

their appreciation to the Research Corporation for a grant in partial support of this work. They also wish to thank Dr. E. O. Brimm of Linde Air Products Company for samples of acetylferro-

cene and 1,1'-diacetylferrocene and Dr. Madison Hunt of E. I. du Pont de Nemours and Company for samples of ferrocene.
URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Fluorocarbon Derivatives. I. Derivatives of Sulfur Hexafluoride¹

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RECEIVED NOVEMBER 15, 1956

The electrofluorination of dialkyl and cyclic sulfides and dialkyl disulfides in anhydrous hydrogen fluoride by the Simons process was investigated. Dialkyl sulfides were found to yield the corresponding di-perfluoroalkyl sulfur tetrafluorides, $(R_F)_2SF_4$ (I), together with degradation products. Dialkyl disulfides failed to give the corresponding di-(perfluoroalkyl) disulfur decafluorides, $(R_FSF_4)_2$, but yielded instead I and cleavage products.

Introduction

Direct as well as cobalt trifluoride fluorination of both methyl mercaptan and carbon disulfide result in the formation of trifluoromethyl sulfur pentafluoride, CF_3SF_5 ³ (II). Clifford, El-Shemy, Emeleus and Haszeldine⁴ obtained the same compound by electrochemical fluorination of dimethyl sulfide in anhydrous hydrogen fluoride (Simons process)⁵ together with bis-(trifluoromethyl) sulfur tetrafluoride, $(CF_3)_2SF_4$ (III), the fully fluorinated analog of the starting material. II and III, which can be regarded as mono- and di-(perfluoroalkyl) derivatives of sulfur hexafluoride, respectively, seem to be the only representatives of these two classes of compounds reported in the literature.

The successful conversion of dimethyl sulfide to III and to the cleavage product II suggested that the relatively mild conditions prevailing in the Simons cell might permit the preparation of higher homologs of the two series of sulfur hexafluoride derivatives, $(R_F)SF_5$ (I) and $(R_F)_2SF_4$ (IV), respectively, from the corresponding dialkyl sulfides. Therefore, the behavior of several open-chain and cyclic sulfides and of three dialkyl disulfides during low-voltage electrolysis in anhydrous hydrogen fluoride was studied in the course of a program for the investigation of new sulfur- and nitrogen-containing fluorocarbon derivatives. This investigation resulted in the synthesis of several open-chain and one cyclic fluorocarbon derivatives of sulfur hexafluoride. The physical constants and analyses of these new compounds are listed in Table I.

After the Experimental part of our investigation had been completed, Severson, Brice and Coon⁶ reported the preparation of $(C_4F_9)_2SF_4$ (X),

$C_4F_9SF_5$ (IX) and $CF_2CF_2OCF_2CF_2SF_4$ (XI) by the Simons process. These compounds also had been obtained in our study.

Experimental

Apparatus.—The large scale runs were performed in a cell of 3600-ml. capacity and a nominal rating of 50 amperes (cell A). The cell casing was constructed of nickel with an electrode pack of alternating anodes and cathodes (9 each, spaced $1/8$ inch apart) of $8.9 \times 17.8 \times 0.16$ cm. nickel sheeting and was provided at the bottom with a valve for the removal of insoluble liquid fluorinated product. Any gaseous reaction product, or low boiling materials entrained in the effluent hydrogen, were condensed in attached traps cooled with Dry Ice-acetone and liquid nitrogen. The effluent from the cell was passed through a low temperature reflux condenser and subsequently through a bed of sodium fluoride pellets in order to remove hydrogen fluoride from the gas stream before condensation in the attached cold traps.

Small cell runs were carried out in either of two nickel cells provided with Kel-F windows for observation of the electrolyte during the reaction. One of the cells (cell B), of 900-ml. capacity, had a cathode area of 250 sq. cm., the cell body served as the anode and the cell was rated at 10 amperes. The other small cell (cell C), of 1000-ml. capacity, was equipped with four anodes and four cathodes ($14.0 \times 12.7 \times 0.16$ cm. each) arranged alternately and was rated at 25 amperes. Cells A and C were provided with a mantle through which a refrigerant could be circulated. The coolant for the cell condensers and jacket was obtained from a Mayer Junior Chiller (Mayer Refrigerating Engineers) model J-4, using a brine of ethylene glycol and water.

The power for cell A was supplied by a Sorenson Natratron model E-6-100a and for cells B and C by a Mallory Rectopower, model 6RS25-1.

Materials.—The organic starting materials used in the electrofluorination were commercial products or were synthesized by conventional methods.

The hydrogen fluoride employed was commercial grade anhydrous hydrogen fluoride (Mathieson Chemical Corp. and Pennsylvania Salt Manufacturing Co.) which was distilled before use through a 122-cm. Monel column of 12.7 cm. inside diameter and packed with nickel Heli-pak (Podbielniak, Inc.).

The sodium fluoride pellets used for the removal of entrained hydrogen fluoride from the effluent gas stream were obtained as NaF·HF pellets (Harshaw Chemical Co.) and converted to NaF by the passage of dry air or nitrogen over the pellets at 450° for 10 hr.

Operation of the Cells.—Drying of the distilled anhydrous hydrogen fluoride (which contained approximately 0.5% of water) was accomplished by electrolyzing the cell charge of hydrogen fluoride at 5.5 to 6.0 volts. During the drying of the hydrogen fluoride some care had to be exercised to avoid undesirable explosions due to the formation of oxygen difluoride. The tendency for explosions was greatest during low flow rates of the effluent gases and could be prevented by increasing the gas flow with dry nitrogen.

(1) Presented in part at the 130th Meeting of the American Chemical Society in Atlantic City, September 16-21, 1956.

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TABLE I
 NEW COMPOUNDS

Compound	B.p., °C.	n_D^{25}	d_{4}^{25}	Carbon		Fluorine		Analyses, % Sulfur		MRD	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd. ^a	Found ^b
C ₂ F ₅ SF ₅ (V)	14										
(C ₂ F ₅) ₂ SF ₄ ^c (VI)	70	1.2754	1.836	13.9	14.1	76.8	76.7	9.2	9.2	33.05	32.6
C ₃ F ₇ SF ₅ (VII)	42	1.2594	1.801	12.1	12.8	76.8	76.5	10.8	11.2	28.15	26.87
(C ₃ F ₇) ₂ SF ₄ ^d (VIII)	116	1.2856	1.865	16.1	16.1	76.7	76.8	7.18	7.18	42.29	42.75
C ₄ F ₉ SF ₅ ^e (IX)	70.5	1.2701	1.839	13.9	13.6	76.6	76.7	9.2	10.3	32.77	31.94
(C ₄ F ₉) ₂ SF ₄ ^f (X)	154	1.2943	1.903	17.6	17.8	76.4	76.1	5.9	6.5	51.53	52.73
OCF ₂ CF ₂ SF ₄ CF ₂ CF ₂ (XI)	80-80.5	1.3015	1.859	14.6	14.3	70.4	70.2	9.87	10.4	32.49	32.7
(C ₂ F ₅) ₂ NCF ₂ CF ₂ SF ₅ ^g (XII)	124	1.2921	1.86	15.0	15.3			6.7	7.1	45.9	47.00

^a The MRD values were calculated using the following atomic refractions: S (in SF₄) 7.97, S (in SF₅) 7.69, F 1.10, C 2.42, N 2.84, -O- 1.64. ^b Calculated by the Lorentz-Lorenz equation. ^c Molecular weight, found 243, calculated 246. ^d Dielectric constant, liquid, 1.923. ^e Dielectric constant, liquid, 2.068. ^f Dielectric constant, liquid, 1.951. ^g Anal. Calcd.: N, 2.9; Found: N, 2.27.

The cells normally were operated at the reflux temperature of the electrolyte. However, cooling the cell charge was found to be desirable before addition of organic starting material, before emptying the cell after completion of a run, during temporary shut-downs over the week-ends, and in case of a leak or clogging of the exit gas lines. In general, the runs in cell A were carried out with 4 to 7 mole % of solute at 5.2-5.8 volts for extended periods on a 24-hr. day basis for 5 days per week with intermittent shut-downs of 65-70 hr. over the week-ends. If at all possible, cells B and C were also operated on this semi-continuous basis. During the course of all runs in cell A, hydrogen fluoride and organic starting materials were added intermittently in order to maintain an approximately constant concentration. Further addition of starting material was based on a measure of the hydrogen produced (as measured by a wet test meter) in the electrofluorination. The experimental data given in the original paper by Simons⁵ on the electrofluorination process show that the replacement of one atom of hydrogen by fluorine proceeds with the consumption of two faradays and the formation of 1 mole of hydrogen with approximately 90% efficiency. In calculating the faradays required for fluorinating organic sulfur compounds and, thus, the hydrogen produced, it was assumed that the initial attack occurred at the sulfur atom and that this addition of fluorine would require only one faraday per fluorine atom. For example, the complete fluorination of one mole of dipropyl sulfide will require on this basis the passage of at least 32 faradays and result in the production of 358.4 liters of hydrogen (S.T.P.).

In runs performed in cells B and C the starting material was added in one portion to the hydrogen fluoride charge, and the electrofluorination was continued until the electrolyte was depleted of starting material.

Purification of Liquid Cell Products.—Liquid products obtained from the electrochemical cell were washed with water, dilute aqueous sodium bicarbonate solution and again with water. The heavy layer of insoluble, fluorinated product was separated and refluxed with 30-50% aqueous potassium hydroxide to remove hydrolyzable impurities. The insoluble fluorinated material was then washed with water, left in contact with Drierite or magnesium sulfate and the dried material was finally fractionated through a modified Todd column of approximately 40 plates. Center fractions of constant boiling point and refractive index were taken for analysis and determination of physical properties. The purity of the sample was checked by infrared and NMR analysis.

Gaseous products were passed over sodium fluoride pellets to remove entrained hydrogen fluoride and dried by passage over phosphorus pentoxide. If the gaseous cell effluents were found to attack mercury, they were purified further by passing through 30% aqueous potassium hydroxide solution. The purified gaseous material was then fractionally distilled in a low temperature column of approximately 25 plates. Molecular weights were determined by the vapor density method employing a gas density balance.⁷

Electrochemical Fluorinations.—The experimental conditions employed in the various runs are listed in Table II together with the weight-yields of the main products. In

some of the runs, only portions of the cell products were worked up; in these cases, the amounts of products indicated in the table were calculated from the data obtained by fractionation of aliquots of the crudes.

Only the isolation of the major products from the insoluble, liquid cell drainings and the cold trap condensates is described in detail in the following for the various sulfur-containing starting materials.

Diethyl Sulfide.—The crude, liquid cell drainings (36.5 g.) were stabilized with aqueous alkali and refluxed under the column with overhead removal of the volatile material which was recondensed in an attached Dry Ice-acetone cold trap. Fractionation of the material remaining in the distillation flask yielded after a forerun of 5 g., b.p. 31-70.0°, 12.5 g. of di-(perfluoroethyl)-sulfur tetrafluoride (VI), b.p. 70.0-70.2°, n_D^{25} 1.2753.

The volatile material (14.5 g.) from the cell drainings was combined with the Dry Ice condensate (70 g.) from the cell effluents. The mixture was stabilized with alkali (89% recovery) and fractionated in a low temperature still to yield 20 g. of sulfur hexafluoride, b.p. -65 to -60°; 46 g. of pentafluoroethyl-sulfur pentafluoride (V), b.p. 13.5°, molecular weight 244 (calcd. 246); and 4 g. of pot residue. The identities of both V and VI were confirmed by nuclear magnetic resonance (NMR) analysis.

Di-*n*-propyl Sulfide.—The electrofluorination of 826 g. of di-*n*-propyl sulfide (Eastman Kodak, white label) gave during 215 hr. of operation 2052 l. of hydrogen at an average current of 23.5 amp. The run yielded 536 g. of HF-insoluble liquid product, 695 g. of Dry Ice-acetone trap condensate and 215 g. of condensate in the liquid nitrogen trap.

The combined Dry Ice and liquid nitrogen condensates were vaporized, passed over sodium fluoride, dried and separated into four arbitrary fractions: (1) b.p. -140 to -70°, approximately 200 g.; (2) b.p. -70 to 0°, 227 g.; (3) b.p. 0-25°, approximately 60 g.; (4) b.p. above 25°, 430 g.

Cut 1 was found to attack mercury. Therefore, a portion of 95 g. was passed through 30% aqueous potassium hydroxide solution to remove the reactive, unidentified contaminants; 59% of purified condensate was recovered. Low temperature distillation of the purified material yielded approximately 7 g. of crude carbon tetrafluoride, b.p. -140 to -80° (reported⁸ b.p. 129°), molecular weight 78-86 (calcd. 88); 28 g. of crude sulfur hexafluoride, b.p. -80 to -60°, molecular weight 120-144 (calcd. 146) (identified by infrared analysis).⁹

Low temperature distillation of 219 g. of fraction 2 yielded 136.2 g. of sulfur hexafluoride, b.p. -62 to -57° (reported¹⁰ b.p. -63.9°), molecular weight 138-147; and 52.8 g. of hexafluoropropane, b.p. -36 to -33° (reported⁸ b.p. -38°) molecular weight 185 (calcd. 188). Fraction 3 of the original distillation did not yield any identifiable material.

Fraction 4 was stabilized with aqueous potassium hydroxide, dried with Drierite (88.4% recovery) and distilled to give the cuts: (4a) b.p. 27-42°, 42 g.; (4b) b.p. 42.0-

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TABLE II
 EXPERIMENTAL CONDITIONS

Organic starting material	Mole % organic	Total organic used, g.	Potential applied, v.	Av. amp.	Cell used	Faradays	Products ^a Compound	Wt., g.
(C ₂ H ₅) ₂ S	7.0	198	5.8	4.0	C	33	V	46
(C ₃ H ₇) ₂ S	3.5	826	5.4	23.5	A	189	VI	12.5
(<i>n</i> -C ₄ H ₉) ₂ S	3.5	1746	5.4	24	A	472	VII	312
(<i>n</i> -C ₄ H ₉) ₂ S	3.5	1746	5.4	24	A	472	VIII	316
(<i>n</i> -C ₄ H ₉) ₂ S	4.0	1964	5.3	39.5	A	890	IX	724
(<i>n</i> -C ₄ H ₉) ₂ S	4.0	1964	5.3	39.5	A	890	X	695
(<i>t</i> -C ₄ H ₉) ₂ S	3.4	849	5.5	22.4	A	113.8	IX	838
(<i>t</i> -C ₄ H ₉) ₂ S	3.4	849	5.5	22.4	A	113.8	X	180
(<i>t</i> -C ₄ H ₉) ₂ S	3.0	713	4.5	12.7	A	171	Liquid products ^b	178
(<i>t</i> -C ₄ H ₉) ₂ S	3.0	713	4.5	12.7	A	171	Gaseous products	825
(<i>t</i> -C ₄ H ₉) ₂ S	3.0	713	4.5	12.7	A	171	Liquid products ^b	522
(<i>t</i> -C ₄ H ₉) ₂ S	3.0	713	4.5	12.7	A	171	Gaseous products	1051
CH ₂ CH ₂ SCH ₂ CH ₂	3.0	100	5.4	4.0	B	17.2	Liq. product mixt. ^c	17.0
CH ₂ CH ₂ OCH ₂ CH ₂ S	2.1	78	5.2	4.9	B	15.2	XI	19.0
[(C ₂ H ₅) ₂ NCH ₂ CH ₂ S] ₂	0.7	62	5.3	6.0	B	15.1	XII	30
(C ₄ H ₉) ₂ SO	1.3	81	5.2	4.4	C	14.3	IX	3
(C ₄ H ₉) ₂ SO	1.3	81	5.2	4.4	C	14.3	X	4

^a Sulfur hexafluoride was obtained in all runs. ^b No effective separation was possible. ^c Mixture of XV, VI, IX and C₃F₇SF₄CF₃.

42.5°, *n*_D²⁰ 1.2594, 312 g.; (4c) b.p. 43–46.0°, 21 g. Elemental and NMR analysis of cut 4b led to its identification as perfluoropropyl sulfur pentafluoride, C₃F₇SF₅ (VII), which was also the main component of the cuts 4a and 4c.

The fractionation of the purified cell drainings (493 g.) yielded after a forerun of 42 g. of material, b.p. 43–116°, 360 g. of di-(perfluoropropyl) sulfur tetrafluoride (VIII), colorless liquid, b.p. 116.0–116.5°, *n*_D²⁰ 1.2856–1.2858; and 29.3 g. of less pure VIII, b.p. 117.0–118.0°, *n*_D²⁰ 1.2868. An analytical cut of VIII, b.p. 116.0°, gave a NMR spectrum which confirmed its identity.

Di-*n*-butyl Sulfide.—From 1746 g. of di-*n*-butyl sulfide (Eimer & Amend, Highest Purity) were obtained 1530 g. of liquid cell products, 2330 g. of Dry Ice-acetone condensate and 600 g. of liquid nitrogen condensate.

Distillation of portions of the material condensed at –78° showed that its composition changed during the run and depended apparently on a variety of factors, such as cell voltage, flow rate of effluent gas and cell temperature. Dry Ice condensate (900 g.) collected during the first half of the run was separated into a gaseous and a liquid fraction (boiling above room temperature). A portion of 195 g. of the low boiling material (about 57% of the total amount of crude Dry Ice condensate) subjected to a low temperature distillation at 761 mm. gave 10.2 g. of unidentified product, b.p. –23 to –4°, average molecular weight 154; 173.3 g. of perfluorobutane, b. 1–3°, molecular weight 223–235 (calcd. 238); and 13.2 g. material, b. 3–15°. The weights of the three fractions correspond to 4.7, 88.4 and 6.3%, respectively, of the total charge.

A portion of 110 g. of low boiling material from the Dry Ice condensate collected at a later stage of the electrofluorination gave the following fractions: (1) b.p. 1–2°, 48.5 g., molecular weight 230–238; (2) b.p. 10–24°, 36.4 g., molecular weight 226–196; (3) b.p. above 24°, 20 g. The weights of the fractions 1 to 3 correspond to 44, 33.1 and 18.2%, respectively, of the total charge. The NMR spectrum indicated fraction 1 to be pure *n*-decafluorobutane (XIII), while fraction 2 gave a spectrum consistent with that expected for a mixture of nonafluorobutane (XIV) isomers (reported¹¹ C₄F₉H, b.p. 14–15°).

The higher boiling material from the various Dry Ice-acetone condensates was combined (1006 g.), and a portion of 268 g. was fractionated through an 18-in. heated column (packed with Heli-pak) to give after a forerun of 5.4 g., b.p. 61–68°, 95.1 g. of crude nonafluorobutyl sulfur pentafluoride (IX), b.p. 68–71°, *n*_D²⁰ 1.2740–1.2728; and 25.0 g. of pot residue, *n*_D²⁰ 1.2740. The NMR spectrum of the crude IX suggested the presence of approximately 25% of

the cyclic compound perfluorothiophane tetrafluoride,

CF₂(CF₂)₂SF₄ (XV), as a contaminant. One hundred thirty-seven grams of condensate was collected in a cold trap attached to the still. Redistillation of this material showed it to consist mainly of XIV isomers.

The total amount of mixture of IX and XV obtained by rectification of the Dry Ice condensate was 406 g. A separation of this mixture by careful redistillation was not possible.

Distillation of the purified liquid cell drainings (1416 g.) yielded 659 g. of bis-(nonafluorobutyl) sulfur tetrafluoride (X), b. 90.5–98.5° (100 mm.), *n*_D²⁰ 1.2940–1.2948. A middle cut of this material was taken and redistilled at atmospheric pressure to give an analytical sample, b.p. 154.0°, *n*_D²⁰ 1.2943. The lower boiling portion of the liquid cell product gave a cut of 318 g. of impure IX, b.p. 67–76°, *n*_D²⁰ 1.2720–1.2709. An analytical cut, b.p. 70.5–70.7°, *n*_D²⁰ 1.2709, gave a NMR spectrum similar to that for the mixture of IX and XV obtained from the Dry Ice condensate.

Low temperature distillation of the gaseous products condensed in the liquid nitrogen trap led to the identification of sulfur hexafluoride and XIII by infrared analysis.

Di-*n*-butyl Sulfoxide.—Rectification of the stabilized cell drainings (9.5 g. of crude material) yielded 3 g. of colorless distillate, b.p. 69.0–71.0°, *n*_D²⁰ 1.2768–1.2770, identified by its NMR spectrum as impure IX, and 4 g. of colorless distillate, b. 155°, *n*_D²⁰ 1.2945, identified as X. Low temperature distillation of the Dry Ice-acetone condensate (28 g.) led to the identification of sulfur hexafluoride and XIII.

Thiophane.—Fractionation of 60 g. of insoluble cell drainings, obtained from 100 g. of thiophane, b. 118–120°, gave 8 g. of forerun, b.p. up to 68.0°; 17.0 g. of colorless distillate, b. 68.0–72.5°, *n*_D^{21.5} 1.2768–1.2762; 11 g. of higher boiling material at 72.5–120°; and 16 g. of distillation residue. The material, b. 68.0–72.5°, was redistilled and a middle cut taken at 70.0°, *n*_D²⁰ 1.2766, for analysis.

Anal. Calcd. for C₄F₁₂S: C, 15.59; F, 74.0; S, 10.41. Found: C, 15.4; F, 74.6; S, 10.0.

Although the analysis of this cut is in fair agreement with the values calculated for perfluorothiophane tetrafluoride (XV), its NMR spectrum showed considerable contamination with VI, IX and possibly C₃F₇SF₄CF₃. A cut, b.p. 72.5–73.5°, *n*_D^{21.5} 1.2758, of the higher boiling distillate showed the same NMR resonance peaks as the analytical samples of XV, but with variations in the intensities.

The pot residue was not further investigated.

Thioxane.—Electrofluorination of 78 g. of thioxane (Carbon & Carbide Chemicals Co.) yielded 55 g. of liquid

(11) A. F. Benning and J. D. Parks, U. S. Patent 2,490,760 (1950).

cell drainings and 1 g. of Dry Ice-acetone condensate. Distillation of the liquid product gave in addition to 25.0 g. of lower boiling cuts 19.0 g. of colorless liquid, b.p. 78.2–78.8°, n_D^{25} 1.3019, and left 11 g. of residue. The main fraction was identified as perfluorothioxane tetrafluoride (XI), but infrared analysis indicated the presence of an acid fluoride impurity. The material, therefore, was refluxed for 3 hr. with excess ammonium hydroxide and redistilled to yield the pure XI, b.p. 80.0–80.5°, n_D^{25} 1.3015, as indicated by its infrared and NMR analysis. No identification of the Dry Ice condensate or of the lower boiling fractions was attempted.

Di-*n*-butyl Disulfide.—In this run, 1900 g. of HF-insoluble, liquid cell drainings, 2010 g. of Dry Ice condensate and 1044 g. of liquid nitrogen condensate were obtained from 1964 g. of di-*n*-butyl disulfide (Fisher, Highest Purity). Rectification of the stabilized liquid product gave after a forerun of 71.3 g., b. 45–70°, a fraction of 833 g. of crude IX, b. 70–72°, n_D^{25} 1.2704, and a fraction of 179.5 g. of X, b.p. 61–62° (21 mm.), n_D^{25} 1.2960. The NMR spectrum of the crude IX indicated 10–15% contamination with XV. A careful fractionation of the crude material gave a constantly boiling cut of IX, b.p. 70.5°, n_D^{25} 1.2701, which on the basis of its NMR spectrum was free from the cyclic compound XV.

A portion of the liquid nitrogen condensate was screened and found to contain approximately 60% of sulfur hexafluoride and 20% of decafluorobutane (XIII) together with products which attacked mercury and reacted with 20% aqueous potassium hydroxide solution. The remainder of this condensate was not investigated.

Careful rectification of the Dry Ice condensate gave a fraction of XIII, b.p. –12 to –11° (462 mm.), and a cut, b.p. 2–4° (462 mm.), consisting of a mixture of isomeric C_4F_8H (XIV). The NMR spectrum of the XIII showed it to contain approximately 15% of the isomeric decafluoroisobutane, $(CF_3)_3CF$ (XVI). The higher boiling portion of the –78° condensate consisted to a large extent of IX but was not processed further.

Di-*t*-butyl Disulfide.—Electrofluorination of 849 g. of di-*t*-butyl disulfide (Eastman Kodak, Practical Grade, b.p. 198–204°) gave 178 g. of HF-insoluble, liquid product, 502 g. of Dry Ice-acetone condensate and 323 g. of liquid nitrogen condensate. The rectification of the alkali-treated liquid product did not yield any constantly boiling fraction. NMR analysis of several arbitrary cuts indicated complex mixtures of fluorocarbons and derivatives of sulfur hexafluoride containing both normal and branched chains. Low temperature distillation of the gaseous products gave sulfur hexafluoride and decafluorobutane. The NMR analysis of the decafluorobutane fraction showed that the major component was XIII contaminated with 10–15% of XVI.

A second run with 713 g. of di-*t*-butyl disulfide at a lower voltage resulted in the formation of 522 g. of liquid cell drainings, 734 g. of Dry Ice condensate and 317 g. of condensate collected in the liquid nitrogen trap. In spite of the larger amount of liquid cell product from this run, we were unsuccessful in isolating any pure material. The results of the NMR analyses of several arbitrary cuts were similar to those obtained with the material from the run performed at 5.5–5.6 v.

Di-(β -diethylaminoethyl) Disulfide.—Di-(β -diethylaminoethyl) disulfide (62 g., 0.235 mole), b.p. 117° (35 mm.) to 119° (50 mm.), n_D^{25} 1.4977–1.4981, yielded 81 g. of liquid cell product and 16 g. of Dry Ice condensate which boiled above room temperature and gave upon fractionation a series of small, unidentified cuts in the range from 23 to 58°. Rectification of the liquid product gave after a forerun of 12.6 g., b.p. 60–120°, a fraction of 30 g. of $(C_2F_5)_2NCF_2CF_2SF_6$ (XII), b.p. 122–124°, n_D^{25} 1.2921, and left 15 g. of distillation residue which was not further investigated.

Small amounts of partly fluorinated tar-like products deposited in the cell in all runs. The tars isolated from the electrochemical fluorinations of di-*n*-butyl sulfide and disulfide and of di-*t*-butyl disulfide were analyzed and found to have the approximate compositions $C_{10}H_{11}F_{10}S$, $C_{11}H_6F_{13}S$ and $CH_2F_2S_2$, respectively.

Pyrolysis of Perfluorobutyl Sulfur Pentafluoride.—Perfluorobutyl sulfur pentafluoride (173 g., 0.3 mole) was passed at a rate of approximately 0.25 mole per hour through a metal tube packed with aluminum oxide-aluminum fluoride pellets heated to 650–700°. The effluent gases were con-

densed in attached Dry Ice-acetone and liquid nitrogen traps. Distillation of the combined condensate (147 g.) gave 44 g. of distillate, b.p. –130 to –75°; 74 g. of material boiling below 25°; and 29 g. of liquid, boiling above 25°. Further fractionation of the higher boiling liquid fraction yielded three distinct cuts: (1) b.p. 56–58°, n_D^{25} 1.2513, 3 g.; (2) b.p. 80–83°, n_D^{25} 1.2610, 3 g.; (3) b.p. 102–104°, n_D^{25} 1.2670, 4 g.; which were identified tentatively by their physical constants as perfluorohexane (reported¹² b.p. 57.23°, n_D^{25} 1.2515); perfluoroheptane (reported¹³ b.p. 82.51°, n_D^{25} 1.26019) and perfluoroöctane (reported¹⁴ b.p. 103.5°, n_D^{25} 1.2830) respectively.

Reaction of Perfluorodibutyl Sulfur Tetrafluoride with Aluminum Chloride.—Di-(perfluorobutyl) sulfur tetrafluoride (100 g., 0.183 mole) was cautiously added to 15 g. of anhydrous sublimed aluminum chloride in a 500-ml. flask equipped with stirrer. The temperature of the stirred mixture was slowly raised to 80° where a violent reaction occurred. When the reaction subsided, the material was heated to 100° and held at this temperature for 5 hr. Distillation of the reaction product after drying over Drierite gave 15 g. of a greenish yellow liquid, b.p. 96–97°, n_D^{25} 1.3489. Infrared analysis indicated that this material contained a C_4F_9 -group and that its spectrum was very similar to that of $(C_4F_9)_2SF_4$, with some major differences in the long wave lengths. Elemental analysis gave 49.2% fluorine and 30.52% chlorine.

Summary of Results

The stability of alkyl sulfides and saturated cyclic sulfur compounds in anhydrous hydrogen fluoride makes these compounds suitable starting materials for conversion by the Simons process to the corresponding fully fluorinated analogs. Similarly to the behavior of dialkyl ethers the sulfides form in hydrogen fluoride more or less colored solutions which exhibit a high degree of conductivity. The conductivity of these sulfide solutions is undoubtedly the result of the formation of a salt-like addition compound between sulfide and hydrogen fluoride of the type $(R_2S-H)^+ F^-$, which ionizes readily in the liquid hydrogen fluoride.

While a considerable part of the sulfide is degraded with rupture of the sulfur-carbon and even the carbon to carbon bonds during the electrolysis, some of the starting material is converted without apparent change of the original skeleton to the fully fluorinated analog. The partial degradation of the starting material was observed in all electrolytic runs to varying degrees and was noticed to increase with increasing voltage; it is definitely responsible for the relatively low conversion of a given organic compound to the fully fluorinated analog.

The sulfur-containing fluorocarbon analogs obtained from dialkyl sulfides were in all runs of the types $R_F SF_6$, $(R_F)_2 SF_4$ and $R_F' SF_4$, where R_F represents a $C_n F_{2n+1}$ group and R_F' represents $C_n F_{2n}$ and is part of a heterocyclic system incorporating the sulfur atom. In no case could any sulfur derivatives of a lower oxidation state be obtained. Although the absolute amount of bis-(heptafluoropropyl) sulfur tetrafluoride (VIII) was, in the run with dipropyl sulfide, larger than that of heptafluoropropyl sulfur pentafluoride (VII), the relative yield of VII on a molar basis was higher than that of VIII. In the runs starting with diethyl and di-*n*-butyl sulfide the yields of $R_F SF_6$ exceeded by far those of $(R_F)_2 SF_4$, even on an absolute weight basis. Cleavage of the carbon-sul-

(12) V. E. Stiles and G. H. Cady, *THIS JOURNAL*, **74**, 3771 (1952).

(13) H. T. Milton and G. D. Owler, *ibid.*, **74**, 3951 (1952).

(14) R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951).

fur bonds was thus rather pronounced in all these runs. Whether this cleavage occurs by a rupture of one of the C-S bonds in the original or only partly fluorinated sulfide or whether it is the result of a degradation of the $(R_F)_2SF_4$ cannot be decided on the basis of our experiments; but the formation of partly fluorinated tar-like products in all cell runs might well be interpreted by an at-random attack on the carbon-to-sulfur and carbon-to-carbon bonds of the sulfide at any time during the electrolysis. Rupture of the C-S bond in the original sulfide should lead to gaseous monofluorohydrocarbon derivatives which, however, were not found, at least not in amounts sufficient for identification. The lack of solubility in the hydrogen fluoride and the great stability of the bis-(perfluoroalkyl) sulfur tetrafluorides argues against its degradation in the cell. The presence of the sulfur in its highest valence state in all products, except perhaps the cell tars, suggests that the oxidation of the sulfur occurs in the initial stages of the electrofluorination of the sulfides and disulfides before the fluorination of the carbon chain is completed. In contrast to this observation, Haszeldine and Nyman¹⁵ were able to isolate from an electrofluorination run of thioglycolic acid in addition to $SF_5CF_2CO_2H$ the incompletely fluorinated product $SF_3CF_2CO_2H$ which demonstrates that in this case the substitution reaction on the carbon is completed before the oxidation of the sulfur atom is accomplished.

It was hoped that fluorocarbon derivatives of the type $(R_FSF_4)_2$, the symmetrical bis-(perfluoroalkyl) derivatives of disulfur decafluoride, S_2F_{10} , might be obtainable by the electrofluorination of dialkyl disulfides in hydrogen fluoride. However, in the runs performed with di-*n*-butyl disulfide and di-*t*-butyl disulfide, no indications for the formation of a derivative of S_2F_{10} were obtained. The results of these two runs were rather surprising insofar as in addition to the expected cleavage product, R_FSF_5 , the second major, higher boiling reaction product was the SF_6 derivative of the type $(R_F)_3SF_4$. In the run starting with di-*n*-butyl disulfide, the main reaction product was identical with the compound obtained from di-*n*-butyl sulfide.

That the effect of the electrofluorination on a given carbon skeleton of an organic compound is far deeper reaching than that of a simple replacement of hydrogen by fluorine becomes obvious in the examination of the NMR spectra of the gaseous cleavage products from the runs with di-*n*-butyl and di-*t*-butyl disulfide. The decafluorobutane fraction, b.p. about 0°, was in both cases a mixture of the two possible isomers, *n*- C_4F_{10} and $(CF_3)_3CF$, containing 10-15% of the branched isomer. The observed rearrangement of a tertiary carbon arrangement as in $(C)_3\equiv C$ to a normal chain does not have a counterpart in the organic radical or carbonium ion chemistry and seems to be unique, but nevertheless general, in the chemistry of fluorocarbons. This type of rearrangement was also observed in the cleavage of substituted pyridines during electrochemical fluorination (see paper II of this series).¹⁶ It is noteworthy that the ratio of

normal to branched isomers seemed to be the same, regardless of the structure of the parent compound.

A unique side-reaction, involving an interesting cyclization, was demonstrated by the presence of 20-25% of an impurity in the $C_4F_9SF_5$ (IX) fraction (from di-*n*-butyl sulfide and disulfide) which was identified as perfluorothiophane tetrafluoride (XV) on the basis of the similarity of the additional peaks in the NMR spectrum of the crude IX with those expected and also found in the reaction product obtained from thiophane. A similar cyclization was observed previously¹⁷ in the electrofluorination of $(C_2H_5)_2NCOF$ which resulted in the formation of perfluoro-3-ethyloxazolidine, $C_2F_5NCF_2$ -

CF_2OCF_2 . It is interesting to note that the IX obtained by electrofluorination of di-*n*-butyl disulfide contained only 10% of the cyclic impurity XV.

The NMR analysis of the higher boiling products from the electrofluorination of di-*t*-butyl sulfide indicated all of these fractions to be complex mixtures of normal and branched chain fluorinated compounds. Only a small part of the high boiling material consisted of sulfur-containing compounds, the majority was a mixture of fluorocarbons. The presence of fluorocarbons in these fractions, b.p. 70-85° (18 mm.), would require that these fluorocarbons contain at least six to twelve carbon atoms; in other words, they are coupling products of fragments of various chain lengths.

The fluorination of the cyclic 1,4-thioxane and thiophane indicates that a part of the starting material survives the electrolysis without cleavage of the original bonds. The NMR spectrum of the liquid product obtained in the electrofluorination of thiophane, on the other hand, showed absorption peaks which were attributed to the cyclic compound XV and the three possible cleavage products retaining the sulfur atom, *i.e.*, IX, VI and $C_3F_7SF_4CF_3$. The formation of these cleavage products demonstrates the susceptibility of each of the carbon-carbon bonds and of the sulfur-to-carbon bond toward cleavage. The stability of the various bonds in the five-membered ring system appears to be lower than in the six-membered ring of the 1,4-thioxane since the yield of the cyclic, completely fluorinated product is much higher from thioxane than from thiophane.

Since the electrofluorination runs carried out in the 10 and 25 ampere cells (B and C) employed relatively small amounts of starting materials, only the main products were obtained in amounts sufficiently large for identification. From the run with di-*n*-butyl sulfoxide, again only products with the sulfur in its highest oxidation state could be isolated. The products were identical with the two SF_6 derivatives obtained from di-*n*-butyl sulfide, and disulfide. The small-scale electrofluorination of bis-(2-diethylaminoethyl) disulfide yielded a substantial amount of the perfluoroalkyl sulfur pentafluoride, $(C_2F_5)_2NCF_2CF_2SF_5$, formed by scission of the original S-S bond confirming, thus, the results from the runs with the isomeric dibutyl disulfides.

(15) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).

(16) T. C. Simmons, F. W. Hoffmann and co-workers, *THIS JOURNAL*, **79**, 3129 (1957).

(17) J. A. Young, T. C. Simmons and F. W. Hoffmann, *Ibid.*, **78**, 5637 (1956).

The pyrolysis of IX at 650–700° gave small amounts of perfluorooctane, perfluoroheptane and perfluorohexane with extensive decomposition of the starting material. Recent reports^{6,13} on the pyrolysis of similar compounds under less drastic conditions demonstrated the possible free radical nature of these reactions.

The reaction of X with aluminum chloride was violent and could not be controlled effectively to obtain sufficient quantities of product for study.

A paper is in preparation by members of the Spectroscopy Group, Physical Measurements Branch, which will contain a more detailed discus-

(18) R. D. Dresdner, *THIS JOURNAL*, **77**, 6633 (1955).

sion of the infrared spectra of the compounds reported in this paper. A study of the NMR spectra of these compounds was published recently by Muller, *et al.*¹⁹

Acknowledgments.—We are indebted to members of the Analytical Research Branch for the elemental analyses, the Spectroscopy Group for determination of the NMR and infrared spectra and to members of the Physical Measurements Branch for determination of some of the physical constants reported.

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(19) N. Muller, P. C. Lauterbur and G. F. Svatos, *ibid.*, **79**, 1043 (1957).

[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

Fluorocarbon Derivatives. II.¹ Cyclic Nitrides

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RECEIVED NOVEMBER 15, 1956

The electrofluorination of some secondary and tertiary cyclic amines in anhydrous hydrogen fluoride by the Simons process³ was investigated. Pyridine, C-substituted pyridines and morpholine yielded the corresponding fully fluorinated, secondary cyclic nitrides, while N-substituted piperidines and 1-methylmorpholine gave the corresponding tertiary fluorocarbon nitrides. In all cases, considerable amounts of cleavage products also were formed; some of them were isolated in pure state and identified.

Introduction

The electrofluorination of cyclic amines, such as pyridine, piperidine and 1-alkylpiperidines by the Simons process has been reported to yield the corresponding cyclic fluorocarbon nitrides^{4,5}; however, the information given in the literature on this class of compounds is rather scanty.

While N-alkyl-substituted piperidines and related compounds, such as N-substituted morpholines, will be converted by electrofluorination in anhydrous hydrogen fluoride to the corresponding, unreactive, cyclic tertiary nitrides (I with X = O or CF₂, and Y = C_nF_{2n+1}), unsubstituted pyridine, piperidine, morpholine, as well as their C-substituted derivatives, are expected to yield the corresponding secondary cyclic nitrides (I with X = O or CF₂, and Y = F). The secondary nitrides, by virtue of their NF group, may possibly undergo chemical reactions allowing thus the introduction of cyclic fluorocarbon nitride groups into other molecules.

Only two secondary cyclic fluorocarbon nitrides appear to have been described in the literature, *i.e.*, perfluoropiperidine, obtained either by electrofluorination of piperidine or piperidine⁵ or by fluorination of pyridine with cobaltic fluoride⁶ and perfluoro-

(2,6-dimethylpiperidine) prepared by Haszeldine⁷ from 2,6-dimethylpyridine with cobalt trifluoride.

The purpose of this investigation was to study the general behavior of cyclic amines in the Simons cell and to characterize the resulting electrofluorination products. Pyridine, 4-alkyl-substituted pyridines and morpholine were chosen as starting materials for the preparation of secondary nitrides. N-methylmorpholine and 1,1'-dipiperidylmethane were expected to yield the corresponding tertiary fluorocarbon nitrides. The physical constants and analyses of the purified secondary and tertiary nitrides obtained in this study are listed in Table I.

Experimental

Electrochemical Fluorinations.—With the exception of N-methylmorpholine, which was electrofluorinated in the 10-amp. cell (B), all other runs were performed in the 50-amp. cell (A) in the manner described previously.¹ The experimental conditions for the electrochemical fluorination runs and the major reaction products are listed in Table II. The crude liquid and gaseous products were subjected to the same preliminary purification with alkali or sodium fluoride, as described for the runs using dialkyl sulfides and disulfides¹ as starting materials.

The hydrogen fluoride employed was commercial grade, anhydrous material (Mathieson Chemical Corp. and Pennsylvania Salt Manufacturing Co.) which was distilled and dried electrolytically¹ before use. The organic starting materials were commercial products with the exception of 1,1'-dipiperidylmethane, b.p. 77.0–79.5° (2.6–2.7 mm.), *n*_D²⁰ 1.4810, which was prepared by the method of Knoevenagel⁸ from piperidine and formaldehyde.

Only the isolation of the major reaction products from the HF-insoluble liquid cell drainings and the cold trap condensates is described in the following for the various runs employing nitrogen-containing heterocyclic compounds as

(1) Paper I of this series: F. W. Hoffmann and T. C. Simmons with co-workers, *THIS JOURNAL*, **79**, 3424 (1957).

(2) To whom inquiries about this paper should be directed: Chemical Research Division, Chemical Warfare Labs., Army Chemical Center, Maryland.

(3) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1947).

(4) E. A. Kauck and J. H. Simons, U. S. Patent 2,616,927 (1952).

(5) J. H. Simons, U. S. Patent 2,490,098 (1949).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 1966 (1950).

(7) R. N. Haszeldine, *ibid.*, 1638 (1950).

(8) F. Knoevenagel, *Ber.*, **31**, 2585 (1898).