. Up to this point we have considered only reactions involving the attack of a nucleophile at the carbon atom of a carbonyl group. We now extend our investigations to a range of reaction types, including attack of thiolate ions on  $ArC_2Br$ , attack of nucleophiles on divalent sulfur, and oxidation of sulfides. The data for these and other reactions of sulfur compounds bearing alkyl groups are given in the Supplementary Material. Results of best correlations with the modified Taft equation are in Table II and the others are in Supplementary Material. Set 8 involves the exchange of acetyl groups between  $^{14}C$ -labeled  $Ac_2O$  and alkyl thiolacetates, catalyzed by  $AlCl_3$ . The reaction is reported to occur at the S atom, with the acetyl groups of the  $Ac_2O$  being equivalent.<sup>7</sup> A possible mechanism is shown in Scheme I. Correlations were carried out with  $v_{SX}$  and  $v_X$ . Best results were obtained with  $v_{SX}$ . This is in accord with a resemblance between the tetrahedral intermediates I and II and the transition state IV.

According to Fava and Illiceto,<sup>8</sup> the rates for the reactions



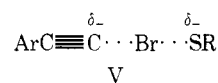
and



show almost the same dependence on steric effects. They conclude that this means that the reaction of the Bunte salt with sulfite goes by the same mechanism as that of the alkylmethyl bromide with bromide ion, that is, by way of a species in which the entering and leaving groups occupy the apical positions of a trigonal bipyramid. Pryor and Smith<sup>9</sup> have observed, however, that for a number of reactions in which the alkyl group is varied, the rate constants give excellent correlations with each other even though the mechanisms are very different. This is not at all surprising, as the success of these correlations merely implies that the steric effect of the alkyl groups is comparable in these different reactions. What this means in terms of the interpretation of correlations with the  $v$  parameters is that if two reactions are both well correlated by the same  $v$  parameter, they may or may not occur by the same or similar mechanisms, while if the two reactions are best correlated by different  $v$  parameters, they probably occur by different mechanisms. We find that the rates for the reaction of the Bunte salts with  $SO_3^{2-}$  give somewhat better correlation (set 9D) with the  $v_X$  constants which were defined from rates of esterification of carboxylic acids<sup>5</sup> than with the  $v_X'$  constants which were defined from rates of reaction of  $RCH_2Br$  with  $^*Br^-$ .<sup>10</sup> Thus, the conclusions of Fava and Illiceto seem unwarranted.

The reaction of alkylsulfenyl chlorides with water (set 10) should presumably be analogous to the reaction of Bunte salts with sulfite. In fact, however, correlation with the  $v_X$  constants is not significant while correlation with the  $v_X'$  constants is poor. Better results are obtained with the  $v_{SX}$  values (set 10C). To obtain the correlation with the  $v_{SR}$  values, it was necessary to calculate an  $v_{SR}$  value for  $R = CH_2-t-Bu$  from eq 8. A value of 1.16 was obtained for  $v_{SCH_2-t-Bu}$ . The results obtained indicate that the hydrolysis of alkylsulfenyl chlorides proceeds by a different mechanism from that of the reaction of Bunte salts with sulfite.

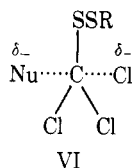
The reaction of 4-substituted phenylethynyl bromides with alkylthiolate ions occurs by displacement of bromine.<sup>11</sup> Data were correlated with the  $v_{SX}$ ,  $v_X$ , and  $v_X'$  constants (sets 11-14C, 11-14D, and 11-14E, respectively). Best results were obtained with the  $v_{SX}$  constants. These constants constitute a measure of the size of the alkyl thiolation. The fact that the correlations obtained with  $v_{SX}$  were not only significant, but in three of the four sets excellent, indicates that steric effects definitely exist. In that case we may rule out a linear transition state such as V, for which steric effects should be negligible.



It might be noted that V is positive for sets 11-14, indicating steric acceleration of the reaction.

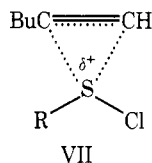
Set 15 is said to proceed by a near  $S_N1$  mechanism involving a chlorine atom on the  $CCl_3$  group of the  $CCl_3SSR$ .<sup>12</sup> In the absence of information on what type of steric effect, if any,

might be encountered here, we have correlated the data with the  $\nu_{SX}$ ,  $\nu_X$ , and  $\nu_X'$  constants. Best results were obtained with the  $\nu_X$  constants, but were only significant at the 90.0% confidence level. Had more data been available, better correlation would probably have been obtained. Sets 16 and 17 are said to occur by a near  $S_N2$  reaction. The leaving group is a Cl atom on the  $CCl_3$  group. Thus, the transition state should be close to VI, where  $Nu^-$  is the nucleophile. What are really required



then for optimum correlation are  $\nu_{SSR}'$  constants, which are of course unavailable. We have carried out correlations with the  $\nu_{SX}$ ,  $\nu_X$ , and  $\nu_X'$  constants. The reaction with  $OMe^-$  gives best results with the  $\nu_X$  constants (set 16D), an excellent correlation being obtained. The reaction with 2-thiolbenzothiazole anion also gives best results with the  $\nu_X$  constants (set 17D), the correlation is good. The value of  $\psi$  is slightly greater for the reaction with 2-thiolbenzothiazole anion than for the reaction with methoxide ion. The small difference between the  $\psi$  values suggests that the  $Nu^-$  to C bond is less than half formed, thereby minimizing interaction between the attacking nucleophile and the SSR group.

The mechanism for the addition of alkylsulfenyl halides to 1-butyne is uncertain. Thus, DiNunno and Scorrano<sup>13</sup> have observed that the regioselectivity of the reaction is anti-Markownikoff and the stereoselectivity is trans. They further note a significant solvent effect on the reaction rate. The addition of arylsulfenyl chlorides to acetylenes has been shown to involve electrophilic attack by a sulfur atom bearing an increment of positive charge.<sup>14</sup> As VII does not resemble any



of the transition states used to define  $\nu$  parameters, the data were correlated with the  $\nu_{SX}$ ,  $\nu_X$ , and  $\nu_X'$  constants. The best results were obtained with the  $\nu_X'$  constants, for which excellent and very good correlations were obtained (sets 18E and 19E).

The mechanism of the reaction of alkyl sulfides with oxygen in the vapor phase over  $V_2O_5$  does not seem to be known. The data have been correlated with the equation

$$\log k_X = \psi \sum \nu_X + h \quad (9)$$

as this equation was previously found applicable to biomolecular nucleophilic substitutions at carbon.<sup>10</sup> The data have also been correlated with the equation

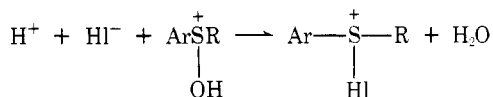
$$\log k_X = \psi_1 \nu_{X(1)} + \psi_2 \nu_{X(2)} + h \quad (10)$$

where  $\nu_{X(1)}$  and  $\nu_{X(2)}$  are the steric parameters for the larger and smaller substituents, respectively ( $\nu_{X(1)} \geq \nu_{X(2)}$ ).

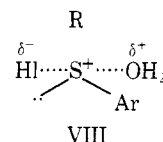
The results of the correlations with eq 10 (set 20F) are given in Table IV, and those with eq 9 (set 20D) are reported in

Table II. Better results were obtained with eq 9, but no conclusion can be reached as to the validity of eq 10 as  $\nu_{X(1)}$  and  $\nu_{X(2)}$  are collinear. The reaction of the alkyl sulfides with  $N_2O_4$  in  $CCl_4$  was also correlated with eq 9 and 10 (sets 21D and F, respectively) with results which are about the same. Thus, both correlations were significant at the 99.9% CL, and whereas the correlation coefficient for 21F is greater than that for 21D, the  $F$  value for 21D is greater than that for 21F.

The  $pK_a$  values of the disulfoniomethanes were also correlated with eq 9 and 10 (sets 22D and 22F). In this set, best results were obtained with eq 10. We are in doubt as to the significance of this correlation, since  $\nu_2$  is more than five times greater than  $\nu_1$ . We are unable to explain this observation, since it seems to us that the larger group should have the greater steric effect. Thus, at least for the sets we have studied involving multiple substitution (sets 20–22), eq 9 seems more useful than eq 10. With regard to sets 23 and 24, according to



Kice, the rate-determining step is the reaction given in eq 11, for which a possible transition state is VIII. This transition



state resembles an  $S_N2$  transition state. Correlations have therefore been carried out with the  $\nu_X$  and  $\nu_X'$  constants. Both sets give somewhat better results with the  $\nu_X$  constants. This suggests that steric effects in these reactions resemble those for the reaction of Bunte salts with sulfite.

In conclusion, data for a number of reactions involving alkyl groups attached to sulfur has been successfully correlated with the modified Taft equation using the  $\nu_{SX}$  parameters defined here or the  $\nu_X$  or  $\nu_X'$  parameters previously defined. Of the 24 sets studied, 23 gave significant results. Thus, the effect of alkyl groups attached to sulfur upon reaction rates and equilibria is largely, if not wholly, steric.

**Supplementary Material Available:** Tables of the data used in the correlations and the results of all the correlations (6 pages). Ordering information is given on any current masthead page.

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