

tained by oxidation of the phenylacetic acid product had a specific radioactivity of 0.0036 mc./mole.

The above 2-phenylacrylic-2-C¹⁴ acid (0.82 g., 0.472 mc./mole) was fused with potassium hydroxide (3.1 g.) in the same fashion. The purified phenylacetic acid product, m.p. 76.5–77°, had a specific radioactivity of 0.482 mc./mole. The benzoic acid obtained on its oxidation had a specific radioactivity of 0.478 mc./mole. The S-1-naphthylmethylthiuronium formate derivative obtained in this experiment had a specific radioactivity of 0.069 mc./mole.

Gaseous Products from the Alkali Fusion of 2-Phenylacrylic Acid.—2-Phenylacrylic acid (254.7 mg., 1.73 mmoles) and powdered potassium hydroxide (1.100 g., 19.6 mmoles) were mixed thoroughly in a small flask and attached into a volume-calibrated vacuum line. Fusion of the mixture was accomplished by gentle flaming as described above, resulting in the evolution of 2.54 mmoles of gas. Mass spectrometric analysis of a sample of this gas indicated the composition: hydrogen, 98%; carbon dioxide < 1%; water < 1%; ethanol < 0.5%. The volume of hydrogen liberated during the above fusion was 147% of the quantity required by eq. 8.

The Alkali Fusion of Paraformaldehyde.—Paraformaldehyde (63.6 mg., 2.13 mmoles) and powdered potassium hydroxide (1.00 g., 17.9 mmoles) were mixed in a small flask, attached into the vacuum line and subjected to fusion as described above; 1.47 mmoles of gas was liberated. Mass spectrometric analysis of the gas sample showed the composition: hydrogen, 75%; methanol, 20%; acetone, 3%; water, trace; unidentified peaks at mass 72, 73, < 1%; formaldehyde, nil. The volume of hydrogen liberated in this experiment corresponded to approximately 52% of that required by eq. 5. A blank fusion of potassium hydroxide (1 g.) alone led to only a negligible evolution (7×10^{-4} mmole) of gas.

In another experiment paraformaldehyde (0.25 g.) and powdered potassium hydroxide (3.80 g.) were fused as before. The cooled melt was dissolved in water and the solution was acidified and extracted continuously with ether for 24 hours. The ether extract was extracted repeatedly with water, titrating each water layer with standard alkali to the phenolphthalein end-point. After 6 extractions, removal of formic acid (0.148 g. by titration) appeared approximately complete and the neutral aqueous extracts were evaporated *in vacuo* to dryness. The residue was treated with S-1-naphthylmethylthiuronium chloride as before, affording 0.62 g. (74% based on formic acid titer, 28% based on paraformaldehyde) of S-1-naphthylmethylthiuronium formate, m.p. 183.2° dec., mixed m.p. with an authentic sample undepressed.

The Alkali Fusion of Sodium Formate.—To demonstrate that the anomalously high hydrogen evolution during the alkali fusion of 2-phenylacrylic acid arose from the formic acid produced in its cleavage, the following experiment was undertaken. Sodium formate (142.6 mg., 2.10 mmoles) and potassium hydroxide (1.5 g.) were mixed in a small flask and attached into the vacuum line as usual. During the fusion there was liberated 1.82 mmoles of hydrogen (87% of the theoretical volume required by eq. 9). When phenylacetic acid (1 g.) and potassium hydroxide (3.5 g.) were fused in the vacuum line, the final pressure of the system was 26 mm., the vapor pressure of the water of neutralization at the temperature of the experiment. No discernible hydrogen evolution was noted.

The Alkali Fusion of Cinnamic Acid.—When cinnamic acid (1.85 mmoles) and potassium hydroxide (18 mmoles) were fused as before, considerable charring was noted and no clean melt was obtained as with 2-phenylacrylic acid. The volume of gas liberated corresponded to 2.29 mmoles. It had the following mass spectrometrically determined composition: hydrogen, 94%; methane, 1.6%; carbon dioxide, 2%; benzene, < 1%; toluene, 0.5%; water, 0.5%.

In a larger scale fusion of cinnamic acid (1.25 g.) with potassium hydroxide (5 g.) an attempt was made to isolate any benzyl alcohol formed by the Cannizzaro reaction. The cooled fusion mixture was dissolved in water and the alkaline solution was extracted thoroughly with ether. Evaporation of the extract yielded only a negligible amount (0.04 g.) of yellow solid and no benzyl alcohol. The alkaline layer was acidified and extracted twice with ether. The extract was dried, decolorized and freed of solvent to yield 1.0 g. (97%) of crude benzoic acid, m.p. 90–95°. This was purified by vacuum sublimation, m.p. 119–120°, mixed m.p. with an authentic sample 120–121.5°. Continuous extraction of the acidified aqueous layer for 24 hours with ether gave an extract, evaporation of which afforded a small liquid residue. This was titrated with alcoholic potassium hydroxide and found to contain approximately 0.31 g. (60%) of acetic acid. The latter was converted to its S-1-naphthylmethylthiuronium salt as usual, m.p. 159.6°, mixed m.p. with an authentic sample 160.5°.

The Alkali Fusion of Hydratropaldehyde.—Hydratropaldehyde (1.5 mmoles) and powdered potassium hydroxide (3 g.) were mixed by stirring and fused as usual in the vacuum line. Comparatively strong flaming for a longer period of time was required before gas evolution (1.02 mmoles, 68%) was noted. Mass spectrometric analysis of the liberated gas indicated the composition: hydrogen, 90%; ethylbenzene, 2%; air, 3%; water, 2%; benzene < 0.5%; methane, < 1%.

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The Synthesis and Chemistry of Fluoroazoalkanes

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Fluoroazoalkanes ($R_fN=NR_f$) have been synthesized by reactions of lower valent metal fluorides and chlorine or bromine with cyanogen chloride and with carbonitriles of fluorocarbons and chlorocarbons. The fluoroazoalkanes have been found to serve as a source of fluoroalkyl radicals and to participate in various syntheses. Thus, with carbon monoxide they yield fluoroalkyl isocyanates; in Diels–Alder additions with 1,3-dienes they form substituted 1,2,3,6-tetrahydropyridazines; and defluorination by a metal carbonyl gives bis-(fluoroalkylidene)-azines ($R_fCF=N=N=CFR_f$). Bis-(perfluoropropylidene)-azine with sodium methoxide yields the symmetrical dimethoxy and tetramethoxy derivatives.

The fluoroazoalkanes as a class have been almost neglected except for the synthesis of the first members. Hexafluoroazomethane has been obtained from silver cyanide and fluorine,¹ from cyanogen iodide and iodine pentafluoride,^{2–4} from cyanogen chloride with silver(II) fluoride,⁵ by reaction of

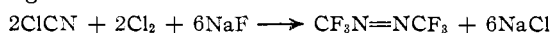
ethylenediamine or ethyleneimine with fluorine,^{6a,b} and by fluorination of hydrogen cyanide with cobalt(III) fluoride.^{7,8} Perfluoroazoethane was prepared in good conversions by the reaction of silver(II) fluoride with trifluoroacetone or pentafluoroethyl isocyanate, and perfluoroazobutane was

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- (2) O. Ruff and W. Willenberg, *ibid.*, **73**, 724 (1940).
- (3) J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).
- (4) G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956).
- (5) O. Glemser, H. Schroeder and H. Haeseler, *Z. anorg. allgem. Chem.*, **282**, 80 (1955).

- (6) (a) J. A. Gervasi, M. Brown and L. A. Bigelow, *J. Am. Chem. Soc.*, **78**, 1679 (1956); (b) F. P. Avondia, J. A. Gervasi and L. A. Bigelow, *ibid.*, **78**, 2798 (1956).
- (7) G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, 2762 (1951).
- (8) J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

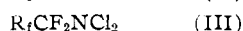
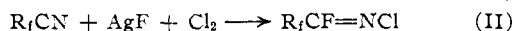
obtained similarly from perfluorobutyronitrile.⁹ The syntheses of perfluoroazoethane and perfluoroazopropane in low yields also have been reported recently by reaction of fluorine with trifluoroacetonitrile and with pentafluoropropionitrile, respectively.¹⁰ These routes used either elemental fluorine or a higher valent metal fluoride prepared by means of fluorine. This paper describes a new synthesis of fluoroazoalkanes that does not require the use of elemental fluorine nor a higher valent metal fluoride prepared by use of elemental fluorine and outlines the chemistry of this class of compounds.

Synthesis of Fluoroazoalkanes.—The new synthesis of fluoroazoalkanes involves reaction of a carbonitrile with a lower valent metal fluoride admixed with chlorine or bromine. It is best illustrated by the preparation of hexafluoroazomethane from cyanogen chloride, chlorine and sodium fluoride. These reactants in 1:1:3.5 mole ratio at 225° under autogenous pressure have given crude hexafluoroazomethane in 31% conversion based on cyanogen chloride.



The proportions of reactants used were important, and excess cyanogen chloride lowered the conversion drastically. The crude hexafluoroazomethane was freed of excess chlorine by separation of the immiscible chlorine layer at -70 to -80° followed by storage over sulfur. The sulfur chlorides formed were separated by distillation.

This synthesis using chlorine or bromine with the more reactive silver(I) fluoride instead of with sodium fluoride has been found applicable to the carbonitriles of fluorocarbons and chlorocarbons. The figures in parentheses note the conversions to fluoroazoalkanes obtained with the nitriles R_tCN in which R_t equals CF_3 (60%), C_2F_5 (22%), C_3F_7 (84%), C_8F_{17} (65%), $\text{H}(\text{CF}_2)_3$ (43%), $\text{H}(\text{CF}_2)_6$ (58%) and also Cl_3C (65%). In contrast to the behavior of cyanogen chloride, trichloroacetonitrile retained the carbon-chlorine bonds. Other products frequently formed included the N-chloro (or N-bromo)-fluoro-alkylidenimines (II) and N,N-dichlorofluoroalkylamines (III). Cyanogen chloride did not yield a compound corresponding to II ($\text{R}_t = \text{F}$) in any of the fluorinations.



As an illustration of these competitive reactions, the N-chlorofluoroalkylidenimines (II) were the major products formed in low conversions in fluorinations with lead(II) fluoride and chlorine. Silver(I) fluoride and chlorine at 125° converted 5H-octafluoropentanenitrile to mixtures of 5H-5'H-eicosafluoroazopentane and N-chloro-5H-nonafluoropentylidenimine in 37% and 23% conversions, respectively. Similarly, perfluorobutyronitrile with silver(I) fluoride and bromine gave N-bromo-octafluorobutylidenimine and perfluoroazobutane, each in 25% conversion. Also, reaction products from

cyanogen chloride, silver(I) fluoride and chlorine were found to give nuclear magnetic resonance signals and mass spectrographic analyses indicative of the presence of the dichloroamine III ($\text{R}_t = \text{F}$) which, however, was not isolated in a pure state.

In general, the preferred temperature for fluorination of carbonitriles by silver(I) fluoride with chlorine or bromine ranged from 50–125°, although several successful preparations were carried out at 190°. Above 250°, cleavage of the fluoroazoalkanes occurred to form chloro- or bromofluoroalkanes. With molar ratios of silver(I) fluoride to halogen greater than four, the fluoroazoalkane was usually the sole product. With ratios of two or less, N-chloro- or N-bromofluoroalkylidenimines (II) were usually formed in 5–25% conversions along with fluoroazoalkanes as the major product. The N,N-dichlorofluoroalkylamines (III) were usually absent from or present in only small amounts in products prepared at temperatures above 100°, which suggests that the N,N-dichloroamines are less stable thermally than the fluoroazoalkanes or the N-chlorofluoroalkylidenimines. An exception was the preparation of N,N-dichlorotrifluoromethylamine at 140°.

The fluoroazoalkanes are yellow-colored liquids or gases that resist hydrolysis by hot aqueous 10% sodium hydroxide. In contrast, the by-product N-chloro- or N-bromofluoroalkylidenimines are nearly colorless liquids or gases that hydrolyze rapidly at 25° and quantitatively liberate iodine from aqueous potassium iodide. The N,N-dichlorofluoroalkylamines also are rapidly destroyed by aqueous alkali at 25° and quantitatively liberate iodine from potassium iodide.

Chemistry of Fluoroazoalkanes. Fluoroalkyl Radicals from Fluoroazoalkanes.—Hexafluoroazomethane has been reported to form hexafluoroethane, tetrakis-(trifluoromethyl)-hydrazine and hexakis-(trifluoromethyl)-tetrazine when heated at 300° or when irradiated at ordinary temperatures.²⁻⁴ This indication that fluoroazoalkanes can serve as a source of fluoroalkyl radicals and participate in other free radical reactions has been confirmed.

When heated at 325° for 8 hr. under autogenous pressure, hexafluoroazomethane gave crude tetrakis-(trifluoromethyl)-hydrazine in 49% conversion and 66% yield. At 483° for 6 hr. 30% conversion to the tetrasubstituted hydrazine occurred, and perfluoro-2-azapropene comprised about 30% of the product. When hexafluoroazomethane and carbon monoxide were passed through a nickel tube at 465°, hexafluoroethane was formed in 91% conversion.

Trifluoromethyl radicals generated from the azoalkane are useful in inducing vinyl polymerization. When hexafluoroazomethane in admixture with tetrafluoroethylene was irradiated by ultraviolet light at 0–30°, polytetrafluoroethylene was formed in 93% conversion. The trifluoromethyl radicals generated in a similar way were found to induce the copolymerization of hexafluoropropylene with tetrafluoroethylene and with vinylidene fluoride and to bring about the homopolymerization of acrylonitrile and of vinyl acetate. Trifluoromethyl radicals generated thermally at 180° induced the polymeri-

(9) J. A. Young, R. D. Dresdner, *ASTIA*, 228,621. "Fluorocarbon N-F Compounds," 1959.

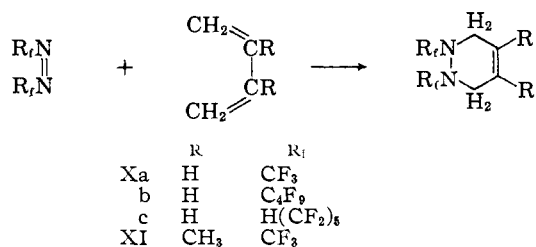
(10) J. A. Attaway, R. H. Groth and L. A. Bigelow, *J. Am. Chem. Soc.*, **81**, 3599 (1959).

zation of ethylene at 1080 atm. to give high molecular weight polyethylene.

Certain elements also reacted with hexafluoroazomethane as though trifluoromethyl radicals were intermediates. Thus, elemental fluorine gave mainly CF_4 , bromine gave CF_3Br , and refluxing sulfur gave $\text{CF}_3(\text{S})_3\text{CF}_3$ and other polysulfides.

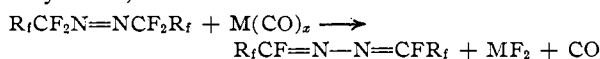
Fluoroalkyl Isocyanates.—A new synthesis of fluoroalkyl isocyanates by reaction of carbon monoxide with fluoroazoalkanes suggests that the nitrene $\text{R}_f\text{N}:$ may have been an intermediate. Thus, trifluoromethyl isocyanate was obtained in 88% conversion in 5 hr. by reaction of hexafluoroazomethane with carbon monoxide at 325° under 650 atm. Higher homologs of hexafluoroazomethane also reacted with carbon monoxide to give the corresponding fluoroalkyl isocyanates but in much lower conversions. For example, perfluoroazopropane gave perfluoropropyl isocyanate in 11% conversion along with 20% conversion to perfluorohexane, and perfluoroazobutane and 3H-3'H-hexafluoroazopropane gave perfluorobutyl isocyanate and 3H-hexafluoropropyl isocyanate, respectively.

Diels-Alder Adducts from Fluoroazoalkanes.—Azodiformic esters and 4,4'-dinitroazobenzene are reported to form Diels-Alder adducts with selected 1,3-dienes.¹¹ The fluoroazoalkanes have now been found to undergo similar type additions with 1,3-dienes at relatively low temperatures to form fluoroalkyl-substituted 1,2,3,6-tetrahydropyridazines. Thus, hexafluoroazomethane, perfluoroazobutane and 5H-5'H-eicosafluoroazopentane reacted with 1,3-butadiene to give the corresponding colorless distillable liquid 1,2,3,6-tetrahydro-1,2-bis-(fluoroalkyl)-pyridazines (Xa, b, c), and 2,3-dimethylbutadiene with hexafluoroazomethane gave the 4,5-dimethyl-substituted pyridazine XI in 45% conversion.



The pyridazines reacted rapidly with bromine to form dibromo derivatives. For example 1,2-bis-(trifluoromethyl)-4,5-dimethyl-1,2,3,6-tetrahydropyridazine gave the corresponding dibromo derivative when treated with bromine in carbon tetrachloride at room temperature.

Synthesis of Bis-(fluoroalkylidene)-azines.—Defluorination of fluoroazoalkanes by reaction with metal carbonyls has given the novel bis-(perfluoroalkylidene)-azines.



Thus, perfluoroazopropane with nickel carbonyl at 170° under autogenous pressure gave bis-(fluoro-propylidene)-azine ($\text{R}_f = \text{C}_2\text{F}_5$) in 60% conversion, and 5H-5'H-eicosafluoroazopentane with iron pen-

tacarbonyl at 160° formed bis-(5H-nonafluoropentylidene)-azine ($\text{R}_f = \text{H}(\text{CF}_2)_4$) in 70% conversion. The bis-(fluoroalkylidene)-azine structures were established by elemental analyses, nuclear magnetic resonance analyses and other spectral data. A gaseous product believed to be $\text{CF}_2=\text{N}-\text{N}=\text{CF}_2$, the first member of the bis-(fluoroalkylidene)-azines, was obtained by the defluorination of hexafluoroazomethane in reactions with iron pentacarbonyl. It had a molecular weight (by gas density) of 130 and showed strong infrared absorption at 5.72 μ indicative of a C=N linkage, but it was not characterized further. The bis-(perfluoropropylidene)-azine was found to react with sodium methoxide in ether to form two products that were isolated and identified as the new symmetrical dimethoxy and tetramethoxy derivatives.

Experimental

Syntheses of the fluoroazoalkanes were carried out under autogenous pressure with gentle rocking in Hastelloy C lined pressure reactors free of air. Unless otherwise indicated, the vessel was of 500-ml. capacity. The gaseous products were collected by transfer to a liquid nitrogen-cooled, evacuated stainless steel cylinder and were distilled through a low-temperature column. The infrared measurements, reported as mole %, were made on a Perkin-Elmer model 21 double beam spectrophotometer. The mass spectra were obtained using Consolidated Electrodynamic Corporation mass spectrometer model 21-103-C.

Nuclear magnetic resonance spectra of the various products were measured with a Varian high resolution nuclear magnetic resonance spectrometer and an associated electromagnet. Fluorine magnetic resonance spectra were obtained at 56.4 Mc. in a field of approximately 14,081 gauss. A capillary of 1,2-difluorotetrachloroethane was placed in each sample, and the spectra were calibrated in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of 1,2-difluorotetrachloroethane. Except as noted, all peaks were to the high field side.

The analytical vapor phase chromatography experiments were carried out using a 2 meter by 3/16" copper column packed with 20% Kel-F acid (8114) ethyl ester on Chromosorb at temperatures approximating the boiling point of the main component.

A. Synthesis of Fluoroazoalkanes. Hexafluoroazomethane.—Cyanogen chloride (60 g.), sodium fluoride (200 g.) and chlorine (60 g.) were heated with shaking for 2 hr. at 80° and for 5 hr. at 225° in a 1-l. Hastelloy C pressure vessel. (The vessel had been preconditioned by heating with sodium fluoride (20 g.) and chlorine (20 g.) at 225° for several hours.) Six such preparations gave 459.8 g. of volatile material which was condensed in a liquid nitrogen-cooled trap and 1471 g. of a light-yellow solid which evolved chlorine. The volatile products collected in the liquid nitrogen-cooled trap were separated into two layers in a separatory funnel cooled to -70 to -80°. Chlorine which formed the bottom layer was drawn off and discarded. The upper layer was hexafluoroazomethane¹² which contained some free chlorine. The crude hexafluoroazomethane was stored overnight over 80 g. of sulfur and was then passed over solid sodium hydroxide. There was thus obtained 189.4 g. of crude hexafluoroazomethane. Distillation through a 90-cm. low-temperature still gave 154 g. (31% conversion based on cyanogen chloride) of hexafluoroazomethane (b.p. -32° to -30°) judged by gas chromatography to be 98% pure. When hexafluoroazomethane alone or in admixture with air was exploded by a hot wire or by a spark, the rate of pressure development was extremely high. The high rate suggests that the azomethane should be considered more hazardous than acetylene and should be adequately barricaded when used in pressure systems. The infrared spectrum of the gas showed major absorptions at 7.16, 7.91, 8.32, 8.80 and 9.10 μ . The fluorine magnetic resonance spectrum consisted of a single peak at 675 c.p.s.

In another experiment, cyanogen chloride (20 g.), silver(I) fluoride (203 g.) and chlorine (64 g.) were heated with

(11) K. Alder and H. Niklas, *Ann.*, **555**, 81 (1954); P. Branger, J. Levisaites and M. Vuidart, *Compt. rend.*, **236**, 1365 (1953).

(12) C. W. Tullock, U. S. Patent 2,912,429, November 10, 1959.

shaking for 1 hr. at 75° and for 3 hr. at 140° in a 1-l. pressure vessel. The volatile material (66 g.) was condensed in a liquid nitrogen-cooled trap and distilled through a low-temperature still, giving 2 g. of chlorotrifluoromethane (not trapped by the solid carbon dioxide-acetone-cooled receiver), and 42 g. of product (b.p. -47° to -11°) which was stored over sulfur under autogenous pressure to remove chlorine, leaving 8 g. which infrared analysis showed to contain 40% hexafluoroazomethane, 40% chlorotrifluoromethane and less than 5% each of dichlorodifluoromethane and bis-(trifluoromethyl)-amine. The next fraction (5 g.) distilled at -11° to +6° and the remainder (6 g.) distilled at +6° to +13°. Infrared and mass spectrometric analyses suggested that the latter two fractions were chiefly N,N-dichlorotrifluoromethylamine and that the fraction distilling at +6° to +13° contained the larger amount. Principal impurities, both probably present in less than 5% as judged by infrared analysis, were hexafluoroazomethane and N-chlorobis-(trifluoromethyl)-amine.¹³ Mass spectrographic analysis indicated the major product had parent peaks at 153, 155 and 157 resulting from Cl³⁵ and Cl³⁷ isotopes and the nuclear magnetic resonance spectrum showed the presence of a CF₃ group.

The dichloride slowly underwent disproportionation to hexafluoroazomethane and probably chlorine at 25°. After storage in a stainless steel vessel for about 2 months at 25°, the dichloride was converted almost wholly to hexafluoroazomethane.

Perfluoroazoethane.—Trifluoroacetonitrile (20 g.), silver(I) fluoride (75 g.) and bromine (35 g.) were heated under autogenous pressure at 100° for 1 hr., at 150° for 1 hr. and at 190° for 2 hr. The volatile reaction product (30 g.) was distilled. The fraction boiling at 16–20° (13 g.) was found by mass spectroscopy analysis to contain, on a molar basis, 90% perfluoroazoethane, 3–8% N-bromotetrafluoroethylideneimine and 1% bromopentafluoroethane. Careful redistillation gave essentially pure perfluoroazoethane as a yellow-green liquid boiling at 18–20° (the literature reports b.p. 22°¹⁰). The conversion was 60%.

Anal. Calcd. for C₂F₁₀N₂: F, 71.50. Found: F, 71.27.

The infrared spectrum of the gas showed major absorption at 7.35, 7.45, 8.05, 9.33, 13.25, 14.12 and 14.77 μ. The fluorine magnetic resonance spectrum consisted of a CF₃-resonance at 1059 c.p.s. and a -CF₂- resonance at 2709 c.p.s. The still residue (6 g.) was found by infrared analysis to contain 75 mole % perfluoroazoethane. The N-bromotetrafluoroethylideneimine codistilled with perfluoroazoethane in the 12–19° range. The imine was identified by mass spectrometric analysis which showed the presence of parent peaks at 193 and 195 resulting from Br⁷⁹ and Br⁸¹, and by the infrared absorption spectrum which showed a major band at 5.85 μ corresponding to the C=N bond and at 7.45 and 8.95 μ. The imine is readily removed from the azo compound by washing with 10% aqueous sodium hydroxide solution.

A mixture of 43 g. of CF₃CN, 100 g. of KF (mole ratio KF/CF₃CN 3.8:1) and 19 g. of Cl₂ was heated under autogenous pressure at 100° for 1 hr., 150° for 1 hr. and 200° for 6 hr. Distillation of the volatile reaction product (58 g.) gave first 44 g. boiling between -62 and -10°, which infrared analysis showed to contain 60–65% CF₃CN, about 5% each of CF₃CF=NCl and C₂F₅N=NC₂F₅, and a trace of C₂F₅Cl; then 10 g. distilling between -8.5 and +5°, together with a small amount of higher boiling material which was not examined. The distilled fraction was shown by infrared analysis to contain 50 mole % of CF₃CF=NCl and 50 mole % of C₂F₅N=NC₂F₅. The analyses indicated an 11% conversion to C₂F₅N=NC₂F₅ and a 5% conversion to CF₃CF=NCl had resulted, based on CF₃CN.

A mixture of 35 g. of CF₃CN, 200 g. of PbF₂ and 26 g. of Cl₂ was heated at 100° for 1 hr., 150° for 1 hr. and 200° for 6 hr. under autogenous pressure. The volatile products from two such experiments were combined. Distillation gave, after removal of unreacted CF₃CN and Cl₂, 27 g. of a fraction boiling between +1 to +6° which was shown to be CF₃CF=NCl, and 14 g. of a higher boiling residue which infrared analysis showed to contain 50% of CF₃CF=NCl, 25–30% C₂F₅N=NC₂F₅ and small amounts of an unknown which mass spectrometric analysis suggested may have been

(13) J. A. Young, S. N. Tsoukias and R. D. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958), reports the preparation and properties of this compound.

CF₃CF=NCl. The CF₃CF=NCl was shown by n.m.r. to contain two different fluorines in a 3:1 ratio, and gas chromatography showed that only one product was present. The compound was further characterized by its compositional analysis. The analyses corresponded to a 30% conversion to CF₃CF=NCl and about a 7% conversion C₂F₅N=NC₂F₅ based on CF₃CN. Mass spectrometric analyses showed major peaks at 31, 35, 37, 45, 50, 69, 80, 82, 130, 132, 149 and 151. Infrared analysis showed major peaks in the spectrum at 5.86, 7.34, 8.02, 8.38, 8.82, 8.86, 11.81, 13.12 and 14.13 μ.

Anal. Calcd. for C₂F₄ClN: F, 50.70; Cl, 23.70; active Cl, 23.70. Found: F, 51.80; Cl, 23.32; active Cl, 22.92.

N,N-Dichloroperfluoroethylamine.—Pure N,N-dichloroperfluoroethylamine was prepared by reaction of silver(I) fluoride (100 g.), trifluoroacetonitrile (35 g.), and chlorine (65 g.) in a 500-ml. pressure vessel at 50° for 1 hr. and at 75° for 2 hr. The 97 g. of volatile product was distilled to obtain 9 g. boiling above 25°. A specimen boiling at 44° gave mass spectrometric and nuclear magnetic resonance analyses in accord with the structure N,N-dichloroperfluoroethylamine. Infrared analysis (gaseous) showed major peaks in the spectrum at 7.43, 8.08, 8.35, 8.66, 9.31, 11.85, 12.80 and 13.90 μ. Mass spectrometric analysis showed major peaks at 31, 35, 37, 49, 50, 51, 69, 80, 82, 99, 100, 101, 119, 134, 136, 138, 203, 205 and 207.

Anal. Calcd. for C₂F₄NCl₂: F, 46.57; Cl, 34.80; active Cl, 34.80. Found: F, 47.17; Cl, 33.62; active Cl, 33.25.

Perfluoroazopropane.—Perfluoroazopropionitrile (30 g.), silver(I) fluoride (75 g.) and bromine (40 g.) were heated at 100° for 1 hr., then at 160° for 3 hr. under autogenous pressure. Distillation of the volatile reaction product gave 8 g. (22% conversion) of a yellow-green liquid, b.p. 68–71° (the literature reports b.p. 69°¹⁰), which was shown by nuclear magnetic resonance and elemental analysis to be perfluoroazopropane. Infrared analysis (gaseous) showed major peaks at 7.39, 7.62, 7.94, 8.05, 8.28, 8.59, 8.80, 9.00, 9.12, 10.10, 13.07, 13.28, 13.82 and 14.30 μ. The fluorine magnetic resonance spectrum of this product showed a perfluoropropyl group with resonance at 928 c.p.s. (CF₃-), 2507 and 3582 c.p.s. (two -CF₂- groups).

Anal. Calcd. for C₃F₁₄N₂: C, 19.67; F, 72.68; N, 7.65. Found: C, 19.90; F, 71.93; N, 8.03.

There was also obtained 1 g. of product (b.p. 51–61°) that mass spectrographic analysis indicated to be N-bromohexafluoropropylideneimine.

Perfluoroazobutane.—Perfluorobutyronitrile (30 g.), silver(I) fluoride (49 g.) and bromine (20 g.) were heated at 100° for 1 hr. and at 160° for 2 hr. under autogenous pressure. Distillation of the volatile reaction product gave (A) 8 g. (25% conversion) of N-bromo-octafluorobutylideneimine (b.p. 75–77°) and (B) 9 g. (25% conversion) of perfluoroazobutane. (A) The nuclear magnetic resonance spectrum of N-bromo-octafluorobutylideneimine contained three different fluorine peaks in the ratio of 3:2:2 which is in accord with the C₃F₇ group. In addition there was a CF peak in 1:3 ratio with respect to the CF₃ group. The infrared spectrum showed major absorption at 5.90 μ (corresponding to the C=N bond), and at 7.36, 7.80, 8.03, 8.77, 9.00, 9.32, 10.37, 10.82, 12.75 and 13.40 μ.

Anal. Calcd. for C₄F₈BrN: C, 16.32; F, 51.70; Br, 27.20; N, 4.76. Found: C, 17.18; F, 52.15; Br, 26.62; N, 4.76.

Redistillation of B gave perfluoroazobutane as a yellow-green liquid boiling at 113°. It was identified by nuclear magnetic resonance and elemental analyses. The infrared spectrum of the liquid showed major absorption at 7.35, 8.04, 8.17, 8.65, 8.79, 11.26, 13.22, 13.40 and 13.74 μ. The fluorine magnetic resonance spectrum consisted of a CF₃-resonance at 935 c.p.s. and three -CF₂- resonances at 2460, 3371 and 3441 c.p.s.

Anal. Calcd. for C₃F₁₀N₂: F, 73.40. Found: F, 72.76.

When different proportions of reactants were used, e.g., 50 g. of perfluorobutyronitrile, 98 g. of silver(I) fluoride and 50 g. of bromine, perfluoroazobutane was formed in 84% conversion.

N-Chloro-(octafluorobutylidene)-imine.—A mixture of 25 g. of C₃F₇CN, 65 g. of PbF₂ (mole ratio PbF₂/C₃F₇CN 4:1) and 9 g. of Cl₂ was heated under autogenous pressure at 100° for 1 hr., 150° for 1 hr. and 200° for 2 hr. Distillation of the volatile reaction product (34 g.) gave, after removal of the

unchanged C_4F_7CN and chlorine, 4 g. (9% conversion based on C_4F_7CN) of a colorless liquid boiling at 55° . This was identified as $C_3F_7CF=NCl$ by infrared, nuclear magnetic resonance and compositional analysis. The infrared spectrum (gaseous) showed major peaks at 5.89, 7.34, 7.67, 7.80, 8.02, 8.30, 8.74, 8.96, 9.27, 10.34, 10.74, 12.55, 13.53 and 14.38μ . The fluorine magnetic resonance spectrum showed CF_2^- resonance at 881 c.p.s. and two $-CF_2^-$ resonances at 2880 and 3458 c.p.s. and the $CF=N$ resonance at 1714 c.p.s. on the low field side.

Anal. Calcd. for C_4F_7ClN : C, 19.24; F, 61.00; Cl, 14.23. Found: C, 20.20; F, 60.42; Cl, 13.60.

Perfluoroazooctane.—The perfluoroazooctane, $C_7F_{15}CN$, used comprised a mixture of isomers derived from a commercial sample of perfluoroazooctanoic acid that contained approximately 70% $CF_2(CF_2)_6COOH$, the remainder consisting of the isomeric perfluoro-2,4-dimethylhexanoic, perfluoro-3,5-dimethylhexanoic and perfluoro-3-methylheptanoic acids. The perfluoroazooctane (28 g.), silver(I) fluoride (81 g.) and chlorine (5 g.) were heated under autogenous pressure at 100° for 1 hr., then at 140° for 2 hr. The crude reaction product was removed from the reactor and was distilled at 155° (0.35 mm.) to obtain a volatile liquid (22 g.) which solidified. Redistillation (b.p. $67-75^\circ$ (0.02 mm.)) gave 20 g. (65% conversion) of a yellow-green, low-melting solid shown by analysis to be perfluoroazooctane.

Anal. Calcd. for $C_8F_{15}N_2$: C, 22.17; F, 74.60. Found: C, 22.31; F, 74.50.

3H-3'H-Dodecafluoroazopropane.—2,2,3,3-Tetrafluoropropionitrile¹⁴ (18 g.), silver(I) fluoride (60 g.) and chlorine (11 g.) were heated at 75° for 1 hr. and at 125° for 1 hr. under autogenous pressure. The reaction mixture was removed from the bomb and heated at 150° (0.15 mm.) to recover the volatile product. Distillation of the latter gave fraction I (2 g.) boiling at 58° and fraction II (10 g.) boiling at $106-108^\circ$.

Fraction I was identified by nuclear magnetic resonance as N-chloro-3H-pentafluoropropylideneimine, obtained in 8% conversion.

Anal. Calcd. for C_3HF_5ClN : F, 52.30; Cl, 19.60. Found: F, 52.49; Cl, 18.85.

Fraction II was identified in the same manner as $H(CF_2)_3N=N(CF_2)_3H$, obtained in 43% conversion.

Anal. Calcd. for $C_6H_2F_{12}N_2$: F, 69.09; N, 8.49. Found: F, 68.83; N, 8.73.

The infrared spectrum (liquid) showed major peaks at 3.32, 7.12, 7.33, 7.70, 7.98, 8.25, 8.60, 8.89, 9.56, 9.95, 10.40, 11.25, 12.20, 13.70 and 14.27μ . The fluorine magnetic resonance spectrum showed three resonances: (a) two single peaks at 2507 and 2721 c.p.s. due to the two internal $-CF_2-$ groups and (b) a doublet with components at 4045 and 4094 c.p.s. due to the terminal CF_2H group characteristic of the splitting by hydrogen.

5H-5'H-Eicosafluoroazopentane.—5H-Octafluorovaleronitrile (39 g.), silver(I) fluoride (60 g.) and chlorine (12 g.) were heated under autogenous pressure at 75° for 1 hr. and at 125° for 1 hr. A liquid (17 g.) was decanted from the reaction mixture, and another portion (18 g.) was recovered by heating the solids at 125° (1-2 mm.). Distillation of the combined liquids gave fraction I (11 g.), a colorless liquid boiling at $100-102^\circ$ (760 mm.), and fraction II (17 g.), a yellow liquid boiling at $85-86^\circ$ (28 mm.).

Fraction I was identified by nuclear magnetic resonance and elemental analysis as N-chloro-5H-nonafluoropentylideneimine obtained in 23% conversion.

Anal. Calcd. for C_5HF_9ClN : F, 60.75; Cl, 12.61. Found: F, 60.54; Cl, 12.76.

Fraction II was identified as 5H-5'H-eicosafluoroazopentane formed in 37% conversion.

Anal. Calcd. for $C_{10}H_2F_{20}N_2$: F, 71.70. Found: F, 71.55.

The infrared spectrum (liquid) showed major absorption at 3.32, 7.12, 7.32, 7.56, 7.70, 8.14, 8.40, 8.69, 8.80, 11.02, 11.40, 11.70, 12.49, 12.86, 13.20 and 13.85μ . The fluorine magnetic resonance spectrum showed five resonances: (a) four single peaks at 2426, 3253, 3296 and 3629 c.p.s. due to internal $-CF_2-$ groups and (b) a doublet having components at 4049 and 4102 c.p.s. due to the terminal $-CF_2H$ group.

(14) D. C. England, R. V. Lindsey and L. R. Melby, *J. Am. Chem. Soc.*, **80**, 6442 (1958).

In another experiment, 5H-octafluorovaleronitrile (64 g.), silver fluoride (102 g.) and bromine (61 g.) were heated at $100^\circ/2$ hr. and $160^\circ/1$ hr. under autogenous pressure in a 1-l. Hastelloy C pressure vessel. The liquid was decanted from the reaction mixture, and more liquid was recovered by heating the solid residue at 100° (0.1 mm.). The combined liquids were washed with 4% aqueous sodium hydroxide and distilled. After a small forerun there was obtained 42 g. (58%) of 5H-5'H-eicosafluoroazopentane, b.p. $74-76^\circ$ (14 mm.).

1,1,1',1'-Tetrafluoro-2,2,2',2'-hexachloroazoethane.—A Hastelloy C pressure vessel (1-l. capacity) was conditioned by heating for 4 hr. at 160° while loaded with bromine (20 g.) and silver(I) fluoride (20 g.). This vessel was then used without cleaning. The contents were discharged, and the vessel was reloaded with trichloroacetonitrile (72.2 g.), silver(I) fluoride (190 g.) and bromine (114 g.). The contents were heated with shaking for 2 hr. at 100° and for 1 hr. at 160° . The products from two such runs were combined and shaken with 4% caustic to discharge the bromine. The product was separated, dried, and distilled to obtain three fractions: fraction I, 2 g., b.p. $42-77^\circ$ (6 mm.); fraction II, 118 g., b.p. $77-79^\circ$ (6 mm.), corresponding to a 65% conversion to $CCl_2CF_2N=NCF_2CCl_2$; fraction III, 3 g., b.p. $79-82^\circ$ (6 mm.).

Anal. Calcd. for $C_4N_2Cl_6F_4$: C, 13.16; N, 7.68; Cl, 58.36; F, 20.83. Found: C, 13.68; N, 8.18; Cl, 57.77; F, 20.71. The infrared spectrum (liquid) showed major peaks at 8.29 and 8.9μ (C-F), 11.35, 12.85 (C-Cl), 14.34 and 14.85μ . The fluorine magnetic resonance spectrum showed one resonance due to $-CF_2-$ at 2016 c.p.s. This compound is reported in the literature, but no physical constants are given.¹⁵

B. Chemistry of Fluoroazoalkanes. 1. Fluoroazoalkanes as Free Radical Source. Polymerization of Tetrafluoroethylene.—An evacuated 100-ml. Pyrex tube cooled in liquid nitrogen was charged with 8.4 g. of tetrafluoroethylene and 0.14 g. of hexafluoroazomethane, after which the tube was evacuated to remove the air and was sealed. The tube and its contents were irradiated with the light from a 110 volt, 275 watt RS sun lamp at $0-30^\circ$ for 1.5 hr. There was obtained 7.2 g. of colorless polytetrafluoroethylene which had a molecular weight of approximately 2,000,000, as determined by melt viscosity measurements. End groups were not apparent by inspection of the infrared spectrum. When hexafluoroazomethane was omitted, polymerization did not occur.

Copolymerization of Tetrafluoroethylene with Hexafluoropropylene.—An evacuated 100-ml. Pyrex tube cooled in liquid nitrogen was charged with 8 g. of tetrafluoroethylene, 6 g. of hexafluoropropylene and 0.2 g. of hexafluoroazomethane. The tube was evacuated, sealed, and irradiated with the light of an RS sun lamp for 4 hr. at $20-60^\circ$. There was obtained 5.7 g. of a colorless tetrafluoroethylene-hexafluoropropylene copolymer containing approximately 3 mole % of combined hexafluoropropylene, as indicated by its infrared spectrum. The molecular weight of the copolymer was estimated as 300,000-500,000 by melt viscosity measurements at 380° .

Copolymerization of Hexafluoropropylene with Vinylidene Fluoride.—An 80-ml. stainless steel vessel containing 30 g. of vinylidene fluoride, 30 g. of hexafluoropropylene and 0.5 g. of hexafluoroazomethane was heated for 12 hr. at 170° under autogenous pressure. There was obtained a tough, colorless vinylidene fluoride-hexafluoropropylene copolymer (9.4 g.) that contained 72% by weight of combined vinylidene fluoride. It had an inherent viscosity of 0.73 as measured at 30° on a 0.1% solution in an 87:13 by weight mixture of tetrahydrofuran and dimethylformamide.

Tetrakis-(trifluoromethyl)-hydrazine.—Hexafluoroazomethane (32 g.) was heated¹⁶ under autogenous pressure in an 80-ml. stainless steel vessel for 8 hr. at 325° . Two such preparations gave 51.8 g. of volatile material that was condensed in a liquid nitrogen-cooled trap. Careful fractionation through a 25-cm. low-temperature still gave 14.1 g. of fraction I (a complex mixture, b.p. -30° to $+28^\circ$); 29.9 g. (49% conversion) of fraction II crude tetrakis-(trifluoro-

(15) O. Ruff, *Ber.*, **69A**, 193 (1936).

(16) Care should be taken when heating hexafluoroazomethane above 400° in view of its extremely rapid rate of detonation. Minor explosions were noted when undiluted hexafluoroazomethane was passed through the heated tube at temperatures above 400° .

methyl)-hydrazine, b.p. 28° to 32° (lit.³ b.p. 32°); and 2.6 ml. of fraction III (b.p. 41° to 63°). Gas chromatography showed fraction II to contain several components. By preparative scale gas chromatography, 16.3 g. of pure tetrakis-(trifluoromethyl)-hydrazine was obtained from 18.5 g. of the crude product. For the separation, 2-g. charges were introduced into a 6 ft. \times 0.75" copper tubing packed with 20% of the ethyl ester of Kel-F Acid 8114 on 35/60 mesh Chromosorb at -5°, using a helium flow of 210 ml./min. The infrared spectrum (gas) of the purified tetrakis-(trifluoromethyl)-hydrazine showed major absorptions at 7.46, 7.61, 7.71, 8.26, 8.44, 10.09, 11.25, 13.45 and 13.82 μ . The fluorine magnetic resonance spectrum was a single resonance at 244 c.p.s. on the low field side.

When hexafluoroazomethane (32 g.) was heated cautiously under autogenous pressure in a 145-ml. Hastelloy C vessel for 6 hr. at 483°, the temperature being increased gradually during the initial 4 hr. to avoid violent decomposition of the azomethane, there was recovered 28.2 g. of volatile material by condensation in a liquid nitrogen-cooled trap. The identities of the components and the composition of the crude product as indicated below were determined by gas chromatography and quantitative infrared data.

CF ₄	20%
CF ₃ N=NCF ₃	3%
CF ₃ N=CF ₂	30%
(CF ₃) ₂ N-N(CF ₃) ₂	30%
(FCN) ₂ , (CF ₃) ₂ NH, COF ₂	small amounts

The separation was made using a 300-cm. \times 3/16 in. copper tube packed with 20% of the ethyl ester of Kel-F Acid 8114 on 48/65 mesh Chromosorb. The analysis was carried out at -36° with 8-lb. helium back pressure.

Pyrolysis of Hexafluoroazomethane.—The fluoroazomethane and carbon monoxide, at atmospheric pressure and in a mole ratio of 1:6, were passed through an unpacked nickel tube 24 in. \times 1 in. at 465° at a rate corresponding to 9.3 g./hr. of hexafluoroazomethane. The chief product was identified as hexafluoroethane by infrared spectroscopy, and gas chromatography indicated the reaction product to contain 90% C₂F₆. Under similar conditions of flow at 336°, the hexafluoroazomethane was recovered unchanged.

Trifluoromethyl Isocyanate.—Hexafluoroazomethane (56 g.) and carbon monoxide (104 g.) were heated for 4 hr. at 325° (650 atm.) in a stainless steel 400-ml. vessel. The vessel was cooled, and the volatiles were condensed in a liquid nitrogen-cooled trap to obtain 67.9 g. of product which contained 95.2 mole% trifluoromethyl isocyanate, b.p. -36° (corresponding to 88% conversion), as judged by gas chromatography. The infrared spectrum (gas) showed absorption at 4.34 and 4.38 μ (-NCO) with other major peaks at 6.82, 8.28, 8.60 and 8.65 μ .¹⁷ The fluorine magnetic resonance spectrum consisted of a single resonance at 989 c.p.s. on the low field side.

Perfluoropropyl Isocyanate.—Perfluoroazopropane (26.3 g.) and carbon monoxide (44 g.) were heated for 8 hr. at 300° and 800 atm. in a stainless steel vessel. The volatile product collected consisted of perfluoropropyl isocyanate,¹⁷ b.p. 24-28°, formed in 11% conversion, and perfluorohexane (C₆F₁₄), b.p. 52-59°, identified by a gas density molecular weight of 339 and 340 and an infrared spectrum identical with that published in the literature.¹⁸

Reaction of Hexafluoroazomethane with Elemental Fluorine.—Fluorine, hexafluoroazomethane and helium in the mole ratio 8:3:1 were passed through an unpacked 24 in. \times 1 in. nickel tube at 162-164° at a rate corresponding to 16.8 g./hr. of hexafluoroazomethane. The products identified by mass spectroscopy comprised CF₄, C₂F₆ and unchanged CF₃N=NCF₃ in the ratio 6:0.2:3, corresponding to a 50% conversion of hexafluoroazomethane to carbon tetrafluoride.

Reaction of Hexafluoroazomethane with Bromine.—Hexafluoroazomethane (25 g.) and bromine (32 g.) were heated in an 80-ml. Hastelloy C pressure vessel at 325° for 4 hr. There was obtained 50 g. of condensable material. Dis-

tillation of the crude product gave 14 g. (23%) of bromotrifluoromethane, b.p. -56° to -55°. In addition 7 g. (29%) of the hexafluoroazomethane was recovered. The identity of the bromotrifluoromethane was confirmed by the infrared spectrum.

Reaction of Hexafluoroazomethane with Sulfur.—Hexafluoroazomethane (28.7 g.) was passed through a zone of refluxing sulfur (40 cm. long) at atmospheric pressure over a period of 3 hr. The product was collected in a trap cooled in a liquid nitrogen-bath. There was obtained a complex mixture. Careful fractionation gave a small amount (3.1 g.) of liquid having a boiling point of 80° which was identified by elemental analysis.

Anal. Calcd. for C₂F₆S₃: C, 10.25; S, 41.03; F, 48.72. Found: C, 10.87; S, 41.22; F, 49.59.

In addition to some unreacted hexafluoroazomethane, the reaction product apparently was a mixture of bis-(trifluoromethyl) trisulfide and other polysulfides.

2. Diels-Alder Adducts from Fluoroazoalkanes. Addition of Hexafluoroazomethane to 1,3-Butadiene.—An 80-ml. pressure vessel charged with 1,3-butadiene (6 g.) and hexafluoroazomethane (20 g.) was heated for 2 hr. at 50°, then for 2 hr. at 100°. Fractionation of the liquid product gave 9.53 g. boiling at 45° (46 mm.), *n*_D^{24.5} 1.3528. The infrared and nuclear magnetic resonance analyses were in accord with the structure 1,2-bis-(trifluoromethyl)-1,2,3,6-tetrahydropyridazine.

Anal. Calcd. for C₆H₈F₆N₂: C, 32.72; H, 2.75; F, 51.81; N, 12.74. Found: C, 33.88; H, 2.81; F, 52.59; N, 12.89.

The infrared spectrum (liquid) showed absorption at 3.28 (=CH), 3.42 and 3.47 μ (saturated CH) with other major peaks at 6.87, 7.12, 7.35, 7.42, 7.87, 8.10, 8.20, 8.89, 9.17, 9.52, 9.82, 10.48 and 11.05 μ . The fluorine magnetic resonance spectrum showed a single resonance at 3 c.p.s.

Addition of Hexafluoroazomethane to 2,3-Dimethylbutadiene.—A sealed glass pressure tube containing 3.29 g. of 2,3-dimethylbutadiene and 6.64 g. of hexafluoroazomethane was heated at 100-137° for 30 min. The product was fractionally distilled under reduced pressure to obtain 4.47 g. of a colorless liquid boiling at 69° (40 mm.), 59° (22 mm.); *n*_D^{24.5} 1.3740. The infrared and nuclear magnetic resonance analyses were in accord with the structure 1,2-bis-(trifluoromethyl)-4,5-dimethyl-1,2,3,6-tetrahydropyridazine.

Anal. Calcd. for C₈H₁₀F₆N₂: C, 38.70; H, 4.06; F, 45.96; N, 11.29. Found: C, 39.12; H, 5.04; F, 45.16; N, 10.61.

The dibromo derivative, 1,2-bis-(trifluoromethyl)-4,5-dibromo-4,5-dimethyl-1,2,3,6-tetrahydropyridazine, was prepared by treating a small amount of the pyridazine with an excess of bromine in carbon tetrachloride at 24-26°. The product was purified by sublimation at 68° (0.1 mm.). The white crystalline solid obtained melted over a wide range but was completely melted at 70°.

Anal. Calcd. for C₈H₁₀N₂F₆Br₂: N, 6.86; Br, 39.19. Found: N, 6.53; Br, 39.22.

Addition of Perfluoroazobutane to 1,3-Butadiene.—1,3-Butadiene (4 g.) and perfluoroazobutane (30 g.) were heated and shaken for 4 hr. at 144° in an 80-ml. pressure vessel. Distillation of the reaction mixture gave 9.68 g. of unreacted perfluoroazobutane and 15 g. (66% yield) of a liquid boiling at 70.5° (4 mm.) which was shown by elemental and infrared analyses to be 1,2-bis-(perfluorobutyl)-1,2,3,6-tetrahydropyridazine.

Anal. Calcd. for C₁₂H₈F₁₈N₂: F, 65.76; N, 5.39. Found: F, 65.42; N, 5.68.

The infrared spectrum (liquid) showed absorption at 3.27 (=CH), 3.40 and 3.46 μ (saturated CH) with other major peaks at 7.38, 7.45, 7.73, 8.15, 8.79, 9.53, 11.54, 11.87, 13.35, 13.48, 13.90 and 14.16 μ . The fluorine magnetic resonance spectrum showed resonances at 882 c.p.s. (CF₃-); a quadruplet having weak-strong-strong-weak components at 1361, 1574, 1674 and 1891 c.p.s. (possibly due to restricted rotation); and two singlets at 3157 and 3412 c.p.s. (internal -CF₂-). The single peaks showed multiple splitting.

Addition of 5H-5'H-Eicosafuoroazopentane to 1,3-Butadiene.—A metal pressure vessel containing 3.4 g. of 1,3-butadiene and 15.8 g. of 5H-5'H-eicosafuoroazopentane was heated with shaking for 6 hr. at 167°. Distillation of the

(17) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956), report a boiling point of -36° and infrared absorption peaks at 4.33, 4.40 and 6.48 μ for -NCO. Perfluoropropyl isocyanate was reported to boil at 24.5°; W. Hücker, *Nachr. Akad. Wiss. Göttingen Math.-physik Klasse*, No. 1, 55 (1946); *C. A.*, 44, 4359 (1950). Trifluoromethyl isocyanate was reported to cause unpleasant physiological effects.

(18) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, 74, 4155 (1952).

resulting viscous liquid gave first about 1 g. of liquid boiling at 66–98° (1.1 mm.), then 9.66 g. (55% yield) of a liquid boiling at 105–106° (1.1 mm.) which was shown by elemental and infrared analyses to be 1,2-bis-(5H-decafluoropentyl)-1,2,3,6-tetrahydropyridazine.

Anal. Calcd. for $C_{14}H_8F_{20}N_2$: F, 65.07; N, 4.79. Found: F, 65.18; N, 5.24.

The infrared spectrum (liquid) showed absorptions at 3.26 μ and 3.32 μ (=CH), and at 3.40 and 3.46 μ (saturated CH) with other major peaks at 7.15, 7.36, 7.46, 7.60, 7.95, 8.15, 8.42, 8.80, 9.74, 12.55, 13.00 and 13.86 μ . The fluorine magnetic resonance spectrum consisted of (a) a quadruplet (weak-strong-strong-weak) with components at 1344, 1552, 1652 and 1889 c.p.s.; (b) three singlets at 3097, 3254 and 3617 c.p.s. ($-CF_2-$); and (c) a doublet with components at 4028 and 4079 c.p.s. due to the terminal $-CF_2H$ group.

3. Synthesis of Bis-(fluoroalkylidene)-azines. Bis-(difluoromethylene)-azine.—A mixture of 14 g. (0.084 mole) of hexafluoroazomethane and 17 g. (0.087 mole) of iron pentacarbonyl was heated in an 80-ml. shaker tube at 200° for 6 hr. There was obtained 5.9 g. of gaseous reaction product which was identified as bis-(difluoromethylene)-azine by determination of its molecular weight on a gas density balance. The identity of the product was confirmed by its infrared spectrum which showed strong absorption at 5.72 μ for a $C=N$ linkage and at 7.54, 7.92 and 8.34 μ for a $C-F$ linkage. Additional analytical data were not obtainable because of the instability of the compound.

Anal. Calcd. for $C_2N_2F_4$: mol. wt., 128. Found: mol. wt., 130.

Bis-(perfluoropropylidene)-azine.—An 80-ml. shaker tube charged with a mixture of 36.6 g. (0.1 mole) of perfluoroazopropane and 17.1 g. (0.1 mole) of nickel tetracarbonyl was heated for 6 hr. at 170° with agitation. Distillation of the volatile product in a low-temperature still gave 20 g. (61% conversion) of a liquid boiling at 35° (131 mm.). Elemental analysis showed the product to be bis-(perfluoropropylidene)-azine, $C_2F_5CF=N-N=CFC_2F_5$.

Anal. Calcd. for $C_6F_{12}N_2$: F, 69.51. Found: F, 69.08.

The azine structure assigned to the product was in accord with the infrared spectrum and the fluorine magnetic resonance spectrum. The infrared spectrum (liquid) showed the $CF=N$ double bond absorption at 5.81 μ with other major peaks at 7.31, 7.46, 7.58, 8.17, 8.78, 9.40, 9.87 and 13.34 μ . The fluorine magnetic resonance spectrum consisted of three chemically shifted resonances in the approximate ratios 3:2:1, a CF_3- resonance at 1072 c.p.s., a $-CF_2-$ resonance centered at 3140 c.p.s. and on the low field side resonance at 334 c.p.s. due to the $CF=N$ group.

Defluorination of perfluoroazopropane to obtain bis-(perfluoropropylidene)-azine was also brought about by use of dicobalt octacarbonyl at 150° for 4 hr. followed by 4 hr. at 200° in a sealed vessel.

Bis-(perfluorobutylidene)-azine.—A mixture of 9.98 g. (0.02 mole) of perfluoroazobutane, 3.42 g. (0.01 mole) of dicobalt octacarbonyl and 20 ml. of hexane was stirred at 24–26° for about 16 hr., then heated for 1 hr. at 45°. The solvent was removed by distillation at atmospheric pressure, and the residue was fractionated under reduced pressure. There was obtained 2.86 g. of material boiling at 47° (41 mm.) which was shown by vapor phase chromatography to consist of 89% of bis-(perfluorobutylidene)-azine, and 11% of unreacted perfluoroazobutane. The purified material was identified by elemental analysis. The assigned structure was in accord with the infrared absorption and fluorine magnetic resonance data. Infrared analysis (liquid) showed

$CF=N$ double bond absorption at 5.78 μ with other major peaks at 7.35, 7.55, 7.66, 7.82, 8.06, 8.36, 8.79, 8.93, 9.20, 9.31, 9.82, 10.53, 10.85, 12.20 and 13.39 μ .

Anal. Calcd. for $C_8F_{16}N_2$: C, 22.45; F, 71.03; N, 6.54. Found: C, 22.95; F, 70.96; N, 6.03.

The fluorine magnetic resonance spectrum consisted of four chemically shifted resonances having intensities in the ratios 3:2:2:1, a CF_3- resonance at 909 c.p.s., two $-CF_2-$ resonances at 2982 and 3487 c.p.s., and on the low field side the $-CF=N-$ resonance at 460 c.p.s. All four resonances contained fine structure.

Bis-(perfluorobutylidene)-azine was also obtained by heating perfluoroazobutane with an equimolar amount of iron pentacarbonyl in a vessel under autogenous pressure at 160° for 4 hr.

Bis-(5H-nonafluoropentylidene)-azine.—An 80-ml. shaker tube charged with 21.2 g. (0.04 mole) of 5H-5'-H-eicosafuoroazopentane and 9.8 g. (0.05 mole) of iron pentacarbonyl was heated at 160° with agitation for 4 hr. There was recovered 17 g. of liquid containing a small amount of solid. The solid was removed by filtration, and the liquid was distilled under reduced pressure to obtain 13.8 g. (70% conversion) of bis-(5H-nonafluoropentylidene)-azine, b.p. 74–80.5° (14 mm.). On refractionation, the purified product boiled at 82–82.5° (14 mm.). The spectral data supported the assigned structure. For example, the infrared spectrum (liquid) showed the $CF=N$ double bond absorption at 5.81 μ and the CF_2-H absorption at 3.32 μ . Other major bands were at 7.56, 7.87, 8.13, 8.40, 8.55, 8.80, 12.52 and 12.97 μ .

Anal. Calcd. for $C_{10}H_2F_{18}N_2$: F, 69.51; N, 5.69. Found: F, 69.85; N, 5.22.

The fluorine magnetic resonance spectrum consisted of five chemically shifted resonances, a doublet having components at 4049 and 4106 c.p.s. (CF_2H), three singlets at 3610, 3316 and 2932 c.p.s. (internal $-CF_2-$), and on the low field side at 524 c.p.s. ($-CF=N-$). The resonances also showed complex fine structure.

Bis-(perfluoropropylidene)-azine and Sodium Methoxide.—To a stirred mixture of 12.7 g. (0.039 mole) of bis-(perfluoropropylidene)-azine in 60 ml. of anhydrous ether under a dry nitrogen atmosphere was added 4.75 g. (0.088 mole) of dry sodium methoxide at a rate sufficient to keep the solvent refluxing. The mixture was stirred for 1 hr. and was allowed to stand at 24–26° for 16 hr. The inorganic salt was removed by filtration, and the solvent was removed by distillation. The residue was fractionated under reduced pressure to obtain 5.46 g. (38% of theory) of bis-[(α -methoxy)pentafuoropropylidene]-azine, b.p. 64–66° at 25 mm. The infrared spectrum showed the $C=N$ double bond absorption at 6.05 μ with other major peaks at 3.32, 3.37, 3.49 μ , 6.85, 6.90, 7.60, 8.1–8.7 (broad $C-F$), 9.33, 9.67, 12.32 and 13.43 μ .

Anal. Calcd. for $C_8H_8F_{10}N_2O_2$: C, 27.27; H, 1.70; F, 53.97; N, 7.95. Found: C, 27.95; H, 1.93; F, 54.93; N, 7.83.

There was also obtained 1.54 g. (9%) of bis-[(α,β -dimethoxy)-tetrafluoropropylidene]-azine, b.p. 117–119° at 25 mm. The infrared spectrum showed the $C=N$ double bond absorption at 6.07 μ with other major peaks at 3.34, 3.38, 3.50, 6.88, 6.90, 7.73, 8.1–8.9 (broad $C-F$), 9.02, 9.35, 9.55, 9.65, 12.45 and 13.43 μ .

Anal. Calcd. for $C_{10}H_{12}F_8N_2O_4$: C, 31.91; H, 3.19; F, 40.44; N, 7.45. Found: C, 31.95; H, 3.15; F, 42.47; N, 7.51.