tate disappeared completely after 18 hours. A control without added enzyme remained turbid. Crystalline trypsin and chymotrypsin produced no visible effect on the mixture.

Cysteine ethyl ester, glycine ethyl ester and arginine methyl ester were not converted to insoluble compounds by chymotrypsin. Crystalline trypsin and crystalline carboxypeptidase did not produce insoluble compounds from L-phenylalanine ethyl ester.

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The Fluorination of Thiophene with Cobalt Trifluoride

BY JULIUS SCHULTZ AND MURRAY HAUPTSCHEIN

The fluorination of thiophene over cobalt trifluoride in a Fowler-type[1] apparatus resulted in extensive cleavage of the molecule with the formation of various low boiling sulfur fluorides and fluorocarbon cleavage products. Two compounds of interest were isolated, one a sulfur-free fluorinated butane derivative, and the other a fluorine-free sulfur-containing polymer.

A series of ten fluorinations was carried out in the usual manner. In each case a 21-g. sample of thiophene was introduced at the rate of 30.0 g. per hour in a stream of dry nitrogen at a rate of 30–35 cc. per minute. The reactor temperature was varied from 150–250°, and 350 g. of cobalt trifluoride was used in each case. Nearly complete reduction to cobalt difluoride was noted. The yield of products was not very much dependent on the temperature of the reaction, which on the introduction of the charge would increase suddenly from 30 to 50° due to the very exothermic reaction.

The two products of interest were isolated from the two traps closest to the system, cooled in water–ice and Dry Ice-acetone, respectively. The average weight of products collected in these traps was 59 g. resulting from the fluorination of 21 g. of thiophene. Approximately 16 g. of product boiling at 30–40° was recovered. On further rectification of this fraction, most of the product boiled at 36.5–37°, f.p. app. −55°, d^{0}_{4} 1.5653, $d^{10.5}_{4}$ 1.5404, $\Delta d/\Delta t$ −0.0024, and corresponded to the dihydride $C_4H_2F_8$.

Anal.[2] Calcd. for $C_4H_2F_8$: C, 23.76; H, 1.00; F, 75.24; mol. wt., 202. Found: C, 23.67; H, 1.08; F, 75.76; mol. wt., 203.

The dihydrofluorocarbon is alkali resistant, reduces permanganate, and is chlorinated slowly in the vapor phase under ultraviolet illumination, to form the corresponding dichloride, b.p. 62–63°, mol. wt., found, 270; mol. wt., calcd. for $C_4Cl_2F_8$: 271.

The other product isolated in the first copper trap cooled in water–ice was a brown solid (5 to 6 g.), which was formed only when the system did not include a sodium fluoride tube for removing the hydrogen fluoride formed. No evidence was found for the formation of this solid in either the fluorinator or the copper tubing connecting lines. After washing this solid with dilute bicarbonate solution to remove any hydrogen fluoride, it was extracted with hot glacial acetic acid to remove any copper contamination. The insoluble powder was then freed of acid and exhaustively extracted with ether. The ether extracts were negligible. The dried powder, which was essentially insoluble in the common organic solvents (except carbon disulfide in which it was slightly soluble) as well as in 10% acid and alkali, could be dissolved in hot fuming nitric acid. Analysis[2] of the purified product gave on an ash-free basis C, 55.8; H, 3.92; S, 40.3. This corresponds closely to the formula $(C_4H_{3.4}S_{1.1})_x$. This formula does not differ greatly from that for a polymer of thiophene, *i.e.*, $(C_4H_4S)_x$, but the deficiency in hydrogen may be significant.

Acknowledgment.—The authors wish to express their sincere appreciation to the U. S. Air Force, Air Materiel Command, for their financial support of part of this work.

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[1] R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 292 (1947).

[2] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

Perfluoroalkyl Halides Prepared from Silver Perfluoro-Fatty Acid Salts. III. 1,3-Dibromohexafluoropropane and 1,3-Dichlorohexafluoropropane

BY MURRAY HAUPTSCHEIN, CHARLES S. STOKES AND ARISTID V. GROSSE

In our first paper of this series[1] we reported the preparation of an 18% yield of 1,3-diiodohexafluoropropane by the thermal degradation of silver hexafluoroglutarate by an excess of iodine. That reaction was shown to proceed mainly with formation of perfluorobutyrolactone probably through cyclization of the intermediate gamma iodo salt, $ICF_2CF_2CF_2CO_2Ag$. We have now treated silver hexafluoroglutarate with bromine and chlorine by the method previously described[2] and have isolated the new compound 1,3-dibromohexafluoropropane and 1,3-dichlorohexafluoropropane in 80.3 and 64.5% yield, respectively. No evidence was found for the formation of any perfluorobutyrolactone. The larger size of the iodine atom, *i.e.*, the closer spacial proximity to the silver atom, may be the principal factor in favoring cyclization and lactone formation in the previous case only.

Since the yield of AgBr was 100% and that of AgCl was 90% of theory (*vide infra*), it is likely that similar proportions of dihalides were formed in the reaction, and the lower yields actually isolated resulted from losses in the recovery processes.

The infrared spectra[3] are shown in Figs. 1 and 2. It is of interest to note the absence of any prominent bands below 7.85 microns in the spectra of these 1,3-dihaloperfluoropropanes. This picture is consistent with that for 1,3-diiodohexafluoropropane given previously,[1] and in marked contrast with that for perfluoroalkyl halides containing $-CF_3$ groups where intense absorption bands appear at 7.3 to 7.52 microns.[1,2]

Experimental

Preparation of $CF_2BrCF_2CF_2Br$.—A 45.38-g. (0.10 mole) sample of finely powdered silver hexafluoroglutarate reacted with 42 g. (0.26 mole) of bromine. The reaction was carried out at 80–90° and was completed in four hours. The yield of AgBr was 37.5 g. (100%). There was obtained 24.84 g. (80.3% yield) of washed and dried dibromide. 1,3-Dibromohexafluoropropane is a water-white liquid, b.p. 74.2°, $n^{0.5}_{D}$ 1.3684, $n^{30.2}_{D}$ 1.3536, $d^{0.0}_{4}$ 2.1966, $d^{27.8}_{4}$ 2.1162, MR (found) 31.81, AR_F 1.14.

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[1] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

[2] M. Hauptschein and A. V. Grosse, XIIth International Congress of Pure and Applied Chemistry, New York City, September 10–13, 1951.

[3] Determined with a Baird Associates Infrared Recording Spectrophotometer of Samuel P. Sadtler & Sons, Inc., Philadelphia.

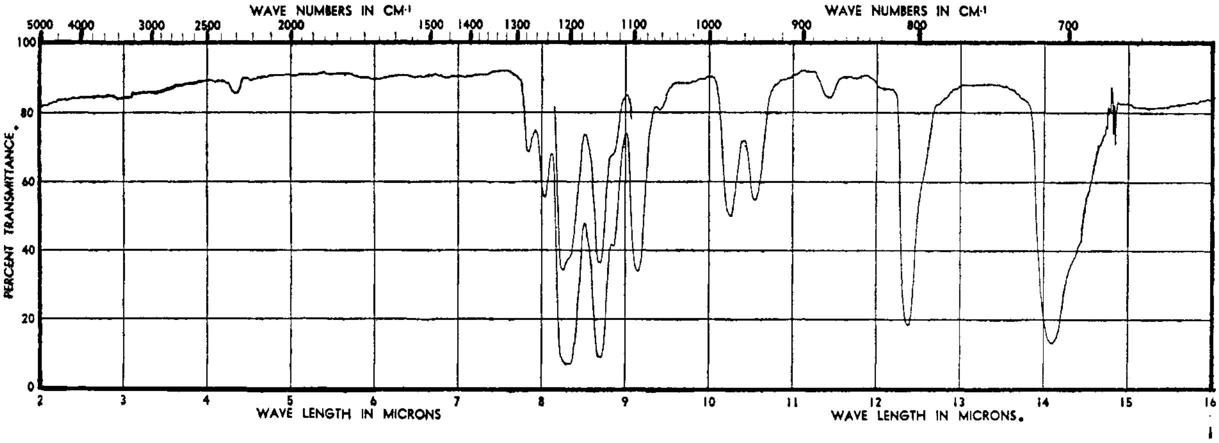

Fig. 1.—Infrared spectrum of 1,3-dibromohexafluoropropane. The spectra of Figs. 1 and 2 were taken in a 5-cm. gas cell. In these figures the lowest curve is for the vapor at 760 mm., and the other curve for vapor diluted with dry nitrogen gas.

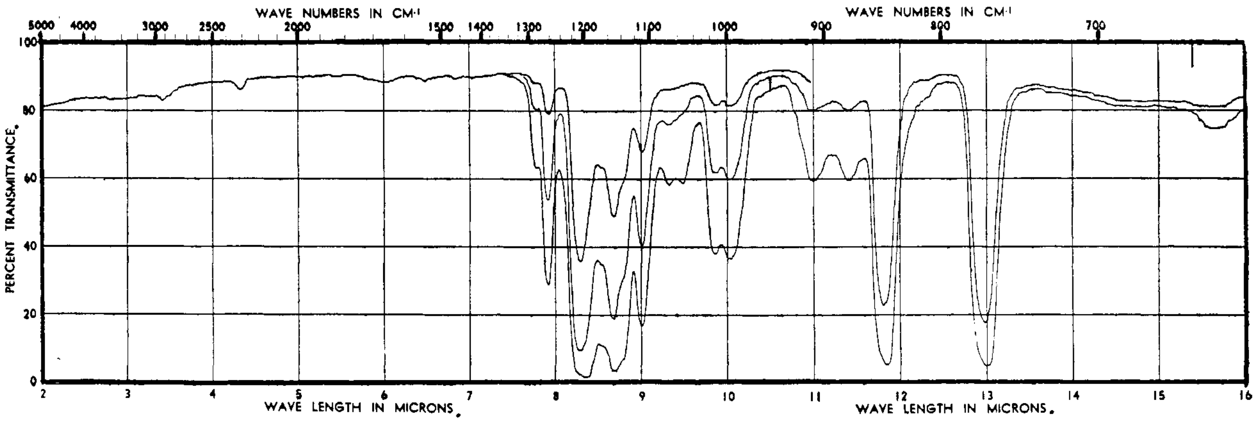

Fig. 2.—Infrared spectrum of 1,3-dichlorohexafluoropropane in vapor phase. The spectrum of this compound over the range of 9 to 15 microns has been given previously.[8] The main discrepancy in this range is the presence of a small band at 14.4 microns which is absent in our case. We have also taken infrared spectra in a 0.01-mm. liquid cell, and while they are very similar to that of Young and Murray,[8] the weak band at 14.4 microns is again absent in our case.

Anal.[4] Calcd. for $C_3F_6Br_2$: C, 11.63; Br, 51.58; mol. wt., 309.9. Found: C, 11.86; Br, 50.73; mol. wt. (gas density balance), 309.

Preparation of $CF_2ClCF_2CF_2Cl$.—An excess of chlorine was slowly passed through a long Pyrex tube, equipped with a Dry Ice refluxer and refrigerated collecting traps. This tube contained 45.38 g. (0.10 mole) of powdered silver hexafluoroglutarate. The reaction tube was heated intermittently with a bunsen flame at approximately 100° for eight hours. The yield of AgCl was 25.8 g. (90%). After washing and drying there was isolated 12.9 g. (64.5% yield) of 1,3-dichlorohexafluoropropane,[5] b.p. 35.7°, mol. wt. (found) 221, $n^{0.5}{}_D$ 1.3134, $n^{22.2}{}_D$ 1.3022, $d^{0.0}{}_4$ 1.6225, $d^{27.2}{}_4$ 1.5518, *MR* (found) 26.52, AR_F 1.22; known for $CF_2ClCF_2CF_2Cl$[5]: b.p. 35.8°, mol. wt. (calcd.) 221, $n^{20}{}_D$ 1.3030, $d^{20}{}_4$ 1.5730.

It should be noted that the boiling points of both 1,3-isomers are 1.2° higher than that of the 1,2-isomers: known b.p. $CF_3CFBrCF_2Br$, 73.0[6]; known b.p. $CF_3CFClCF_2Cl$, 34.5°,[6] 34.7°,[7] 34.5°.[8]

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[4] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

[5] B. L. Baker and A. M. Whaley, THIS JOURNAL, **73**, 4010 (1951), prepared this compound by a three-step procedure from 1,2-dichloro-2-propene. Other references are cited therein.

[6] M. Hauptschein and L. A. Bigelow, *ibid.*, **73**, 1428 (1951).

[7] A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

[8] E. G. Young and W. S. Murray, *ibid.*, **70**, 2814 (1948).

Perfluoroalkyl Halides Prepared from Silver Perfluoro-fatty Acid Salts. IV. 1-Haloundecafluoropentanes

BY MURRAY HAUPTSCHEIN, RICHARD L. KINSMAN AND ARISTID V. GROSSE

The silver salt of *n*-perfluorocaproic acid has been prepared and converted to the new 1-iodo-, 1-bromo- and 1-chloroperfluoropentanes by the previously reported procedures.[1,2]

The reaction of silver *n*-undecafluorocaproate and an excess of halogen resulted in the formation of 1-iodoundecafluoropentane, 1-bromoundecafluoropentane and 1-chloroundecafluoropentane in yields of 73.9, 82.5 and 71.2%, respectively.

The physical constants of the perfluoroamyl halides are presented in Table I, and the infrared spectra[3] are shown in Figs. 1–4. The spectrum of

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[1] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

[2] M. Hauptschein and A. V. Grosse, XIIth International Congress of Pure and Applied Chemistry, New York City, September 10–13, 1951.

[3] Determined with a Baird Associates Infrared Recording Spectrophotometer of Samuel P. Sadtler & Sons, Inc., Philadelphia.