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

Walter W. Schmiegel,[1] Fred A. Litt,[2]
and Dwaine O. Cowan

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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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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(1) National Science Foundation Graduate Trainee, 1965–1968.

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

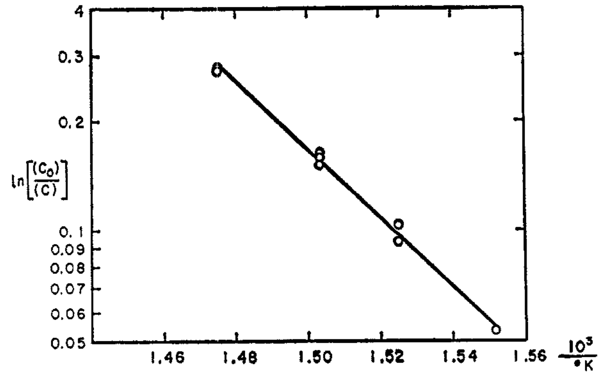

Figure 1.—Semilogarithmic plot of ln (C_0/C) *vs.* reciprocal of injection block absolute temperature for *cis*-stilbene isomerization.

several hours after devising a suitable product analysis. For the analytical separations 0.125 in. × 5 ft packed columns were used: for the stilbenes, 5% SE-30, on 60/80 Chromosorb W; for the allyl phenyl ether system, 2% xylenyl phosphate, on 80/100 Chromosorb G; for the norbornene system, 15% Apiezon L, on 60/80 Chromosorb W.

Figure 1 is a semilogarithmic plot of ln (C_0/C) *vs.* the reciprocal of the absolute temperature of the injection block for the isomerization of *cis*-stilbene. The activation energy obtained from the slope of this plot is 42.6 ∓ 1.0 kcal mol^{-1} (lit.[3] 42.8 kcal mol^{-1}). Similarly the activation energy for the Diels-Alder retrogression of norbornene was found to be 41.3 ∓ 1.5 kcal mol^{-1} (lit.[4] 42.8 ∓ 0.6 kcal mol^{-1}), and that for the Claisen rearrangement of allyl phenyl ether was found to be 33.2 ∓ 1.5 kcal mol^{-1} (lit.[5] 32.2 kcal mol^{-1} in Carbitol).

Several notes of caution should be given. Owing to the nature of the logarithmic function the spread of experimental points is expected to be greater at low rather than at high conversions under conditions of equal precision in temperature measurement, flow rate regulation, sample introduction, and analysis. Nonlinearity, however, is also observed at very high temperatures, where appreciable back reaction becomes evident for *cis*-stilbene or, in the case of the Claisen rearrangement of allyl phenyl ether, where a concurrent reaction with a greater temperature coefficient becomes important. In the allyl phenyl ether reaction at high temperatures cleavage to phenol competes favorably with *ortho* rearrangement and is the preferred reaction above 380° at a helium flow rate of 6 cc min^{-1} with the particular block geometry of our instrument. The activation energy given in the case of allyl phenyl ether is that for its disappearance, determined from the linear, lower temperature portion of the plot analogous to Figure 1.

An increase in flow rate from 10 to 14 cc min^{-1} did not afford an experimentally significant difference (>1.0 kcal mol^{-1}) in activation energy for the *cis*-stilbene isomerization, although it decreased the extent of reaction.

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On a Supposed Preparation of α-Chloroanisole

MAURICE SHAMMA, LUDVIK NOVAK, AND MICHAEL G. KELLY

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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Because of a need for α-chloroanisole (chloromethyl phenyl ether) in connection with some synthetic work in progress, we had a chance to repeat the most recent preparation for this compound given in the literature.[1] Following the instructions given in ref 1, anisole in methylene chloride solution was brought to reflux temperature, and sulfuryl chloride was added dropwise, exactly as specified. The product was distilled and exhibited the physical constants quoted, namely, bp 74–77° (13 mm) and n^{25}D 1.5342.

To our surprise, however, the product was insensitive to silver nitrate solution and did not react with benzyldimethylamine.[2] The nmr spectrum in $CDCl_3$ solution clearly showed two doublets centered at δ 6.78 and 7.31 (J = 10 cps), characteristic of an aromatic AB system. It therefore appeared probable that our product was *p*-chloroanisole rather than the expected α-chloroanisole. The preparation was repeated four times with identical results, so that aromatic chlorination always occurred. Spectral (nmr and ir) comparison of the synthetic material with an authentic sample (Eastman Distillation Products) of *p*-chloroanisole indicated the two compounds to be essentially identical, but gas chromatography showed our product to be only 90% pure, as specifically stated in the preparation given.[1]

Aromatic chlorination by means of sulfuryl chloride is not unusual, and has been amply recorded in the literature.[3] It is claimed that the procedure utilized in ref 1 is that of Bordwell and Pitt. These authors prepared a number of α-chloromethyl sulfides by this procedure, but it was never suggested that the method could be extended to prepare α-chloromethyl ethers.[4]

It is easy to see in retrospect how *p*-chloroanisole could be mistaken for α-chloroanisole. Besides having identical elemental analyses, the two compounds possess very close boiling points and refractive indices as indicated in Table I.

TABLE I

	Bp, °C (mm)	nD
p-Chloroanisole	90–92 (18)	1.5351 at 20°
α-Chloroanisole	88–90 (15)	1.5362 at 20°

In conclusion, therefore, the best method for preparing α-chloroanisole is still that used by Schollkopf and coworkers.[5] The supposed preparation of α-chloroanisole given in ref 1 is at best a procedure for obtaining slightly impure *p*-chloroanisole.

Registry No.—α-Chloroanisole, 6707-01-3; *p*-chloroanisole, 623-12-1.

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