gas, isobutylene, and bromine in carbon tetrachloride [δ 1.90 (six protons) and 3.88 (two protons)]. From the nmr the product was judged to be about 90% pure.

Pyrolysis of Hyponitrites.—In a 10-ml, round-bottom flask fitted with a reflux condenser, 0.66 g (3.79 mmol) of *t*-butyl hyponitrite[13] was slowly mixed with 3.86 g (19.1 mmol) of tri-*n*-butylphosphine while external control kept the temperature near 55° (below 50° the two liquids appear to be immiscible). After stirring for 20 hr at this temperature, *t*-butyl alcohol was detected in 35% yield by measuring peak areas by vpc from an SE-30 10-ft column operated at 60°. Standards for comparison in calculating yield consisted of prepared mixtures of tri-*n*-butylphosphine and *t*-butyl alcohol. *Caution.* In one experiment with inadequate external control of the reaction temperature, the mixture of *t*-butyl hyponitrite and tri-*n*-butylphosphine became explosive.

In a similar reaction, 0.1471 g (0.608 mmol) of benzyl hyponitrite, mp 44–46° dec,[17] and 0.5846 g (2.89 mmol) of tri-*n*-butylphosphine were stirred overnight at room temperature. The initially clear solution became dark brown after 24 hr and then yellow. Benzyl alcohol was detected in 38.2% yield by vpc. Standards for comparison in calculating yield consisted of prepared mixtures of tri-*n*-butylphosphine and benzyl alcohol.

Registry No.—Benzyl nitrite, 935-05-7; *t*-butyl nitrite, 540-80-7.

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[17] J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2071 (1931).

The Timing of Covalency Changes in Nucleophilic Substitutions at Sulfenyl Sulfur. The Influence of *meta* and *para* Substituents on the Rate of Reaction of Aryl Bunte Salts with Cyanide Ion[1]

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Nucleophilic substitution at a sulfenyl sulfur, shown in a generalized representation in eq 1, is one of

$$\mathrm{Nu^- + R{-}S{-}Y \longrightarrow R{-}S{-}Nu + Y^-} \qquad (1)$$

the most important and fundamental reactions of organic sulfur chemistry.[2] As a consequence, detailed knowledge about all aspects of its mechanism is highly desirable.

In a classic study, Fava and Ilceto[3] have shown, through examination of the effect of changes in R on rate, that the steric requirements of the displacement reaction

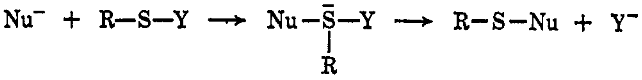
$$\mathrm{{}^*SO_3{}^{2-} + R{-}S{-}SO_3{}^- \longrightarrow R{-}S{-}{}^*SO_3{}^- + SO_3{}^{2-}} \qquad (2)$$

are remarkably similar to those for bimolecular nucleophilic substitution at primary carbon (eq 3). They

$$\mathrm{Nu^- + RCH_2Y \longrightarrow RCH_2Nu + Y^-} \qquad (3)$$

have suggested that this means that the preferred transition-state geometry for nucleophilic substitution at sp^3 carbon and sulfenyl sulfur is the same, namely, a trigonal bipyramid with the entering and leaving groups occupying the apical positions.

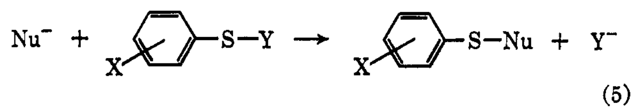
This clarification of transition-state geometry does not, however, tell us anything about the relative progress of bond making *vs.* bond breaking in the transition states of eq 1 or 2. In SN2 displacements at sp^3 carbon bond making and bond breaking are synchronous. The same could well be true for nucleophilic displacements at sulfenyl sulfur, but, at the same time, given the ability of sulfur to expand its valence shell, serious consideration must also be given to the possibility that bond making may well be ahead of bond breaking when the transition state is reached. In the most extreme representation one might even conceive of an actual intermediate (I) being formed during the reaction, *i.e.*



$$\mathrm{Nu^- + R{-}S{-}Y \longrightarrow Nu{-}\underset{\underset{\textstyle R}{|}}{\bar{S}}{-}Y \longrightarrow R{-}S{-}Nu + Y^-}$$

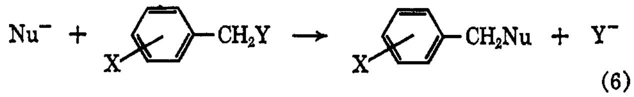
I (4)

One way of probing this matter of the timing of the several covalency changes involved in eq 1 is through measurement of the effect of selected *meta* and *para* substituents on the rate of a substitution of the type



(5)

One can then compare the results with those for analogous displacements at sp^3 carbon (eq 6) and silicon (eq 7). Those substitutions at silicon, where bond making



(6)

$$\mathrm{Nu^- + R_3Si{-}Y \longrightarrow R_3Si{-}Nu + Y^-} \qquad (7)$$

is well ahead of bond breaking in the transition state, owing to the use of silicon d orbitals, are characterized[4] by a very pronounced dependence of rate on substituents and large positive values of ρ.* In contrast, substitutions at a benzylic sp^3 carbon (eq 6), where bond making and brond breaking are truly synchronous, show relatively little dependence of rate on X and no satisfactory correlation with the Hammett equation, rates frequently being faster for both electron-withdrawing and electron-releasing substituents than they are for the unsubstituted compound.[5] There is thus reason to feel that, if the substitution at sulfenyl sulfur (eq 5) involves the use of the d orbitals on that atom, as in eq 4, it will show a considerably different response to changes in the nature of X than if it involves essentially synchronous bond making and bond breaking.

The specific example of eq 5 examined in the present work was the reaction of cyanide ion with S-aryl thio-

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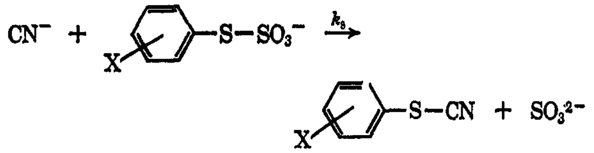
[1] This research supported by the National Institutes of Health under Grant GM-12104.

[2] (a) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959); (b) O. Foss in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Oxford, Chapter 9, 1961.

[3] A. Fava and A. Ilceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958).

[4] (a) O. W. Steward and O. R. Pierce, *ibid.*, **83**, 1916 (1961); (b) for a summary of all studies of this type, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 127–146.

[5] (a) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962); (b) R. Fuchs and D. M. Carlton, *J. Amer. Chem. Soc.*, **85**, 104 (1963); (c) for a summary of various earlier data, see A. Streitwieser, *Chem. Rev.*, **56**, 591 (1956).


(8)

sulfates (eq 8).[6] Reaction rates can be followed spectrophotometrically (see Experimental Section). The reactions were studied in aqueous carbonate–bicarbonate buffers (pH 9.00–10.36). Other experiments showed that the rate of disappearance of the Bunte salt in the absence of cyanide ion at these pH's was negligible. The reactions were run using a large stoichiometric excess of cyanide over Bunte salt. The concentration of free cyanide ion was varied by using a fixed amount of sodium cyanide (0.016 M) for all runs and varying the pH at which runs were carried out. Since K_a for HCN is 7×10^{-10}, only 41% of the total cyanide is present as CN^- at pH 9, while at pH 10.36 94% is present as CN^-. The initial concentration of Bunte salt was varied over the range $1.0–8.0 \times 10^{-4}$ M. Because the final optical density of the solution shows significant drift (due, presumably, to subsequent reactions of ArSCN), rate constants were determined from the initial rate of change of the optical density of the solution, assuming the kinetics of eq 8 to be given by

$$\text{initial rate} = k_8(\text{ArSSO}_3^-)_0(\text{CN}^-) \tag{9}$$

The constancy of k_8 for a given Bunte salt as determined from

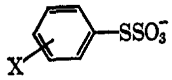
$$k_8 = \frac{\text{initial rate}}{(\text{ArSSO}_3^-)_0(\text{CN}^-)}$$

for a series of runs in which both the initial concentration of Bunte salt and the concentration of cyanide ion were varied (see Experimental Section for typical results) established that the kinetics of reaction 8 are indeed correctly given by eq 9.

Table I lists the rate constants for the reaction of six *meta-* and *para-*substituted S-aryl thiosulfates with cyanide ion at 25° in aqueous solution at an ionic strength of 2.0. Examination of Table I reveals that the rate constant for eq 8 shows no obvious dependence on the electron-withdrawing or electron-releasing character of the substituent attached to the aromatic ring. Although one electron-withdrawing substituent, *p*-Cl (σ = +0.23), causes a fairly substantial increase in rate, others, much more strongly electron withdrawing, such as *m*-NO_2 (σ = +0.71) and *p*-NO_2 (σ = +0.78), lead to only small increases in rate. These are, in fact, not much larger than that caused by *p*-CH_3 (σ = −0.17), an electron-releasing substituent. Because of the necessity of evaluating k_8 from initial rate measurements the values given in Table I are probably accurate to no better than ±15%. This could perhaps be responsible for the apparent anomalously high rate for the *p*-Cl compound. However, even if the k_8 values were subject to even greater uncertainty (±50%) this would not change the basic conclusion from these results, which is that the electron density at the sulfenyl sulfur must be essentially the same in the transition state for eq 8 as it is in the Bunte salt itself. This is hardly in accord with what would be expected if the mechanism were as shown in eq 4, or in any variant of it in which bond making is significantly ahead of bond breaking at the transition state. We conclude that in the transition state for eq 8 the making of the new bond has progressed no further than the breaking of the old one. Its structure should therefore be represented as

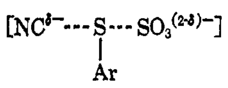
TABLE I

RATE CONSTANTS FOR REACTION OF CYANIDE ION WITH ARYL BUNTE SALTS[a]



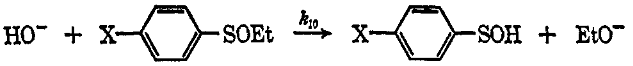
X[b]	$k_8 \times 10^2$, M^{-1} sec^{-1}	$(k_X/k_{p\text{-H}})$
p-CH_3	1.0	1.1
p-H	0.91	(1.0)
p-Cl	1.6	1.8
p-Br	1.2	1.3
m-NO_2	1.1	1.2
p-NO_2	1.2	1.3

[a] All runs were at 25° in water at pH 10.36 and an ionic strength of 2.0. [b] Registry numbers are given in consecutive order: 16727-96-1, 16723-24-3, 16723-25-4, 16723-26-5, 16723-27-6, 16723-28-7.



$$[\text{NC}^{\delta-}\cdots\underset{\substack{|\\ \text{Ar}}}{\text{S}}\cdots\text{SO}_3^{(2-\delta)-}]$$

Despite the availability of the d orbitals on sulfur the timing of the various covalency changes in this nucleophilic substitution seems to be closely comparable with the timing for an SN2 reaction at sp^3 carbon and quite different from the timing for substitutions at silicon. This conclusion is also in accord with the results of another recent study[7] dealing with the effect of substituents on the rate of a nucleophilic substitution involving aryl sulfenyl compounds. Equation 10 represents the rate-determining step in the alkaline hydrolysis of a series of *p*-substituted ethyl benzenesulfenates.


(10)

The observed[7] variation of k_{10} with X was as follows: X, $(k_X/k_{p\text{-H}})$; CH_3, 1.21; Cl, 3.0; CF_3, 1.47. Although substituents exert generally a somewhat larger effect than in the Bunte salt–cyanide reaction, one still finds that a strong electron-withdrawing group, *p*-CF_3 (σ = +0.54), accelerates the rate considerably less than *p*-Cl and not much more than *p*-CH_3.

Acceleration of the rate by both electron-withdrawing and electron-releasing *para* substituents has, as noted earlier, also been observed in a number of nucleophilic displacements involving substituted benzyl halides (eq 6).[5] Unlike the two substitutions at sulfenyl sulfur, however, in most of the benzyl halide reactions the acceleration produced by a strong electron-withdrawing substituent like *p*-NO_2 clearly exceeds that produced by either a weaker electron-withdrawing one like *p*-Cl or an electron-releasing one like *p*-CH_3. One case (Y = Cl, Nu = $S_2O_3^{2-}$) is known,[5b] however, where $k_{m\text{-NO}_2}/k_{p\text{-H}}$ is slightly less than $k_{p\text{-Cl}}/k_{p\text{-H}}$.

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[6] H. B. Footner and S. Smiles, *J. Chem. Soc.*, **121**, 2887 (1925).

[7] C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

[8] A. Fava, private communication.

In conclusion one should also note some unpublished work by Fava,[8] in which he studied the effect of *para*

$$^{*}SO_3^{2-} + ArSSO_3^- \xrightarrow{k_{11}} ArS\text{—}\overset{*}{S}O_3^- + SO_3^{2-} \qquad (11)$$

substituents on the rate of the exchange reaction in eq 11 involving aryl Bunte salts. The variation of k_{11} with *para* substituent X was as follows: X, ($k_{p\text{-X}}/k_{p\text{-H}}$); CH_3, 0.76; Cl, 1.70; NO_2, 5.22. Even though in this instance the rate for the *p*-NO_2 compound is considerably faster than the rate for the *p*-chloro compound, substituent effects are still rather small ($\rho = +0.85$), and Fava[8] has concluded, like ourselves and Brown and Hogg,[7] that little if any d orbital participation involving sulfur occurs in such substitutions at sulfenyl sulfur.

Experimental Section

Preparation of Bunte Salts.—Except for the *m*-nitrophenyl compound[9] all of the Bunte salts were first prepared as pyridinium S-aryl thiosulfates.[9] They were then converted into the sodium S-aryl thiosulfates using the ion-exchange procedure previously described.[9] Analytical data were obtained on those salts which had not been previously prepared. All were isolated as the monohydrate: sodium S-*p*-tolyl thiosulfate (Calcd for $C_7H_7NaO_3S_2 \cdot H_2O$: C, 34.42; H, 3.71. Found: C, 34.41; H, 3.88), sodium S-*p*-chlorophenyl thiosulfate (Calcd for $C_6H_4ClNaO_3S_2 \cdot H_2O$: C, 27.23; H, 2.29. Found: C, 27.28; H, 2.43), sodium S-*p*-bromophenyl thiosulfate (Calcd for $C_6H_4BrNaO_3S_2 \cdot H_2O$: C, 23.34; H, 1.96. Found: C, 23.26; H, 2.03), sodium S-*p*-nitrophenyl thiosulfate. (Calcd for $C_6H_4NNaO_5S_2 \cdot H_2O$: C, 26.18; H, 2.20. Found: C, 26.00; H, 2.29).

Procedure for Kinetic Runs.—Bicarbonate–carbonate buffer solutions of the proper pH and containing the desired amount of sodium cyanide were made up volumetrically. A solution of the appropriate Bunte salt in water was made up separately. The reaction vessel used for the kinetic runs was the type described in another paper.[10] For a run measured aliquots of the buffer-cyanide and the Bunte salt solutions were placed separately in chambers A and B of the reaction vessel and brought to temperature. They were then mixed rapidly, and the resulting solution was poured into the 1-cm cell which was attached to the side of chamber B. The apparatus was placed in the cell compartment of Cary Model 15 spectrophotometer, which was equipped to permit thermostatting of the 1-cm cell. The decrease in the absorbance of the reaction solution was then followed at a wavelength between 260 and 268 mμ. Because the final optical density of the solution tended to drift significantly, rates were evaluated from the initial rate of change of the optical density. This was determined by drawing a line tangent to the initial portion of the absorbance *vs.* the time curve. At least three separate runs were made for each set of reaction conditions. Some typical results obtained upon variation of the initial concentrations of Bunte salt and cyanide ion are shown in Table II.

TABLE II

$(ArSSO_3^-)_0$, M	(CN^-), M	$-d(ArSSO_3^-)_0/dt$, M sec^{-1}	$k_8 = \dfrac{-d(ArSSO_3^-)_0/dt}{(ArSSO_3^-)_0(CN^-)}$
8×10^{-4}	1.5×10^{-2}	1.1×10^{-7}	0.0092
4×10^{-4}	1.5×10^{-2}	0.55×10^{-7}	0.0091
4×10^{-4}	0.66×10^{-2}	0.26×10^{-7}	0.0098

(The data in question are for the S-phenyl Bunte salt.) Similar sorts of results were found with the other Bunte salts. It therefore seems clear that the Bunte salt–cyanide reaction is first order in each reactant, and also that the procedure of determining its rate constant from initial rates does not lead to any significant error.

Registry No.—Cyanide ion, 57-12-5.

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[9] J. L. Kice, J. M. Anderson, and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **88**, 5245 (1966).

[10] J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966).

Chemistry of Trialkylthiomethyl Ions. II. A Convenient Synthesis of Tetrathioorthocarbonate Esters

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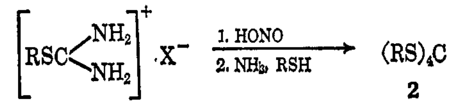
Received March 26, 1968

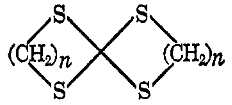
Our investigation into the chemistry of trimethylthiomethyl cation (1) has utilized the corresponding tetrathioorthocarbonate esters (2) as precursors for 1 and its homologs.[1] Orthocarbonates of this type have been known for many years but their synthesis has been indirect and laborious. Arndt[2,3] and, later, Backer and Stedehouder[4] prepared several aromatic tetrathioorthocarbonates in unspecified yields by nitrosation of isothiouronium salts followed by the decomposition of the nitrosated adduct in aqueous or methanolic ammonia (eq 1). This method was extended to a series of alkyl tetrathioorthocarbonates in yields averaging about 20%.[4–6]



$$\left[RSC\begin{matrix}NH_2\\NH_2\end{matrix}\right]^+ X^- \xrightarrow[2.\ NH_3,\ RSH]{1.\ HONO} \underset{\mathbf{2}}{(RS)_4C} \qquad (1)$$

More recently the preparation of 2 has been achieved by a sequence of reactions involving removal of the proton from an orthothioformate and thioalkylation of the resulting anion with the appropriate disulfide (eq 2).[7–9] The synthesis of the spiran derivative 3, a special case of 2, by methods whose general applicability has not been tested, was reported by Johnson[10] and by D'Amico and Campbell.[11]

$$(RS)_3CH \xrightarrow[\text{or } n\text{-}C_4H_9Li]{\overline{N}H_2,\ NH_3} (RS)_3C^- \xrightarrow{(RS)_2} \mathbf{2} \qquad (2)$$



3, $n = 2$ or 3

We have found that trimethylthiomethyl fluoroborate (1), which is an easily prepared and stable material,[1] serves as a convenient intermediate in the preparation

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[1] W. P. Tucker and G. L. Roof, *Tetrahedron Lett.*, 2747 (1967).

[2] F. Arndt, *Ann.* **384**, 322 (1911).

[3] F. Arndt, *ibid.*, **396**, 1 (1913).

[4] H. J. Backer and P. L. Stedehouder, *Rec. Trav. Chim. Pays-Bas*, **52**, 1039 (1933).

[5] H. J. Backer and P. L. Stedehouder, *ibid.*, **52**, 923 (1933).

[6] We have prepared most of the compounds listed in Table I by this method but always in low and unsatisfactory yields.

[7] A. Fröling and J. F. Arens, *Rec. Trav. Chim. Pays Bas*, **81**, 1009 (1962).

[8] D. Seebach, *Angew. Chem. Intern. Ed.*, **6**, 442 (1967).

[9] Yields in this reaction are on the order of 50% but we have encountered difficulty in separation of the desired product from the tetrakisalkylthioethylene which is produced in a side reaction.[7]

[10] T. P. Johnson, C. R. Stringfellow, and A. Gallagher, *J. Org. Chem.*, **27**, 4068 (1962).

[11] J. J. D'Amico and R. H. Campbell, *ibid.*, **32**, 2567 (1967).