

solution was used to rinse the syringe, removing traces of residual moisture, before the syringe was utilized to transfer the standard diborane solution.

The disiamylborane reagent was prepared as follows. To the carefully dried 200-ml. reaction flask, flushed with nitrogen and fitted with a side-arm containing a rubber serum cap, was added 20 ml. of the standard tetrahydrofuran solution, 6.0 *M* in 2-methyl-2-butene (120 mmoles). The flask was cooled to -20° to compensate for the heat of reaction and 24.25 ml. of the diborane solution in tetrahydrofuran (2.47 *M*, 60 mmoles) was added slowly. The reaction was permitted to proceed over 6 to 9 hours in order to attain 98-99% reaction of the 2-methyl-2-butene, maintaining a slight excess static nitrogen pressure.

To the reagent was added 85.5 ml. of tetrahydrofuran (0°) and the entire mixture was cooled to -2° . A standard solution of cyclopentene, 3.0 *M*, and methylcyclohexane, 1.5 *M*, in tetrahydrofuran was prepared and maintained at 0° . The reaction was initiated by injecting over 30 seconds 20 ml. of this solution, containing 4.08 g. (60 mmoles) of cyclopentene and 2.94 g. (30 mmoles) of methylcyclohexene. The heat of mixing brought the temperature of the reaction mixture, 150 ml. of a homogeneous solution, to 0° , where it was maintained during the reaction.

To follow the course of the reaction, aliquots of 0.50 ml. were withdrawn with a syringe (precooled to 0°) and in-

jected into rubber-capped vials, which contained 0.10 ml. of 1-decene to react with residual disiamylborane and quench the reaction. The vials were maintained at -78° until the reaction mixtures were analyzed.

The samples, 1-3 μ l., for the v.p.c. analysis were removed with a Hamilton syringe, precooled to -78° and injected into the Perkin-Elmer 154C fractometer containing a 1-m. adiponitrile column maintained at $40-50^{\circ}$. The injection block was maintained at a low temperature, $50-70^{\circ}$, to avoid pyrolysis of the injected mixture. Symmetrical peaks were obtained and the areas determined by graphical integration.

Data for a typical kinetic study are presented in Table I. Other kinetic data are shown graphically in Figs. 2 and 3.

Acknowledgment.—The financial assistance provided by the National Science Foundation (G-6273) and the Petroleum Research Fund of the American Chemical Society (585-C) is gratefully acknowledged. We are also deeply indebted to Dr. Kenneth S. Greenlee of the American Institute Project 45 at Ohio State University, who generously made available a large number of pure olefins and thereby greatly facilitated this study.

[CONTRIBUTION NO. 683 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

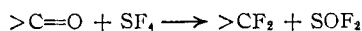
Chemistry of Sulfur Tetrafluoride.¹ VI. Fluorination of Thiocarbonyl Compounds

BY R. J. HARDER AND W. C. SMITH

RECEIVED MARCH 13, 1961

The reactions of several thiocarbonyl compounds with SF_4 have been investigated. Fluorine atoms are introduced with ease at specific sites in the molecule by replacement of sulfur, with complete utilization of the fluorine in SF_4 .

An earlier paper² in this series described the use of sulfur tetrafluoride (SF_4) as a highly selective agent for the replacement of oxygen by fluorine in organic compounds. Thus, SF_4 converts a carbonyl group to a difluoromethylene group, thionyl fluoride being formed as a by-product.



We have found that the thiocarbonyl group is fluorinated by SF_4 in a similar manner. This reaction differs from that of SF_4 with carbonyl compounds, however, in that a formal oxidation-reduction of the sulfur atoms in the thiocarbonyl compound and SF_4 occurs, resulting in the formation of free sulfur and the complete utilization of the fluorine atoms in SF_4 .



The course of reaction, therefore, parallels that of SF_4 with inorganic sulfides, which are converted to the corresponding fluorides and sulfur.³

Ethylene trithiocarbonate reacts smoothly with SF_4 at 110° in the absence of catalyst to give 2,2-difluoro-1,3-dithiolane (I) in 82% yield, by-product sulfur being obtained in 90% of the theoretical amount. Dithiolane I is readily hydrolyzed

(1) Paper V, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3838 (1960). See also papers VII, C. W. Tullock, R. A. Carboni, R. J. Harder, W. C. Smith and D. D. Coffinan, *ibid.*, **82**, 5107 (1960), and VIII, W. C. Smith, *ibid.*, **82**, 6178 (1960).

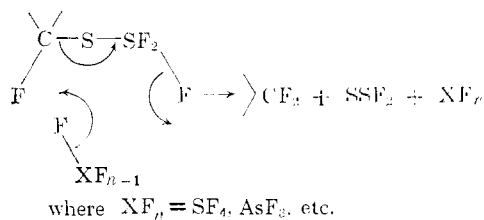
(2) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(3) A. L. Oppgaard, W. C. Smith, E. L. Muettterties and V. A. Engelhardt, *ibid.*, **82**, 3835 (1960).

to ethylene dithiocarbonate, demonstrating that no rearrangement of the ring system occurred during fluorination.

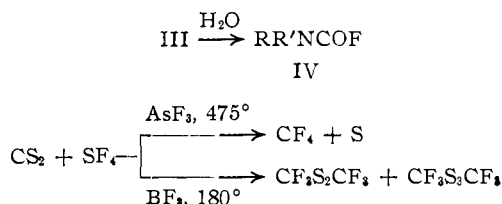
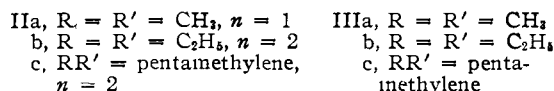
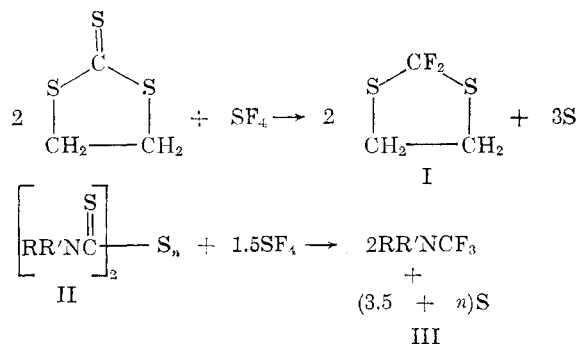
Fluorination of thiuram sulfides (II) with SF_4 also proceeds with ease, affording a novel series of compounds, the dialkyltrifluoromethylamines (III). Typical of this transformation is the reaction of SF_4 with bis-(pentamethylene)-thiuram disulfide (IIc) at 100° , providing a 70% yield of 1-trifluoromethylpiperidine (IIIc). It is interesting to note that both the thione and sulfidic sulfur atoms of the thiuram compound and the sulfur atom of SF_4 appear as free sulfur among the products.

A mechanism can be written for the initial stages of the SF_4 -thiocarbonyl reaction which parallels that proposed for the SF_4 -carbonyl reaction.² However, if the analogy between these two reactions were carried to completion, the result would be the elimination of a fragment SSF_2 .



A fluoride of sulfur, S_2F_2 , is known, but the structure has not been determined. It has been found in this Laboratory that S_2F_2 disproportionates moderately fast at room temperature to give SF_4 and

sulfur,⁴ and therefore transient formation of S_2F_2 is not inconsistent with the observed course of reaction, but an understanding of the intimate details of this reaction must await further study.



The dialkyltrifluoromethylamines are highly susceptible to hydrolysis, as expected by analogy with the dialkyltetrafluoroethylamines.⁵ Diethyltrifluoromethylamine (IIIb) reacts vigorously with water, and all of the amines prepared in this study fume in air. In the case of 1-trifluoromethylpiperidine (IIIc), the initial product of hydrolysis, 1-piperidinecarbonyl fluoride (IV, RR' = pentamethylene), is much less easily hydrolyzed than its precursor, so that the carbonyl fluoride can be isolated in high yield.

Carbon disulfide gives an essentially quantitative yield of carbon tetrafluoride on reaction with SF₄ at 450° in the presence of arsenic trifluoride catalyst, the major by-product again being sulfur. At lower temperatures (180–225°), bis-(trifluoromethyl) polysulfides are formed if a catalyst is present, and no reaction occurs in the absence of catalyst.⁶ Sulfur tetrafluoride and carbon disulfide at 180° in the presence of boron trifluoride catalyst gave a mixture of bis-(trifluoromethyl) polysulfides from which a 28% yield of bis-(trifluoromethyl) trisulfide was obtained.

Acknowledgment.—The authors gratefully acknowledge helpful suggestions given by Dr. V. A. Engelhardt of this laboratory.

(4) Unpublished observation by W. C. S. This is in contrast with the report by L. M. Dubnikov and N. I. Zorin, *J. Gen. Chem. U.S.S.R.*, **17**, 185 (1947), that S₂F₂ disproportionates to SF₂ and sulfur, and at a significant rate only above 140°.

(5) D. C. England, L. R. Melby, M. A. Dietrich and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5116 (1960). The facile hydrolysis of R₂NCF₂CF₂H to R₂NCOF is reported.

(6) We are indebted to Dr. A. L. Oppgaard of this laboratory for carrying out some of the carbon disulfide reactions.

Experimental⁷

Sulfur tetrafluoride was prepared by the method of Tullock, *et al.*⁸

Reactions were carried out in high-pressure shaker vessels lined with Hastelloy or stainless steel. The solid or liquid reactants were charged into the vessel under nitrogen and after cooling with an acetone–solid carbon dioxide-bath the reactor was evacuated. The required amount of sulfur tetrafluoride then was added. Volatile products were collected in stainless steel cylinders and liquid products were transferred to polyethylene bottles.

2,2-Difluoro-1,3-dithiolane (I).⁹—A 400-ml. high-pressure vessel charged with 88 g. (0.65 mole) of ethylene trithiocarbonate and 145 g. (1.34 moles) of sulfur tetrafluoride was heated for 8 hours at 110°. There was obtained 140 g. of a mixture of liquid and solid. The liquid fraction (90 g.) was removed and distilled through an oven-dried Vigreux column, giving 75 g. (82%) of pale yellow liquid, b.p. 51° (11 mm.). Some etching of the column occurred during distillation, and the product fumed slightly in the air. The n.m.r. F¹⁹ spectrum had a single unsplit resonance at –1488 c.p.s.

Anal. Calcd. for C₂H₄F₂S₂: F, 26.73; S, 45.10. Found: F, 26.82; S, 44.94.

The solid fraction was washed with small amounts of ether and acetone, and the residue was extracted continuously with carbon disulfide. The solvent was removed from the extracts and the residue was recrystallized from chloroform, giving 28 g. (90%) of sulfur.

Hydrolysis of 2,2-Difluoro-1,3-dithiolane (I).—Twelve grams of 2,2-difluoro-1,3-dithiolane (I) was stirred with 50 ml. of ice-water while a slight excess of saturated aqueous sodium bicarbonate solution was added. The mixture was allowed to warm to room temperature and then was filtered, giving 9 g. (90%) of ethylene dithiocarbonate, identified by melting point and mixed melting point with an authentic sample.

1-Trifluoromethylpiperidine (IIIc).⁹—A 145-ml. Hastelloy shaker vessel charged with 47 g. (0.15 mole) of bis-(pentamethylene)-thiuram disulfide (IIc) and 49 g. (0.45 mole) of sulfur tetrafluoride was heated for 6 hours at 100°. There was obtained 69 g. of a mixture of magenta colored liquid and yellow solid. Filtration gave 23 g. (88%) of sulfur. Distillation of the filtrate through an oven-dried Vigreux column gave 34 g. (70%) of 1-trifluoromethylpiperidine (IIIc), b.p. 44° (68 mm.); some decomposition occurred during distillation. The amine is quite sensitive to traces of moisture, decomposing fairly rapidly in the presence of glass, and a satisfactory analysis could not be obtained.

Anal. Calcd. for C₈H₁₀F₃N: C, 47.05; H, 6.58; F, 37.22; N, 9.15. Found: C, 48.37; H, 6.76; F, 36.16; N, 8.42.

The n.m.r. F¹⁹ spectrum consisted of a strong unsplit resonance at –375 c.p.s. and a very weak resonance at –1920 c.p.s., the latter being due to 1-piperidinecarbonyl fluoride (IV, RR' = pentamethylene) formed by hydrolysis of IIIc.

Hydrolysis of 1-Trifluoromethylpiperidine.—To 100 ml. of ice-water was added with stirring 12 g. of 1-trifluoromethylpiperidine (IIIc). The mixture was stirred occasionally during 10 minutes, the insoluble oil was removed, diluted with ether, and dried over sodium sulfate. Distillation gave, after removal of ether, 7.5 g. (73%) of 1-piperidinecarbonyl fluoride (IV, RR' = pentamethylene), b.p. 61° (11 mm.). The n.m.r. F¹⁹ spectrum had a single unsplit resonance at –1920 c.p.s. The infrared spectrum (liquid) had very strong C=O absorption at 5.6 μ.

(7) All melting points are corrected and all boiling points are uncorrected. We are indebted to Dr. Harlan Foster and Mr. Charles Matthews of this Laboratory for the determination and interpretation of the n.m.r. spectra. Spectra were obtained by means of a high-resolution magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc./sec. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F¹⁹ resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field than the reference.

(8) C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

(9) W. C. Smith, U. S. Patent 2,957,001 (1960).

Anal. Calcd. for $C_8H_{10}FNO$: C, 54.94; H, 7.69; N, 10.68; F, 14.49. Found: C, 55.17; H, 7.47; N, 10.78; F, 14.46.

Dimethyltrifluoromethylamine (IIIa).⁹—A 145-ml. Hastelloy shaker tube was charged with 21 g. (0.10 mole) of bis-(dimethylthiocarbamoyl) disulfide (IIa), 0.5 g. of arsenic trifluoride catalyst, and 35 g. (0.32 mole) of sulfur tetrafluoride. The mixture was heated at 120° for 2 hours and then at 150° for 6 hours. The tube was cooled to room temperature and the volatile product was vented into an evacuated, liquid nitrogen-cooled cylinder. There remained in the tube 11 g. (77%) of sulfur.

Mass spectrometric analysis of the volatile products indicated that the sole organic product was dimethyltrifluoromethylamine, the inorganic portion consisting mainly of sulfur tetrafluoride. Strong peaks appeared at the following *M/e* values: 113, parent ion; 112, $CH_3(CH_2)NCF_2^+$ (most abundant); 94, $(CH_3)_2NCF_2^+$; 78, $CH_2NCF_2^+$; 69, CF_3^+ ; 60, CH_3NCF^+ ; 44, $(CH_3)_2N^+$; 15, CH_3^+ .

In a larger run, a small amount of the amine, b.p. 20°, remained in the bomb after venting into a cylinder as above. The n.m.r. F^{19} spectrum consisted of a strong unsplit resonance at -302 c.p.s.

Diethyltrifluoromethylamine (IIIb).⁹—A 400-ml. stainless steel shaker vessel charged with 90 g. (0.30 mole) of bis-(diethylthiocarbamoyl) disulfide (IIb) and 110 g. (1.02 moles) of sulfur tetrafluoride was heated at 120° for 8 hours. There was obtained 121 g. of a mixture of yellow liquid and solid. The latter was removed by filtration, slurred with a little ether, and recrystallized from chloroform, giving 49 g. (92%) of sulfur. The filtrate was distilled from 0.5 g. of sodium fluoride through an oven-dried Vigreux column, giving 50 g. (58%) of diethyltrifluoromethylamine (IIIb), b.p. 34-35° (180 mm.). The n.m.r. F^{19} spectrum consisted of a strong unsplit resonance at -690 c.p.s.

Anal. Calcd. for $C_8H_{10}F_3N$: C, 42.55; H, 7.14; F, 40.39. Found: C, 43.15; H, 7.64; F, 40.03.

Reaction of Sulfur Tetrafluoride with Carbon Disulfide.
A. Synthesis of Carbon Tetrafluoride.¹⁰—A 145-ml. Hastelloy shaker tube charged with 20 g. (0.26 mole) of carbon disulfide, 60 g. (0.55 mole) of sulfur tetrafluoride and 2 g. of arsenic trifluoride catalyst was heated at 200° for 2 hours, 300° for 3 hours, 400° for 4 hours and at 475° for 3.5 hours. The tube was cooled to room temperature and the volatile products were vented into a liquid nitrogen-cooled stainless steel cylinder. There remained in the bomb 24 g. of solid from which free sulfur was isolated by extraction with carbon disulfide.

Mass spectrometric analysis showed that the volatile product (48 g.) consisted of approximately 50 weight per cent. (103%) of carbon tetrafluoride and approximately 45 weight per cent. of sulfur tetrafluoride, the remainder being mainly thionyl fluoride (4.5 weight per cent.).

B. Synthesis of Bis-(trifluoromethyl) Polysulfides.—A 145-ml. Hastelloy pressure vessel charged with 35 g. (0.46 mole) of carbon disulfide, 28 g. (0.26 mole) of sulfur tetrafluoride and 3 g. of boron trifluoride catalyst was heated at 150° for 2 hours and at 180° for 8 hours. There was obtained 41 g. of lavender-colored liquid containing a small amount of solid. The decanted liquid was distilled at atmospheric pressure to give a forerun consisting of a mixture of carbon disulfide and bis-(trifluoromethyl) disulfide (identified qualitatively by infrared and n.m.r.) and 11 g. (28% based on SF_4) of bis-(trifluoromethyl) trisulfide, b.p. 78-80°, n_D^{25} 1.3978 (lit.¹¹ b.p. 86.4°, n_D^{20} 1.4023). The infrared spectrum was identical with that of authentic $CF_3-S_3-CF_3$.¹²

Anal. Calcd. for $C_2F_6S_3$: C, 10.26; F, 48.67; S, 41.07. Found: C, 10.40; F, 48.25; S, 40.98.

(10) W. C. Smith, U. S. Patent 2,922,825 (1960).

(11) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

(12) Butterworths Scientific Publications, London, England, *Chem. Soc.*, No. 51.

[CONTRIBUTION NO. 647 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Bis-(polyfluoroalkyl)-acetylenes. I. Synthesis of Bis-(polyfluoroalkyl)-acetylenes

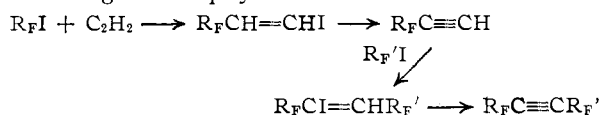
BY C. G. KRESPAN, R. J. HARDER AND J. J. DRYSDALE

RECEIVED JANUARY 31, 1961

Two new routes to 1,2-dichloro-1,2-bis-(polyfluoroalkyl)-ethylenes are presented. These routes involve coupling of 1,1,1-trichloropolyfluoroalkanes with copper, and reaction of a fluorinated acid chloride with 1,1-dichloro-2,2-difluoroethylene and nickel carbonyl. Dechlorination of two of the dichloroolefins to produce new bis-(polyfluoroalkyl)-acetylenes is described.

Recent syntheses¹⁻³ of hexafluoro-2-butyne by dehalogenation of 2,3-dichlorohexafluoro-2-butene have made this acetylene readily available. However, since the dihalides required as precursors to other bis-(polyfluoroalkyl)-acetylenes are not easily obtained, the dehalogenation reaction has not been a useful general reaction.

Dehydrohalogenation of 2-halo-1,1,1,4,4,4-hexafluoro-2-butenes also gives hexafluoro-2-butyne, but again syntheses of other precursors require several steps. Perhaps the shortest known general route to bis-(polyfluoroalkyl)-acetylenes is the following four-step synthesis.³⁻⁵



(1) A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71**, 298 (1949).

(2) C. I. Gochenour, U. S. Patent 2,546,997 (1951).

A third synthesis of hexafluoro-2-butyne, the reaction of sulfur tetrafluoride with acetylenedicarboxylic acid,⁶ gives a high yield in one step, but is, of course, limited to the introduction of CF_2 - or $-CF_2$ - groups.

This paper describes two new routes to symmetrical bis-(polyfluoroalkyl)-acetylenes *via* the corresponding dihaloolefins. One method starts from relatively inexpensive materials and consists of three steps: (1) preparation of a 1,1,1-trihaloalkane, (2) coupling of the trihaloalkane to give a dihaloolefin and (3) dehalogenation. For example, bis-(polyfluoroalkyl)-acetylenes can be made from carbon tetrachloride and tetrafluoroethylene by the following series of reactions.

(3) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952).

(4) R. N. Haszeldine and K. Leedham, *ibid.*, 1634 (1954).

(5) R. N. Haszeldine, *ibid.*, 588 (1951).

(6) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).