Photolytic Procedures.—The apparatus used in these studies consisted of a Vycor filtered 450-W medium-pressure Hanovia mercury arc lamp placed in a water-cooled quartz jacket fitted with a 45/50 male joint. This assembly was placed in a 700-ml glass finger with a 45/50 female joint. The quartz jacket was of sufficient depth to permit the lamp to be below the surface of 500 ml of liquid contained in the glass finger. The glass portion of the apparatus had a gas inlet tube and a 24/40 side arm to which a water-cooled condenser was attached. All solvents were purified prior to their use.[11] In a typical photolysis, sufficient thiocyanate or isothiocyanate starting material was diluted to 500 ml in solvent to afford the desired concentration. This solution was placed in the glass portion of the apparatus, the lamp assembly was inserted, and argon gas was passed through the solution for a minimum of 1 hr before the lamp was turned on. During argon gas flushing and photolysis the solution was magnetically stirred. At intervals after lamp ignition, aliquots (10 ml for gc analysis and 40 ml for nmr) were removed, the solvent was evaporated, and the residue was analyzed by gc and mass spectrum. Gc was used to analyze the products from the photolyses of **1a**, **2a**, and **3**. On a 2 ft × 0.125 in. 15% diethylene glycol succinate on Chromosorb W column at 150° with a helium carrier gas flow of 75 ml/min, **1a** and **2a** showed retention times of 5.5 and 3.5 min, respectively. In the remaining benzyl systems, nmr analysis was accomplished by comparing the relative peak areas for the benzyl methylene protons of the thiocyanates and isothiocyanates within a given sample. The relative peak areas were measured by integration on the nmr and these results were compared with the relative areas measured with a planimeter. These methods were mutually consistent.

Dicyclohexyl Sulfide (4).—To 1.67 g (0.011 mol) of cyclohexanethiol in 15 ml of anhydrous nitrogen-flushed pyridine was added 2.87 g (0.011 mol) of cyclohexyl *p*-toluenesulfonate. The reaction mixture was heated at reflux for 24 hr, cooled, and poured into 100 ml of water. The water solution was extracted three times with 20-ml portions of ether. The ether extracts were combined and washed successively with water, 10% hydrochloric acid solution, and saturated sodium bicarbonate solution. Drying of the resultant ether solution followed by solvent removal afforded 2.4 g of a crude product. Gas chromatographic analysis of this mixture using conditions identical with those used for analysis of the photolysis products from **1a** and **2a** indicated a component with a retention time of 0.80 min. Gc collection of this material afforded dicyclohexyl sulfide: mass spectrum *m/e* (rel intensity) 198 (17), 117 (94), 115 (16), 83 (100), 82 (54), 81 (21), 67 (37), 55 (70), 41 (40), 39 (20).

The mass spectrum and gc retention time of **4** were identical with those shown by the by-product from the photolyses of **1a** and **2a**.

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Registry No.—**1a**, 3012-37-1; **1b**, 18991-39-4; **1c**, 19927-28-7; **1d**, 2082-64-6; **1e**, 41499-20-1; **2a**, 622-78-6; **2b**, 3694-46-0; **2c**, 3694-57-3; **2d**, 3694-45-9; **2e**, 41499-21-2; **4**, 7133-46-2; *p*-trifluoromethylbenzyl bromide, 402-49-3.

Perfluorovinyl Isocyanates

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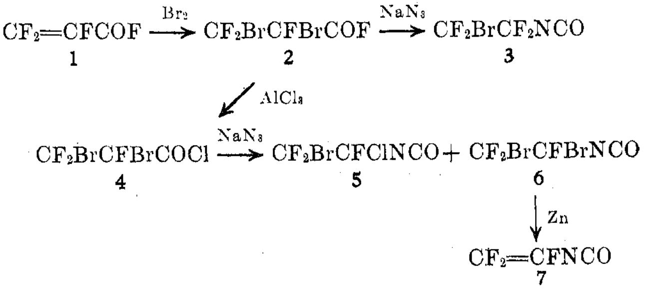
Two new polymerizable monomers, trifluorovinyl isocyanate (**7**) and 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate (**18**), were prepared by dehalogenation of dichloro- (and dibromo-) trifluoroethyl isocyanates (**6** and **13**) and 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate (**17**), respectively. The isocyanates **6** and **13** were prepared by the Curtius reaction from the corresponding propionyl chlorides (**4** and **11**) which were in turn prepared by halogenation of trifluoroacryloyl fluoride (**1**) and replacement of the acyl fluorine with chlorine from $AlCl_3$. The isocyanate **17** was prepared in one step by reaction of 1,3-chloropentafluoroacetone imine with oxalyl chloride. Hexafluoroacetone imine and dichlorotetrafluoroacetone imine also gave α-chloro isocyanates with oxalyl chloride. The new vinyl isocyanates, **7** and **18**, add nucleophiles to the isocyanate group in preference to the carbon–carbon double bond.

Although many perfluoroalkyl isocyanates are known,[1] trifluorovinyl isocyanate and other perfluoro isocyanates with α,β double bonds have not been reported previously. Such isocyanates would be expected to polymerize easily and could be used to prepare perfluorinated polymers containing isocyanate groups.

We have prepared trifluorovinyl isocyanate (**7**) in several steps from trifluoroacyloyl fluoride (**1**)[2] (Scheme I). Reaction of **1** with sodium azide to give **7** directly by means of the Curtius reaction failed and gave instead an unidentified, highly explosive material. This explosive material probably resulted from an attack of azide ion on the β-carbon atom of **1**, since it is known that nucleophiles preferentially replace the vinylic β-fluorine atoms of **1** instead of the acyl fluoride.[3]

Scheme I



$$CF_2{=}CFCOF\ (\mathbf{1}) \xrightarrow{Br_2} CF_2BrCFBrCOF\ (\mathbf{2}) \xrightarrow{NaN_3} CF_2BrCF_2NCO\ (\mathbf{3})$$

$$\mathbf{2} \xrightarrow{AlCl_3} CF_2BrCFBrCOCl\ (\mathbf{4}) \xrightarrow{NaN_3} CF_2BrCFClNCO\ (\mathbf{5}) + CF_2BrCFBrNCO\ (\mathbf{6}) \xrightarrow{Zn} CF_2{=}CFNCO\ (\mathbf{7})$$

To circumvent this problem, the double bond was protected by bromination, with the idea that it could be regenerated after the isocyanate was formed by the Curtius reaction. The dibromopropionyl fluoride **2** reacted smoothly with sodium azide, but the major product was the monobromo isocyanate **3**. The sodium fluoride formed in the reaction had apparently replaced the α bromine with fluorine in either the intermediate dibromopropionyl azide or in the expected dibromo isocyanate **6**. It seems most likely that the halogen exchange occurs with **6**, since it could be

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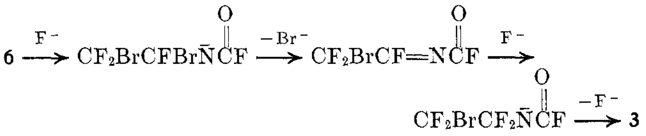
[1] W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969.

[2] R. E. Banks, J. M. Birchall, T. Clarke, R. M. Haszeldine, M. J. Stevenson, and H. Iserson, *J. Chem. Soc. C*, 266 (1968).

[3] Y. A. Cheburkov and M. D. Bargamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 833 (1967).

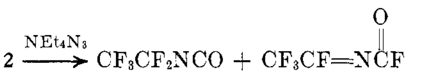
facilitated by a series of addition and elimination reactions as illustrated in Scheme II. More soluble azides,

SCHEME II



$$6 \xrightarrow{\mathrm{F^-}} \mathrm{CF_2BrCFBr\bar{N}\overset{O}{\overset{\|}{C}}F} \xrightarrow{\mathrm{-Br^-}} \mathrm{CF_2BrCF{=}N\overset{O}{\overset{\|}{C}}F} \xrightarrow{\mathrm{F^-}} \mathrm{CF_2BrCF_2\bar{N}\overset{O}{\overset{\|}{C}}F} \xrightarrow{\mathrm{-F^-}} 3$$

such as tetraethylammonium azide, reacted with 2 to give completely fluorinated products, including pentafluoroethyl isocyanate (8)[4] and the isomeric carbamoyl fluoride 9.



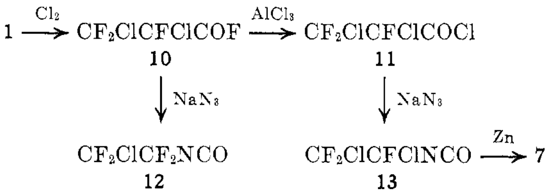
$$2 \xrightarrow{\mathrm{NEt_4N_3}} \underset{8}{\mathrm{CF_3CF_2NCO}} + \underset{9}{\mathrm{CF_3CF{=}N\overset{O}{\overset{\|}{C}}F}}$$

So that no sodium fluoride would be formed in the Curtius reaction, 2 was converted to the corresponding acid chloride 4 by treatment with aluminum chloride in methylene chloride. This dibromo acid chloride (4) reacted smoothly with sodium azide to give the dibromo isocyanate 6 as the principal product. Some bromochloro isocyanate 5 was also formed.

Trifluorovinyl isocyanate (7) was formed in 81% yield by debromination of 6 with activated zinc dust in diglyme at room temperature. It is a colorless, low-boiling liquid (bp 19-20°) that polymerizes spontaneously if stored uninhibited at room temperature. The polymerization can be inhibited if small amounts of conventional radical inhibitors such as D-limonene or 2-(trifluoromethyl)phenothiazine are added to the liquid monomer.

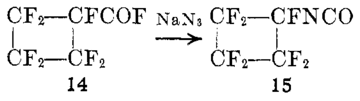
Trifluorovinyl isocyanate (7) can also be prepared from 1 by protecting the double bond with chlorine, as illustrated in Scheme III.

SCHEME III



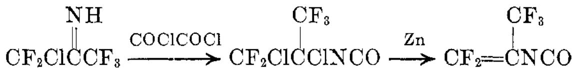
$$\begin{tikzcd} 1 \arrow[r, "\mathrm{Cl_2}"] & \underset{10}{\mathrm{CF_2ClCFClCOF}} \arrow[r, "\mathrm{AlCl_3}"] \arrow[d, "\mathrm{NaN_3}"] & \underset{11}{\mathrm{CF_2ClCFClCOCl}} \arrow[d, "\mathrm{NaN_3}"] & \\ & \underset{12}{\mathrm{CF_2ClCF_2NCO}} & \underset{13}{\mathrm{CF_2ClCFClNCO}} \arrow[r, "\mathrm{Zn}"] & 7 \end{tikzcd}$$

An attempt to prepare 7 by the pyrolysis of perfluorocyclobutyl isocyanate (15) failed, presumably because of the instability of 7 in the presence of radicals generated in the pyrolysis. Isocyanate 15 was prepared by a normal Curtius reaction of the corresponding acyl fluoride 14.



14 15

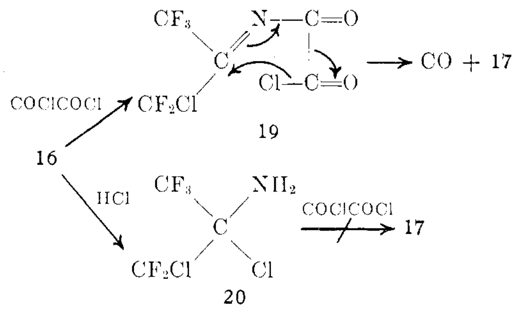
Perfluoroisopropenyl isocyanate (18) was also prepared by zinc dehalogenation of the corresponding dichloro isocyanate (17) and was obtained in 91% yield as a colorless liquid, bp 42°. Isocyanate 18 does not spontaneously polymerize when stored at room temperature, but it can be polymerized and copolymerized with radical or anionic catalysts.



$$\underset{16}{\mathrm{CF_2Cl\overset{NH}{\overset{\|}{C}}CF_3}} \xrightarrow{\mathrm{COClCOCl}} \underset{17}{\mathrm{CF_2Cl\overset{CF_3}{\overset{|}{C}}ClNCO}} \xrightarrow{\mathrm{Zn}} \underset{18}{\mathrm{CF_2{=}\overset{CF_3}{\overset{|}{C}}NCO}}$$

The dichloro isocyanate (17) precursor to 18 was prepared conveniently in one high-yield step by the reaction of oxalyl chloride with chloropentafluoroacetone imine.[5] This reaction is believed to proceed through the oxalyl derivative (19) which either undergoes a concerted reaction as illustrated in Scheme IV or adds a chloride ion with elimination of CO and chloride to give 17.

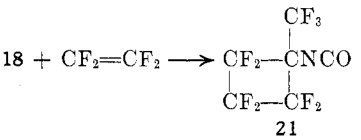
SCHEME IV



Another possible mechanism would be the addition of hydrogen chloride to 16 to give the α-chloro amine 20, and then oxalylation of this amine to give 17. This mechanism appears unlikely, however, since 20, which can be prepared by the addition of anhydrous hydrogen chloride to the imine 16, will not react with oxalyl chloride under the same conditions that 16 will react.

The reaction of perhalo ketone imines with oxalyl chloride to give α-chloro isocyanates appears to be a general reaction. Hexafluoroacetone imine[5] and 1,3-dichlorotetrafluoroacetone imine[5] also react with oxalyl chloride to give the corresponding α-chloro isocyanates.[6]

Nucleophiles react with both 7 and 18 preferentially at the isocyanate group instead of the double bond. For example, alcohols add to give carbamates and amines add to give ureas. Bromine, however, adds to the double bond. Tetrafluoroethylene also adds to the double bond of 18 in low yield to give the cyclic isocyanate 21.



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Experimental Section[7]

2,3-Dichloro-2,3,3-trifluoropropionyl Fluoride (10).—Chlorine, 60 ml measured at −78° (*ca.* 93 g, 1.31 mol), was slowly distilled into a Pyrex flask containing 100 ml (*ca.* 168 g, 1.31 mol) of trifluoroacryloyl fluoride that was irradiated with a 275-W sun

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[4] A. H. Ahlbrecht and D. R. Husted, U. S. Patent 2,617,817 (1952).

[5] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

[6] R. F. Swindell and J. M. Shreeve, *J. Fluorine Chem.*, **2**, 191 (1972–1973), describe the preparation of 1-chloro-2,2,2-trifluoro-1-(trifluoromethyl)ethyl isocyanate by reaction of oxalyl chloride with the lithium salt of hexafluoroacetone imine. L. I. Samarai, V. P. Belaya, O. U. Vishneuskii, and G. I. Derkach, *Zh. Org. Khim.*, **4**, 720 (1968), report that benzophenone imine is converted to chlorodiphenylmethyl isocyanate by treatment with oxalyl chloride.

[7] All boiling points are uncorrected.

lamp at a 6-in. distance. The temperature was kept between 0 and 20°, and the addition required 6 hr. Distillation of the reaction mixture gave 188 g (72%) of 2,3-dichloro-2,3,3-trifluoropropionyl fluoride as a colorless liquid: bp 49–50°; n^{25}D 1.3294; ir (liquid) 5.35 μ (COF); ^{19}F nmr (CCl$_3$F) δ 21.7 (d, J = 15 Hz coupled to d, J = 10.3 Hz coupled to d, J = 10.3 Hz, 1 F) −64.7 (d, J = 173 Hz coupled to d, J = 10.3 Hz coupled to d, J = 8.6 Hz, 1 F), −68.8 (d, J = 173 Hz coupled to d, J = 10.3 Hz coupled to d, J = 10.3 Hz, 1 F), and −123.7 ppm (d, J = 15 Hz coupled to d, J = 10.3 Hz coupled to d, J = 8.6 Hz, 1 F).

Anal. Calcd for C$_3$Cl$_2$F$_4$O: C, 18.11; Cl, 35.65; F, 38.20. Found: C, 18.20; Cl, 34.87; F, 38.33.

2,3-Dichloro-2,3,3-trifluoropropionyl Chloride (11).—A 100-g sample (0.5 mol) of 2,3-dichloro-2,3,3-trifluoropropionyl fluoride was added dropwise to a stirred suspension of 34 g (0.25 mol) of aluminum chloride in 200 ml of methylene chloride. The reaction mixture was stirred for 2 hr, and the volatile portion was distilled under reduced pressure into a Dry Ice cooled trap. Redistillation gave 70.6 g (66%) of 2,3-dichloro-2,3,3-trifluoropropionyl chloride as a colorless liquid: bp 87.5–88°; n^{25}D 1.3812; ir (liquid) 5.57 μ (C═O); ^{19}F nmr (CCl$_3$F) δ −64.2 (d, J = 173 Hz to d, J = 8 Hz, 1 F), −65.7 (d, J = 173 Hz to d, J = 10 Hz, 1 F), and −117.4 ppm (d, J = 10 Hz to d, J = 8 Hz, 1 F).

Anal. Calcd for C$_3$Cl$_3$F$_3$O: C, 16.73; Cl, 49.38; F, 26.46. Found: C, 16.87; Cl, 49.07; F, 26.56.

2-Chloro-1,1,2,2-tetrafluoroethyl Isocyanate (12) and 1,2-Dichloro-1,2,2-trifluoroethyl Isocyanate (13).—A 40-g sample *(0.2 mol) of 2,3-dichloro-2,3,3-trifluoropropionyl fluoride* was added dropwise to a stirred suspension of 14.3 g (0.22 mol) of powdered sodium azide in 200 ml of xylene. The reaction mixture was stirred for 18 hr at 25° and then warmed slowly to 110°. When the evolution of nitrogen ceased, the volatile portion of the reaction mixture was distilled to give 10.14 g (29%) of 2-chloro-1,1,2,2-tetrafluoroethyl isocyanate as a colorless liquid, bp 31–31.5°, n^{25}D 1.3122, ^{19}F nmr (CCl$_3$F) δ −73.1 (t, J = 4 Hz, 2 F) and −83.6 ppm (broad t, 2 F), and 3.03 g (8%) of 1,2-dichloro-1,2,2-trifluoroethyl isocyanate as a colorless liquid, bp 67–68°, n^{25}D 1.3650, ^{19}F nmr (CCl$_3$F) δ −69.9 (q, 2 F) and −77.9 ppm (broad t, 1 F).

Anal. Calcd for C$_3$ClF$_4$NO: C, 20.30; Cl, 19.98; F, 42.82; N, 7.89. Found: C, 20.69; Cl, 20.23; F, 43.11; N, 7.59.

Anal. Calcd for C$_3$Cl$_2$F$_3$NO: C, 18.58; Cl, 36.56; F, 29.39; N, 7.22. Found: C, 19.01; Cl, 36.19; F, 29.52; N, 6.96.

1,2-Dichloro-1,2,2-trifluoroethyl Isocyanate (13).—A 65-g sample (0.3 mol) of 2,3-dichloro-2,3,3-trifluoropropionyl chloride was added dropwise to a suspension of 21.67 g (0.33 mol) of powdered sodium azide in 300 ml of dry xylene. The reaction mixture was stirred at 25° for 20 hr, and then slowly warmed to 112° over a period of 6 hr. The material boiling below xylene was distilled from the reaction mixture and then redistilled to give 32.2 g (62% yield, 55% conversion) of 1,2-dichloro-1,2,2-trifluoroethyl isocyanate as a colorless liquid, bp 68–69°, n^{25}D 1.3654, ir (liquid) 4.40 μ (NCO), and 7.8 g of recovered 2,3-dichloro-2,3,3-trifluoropropionyl chloride.

Anal. Calcd for C$_3$Cl$_2$F$_3$NO: C, 18.58; Cl, 36.56; F, 29.39; N, 7.22. Found: C, 18.86; Cl, 36.97; F, 28.92; N, 7.32.

2,3-Dibromo-2,3,3-trifluoropropionyl Fluoride (2).—A 128-g sample (1 mol) of trifluoroacryloyl fluoride was slowly distilled into 160 g (1 mol) of bromine cooled to 0°. The reaction mixture was stirred for 3 days at room temperature and then distilled to give 261 g (93%) of 2,3-dibromo-2,3,3-trifluoropropionyl fluoride as a colorless liquid: bp 88–89°; n^{25}D 1.3938; ir (liquid) 5.33 μ (COF); ^{19}F nmr (CCl$_3$F) δ 21.3 (d, J = 11.0 Hz to d, 13.3 Hz to d, 14.3 Hz, 1 F), −56.3 ppm (d, J = 177 Hz to d, 15.2 Hz to d, 14.3 Hz, 1 F), 60.9 (d, J = 177 Hz to d, 16.8 Hz to d, 11.0 Hz), and −125.4 ppm (d, J = 16.8 Hz to d, 15.2 Hz to d, 13.3 Hz).

Anal. Calcd for C$_3$Br$_2$F$_4$O: C, 12.52; Br, 55.52; F, 26.40. Found: C, 12.75; Br, 55.32; F, 26.69.

2,3-Dibromo-2,3,3-trifluoropropionyl Chloride (4).—A 163-g sample (0.56 mol) of 2,3-dibromo-2,3,3-trifluoropropionyl fluoride was added dropwise to a mechanically stirred suspension of 76 g (0.56 mol) of aluminum chloride in 282 ml of methylene chloride. The reaction mixture warmed spontaneously to 40°. After cooling, the volatile portion of the reaction mixture was distilled under reduced pressure into a Dry Ice cooled trap. Redistillation gave 97.5 g (57%) of 2,3-dibromo-2,3,3-trifluoropropionyl chloride as a colorless liquid: bp 128–129°; n^{25}D 1.4436; ir (liquid) 5.57 μ (COCl); ^{19}F nmr (CCl$_3$F) δ −55.7 (d, J = 175 Hz to d, J = 14.5 Hz, 1 F), −57.9 (d, J = 175 Hz to d, J = 16 Hz, 1 F), and 116.5 ppm (d, J = 16 Hz to d, J = 14.5 Hz, 1 F).

Anal. Calcd for C$_3$Br$_2$ClF$_3$O: C, 11.84; Br, 52.52; Cl, 11.65; F, 18.73. Found: C, 12.09; Br, 52.32; Cl, 11.55; F, 18.99.

1,2-Dibromo-1,2,2-trifluoroethyl Isocyanate (6) and 2-Bromo-1-chloro-1,2,2-trifluoroethyl Isocyanate (5).—A 27.4-g sample (0.09 mol) of 2,3-dibromo-2,3,3-trifluoropropionyl chloride was added dropwise to a stirred suspension of 6.5 g (0.1 mol) of powdered sodium azide in 100 ml of xylene. The reaction mixture was stirred for several hours at 25°, and then heated gently to reflux until nitrogen evolution ceased. The most volatile portion was distilled out of the reaction mixture and then redistilled to give 2.5 g (12%) of 2-bromo-1-chloro-1,2,2-trifluoroethyl isocyanate as a colorless liquid, bp 89–91°, ir (liquid) 4.43 μ (NCO), ^{19}F nmr (CCl$_3$F) δ −63.8 (d, J = 10 Hz, 2 F) and −75.7 ppm (broad t, J = 10 Hz, 1 F), and 6.7 g (26%) of 1,2-dibromo-1,2,2-trifluoroethyl isocyanate as a colorless liquid, bp 107–110°, ir (liquid) 4.43 μ (NCO), ^{19}F nmr (CCl$_3$F) δ −61.3 (d to d, 2 F) and −71.7 ppm (broad t, 1 F).

Anal. Calcd for C$_3$BrClF$_3$NO: C, 15.11; Br, 33.52; Cl, 14.88; F, 23.91; N, 5.87. Found: C, 15.50; Br, 33.60; Cl, 15.01; F, 24.14; N, 5.99.

Anal. Calcd for C$_3$Br$_2$F$_3$NO: C, 12.74; Br, 56.50; F, 20.15; N, 4.96. Found: C, 13.10; Br, 57.00; F, 20.17; N, 5.30.

2-Bromo-1,1,2,2-tetrafluoroethyl Isocyanate (3).—A 25-g sample (0.087 mol) of 2,3-dibromo-2,3,3-trifluoropropionyl fluoride was added dropwise to a stirred suspension of 6.5 g (0.1 *mol) of powdered sodium azide in 100 ml of xylene.* The mixture was stirred for several hours at about 25°, and then heated gently to about 110° until no further evolution of nitrogen occurred. The most volatile portion was distilled out of the reaction mixture and then redistilled to give 8.35 g (43%) of 2-bromo-1,1,2,2-tetrafluoroethyl isocyanate as a colorless liquid: bp 50°; ir (liquid) 4.40 μ (NCO); ^{19}F nmr (CCl$_3$F) δ −68.0 (t, J = 5 Hz, 2 F) and −79.3 ppm (broad t, J = 5 Hz, 2 F).

Anal. Calcd for C$_3$BrF$_4$NO: C, 16.23; Br, 36.01; F, 34.24; N, 6.13. Found: C, 16.37; Br, 35.61; F, 34.79; N, 6.39.

Trifluorovinyl Isocyanate (7). Method A.—A 35.2-g sample (0.18 mol) of 1,2-dichloro-1,2,2-trifluoroethyl isocyanate was added dropwise to a stirred suspension of 23.5 g of activated zinc dust in 100 ml of diglyme heated to 60°. The temperature was maintained at 60–70°, and stirring was continued at this temperature for 1 hr after the addition was completed. The volatile products (7.8 ml) were distilled from the reaction mixture and then redistilled to give 4 ml (at −78°, about 7 g, 32%) of trifluorovinyl isocyanate, bp 19–20°, and 1.7 g of 2-chloro-1,1,2,2-tetrafluoroethyl isocyanate, bp 31°. The trifluorovinyl isocyanate was identified by its ^{19}F nmr spectrum in CCl$_3$F: δ −112.6 (d, J = 85 Hz to d, J = 50 Hz, 1 F), −123.0 ppm (d, J = 121 Hz to d, J = 85 Hz, 1 F), and −145.4 ppm (d, J = 121 Hz to d, J = 50 Hz, 1 F).

Method B.—A solution of 5.66 g (0.02 mol) of 1,2-dibromo-1,2,2-trifluoroethyl isocyanate in 10 ml of diglyme was added dropwise to a stirred suspension of 2.6 g (0.04 mol) of zinc dust and 0.1 g of zinc chloride in 25 ml of diglyme. The reaction mixture became warm. The most volatile portion was distilled out under reduced pressure (5 mm) into a Dry Ice cooled trap, and the condensate in the trap was redistilled to give 1.2 ml (2.0 g, 81%) of trifluorovinyl isocyanate, bp 19–20° (identified by ^{19}F nmr).

Method C.—A solution of 19.0 g (0.085 mol) of 2-bromo-1,1,2,2-tetrafluoroethyl isocyanate in 20 ml of diglyme was added dropwise to a suspension of 13 g (0.2 mol) of zinc dust and 0.1 g of zinc chloride in 100 ml of diglyme heated to 80°. The reaction temperature was maintained at 80–90° during the addition, and then the most volatile portion was distilled from the reaction mixture and redistilled to give 2.1 ml (*ca.* 3.6 g, 29%) of a colorless liquid, bp 18–21°. The ^{19}F nmr spectrum indicated that the product was 90% trifluorovinyl isocyanate.

Spontaneous Polymerization of Trifluorovinyl Isocyanate.—A sample of trifluorovinyl isocyanate sealed in a glass tube was allowed to remain at room temperature (*ca.* 25°) for 17 days. The tube was broken open, and the polymer was removed as a clear, colorless, flexible rod, mp >250°, ir (film) 4.40 μ (NCO).

Anal. Calcd for (C$_3$F$_3$NO)$_n$: C, 29.29; F, 46.33; N, 11.38. Found: C, 29.07; F, 45.55; N, 10.75.

The polymerization can be inhibited and the monomer can be stored at room temperature if small amounts of conventional radical inhibitors such as D-limonene or 2-(trifluoromethyl)-phenothiazine are added to the liquid monomer.

Curtius Reaction with Tetraethylammonium Azide.—A 83.65-g sample (0.29 mol) of 2,3-dibromo-2,3,3-trifluoropropionyl fluoride was added dropwise to a stirred mixture of 51.7 g (0.3 mol) of tetraethylammonium azide in 300 ml of diglyme. The mixture was then heated slowly to 110° until nitrogen evolution ceased. The more volatile products were distilled from the reaction mixture and condensed in a cold trap to give 15 ml of a colorless liquid, bp −15 to 30°. Redistillation through a low-temperature still gave 9.1 g (20%) of pentafluoroethyl isocyanate, bp −10 to −5° [identified by its ^{19}F nmr spectrum (CCl_3F) δ −85.3 (broad singlet, 2 F) and −87.4 ppm (s, 3 F), and by comparison of its ir spectrum with that of an authentic sample] and 6.1 g (13%) of $CF_3CF{=}NCOF$ as a colorless liquid: bp 28–29°; ir (gas) 5.31 (COF) and 5.42 μ (C=N); ^{19}F nmr (CCl_3F) δ 20.2 (d, J = 20 Hz to q, J = 8 Hz, 1 F), −78.7 (d, J = 9 Hz to d, J = 8 Hz, 3 F), and −136.5 ppm (d, J = 20 Hz to q, J = 9 Hz, 1 F).

Anal. Calcd for C_3F_5NO: C, 22.37; F, 59.00; N, 9.69. Found: C, 22.67; F, 58.73; N, 8.71.

1,2-Dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl Isocyanate (17).—A mixture of 465 g (2.5 mol) of chloropentafluoroacetone imine, 381 g (2.5 mol) of oxalyl chloride, and 2.5 ml of pyridine was refluxed for 3 days. Distillation gave 205 g of a mixture of unreacted starting materials and **17**, bp 60–81°, and 315 g (52% conversion) of **17** as a colorless liquid: bp 85–85.5°; $n^{25}\text{D}$ 1.3580; ir (liquid) 4.42 μ (NCO); ^{19}F nmr (CCl_3F) δ −62.9 (q, J = 24 Hz, 2 F) and −75.7 ppm (t, J = 24 Hz, 3 F).

Anal. Calcd for $C_4Cl_2F_5NO$: C, 19.69; Cl, 29.07; F, 38.94; N, 5.74. Found: C, 19.39; Cl, 28.81; F, 38.76; N, 5.67.

1,2-Dichloro-2,2-difluoro-1-(trifluoromethyl)ethylamine (20).—An 18.2-g sample of chloropentafluoroacetone imine was saturated with dry hydrogen chloride gas and then distilled to give 15.73 g of 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethylamine as a colorless liquid that becomes cloudy on exposure to moist air: bp 65–65.5°; ^{19}F nmr (CCl_3F) δ −62.0 (q, J = 11 Hz, 2 F) and −75.5 ppm (t, J = 11 Hz, 3 F); ir (liquid) 2.90 and 2.96 μ (NH_2).

Anal. Calcd for $C_3H_2Cl_2F_5N$: C, 16.53; H, 0.92; Cl, 32.53; F, 43.58; N, 6.42. Found: C, 17.64; H, 0.79; Cl, 32.03; F, 46.68; N, 6.25.

1-Chloro-2,2,2-trifluoro-1-(trifluoromethyl)ethyl Isocyanate.—A mixture of 127 g (1 mol) of oxalyl chloride, 165 g (1 mol) of hexafluoroacetone imine, and 5 ml of pyridine was heated in a 600-ml Hastelloy bomb at 100° for 4 hr at 150° for 4 hr, and at 200° for 4 hr. The bomb was cooled and vented, and the contents were filtered to remove the suspended solid. Distillation gave 102.3 g of a 25:75 mixture (by gc and ^{19}F nmr) of $(CF_3)_2CClNH_2$ and the isocyanate, bp 46.0–46.5°, and 29.3 g of the pure isocyanate as a colorless liquid: bp 50.5–51.0°; ^{19}F nmr (CCl_3F) δ −78.0 (s); ir (liquid) 4.40 μ (NCO).

Anal. Calcd for C_4ClF_6NO: C, 21.12; Cl, 15.58; F, 50.11; N, 6.16. Found: C, 21.11; Cl, 16.01; F, 49.52; N, 6.16.

2-Chloro-1,1,1,3,3,3-hexafluoro-2-propylamine (22).—A 25-ml sample of hexafluoroacetone imine was cooled to 0° and saturated with dry hydrogen chloride gas. The reaction mixture was filtered to remove some white solid, and the filtrate was distilled to give 37.1 g (74%) of **22** as a colorless liquid: bp 51.5–52.5°; $n^{25}\text{D}$ 1.3166; ^{19}F nmr (neat) δ −77.5 ppm (s); ^{1}H nmr (neat) δ 2.82 ppm.

Anal. Calcd for $C_3H_2ClF_6N$: C, 17.88; H, 1.00; F, 56.57; N, 6.95. Found: C, 18.09; H, 1.13; F, 56.59; N, 7.14.

1,2-Dichloro-2,2-difluoro-1-(chlorodifluoromethyl)ethyl Isocyanate.—A mixture of 39.6 g (0.2 mol) of 1,3-dichlorotetrafluoroacetone imine and 31.8 g (0.25 mol) of oxalyl chloride was refluxed for 5 days. Distillation of the reaction mixture gave 33.5 g (64%) of the isocyanate as a colorless liquid: bp 121.5–122°; $n^{25}\text{D}$ 1.3953; ir (liquid) 4.39 μ (NCO); ^{19}F nmr (CCl_3F) δ −60.9 ppm (s).

Anal. Calcd for $C_4Cl_3F_4NO$: C, 18.45; Cl, 40.85; F, 29.18; N, 5.38. Found: C, 18.50; Cl, 40.61; F, 29.22; N, 5.69.

2,2-Difluoro-1-(trifluoromethyl)vinyl Isocyanate (18).—A 244-g sample (1.0 mol) of 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate was added dropwise to a stirred suspension of 98 g (1.5 g-atoms) of powdered zinc in 1000 ml of diglyme at such a rate that the temperature warmed to 45° and remained between 45 and 50°. The reaction mixture was stirred for 1 hr after the addition, and then the most volatile portion was distilled under reduced pressure (5 mm) into a trap cooled to −78°. The condensate in the trap was redistilled to give 158 g (91%) of 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate as a colorless liquid: bp 42.3–42.5°; ir (liquid) 4.38 (NCO) and 5.67 μ (=CF_2); ^{19}F nmr (CCl_3F) δ −66.6 (d, J = 9 Hz to d, J = 23 Hz, 3 F), −82.9 (d, J = 21 Hz to q, J − 9 Hz, 1 F), and −89.7 ppm (d, J = 21 Hz to d, J = 23 Hz, 1 F).

Anal. Calcd for C_4F_5NO: C, 27.76; F, 54.90; N, 8.10. Found: C, 27.70; F, 54.46; N, 7.74.

Perfluorocyclobutyl Isocyanate (15).—Perfluorocyclobutanecarbonyl fluoride, 22.6 g (0.1 mol), was added dropwise to a stirred suspension of 7.2 g (0.11 mol) of powdered sodium azide in 100 ml of xylene. The reaction mixture was stirred overnight and then heated to 80–85° until evolution of nitrogen ceased. The volatile portion of the reaction mixture was distilled out under reduced pressure into a cold trap (−78°), and then redistilled to give 10.05 g (45%) of perfluorocyclobutyl isocyanate as a colorless liquid: bp 53°; ir (CCl_4) 4.41 μ (NCO); ^{19}F nmr (CCl_3F) δ −152.8 ppm (m, 1 F) and six other F.

Anal. Calcd for C_5F_7NO: C, 26.92; F, 59.62; N, 6.28. Found: C, 26.74; F, 59.67; N, 6.26.

1,2-Dibromo-2,2-difluoro-1-(trifluoromethyl)ethyl Isocyanate.—A 8.65-g sample (0.05 mol) of 2,2-difluoro-1-(trifluoromethyl)-vinyl isocyanate was mixed with 8.0 g (0.05 mol) of bromine. When the bromine color faded, the sample was distilled to give 13.79 g (83%) of the dibromide as a colorless liquid: bp 45° (39 mm); $n^{25}\text{D}$ 1.4056; ir (liquid) 4.40 μ (NCO); ^{19}F nmr (CCl_3F) δ 55.0 (ABX_3, J_{AB} = 165, J_{AX} = 11.6, J_{BX} = 12.6, $\Delta\mu_{AB}$ = 77 Hz) and −72.9 ppm (ABX_3).

Anal. Calcd for $C_4Br_2F_5NO$: C, 14.43; Br, 48.01; F, 28.54; N, 4.21. Found: C, 14.66; Br, 48.15; F, 29.21; N, 4.20.

2,2,3,3,4,4-Hexafluoro-1-(trifluoromethyl)cyclobutyl Isocyanate (21).—A mixture of 34.6 g (0.2 mol) of 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate, 20 g (0.2 mol) of tetrafluoroethylene, and 0.5 g of hydroquinone was heated at autogenous pressure at 180° for 8 hr in a 80-ml Hastelloy tube. The tube was cooled and vented, and the contents were distilled to give 28.1 g (81%) of recovered vinyl isocyanate, bp 43–43.5°, and 3.05 g (6% conversion, 30% yield) of **21** as a colorless liquid: bp 67–68°; ir (liquid) 4.37 μ (NCO); ^{19}F nmr (CCl_3F) δ −71.8 (m, 3 F), −125.4 (m, 4 F), and −131.0 ppm (m, 2 F).

Anal. Calcd for C_6F_9NO: C, 26.4; F, 62.7; N, 5.13. Found: C, 25.8; H, 0.48; F, 62.7; N, 5.33.

2,2,3,3,4,4-Hexafluoro-1-(trifluoromethyl)cyclobutylamine.—A 4.6-g sample (0.017 mol) of 2,2,3,3,4,4-hexafluoro-1-(trifluoromethyl)cyclobutyl isocyanate was added to a solution of 1.5 ml (0.017 mol) of concentrated hydrochloric acid in 25 ml of diglyme. To this solution was added 1.5 ml of a 30% sodium hydroxide solution, and the most volatile portion was distilled from the reaction mixture. The lower layer of this distillate was separated and redistilled to give 2.55 g (61%) of 2,2,3,3,4,4-hexafluoro-1-(trifluoromethyl)cyclobutylamine as a colorless liquid: bp 74–75°; $n^{25}\text{D}$ <1.3; ir (liquid) 2.90, 2.96, and 6.13 μ (NH_2); ^{1}H nmr (CCl_3F) δ 2.0 ppm (broad peak); ^{19}F nmr (CCl_3F) δ −72.8 (m, 3 F), −129.1 (m, 4 F), 131.4 (AB, J = 230 Hz), and −133.1 ppm (AB, J = 230 Hz to q, J = 4 Hz, 1 F).

Anal. Calcd for $C_5H_2F_9N$: C, 24.30; H, 0.82; F, 69.21; N, 5.67. Found: C, 24.70; H, 1.21; F, 68.81; N, 5.37.

Methyl 2,2-Difluoro-1-(trifluoromethyl)vinylcarbamate.—A 2.05-ml sample (0.05 mol) of methanol was added dropwise to a stirred solution of 8.7 g (0.05 mol) of 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate in 22 ml of ether. The reaction mixture was distilled to give 8.2 g of methyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate as a colorless liquid: bp 67–68° (13.2 mm); $n^{25}\text{D}$ 1.3554; ir (liquid) 3.02 (NH), 5.65 ($C{=}CF_2$), 5.77 (C=O), and 6.55 μ (amide II); ^{19}F nmr (CCl_3F) δ −66.1 (d, J = 22 Hz to d, J = 9.5 Hz, 3 F), −78.8 (m, 1 F), and −82.3 ppm (m, 1 F); ^{1}H nmr (CCl_3F) δ 7.25 (NH) and 3.76 ppm (s, OCH_3).

Anal. Calcd for $C_5H_4F_5NO_2$: C, 29.43; H, 1.97; F, 46.32; N, 6.83. Found: C, 29.63; H, 2.21; F, 46.30; N, 6.98.

Hydrolysis of 2,2-Difluoro-1-(trifluoromethyl)vinyl Isocyanate.—A mixture of 17.3 g (0.1 mol) of 2,2-difluoro-1-(trifluoromethyl)vinyl isocyanate and 50 ml of water was stirred at 25° for 1.5 hr. The white solid that formed was collected on a filter, washed with water, and recrystallized from 50% ethanol to give 10.1 g of 1,3-bis[2,2-difluoro-1-(trifluoromethyl)vinyl]urea as colorless needles: mp 211–213°; ir (KBr) 3.01 (NH), 5.68 ($C{=}CF_2$), 5.98 (C=O), and 6.30 μ (amide II); ^{19}F nmr (acetone) δ −65.2

(d, J = 22.5 Hz to d, J = 10 Hz, 3 F), −78.6 (m, 1 F), and −82.3 ppm (m, 1 F).

Anal. Calcd for $C_7H_2F_{10}N_2O$: C, 26.26; H, 0.65; F, 59.35; N, 8.75. Found: C, 26.49; H, 0.84; F, 58.82; N, 8.59.

Reaction of 18 with 2*H*-Hexafluoroisopropyl Alcohol.—A solution of 4.33 g (0.025 mol) of **18** in 10 ml of 2*H*-hexafluoroisopropyl alcohol was allowed to remain at room temperature for 5 days. The crystals that precipitated were collected on a filter and dried in air (4.04 g). A second crop was obtained by mixing the filtrate with water (3.22 g). The combined samples were recrystallized from benzene to give 5.3 g of 2,2,2-trifluoro-1-(trifluoromethyl)ethyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate as colorless crystals: mp 78–80°; ^{19}F nmr (CCl_3F) δ −69.1 (d, J = 21 Hz to d, J = 10 Hz, 3 F), −73.7 (d, J = 7 Hz, 6 F), −77.3 (m, 1 F), and −81.0 ppm (m, 1 F); ir (KBr) 5.70 μ (C═O).

Anal. Calcd for $C_7H_2F_{11}NO_2$: C, 24.65; H, 0.59; F, 61.27; N, 4.11. Found: C, 25.02; H, 0.81; F, 60.71; N, 4.60.

1-(*p*-Chlorophenyl)-3-(trifluorovinyl)urea.—A solution of 2.40 g (0.019 mol) of *p*-chloroaniline in 10 ml of ether was added dropwise to a stirred solution of 2.34 g (0.019 mol) of trifluorovinyl isocyanate in 25 ml of ether. The solid that precipitated was collected on a filter and washed with ether. There was obtained 3.77 g (80%) of the urea as colorless plates: mp 170–172° dec; ir (KBr) 3.02 (NH), 5.47 (CF_2═C), and 6.00 μ (C═O); ^{19}F nmr (acetone) δ −106.8 (d, J = 72 Hz to d, J = 44 Hz to m, 1 F), −118.5 (d, J = 72 Hz to d, J = 113 Hz to m, 1 F), and −127.7 ppm (d, J = 113 Hz to d, J = 44 Hz to m, 1 F).

Anal. Calcd for $C_9H_6ClF_3N_2O$: C, 43.13; H, 2.42; Cl, 14.15; F, 22.74; N, 11.18. Found: C, 43.24; H, 1.94; Cl, 14.01; F, 22.75; N, 10.86.

1-(*p*-Chlorophenyl)-3-(1,1,2,2,2-pentafluoroethyl)urea.—A solution of 2.54 g (0.02 mol) of *p*-chloroaniline in 25 ml of ether cooled to −50° was mixed with 3.22 g (0.02 mol) of pentafluoroethyl isocyanate. The reaction mixture was warmed to 25°, and the white solid that precipitated was collected on a filter, washed with cold ether, and dried to give 4.6 g of the urea as white crystals: mp 133–40° dec; ir (KBr) 5.98 μ (C═O); ^{19}F nmr (acetone) δ −79.4 (s, 2 F) and −87.4 ppm (s, 3 F).

Anal. Calcd for $C_9H_6ClF_5N_2O$: Cl, 12.29; F, 32.91; N, 9.71. Found: Cl, 12.83; F, 32.51; N, 9.51.

Methyl 1,2-Dichloro-2,2-difluoro-1-(trifluoromethyl)ethylcarbamate.—Methanol (4.1 ml, 0.1 mol) was added dropwise to a 24.4-g sample (0.1 mol) of 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate cooled in an ice bath. The reaction mixture solidified. Recrystallization from pentane gave 22.0 g (80%) of the carbamate as colorless crystals: mp 46–47°; ^{19}F nmr (CCl_3F) δ −62.0 (m, 2 F) and −72.1 ppm (d, J = 14 Hz to d, J = 12 Hz, 3 F); ir (KBr) 3.92 (NH), 5.64, and 5.73 μ (CO).

Anal. Calcd for $C_5H_4Cl_2F_5NO_2$: C, 21.76; H, 1.46; Cl, 25.69; F, 34.42; N, 5.07. Found: C, 22.17; H, 1.48; Cl, 25.27; F, 34.72; N, 4.79.

1-(*p*-Chlorophenyl)-3-(2-chloro-1,1,2,2-tetrafluoroethyl)urea.—A solution of 2.04 g (0.016 mol) of *p*-chloroaniline in 10 ml of ether was added dropwise to a solution of 2.85 g (0.016 mol) of 2-chloro-1,1,2,2-tetrafluoroethyl isocyanate in 25 ml of ether cooled to 0°. The precipitate that formed was collected on a filter, washed with cold ether, and dried in air to give 3.92 g (80% yield) of the urea as colorless crystals: mp 137–138° dec (gas); ir (KBr) 3.02 (NH), 5.97, 6.40, 6.24, and 6.68 μ; ^{19}F nmr (acetone) δ 71.5 (t, J = 8 Hz, 2 F) and −91.7 ppm (m, 2 F).

Anal. Calcd for $C_9H_6Cl_2F_4N_2O$: C, 35.43; H, 1.98; Cl, 23.24; F, 24.91; N, 9.19. Found: C, 35.56; H, 1.75; Cl, 23.22; F, 24.06; N, 8.97.

Registry No.—**1**, 667-49-2; **2**, 17773-81-8; **3**, 41594-54-1; **4**, 17773-79-4; **5**, 41594-56-3; **6**, 41594-24-5; **7**, 41594-57-4; **7** polymer, 41588-59-4; **8**, 356-74-1; **10**, 41594-59-6; **11**, 422-43-5; **12**, 41594-60-9; **13**, 41594-61-0; **14**, 710-53-2; **15**, 41594-63-2; **16**, 3749-02-8; **17**, 41594-65-4; **18**, 41594-66-5; **20**, 41594-67-6; **21**, 41594-68-7; **22**, 41594-69-8; tetraethylammonium azide, 993-20-4; hexafluoroacetone imine, 1645-75-6; 1-chloro-2,2,2-trifluoro-1-(trifluoromethyl)ethyl isocyanate, 39095-53-9; 1,2-dichloro-2,2-difluoro-1-(chlorodifluoromethyl)ethyl isocyanate, 41594-25-6; 1,3-dichlorotetrafluoroacetone imine, 1619-97-2; 1,2-dibromo-2,2-difluoro-1-(trifluoromethyl)ethyl isocyanate, 41594-27-8; 2,2,3,3,4,4-hexafluoro-1-(trifluoromethyl)cyclobutylamine, 41594-28-9; methyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate, 41594-29-0; 1,3-bis[2,2-difluoro-1-(trifluoromethyl)vinyl]urea, 41594-30-3; 2*H*-hexafluoroisopropyl alcohol, 920-66-1; 2,2,2-trifluoro-1-(trifluoromethyl)ethyl 2,2-difluoro-1-(trifluoromethyl)vinylcarbamate, 41594-32-5; 1-(*p*-chlorophenyl)-3-(trifluorovinyl)urea, 41594-33-6; *p*-chloroaniline, 106-47-8; 1-(*p*-chlorophenyl)-3-(1,1,2,2,2-pentafluoroethyl)urea, 41594-34-7; methyl 1,2-dichloro-2,2-difluoro-1-(trifluoromethyl)ethylcarbamate, 41594-35-8; 1-(*p*-chlorophenyl)-3-(2-chloro-1,1,2,2-tetrafluoroethyl)urea, 41594-36-9.

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syn-8,16-Difluoro[2.2]metacyclophane-1,9-diene[1]

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Normally, syntheses of metacyclophanes lead to the anti conformational isomer. In sharp contrast to this generalization, the condensation of 2,6-bis(bromomethyl)fluorobenzene (**3**) with sodium sulfide gives exclusively the syn isomer of 9,18-difluoro-2,11-dithia[3.3]metacyclophane (**4**) in 37% yield. When **4** is carried through the two-step reaction sequence of a Stevens rearrangement followed by a Hofmann elimination, the corresponding *syn*-8,16-difluoro[2.2]metacyclophane-1,9-diene (**7**) is formed in good yield. Although **7** does not spontaneously undergo valence tautomerization to *cis*-15,16-difluorodihydropyrene (**10**), thermal rearrangement of **7** gives 1-fluoropyrene (**11**), suggesting the intervention of *cis*-15,16-difluorodihydropyrene (**10**) as a transient intermediate.

In previous publications we have indicated the synthetic utility of the two-step reaction sequence—Stevens rearrangement and Hofmann elimination—for transforming sulfide linkages to carbon–carbon double bonds.[2,3] This procedure has been especially useful for preparing derivatives of 15,16-dihydropyrene.[2] One of the striking features of such derivatives is their valence tautomerization, both thermally and photochemically, to the corresponding [2.2]metacyclophane-1,9-diene derivatives ($1 \rightleftharpoons 2$). Thus far this valence tautomerization has only been studied for examples where the substituents at the 15 and 16 positions are hydrogen or alkyl.[2,4,5] However, Schmidt, on the basis of an extended Hückel calculation, has made the theoretical prediction that in this valence tautomerization ($1 \rightleftharpoons 2$) the *trans*-15,16-dihydropyrene moiety **1** will be preferred for other substituents as well, namely fluoro.[6]

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