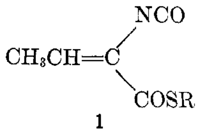
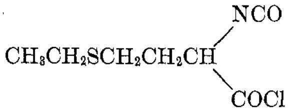
carbon tetrachloride. Infrared and nmr spectral data in conjunction with elemental analysis conclusively demonstrated the structure of the unknown material to be methyl 2-isocyanato-2-butenethiolate (**1**, R = $CH_3$).



$CH_3CH{=}C(NCO)COSR$

**1**

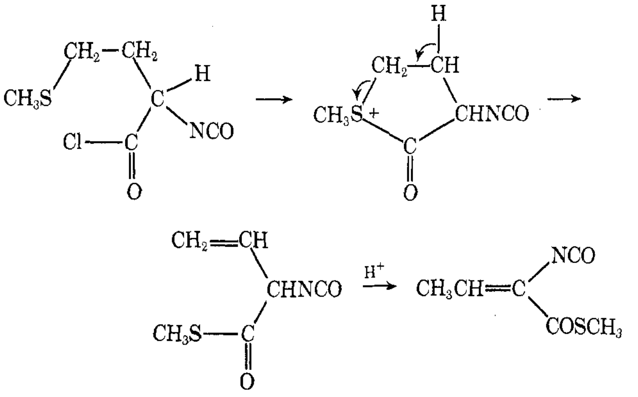
When an identical reaction was carried out using ethionine in place of methionine, distillation at reduced pressure afforded two materials. These were identified as the expected α-isocyanato acid chloride **2** and the



$CH_3CH_2SCH_2CH_2CH(NCO)COCl$

**2**

corresponding rearrangement product **1** (R = $C_2H_5$). While no mechanistic studies of this rearrangement have been undertaken, it is quite likely that in intramolecular rearrangement occurs *via* a sulfonium ion intermediate. A possible mechanism is shown below.



An investigation of the intermolecular interaction between acyl chlorides and sulfur has been shown to form thiolactones and alkyl halides *via* an acyl sulfonium salt.[2] Thus, 4-(*n*-propylthio)butyryl chloride provides γ-thiobutyrolactone and *n*-propyl chloride. In contrast, the present study reveals that formation of the 2-isocyanatoacylsulfonium chloride undergoes loss of hydrogen chloride to form an unsaturated 2-isocyanatothiol ester.

### Experimental Section

Infrared and nuclear magnetic resonance spectra were determined on a Beckman IR-5 spectrophotometer and a Varian Model A-60 spectrometer, respectively.

**Preparation of Methyl 2-Isocyanato-2-butenethiolate.**—Methionine (50 g) was suspended in 500 ml of dry dioxane; phosgene was then passed through the mixture at 45° for 4 hr. The solution was cooled to 0° and dry hydrogen chloride passed through the mixture for 2 hr; the resultant mixture was allowed to stand overnight. The solution was then heated to 50° and phosgene was passed through for 4 hr, and then the solution was allowed to stand for 2 days. The solvent was removed *in vacuo* and the residue was distilled at 70–80° (*ca.* 1 mm). Prior to the distillation temperature, evolution of hydrogen chloride occurred. The product (10.2 g, 21%) was identified as the title compound by its infrared and nmr spectra in conjunction with elemental analysis.

*Anal.* Calcd for $C_6H_7NO_2S$: C, 45.84; H, 4.49; S, 20.40. Found: C, 45.62; H, 4.51; S, 20.18.

When the reaction was carried out in an identical fashion using ethionine, distillation at 70–75° (0.45 mm) provided 20 g of a 3:2 mixture of compounds **2** and **1** (R = $C_2H_5$). Further distillation at 77° (0.35 mm) provided 9.7 g (18%) of pure **1** (R = $C_2H_5$). The nmr spectrum of the latter had proton resonances centered at 1.3 (t, 3 H), 1.9 (d, 3 H), 2.95 (q, 2 H), and 6.4 ppm (q, 1 H).

**Registry No.**—**1** (R = $CH_3$), 31600-83-6; **1** (R = $C_2H_5$), 31600-84-7; **2**, 31600-85-8.

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[2] W. E. Truce and D. J. Abraham, *J. Org. Chem.*, **28**, 964 (1963).

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# Trifluoroacetic Anhydride Ring Opening Addition to Cyclic Ethers

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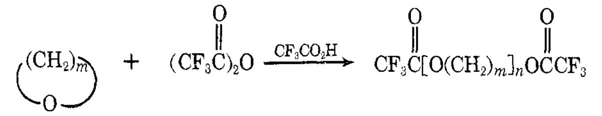
Cyclic ethers such as ethylene oxide (EO) and tetrahydrofuran (THF) are readily opened by acids to the corresponding adducts;[1,2] for example, acetic acid condenses rapidly with EO to give 2-acetoxyethanol. Recently, on attempting a trifluoroacetylation with trifluoroacetic anhydride (TFAA) in THF, we obtained mainly the products resulting from addition of TFAA to THF and an oligomer.[3] This reaction is definitely acid catalyzed since higher yields at lower reaction temperature result by addition of a catalytic amount of trifluoroacetic acid. In the series of cyclic ethers the relative yields of oligomer *vs.* 1:1 adduct vary with the size of the ring. Relative concentration and possibly temperature are also important, but insufficient data have been collected to establish any quantitative conclusions. The reaction was run under autogenous pressure in a sealed autoclave in order to attain temperatures over 100° that appeared to be required for reasonable reaction rate. No significant yield of product was found in refluxing THF at atmospheric pressure. For ethylene oxide (*m* = 2), products with *n* = 1, 2, 3, 4, and greater are isolated. For tetramethylene oxide (*m* = 3) and THF (*m* = 4), both 1:1 and 2:1 adducts are obtained. For tetrahydropyran, only the 1:1 adduct was found. The product yields are given in Table I and physical and analytical data on all new compounds are listed in Table II.



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[1] A. Rosowski in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 349.

[2] R. C. Elderfield, *Heterocycl. Compounds*, **1**, 175 (1950).

[3] The ring opening addition of acetic anhydride to THF has been reported: Netherlands Patent Application 6,516,827 (Farwerke Hoechst A.-G., July 1966) [*Chem. Abstr.*, **66**, 2194b (1967)]; R. M. Ispiryan, L. I. Belen'kii, Ya. I. Gol'farb, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, **11**, 513 (1967) [*Chem. Abstr.*, **69**, 66866t (1968)].

TABLE I

REACTION OF CYCLIC ETHERS WITH TRIFLUOROACETIC ANHYDRIDE (TFAA)

| Ether | Amount, g (mol) | TFAA,[a] g (mol) | Conditions | Product | n | Yield, g | Yield, % based on ether | Yield, % based on TFAA[a] |
|---|---|---|---|---|---|---|---|---|
| Ethylene oxide | 8.9 (0.20) | 42 (0.20) | 50 ml of $CCl_3F$ solvent, 120°, 20 hr | $CF_3\overset{\overset{O}{\|}}{C}(OCH_2CH_2)_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 11.6 | 22.8 | 22.8 |
| | | | | | 2 | 17.6 | 59 | 29.5 |
| | 44.5 (1.0) | 42 (0.20) | 120°, 20 hr | | 1 | 9.3 | 3.7 | 18.3 |
| | | | | | 2 | 23.2 | 15.6 | 40.0 |
| | | | | | 3 | 12.8 | 11.1 | 18.5 |
| | | | | | (4)[b] | 7.7 | 8.2 | (10.0) |
| Trimethylene oxide | 11.6 (0.20) | 42 (0.20) | 50 ml of $CCl_3F$ solvent, 120°, 18 hr | $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_3]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 14.0 | 25.6 | 25.6 |
| | | | | | 2 | 18.1 | 55.4 | 27.7 |
| Tetrahydrofuran | 14.4 (0.20) | 42 (0.20) | 120°, 18 hr | $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_4]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 1.9 | 3.4 | 3.4 |
| | | | | | 2 | 0.3 | 0.9 | 0.5 |
| | 14.4 (0.20) | 42 (0.20) | 180°, 18 hr | | 1 | 41.7 | 73.9 | 73.9 |
| | | | | | 2 | 6.2 | 17.5 | 8.7 |
| | 72 (1.0) | 42 (0.20) | 120°, 18 hr | | 1 | 6.6 | 2.3 | 11.7 |
| | | | | | 2 | 5.0 | 2.8 | 7.0 |
| | 72 (1.0) | 42 (0.20) | 1.0 g of $CF_3CO_2H$, 120°, 18 hr | | 1 | 14.6 | 5.2 | 25.9 |
| | | | | | 2 | 26.5 | 15.0 | 37.4 |
| Tetrahydropyran | 17.2 (0.2) | 42 (0.20) | 200°, 18 hr | $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_5]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 45.3 | 76.5 | 76.5 |
| | 17.2 (0.2) | 42 (0.20) | 120°, 18 hr | | | 0 | 0 | 0 |

[a] TFAA = trifluoroacetic anhydride. [b] The fraction of bp 112° (0.225 mm) appeared to be primarily oligomer with $n = 4$.

TABLE II

PHYSICAL AND ANALYTICAL DATA ON ETHER–TFAA ADDUCTS

| Compd | n | Registry no. | Bp, °C (mm) | $n^{25}D$ | Formula | C, % Calcd | C, % Found | H, % Calcd | H, % Found | F, % Calcd | F, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3\overset{\overset{O}{\|}}{C}(OCH_2CH_2)_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 2613-44-7 | 47 (6.5) | 1.3275 | $C_6H_4F_6O_4$[a] | | | | | | |
| | 2 | 31580-02-6 | 71 (1.5) | 1.3516 | $C_8H_8F_6O_5$ | 32.2 | 32.1 | 2.70 | 2.88 | 38.2 | 37.1 |
| | 3 | 31528-86-6 | 61 (0.02) | 1.3696 | $C_{10}H_{12}O_6F_6$ | 35.1 | 35.8 | 3.54 | 3.77 | 33.3 | 32.4 |
| $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_3]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 7647-95-2 | 95.5 (30) | 1.3388 | $C_7H_6O_4F_6$ | 31.4 | 31.2 | 2.26 | 2.24 | 42.5 | 42.3 |
| | 2 | 31528-88-8 | 134 (30) | 1.3604 | $C_{10}H_{12}F_6O_5$ | 36.8 | 37.1 | 3.71 | 3.76 | 35.0 | 34.9 |
| $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_4]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 31528-89-9 | 43–44 (0.1) | 1.3459 | $C_8H_8F_6O_4$ | 34.1 | 33.8 | 2.85 | 2.86 | 40.4 | 40.5 |
| | 2 | 31528-90-2 | 70–75 (0.1) | 1.3709 | $C_{12}H_{16}F_6O_5$ | 40.9 | 40.0 | 4.55 | 4.65 | 32.2 | 32.5 |
| $CF_3\overset{\overset{O}{\|}}{C}[O(CH_2)_5]_nO\overset{\overset{O}{\|}}{C}CF_3$ | 1 | 453-44-1 | 50 (0.25) | 1.3538 | $C_9H_{10}F_6O_4$ | 36.5 | 36.5 | 3.41 | 3.5 | 38.5 | 37.5 |

[a] Lit. bp 151–153°, $n^{25}D$ 1.3286 (at least 95% pure): S. D. Ross and M. Finkelstein, *J. Org. Chem.*, **22**, 847 (1957). Preparation was from a large excess of trifluoroacetic anhydride and ethylene glycol.

The reaction no doubt goes by ring-opening protonation of the ether since trifluoroacetic acid was shown to be a catalyst. To attempt to determine whether polymer was derivable under the reaction conditions using a larger THF–anhydride ratio, ratios of 10:1–100:1 (molar) were used. Under the latter conditions, conversion was low to give predominantly the adduct with two THF units.

### Experimental Section

The typical procedure for reaction was to charge the reactants into a 240-ml stainless steel pressure vessel and heat at autogenous pressure, at temperature and time given in Table I. The reaction mixture was distilled.

No significant reaction occurred when THF and TFAA containing a catalytic amount of trifluoroacetic acid were refluxed for 24 hr at atmospheric pressure.

The physical and analytical data on all new compounds are in Table II. The ir and nmr (proton and $^{19}F$) spectra were in agreement with the proposed structure. In the ir, the trifluoroacetate carbonyl had a strong absorption at 1740 cm$^{-1}$. The $^{19}F$ nmr for the $CF_3$ group was a sharp singlet in the range of 75.8–75.9 ppm relative to $CCl_3F$ (internal standard and solvent, 5% concentration).

**Registry No.**—Trifluoroacetic anhydride, 407-25-0.

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## Reaction of Nitronium Fluoroborate with Olefins in Acetonitrile

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The Ritter reaction[2] is a convenient method of preparing amines or amides by reaction of olefins in acidic

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[2] (a) J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045 (1948); (b) T. Clark, J. Devine, and D. W. Dicker, *J. Amer. Oil Chem. Soc.*, **41**, 78 (1964).