Fluorinated Imines and Hydrazones

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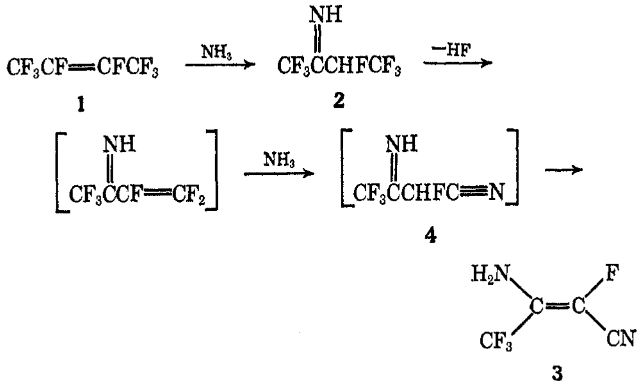
Ammonia and hydrazine react easily with internal fluorinated olefins, acetylenes, and allenes to form α-hydro imines and hydrazones. Depending on substituents, the α-hydro imines can exist preferentially as the imine or as the tautomeric vinylamine.

Recently discovered means of converting fluoro ketones into fluoro imines[2] and fluorohydrazones[1] have made many members of these classes available for study. One notable exception is the type containing α hydrogen. Such compounds are shown in the present work to be obtained directly from reactions of ammonia or hydrazine with fluorinated olefins, acetylenes, and allenes having internal unsaturation.

Imines.—Ammonia was previously shown[3] to give nitriles with terminal fluoro olefins, while primary amines generally were found to form imidyl fluorides and amidines. Secondary amines tended to give saturated adducts under mild conditions and vinylamines with excess secondary amine at elevated temperatures. Secondary amines also formed vinylamines with cyclic fluoro olefins, but ammonia and primary amines gave only 1,3-imino amines.[4-6]

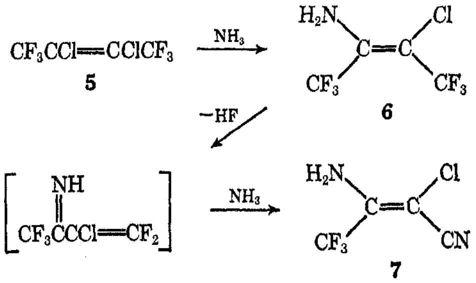
In contrast to these results, octafluoro-2-butene (1) has now been shown to react below 0° with ammonia to form 1-(trifluoromethyl)-2,3,3,3-tetrafluoropropylidenimine (2) in good yield (Scheme I). At 50°, a substantial amount of 3-amino-2,4,4,4-tetrafluoro-2-butenenitrile (3) is also formed by dehydrofluorination of 2 and further reaction with ammonia. None of the imino tautomer 4 was found, and only one isomer of 3 was detected; this isomer was assigned the *trans* CF_3/F structure on the basis of its nmr spectrum. The observed coupling between CF_3 and F is 6.8 Hz, close to the literature average of 9.5 Hz for the *trans* arrangement rather than that of 23 Hz for the *cis* arrangement.[7]

SCHEME I

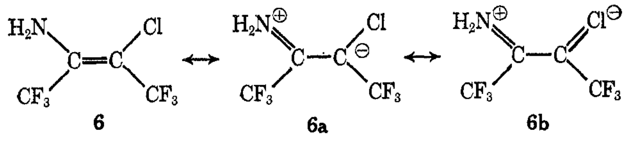


At 25° and slightly above, 2,3-dichlorohexafluoro-2-butene (5) was treated with ammonia with replacement of chlorine to form 2% 2-amino-3-chloro-1,1,1,-4,4,4-hexafluoro-2-butene (6) (Scheme II). Although the imine tautomeric with 6 may have been present in very small amount, it was not isolated. The yield of 6 was not improved by conducting the reaction at −30° under atmospheric pressure because of the low reactivity of olefin 5 compared with 1. At 50°, dehydrofluorination of 6 proceeded so readily that the sole product was 3-amino-2-chloro-4,4,4-trifluoro-2-butenenitrile (7).

SCHEME II



Compound 6 was assigned the *cis* CF_3/CF_3 structure because of the strong coupling (12.5 Hz) between the CF_3 groups.[8] Compound 7 was assigned the *trans* NH_2/CN structure, which allows extended conjugation, in analogy with 3. The preference for the imino form for 2 over the vinylamino form can be attributed to the destabilizing effect of fluorine attached to sp^2 carbon relative to fluorine attached to sp^3 carbon.[9,10] The less electronegative chlorine atom in 6, on the other hand, should not only stabilize a double bond relative to fluorine, but also provide the adjacent partial negative charge developed by resonance (6a) with added stabilization by d-orbital participation (6b).[11]



A case in which the imine and vinylamine tautomers appear to be of comparable stability was provided by the addition of ammonia to hexafluoro-2-butyne (8).

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[1] Contribution No. 1459.

[2] (a) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965); (b) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **153**, 1334 (1963).

[3] For a review of the reactions of nitrogen bases with fluoro olefins, see R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, 62 (1965).

[4] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Amer. Chem. Soc.*, **72**, 3646 (1950).

[5] P. Robson, J. Roylance, R. Stephens, J. C. Tatlow, and R. E. Worthington, *J. Chem. Soc.*, 5748 (1964).

[6] E. T. McBee, J. J. Turner, C. J. Morton, and A. P. Stefani, *J. Org. Chem.*, **30**, 3698 (1965).

[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, pp 909, 910.

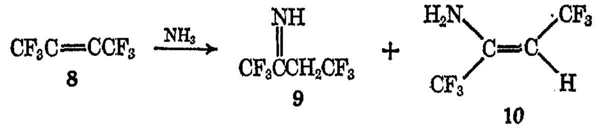
[8] See ref 7, p 911.

[9] J. Hine and P. B. Langford, *J. Amer. Chem. Soc.*, **78**, 5002 (1956).

[10] G. Schröder and J. F. M. Oth, *Angew. Chem. Intern. Ed. Engl.*, **6**, 414 (1967).

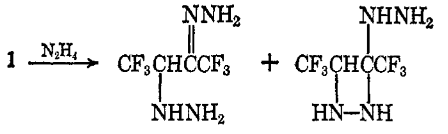
[11] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 71.

Both 1-(trifluoromethyl)-3,3,3-trifluoropropylidenimine (**9**) and 2-amino-1,1,1,4,4,4-hexafluoro-2-butene (**10**) were obtained in 62% combined yield, with vinylamine **10** as the major component of the mixture. The tautomers were separated by vpc and shown to have at least moderate stability at 25°. Only one isomer of **10** was detected; the *trans* CF_3/CF_3 structure was assigned because of the small (1.7 Hz) nmr coupling between the CF_3 groups.[8]



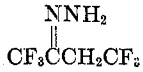
8 **9** **10**

Hydrazones.—Previous additions of hydrazines to unsaturated fluoro compounds have apparently been limited to terminal fluoroolefins. Products were 1,2-dihydro-*s*-tetrazines and hydrazones of acyl fluorides.[12] In this study, hydrazine was found to react readily with **1** or **5** to give two isomeric products of disubstitution. The spectral evidence is in complete accord with 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone (**11**) as the structure for the isomer, mp 124–125°, while the lower melting (54–55°) isomer may be another form of **11** or an unusual cyclic structure. Cryoscopic molecular weight determination showed the lower melting isomer to be monomeric; the absence of a substantial C=N ir absorption and the shift of an NH nmr resonance for the lower melting isomer compared with the higher melting isomer fit ring-closed structure **12** as well as hydrazone structure **11** for the lower melting isomer. The marked similarity between the mass spectra of the two isomers cannot be taken as evidence against a structure such as **12** for the low melting isomer. The mass spectra do establish, however, that oxidation to osazone has not taken place in this case.



11 **12**

Hydrazine reacted at −60° with **8** to form 1,1,1,4,4,4-hexafluoro-2-butanone hydrazone (**13**) in 82% yield. A similar reaction at 0° with tetrakis(trifluoromethyl)allene gave 2,4-bis(trifluoromethyl)-1,1,1,5,5,5-hexafluoro-3-pentanone hydrazone (**14**). The low yield (7%) is probably due to the sensitivity of the product to base.



$$CF_3\overset{NNH_2}{\overset{\|}{C}}CH_2CF_3$$

13

$$(CF_3)_2CH\overset{NNH_2}{\overset{\|}{C}}CH(CF_3)_2$$

14

syn **and** *anti* **Isomers.**—α-Hydro imines **2** and **9** were shown by nmr spectroscopy to be mixtures of isomers in which CF_3 and H are in *syn* and *anti* configurations. Assignments were made following the generalization that coupling between CF_3 and H on an imine double bond is greater for the *syn* case than for the *anti*.[13] Imine **2** was a 5:3 mixture of *syn* CF_3/H ($J_{CF_3/NH}$ = 2.7 Hz) and *anti* CF_3/H ($J_{CF_3/NH}$ = 1.1 Hz) isomers. Imine **9** was a 1:2 mixture of *syn* CF_3/H ($J_{CF_3/NH}$ = 2.6 Hz) and *anti* CF_3/H ($J_{CF_3/NH}$ = 1.3 Hz). Hydrazone **13** was obtained as a single isomer. As indicated above, the presence of an α-hydrazino group may have resulted in the formation of both *syn* and *anti* forms of hydrazone **11** as isolable compounds.

Experimental Section[14]

1-(Trifluoromethyl)-3,3,3-trifluoropropylidenimine (9) **and 2-Amino-1,1,1,4,4,4-hexafluoro-2-butene** (10).—Into a 500-ml round-bottomed flask containing 50 ml of ether was condensed 65 g (40.5 ml at −80°, 0.40 mol) of hexafluoro-2-butyne. The flask was flushed with nitrogen and fitted with a −80° condenser. The mixture was stirred at 0° while ammonia (10.5 g, 0.62 mol, 12.1 ml at −80°) was distilled in over 1 hr. Stirring was continued for 1 additional hr, at which point reflux had ceased and the exothermic reaction was over. Distillation afforded 44.2 g (62%) of a 5:3 mixture of 2-amino-1,1,1,4,4,4-hexafluoro-2-butene and 1-(trifluoromethyl)-3,3,3-trifluoropropylidenimine, bp 66–68°. Composition varied from 5:2 for the first fraction to 5:4 for the last. Analysis of the isomer mixture gave the following values.

Anal. Calcd for $C_4H_3F_6N$: C, 26.83; H, 1.69; F, 63.66; N, 7.82. Found: C, 27.27; H, 2.02; F, 63.87; N, 7.54.

The isomer ratios of the various fractions were unchanged after 2 weeks, indicating the tautomers to be stable with respect to spontaneous interconversion. Preparative vpc on 20% silicone 200–Chromosorb W at 25° served to separate the isomers. The minor product, imine, came off the column first (9.5 min) and the major product, vinylamine, came off second (20.8 min).

Data for the imine were as follows: ir 3.06 and 3.09 (NH), 3.37 (saturated CH), 5.96 μ (C=N); nmr ($CFCl_3$) showed a mixture of *syn* and *anti* isomers, with the *anti* H/CF_3 isomer predominant in close to a 2:1 ratio. Data for the *anti* H/CF_3 were as follows: ^1H at τ 1.1 (broad, NH, atop NH for *syn* isomer) and 6.67 (quadruplet, 2, J_{H/CF_3} = 9.9 Hz, CH_2); ^{19}F at 63.8 (24 lines, 3, triplet $J_{CF_3/H}$ = 9.9 Hz into quadruplets, J_{CF_3/CF_3} = 2.6 Hz into doublets, J_{CF_3NH} = 1.1 Hz, CF_3CH_2), and 77.2 ppm (eight lines, 3, quadruplet, J_{CF_3/CF_3} = 2.6 Hz into overlapping doublets, $J_{CF_3/NH}$ = 1.3 Hz, CF_3C=N). Data for the *syn* H/CF_3 isomer with proportionately less (1:2) area for each peak were as follows: ^1H at τ 1.1 (broad, NH, atop NH for *anti* isomer) and 6.79 (eight lines, 2, quadruplet J_{H/CF_3} = 10.0 Hz into doublets, $J_{H/NH}$ = 1.7 Hz, CH_2); ^{19}F at 64.1 (24 lines partly overlapping CF_3 for *anti* isomer, 3, triplet, $J_{CF_3/H}$ = 10.0 Hz into quadruplets, J_{CF_3/CF_3} = 1.9 Hz into doublets, $J_{CF_3/NH}$ = 0.5 Hz, CF_3CH_2) and 75.7 ppm (eight lines, 3, doublet, $J_{CF_3/NH}$ = 2.6 Hz into quadruplets, J_{CF_3/CF_3} = 1.9 Hz, CF_3C=N); mass spectrum 179 (1), 110 (100), 96 (39), 90 (42), 69 (34), 46 (24).

Data for the vinylamine were as follows: ir 2.84, 2.92, and 3.09 (NH_2), 3.18 and 3.20 (vinyl CH), 5.89 (C=C), 6.16 μ (NH_2); nmr ($CFCl_3$), ^1H at τ 5.11 (quadruplet, 1, J_{H/CF_3} = 8.4 Hz, =CH) and 5.67 (broad, 2, NH_2); ^{19}F at 58.7 (eight lines, 3, doublet, $J_{CF_3/H}$ = 8.4 Hz into quadruplets, J_{CF_3/CF_3} = 1.7 Hz, CF_3CH=] and 72.8 ppm [quadruplet, 3, J_{CF_3/CF_3} = 1.7 Hz, $CF_3C(NH_2)$=]; mass spectrum 179 (49), 160 (42), 110 (42), 90 (100), 69 (15).

1-(Trifluoromethyl)-2,3,3,3-tetrafluoropropylidenimine (2).—Octafluoro-2-butene (50 g, 0.25 mol, 28 ml at −80°) was condensed into a cooled 1-l. flask containing 250 ml of ether and fitted with a −80° reflux condenser, stirrer, and gas inlet tube. Ammonia (25.5 g, 1.5 mol, 31 ml at −80°) was distilled into the flask over 45 min while the reaction mixture was being stirred at −15°. Stirring was continued for 30 min more at −10°, and the mixture was allowed to warm to room temperature. The mixture was then filtered, and the filter cake was rinsed with ether. The combined filtrate and washings were distilled to give

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(12) R. A. Carboni and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **80**, 5793 (1958).

(13) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, in press.

(14) Melting points and boiling points are uncorrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer. Peak center positions for protons are reported as $\tau = 10 - \delta_H$ ppm. Fluorine nmr spectra were obtained with Varian A-56 and -60 spectrometers using trichlorofluoromethane as an internal standard. Peak center positions for fluorine are reported in parts per million upfield from $CFCl_3$. Nmr data are reported thus, chemical shift (absorption description, intensity, pattern with coupling constant, assignment). Mass spectra were taken on a CEC 21-103C instrument; peaks of 15% or greater relative intensity are reported thus, *m/e* (relative intensity).

20.7 g (42%) of 1-(trifluoromethyl)-2,3,3,3-tetrafluoropropylidenimine: bp 57°; ir 3.06 (NH), 3.35 (saturated CH), 5.93 μ (C=N); nmr ($CFCl_3$) showed a 5:3 mixture of isomers with NH *syn* and *anti* to CF_3. Data for the *syn* H/CF_3 isomer are as follows: ^1H at τ 1.7 (broad, NH, atop NH for *anti* isomer) and 4.63 (16 lines, 1, doublet, J_{HF} = 3.6 Hz into quadruplets, $J_{\mathrm{HCF_3}}$ = 5.5 into doublets, $J_{\mathrm{H/NH}}$ = 1.2 Hz, CHF); ^{19}F at 73.2 (nine lines, 3, quadruplet, $J_{\mathrm{CF_3/CF_3}}$ = 5.5 Hz into doublets, $J_{\mathrm{CF_3/F}}$ = 2.7 Hz into overlapping doublets, $J_{\mathrm{CF_3/NH}}$ = 2.7 Hz, $CF_3C{=}N$), 79.0 (eight lines, 3, doublet, $J_{\mathrm{CF_3/F}}$ = 12.8 Hz into overlapping quadruplets, $J_{\mathrm{CF_3/CF_3}}$ = 5.5 Hz into overlapping doublets, $J_{\mathrm{CF_3/H}}$ = 5.5 Hz, CF_3CHF), and 206.1 ppm (seven lines, 1, doublet, $J_{\mathrm{F/H}}$ = 43.6 Hz into overlapping quadruplets, $J_{\mathrm{F/CF_3}}$ = 12.8 Hz with unresolved fine structure, CHF). Data for the *anti* H/CF_3 isomer with proportionately less (3:5) area for each peak are as follows: ^1H at τ 1.7 (broad, NH, atop NH for *syn* isomer) and 4.53 (16 lines, 1, doublet, J_{HF} = 43.8 Hz into quadruplets, $J_{\mathrm{H/CF_3}}$ = 5.9 Hz into rough doublets, $J_{\mathrm{H/NH}}$ = 0.7 Hz, CHF); ^{19}F at 75.2 (14 lines, 3, doublet, $J_{\mathrm{CF_3/F}}$ = 10.2 Hz into overlapping quadruplets, $J_{\mathrm{CF_3/CF_3}}$ = 3.4 Hz into doublets, $J_{\mathrm{CF_3/NH}}$ = 1.1 Hz, $CF_3C{=}N$), 78.3 (ten lines, 3, doublet, $J_{\mathrm{CF_3/F}}$ = 11.9 Hz into doublets, $J_{\mathrm{CF_3/H}}$ = 5.9 Hz into overlapping quadruplets, $J_{\mathrm{CF_3/CF_3}}$ = 3.4 Hz, CF_3CHF), and 208.8 ppm (nine lines, 1, doublet, J_{FH} = 43.8 Hz into quadruplets, $J_{\mathrm{F/CF_3}}$ = 11.9 Hz into overlapping quadruplets, $J_{\mathrm{F/CF_3C{-}H}}$ = 10.2 Hz, CHF); mass spectrum 197 (1), 128 (100), 96 (74), 69 (56), 51 (23), 46 (21), 31 (16).

Anal. Calcd for $C_4H_2F_7N$: C, 24.38; H, 1.03; F, 67.49; N, 7.11; mol wt, 197. Found: C, 24.14; H, 1.48; F, 66.99; N, 6.89; mol wt, 197 (mass spectrometer).

3-Amino-2,4,4,4-tetrafluoro-2-butenenitrile (3). A.—Using the same apparatus as in the preceding experiment, a mixture of 100 g (0.5 mol) of octafluoro-2-butene and 250 ml of ether was cooled to between −35 and −40°, and ammonia (51 g, 3 mol, 62 ml at −80°) was distilled into the stirred solution over 2.5 hr. The mixture was then stirred for 1 additional hr at −35°, allowed to warm to room temperature overnight, and filtered. Distillation of the filtrate gave first 58.0 g (59%) of 1-(trifluoromethyl)-2,3,3,3-tetrafluoropropylidenimine, bp 57° at atmospheric pressure, then 3.9 g (5%) of 3-amino-2,4,4,4-tetrafluoro-2-butenenitrile, bp 54° (5 mm). The latter product was shown to be a single compound by vpc: ir 2.88, 3.00, and 3.11 (NH_2), 4.51 (conjugated CN), 5.96 (C=C); 6.18 μ (NH_2); nmr ($CFCl_3$), ^1H at τ 5.07 (broad, NH_2); ^{19}F at 67.0 (doublet, 3, J_{FF} = 6.8 Hz, CF_3) and 165.2 ppm (12 lines, 3, from quadruplet, J_{FF} = 6.8 Hz into triplets, J_{FH} = 1.4 Hz, CF); mass spectrum 154 (100), 135 (24), 134 (18), 115 (21), 85 (72), 84 (57), 69 (33), 64 (21), 58 (31), 38 (43), 31 (30), 28 (31).

Anal. Calcd for $C_4H_2F_4N_2$: C, 31.18; H, 1.31; F, 49.32; N, 18.19; mol wt, 154. Found: C, 31.14; H, 1.50; F, 49.88; N, 18.18; mol wt, 154 (mass spectrometer).

B.—A higher yield of the butenenitrile is obtainable by carrying out the reaction at higher temperature.

A mixture of 100 g (0.5 mol) of octafluoro-2-butene, 100 g (6 mol) of ammonia, and 200 ml of ether was heated at 50° for 10 hr under autogenous pressure in an agitated 1-l. steel tube. The reaction mixture was filtered, and the solids were rinsed with ether. Distillation of the combined filtrate and washings gave 48.2 g (49%) of 1-(trifluoromethyl)-2,3,3,3-tetrafluoropropylidenimine, bp 55°, and 21.3 g (28%) of 3-amino-2,4,4,4-tetrafluoro-2-butenenitrile, bp 80–81° (20 mm).

2-Amino-3-chloro-1,1,1,4,4,4-hexafluoro-2-butene (6).—A 150-ml thick-walled tube was loaded with 58 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene, 50 ml of ether, and 13 g (0.75 mol, 15.5 ml at −80°) of ammonia. The tube was evacuated cold, sealed, and allowed to stand at 25° overnight. The plug of solid which formed was broken by shaking, after which spontaneous warming occurred. After a total of 24 hr, no further reaction was apparent, so the tube was cooled and opened. The mixture was filtered, and the filtrate was distilled to give 5 g of liquid, bp 25–28° (80 mm), as low-boiling product. Redistillation gave 1.1 g (2%) of 2-amino-3-chlorohexafluoro-2-butene, bp 70° (170 mm). Vpc indicated a single compound with a small amount of starting butene present: ir 2.86 and 2.96 (NH_2), 6.07 (C=C), and 6.26 μ (NH_2); nmr ($CFCl_3$), ^1H at τ 5.52 (broad, NH_2); ^{19}F at 59.5 (quadruplet, 3, J_{FF} = 12.5 Hz, CF_3) and 63.9 ppm (quadruplet, 3, J_{FF} = 12.5 Hz, CF_3).

An early fraction from the redistillation contained a second product in even smaller amount which came off the gc column before the vinylamine. This second product, possibly the isomeric imine, was not isolated.

3-Amino-2-chloro-4,4,4-trifluoro-2-butenenitrile (7).—A mixture of 58 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene, 26 g (1.5 mol) of ammonia, and 100 ml of ether was heated at 50° for 10 hr in an agitated steel tube under autogenous pressure. The resulting mixture was filtered, and the solids were rinsed with ether. Distillation of the combined filtrate and washings gave 25.8 g (61%) of 3-amino-2-chloro-4,4,4-trifluoro-2-butenenitrile: bp 62° (0.5 mm); $n^{25}D$ 1.4688; ir 2.88, 3.01, and 3.13 (NH_2), 4.52 (conjugated CN), 6.06 (C=C), 6.06 (sh, NH_2), and 12.06 μ (C–Cl); nmr ($CFCl_3$), ^1H at τ 4.53 (broad, NH_2); ^{19}F at 66.8 ppm (suggestion of triplet splitting).

Anal. Calcd for $C_4H_2ClF_3N_2$: C, 28.17; H, 1.18; Cl, 20.80; F, 33.43; N, 16.43. Found: C, 28.37; H, 1.22; Cl, 20.71; F, 33.21; N, 16.44.

1,1,1,4,4,4-Hexafluoro-2-butanone Hydrazone (13).—Hexafluorobutyne (65 g, 0.4 mol) was condensed into a flask containing 100 ml of ether cooled to −60° and 19.2 g (0.6 mol) of anhydrous hydrazine was added dropwise with stirring, after which an additional 32 g (0.2 mol) of hexafluorobutyne was distilled into the flask. The exothermic reaction was controlled by maintaining the mixture at a temperature of −60°. After it had subsided, the stirred mixture was allowed to warm to room temperature, then distilled to give 95.3 g (82%) of 1,1,1,4,4,4-hexafluoro-2-butanone hydrazone: bp 71° (60 mm); $n^{28}D$ 1.3534; ir (CCl_4) 2.87, 2.97, and 3.08 (NH_2), 3.30 and 3.36 (saturated CH), 6.05 (sh, C=N), and 6.15 μ (NH_2); nmr ($CFCl_3$), ^1H at τ 3.52 (broad, 2, NH_2) and 6.78 (quadruplet, 2, J_{HF} = 10.5 Hz, CH_2); ^{19}F at 56.4 (decet, 3, from triplet, J_{HF} = 10.5 Hz, into overlapping quadruplets, J_{FF} = 3.5 Hz, CF_3CH_2) and 67.2 ppm (quadruplet, 3, J_{FF} = 3.5 Hz, $CF_3C{=}N$); mass spectrum 194 (62), 175 (15), 125 (100), 111 (34), 75 (33), 69 (57), 43 (24), 29 (18).

Anal. Calcd for $C_4H_4F_6N_2$: C, 24.75; H, 2.08; F, 58.73; N, 14.44; mol wt, 194. Found: C, 24.78; H, 2.08; F, 58.17; N, 14.52; mol wt, 194 (mass spectrometer).

2,4-Bis(trifluoromethyl)-1,1,1,5,5,5-hexafluoro-3-pentanone Hydrazone (14).—To a stirred solution of 1.6 g (0.05 mol) of hydrazine in 25 ml of ether cooled to 0–5° was added dropwise over 30 min 15.6 g (0.05 mol) of tetrakis(trifluoromethyl)allene. The volatile materials were then distilled from the reaction mixture, and the reaction product was sublimed from the residue at 25° (1 mm) to give 1.2 g (7%) of 2,4-bis(trifluoromethyl)-1,1,1,5,5,5-hexafluoro-3-pentanone hydrazone: mp 41–42°; ir (Nujol mull) 2.89, 2.97, and 3.05 (NH_2), 6.03 (C=N), 6.17 μ (NH_2); nmr ($CFCl_3$), ^1H at τ 3.70 (broad, 2, NH_2) and 5.97 (septet, 2, $J_{\mathrm{H/CF_3}}$ = 7.5 Hz, CH); ^{19}F at 62.9 (broad, 6) and 65.1 ppm (broad, 6); mass spectrum 344 (27), 193 (100), 69 (27).

Anal. Calcd for $C_7H_4F_{12}N_2$: C, 24.43; H, 1.17; F, 66.26; N, 8.14; mol wt, 344. Found: C, 24.57; H, 1.35; F, 66.57; N, 7.95; mol wt, 344 (mass spectrometer).

1,1,1,4,4,4,4-Hexafluoro-3-hydrazino-2-butanone Hydrazones (11 and 12).—Two isomers were obtained starting with either octafluoro-2-butene or 2,3-dichlorohexafluoro-2-butene. The highest yields attained of each are given below.

A. **High-Melting Isomer.**—Octafluoro-2-butene (50 g, 0.25 mol, 28 ml at −80°) was evaporated over 30 min into a stirred mixture of 32 g (1.0 mol) of anhydrous hydrazine and 200 ml of ether in a flask cooled to 0° and topped with a −80° reflux condenser. The resulting yellow reaction mixture was stirred an additional 30 min at 0° and allowed to warm slowly to 25° to distil off the unreacted octafluoro-2-butene (2.5 ml). The mixture was then filtered, and the filter cake was rinsed with three 50-ml portions of ether. The combined filtrate and washings were evaporated under reduced pressure to give a residual oil from which crystals deposited. The crystalline solid was filtered off, rinsed with ether and then water, and dried to give 4.1 g of the high-melting isomer of 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone, mp 123–125°. The filtrate gave, on distillation, a small amount of the low-melting isomer which volatilized and solidified as feathery white needles, mp 54–55°. The residue from this distillation was extracted with ether, then with benzene, to provide a second crop of the high-melting isomer (0.8 g). The two crops of high-melting isomer were combined and recrystallized from benzene–ether to give 3.5 g (6%) of 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone: mp 124–125°; ir (KBr) 2.97 (sh), 3.00 3.03, (sh), and 3.15 (NH, NH_2), 3.35, (saturated CH), 5.89 (C=N), 6.17 and 6.25 μ (NH_2); nmr (acetone-*d*), ^1H at τ 2.23 (broad, 2, $=NNH_2$), 4.37 (broad doublet, 1, $J_{NH/CH}$ = 9.5 Hz, $-NHNH_2$), 5.22 (eight lines, 1, doublet ($J_{CH/NH}$ = 9.5 Hz into overlapping quadruplets, J_{H/CF_3} = 7.3 Hz, CH), and 6.66 (singlet, 2, $NHNH_2$); ^{19}F at 68.2 (quadruplet, 3, J_{CF_3/CF_3} = 3.2 Hz, $CF_3C{=}N$) and 73.4 ppm (eight lines, 3, doublet, $J_{CF_3/H}$ = 7.3 Hz into overlapping quadruplets, J_{CF_3/CF_3} = 3.2 Hz, CF_3CH); mass spectrum 224 (5), 194 (42), 155 (21), 145 (16), 113 (27), 111 (17), 105 (23), 95 (28), 93 (20), 75 (19), 69 (48), 43 (39), 31 (100), 29 (23), 28 (52).

Anal. Calcd for $C_4H_6F_6N_4$: C, 21.43; H, 2.70; F, 50.86; N, 25.00; mol wt, 224. Found: C, 22.10; H, 2.88; F, 50.94; N, 24.86; mol wt, 224 (mass spectrometer).

B. Low-Melting Isomer.—A mixture of 32 g (1.0 mol) of anhydrous hydrazine and 100 ml of acetonitrile was stirred and cooled at 0° while 58 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene was added dropwise over 30 min. The mixture was stirred an additional 0.5 hr, during which time it was allowed to warm spontaneously to 34°. It was then filtered, and the solid filter cake was rinsed with acetonitrile. Evaporation of the solvent from the combined filtrate and washings, followed by distillation in a short-path still, afforded 26 g of the crude hydrazone (low-melting isomer), bp *ca.* 80° (0.5 mm). Redistillation in a molecular still under 0.5-mm pressure with the pot at 90° gave 23.8 g (42%) of hydrazone as a distillate which solidified to a white solid, mp 51–53°.

A 17.4-g sample of this hydrazone was dissolved in methylene chloride, and the less soluble high-melting isomer was filtered off. The filtrate was evaporated to a low volume, and petroleum ether (bp 30–60°) was added until cloudiness persisted. The mixture was filtered again and cooled to 0°. The precipitate of low-melting isomer was filtered off and further purified by sublimation at 45° (1 mm) to give 12.1 g of the low-melting isomer of 1,1,1,4,4,4-hexafluoro-3-hydrazino-2-butanone hydrazone as colorless crystals, mp 52–53°. This was resublimed before analysis: ir (KBr) 2.92 (sh), 3.00, 3.05, and 3.13 (sh) (NH, NH_2), 3.45 (saturated CH), 6.15 (sh) and 6.25 μ (NH_2); nmr ($CDCl_3$), ^1H at τ 2.40 (broad, 2, $=NNH_2$), 5.77 (quadruplet, 1, J_{H/CF_3} = 7.5 Hz, CH), and 6.55 (singlet, 3, $NHNH_2$); ^{19}F at 67.6 (quadruplet, 3, J_{CF_3/CF_3} = 3.7 Hz, $CF_3C{=}N$) and 70.2 ppm (six lines, 3, doublet, $J_{CF_3/H}$ = 7.5 Hz into overlapping quadruplets, J_{CF_3/CF_3} = 3.7 Hz, CF_3CH); mass spectrum 224 (10), 194 (79), 174 (24), 155 (38), 125 (16), 113 (30), 111 (29), 105 (41), 93 (33), 75 (22), 69 (60), 66 (17), 43 (54), 32 (39), 31 (100), 29 (35), 28 (57), 17 (25).

Anal. Calcd for $C_4H_6F_6N_4$: C, 21.43; H, 2.70; F, 50.86; N, 25.00; mol wt, 224. Found: C, 21.90; H, 2.88; F, 50.78; N, 25.69; mol wt, 222, 238 (fp benzene); 224 (mass spectrometer).

Registry No.—*syn* **2**, 17603-96-2; *anti* **2**, 17603-97-3; **3**, 17603-98-4; **6**, 17603-99-5; **7**, 17604-00-1; *syn* **9**, 17604-01-2; *anti* **9**, 17604-02-3; **10**, 17604-03-4; **11**, 17604-30-7; **12**, 17604-31-8; **13**, 17604-32-9; **14**, 17604-33-0.

Fluoronitroaliphatics. IV.[1] Some Reactions of 2-Fluoro-2,2-dinitroethanol

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A variety of reactions of 2-fluoro-2,2-dinitroethanol, primarily involving its hydroxyl function, are described. In certain of its reactions this material parallels other polynitroethanols; in others its reactivity behavior differs markedly. A possible basis for this dual reactivity is suggested.

In a previous paper[2] we reported the first synthesis of fluorodinitromethyl compounds by the perchloryl fluoride fluorination of the corresponding 1,1-dinitroalkane salts as well as improvements and extensions in scope of the preparative methods for such materials which resulted from the Grakauskas aqueous fluorination procedure.[3] In the light of the extensive polynitroaliphatic chemistry which has centered on 2,2,2-trinitroethanol, 2,2-dinitroethanol and 2,2-dinitropropanol as intermediates,[4,5] 2-fluoro-2,2-dinitroethanol (**1**) seemed the most interesting and potentially the most useful of the new fluoro derivatives described. We have therefore investigated the chemistry of **1** in greater detail and wish now to report that it is, indeed, a highly versatile reagent for the introduction of the fluorodinitroethoxy, the fluorodinitroethyl and, indirectly, the fluorodinitromethyl groups into organic molecules.

It was expected that in its reactivity **1** would resemble other highly negatively substituted acidic alcohols such as 2,2,2-trinitroethanol, 2-substituted 2,2-dinitroethanols, and 2,2,2-trifluoroethanol.[4–6] In the course of the present investigation this expectation was confirmed in a number of respects. It will be shown, however, that, in certain other regards, primarily in its behavior with bases, the reactions of **1** deviate considerably from established pathways.

Esterification.—Reactions of fluorodinitroethanol with a variety of acid chlorides proceeded smoothly in the manner described previously for 2,2-dinitroalkanols.[7] Acetyl chloride, for example, reacted readily with **1** in the absence of catalyst or base. With *p*-toluenesulfonyl chloride, the condensation reaction proceeded in the presence of pyridine or pyridine N-oxide.[8]

As with 2,2,2-trichloro-, tribromo-, trifluoro-, and trinitroethanol,[9,10] aluminum chloride has proven an effective catalyst for the esterification of **1** with less reactive acid chlorides. A preferred method of effecting the reaction is to treat **1** with 1 equiv of aluminum chloride in an inert solvent to form the soluble fluoro-

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(1) Part III: H. G. Adolph, R. E. Oesterling, and M. E. Sitzmann, *J. Org. Chem.*, **33**, 4296 (1968).

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(3) V. Grakauskas and K. Baum, *ibid.*, **33**, 3080 (1968).

(4) A detailed review of the chemistry of 2,2,2-trinitroethanol and 2,2-dinitroethanol may be found in Reports No. 461 and 494, Aerojet Engineering Corp., Azusa, Calif., available through the Defense Documentation Center, Cameron Station, Alexandria, Va.

(5) Several dozen papers and scores of patents describe derivatives of these polynitro alcohols. An excellent review through 1962 is given by P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **61**, 19 (1964).

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