

were obtained with a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were obtained on a Varian A-60D spectrometer and in reference to benzene as an internal standard.

**Nitration of Pentachlorobenzene (Runs 1, 2, and 3).**—Pentachlorobenzene (25.0 g, 0.1 mol) was heated to 140°. The nitrating mixture, consisting of 9.0 ml of fuming nitric acid (Baker analyzed reagent) in 31.0 ml of fuming sulfuric acid (Baker analyzed reagent, 30–33%), was added to the liquid pentachlorobenzene, maintaining a temperature of 140–145° during the addition. After addition of the nitrating mixture was completed, the temperature was held at 150–155° for a period of 1.5 hr. The reaction mixture was cooled to room temperature and the solid product was collected by suction filtration, followed by thorough washing with cold water. The product was dried under reduced pressure.

**Run 4.**—The procedure was identical with that employed in runs 1–3, except 75.0 g of pentachlorobenzene was used. The nitrating mixture consisted of 27.0 ml of fuming nitric acid and 93.0 ml of fuming sulfuric acid. Gas chromatographic analysis of the reaction mixture on the OV-17 and on the more polar Carbowax columns showed only two products, pentachloronitrobenzene (PCNB) and hexachlorobenzene (HCB). Identification was based upon retention times on the two columns and the lack of evidence from either column of additional components when standard HCB was added to the mixture of products. Experimental results are summarized in Tables I and II.

TABLE I

Run	Unchanged PCB, g	Yield of PCNB, g	% yield, PCNB
1	3.4	22.2	89.5
2	4.7	21.5	83.7
3	4.0	20.6	83.0
4	18.5	55.5	85.9

TABLE II

Run	GAS CHROMATOGRAPHIC ANALYSIS		
	Reactant (PCB), %	Product mixture, % by wt	
		PCNB	HCB
1	100	99	1
2	100	98.5	1.5
3	100	98.1	1.9
4	100	98.4	1.6

**Collection and Inspection of Off Gases.**—The gases liberated during the nitration of pentachlorobenzene were collected as follows.

Fraction 1: off-gases passed into a 50-ml portion of benzene for a 30-min period.

Fraction 2: off-gases passed into a fresh 50-ml portion of chloroform for a 30-min period.

Fraction 3: off-gases passed into a 10% aqueous solution of silver nitrate for a 2-min period. A heavy precipitate, identified as silver chloride, formed.

Fraction 4: off-gases passed into a fresh 50-ml portion of chloroform for a 20-min period.

**Ir, Nmr, and Gc Analysis (Fractions 1, 2, and 4).**—Ir spectra of fractions 1, 2, and 4 exhibited an intense band at 5.74  $\mu$  and a broad, intense band at 3.3  $\mu$  indicative of C=O stretching and OH stretching, respectively, in a carboxylic acid dimer. No absorption was observed in the aromatic region of the spectra of fractions 2 and 4.

The nmr spectrum of fraction 1 exhibited a singlet at  $\delta$  10.33, representing the carboxylic acid proton. Spectra of fractions 2 and 4 exhibited no acid proton signal, likely due to the use of chloroform as a solvent. Spectra of fractions 2 and 4 also exhibited no aromatic proton signal.

Samples taken from the off-gas stream in front of the solution phase collector were chromatographed on Arochlor 1232. The presence of chlorine in these samples was established by retention time and by increase in chlorine peak area, without evidence of resolution, on addition of chlorine to the off-gas mixture.

**Treatment of Pentachlorobenzene with Fuming Sulfuric Acid.**—A 5.0-g sample of pentachlorobenzene was added to 18.0 ml of fuming sulfuric acid and the mixture was heated at 150–160° for periods of 1–8 hr. The mixture was cooled to room temperature and poured over crushed ice. The product was collected by

suction filtration, thoroughly washed with cold water, and dried. Solid material (5.0 g) was collected. The product was subjected to gas chromatographic analysis and was found to be pure pentachlorobenzene. No trace quantities of other materials were detected.

**Treatment of Pentachlorobenzene with Fuming Nitric Acid.**—The procedure was identical with that employed in using fuming sulfuric acid. The product was subjected to gas chromatographic analysis and hexachlorobenzene, pentachloronitrobenzene, and pentachlorobenzene were found to be present. The procedure was repeated and anhydrous chlorine was passed through the mixture. It was observed that the amount of hexachlorobenzene forming in a given time increased.

**Treatment of Pentachlorobenzene with Hydrogen Chloride and Chlorine.**—A 5.0-g sample of pentachlorobenzene was melted and anhydrous hydrogen chloride and chlorine were passed through the melt for 1.5 hr. The mixture was cooled to room temperature, thoroughly washed with water, and collected. The product was subjected to gas chromatographic analysis and was found to be unchanged pentachlorobenzene. No detectable quantities of other materials were detected. The process was repeated using 20.0 ml of concentrated hydrochloric acid rather than anhydrous hydrogen chloride. The result was the same as above.

**Registry No.**—PCB, 608-93-5; PCNB, 82-68-8; HCB, 118-74-1.

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## A Novel Rearrangement of 2-Isocyanato-4-(alkylthio) Acid Chlorides

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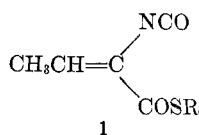
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$\alpha$ -Isocyanato acid chlorides have been prepared from amino acids, phosgene, and hydrogen chloride.<sup>1</sup> While studying a series of reactions of these materials with various amines, the need arose for 2-isocyanato-(4-methylthio)butyryl chloride. Utilizing the method of Iwakura, Uno, and Kang,<sup>1</sup> methionine was converted to the expected  $\alpha$ -isocyanato acid chloride. This was evidenced by the infrared spectrum of the crude product which exhibited peaks at 4.5 (NCO) and 5.65  $\mu$  (COCl). However, upon attempted purification by vacuum distillation a vigorous evolution of hydrogen chloride was found to occur. After the evolution of the gas had ceased, the distillation proceeded without further incident.

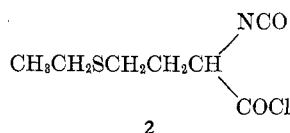
The infrared spectrum of the reaction product finally obtained after distillation exhibited an intense peak at 4.5  $\mu$  characteristic of the isocyanate grouping but lacked the characteristic acid chloride absorbance at 5.65  $\mu$ . There was, however, an additional intense absorption at 6.05  $\mu$  attributable to a thiol ester grouping. The nuclear magnetic resonance spectrum of this unknown material consisted of a doublet at 1.91 (3 H), a singlet at 2.42 (3 H), and a quartet at 6.53 ppm (1 H) downfield from an internal tetramethylsilane standard in

(1) Y. Iwakura, K. Uno, and S. Kang, *J. Org. Chem.*, **30**, 1158 (1965).

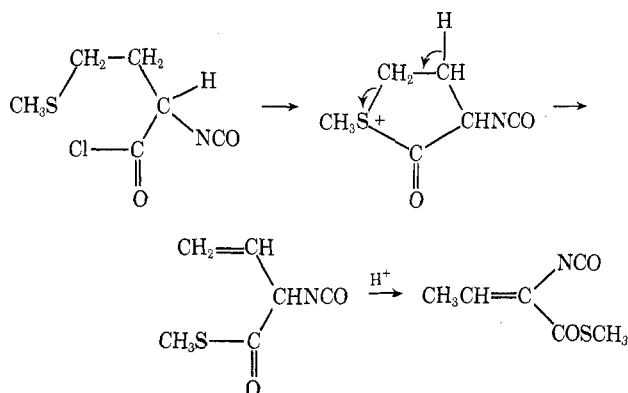
carbon tetrachloride. Infrared and nmr spectral data in conjunction with elemental analysis conclusively demonstrated the structure of the unknown material to be methyl 2-isocyanato-2-butenethiolate (1, R = CH<sub>3</sub>).



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  $\alpha$ -isocyanato acid chloride 2 and the



corresponding rearrangement product 1 (R = C<sub>2</sub>H<sub>5</sub>). 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.<sup>2</sup> Thus, 4-(*n*-propylthio)butyryl chloride provides  $\gamma$ -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.

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

*Anal.* Calcd for C<sub>6</sub>H<sub>7</sub>NO<sub>2</sub>S: 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<sub>2</sub>H<sub>5</sub>). Further distillation at 77° (0.35 mm) provided 9.7 g (18%) of pure 1 (R = C<sub>2</sub>H<sub>5</sub>). 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<sub>3</sub>), 31600-83-6; 1 (R = C<sub>2</sub>H<sub>5</sub>), 31600-84-7; 2, 31600-85-8.

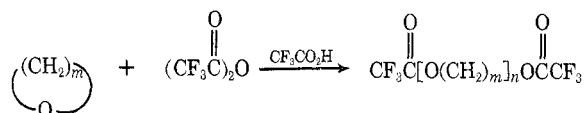
### Trifluoroacetic Anhydride Ring Opening Addition to Cyclic Ethers

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Cyclic ethers such as ethylene oxide (EO) and tetrahydrofuran (THF) are readily opened by acids to the corresponding adducts;<sup>1,2</sup> 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.<sup>3</sup> 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.

(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**, 66860t (1968)].