

*Anal.* Calcd. for  $C_8H_{10}FNO$ : C, 54.94; H, 7.69; N, 10.68; F, 14.49. Found: C, 55.17; H, 7.47; N, 10.78; F, 14.46.

**Dimethyltrifluoromethylamine (IIIa).**<sup>9</sup>—A 145-ml. Hastelloy shaker tube was charged with 21 g. (0.10 mole) of bis-(dimethylthiocarbamoyl) sulfide (IIa), 0.5 g. of arsenic trifluoride catalyst, and 35 g. (0.32 mole) of sulfur tetrafluoride. The mixture was heated at 120° for 2 hours and then at 150° for 6 hours. The tube was cooled to room temperature and the volatile product was vented into an evacuated, liquid nitrogen-cooled cylinder. There remained in the tube 11 g. (77%) of sulfur.

Mass spectrometric analysis of the volatile products indicated that the sole organic product was dimethyltrifluoromethylamine, the inorganic portion consisting mainly of sulfur tetrafluoride. Strong peaks appeared at the following *M/e* values: 113, parent ion; 112,  $CH_3(CH_2)NCF_3^+$  (most abundant); 94,  $(CH_3)_2NCF_2^+$ ; 78,  $CH_2NCF_2^+$ ; 69,  $CF_3^+$ ; 60,  $CH_3NCF^+$ ; 44,  $(CH_3)_2N^+$ ; 15,  $CH_3^+$ .

In a larger run, a small amount of the amine, b.p. 20°, remained in the bomb after venting into a cylinder as above. The n.m.r.  $F^{19}$  spectrum consisted of a strong unsplit resonance at -302 c.p.s.

**Diethyltrifluoromethylamine (IIIb).**<sup>9</sup>—A 400-ml. stainless steel shaker vessel charged with 90 g. (0.30 mole) of bis-(diethylthiocarbamoyl) disulfide (IIb) and 110 g. (1.02 moles) of sulfur tetrafluoride was heated at 120° for 8 hours. There was obtained 121 g. of a mixture of yellow liquid and solid. The latter was removed by filtration, slurried with a little ether, and recrystallized from chloroform, giving 49 g. (92%) of sulfur. The filtrate was distilled from 0.5 g. of sodium fluoride through an oven-dried Vigreux column, giving 50 g. (58%) of diethyltrifluoromethylamine (IIIb), b.p. 34-35° (180 mm.). The n.m.r.  $F^{19}$  spectrum consisted of a strong unsplit resonance at -690 c.p.s.

*Anal.* Calcd. for  $C_8H_{10}F_3N$ : C, 42.55; H, 7.14; F, 40.39. Found: C, 43.15; H, 7.64; F, 40.03.

**Reaction of Sulfur Tetrafluoride with Carbon Disulfide.**  
**A. Synthesis of Carbon Tetrafluoride.**<sup>10</sup>—A 145-ml. Hastelloy shaker tube charged with 20 g. (0.26 mole) of carbon disulfide, 60 g. (0.55 mole) of sulfur tetrafluoride and 2 g. of arsenic trifluoride catalyst was heated at 200° for 2 hours, 300° for 3 hours, 400° for 4 hours and at 475° for 3.5 hours. The tube was cooled to room temperature and the volatile products were vented into a liquid nitrogen-cooled stainless steel cylinder. There remained in the bomb 24 g. of solid from which free sulfur was isolated by extraction with carbon disulfide.

Mass spectrometric analysis showed that the volatile product (48 g.) consisted of approximately 50 weight per cent. (103%) of carbon tetrafluoride and approximately 45 weight per cent. of sulfur tetrafluoride, the remainder being mainly thionyl fluoride (4.5 weight per cent.).

**B. Synthesis of Bis-(trifluoromethyl) Polysulfides.**—A 145-ml. Hastelloy pressure vessel charged with 35 g. (0.46 mole) of carbon disulfide, 28 g. (0.26 mole) of sulfur tetrafluoride and 3 g. of boron trifluoride catalyst was heated at 150° for 2 hours and at 180° for 8 hours. There was obtained 41 g. of lavender-colored liquid containing a small amount of solid. The decanted liquid was distilled at atmospheric pressure to give a forerun consisting of a mixture of carbon disulfide and bis-(trifluoromethyl) disulfide (identified qualitatively by infrared and n.m.r.) and 11 g. (28% based on  $SF_4$ ) of bis-(trifluoromethyl) trisulfide, b.p. 78-80°,  $n_D^{25}$  1.3978 (lit.<sup>11</sup> b.p. 86.4°,  $n_D^{20}$  1.4023). The infrared spectrum was identical with that of authentic  $CF_3-S_3-CF_3$ .<sup>12</sup>

*Anal.* Calcd. for  $C_2F_6S_3$ : C, 10.26; F, 48.67; S, 41.07. Found: C, 10.40; F, 48.25; S, 40.98.

(10) W. C. Smith, U. S. Patent 2,922,825 (1960).

(11) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

(12) Butterworths Scientific Publications, London, England, *Chem. Soc.*, No. 51.

[CONTRIBUTION NO. 647 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

## Bis-(polyfluoroalkyl)-acetylenes. I. Synthesis of Bis-(polyfluoroalkyl)-acetylenes

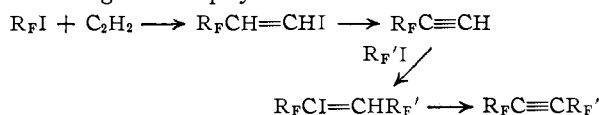
BY C. G. KRESPAN, R. J. HARDER AND J. J. DRYSDALE

RECEIVED JANUARY 31, 1961

Two new routes to 1,2-dichloro-1,2-bis-(polyfluoroalkyl)-ethylenes are presented. These routes involve coupling of 1,1,1-trichloropolyfluoroalkanes with copper, and reaction of a fluorinated acid chloride with 1,1-dichloro-2,2-difluoroethylene and nickel carbonyl. Dechlorination of two of the dichloroolefins to produce new bis-(polyfluoroalkyl)-acetylenes is described.

Recent syntheses<sup>1-3</sup> of hexafluoro-2-butyne by dehalogenation of 2,3-dichlorohexafluoro-2-butene have made this acetylene readily available. However, since the dihalides required as precursors to other bis-(polyfluoroalkyl)-acetylenes are not easily obtained, the dehalogenation reaction has not been a useful general reaction.

Dehydrohalogenation of 2-halo-1,1,1,4,4,4-hexafluoro-2-butenes also gives hexafluoro-2-butyne, but again syntheses of other precursors require several steps. Perhaps the shortest known general route to bis-(polyfluoroalkyl)-acetylenes is the following four-step synthesis.<sup>3-5</sup>



(1) A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **71**, 298 (1949).

(2) C. I. Gochenour, U. S. Patent 2,546,997 (1951).

A third synthesis of hexafluoro-2-butyne, the reaction of sulfur tetrafluoride with acetylenedicarboxylic acid,<sup>6</sup> gives a high yield in one step, but is, of course, limited to the introduction of  $CF_2$ - or  $-CF_2$ - groups.

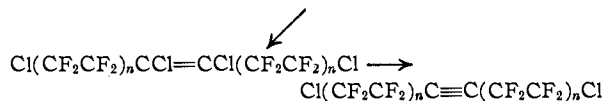
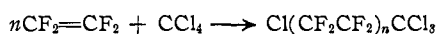
This paper describes two new routes to symmetrical bis-(polyfluoroalkyl)-acetylenes *via* the corresponding dihaloolefins. One method starts from relatively inexpensive materials and consists of three steps: (1) preparation of a 1,1,1-trihaloalkane, (2) coupling of the trihaloalkane to give a dihaloolefin and (3) dehalogenation. For example, bis-(polyfluoroalkyl)-acetylenes can be made from carbon tetrachloride and tetrafluoroethylene by the following series of reactions.

(3) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952).

(4) R. N. Haszeldine and K. Leedham, *ibid.*, 1634 (1954).

(5) R. N. Haszeldine, *ibid.*, 588 (1951).

(6) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

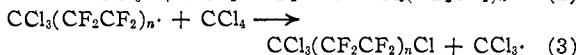
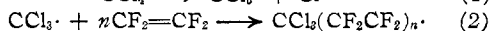
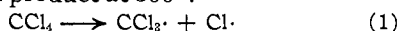


The other method involves preparation of the intermediate dichloroolefin by interaction of a fluorinated acid chloride with 1,1-dichloro-2,2-difluoroethylene and nickel carbonyl.

**Thermally Initiated Telomerization of Tetrafluoroethylene with Carbon Tetrachloride.**—A number of 1,1,1-trihalopolyfluoroalkanes that appear suitable for coupling to dichloroolefins are already available. Among these are 1,1,1-trichlorotrifluoroethane,<sup>7</sup> 1,1,1-trichloro-2,2-difluoroethane,<sup>8</sup> 1,1,1,3-tetrachlorotetrafluoropropane<sup>9</sup> and 1,1,1-trichloroheptafluoro-*n*-butane.<sup>10</sup>

A series of useful  $\alpha,\alpha,\alpha,\omega$ -tetrahaloperfluoroalkanes also might be obtainable readily by telomerization of carbon tetrahalides with tetrafluoroethylene, but previous work on reactions of this type showed that initiation by conventional free radical catalysts at moderate temperatures does not give a desirable distribution of low telomers. Carbon tetrachloride leads to waxes of high molecular weight,<sup>11</sup> because of its reluctance to participate in chain transfer with the growing radical chain. Bromo compounds, on the other hand, react so readily with fluoroalkyl radicals that only 1:1 adducts are formed in acceptable yield.<sup>12</sup>

The tendency of carbon tetrachloride to give telomers of high molecular weight has been overcome by raising the temperature at which the telomerization is run. At 250° or above, the rate of chain transfer (eq. 3) has increased so much more than the rate of propagation (eq. 2) that telomers containing from one to four tetrafluoroethylene units predominate in the product. Under ten to twenty atmospheres of tetrafluoroethylene, the telomers containing from one to three tetrafluoroethylene units are major products at 250°, while telomer containing one tetrafluoroethylene unit is the main product at 300°.



An initiator is not required, since thermal decomposition of carbon tetrachloride at reaction temperature (eq. 1) provides the free radicals necessary to start the chain reaction. Similar cases of initiation by thermal decomposition of bromo and iodo compounds have been described in the literature.<sup>13,14</sup>

(7) J. H. Simons and T. J. Brice, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 346.

(8) A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

(9) D. D. Coffman, R. Cramer and G. W. Rigby, *ibid.*, **71**, 979 (1949).

(10) E. T. McBee, D. H. Campbell and C. W. Roberts, *ibid.*, **77**, 3149 (1955).

(11) W. E. Hanford and R. M. Joyce, U. S. Patent 2,562,547 (1951).

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 250-252.

(13) W. A. Skinner, E. Bishop, D. Tieszen and J. D. Johnston, *J. Org. Chem.*, **23**, 1710 (1958).

(14) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.* (1956).

Table I summarizes the results obtained by this technique over a temperature range of 200-275°. Constant partial pressure of tetrafluoroethylene was maintained by continuous injection of this reactant into an excess of carbon tetrachloride. Although the telomerization was exothermic under these conditions, no difficulty with runaway reactions was encountered.<sup>15</sup>

TABLE I

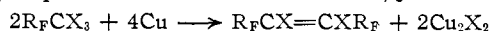
SYNTHESIS OF LOW TELOMERS FROM TETRAFLUOROETHYLENE<sup>a</sup>

Temp., °C.	Time, min. <sup>b</sup>	Yield of $\text{CX}_2(\text{CF}_2\text{CF}_2)_n\text{X}$ , %			
		$n = 1$	2	3	4
200	90	Waxy polymer			
260	165	34	18	7	..
260	50	20	17	11	6
260	25	13	15	10	8
275	25	30	14	7	..
225 <sup>c</sup>	60	26	..	..	..

<sup>a</sup> Used 2.0 moles of  $\text{CCl}_4$  and 1.0 mole of  $\text{C}_2\text{F}_4$  in a 400-ml. shaker tube. <sup>b</sup> Time required to inject the tetrafluoroethylene continuously at reaction temperature. <sup>c</sup> Used 1.3 moles of  $\text{CBr}_4$  and 0.94 mole of  $\text{C}_2\text{F}_4$ .

Carbon tetrabromide, included for comparison, readily gives the lowest telomer, a result expected from an efficient chain transfer step. The presence of free bromine and considerable low-boiling product in this reaction mixture indicated that a temperature well below 225° would give more satisfactory results. Chloroform, chosen as an example of a telogen containing a modest amount of hydrogen, underwent gross decomposition rather than telomerization at 250°.

**Preparation of Fluorinated Dihaloolefins.**—2,3-Dichlorohexafluoro-2-butene is apparently the only easily accessible acyclic 1,2-dihalo-1,2-bis-(polyfluoroalkyl)-ethylene.<sup>2,6</sup> Therefore, a general route to this class of compounds was sought in the coupling of 1,1,1-trihalopolyfluoroalkanes. The reaction of copper with carbon tetrachloride at elevated temperature is a known method for the preparation of hexachloroethane.<sup>16</sup> Arylated trichlorides such as benzotrichloride and 1,1,1-trichloro-2,2-diphenylethane have also been coupled with metals to give saturated and olefinic products.<sup>17</sup> This procedure has been found to be adapted readily to the conversion of 1,1,1-trichloro- or 1,1,1-tribromopolyfluoroalkanes to the corresponding 1,2-dihalo-1,2-bis-(polyfluoroalkyl)-ethylenes.<sup>18</sup> The 1:1 and 2:1 tetrafluoroethylene-carbon tetrachloride telomers and the 1:1 tetrafluoroethylene-carbon tetrabromide telomer have been coupled with copper powder at 140-200° in 40-65% conversion.



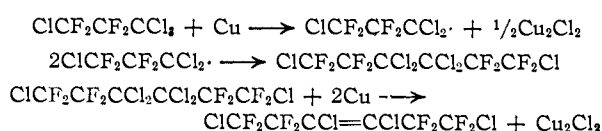
(15) Since the handling of tetrafluoroethylene under pressure can be hazardous due to the exothermic nature of its polymerization and decomposition, care must be taken to exclude possible initiators such as oxygen (*cf.*, M. A. Dietrich and R. M. Joyce, U. S. Patent 2,407,405 (1946)). In the present work, both metering and injection of tetrafluoroethylene were accomplished by positive displacement of the cold liquid with a piston in apparatus designed and supervised by Mr. P. J. Reynolds of these laboratories.

(16) B. Radziszewski, *Ber.*, **17**, 834 (1884).

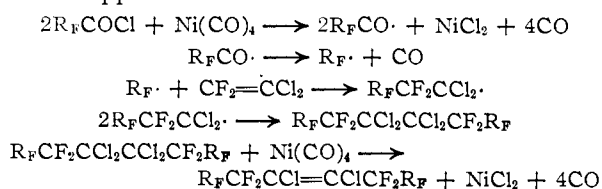
(17) T. L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 42-43.

(18) The coupling of a 1,1,1-trichloropolyfluoroalkane with copper to give a 1,2-dichloroolefin was first carried out by Dr. R. D. Cramer of these laboratories.

The products from all three telomers mentioned above were shown by nuclear magnetic resonance spectroscopy to be mixtures of the *cis* and *trans* isomers. Indirect evidence was also obtained that in one case the crude product from 1,1,1,3-tetrachlorotetrafluoropropane contained a substantial amount of the saturated coupling product, 1,3,3,4,4,6-hexachlorooctafluoro-*n*-hexane. After removal of all dichloroolefin from this crude product by distillation, the high-boiling residue was made to yield more dichloroolefin by heating it with a fresh portion of copper powder. This result is evidence that little of the dichloroolefin is formed by dimerization of a carbene intermediate. More probable is the following sequence of reactions involving a saturated intermediate similar to the hexachloroethane obtained earlier from carbon tetrachloride.



Another synthesis of dichloroolefins discovered in this work is a complex reaction that apparently involves radical species. The method consists of heating a fluorinated acid chloride, nickel carbonyl and 1,1-dichloro-2,2-difluoro-ethylene at 150° to obtain a dichloroolefin directly. Although carbene formation is also possible here, the reaction is best formulated as an additive dimerization<sup>19</sup> similar to the preparation of octachloro-1,4-difluoro-*n*-butane by the fluorination of tetrachloroethylene.<sup>20</sup> Dechlorination of a saturated intermediate by nickel carbonyl would provide the olefin in a last step analogous to that suggested above for couplings with copper.



**Dechlorination of 1,2-Dichloro-1,2-bis-(polyfluoroalkyl)-ethylenes.**—The well-known use of zinc dust to dehalogenate 1,2-dihalides to ethylenes and acetylenes already has been applied to the synthesis of hexafluoro-2-butyne from the corresponding dichloride.<sup>1,2</sup> Yields of 60–70% are reported, but the dichloride must be treated with care to avoid formation of excessive amounts of by-products. As ordinarily carried out in an alcoholic medium, reactions such as reduction can predominate if conditions are not carefully controlled.

In our use of three dechlorination systems—zinc and ethanol, zinc and acetic anhydride, and magnesium and tetrahydrofuran—the most satisfactory results have been obtained with zinc and acetic anhydride. High temperature and rapid addition of dichloroolefin had no adverse effect on yields of bis-(polyfluoroalkyl)-acetylene with this combination, while such a procedure with zinc and

ethanol resulted in low yields. Magnesium in tetrahydrofuran gave modest yields of one bis-(polyfluoroalkyl)-acetylene, but no product in another case. In the attempted synthesis of 1,6-dichlorooctafluoro-3-hexyne from 1,3,4,6-tetrachlorooctafluoro-3-hexene, magnesium reacted to give a dark solid. Zinc and acetic anhydride dechlorination, however, gave the desired acetylene in 70% yield.

These highly fluorinated acetylenes have unusual reactivity, as subsequent papers will show.

### Experimental<sup>21</sup>

**Low Telomers from Tetrafluoroethylene and Carbon Tetrachloride.**—The telomerizations in Table I were carried out by heating 2 moles of carbon tetrachloride at reaction temperature in a 400-ml. shaker tube lined with stainless steel while 1 mole of tetrafluoroethylene was injected continuously. The following reaction is a typical example of the procedure.

Ninety-seven grams (1.0 mole) of tetrafluoroethylene was injected over a period of 50 minutes into 308 g. (2.0 moles) of carbon tetrachloride heated at 260°. Onset of the reaction was marked by a slight rise in temperature and pressure, and termination of the addition of tetrafluoroethylene resulted in a slight drop in temperature and pressure. The reaction mixture was heated for an additional 30 minutes. Distillation of the resulting mixture, 381 g. of liquid, gave 230 g. of recovered carbon tetrachloride and four low telomers. 1,1,1,3-Tetrachlorotetrafluoropropane<sup>22</sup> was obtained as 49.0 g. (20% yield based on tetrafluoroethylene) of colorless liquid, b.p. 112–114°, *n*<sub>D</sub><sup>20</sup> 1.3948.

1,1,1,5-Tetrachlorooctafluoro-*n*-pentane, 29.8 g. (17% yield), had b.p. 98–100° (140 mm.), *n*<sub>D</sub><sup>20</sup> 1.3723.

*Anal.* Calcd. for C<sub>5</sub>Cl<sub>4</sub>F<sub>8</sub>: Cl, 40.08; F, 42.95. Found: Cl, 40.19; F, 43.17.

1,1,1,7-Tetrachlorododecafluoro-*n*-heptane, 15.4 g. (11% yield), had b.p. 90–91° (25 mm.), *n*<sub>D</sub><sup>20</sup> 1.3621.

*Anal.* Calcd. for C<sub>7</sub>Cl<sub>4</sub>F<sub>12</sub>: Cl, 31.25; F, 50.23. Found: Cl, 31.20; F, 49.85.

1,1,1,9-Tetrachlorohexadecafluoro-*n*-nonane, 8.1 g. (6% yield), had b.p. 113–120° (25 mm.). This product, which solidified in the receiver, was not characterized further. The liquid products, however, gave nuclear magnetic resonance spectra for F<sup>19</sup> that are compatible with the postulated structures.

**1,1,1,3-Tetrabromotetrafluoropropane.**—A 400-ml. shaker tube lined with stainless steel was charged with 431 g. (1.3 moles) of carbon tetrabromide and heated at 225° while 94 g. (0.94 mole) of tetrafluoroethylene was injected continuously over a period of 1 hour. Distillation of the resulting mixture, 497 g., gave a considerable amount of low boiling material, including free bromine, and recovered carbon tetrabromide. The product was obtained as 105 g. (26% yield based on tetrafluoroethylene) of colorless oil, b.p. 90–93° (25 mm.), *n*<sub>D</sub><sup>20</sup> 1.5019. The nuclear magnetic resonance spectrum for F<sup>19</sup> consisted of the expected two peaks of equivalent size.

*Anal.* Calcd. for C<sub>3</sub>Br<sub>4</sub>F<sub>4</sub>: Br, 74.05; F, 17.61. Found: Br, 73.78; F, 18.04.

**1,3,4,6-Tetrachlorooctafluoro-3-hexene.**—A mixture of 187 g. (0.74 mole) of 1,1,1,3-tetrachlorotetrafluoropropane and 114 g. (1.8 moles) of copper powder was heated in a 400-ml. shaker tube at 180° for 15 hours. Continuous extraction of the product with methylene chloride and distillation of the extracts gave 88.0 g. (65% yield) of 1,3,4,6-

(21) All boiling points are uncorrected. The nuclear magnetic resonance 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 56.4 mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the H<sup>1</sup> resonance of water and the F<sup>19</sup> resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field than the reference. The copper powder used in the coupling reactions was obtained from Metals Disintegrating Co., Grade No. 105.

(22) This compound has been reported previously (ref. 9) to have b.p. 114.5°, *n*<sub>D</sub><sup>20</sup> 1.3974.

(19) D. D. Coffman and E. L. Jenner, *J. Am. Chem. Soc.*, **80**, 2872 (1958).

(20) W. T. Miller, *ibid.*, **62**, 341 (1940).

tetrachloroöctafluoro-3-hexene, b.p. 95–98° (100 mm.). The infrared spectrum showed the presence of a double bond (6.4  $\mu$ ). The presence of both *cis* and *trans* forms of the olefin was indicated by the nuclear magnetic resonance spectrum for  $F^{19}$ , since two sets of the expected two peaks of equivalent size were found.

*Anal.* Calcd. for  $C_6Cl_4F_8$ : Cl, 38.77; F, 41.54. Found: Cl, 38.49; F, 41.55.

Another coupling reaction carried out under ostensibly similar conditions gave 23% of recovered chlorofluoropropane, 23% conversion to the olefin, and a large amount of residual oil. Reaction of the residue with additional copper powder at 200° for 6 hours resulted in the formation of an additional 14% of the olefin. In view of this result, a reaction temperature of 200° should prove more reliable.

**1,5,6,10-Tetrachlorohexadecafluoro-5-decene.**—A mixture of 25.0 g. (0.07 mole) of 1,1,1,5-tetrachloroöctafluoropentane and 15.0 g. (0.24 mole) of copper powder was heated to reflux under atmospheric pressure for 12 hours, during which time the boiling point rose from 152° to 187°. The liquid was decanted, and the solid was washed with methylene chloride. The liquid product and washings were then combined and distilled to give 7.1 g. (36% yield) of 1,5,6,10-tetrachlorohexadecafluoro-5-decene, b.p. 98–99° (10 mm.). The infrared spectrum showed the presence of a double bond (6.35  $\mu$ ), and the nuclear magnetic resonance spectrum for  $F^{19}$  fitted a mixture of *cis* and *trans* isomers of the desired olefin.

*Anal.* Calcd. for  $C_{10}Cl_4F_{16}$ : Cl, 25.06; F, 53.72. Found: Cl, 24.89; F, 53.63.

**1,3,4,6-Tetrabromoöctafluoro-3-hexene.**—A mixture of 104 g. (0.24 mole) of 1,1,1,3-tetrabromotetrafluoropropane and 38.1 g. (0.60 mole) of copper powder was heated at 120° for 20 hours and then at 140° for 8 hours. The mixture was extracted exhaustively with methylene chloride, and the extracts were distilled to give 29.2 g. (28%) of recovered bromofluoropropane and 25.4 g. (39% conversion) of 1,3,4,6-tetrabromoöctafluoro-3-hexene, b.p. 83–88° (5 mm.). The infrared spectrum showed the presence of a double bond (6.35  $\mu$ ), and the presence of both *cis* and *trans* isomers was established by the nuclear magnetic resonance spectrum for  $F^{19}$ . *Anal.* Calcd. for  $C_6Br_4F_8$ : Br, 58.79; F, 27.96. Found: Br, 58.85; F, 28.07.

**1,6-Dichloroöctafluoro-3-hexyne.**—A 500-ml. flask fitted with a stirrer, a dropping funnel and a 6-inch Vigreux still was charged with 20 g. (0.31 mole) of zinc dust and 60 ml. of acetic anhydride. The mixture was heated until the head temperature reached 135°, and then a solution of 44.2 g. (0.12 mole) of 1,3,4,6-tetrachloroöctafluoro-3-hexene in 20 ml. of acetic anhydride was added in small portions during 4 hours. The hexyne was removed continuously as formed at a head temperature of 83–93°. There was thus obtained 36.5 g. of colorless distillate which was washed with water, 5% sodium bicarbonate, and again with water to remove co-distilled acetic anhydride. After having been dried over anhydrous sodium sulfate, the product was distilled to give 25.0 g. (70%) of the hexyne, b.p. 82–84°,  $n_D^{20}$  1.3210. The nuclear magnetic resonance spectrum for  $F^{19}$  consisted of the expected two peaks of equal intensity, one at –290 c.p.s. for the chlorodifluoromethyl group and the other at +1409 c.p.s. for the difluoromethylene group adjacent to the triple bond. The infrared spectrum had no absorption in either the double bond region or the carbon–hydrogen stretching region.

*Anal.* Calcd. for  $C_6Cl_2F_8$ : Cl, 24.04; F, 51.53. Found: Cl, 24.44; F, 51.61.

When an attempt was made to carry out this dehalogena-

tion with magnesium in tetrahydrofuran, only a black intractable solid was obtained.

**Hexafluoro-2-butyne.**—A 1-l. flask fitted with a stirrer, a dropping funnel and a 10-inch Vigreux still connected to a –80° trap was charged with 80 ml. of acetic anhydride and 60 g. of zinc dust. The mixture was heated to reflux with vigorous stirring. With the still-head set for total reflux, a solution of 84 g. (0.36 mole) of 2,3-dichlorohexafluoro-2-butene in 50 ml. of acetic anhydride was added dropwise over a 4-hour period. The heat and rate of addition were adjusted so that the head temperature did not exceed 50°; 30 g. of zinc dust then was added, and the mixture was refluxed for an additional 3 hours. The contents of the –80° trap were transferred to another trap by warming slowly to room temperature, giving 34 g. (63%) of hexafluoro-2-butyne, identified by its infrared spectrum.

**1,12-Dihydroeicosafafluoro-6-dodecyne.**—A mixture of 150 g. (0.56 mole) of  $\omega$ -H-octafluorovaleryl chloride, b.p. 86–88°, 53 g. (0.40 mole) of 1,1-dichloro-2,2-difluoroethylene and 50 g. (0.29 mole) of nickel carbonyl was heated at 150° for 6 hours in a 1-l. bomb. The moist solid products from five such reactions were stirred slowly into 1500 ml. of ice-water, and the resulting mixture was allowed to stand overnight. The lower phase was separated, washed twice with water, dried over anhydrous calcium chloride, filtered and distilled to give 128 g. of a fraction boiling at 90–110° (8 mm.). The nuclear magnetic resonance spectrum for  $F^{19}$  was compatible with a mixture of *cis*- and *trans*-6,7-dichloro-1,12-dihydroeicosafafluoro-6-dodecene, and the infrared spectrum contained an absorption band for a double bond at 6.3  $\mu$ . Calculated on the basis of this product, the yield was 30% from nickel carbonyl.

The olefin was dehalogenated in the following manner without further characterization. To 3.68 g. (0.15 mole) of magnesium turnings in 20 ml. of tetrahydrofuran was added 15 ml. of a solution of 25.0 g. (0.042 mole) of the olefin in 100 ml. of tetrahydrofuran. Reaction soon set in at room temperature, and the mixture was cooled with an ice-bath. The remainder of the olefin solution was added at a rate of one drop per second, and the dark solution was then stirred for 2 hours at 0°. After removal of 75 ml. of the solvent by distillation under reduced pressure, the excess magnesium was removed by filtration, and the filtrate was poured into 750 ml. of water. Dilute sulfuric acid was added to break the dark emulsion, and the organic material was extracted with ether. Fractionation of the dried ether extracts gave 4.55 g. (20% yield) of the desired acetylene as a colorless liquid, b.p. 71–76° (18 mm.),  $n_D^{20}$  1.3055, and 5.5 g. of a mixture of the acetylene and starting material.

*Anal.* Calcd. for  $C_{12}F_{20}H_2$ : C, 27.39; H, 0.38; F, 72.22. Found: C, 27.71; H, 0.90; F, 71.90.

The nuclear magnetic resonance spectra (proton and  $F^{19}$ ) are consistent with the proposed structure. The resonance for the terminal hydrogen was a triplet centered at –47 c.p.s. with the smaller peaks at –99 and +5 c.p.s. The fluorine spectrum consisted of a doublet at +3409 and +3463 c.p.s. for the terminal difluoromethylene group, bands at +2995 and +2582 c.p.s. (double intensity) for the internal difluoromethylene groups, and a band at +1436 c.p.s. for the difluoromethylene group adjacent to the triple bond. The infrared spectrum had no absorption in the double bond region, but did show a sharp carbon–hydrogen stretching absorption at 3.32  $\mu$ .

A solution of the acetylene in acetic acid rapidly absorbed 95% of the theoretical amount of hydrogen at 33° in the presence of  $PtO_2$  (2 moles of hydrogen per mole of substrate).