In conclusion one should also note some unpublished work by Fava,[8] in which he studied the effect of *para*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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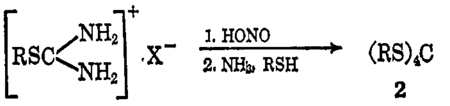
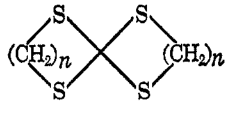
Our investigation into the chemistry of trimethylthiomethyl cation (1) has utilized the corresponding tetrathioorthocarbonate esters (2) as precursors for **1** and its homologs.[1] Orthocarbonates of this type have been known for many years but their synthesis has been indirect and laborious. Arndt[2,3] 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]



(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).

of a variety of tetrathioorthocarbonates in good yields. Although the reaction between **1** and thiols represents an equilibrium (eq 3), the removal of the very volatile

$$\underset{\mathbf{1}}{(CH_3S)_3C^+BF_4^-} + 4RSH \rightleftharpoons \underset{\mathbf{2}}{(RS)_4C} + 3CH_3SH + HBF_4 \quad (3)$$

methanethiol displaces the reaction in favor of **2**. A second equilibrium is thereby established (eq 4),

$$\mathbf{2} + H^+ \rightleftharpoons (RS)_3C^+ + RSH \quad (4)$$

but the formation of **2** can be favored by using excess thiol (method A) or by using sodium bicarbonate to remove the acid which promotes the equilibrium (method B). Method A was employed for the synthesis of alkyl tetrathioorthocarbonates and method B was used for the preparation of aryl derivatives.

The properties and yields of the tetrathioorthocarbonates prepared from **1** are given in Table I.

Table I

Tetrathioorthocarbonate Esters (**2a–h**)

R	Method of preparation[a]	% yield[b]	Recrystn solvent	Mp, °C[c]	Lit. mp, °C
CH_3 (**a**)	A	97	95% EtOH	65	65[d]
C_2H_5 (**b**)	A	88	95% EtOH	31–32	33–33.5[d]
n-C_3H_7 (**c**)	A	86[e]		[f]	
i-C_3H_7 (**d**)	A	92	95% EtOH	60–61.5	61.5[d]
C_6H_5 (**e**)	B	85	C_6H_6	159–160	159[g,h]
p-$CH_3C_6H_4$ (**f**)	B	85	C_6H_6-heptane	145–146	147[i]
p-ClC_6H_4 (**g**)	B	90[j]	C_6H_6	210–211 dec	212–213[g]
β-$C_{10}H_7$ (**h**)	B	86[k]	$CHCl_3$	189–192 dec	134–136[h]

[a] See Experimental Section. [b] Yields are based on unrecrystallized products. [c] Melting points were taken on a Thomas–Hoover melting point apparatus and are uncorrected. [d] Reference 5. [e] *Anal.* Calcd for $C_{13}H_{28}S_4$: C, 49.94; H, 9.03. Found: C, 50.10; H, 8.90. [f] Bp 123° (0.16 mm). [g] Reference 3. [h] Reference 4. [i] Reference 2. [j] *Anal.* Calcd for $C_{25}H_{16}Cl_4S_4$: C, 51.20; H, 2.75. Found: C, 51.43; H, 2.83. [k] The melting point of our product differed markedly from that reported in ref 4. A good elemental analysis was obtained. *Anal.* Calcd for $C_{41}H_{28}S_4$: C, 75.88; H, 4.35. Found: C, 75.63; H, 4.40.

Experimental Section

Tetrathioorthocarbonate Esters (2). Method A.—A stirred mixture of 1.15 mol of alkanethiol and 0.1 mol of trimethylthiomethyl fluoroborate (**1**) was refluxed for 48 hr.[12] After cooling, 75 ml of 10% sodium hydroxide was added, and the organic layer was separated and washed three times with 10% sodium hydroxide and three times with water. Volatile materials were removed *in vacuo* and the crude product was purified by recrystallization or by distillation under reduced pressure.

Method B.—A stirred mixture of 0.06 mol of arylthiol, 0.01 mol of **1**, and 0.01 mol of solid sodium bicarbonate in 50 ml of dry benzene was refluxed for 12 hr. After removal of the solvent *in vacuo* the residue was washed with 10% sodium hydroxide and then three times with water. The crude product was dried before recrystallization from an appropriate solvent.

Registry No.—**2a,** 6156-25-8; **2b,** 16876-57-6; **2c,** 16876-58-7; **2d,** 16876-59-8; **2e,** 14758-47-5; **2f,** 16915-94-9; **2g,** 16876-61-2; **2h,** 16876-62-3.

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(12) Dry 1,2-dichloroethane was used as a solvent with both methane and ethanethiol. In the first case, methanethiol was bubbled into a suspension of **1** at room temperature until homogeneity was achieved. In the ethyl case, the solvent was used to obtain a higher reaction temperature.

A Convenient Gas Chromatographic Method for Determining Activation Energies of First-Order Reactions

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In the study of the vapor phase thermal isomerization of stilbene it was necessary to determine the activation energy for this first-order reaction rapidly and reasonably accurately. The gas chromatographic method developed to do this should provide a generally useful technique for the rapid determination of activation energies using exceedingly small amounts of compounds and very simple equipment. We envisage this technique as being particularly valuable for the rapid examination of reactions of a series of structurally related organic compounds.

In its simplest form, the technique uses a gas chromatographic injection chamber as a constant time and temperature flow reactor. The reaction is rapidly quenched by the gas chromatographic column which is at a temperature sufficiently low to preclude reaction in this region, yet at a temperature high enough to produce an adequate separation of the reactant and products in a reasonable period of time. The extent of conversion is then determined as a function of the injection block equilibrium temperature while maintaining the same flow rate at each temperature and assuring reproducible injection technique. The conversion can be related to the activation energy in the following way.

$$\ln \ln \left(\frac{C_0}{C}\right) = -\frac{E_a}{RT} + \ln (At)$$

This equation was obtained by taking the logarithims of the integrated first-order rate expression, $\ln (C_0/C) = kt$, and the Arrhenius equation, $k = A \exp(-E_a/RT)$, and eliminating $\ln k$. With a constant preexponential factor A over the range of injector block temperatures studied, as well as a constant time t in the block, it is evident that the slope of a plot of $\ln \ln (C_0/C)$ *vs.* $1/T$ yields the Arrhenius activation energy as $-E_a/R$.

Three unrelated reactions were chosen to test the method; first, the isomerization of *cis*-stilbene; second, the Diels–Alder retrogression of norbornene; and third, the Claisen rearrangement of allyl phenyl ether. All of the measurements described were made on a Wilkins Aerograph Model 600-D gas chromatograph, which was modified only by embedding a thermocouple into a cavity of the injection block, surrounding the block with extra insulation, and adding a Matheson precision gas flow meter. A second thermocouple, placed in the flow section of the block and centered for maximum temperature response, indicated that the block temperature was at the most 2–3° higher at thermal equilibrium than that of the carrier gas. Typical sample sizes were 0.2 to 0.4 μl of neat liquid, permitting the determination of an activation energy with less than 50 μl of sample which need not be pure so long as the impurities do not interfere analytically, and in a period on the order of

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(2) National Institutes of Health Predoctoral Fellow 1965–1966.