Table I. NMR Parameters[a] (in Hertz at 270 MHz) of the CH_2 Protons in 1-Methyl-3-phospholene 1-Oxide

	Neat	9% solution ($CDCl_3$)
$\delta_A - \delta_B$	−53.2	+35.5[b]
$\lvert^2J_{AB}\rvert$	17.4	17.64
$^2J_{AP}$	±14.32	±16.04[c]
$^2J_{BP}$	∓7.95	∓9.18[c]

[a] The olefinic protons H_C give rise to a clean doublet due to coupling with ^{31}P and show no evidence of coupling with the methylene protons H_A and H_B. [b] Absolute shifts: H_A, 2.59; H_B, 2.47 ppm. [c] H_A in I is cis to P→O in accordance with J and δ assignments made for 1,2,5-trimethyl-3-phospholene 1-oxide.[7]

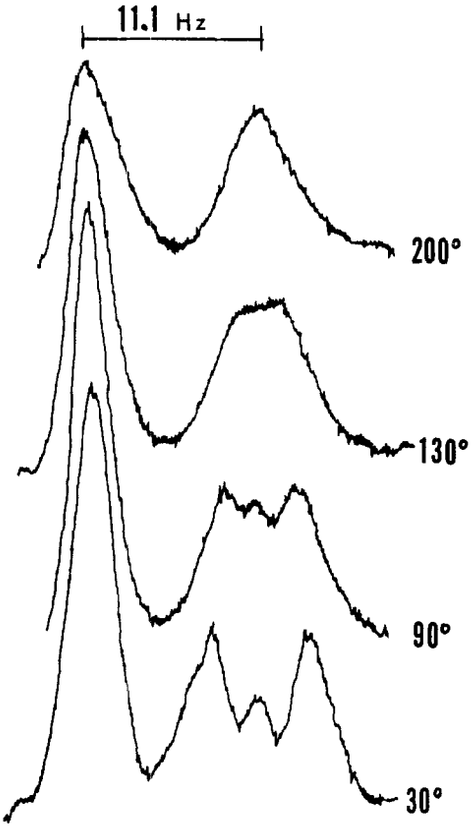

Figure 3. ^1H NMR spectrum (Varian A-50/60) of the CH_2 protons in a neat sample of 1-methyl-3-phospholene 1-oxide at various temperatures.

trations: neat sample I, 50 and 9% *solutions of* I in $CDCl_3$. The spectrum of the neat sample had to be recorded at 50 °C because of the difficulty of preventing the sample from crystallizing at room temperature. The others were recorded at room temperature. In view of the temperature effect discussed below, the spectrum of the neat sample is, therefore, not directly comparable with the corresponding 60-MHz spectrum. The spectra of the neat compound and of the 9% solution, however, are satisfactorily interpreted in terms of the AB part of ABX spectra,[6] with the parameters summarized in Table I. Computer-simulated spectra of I for the two cases of Table I are also shown in Figure 2. While the coupling constants are only slightly affected (to within 12%) by dilution, the chemical shifts reflect an inversion in the relative shielding experienced by A and B.

The spectrum of the 50% solution in Figure 2 cannot be understood as an AB part of an ABX pattern; however, computer simulations revealed that it could qualitatively be explained as the AA'BB' part of an AA'BB'X pattern. Exact parameters were not obtained because of the insufficiency of actual experimental values provided by the spectrum in Figure 2.

These observations show clearly that the methylene protons A and B of I are nonequivalent, basically giving rise to an AA'BB' spectrum, which degenerates, under proper conditions of the environment (dilution, temperature), into apparent ABX or even A_2X spectra.

The temperature dependence of a neat sample at 60 MHz is shown in Figure 3. With increasing temperature the spectrum becomes simpler and more symmetrical, in a way similar to the effect observed upon dilution at 60 MHz. The underlying reason for this is, as in the dilution study, not a dynamical but a shielding effect.

We believe that the reason for these observations, based solely on the present NMR study, is a matter of speculation. It is, however, plausible to suggest that various degrees of molecular association or short-range molecular ordering are the basis of these interesting shielding effects.

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Registry No.—I, 930-38-1.

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A Novel Synthesis of Trifluoromethylthioacetic Acid

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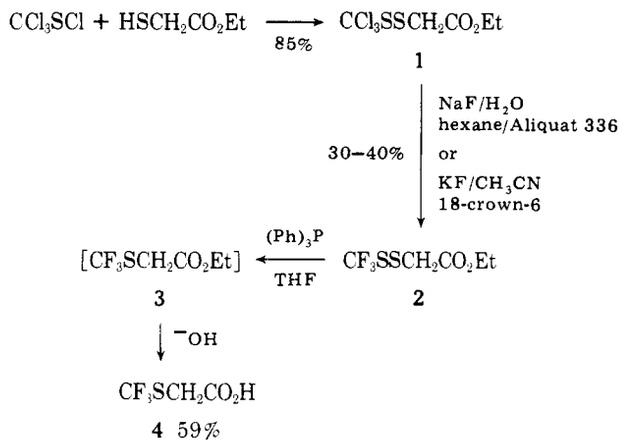
The synthesis of trifluoromethylthioacetic acid,[1,2] an important intermediate in the preparation of the semisynthetic cephalosporin antibiotic cefazaflur (SKF 59962),[3] is made difficult by the limited methods available for the elaboration of the trifluoromethylthio moiety.[4] We wish to report a facile route to this compound from ethyl mercaptoacetate which provides a potentially useful method for the conversion of thiols to trifluoromethyl sulfides.

Chlorination of a methyl group adjacent to sulfur followed by halogen exchange with an inorganic fluoride at elevated temperature is one of the most widely used methods for the synthesis of a trifluoromethylthio group.[5] Thus, our initial approach to the synthesis of trifluoromethylthioacetic acid was to prepare the corresponding trichloride and convert it by existing methods to the trifluoride. However, in methylthioacetic acid the methylene adjacent to the sulfur is sufficiently activated by the carboxyl group to preclude selective chlorination of the methyl.

As an alternate approach we tried fluorination of the readily available disulfide **1**, followed by sulfur extrusion to give an ester of trifluoromethylthioacetic acid. Although the fluoride exchange could not be carried out by the usual method, i.e., antimony trifluoride–antimony pentachloride, we discovered that it occurred rapidly under mild conditions using phase transfer catalysis. Treatment of a hexane solution of **1**, pre-

pared by condensing trichloromethylsulfenyl chloride with ethyl mercaptoacetate, with a twofold excess of aqueous sodium fluoride at room temperature in the presence of a catalytic amount of Aliquat 336[6] gave the trifluoro disulfide **2** in 35% yield. Alternatively, addition of **1** to a cold suspension of



potassium fluoride in acetonitrile containing a catalytic amount of 18-crown-6 also yielded **2** (41%). To our knowledge this represents one of the first examples of a phase-transfer mediated trisubstitution of fluorine for chlorine, and it occurs under unusually mild conditions.[7-9] Treatment of disulfide **2** with an aminophosphine[10] resulted in an extremely exothermic reaction which produced only traces of sulfide **3**. However, when disulfide **2** was added to a THF solution of triphenylphosphine it was smoothly desulfurized to **3**. With one recent exception[11] reports of desulfurizations of disulfides with triphenylphosphine had been limited to acyl or vinylogous disulfides.[12] In the present case, the extremely electronegative trifluoromethyl group may polarize the disulfide sufficiently to render it labile to attack by triphenylphosphine. Since ester **3** was difficult to isolate in good yield because of its tendency to codistill with a variety of solvents, it was hydrolyzed in situ with 5% sodium hydroxide to produce pure trifluoromethylthioacetic acid in 59% yield (from **2**).

Experimental Section

Infrared spectra were obtained in $CHCl_3$ using a Perkin-Elmer Infracord; NMR spectra were obtained in $CDCl_3$ on a Varian T-60 spectrometer using Me_4Si as an internal standard; VPC analyses were carried out on a F & M 700 gas chromatograph with a 6 ft SE-30 column. $MgSO_4$ was used as drying agent for organic extracts.

Ethyl Trichloromethyldithioacetate (1). Ethyl mercaptoacetate (36 g, 0.3 mol) was added dropwise with stirring over 1 h to trichloromethylsulfenyl chloride (55.8 g, 0.3 mol). The mixture was stirred at room temperature for an additional 1 h and then distilled to yield 69 g (85%) of **1** as a pale yellow oil: bp 94–96 °C (0.3 mm); NMR δ 4.20 (q, 2, J = 7 Hz), 3.90 (s, 2), 1.35 ppm (t, 3, J = 7 Hz); IR 1725, 845 cm^{-1}. Anal. Calcd for $C_5H_7Cl_3O_2S_2$: C, 22.28; H, 2.62; Cl, 39.45. Found: C, 22.68; H, 2.67; Cl, 39.83.

Ethyl Trifluoromethyldithioacetate (2). A. A mixture of 30 mL of hexane containing 5.40 g (20 mmol) of disulfide **1** and 30 mL of H_2O containing 5.04 g (120 mmol) of NaF was stirred at room temperature while about 0.7 g of Aliquat 336 in 1 mL of hexane was added. After stirring at room temperature overnight the mixture was diluted with 100 mL of hexane and the organic layer separated, washed with H_2O, dried, filtered, and evaporated. The residue was distilled under aspirator pressure to give 1.4 g (35%) of **2** as a pale yellow liquid: bp 72–74 °C (10 mm); NMR δ 4.24 (q, 2, J = 7 Hz), 3.72 (s, 2), 1.30 ppm (t, 3, J = 7 Hz); IR 1725, 1145 cm^{-1}; m/e M^+ 220.

B. To an ice-cold solution of 1.6 g (6 mmol) of 18-crown-6 in 50 mL of dry CH_3CN was added 7.0 g (120 mmol) of KF and the suspension stirred for 30 min. To this rapidly stirred solution was added dropwise over ~20 min a solution of 5.4 g (20 mmol) of disulfide **1** in 10 mL of CH_3CN. The mixture was stirred in the cold for an additional 1 h and then at room temperature for 2 h. Suspended solids were removed by filtration and the filtrate was evaporated. The residue was triturated with petroleum ether and filtered and the filtrate was concentrated and distilled to give 1.8 g (41%) of **2** as a light tan oil.

Trifluoromethylthioacetic Acid (4). The disulfide **2** (4.4 g, 20 mmol) dissolved in 20 mL of THF was added dropwise to a stirred solution of 5.8 g (22 mmol) of triphenylphosphine in 50 mL of THF. After addition was complete, the mixture was stirred at room temperature for 30 min. An additional 1 g of triphenylphosphine was added in 0.5-g portions and stirring continued for 15 min longer until VPC indicated complete consumption of starting material. Fifty milliliters of 5% NaOH was added and the mixture stirred rapidly for 1 h. Most of the THF was removed under vacuum and the mixture diluted with 200 mL of H_2O. It was washed twice with benzene and twice with Et_2O, acidified to pH 1.5 with 3 N HCl, and extracted with three portions of Et_2O. The latter extracts were combined, dried, filtered, and evaporated to give a brown oil which was distilled to give 1.9 g (59%) of **4** as a pale yellow oil: bp 87–88 °C (11 mm) [lit.[1] 101 °C (31 mm)]; NMR δ 10.25 (s, 1), 3.80 ppm (s, 2); IR 1710, 1240 cm^{-1}.

Registry No.—**1**, 61915-55-7; **2**, 61915-56-8; **4**, 2408-17-5; ethyl mercaptoacetate, 623-51-8; trichloromethylsulfenyl chloride, 594-42-3.

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Neighboring Sulfide Group in Thermal Decomposition of Aryldiazonium Salts

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Aryldiazonium tetrafluoroborates (**1**) are a well-known source of aryl radicals when they undergo reduction by nucleophilic species.[1] The mechanism proposed[2] involves the attack of nucleophilic species at the β nitrogen of the diazonium group to form an intermediate which then fragments homolytically, releasing X·, N_2, and aryl radicals. Recently, we studied[3] this reaction in carbon disulfide and we found that this solvent is a good scavenger for aryl radicals, which add to the carbon–sulfur double bond to give diaryl disulfide (**2**) and diaryl trithiocarbonate (**3**) through an intermediate arylthiothiocarbonyl radical (**4**). Otherwise, the thermal decomposition of **1** gives the aryl cation.[4] When the reaction was carried out in acetone, fluoroarenes (**5**) and phenols (**6**) were obtained;[4] no addition products on the carbon–sulfur double