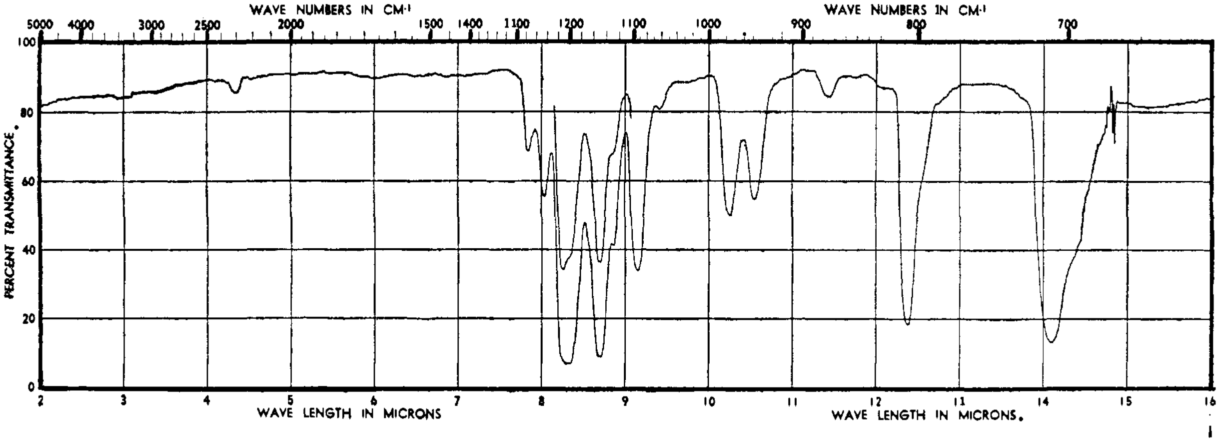

Fig. 1.—Infrared spectrum of 1,3-dibromohexafluoropropane. The spectra of Figs. 1 and 2 were taken in a 5-cm. gas cell. In these figures the lowest curve is for the vapor at 760 mm., and the other curve for vapor diluted with dry nitrogen gas.

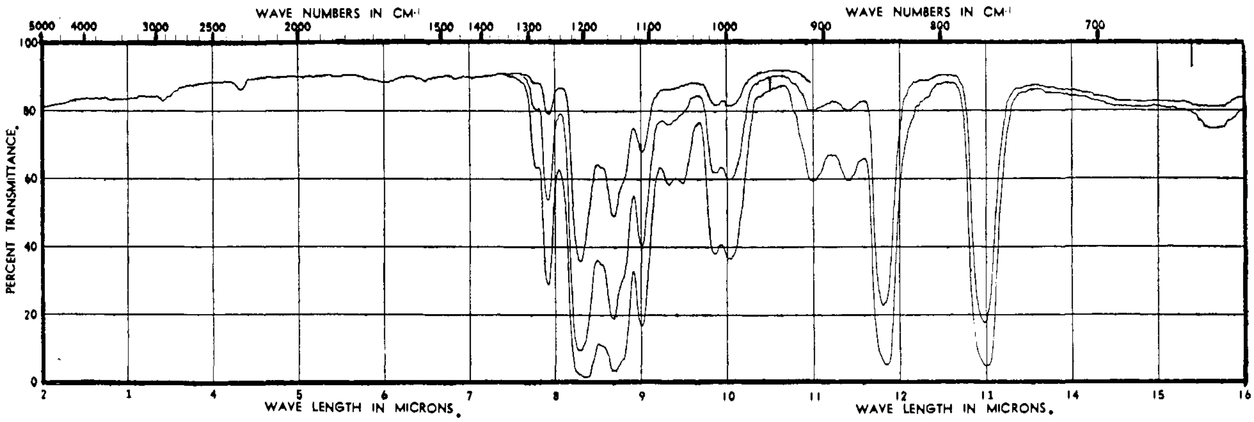

Fig. 2.—Infrared spectrum of 1,3-dichlorohexafluoropropane in vapor phase. The spectrum of this compound over the range of 9 to 15 microns has been given previously.[8] The main discrepancy in this range is the presence of a small band at 14.4 microns which is absent in our case. We have also taken infrared 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.

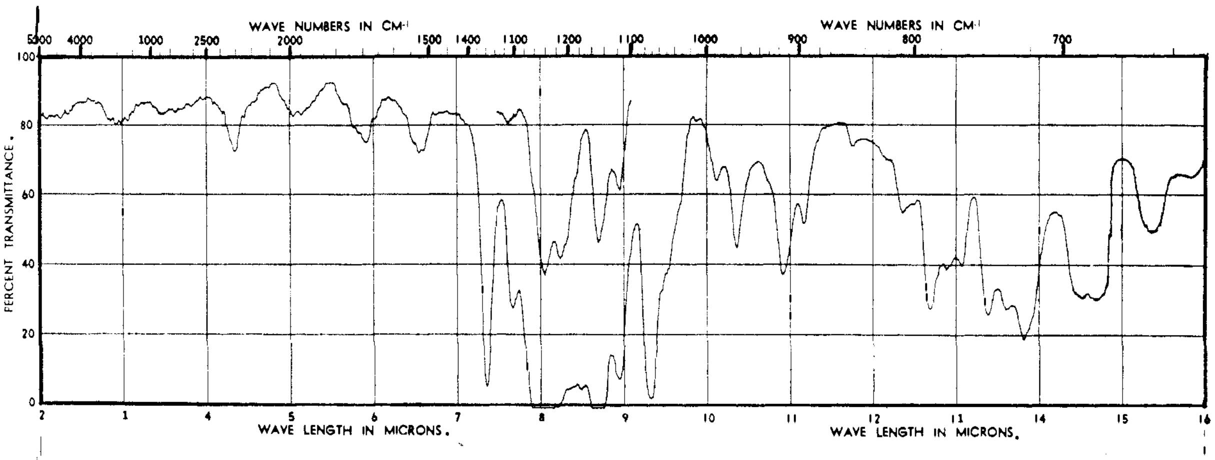

Fig. 1.—Infrared spectrum of 1-iodoundecafluoropentane: lower curve was taken in a 0.01-mm. liquid cell; upper curve was taken in a 0.005-mm. liquid cell.

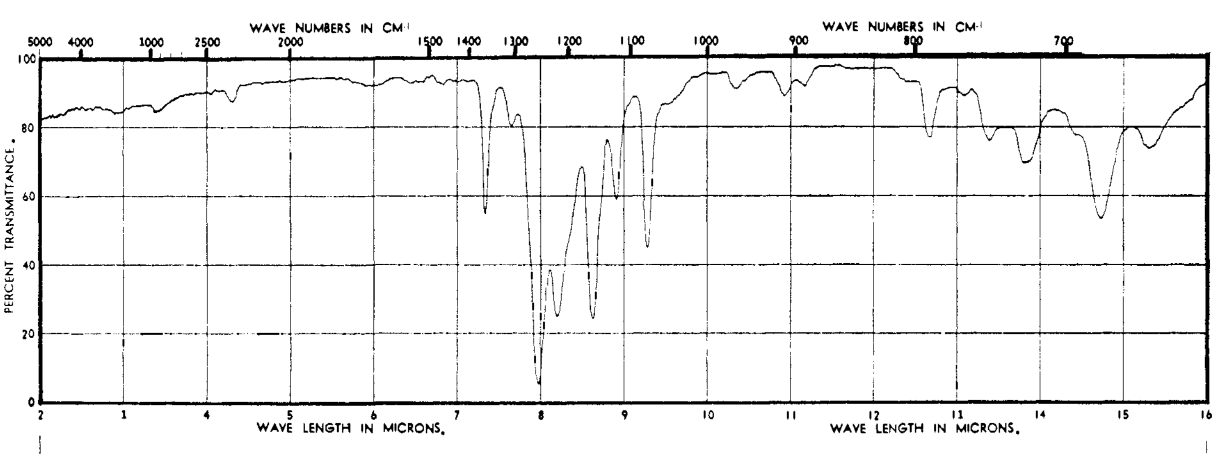

Fig. 2.—Infrared spectrum of 1-iodoundecafluoropentane in vapor phase taken in 5-cm. gas cell.

1-iodoundecafluoropentane is given for both the vapor and liquid phase, and exhibits a slight shift in most of the absorption bands due presumably to differences in physical state.

TABLE I

PHYSICAL PROPERTIES

Compound	B.p., °C.	n^t_D	t	d^t_4	t	*MR* Found[b]	AR_F[c]
$CF_3(CF_2)_3CF_2I$[a]	94.4	1.3243	31.5	2.0349	27.8	39.18	1.20
		1.3389	0.5	2.1141	0.0		
$CF_3(CF_2)_3CF_2Br$	73.9	1.2920	27.8	1.8522	28.4	34.19	1.20
		1.3042	0.0	1.9324	0.0		
$CF_3(CF_2)_3CF_2Cl$	59.5	1.2736	25.4	1.6450	25.8	31.77	1.25
		1.2845	0.0	1.7150	0.0		

[a] Melting point (*ca.*) −50°. [b] *MR* (Found) denotes the molecular refraction calculated by Lorentz–Lorenz formula. [c] AR_F is the atomic refraction for fluorine, obtained from *MR* (Found) by subtracting the customary increments for C, I, Br and Cl.

Experimental

Preparation of Silver *n*-Undecafluorocaproate.—$CF_3CF_2CF_2CF_2CF_2CO_2Ag$ was prepared by adding 10% excess of silver oxide (52.0 g.) to a homogeneous solution of 127.0 g. (0.404 mole) of *n*-perfluorocaproic acid in 340 ml. of water. This quantity of acid was not completely miscible in 200 ml. of water. The reaction mixture was heated on a hot-plate at 50–60°, but the silver *n*-undecafluorocaproate was only partially soluble in the amount of water used. Therefore the product was extracted with an equal amount of ether and the excess silver oxide was filtered off. On evaporation of both the ethereal and aqueous layer 116.7 g. of silver salt was collected from the ether extract and 34.9 g. of silver salt from the water extract or a total yield of 89.2%. The silver salt melted at 286–288°. It was analyzed for silver by the Volhard method.

Anal. Calcd. for $C_5F_{11}CO_2Ag$: Ag, 25.63. Found: Ag, 25.70.

Preparation of 1-Iodoundecafluoropentane.—A 50.0-g. (0.119 mole) sample of powdered silver *n*-undecafluorocaproate was treated with 33.2 g. (10% excess) of powdered iodine at 100° for six hours. The yield of AgI was 28.0 g. (100% of theory). There was obtained 34.7 g. (73.9% yield) of washed and dried *n*-$C_5F_{11}I$, b.p. 93.4–94.4° (almost entirely 94.4° at 760 mm.). This compound distils as a water-white liquid, but on exposure to air and light turns slowly pink.[4]

Anal.[5] Calcd. for $C_5F_{11}I$: C, 15.16; H, none; mol. wt., 396. Found: C, 15.06; H, none; mol. wt. (gas density balance), 398, 396.

Preparation of 1-Bromoundecafluoropentane.—A 40.0-g. (0.095 mole) sample of powdered silver *n*-undecafluorocaproate reacted with 24 g. (0.15 mole) of bromine at 80–90° for 5 hours. The yield of AgBr was 17.8 g. (100%). There was isolated 27.36 g. (82.5% yield) of washed and dried, water-white, *n*-$C_5F_{11}Br$, b.p. 73.1–73.9° (almost entirely 73.9° at 760 mm.).

Anal.[5] Calcd. for $C_5F_{11}Br$: C, 17.21; H, none; mol. wt., 349. Found: C, 17.16; H, none; mol. wt. (gas density balance), 350.

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[4] J. H. Simons and T. J. Brice, U. S. Patent 2,554,219, May 22, 1951, indicated the preparation of $C_5F_{11}I$ by a method differing from the above by the addition of inert silica-containing diluents and *fluorocarbon* solvents.

[5] Microanalysis by Clark Microanalytical Laboratory, Urbana, Illinois.

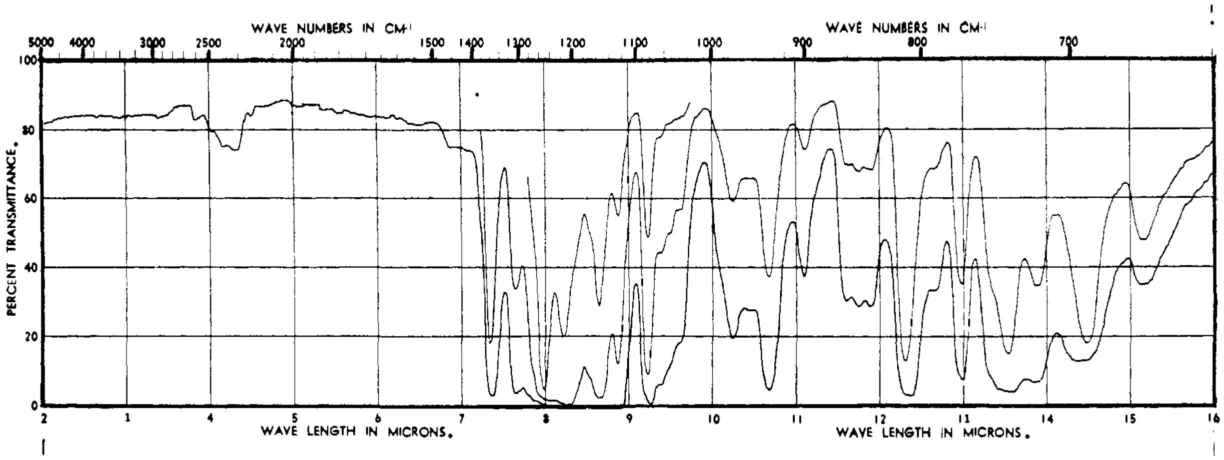

Fig. 3.—Infrared spectrum of 1-bromoundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curves are for vapor diluted with dry nitrogen gas taken in same cell.

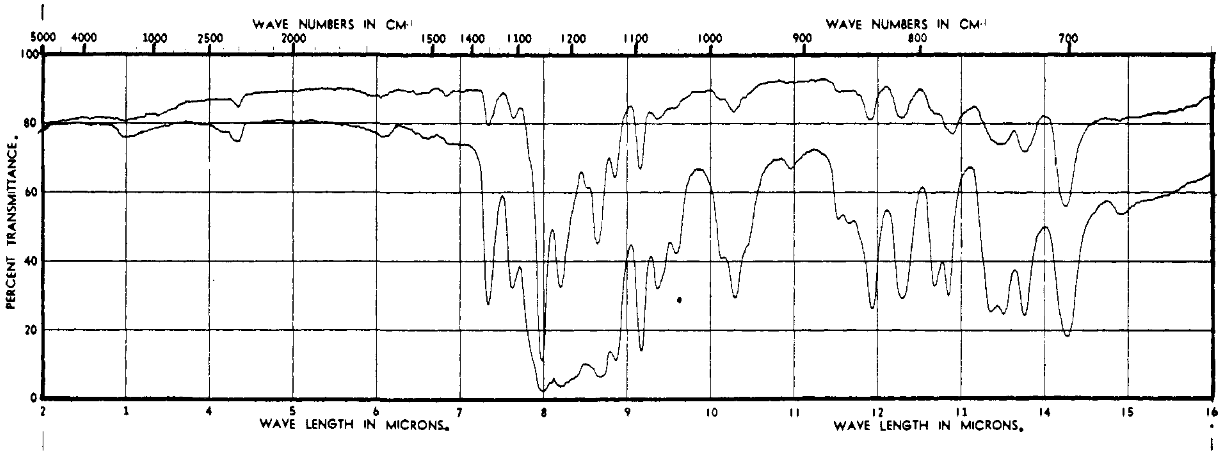

Fig. 4.—Infrared spectrum of 1-chloroundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curve is for vapor diluted with dry nitrogen gas taken in same cell.

Preparation of 1-Chloroundecafluoropentane.—An excess of chlorine was passed through a long Pyrex tube, equipped with a Dry Ice refluxer and refrigerated collecting traps. The tube was partially filled with 23 g. (0.0546 mole) of powdered silver *n*-undecafluorocaproate, which was heated intermittently with a bunsen flame at approximately 100° for eight hours. The yield of AgCl was 93% of theory. After washing and drying there was isolated 11.84 g. (71.2% yield) of the water-white liquid, *n*-$C_5F_{11}Cl$., b.p. 59.0–59.5° (almost entirely 59.5° at 760 mm.).

Anal.[5] Calcd. for $C_5F_{11}Cl$: mol. wt., 304.5; C, 19.72. Found: mol. wt. (gas density balance), 304; C, 19.70.

Acknowledgment—The authors wish to express their sincere appreciation to the Minnesota Mining & Manufacturing Co., Saint Paul, Minnesota, for supplying the perfluorocaproic acid used in these experiments.

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Reductive Cyclization of Butyl Pyroglutamate. Synthesis of a New Nitrogen Heterocycle, Decahydrodipyrrolo[a,d]pyrazine

BY EDWARD SEGEL

The only reported product from the hydrogenation of the α-amido ester, ethyl pyroglutamate, is 5-hydroxymethyl-2-pyrrolidone[1,2]; the amide group does not enter into the observed reaction. However, by using a somewhat higher reaction temperature (250°) than that used by Sauer and Adkins (210–220°),[1] the amide group can be completely hydrogenated. The amino alcohol, 2-hydroxymethylpyrrolidine, logically expected as the product, is not actually isolated; while it may have a transitory existence during the reaction, it cannot remain under the experimental conditions employed. The alkylating action of alcohols on amines at elevated temperatures in the presence of copper-chromium oxide catalyst and hydrogen is well established[3]; ring closure accompanying such alkylation has also been noted.[4,5] Since hydrogenation of the ester group of butyl pyroglutamate results in the formation of two alcohols, butanol, and 5-hydroxymethyl-2-pyrrolidone, either of which can then react with amino nitrogen when it arises by hydrogenation of the amide group. If the two

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(1) J. C. Sauer and H. Adkins, THIS JOURNAL, **60**, 402 (1938).

(2) H. Adkins and H. R. Billica, *ibid.*, **70**, 3121 (1948).

(3) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 26.

(4) J. P. Bain and C. B. Pollard, THIS JOURNAL, **61**, 532, 2704 (1939).

(5) B. G. Wilkes, U. S. Patent 2,479,657.