## Experimental[9]

**Dichlorofluoromethanesulfenyl Chloride.**—The reaction of 90 g. (0.485 mole) of trichloromethanesulfenyl chloride with 100 g. (0.42 mole) of mercuric difluoride was carried out as described by Kober.[2] The product was distilled through a 45-cm. spinning band column to give 32.1 g. (39% yield based on $CCl_3SCl$) of dichlorofluoromethanesulfenyl chloride, b.p. 97–98°, $n^{25}D$ 1.4767.[10]

*Anal.* Calcd for $CCl_3FS$: F, 11.2; S, 18.9. Found: F, 11.0; S, 19.1.

The infrared spectrum was extremely simple and contained absorption at 5.6 μ (medium weak), 9.5 μ, (strong) 10.8 μ (medium), and about 12 μ (very strong, broad).[11] The n.m.r. fluorine spectrum consisted of a single sharp resonance; the $F^{19}$ chemical shift is listed in Table I.

**Bis-(dichlorofluoromethyl) Disulfide.**—A solution of 12.6 g. (0.075 mole) of dichlorofluoromethanesulfenyl chloride in 45 ml. of ether was shaken with a solution of 24.9 g. (0.075 mole) of potassium iodide in 45 ml. of water. A vigorous exothermic reaction was noted, and the dark color of iodine appeared immediately. The ether layer was separated, washed with saturated sodium bisulfite solution until all of the $I_2$ color was removed, and then washed with water and dried over anhydrous magnesium sulfate. The ether was distilled and the residual oil fractionated through a spinning band column. There was thus obtained 3.58 g. (36% yield) of bis-(dichlorofluoromethyl) disulfide, b.p. 103° (36 mm.), $n^{25}D$ 1.5155.

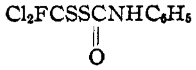
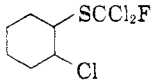
*Anal.* Calcd. for $C_2Cl_4F_2S_2$: C, 9.0; Cl, 52.9; F, 14.2; S, 23.9. Found: C, 9.1; Cl, 52.6; F, 14.4; S, 24.5.

The infrared spectrum was similar to that of the starting material Ib and contained strong absorption at 9.4, 10.95, and 12 μ (broad). The n.m.r. $F^{19}$ chemical shift (single resonance) is given in Table I.

**Reaction of I with Ethyl N-Phenylthionocarbamate.**—A solution of 1.0 g. (0.0059 mole) of I in 5 ml. of benzene was added all at once to a solution of 1.07 g. (0.0059 mole) of ethyl N-phenylthiocarbamate in 15 ml. of benzene. The mixture was stoppered at once and allowed to stand for 1 hour. The mixture was then filtered to remove a small amount of suspended solid, and the filtrate was allowed to evaporate to dryness. There was thus obtained 1.55 g. (92%) of crude dichlorofluoromethyl N-phenylcarbamoyl disulfide melting at 88–93°. After several recrystallizations from cyclohexane, the product was obtained as small white needles, m.p. 95–96°.

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

| Compounds | Frequency displacement,[b] c.p.s. at 40 mc. |
|---|---|
| $Cl_2FCSCl$ | −2025 |
| $Cl_2FCSSCCl_2F$ | −2248 |
|  $Cl_2FCSSC(=O)NHC_6H_5$ | −2110 |
|  | −2500 |

[a] Spectra were obtained by means of a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 9,988 gauss for fluorine. [b] Spectra were calculated in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field relative to the reference.

*Anal.* Calcd. for $C_8H_6Cl_2FNOS_2$: Cl, 24.8; F, 6.6. Found: Cl, 24.0; F, 6.7.

The infrared spectrum was in agreement with the proposed structure. The n.m.r. $F^{19}$ chemical shift (single resonance) is given in Table I.

**Reaction of I with Cyclohexene.**—A mixture of 10 g. (0.059 mole) of I, 20 ml. of cyclohexene and 50 ml. of ethylene chloride was stirred for 1 hour. Upon distillation of the reaction mixture, there was obtained 6.8 g. (46%) of dichlorofluoromethyl 2-chlorocyclohexyl sulfide, b.p. 59° (0.2 mm.)–63° (0.25 mm.), $n^{25}D$ 1.5157.

*Anal.* Calcd. for $C_7H_{10}Cl_3FS$: Cl, 42.3; F, 7.5. Found: Cl, 41.6; F, 7.7.

The n.m.r. $F^{19}$ chemical shift (single resonance) is given in Table I. The structure of the product was further confirmed by the infrared spectrum.

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[9] Melting points are uncorrected.

[10] In ref. 2, the yield of product b.p. 96–101° was reported to be 42.2 g. (51.5%).

[11] The absorption at 5.6 μ is unexpected for this type of molecule. A sample (1.5 ml.) of the compound was gas chromatographed (6 ft., $^3/_4$ in. copper tube column, packed with 20% telomer oil of tetrafluoroethylene-propylene on "Chromosorb" and heated at 50°; helium carrier gas, flow rate 600 ml./min.; retention time 25.5 min.) and no significant amount of impurity was detected. Two fractions of the chromatographed product were shown to have infrared spectra identical to that of the original sample. It would appear that the absorption at 5.6 μ is not due to an impurity.

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[CONTRIBUTION NO. 603 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

# The Chemistry of Sulfur Tetrafluoride. VII. Synthesis of Organic Fluorides by Halogen Exchange with Sulfur Tetrafluoride

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Sulfur tetrafluoride has been found to undergo halogen exchange with chloro- and bromomethanes, chloroalkanes and -alkenes, aryl chlorides, cyanuric chloride and chloropyrimidines. Usually only partial substitution of fluorine for chlorine or bromine resulted. At the elevated temperatures used, chloroalkenes and hexachlorobenzene were converted to chlorofluoroalkanes and chlorofluorocyclohexenes, respectively.

Replacement of chlorine or bromine atoms bonded to carbon by fluorine has been accomplished with such agents as hydrogen fluoride, potassium fluoride, antimony trifluoride, antimony pentafluoride or chlorofluoride, and also by means of the less frequently used silver monofluoride, manganese trifluoride, cobalt trifluoride and chromium trifluoride.[1] Similar replacements have now been carried out by the use of sulfur tetrafluoride, which is a unique agent[2,3] for the replacement of carbonyl oxygen by fluorine and which is readily available from sulfur dichloride and sodium fluoride.[4]

**Fluorohalomethanes from Carbon Tetrachloride or Carbon Tetrabromide.**—Chlorofluoromethanes

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[1] A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958.

[2] W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt and D. D. Coffman, THIS JOURNAL, **81**, 3165 (1959).

[3] W. C. Smith, U. S. Patent 2,859,245 (1958).

[4] C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, THIS JOURNAL, **82**, 539 (1960).

and bromofluoromethanes have been synthesized by metathesis of sulfur tetrafluoride with carbon tetrachloride and with carbon tetrabromide. The details are listed in Table I. Mixtures of trichlorofluoromethane with dichlorodifluoromethane and of dichlorodifluoromethane with chlorotrifluoromethane, in which the components were present in various ratios depending upon the conditions, were formed in combined yields up to 85% by reactions of carbon tetrachloride with excess sulfur tetrafluoride at 225–325° under pressure. Trichlorofluoromethane was the principal product at 225°, while chlorotrifluoromethane was the chief product at 325°. The formation of sulfur monochloride and chlorine as by-products suggests that metathesis proceeded through a transitory, higher-valent sulfur chloride intermediate which decomposed into chlorine and the sulfur monochloride. Similar halogen exchange with carbon tetrachloride has also been effected using sulfur tetrafluoride formed *in situ*. Thus, trichlorofluoromethane and dichlorodifluoromethane were formed in 75 and 9% yields, respectively, by treating carbon tetrachloride with sodium fluoride, sulfur dichloride and chlorine at 235° under pressure.

The products from metathesis of carbon tetrabromide with sulfur tetrafluoride suggest that replacement of bromine by fluorine is more facile than is replacement of chlorine in the chloromethane series. Thus, dibromodifluoromethane was the main fluorination product formed along with tribromofluoromethane at 225°, and bromotrifluoromethane was the chief product formed at 325° in reactions of carbon tetrabromide with excess sulfur tetrafluoride. Also, at the higher temperature some carbon tetrafluoride was formed from carbon tetrabromide but not from carbon tetrachloride.

Higher haloalkanes were less prone to undergo halogen exchange with sulfur tetrafluoride than were the chloro- or bromomethanes. Thus, even under extreme conditions, hexachloroethane gave tetrachlorodifluoroethane, and 2,2,3,3-tetrachlorohexafluorobutane formed 2,2,3-trichloroheptafluorobutane.

**Fluorohalomethanes from Carbon Disulfide, Sulfur Tetrafluoride and a Halogen.**—Mixtures of chlorofluoromethanes and of bromofluoromethanes have been synthesized in reactions of carbon disulfide and sulfur tetrafluoride in admixture with chlorine or bromine, respectively, at 225–350° in a pressure vessel. These syntheses (see Table II) may involve the formation of carbon tetrachloride or carbon tetrabromide *in situ* from carbon disulfide and chlorine or bromine, and then a metathesis of the tetrahalomethane with sulfur tetrafluoride. Carbon disulfide, sulfur tetrafluoride and chlorine at 225–350° gave mixtures containing the same chlorofluoromethanes in about the same ratios as were present in the mixtures formed by reactions of carbon tetrachloride with sulfur tetrafluoride under similar conditions. Trichlorofluoromethane was the chief product at 225°, and chlorotrifluoromethane was the principal product formed at 350° along with dichlorodifluoromethane. In the reaction of carbon disulfide and sulfur tetrafluoride with bromine, bromotrifluoromethane was the principal product formed at both 225° and 325° under autogenous pressure. In contrast, preformed carbon tetrabromide and sulfur tetrafluoride at 225° gave dibromodifluoromethane along with tribromofluoromethane as the products of metathesis.

In the synthesis of fluoromethanes from carbon disulfide, sulfur tetrafluoride and bromine, sulfur bromide was a byproduct when the carbon disulfide:bromine mole ratio was about 0.6. When the proportion of bromine used in the synthesis of bromotrifluoromethane was reduced so that the carbon disulfide:bromine ratio was 2, elemental sulfur was a by-product rather than sulfur bromide.

**Halogen Exchange with Chloroalkenes.**—In reactions with sulfur tetrafluoride, chloroalkenes were converted to chlorofluoroalkanes. Thus, tetrachloroethylene formed 1,2-dichlorotetrafluoroethane and chloropentafluoroethane (see Table III). These same products also were obtained from sulfur tetrafluoride and trichloroethylene. It is thus apparent that at the elevated temperatures used, disproportionation by dehalogenation and/or by dehydrohalogenation and subsequent addition of the fragments to yield saturated products must have preceded or accompanied fluorination. Similar processes must have been involved also in the conversion of hexachlorocyclopentadiene to a mixture of pentachlorotrifluorocyclopentenes.[5] An aromatic halide also displayed this propensity to form more nearly saturated products. Thus, hexachlorobenzene and sulfur tetrafluoride at 200–400° gave chiefly a mixture of dichloroöctafluorocyclohexene and trichlorononafluorocyclohexane. Similar products have been obtained from hexachlorobenzene with antimony pentachloride and hydrogen fluoride[6] and from hexachlorobenzene and bromine trifluoride.[7]

**Cyanuric Fluoride.**—In contrast to the propensity of chloroalkenes and hexachlorobenzene to yield saturated or more nearly saturated chlorofluorides, the heterocyclic cyanuric acid chloride and the closely related chloro-pyrimidines readily underwent exchange to yield the corresponding fluorides. Thus, cyanuric fluoride was the main product from the reaction of cyanuric chloride with sulfur tetrafluoride in 1:6 molar ratio at 250° in a pressure vessel. With lower proportions of sulfur tetrafluoride, cyanuric chlorofluorides were formed. These products recently have been prepared by reaction of cyanuric chloride with antimony trifluoride and chlorine or with antimony pentafluoride.[8]

**Fluopyrimidines.**—In reactions with sulfur tetrafluoride at elevated temperatures under pressure, several chloropyrimidines formed the corresponding fluoropyrimidines. Thus, the 2,4 and 4,6-difluoropyrimidines were prepared from the respective chlorides at 150°, while 2,4,6-trichloropyrimi-

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[5] A. Latif, *J. Indian Chem. Soc.*, **30**, 524 (1953), has reported similar products from reactions of hexachlorocyclopentadiene with antimony trifluoride and chlorine.

[6] E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

[7] W. B. Ligett, E. T. McBee and V. V. Lindgren, U. S. Patent 2,509,156 (1953).

[8] D. W. Grisley, Jr., E. W. Gluesenkamp and S. A. Heininger, *J Org. Chem.*, **23**, 1802 (1958).

dine gave a mixture of the 4,6-dichloro-2-fluoro- and 2,6-dichloro-4-fluoropyrimidines at 225°.

## Experimental

All the experiments were carried out under autogenous pressure in gently rocked sealed vessels of 300–1000-ml. capacity. The gaseous products, collected by condensation in a liquid nitrogen-cooled, evacuated cylinder, were purified by distillation through a low-temperature still. Liquid products were fractionally distilled through a spinning band column or a 10-inch vacuum-jacketed Vigreux column. The infrared measurements, reported on a molar percentage basis, were made on a Perkin-Elmer model 21 double beam spectrophotometer. The presence of chlorine in samples was detected qualitatively by passage through aqueous potassium iodide solution. When chlorine was present and the infrared analysis did not total 100%, chlorine was presumed to make up the difference. The sulfur tetrafluoride[4] employed contained 5–10% thionyl fluoride as an impurity.

**Preparation of Fluorohalomethanes from Carbon Tetrachloride or Carbon Tetrabromide.**—These syntheses were carried out by halogen exchange with sulfur tetrafluoride using the conditions listed in Table I.

TABLE I

SYNTHESIS OF FLUOROHALOMETHANES FROM $CCl_4$ AND $CBr_4$ BY METATHESIS WITH $SF_4$

| Reactants (moles) | Reaction conditions[h] | Conversion (halomethanes to fluoromethanes), % |
|---|---|---|
| $CCl_4$ (1.00) | 100°, 2 hr.; 150°, 2 hr. | $CF_2Cl_2$ (17)[a] |
| $SF_4$ (1.00) | 225°, 4 hr. | $CFCl_3$ (66)[b] |
| $CCl_4$ (0.10) | 100°, 1 hr.; 175°, 1 hr. | $CF_2Cl_2$ (10) |
| $SF_4$ (0.15) | 250°, 1 hr.; 325°, 1 hr. | $CF_3Cl$ (40)[c] |
| $CCl_4$ (1.00) | 100°, 2 hr.; 150°, 2 hr. | $CF_2Cl_2$ (22)[d] |
| $SCl_2$ (1.00) | 225°, 4 hr. | $CFCl_3$ (53)[b] |
| $Cl_2$ (1.00) | | |
| NaF (4.75) | | |
| $CBr_4$ (0.15) | 150°, 2 hr.; 225°, 1 hr. | $CF_2Br_2$ (27)[e] |
| $SF_4$ ( .14) | | $CFBr_3$ (16)[f] |
| $CBr_4$ ( .10) | 150°, 1 hr.; 250°, 1 hr. | $CF_3Br$ (77)[g] |
| $SF_4$ ( .20) | 325°, 1 hr. | $CF_4$ ( 5) |

[a] The fraction containing this product distilled from −38° to −9.5°. Infrared analysis showed it contained 15% $CCl_2F_2$, 45% $SF_4$ and 10% $SOF_2$. The remainder presumably was $Cl_2$. [b] This fraction distilled from 21–23°. Infrared analysis showed it to be pure $CFCl_3$. [c] The product was not distilled. Infrared analysis showed it to contain 10% $CClF_3$, 5% $CCl_2F_2$, 5–10% $SOF_2$. The remainder presumably was $Cl_2$. [d] These products comprised the fraction distilling from −39 to −30°. Infrared analysis showed the presence of 15% $CCl_2F_2$ and 15% $SOF_2$. The remainder presumably was $Cl_2$. [e] This product comprised the fraction distilling from 26–32°. Infrared analysis showed this to contain 65–70% $CBr_2F_2$ and 30% $CS_2$. [f] This product distilled at 103–108°; the literature reports b.p. 106°. [g] These products comprised the fraction distilling <−37°. Infrared analysis showed this fraction to contain 60–65% $CBrF_3$, 5% $CF_4$ and 25% $SOF_2$. [h] The two experiments employing molar amounts of $CCl_4$ were carried out in 1-liter pressure reactors. The other experiments employed a 500-ml. pressure reactor.

**Preparation of Chlorofluoroalkanes from Chloroalkanes. (a) Synthesis of Tetrachloro-1,2-difluoroethane.**—A mixture of 47 g. (0.20 mole) of hexachloroethane and 40 g. of sulfur tetrafluoride (0.37 mole) was heated in a 500-ml. pressure vessel free of air at 150° for 1 hr., at 250° for 1 hr., and at 350° for 1 hr. The liquid product was distilled to obtain 24 g., b.p. 93–95°. Comparison of the infrared spectrum with that of the known compound showed that the product was not 1,1,1,2-tetrachloro-2,2-difluoroethane. Elemental analysis showed the compound to contain two fluorine atoms. Therefore the product must have been 1,1,2,2-tetrachloro-1,2-difluoroethane.

*Anal.* Calcd. for $C_2Cl_4F_2$: F, 18.45. Found: F, 18.74.

(b) **Synthesis of 2,3,3-Trichloroheptafluorobutane.**—A mixture of 40 g. (0.37 mole) of 2,2,3,3-tetrachlorohexafluorobutane and 27 g. (0.25 mole) of sulfur tetrafluoride was heated in a 500-ml. pressure vessel free of air at 150° for 1 hr., at 250° for 1 hr., and at 325° for 1 hr. The product after having been washed with 10% aqueous sodium hydroxide and dried over magnesium sulfate yielded 25 g. (61% conversion) of 2,3,3-trichloroheptafluorobutane, b.p. 97–98°. The Hooker Electrochemical Co. Preliminary Technical Data Sheet No. 339 reports the boiling point of this compound as 98°.

**Preparation of Fluorohalomethanes from Carbon Disulfide, a Halogen and Sulfur Tetrafluoride.**—These syntheses were carried out by the procedures already outlined. The details are given in Table II.

TABLE II

SYNTHESIS OF FLUOROHALOMETHANES FROM CARBON DISULFIDE, A HALOGEN AND SULFUR TETRAFLUORIDE

| Reactants (mole) | Reaction conditions[f] | Conversion ($CS_2$ to fluoromethanes), % |
|---|---|---|
| $CS_2$ (0.25) | 75°, 1 hr.; 150°, 1 hr. | $CF_2Cl_2$ (14)[a] |
| $Cl_2$ ( .56) | 225°, 2 hr. | $CFCl_3$ (54)[b] |
| $SF_4$ ( .27) | | |
| $CS_2$ ( .10) | 75°, 1 hr.; 250°, 1 hr. | $CF_2Cl_2$ (57)[c] |
| $Cl_2$ ( .14) | 325°, 1 hr. | $CF_3Cl$ (19) |
| $SF_4$ ( .15) | | |
| $CS_2$ ( .25) | 150°, 2 hr.; 225°, 4 hr. | $CF_3Br$ (38)[d] |
| $Br_2$ ( .47) | | $CF_4$ ( 8) |
| $SF_4$ ( .37) | | |
| $AsF_3$ ( .05) | | |
| $CS_2$ ( .25) | 200°, 1 hr.; 300°, 1 hr. | $CF_3Br$ (87)[e] |
| $Br_2$ ( .42) | 325°, 1 hr. | $CF_4$ (12) |
| $SF_4$ ( .37) | | |

[a] The fraction containing this product distilled from −41 to −27°. Infrared analysis showed it to contain 15% $CF_2Cl_2$, 65% $SOF_2$ and 20% $SF_4$. [b] This fraction distilled from 14 to 22.5°. Infrared analysis showed it was 95% $CFCl_3$ and 5% $CS_2$. [c] The crude product was stored over sulfur at room temperature under pressure to remove chlorine. Infrared analysis showed the material remaining was 25% $CF_2Cl_2$, 5–10% $CF_3Cl$, 10–15% $SOF_2$ and 55% $SF_4$. [d] These products comprised the fraction distilling below −47°. Infrared analysis showed it to contain 65–70% $CF_3Br$, 15–20% $CF_4$ and 15–20% $SOF_2$. [e] These products made up the fraction distilling from −58 to −50°. Infrared analysis showed it contained 80% $CF_3Br$, 15% $CF_4$ and 5% $SOF_2$. [f] All experiments were carried out in a 500-ml. pressure reactor.

**Halogen Exchange with Chloroalkenes.**—Details of the reactions of sulfur tetrafluoride with chloroalkenes, hexachlorocyclopentadiene and hexachlorobenzene are listed in Table III.

**Preparation of Fluoropyrimidines from Chloropyrimidines and Sulfur Tetrafluoride. (a) Synthesis of 4,6-Difluoropyrimidine.**—A mixture of 20 g. (0.13 mole) of 4,6-dichloropyrimidine which contained a small amount of 2,4,6-trichloropyrimidine and 60 g. of sulfur tetrafluoride (0.55 mole) was heated in a 300-ml. stainless steel bomb with rocking for successive 3-hour periods at 50°, 100° and 150°. The liquid product in the bomb was taken up in diethyl ether and fractionated; 11.2 g. of a yellow liquid, b.p. 35–40° (55 mm.), was obtained. Redistillation gave a main fraction boiling at 50° (100 mm.). Mass spectrometric analysis showed the product to be chiefly 4,6-difluoropyrimidine containing small amounts of chlorodifluoropyrimidine. The yield was about 70%. Mass spectrometric analysis for 4,6-difluoropyrimidine was based on the presence of the parent 116 and 117 peaks, and the 97, 78, 44 and 31 mass peaks.

(b) **Synthesis of 2,4-Difluoropyrimidine and 6-Chloro-2,4-difluoropyrimidine.**—A mixture of 24 g. (0.16 mole) of 2,4-dichloropyrimidine (containing a small amount of 2,4,6-trichloropyrimidine) and 90 g. (0.83 mole) of sulfur tetrafluoride was allowed to react in a manner similar to that described in the preceding example. A fraction amounting

TABLE III

SYNTHESIS OF CHLOROFLUOROALKANES FROM CHLOROALKENES

| Reactants (mole) | | Reaction conditions[d] | Conversion (chlorides to fluorides), % | |
|---|---|---|---|---|
| $Cl_2C{=}CCl_2$ | (0.12) | 200°, 2 hr.; 300°, 2 hr. | $ClCF_2CF_2Cl$ | (35)[a] |
| $SF_4$ | ( .25) | 400°, 6 hr. | $C_2F_5Cl$ | (35) |
| $AsF_3$ | ( .01) | | | |
| $Cl_2C{=}CHCl$ | ( .12) | 200°, 1 hr.; 300°, 1 hr. | $ClCF_2CF_2Cl$ | (25)[a] |
| $SF_4$ | ( .25) | 400°, 2 hr. | $C_2F_5Cl$ | (25) |
| $C_5Cl_6$ | ( .13) | 180°, 1 hr.; 230°, 2 hr. | $C_5Cl_5F_3$ | (38)[b] |
| $SF_4$ | ( .51) | 280°, 2 hr.; 330°, 5 hr. | | |
| $BF_3$ | ( .06) | | | |
| $C_6Cl_6$ | ( .10) | 200°, 2 hr.; 300°, 2 hr. | $C_6F_8Cl_2$ | (20) |
| $SF_4$ | ( .31) | 400°, 4 hr. | $C_6F_9Cl_3$ | (20)[c] |

[a] The crude gaseous product was freed of excess sulfur tetrafluoride, hydrogen fluoride and chlorine by passage through 40% aqueous KOH and was dried by passage over solid KOH. Infrared analysis showed the fraction remaining to contain 40% $ClCF_2CF_2Cl$ and 40% $C_2F_5Cl$. The remainder was unidentified. [b] The crude liquid product, after being treated with NaF to remove HF, yielded 14.4 g., b.p. 146–147°, $n^{25}D$ 1.4420–1.4425. Infrared analysis confirmed the presence of a pentachlorotrifluorocyclopentene structure. *Anal.* Calcd. for $C_5Cl_5F_3$: C, 20.40; Cl, 60.20; F, 19.40. Found: C, 20.85; Cl, 58.69; F, 21.15. A second component, amounting to 4.5 g., b.p. 77–78° (23 mm.), was isolated, $n^{25}D$ 1.4760. *Anal.* Calcd. for $C_5Cl_5F_3$: C, 20.40; Cl, 60.20; F, 19.40. Found: C, 20.79; Cl, 60.49; F, 19.63. [c] The crude liquid product, after having been washed with water to remove sulfur chlorides and dried over magnesium sulfate, yielded 13.1 g., b.p. 100–150°. Careful refractionation yielded 1.05 g. (b.p. 117–118°) which on the basis of nuclear magnetic resonance analysis appeared to be 1,2-dichlorooöctafluorocyclohexene since there were two fluorine peaks in a 2:1 ratio. In addition, the infrared spectrum was satisfactory for a compound of this structure. *Anal.* Calcd. for $C_6F_8Cl_2$: C, 24.40; F, 51.50; Cl, 24.00. Found: C, 24.10; F, 53.00; Cl, 23.40. A second cut, amounting to 1.6 g. (b.p. 139–141°, m.p. 30–32°) was obtained of composition approximating $C_6F_9Cl_3$. *Anal.* Calcd. for $C_6F_9Cl_3$: C, 20.60; F, 48.90; Cl, 30.40. Found: C, 20.10; F, 47.70; Cl, 31.10. [d] All experiments were carried out in a 300-ml. stainless steel pressure reactor. We are indebted to Dr. W. R. Hasek for the experiments with trichloroethylene and with hexachlorobenzene.

to 5.7 g. was collected; b.p. 53° (45 mm.). This was shown by mass spectrometric analysis to be 2,4-difluoropyrimidine containing a small amount of chlorodifluoropyrimidine.

The product was fractionated precisely by vapor-phase chromatography to give two pure specimens which were identified as (a) 2,4-difluoropyrimidine, $n^{25}D$ 1.4278; and (b) 6-chloro-2,4-difluoropyrimidine, $n^{25}D$ 1.4588.

*Anal.* Calcd. for $C_4H_2F_2N_2$ (a): F, 32.73. Found: F, 32.30.

The fluorine magnetic resonance spectrum was in agreement with the 2,4-difluoropyrimidine structure.

*Anal.* Calcd. for $C_4HClF_2N_2$ (b): F, 25.24. Found: F, 25.35.

The fluorine magnetic resonance spectrum showed a single peak (for the 2-F) and a doublet (for the 4-F) which is associated with the splitting from an adjacent hydrogen (5-H). This is in agreement with the 6-chloro-2,4-difluoropyrimidine structure.

**(c) Synthesis of 4,6-Dichloro-2-fluoropyrimidine and 2,6-Dichloro-4-fluoropyrimidine.**—A mixture of 40 g. of 2,4,6-trichloropyrimidine (0.22 mole) and 100 g. of sulfur tetrafluoride (0.93 mole) was heated in a 300-ml. stainless steel bomb at 175° for 4 hr. and then at 225° for 3 hr. Fractionation at reduced pressure yielded, after a low-boiling foreshot, 5 g. of product (b.p. 66–67° (15 mm.), $n^{25}D$ 1.5180) which was a dichlorofluoropyrimidine.

*Anal.* Calcd. for $C_4HCl_2FN_2$: F, 11.38; Cl, 42.47. Found: F, 11.39; Cl, 42.69.

The proton magnetic resonance pattern of the undistilled product showed two very similar hydrogen atoms to be present in about equal amounts. This indicated the initial product before fractionation to have contained approximately equal amounts of 4,6-dichloro-2-fluoro- and 2,6-dichloro-4-fluoropyrimidines.

**Preparation of Cyanuric Fluorides from Cyanuric Chloride and Sulfur Tetrafluoride. (a) Synthesis of Cyanuric Fluoride.**—A mixture of 23.1 g. (0.13 mole) of cyanuric chloride and 81 g. (0.75 mole) of sulfur tetrafluoride was heated in a 300-ml. stainless steel bomb with rocking at 150° for 2 hr., at 200° for 4 hr. and at 250° for 6 hr. The molar ratio of cyanuric chloride to sulfur tetrafluoride was about 1:6. There was obtained 24.5 g. of brown liquid product which was distilled to obtain 6.8 g. (40%) of cyanuric fluoride, $C_3N_3F_3$, b.p. 70–73°.

*Anal.* Calcd. for $C_3N_3F_3$: F, 42.21; mol. wt., 135. Found: F, 42.36; mol. wt., 128.

**(b) Synthesis of Cyanuric Chlorodifluoride and Cyanuric Dichlorofluoride.**—A mixture of 46.2 g. (0.25 mole) of cyanuric chloride and 108 g. (1.00 mole) of sulfur tetrafluoride was heated in a 300-ml. stainless steel bomb successively at 150°, 200° and 250° for a total of 12 hr. There was isolated 49.8 g. of a liquid product which was distilled to obtain 14.9 g. (b.p. 113–114°) and 12.3 g. (b.p. 149–155°). The product boiling at 113–114° was cyanuric chlorodifluoride ($C_3N_3F_2Cl$), isolated in 39% yield.

*Anal.* Calcd. for $C_3N_3F_2Cl$: F, 25.08; Cl, 23.43. Found: F, 24.64; Cl, 23.80.

The product boiling at 149–155° was cyanuric dichlorofluoride, $C_3N_3FCl_2$, which was isolated in a 29% yield.

*Anal.* Calcd. for $C_3N_3FCl_2$: F, 11.31; Cl, 42.26. Found: F, 11.30; Cl, 41.95.