trialkylammonium salts, **5** and **7**. Attempts to methylate **3** and **6** with methyl iodide, methyl *p*-toluenesulfonate, and trimethyloxonium tetrafluoroborate all failed or gave much lower yields. All attempts to alkylate **3** and **6** with groups larger than methyl failed. Some of these experiments are reported briefly in the microfilm edition.

Experimental Section[6]

Materials.—Tris(2-methylallyl)amine (**1**) was prepared from 2-methylallyl chloride (Eastman) and aqueous ammonia,[7] bp 84–88° at 15 Torr (lit.[8] bp 83–85° at 15 Torr). Methyl fluorosulfonate (Aldrich) was distilled and stored over CaH_2 at −20°. Technical 2-methoxyethanol was distilled. *p*-Toluenesulfonyl chloride was purified.[9] All other chemicals were reagent grade and were used as obtained without further purification.

Tris(1-methylcyclopropylmethyl)ammonium Tetrafluoroborate (**2**).—A mixture of 58.8 g of zinc dust, 81.3 g of Cu_2Cl_2, and 150 ml of anhydrous ethyl ether was stirred for 30 min at reflux. A solution of 17.9 g of **1** and 10 ml of ethyl ether was added slowly, and 102.8 g of CH_2I_2 (Eastman) was added dropwise over 45 min. After 21 hr at reflux the mixture was cooled and poured into a mixture of 800 ml of saturated aqueous NH_4Cl and ice. The layers were separated, and the aqueous suspension was washed with 4 × 200 ml portions of ether. The combined ether extract was dried over $MgSO_4$ and distilled through a 30-cm Vigreux column until 150 ml of yellow solution remained. To the ethereal solution 9.7 g of 48–50% aqueous HBF_4 was added slowly with stirring. The resulting precipitate was collected, air dried, and crystallized from methanol–ethyl acetate to give 11.0 g (35.6%) of **2**:[10] white needles; mp 227–228.5° dec (gas evolution); pmr ($CDCl_3$) δ 0.63 (12 H, AA'BB'), 1.24 (9 H, s), 3.28 (6 H, d, *J* = 6 Hz). The pmr spectrum showed a trace of 2-methylallyl groups (<3% of the area of 1-methylcyclopropylmethyl groups) and showed no sign of ^+N-H. A second crop was obtained from acetone–ethyl acetate: 2.1 g, mp 224.5–226° dec.

Tris(1-methylcyclopropylmethyl)amine (**3**).—A 1.19-g sample of **2** was shaken with 6 ml of 1 *M* NaOH and extracted with 10 ml of 30–60° petroleum ether. The organic solution was dried over K_2CO_3 and distilled on a steam bath through a 15-cm Vigreux column. Cooling of the residual liquid formed white solid **3**:[11] 0.85 g; mp 35–41°; pmr (CCl_4) δ 0.25 (12 H, br s), 1.16 (9 H, s), 2.23 (6 H, s). The pmr spectrum also showed a trace of residual petroleum ether, but this slightly impure material was used for subsequent experiments because further attempted removal of petroleum ether by evacuation and by passing a stream of N_2 over the solid resulted in much loss of **3** by sublimation. A sample sublimed at 25° and 1 atm for 7 days from the bottom to the upper walls of a sealed flask had mp 46–46.5°.

Methyltris(1-methylcyclopropylmethyl)ammonium Tetrafluoroborate (**5**).—A solution of 24.4 mmol of **3** and 46.5 mmol of methyl fluorosulfonate in 10 ml of CH_2Cl_2 was refluxed for 4.7 hr under N_2. The resulting dark CH_2Cl_2 solution was poured into 50 ml of water, extracted, washed with 50 ml of 1 *M* aqueous NaOH (which changed its color to beige), and washed with 4 × 25 ml portions of 3 *M* aqueous HBF_4. The combined aqueous wash solutions were extracted with 10 ml of CH_2Cl_2, and the combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to a beige solid. Crystallization from methanol–ethyl acetate gave 5.48 g (70%) of **5**:[10] white needles; mp 188.5–189.5° dec (gas evolution); pmr ($CDCl_3$) δ 0.70 (12 H, AA'BB'), 1.33 (9 H, s), 3.40 (6 H, d, *J* = 6 Hz), 3.47 (3 H, s). A second crop was obtained: 0.76 g, mp 186–187° dec.

Trineopentylammonium Tetrafluoroborate (**4**).—To a solution of 5.05 g of **2** in 175 ml of 2-methoxyethanol in a glass liner was added 4.99 g of 5% rhodium on carbon (Engelhard Industries). The mixture was rocked for 48 hr at 60° and 100 atm of H_2. The catalyst was removed by gravity filtration and washed with methanol. The filtrate was evaporated to ∼10 ml. Addition of 50 ml of ethyl ether and filtration of the resulting mixture gave crude white solid, 4.3 g, mp 191–199°, which was a mixture of two compounds having *tert*-butyl peaks in the pmr. A slurry of the crude solid in 15 ml of CH_2Cl_2 was filtered to give a solution of **4** and an insoluble solid which was not identified. Evaporation of the filtrate gave white solid, 3.51 g, mp 215–220°, which was crystallized three times from ethyl acetate to give **4**:[10] 2.97 g (58%); mp 221–224°; pmr (CH_2Cl_2) δ 1.15 (27 H, s), 3.34 (6 H, d, *J* = 5 Hz).

Trineopentylamine (**6**).—By the method described for conversion of **2** to **3**, 0.97 g of **4** was converted to liquid **6** contaminated with a trace of petroleum ether. Pure samples of **6**[10] for elemental analysis and spectra were collected by preparative glpc on a 10 ft × 0.25 in. column of 20% Apiezon L on 60–80 Chromosorb W at 190°: pmr (CH_2Cl_2) δ 0.93 (27 H, s), 2.21 (6 H, s); mass spectrum (Varian-MAT CH-5, 70 ev) *m/e* 227 (M^+), 212, 170 (base peak), 100, 71.

Methyltrineopentylammonium Tetrafluoroborate (**7**). **A.**—A mixture of 6.24 g of **5**, 5.9 g of 5% rhodium on carbon, and 250 ml of 2-methoxyethanol in a glass liner was rocked for 24 hr at 60° and 100 atm of H_2. The catalyst was removed by gravity filtration and washed with methanol. The filtrate was evaporated to a solid, which was crystallized from methanol–ethyl acetate to give **7**:[10] 2.62 g (41%); fine white flakes; mp 237–239°; pmr ($CDCl_3$) δ 1.25 (27 H, s), 3.32 (3 H, s), 3.44 (6 H, s).

B.—A solution of 0.474 g of **6**, 1.17 g of methyl fluorosulfonate, and 1.0 ml of CH_2Cl_2 was sealed in a heavy-wall glass tube and heated 2.5 hr at 117°. The contents of the tube were poured into 6 ml of 1 *M* aqueous HBF_4 and extracted with 6 × 1 ml portions of CH_2Cl_2. The combined CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated to a white paste, which was extracted with 3 ml of 1 *M* aqueous NaOH and 3 × 2 ml portions of 30–60° petroleum ether. The combined petroleum ether solution contained much unreacted **6** according to its pmr spectrum. The white solid which remained suspended in the aqueous phase during the petroleum ether extractions was isolated by filtration (0.29 g) and crystallized from methanol–ethyl acetate to give **7**, 0.144 g (23%), white needles, mp 234–237° dec, whose pmr spectrum was identical with that of **7** prepared by method A.

Acknowledgments.—I thank the U. S. Public Health Service (GM 16909) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support, Robert McNeil for technical assistance with the hydrogenations, and J. C. Martin for helpful discussion.

Registry No.—**1**, 6321-40-0; **2**, 41143-53-7; **3**, 41143-60-6; **4**, 41143-54-8; **5**, 41143-55-9; **6**, 13369-22-7; **7**, 41143-56-0.

Supplementary Material Available.—A supplementary experimental section will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-3614-73.

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[6] All temperatures including melting points and boiling points are uncorrected. Pmr spectra were obtained on Varian A-60A and HA-100 spectrometers. Microanalyses were performed by J. Nemeth and associates.

[7] G. B. Butler and B. M. Benjamin, *J. Chem. Educ.*, **28**, 191 (1951).

[8] M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[9] S. W. Pelletier, *Chem. Ind.* (*London*), 1034 (1953).

[10] Satisfactory elemental analysis for C, H, and N (±0.3%) was obtained for this compound. The data appears in a supplementary table of this paper in the microfilm edition.

[11] No elemental analysis was obtained for this compound.

Synthesis of 2-Methylene-4-thiazolidinones

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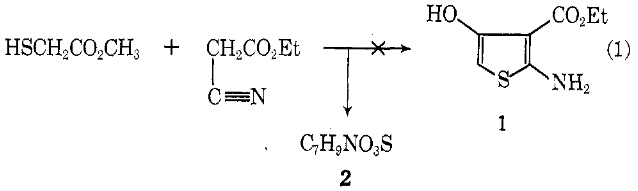
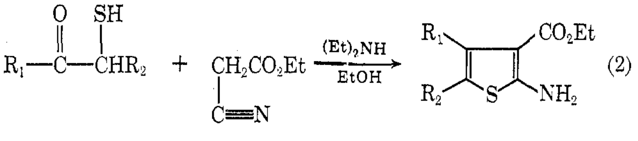
Received May 30, 1972

In recent synthetic work it was anticipated that the base-catalyzed condensation of α-mercapto esters with ethyl cyanoacetate would give 2-amino-3-carbethoxy-4-

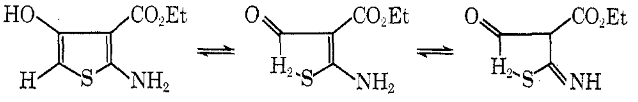
hydroxythiophene (**1**, eq 1) by analogy with the documented formation of 2-amino-3-carbethoxythiophenes from the interaction of α-mercapto ketones with ethyl cyanoacetate (eq 2).[1,2]





R_1 and R_2 = alkyl, aryl, and/or acyl

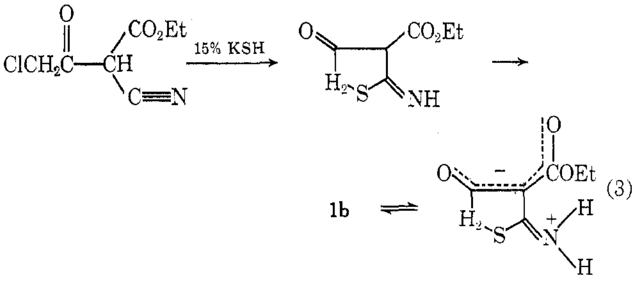
However, it was found that the interaction of methyl mercaptoacetate with ethyl cyanoacetate in diethylamine–ethanol gave a nearly quantitative yield of a product (**2**) whose empirical formula corresponded to **1**, but whose nmr spectrum was inconsistent with **1**. The nmr spectrum of **2** indicated the presence of a carbethoxy group, a singlet methylene absorption at 5.86 ppm, a one-hydrogen singlet that collapsed very slowly upon addition of D_2O, and one singlet hydrogen attached to nitrogen (^{14}N spin decoupled) at 11.50 ppm downfield from TMS. Of the three possible tautomeric forms for **1** (**1a**, **1b**, and **1c**) only **1c** could give rise to this



1a **1b** **1c**

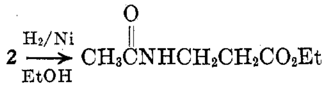
spectrum. However, this tautomer is highly unlikely for **1**, and a large variety of 2-aminothiophenes have been shown to exist entirely in the amino rather than imino form.[3,4]

A subsequent literature search for **1** revealed a reported synthesis of **1c** from the treatment of ethyl chloroacetylcyanoacetate with aqueous potassium hydrosulfide (eq 3).[5-8] Repetition of this procedure gave



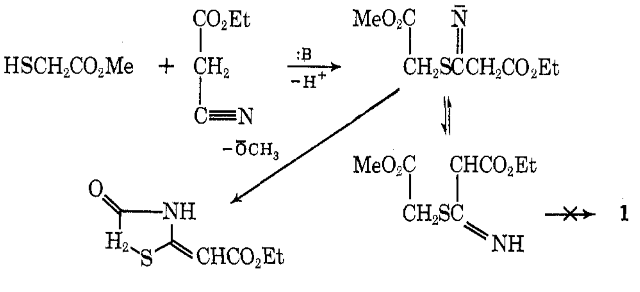
what appeared to be **1**, but as **1b** rather than **1c** from the nmr spectrum, and as expected, the ir, nmr, and mass spectrum of **1b** all differed from those given by the isomeric compound, **2**. It is interesting to note that the nmr spectrum of **1b** displays two different NH protons at room temperature, presumably owing to the rather unque steric arrangement of this vinylogous amide where restricted rotation about the C–N bond gives rise to two magnetically distinct amine hydrogens. The positive character of the nitrogen is evident from the unusually low shift values for the amine protons (8.87 and 9.40 ppm downfield from TMS).

The identity of **2** was established by desulfurization with Raney nickel to give the ethyl ester of *N*-acetyl-β-alanine (eq 4). Reconstruction of **2** from the desulfurization process indicated that **2** is 2-carbethoxymethylene-4-thiazolidenone, resulting from sulfur attack at the nitrile carbon followed by lactam formation (Scheme I).



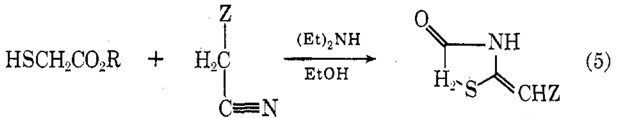
$$\mathbf{2} \xrightarrow[\text{EtOH}]{\text{H}_2/\text{Ni}} \text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NHCH}_2\text{CH}_2\text{CO}_2\text{Et} \qquad (4)$$

SCHEME I



2

It was subsequently found that this type of reaction with α-mercapto esters is general for methylene-active nitriles. Thus, the condensation of methyl mercaptoacetate with malononitrile and with 2-cyanoacetamide gave excellent yields of **3** and **4**, respectively, and constitues a new and facile synthesis of this biologically and industrially important ring system (eq 5).[9]



2, Z = CO_2Et
3, Z = C≡N
4, Z = $CONH_2$

A similar reaction has been previously observed in the thiazole system, where α-mercapto acids or esters react with Schiff bases to give 4-oxothiazolidines.[10,11] The method is restricted to Schiff bases, however, and good yields require preformation of the Schiff base.

Experimental Section

2-Carbethoxymethylene-4-thiazolidinone (**2**).—A solution consisting of 10.0 g (0.094 mol) of ethyl mercaptoacetate, 13.0 g

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(1) K. Gewald, E. Schinke, and H. Bottcher, *Chem. Ber.*, **99**, 94 (1966).
(2) W. Ried and R. Giesse, *Justus Liebigs Ann. Chem.*, **713**, 143 (1968).
(3) M. C. Ford and D. McKay, *J. Chem. Soc.*, 4985 (1956).
(4) R. A. Hoffman and S. Gronowitz, *Ark. Kemi*, **16**, 515 (1961).
(5) Tohl and Eberhard, *Chem. Ber.*, **26**, 2945 (1893).
(6) W. Autenrieth and A. Bruning, *Chem. Ber.*, **36**, 3464 (1903).
(7) E. Benary, *Chem. Ber.*, **41**, 2399 (1908).
(8) E. Benary, *Chem. Ber.*, **43**, 1943 (1910).

(9) For a review of 4-thiazolidinones see F. C. Brown, *Chem. Rev.*, **61**, 463 (1961).
(10) A. R. Surrey, *J. Amer. Chem. Soc.*, **71**, 3105 (1949).
(11) H. D. Troutman and L. M. Long, *J. Amer. Chem. Soc.*, **70**, 3436 (1948).

(slight excess) of ethyl cyanoacetate, and 6 ml of acetic acid in 50 ml of absolute alcohol was stirred at room temperature. Then 10 ml of diethylamine was added in small portions. The temperature rose rapidly to 45°, then began to drop as the last of the diethylamine was added. After 15 min, a white, fluffy precipitate formed. Stirring was continued for an additional 1 hr, then the mixture was cooled in an ice bath for 30 min. The white crystals were filtered, washed with water, and then recrystallized from 95% ethanol to give 16.4 g (93%) of shiny, white flakes: mp 144–149°; ir (KBr) 3260, 3000, 1730, 1725, 1670, and 1575 cm^{-1}; nmr (DMSO-d_6) δ 1.20 (3 H, t, J = 6 Hz), 3.73 (2 H, s), 4.00 (2 H, q, J = 6 Hz), 5.86 (1 H, s), and 11.50 ppm (1 H, broad s, exchanged with D_2O); uv max (CH_3OH) 233 nm (ϵ 11,000) and 284 (22,000); mass spectrum (70 eV) m/e (rel intensity) 187 (60), 173 (7), 159 (18), 142 (82), 115 (100), and 86 (40).

Anal. Calcd for $C_7H_9NO_3S$: C, 44.90; H, 4.84; N, 7.49; S, 17.12. Found: C, 44.85; H, 4.76; N, 7.47; S, 17.06.

2-Cyanomethylene-4-thiazolidinone (**3**).—Five milliliters of piperidine was added to a stirred mixture consisting of 120.17 g (1.0 mol) of ethyl mercaptoacetate, 66.07 g (1.0 mol) of malononitrile, and 5 drops of acetic acid in 200 ml of absolute ethanol. The temperature quickly rose to 60° and was subsequently maintained between 50 and 60° by intermittent use of an ice bath. After a short time, a white precipitate formed a solid mass in the reaction vessel. An additional 100 ml of ethanol was then added and the mixture was stirred for 30 min more. The mixture was then filtered and the white solid was recrystallized from a mixture (v/v) of ethanol–acetonitrile (2:1) to give 80 g (57%) of a white powder that slowly decomposed over 200°: ir (KBr), 3115, 3090, 3000, 2880, 2218, 1770, 1730, and 1600 cm^{-1}; nmr (DMSO-d_6) δ 4.00 (2 H, s), 4.90 (1 H, s), and 11.75 ppm (1 H, broad s, exchanged with D_2O); mass spectrum (70 eV) m/e (rel intensity) 139 (39), 111 (12), 73 (20), 67 (100), 66 (53), 47 (35), 46 (78), 45 (61), and 42 (33).

Anal. Calcd for $C_5H_4N_2OS$: C, 42.87; H, 2.88; N, 20.00; S, 22.84. Found: C, 42.44; H, 2.94; N, 20.01; S, 22.37.

2-Carboxamidomethylene-4-thiazolidinone (**4**).—A mixture of 10.0 g (0.094 mol) of methyl mercaptoacetate, 13.0 g (slight excess) of 2-cyanoacetamide, 2.0 g of ammonium acetate, and 50 ml of ethanol was stirred at room temperature. Then 15 ml of diethylamine was added and stirring was continued for 1 hr, during which time the temperature gradually rose to 48°. At the end of 1 hr, the temperature began to drop and a tan powder came out of solution. After an additional 0.5 hr the solution was filtered and the very insoluble powder was washed liberally with ethanol, then ether. The residue after washing weighed 4.8 g (32%) as a light brown powder that decomposed at 260° and sublimed over 200°, and was homogeneous (tlc): ir (KBr) 3400, 3160, 2783, 1730, 1675, 1630, and 1590 cm^{-1}; nmr (DMSO-d_6) δ 3.60 (2 H, s), 5.59 (1 H, s), 6.60 (1 H, broad s), 7.10 (1 H, broad s), and 10.50 ppm (1 H, broad s); mass spectrum (70 eV) m/e (rel intensity) 158 (100), 142 (16), 115 (19), 84 (28), 73 (42), 68 (42), 46 (53), 44 (53), and 42 (56).

Anal. Calcd for $C_5H_6N_2O_2S$: C, 37.98; H, 3.82; N, 17.71; S, 20.24. Found: C, 37.98; H, 3.79; N, 17.49; S, 20.19.

Desulfurization of 2-Carbethoxymethylene-4-thiazolidinone (**2**).—Three grams of **2** was dissolved in 250 ml of absolute ethanol containing approximately 18 g of W2 Raney nickel and the mixture was stirred and refluxed for 44 hr. The solution was then cooled, filtered through an asbestos plug, and then filtered by gravity through fluted paper to give a clear, colorless filtrate. Removal of the ethanol by evaporation left a colorless oil that was distilled at 137–138° (6 mm) [lit. 136° (6 mm)]: ir (liquid film) 3260, 2950, 1740, and 1650 cm^{-1}; nmr (CCl_4) δ 1.23 (3 H, t, J = 6 Hz), and 2.05 (3 H, s), 2.48 (2 H, t, J = 6 Hz), 3.28 (2 H, q, J = 6 Hz), 4.00 (2 H, q, J = 6 Hz), 7.50 ppm (1, H, broad t). The ir, nmr, and elemental analyses indicated that the product was the ethyl ester of N-acetyl-β-alanine.

Anal. Calcd for $C_7H_{13}NO_3$: C, 52.82; H, 8.23; N, 8.80. Found: C, 52.57; H, 8.51; N, 9.06.

2-Amino-3-carbethoxy-4-hydroxythiophene (**1b**)[8].—Nine grams (0.048 mol) of ethyl chloroacetylcyanoacetate[7] was dissolved in 90 ml of a 15% aqueous potassium hydrosulfide solution. The mixture was warmed gently on a steam bath. After a few minutes, shiny plates began to appear. After 15 min the precipitate was collected, washed with water, and recrystallized from ethanol to give 4.2 g (45%) of shiny, white flakes: mp 219–202; ir (KBr) 3350, 3080, 1673, 1625, and 1490 cm^{-1}; nmr (DMSO-d_6) δ 1.20 (3 H, t, J = 6 Hz), 3.35 (2, H, s), 4.15 (2, H, q, J = Hz), 8.87 (1 H, broad s, sharpened upon ^{14}N spin decoupling), and 9.40 ppm (1, H, broad s, sharpened upon ^{14}N spin decoupling); mass spectrum (70 eV) m/e (rel intensity) 187 (100), 143 (100), 142 (100), 141 (69), 115 (100), 85 (69), 68 (100), and 60 (65).

Anal. Calcd for $C_7H_9NO_3S$: C, 44.90; H, 4.84; N, 17.49. Found: C, 45.00; H, 4.80; N, 17.38.

Registry No.—**1b**, 38555-67-8; **2**, 24146-36-9; **3**, 3364-82-7; **4**, 27653-83-4; ethyl mercaptoacetate, 623-51-8; ethyl cyanoacetate, 105-56-6; malononitrile, 109-77-3; 2-cyanoacetamide, 107-91-5; methyl mercaptoacetate, 2365-48-2; ethyl ester of N-acetyl-β-alanine, 33233-68-0; ethyl chloroacetylcyanoacetate, 26390-99-8.

The Synthesis of the Fluorinated Ethers "Perfluoroglyme" and "Perfluorodiglyme" by Direct Fluorination

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Received March 28, 1973

The synthesis of perfluorinated ethers and polyethers using existing technology is often difficult and in many cases impossible to accomplish. A facile general synthesis with possible commercial importance has been developed in our laboratory by employing modified[1] LaMar[2] direct fluorination techniques. Perfluorinated polyethers are of interest as potential high stability fluids and as solvents. Of the reported products, only "perfluoroglyme" (perfluoro-1,2-dimethoxyethane) has been prepared in 4% yield based on the electrolytic fluorination and cleavage of 1,4-dioxane.[3]

Experimental Section

Perfluoro-1,2-dimethoxyethane.—1,2-Dimethoxyethane (4.015 g, 0.045 mol) was evaporated employing a flow of 50–100 cc of helium into gradient reactor containing four distinct zones which were maintained at −78°, a temperature below the freezing point of the ether (−58°). An initial flow of 0.5 cc/min of fluorine and 20 cc/min of helium was started and after 12 hr the fluorine was increased to 1.0 cc/min. After an additional 12 hr, zone 1 was allowed to run out of Dry Ice. Twelve hours after zone 1 was clear of Dry Ice the fluorine was increased to 1.5 cc/min while helium flow still was maintained at 20 cc/min. The fluorine flow was maintained at 1.5 cc/min. On alternate days the helium was reduced to 10 cc/min, followed by one additional zone being allowed to clear of Dry Ice. Subsequent reductions to 5-, then to 0-cc/min helium flow were followed each time by warming of one additional zone.[4] Finally, as the reactor warmed under a flow of pure fluorine, the fluorinated ether was passed through a metal trap filled with sodium fluoride pellets and into a glass trap maintained at −78°. The raw fluorocarbon ethers collected represented a mass which corresponded to between 50 and 100% of the expected yield based on moles of the parent ether. This mixture contained several hydrofluoro ethers and

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(1) R. J. Lagow and N. J. Maraschin, *J. Amer. Chem. Soc.*, **94**, 8601 (1972).

(2) R. J. Lagow and J. L. Margrave, "The Reaction of Polynuclear Hydrocarbons with Elemental Fluorine," in press; R. J. Lagow and J. L. Margrave, *Chem. Eng. News*, 40 (Jan 12, 1970).

(3) J. H. Simons, U. S. Patent 2,500,388 (1950).

(4) Warmings of successive zones allowed renewal of the reactant surface inside the reactor.