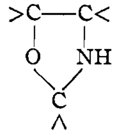
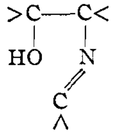
Cope and Hancock used as catalyst Raney nickel or copper chromite at about 150° and 1000–2000 p.s.i., since palladium–charcoal at room temperature reacted very slowly. Also, Senkus could achieve hydrogenation in presence of palladium only at 100° and 1000 p.s.i. Similar observations were made in this Laboratory in hydrogenating the product of the reaction between formaldehyde and ethanolamine.

It seemed interesting to ascertain whether palladium-activated hydrogen could be used to distinguish between oxazolidines (A) and their isomers, Schiff bases type (B), assuming that the former would be hydrogenated at a much slower rate than the latter.

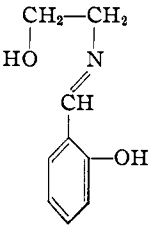
A



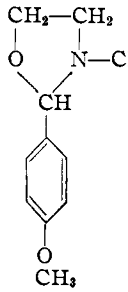
B



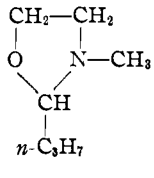
The following three substances were chosen as models



I



II



III

Substance (I) exists only in the form of the Schiff base[3] and does not show any tendency to isomerize to a cyclic structure,[4] whilst (II) and (III), due to the presence of the methyl group at the nitrogen atom, cannot exist in an open form. Hydrogenation of (II) and (III) would, therefore, necessarily be a ring splitting reaction. Contrary to expectation, however, (I), (II) and (III) did not show any outstanding difference in the rate of their hydrogenation at room temperature and a pressure of about four atmospheres.

Experimental

(1) **N-(*o*-Hydroxybenzyl)-2-aminoethanol.**—A solution of 9.2 g. of N-salicylideneaminoethanol (I)[3,4] in 100 cc. of 95% ethyl alcohol was hydrogenated in presence of 0.3 g. of 10% palladium–charcoal.[5] The reaction was carried out at 30° and under a pressure of 55–60 p.s.i. 70% of the theoretical amount of hydrogen was absorbed in seven hours. After completion of the hydrogenation, the product was recovered by filtration and evaporation of the solvent. The oily residue solidified upon standing at 0°; the solid was recrystallized from a benzene–light petroleum mixture (1:1); m.p. 66.5–67°.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.7; H, 7.8; N, 8.4; mol. wt., 167. Found: C, 64.9; H, 7.9; N, 8.6; mol. wt., 182.

The infrared spectrum (0.066 g. plus 1 cc. of chloroform) showed two bands, at 3300 and 3410 cm.$^{-1}$, characteristic for the OH and NH groups, respectively. No absorption was found in the C=N region.

(2) **N-Methyl-N-(*p*-methoxybenzyl)-2-aminoethanol.**—A solution of 9.0 g. of 2-(*p*-methoxyphenyl)-3-methyloxazolidine (II)[4] in 120 cc. of 95% alcohol was hydrogenated in the presence of 0.4 g. of 10% palladium–charcoal catalyst. Carried out at 30° and under 53–56 p.s.i., the reaction was complete in six hours. The liquid product was recovered by evaporation of the solvent and subjected to fractional distillation in a Todd column; b.p. 154° (2 mm.); yield 2.6 g. (30%) of pure product; $n^{29}D$ 1.531.

Anal. Calcd. for $C_{11}H_{17}NO_2$: N, 7.2; mol. wt., 195. Found: N, 7.2; mol. wt., 200.

The infrared spectrum of the hydrogenation product showed a band at 3450 cm.$^{-1}$, corresponding to the hydroxyl group. No absorption was found in the C=N region. The hydrogenation of (II) was also carried out in a mixture of cyclohexane and benzene (80:25) at atm. pressure (II) is only slightly soluble in cyclohexane; it then required about twice the time indicated above.

(3) **N-Methyl-N-*n*-butyl-2-aminoethanol.**—A solution of 16.4 g. of 2-*n*-propyl-3-methyloxazolidine (III)[4] in 110 cc. of 95% ethyl alcohol was hydrogenated at 30° and under 50–60 p.s.i., in the presence of 0.3 g. of the palladium catalyst. The reaction was complete in five and one-half hours. (In a mixture of cyclohexane and benzene (80:25) at atm. pressure, the hydrogenation is about one third as fast.) The oily product which remained after filtration and evaporation of the solvent, boiled (Todd column) at 122–123° (100 mm.); yield 9.5 g. (60%); $n^{31}D$ 1.4389.

Anal. Calcd. for $C_7H_{17}NO$: N, 10.7; mol. wt., 131. Found: N, 10.7, 10.8; mol. wt., 143.

The infrared spectrum showed the OH band at 3450 cm.$^{-1}$ and no absorption in the C=N region.

DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

RECEIVED MAY 31, 1951

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[3] L. W. Daasch and U. E. Hanninen, THIS JOURNAL, **72**, 3673 (1950).

[4] E. Bergmann and co-workers, *Rec. trav. chim.*, **51**, in press (1952).

[5] Preparation according to *Org. Syntheses*, **26**, 78 (1946).

Perfluoroalkyl Halides Prepared from Silver Perfluoro-fatty Acid Salts. II. Perfluoroalkyl Bromides and Chlorides[1]

BY MURRAY HAUPTSCHEIN, EDWARD A. NODIFF AND ARISTID V. GROSSE

In our first paper of this series[2] we reported an excellent method for the preparation of perfluoroalkyl iodides by the degradation of the appropriate silver perfluoro-carboxylic acid salt by an excess of iodine. This method has been demonstrated to be equally well adapted to the preparation of perfluoroalkyl bromides and chlorides. The reaction of an excess of bromine and chlorine with silver trifluoroacetate, silver pentafluoropropionate and silver *n*-heptafluorobutyrate resulted in the formation of high yields of bromotrifluoromethane[3] and chlorotrifluoromethane,[3] bromopentafluoroethane and chloropentafluoroethane, as well as the new compounds, 1-bromoheptafluoropropane and 1-chloroheptafluoropropane. The latter two representative reactions are given by the equation

$$CF_3CF_2CF_2CO_2Ag + Br_2 \longrightarrow CF_3CF_2CF_2Br + AgBr + CO_2 \quad (1)$$

and

$$CF_3CF_3CF_2CO_2Ag + Cl_2 \longrightarrow CF_3CF_2CF_2Cl + AgCl + CO_2 \quad (2)$$

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[1] Presented before the Twelfth International Congress of Pure and Applied Chemistry, New York City, September 10–13, 1951.

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

[3] R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951), has independently prepared bromotrifluoromethane and chlorotrifluoromethane by this method. This reaction is an extension of the method of Hunsdiecker applied to normal "hydrocarbon" silver salts. See, for examples, Hunsdiecker, Hunsdiecker and Vogt, U. S. Patent 2,176,181 (1939), and the review of Kleinberg, *Chem. Revs.*, **40**, 381 (1947).

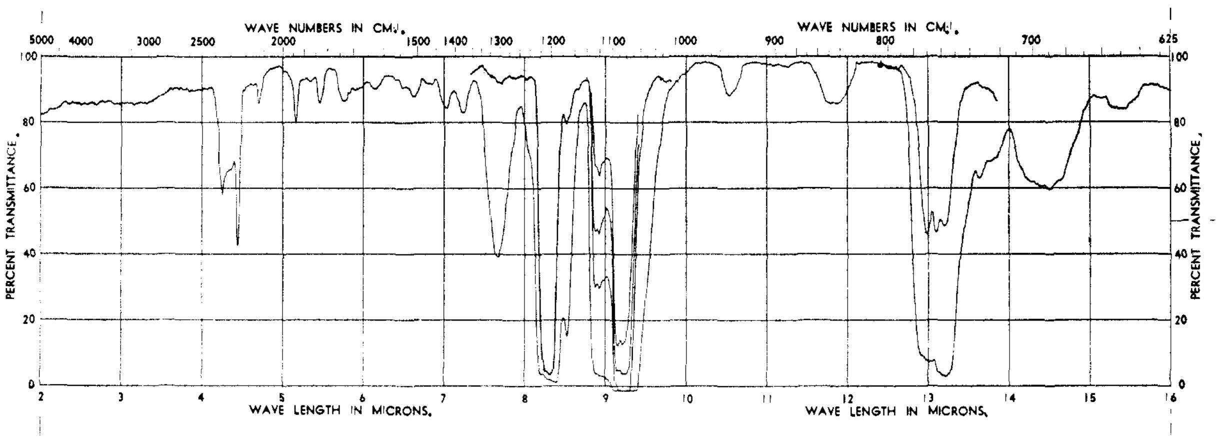

Fig. 1.—Infrared spectrum of bromotrifluoromethane. This spectrum as well as all of the following spectra were taken in a 5-cm. gas cell. In Figs. 1–6, the lowest curve is for vapor at 760 mm. and the other curves are for vapor diluted with varying proportions of dry nitrogen gas.

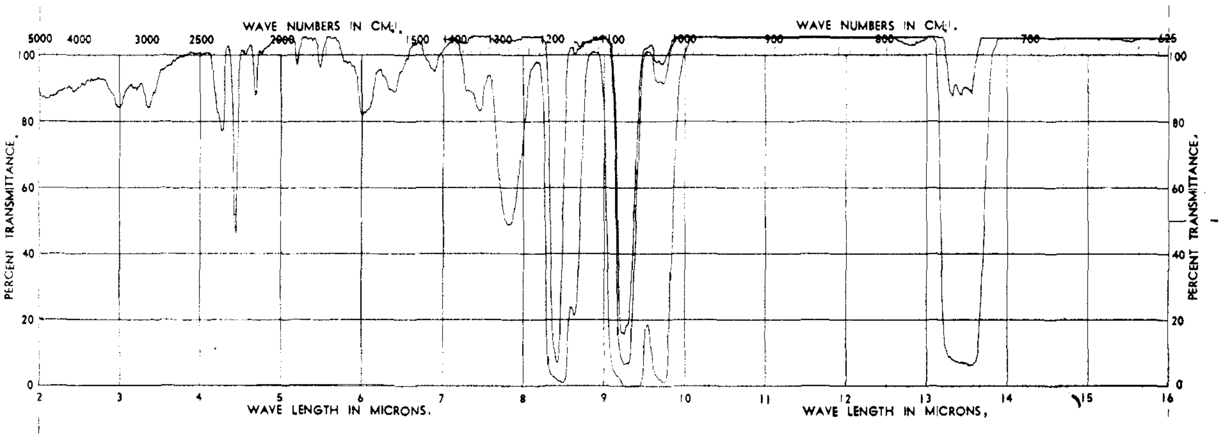

Fig. 2.—Infrared spectrum of iodotrifluoromethane.

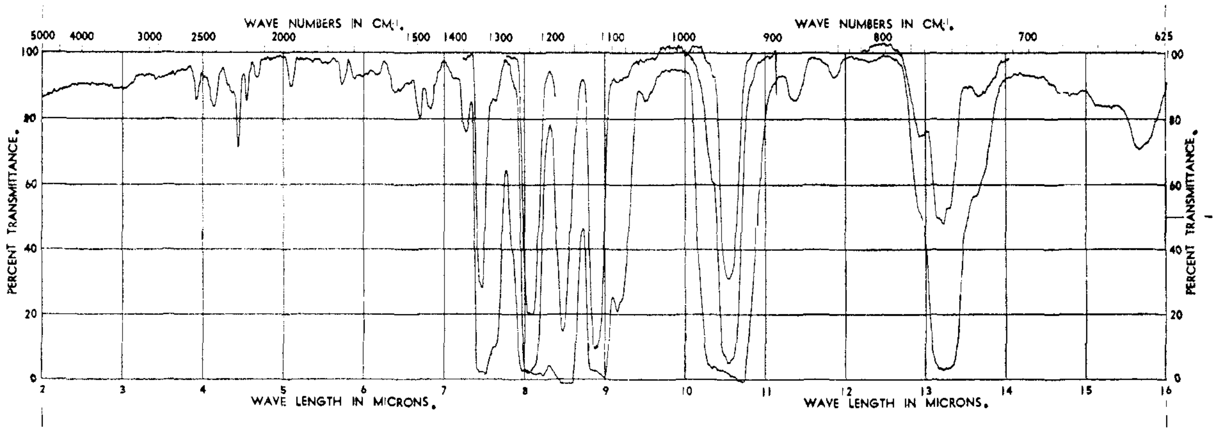

Fig. 3.—Infrared spectrum of bromopentafluoroethane.

It should be particularly emphasized that these reactions are practically quantitative. In equation (1) above all three reaction products were determined *quantitatively* and the yields of n-C_3F_7Br, AgBr and CO_2 were found to be 95.8, 98.8 and 99.5%, respectively. In all other cases the most accurate yield figures were obtained for the silver halides; in the case of three bromides these yields were 98.8, 99.4 and 98% (*vide infra*). Thus the yield of the perfluoroalkyl halides may also be considered practically quantitative and the actual yields will depend on the physical efficiency of the recovery system used and the effort allocated to the recovery.

The physical constants of the perfluoroalkyl bromides and chlorides are presented in Table I, and the infrared spectra[4] are shown in Figs. 1–6. The spectrum of CF_3I, which was not presented in our previous paper is also included.

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

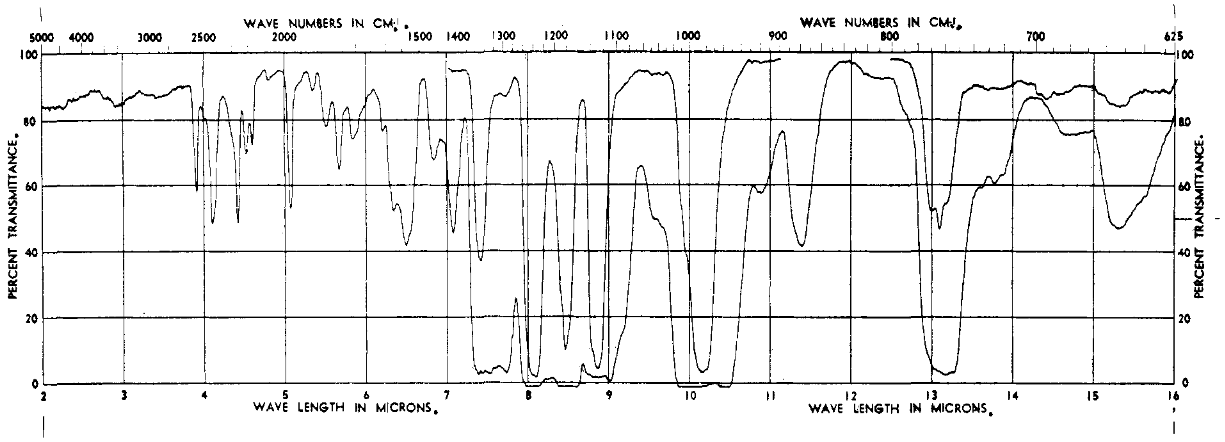

Fig. 4.—Infrared spectrum of chloropentafluoroethane.

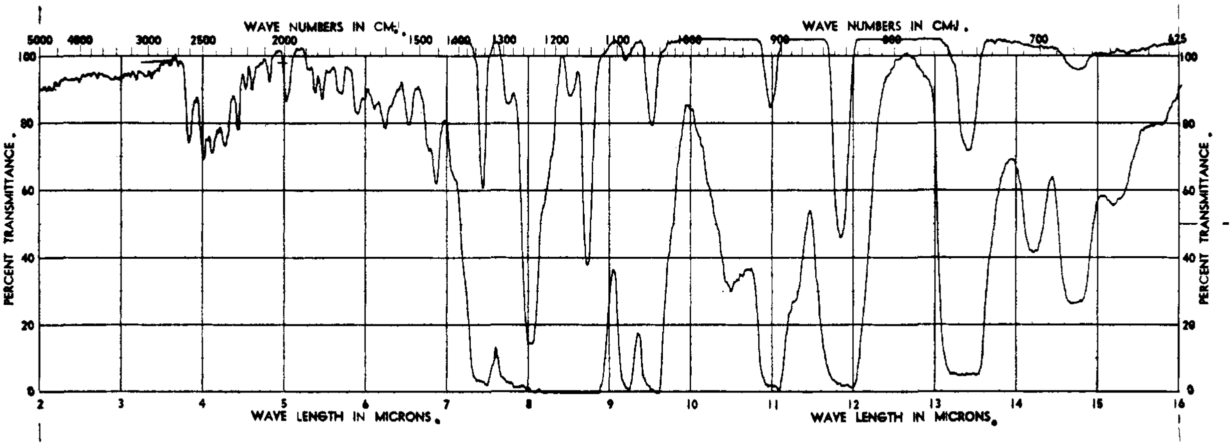

Fig. 5.—Infrared spectrum of 1-bromoheptafluoropropane.

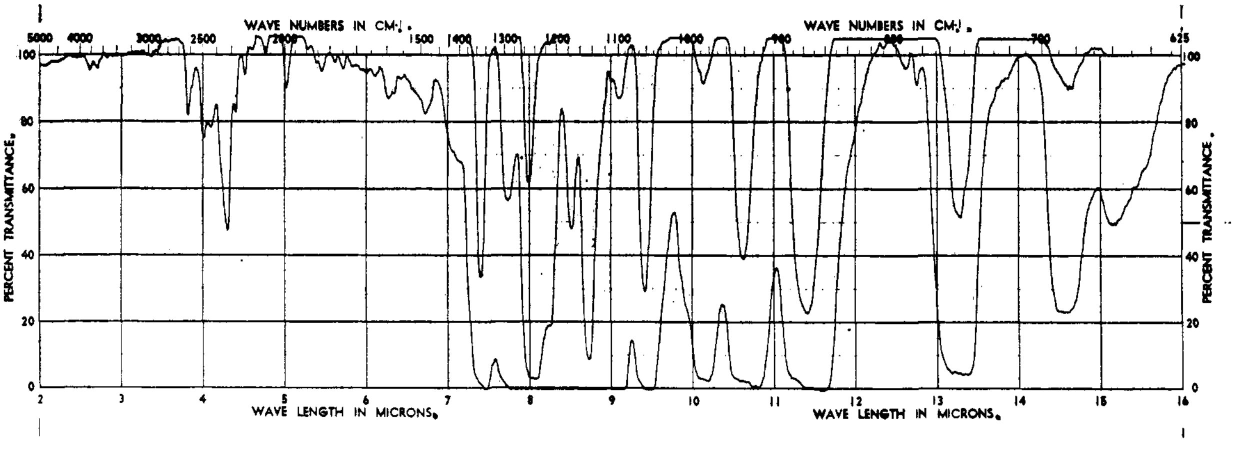

Fig. 6.—Infrared spectrum of 1-chloroheptafluoropropane.

Experimental

Preparation of the Silver Salts.—All of the silver salts were prepared as described previously.[2]

Preparation of 1-Bromoheptafluoropropane.—A 43.92-g. (0.137 mole) sample of finely powdered silver *n*-heptafluorobutyrate was treated with 65.7 g. (0.411 mole) of bromine in the apparatus illustrated in Fig. 7. Bromine was added in small portions to the flask containing the silver salt, while the temperature of the water-bath was slowly raised from 50 to 75° in order to reflux the bromine inside the reaction flask. After a few cc. of liquid bromine was added, steady gas evolution took place. The reaction was completed in 3 hours. During the last half-hour dry air or nitrogen was passed through the system to sweep out any remaining gaseous product. The reaction can be easily controlled by adjusting the rate of addition of bromine and by stirring intermittently with the manually operated glass stirrer. The excess bromine was removed by the first receiver as well as by two potassium hydroxide scrubbers attached to the system which also removed the carbon dioxide generated. The remaining gaseous product was passed over potassium hydroxide pellets and Drierite and finally collected in Dry Ice refrigerated receivers. There was obtained 32.6 g. (95.8% yield) of pure, water-white, 1-bromoheptafluoropropane, b.p. 12°.

Anal.[5] Calcd. for C_3F_7Br: C, 14.47; mol. wt., 249. Found: C, 14.56; mol wt. (gas density balance), 248, 249.

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(5) Microanalyses by Clark Microanalytical Laboratories, Urbana, Ill.

TABLE I

PHYSICAL PROPERTIES

Compound	B.p., °C.	n_D^t[a]	t	d_4^t[b]		MR		AR_F[e]
						Found[c]	Calcd.[d]	
CF_3CF_2Br	−21	1.2966	−29.8	1.8098	0.0	18.97	19.85	1.05
		1.3040	−42.2	1.9492	−32.2			
$CF_3CF_2CF_2Br$	12	1.3070	−29.8	1.8746	0.0	24.05	24.73	1.13
		1.3131	−42.2	1.9845	−32.2			
CF_3CF_2Cl	−38	1.2678	−42.2	1.5678	−42.2	16.60	16.95	1.16
				1.6914	−78.5			
$CF_3CF_2CF_2Cl$	− 2	1.2781	−29.8	1.5572	0.0	21.60	21.83	1.20
		1.2837	−42.2	1.6605	−33.5			

[a] Refractive indices were determined at low temperatures by the method of Grosse, THIS JOURNAL, 59, 2739 (1937). [b] Determined in sealed dilatometer. [c] *MR* (Found) denotes the molecular refraction calculated by Lorentz–Lorenz formula. [d] *MR* (calcd.) denotes the molecular refraction calculated by adding the customary increments for C, Br, Cl and F, using AR_F = 1.23 which is the best value for fluorine in fluorocarbons only. [e] AR_F is the atomic refraction for fluorine, obtained from *MR* (found) by subtracting the customary increments for C, Br and Cl.

This pure isomer is new, although C_3F_7Br (mixture of isomers), b.p. 11–12°, has been prepared previously by the thermal bromination of C_3F_7H.[6]

There were also obtained 25.42 g. (98.8% yield) of AgBr and the stoichiometric amount of carbon dioxide, determined as barium carbonate (99.5% yield). No traces of unreacted silver salt were present. The large excess of bromine was used to ensure complete reaction of the much more expensive silver salt, since it was found that even when a 20% excess of bromine was used the reaction was incomplete due to the loss of bromine vapors.

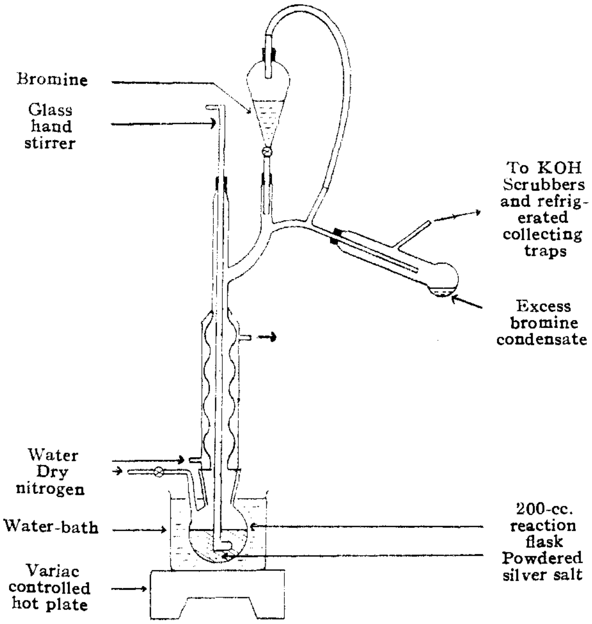

Fig. 7.—Reactor for preparation of perfluoroalkyl bromides.

Preparation of Bromopentafluoroethane.—The preparation of bromopentafluoroethane was accomplished similarly in the apparatus described above. To 36.93 g. (0.136 mole) of silver pentafluoropropionate, 45.0 g. (0.28 mole) of bromine was added over a period of 2.5 hours. The bath temperature was 53–70°. After washing and drying the gaseous product, 26.8 g. (98.9% yield) of water-white bromopentafluoroethane was obtained, b.p. −21°, mol. wt. 199; known[6] for C_2F_5Br, b.p. −23 to −21°, mol. wt. calcd., 199. In addition 25.36 g. (99.4% yield) of AgBr and the stoichiometric amount of CO_2 were formed.

Preparation of Bromotrifluoromethane.—By the same method bromotrifluoromethane was prepared at 65–85° in 98% yield. The water-white liquid boiled at −59°, mol. wt. 148. Known[6] for CF_3Br, b.p. −60.5 to −59°, −58°,[3] mol. wt. calcd., 149.

Preparation of Chlorotrifluoromethane.—In a typical reaction, 2.0 g. (0.00904 mole) of silver trifluoroacetate was mixed with 1.4 g. of chlorine and sealed in a Pyrex tube. The reaction took place almost instantaneously on warming to room temperature, and there was obtained after washing and drying, 0.83 g. (88% yield) of pure water-white chlorotrifluoromethane; mol. wt., 104, 105; calcd. for CF_3Cl: mol. wt., 104.5. There was also obtained 1.28 g. (98.60% yield) of silver chloride.

Preparation of Chloropentafluoroethane.—In a sealed Pyrex tube 1.02 g. (0.00377 mole) of silver pentafluoropropionate reacted with 0.75 g. of chlorine at room temperature to form 0.53 g. of AgCl (98.2% yield) and 0.48 g. (83% yield) of washed and dried chloropentafluoroethane, b.p. −38°, mol. wt. 154; known,[7] b.p. −38°, mol. wt. 154.5.

Preparation of 1-Chloroheptafluoropropane.—The chlorination was carried out at atmospheric pressure. Into a 100-cc. flask, equipped with a side arm and Dry Ice "refluxer" connected to two Dry Ice refrigerated traps, was placed 18.70 g. (0.0582 mole) of silver *n*-heptafluorobutyrate. A large excess of chlorine gas was bubbled through the silver salt. Unreacted chlorine refluxed in the flask. The bottom of the flask was gently heated occasionally with a small micro-burner. The reaction was terminated after 4 hours and all of the gases were allowed to distil into the refrigerated receivers. There were obtained 6.7 g. (82% yield) of silver chloride and 8.4 g. (71% yield) of pure, washed and dried 1-chloroheptafluoropropane, b.p. −2°.

Anal.[5] Calcd. for C_3F_7Cl: C, 17.62; mol. wt., 204.5. Found: C, 17.11; mol. wt. (gas density balance), 204.

This pure isomer is new, and should be compared with the known 2-chloroheptafluoropropane,[8] b.p. −2°. This reaction could be made quantitative by modifying this procedure.

Acknowledgment.—The authors wish to thank Dr. R. D. Fowler, Johns Hopkins University, for the loan of a low-range refractometer.

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(6) T. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, 68, 968 (1946).

(7) J. D. Calfee, N. Fukuhara, D. S. Young and L. A. Bigelow, *ibid.*, 62, 267 (1940).

(8) A. L. Henne and T. P. Waalkes, *ibid.*, 67, 1639 (1945).

RESEARCH INSTITUTE OF TEMPLE UNIVERSITY
PHILADELPHIA, PENNSYLVANIA

RECEIVED OCTOBER 19, 1951

Azulenes. II. Synthesis of 1,4,8-Trisubstituted Azulenes[1]

BY WERNER HERZ

For comparison with azulenes encountered in work with certain natural products it was deemed desirable to prepare azulenes substituted in the 1,4- and 8-positions of the azulene nucleus. The only representative of this class previously described,

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(1) Paper I, W. Herz, THIS JOURNAL, 73, 4295 (1951).