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REACTIONS OF AMINES WITH A DIMER OF HEXAFLUOROPROPENE  
AND WITH A PERFLUOROVINYL SULFIDE PREPARED WITH HEXAFLUOROPROPENE

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SUMMARY

Some reactions of amines with a perfluorovinylsulfide,  $(CF_3)_2CFSCF_3=CFCF(CF_3)_2$ , prepared from hexafluoropropene (HFP) and sulfur [1] are compared to reactions of the same amines with the thermodynamic dimer of HFP,  $(CF_3)_2C=CFCF_2CF_3$ . Many new ketenimines, eneamines, amidines, nitriles, and quinoline derivatives are reported.

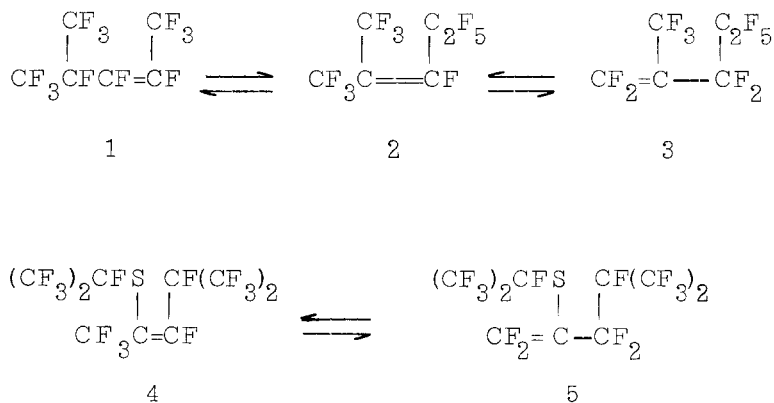
INTRODUCTION

We have reported a facile preparation of the perfluorovinyl sulfide, 2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-1,1,1,3,4,5,5,5-octafluoro-2-pentene (4), from HFP and sulfur and the preparation of an acylketene from it [1], analogous to the preparation of an acylketene from HFP dimer (2) [2]. We now report further similarities in the behavior of these two unsaturated compounds in their reactions with amines. Some reactions of the kinetic HFP dimer 1 with aliphatic amines [3] and some reactions of the thermodynamic HFP dimer 2 with aliphatic amines [4] and with aromatic amines [4,5,6] have been reported. Some of the products

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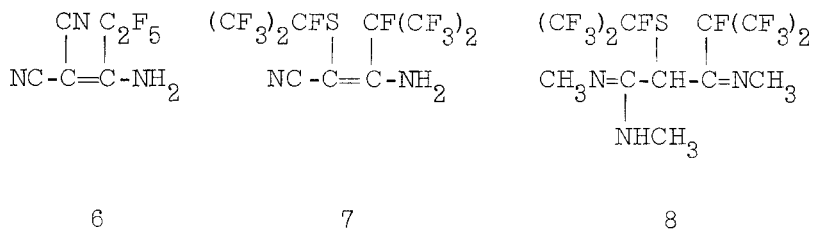
\*Contribution No. 2784

of 1 and 2 with aliphatic amines were accounted for by isomerization to the terminally unsaturated isomer 3. Similarly, we have found some products from 4 which indicate isomerization to 5.

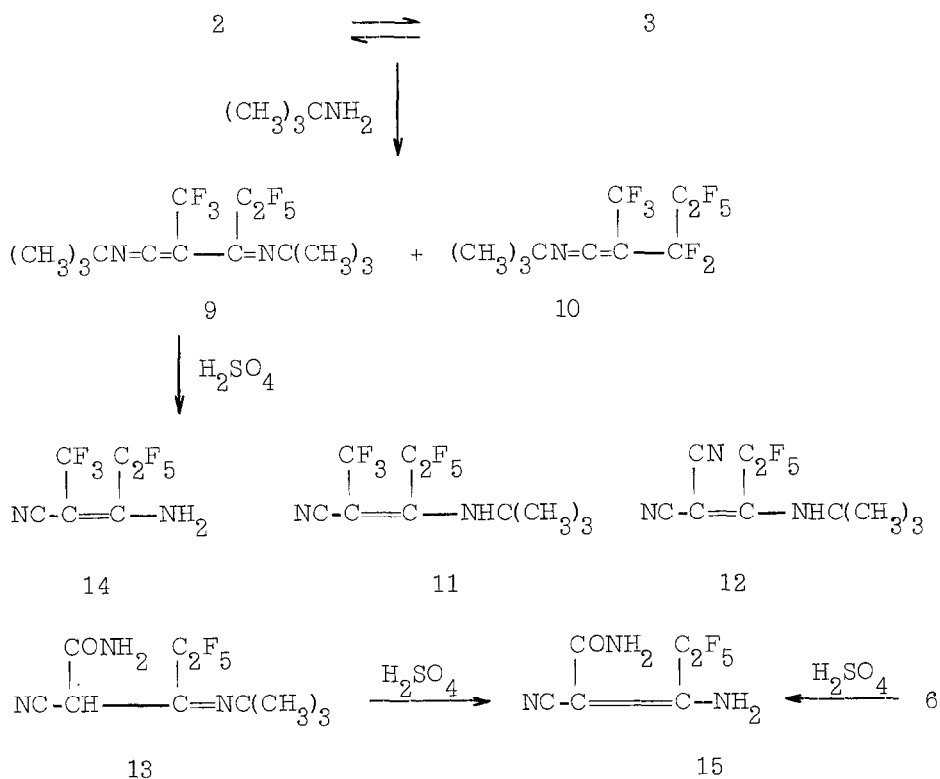


#### RESULTS and DISCUSSION

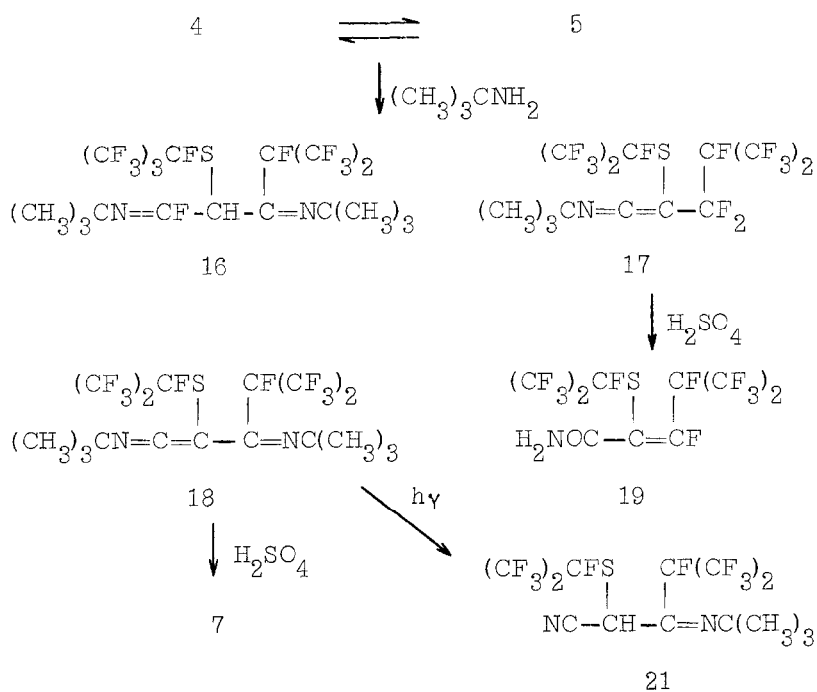
The reaction of 2 with ammonia gave the dicyanoenamine 6 [4] previously prepared from sodiomalonitrile and perfluoropropionitrile [7]. Reaction of 4 with ammonia gave the cyanoenamine 7 which was hydrolyzed in sulfuric acid to the ketone,  $(\text{CF}_3)_2\text{CFSCH}_2\text{COCF}(\text{CF}_3)_2$ , previously reported [1] as the hydrolysis product of the acylketene,  $\text{O}=\text{C}[\text{SCF}(\text{CF}_3)_2]\text{COCF}(\text{CF}_3)_2$ . Reaction of 4 with methylamine gave the amidine 8 which formed a salt with one mole of sulfuric acid.



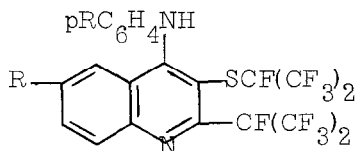
HFP dimer 2 was reported [4] to give 85% yield of 9 with t-butylamine. In our hands, regardless of the order of addition, both 9 (ca. 45%) and 10 (ca. 20%) were isolated indicating the possibility of some isomerization of 2 to 3. From some reactions under different conditions, products of further reaction including hydrolysis and/or pyrolysis (11, 12 and 13) were also isolated. Hydrolyses in sulfuric acid gave 14 from 9 and 15 from 13 as well as from 6.



Reaction of the vinyl sulfide 4 with t-butylamine was analogous to the above in that both 17 and 18 were isolated. In addition, an intermediate to 18, compound 16, was isolated, each in about 20% yield. Hydrolyses in sulfuric acid gave 19 from 17 and 7 from 18. Irradiation with ultraviolet light caused 18 to lose isobutylene and give 21.

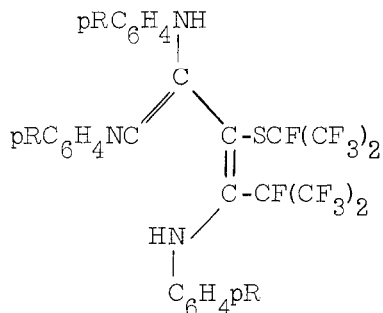


Several products have been reported [4, 5, 6] from reaction of 2 with aromatic primary amines including quinoline derivatives corresponding to 22 prepared from 4 and aniline and 23 prepared from 4 and p-toluidine. In addition to the quinoline derivatives, these reactions gave the amidines 24 and 25, respectively. Analogous amidines were not reported from 2.



22 R = H

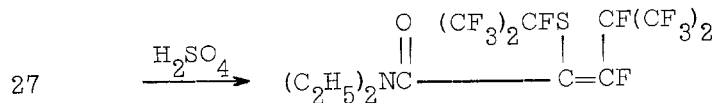
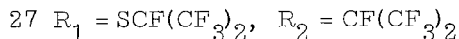
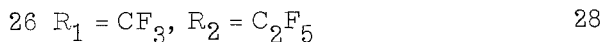
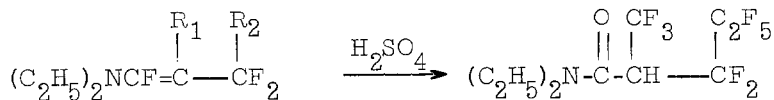
23 R = CH<sub>3</sub>



24 R = H

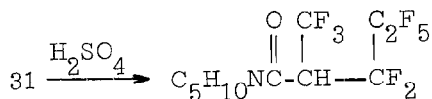
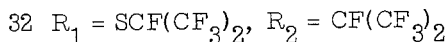
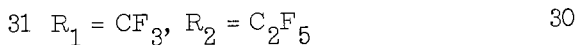
25 R = CH<sub>3</sub>

We have confirmed that the reaction of 2 with diethylamine gives 26 probably through isomerization to 3 [4]. Likewise, the vinylsulfide 4 gives 27 probably through isomerization to 5. Hydrolysis with sulfuric acid gave 28 from 26 as reported [4]. Similar treatment of 27 gave 29 (additional loss of HF).

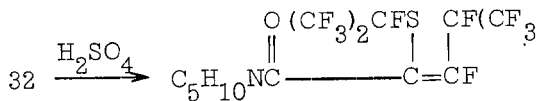


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The main product (86%) reported [4] from the reaction of 2 with piperidine is the enamine 30. However we found 30 to be the minor (16%) product and enamine 31 to be the major (34%) product. The only product (68%) isolated from the reaction of 4 with piperidine was enamine 32. Hydrolysis of 31 in  $H_2SO_4$  gave 33 whereas 32 gave 34 (additional loss of HF).

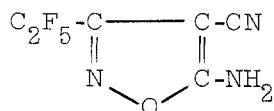
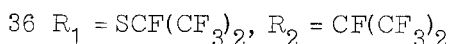
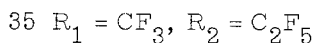


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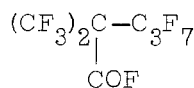


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Reaction of 2 and 4 with hydroxylamine were analogous giving respectively, the tautomeric mixtures 35 and 36. Hydroxylamine reacted with the dicyanoenamine 6 to give the heterocycle 37. The cyanoenamine 7 did not react with hydroxylamine under similar conditions.



37



38

Carbonyl fluoride was added to 2 to give 38.

#### EXPERIMENTAL

Melting points and boiling points are uncorrected. PMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as external standard with the downfield direction taken as positive.  $^{19}\text{F}$  NMR spectra were obtained with a Varian A56/60 spectrometer operating at 56.4 MHz; chemical shifts are reported in ppm downfield from  $\text{CFCl}_3$  as internal standard.

#### Reaction of 2 with Ammonia. (1-Amino-2,2,3,3,3-pentafluoropropylidene)propanedinitrile (6).

Flowers, et al [4] have reported without experimental details a near quantitative yield of 6 from 2. Our yield was less.

In a 2-liter flask fitted with a mechanical stirrer, dropping funnel, and Dry Ice condenser was placed 500 ml of ether. Ammonia (47 g, 65 ml at  $-80^{\circ}$ ) was then condensed into the flask which was stirred while adding dropwise a solution of 75 g (0.25 m) of HFP dimer 2 in 100 ml ether. Reaction was very exothermic, and the mixture was kept at about  $0^{\circ}$  with cooling. There was considerable reaction in the vapor phase also. After addition, the mixture was allowed to stand one-half hour at room temperature, poured into water, the ether layer washed with water, dried over  $MgSO_4$ , and the ether removed. The crystalline residue was recrystallized from nitromethane. Yield 27 g (51%), mp  $190-192^{\circ}$ .

IR:  $3.00 \mu$ ,  $3.13 \mu$  ( $NH_2$ ),  $4.46 \mu$  (CN),  $5.94 \mu$  (C=C). FMR:  $-84.6$  ppm (triplet,  $J = 2.22$  Hz, 3F) and  $-119.0$  ppm (quartet,  $J = 2.22$  Hz, 2F).

This compound had been prepared previously [7] by the reaction of perfluoropropionitrile with the sodium salt of malononitrile. It was hydrolyzed to the amide nitrile 15 as described below.

Hydrolysis of 6 to 15. 3-Amino-2-cyano-4,4,5,5,5-pentafluoro-2-pentenamide (15) (nc)

The dinitrile 6 (5 g) was dissolved in 10 ml of conc. sulfuric acid with stirring (exothermic to  $35^{\circ}$ ). The yellow solution was stirred for one hour and poured into 100 g of ice. There was filtered 5.6 g of 15, which was recrystallized from nitromethane, 4 g (73.5%), mp  $180-182^{\circ}$ .

IR:  $2.87 \mu$ ,  $3.04 \mu$ ,  $3.15 \mu$  ( $NH_2$ ),  $4.50 \mu$  (C=N),  $5.91 \mu$ ,  $6.12 \mu$  (C=C and C=O). FMR:  $-84.6$  ppm (triplet,  $J = 2.20$  Hz, 3F) and  $-120.0$  ppm (multiplet, 2F).

Anal: Calcd. for  $C_6H_4F_5N_3O_2$ : C, 31.47; H, 1.76; F, 41.48; N, 18.35  
 Found : C, 31.64; H, 1.96; F, 41.59; N, 18.14

Reaction of 6 with Hydroxylamine. 5-Amino-3-(pentafluoroethyl)-4-isoxazolecarbonitrile (37). (nc)

The dicyanoenamine 6 (10.5 g, 0.05 m) was added to a solution of 3.5 g (0.05 m) hydroxylamine hydrochloride in a solution of 8 g (0.2 m) sodium hydroxide in 80 ml water, and the resulting solution was stirred overnight. Extraction with ether gave three layers. Removal of ether from the top layer gave 3 g of crystals. Removal of ether from the second layer and acidification with HCl gave 6.8 g of the same crystals. The third layer gave a trace of solid on acidification, which was discarded. Recrystallization from chloroform gave white crystals, m.p. 136-138°C.

IR; 4.38  $\mu$  (CN), 2.91, 3.08  $\mu$  (NH<sub>2</sub>), 5.98  $\mu$  (C=N).

PMR: 7.33 ppm (broad, 2H). FMR: -85.2 ppm (triplet, J = 2.2 Hz, 3F) and -116.4 ppm (quartet, J = 2.2 Hz, 2F).

Anal: Calcd for C<sub>6</sub>H<sub>2</sub>F<sub>5</sub>N<sub>3</sub>O: C, 31.74; H, 0.89; F, 41.85; N, 18.51  
 Found : C, 31.80; H, 0.87; F, 41.93; N, 18.50

An attempt to react 7 with hydroxylamine under similar conditions was unsuccessful.

Reaction of 4 with Ammonia. 3-Amino-4,5,5,5-tetrafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-2-pentenenitrile (7) (nc)

The vinyl sulfide 4 (49 g, *cis* and *trans* mixture) in 100 ml tetrahydrofuran was mechanically stirred in a 1-liter, 3-neck flask evacuated and pressured with ammonia maintained automatically at about 740 mm. As ammonia was absorbed, the temperature was maintained at about 25° with ice-bath cooling. Ammonium fluoride separated giving a thick slurry which later became thinner. When absorption stopped, water was added dissolving the ammonium fluoride and giving a heavy oily layer which solidified when washed again with water. Vacuum dried yield: 43 g (97%). This product was recrystallized from 300 cc toluene to give 35 g (79%), mp 121-123°.



IR: 4.44  $\mu$  (C=N), 6.13  $\mu$  (C=C). PMR: 7.45 ppm (broad).  
 FMR: -159.7 ppm (septet,  $J = 10.0$  Hz, 1F), -74.2 ppm (doublet,  
 $J = 10$  Hz, 6F), -179.3 ppm (very broad, 1F) and -73.95 ppm  
 (broad, 6F).

Anal: Calcd. for  $C_9H_2F_{14}N_2S$ : C, 24.78; H, 0.46; F, 60.98;  
 N, 6.42; S, 7.35  
 Found: C, 24.98; H, 0.52; F, 61.36;  
 N, 6.60; S, 7.18.

Mass spec. calcd. 435.9714, measured 435.9700.

Hydrolysis of 7 with Sulfuric Acid. 3,4,4,4-Tetrafluoro-1-  
[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-3-  
(trifluoromethyl)-2-butanone.

The amino nitrile 7 (5 g) was dissolved in 25 ml conc.  $H_2SO_4$   
 and heated in a sealed tube for 60 hrs at 100°. The reaction mixture  
 separated into two layers. After pouring onto ice, the heavy layer  
 (3 g) was identified as the ketone  $(CF_3)_2CFSCH_2COCF(CF_3)_2$ , bp  
 101° [1].

Reaction of 4 with Methylamine. 4,5,5,5-Tetrafluoro-2-  
[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-  
(trifluoromethyl)-N-methyl-1,3-bis(methylimino)pentanamine (8) (nc).

The vinyl sulfide 4 (50 g, 0.1 m) in 100 ml THF was stirred  
 while adding dropwise with cooling 40% aqueous methyl amine until  
 the mixture remained basic. A total of 64 g (0.8 m) was used. The  
 mixture was poured into cold water and washed with water. The  
 crystalline product was recrystallized from methanol giving 37 g  
 (72%) mp 58-61°. Recrystallization gave 17.5 g, mp 69-70°.

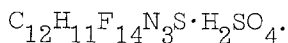
PMR: 2.87 ppm (singlet, 3H), 2.90 ppm (singlet, 3H),  
 3.30 ppm (singlet, 3H) and ca. 4 ppm (broad, 2H). FMR: -73.8  
 ppm (multiplet, 6F), -74.9 ppm (multiplet, 3F), -75.7 ppm (multiplet,  
 1F) and -165.6 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{12}H_{11}F_{14}N_3S$ : C, 29.09; H, 2.22; F, 53.74;  
N, 8.48; S, 6.46.

Found: C, 29.19; H, 2.25; F, 52.94;  
N, 8.34; S, 6.84

Reaction of 8 with Sulfuric Acid (Salt Formation) (nc)

The above product (6.9 g) was stirred in 20 ml of conc.  $H_2SO_4$ . Ice was added and the solution filtered. The solid was recrystallized from water and vacuum dried to give 6.2 g crystals, mp 237-238° (insoluble in ethyl ether and acetone, soluble in methanol and dimethylsulfoxide). Apparently a salt was formed:



Anal: Calcd. for  $C_{12}H_{11}F_{14}N_3S \cdot H_2SO_4$ : C, 24.29; H, 2.21; F, 44.83;  
N, 7.08; S, 10.81.

Found: C, 24.50; H, 2.38; F, 44.84;  
N, 6.48; S, 10.80

Reaction of 2 with t-Butylamine. N,N'-[4,4,5,5,5-Pentafluoro-2-(trifluoromethyl)-1-penten-1,3-diyldene] bis(1,1-dimethylethanamine) (9) and N-[3,3,4,4,5,5,5-Heptafluoro-2-(trifluoromethyl)-1-penten-1-ylidene]-1,1-dimethylethanamine (10) (nc).

Flowers, et al [4] have reported isolation of 9 from this reaction without experimental details.

A solution of 219 g (3.0 m) t-butylamine in 200 ml ether was added dropwise to 150 g (0.5 m) of dimer 2 in 500 ml of ether keeping the temperature about -50° with a Dry Ice-acetone bath. Stirring became difficult during the latter third of the addition. After standing overnight, cold water (500 ml) was added, the ether layer separated, washed twice with water, dried over  $MgSO_4$ , ether removed and the residue distilled under reduced pressure. There was recovered 32 g (19%) of 10, bp 57°/22 mm,  $n_D^{25}$  1.3440 and 80 g (44%) of 9, bp 45°/0.5 mm,  $n_D^{25}$  1.3840.

For 10: IR:  $4.75 \mu$  (C=C=N). PMR: 1.08 ppm (singlet, 9H).  
 FMR: -54.1 ppm (multiplet, 3F), -80.9 ppm (triplet,  $J = 10.5$  Hz, 3F), -103.9 ppm (multiplet, 2F), and -126.5 ppm (quartet,  $J = 5.2$  Hz, 2F)

Anal: Calcd. for  $C_{10}H_9F_{10}N$ : C, 36.05; H, 2.72; F, 57.03; N, 4.20

Found: C, 35.59; H, 2.78; F, 60.27; N, 4.95

For 9: IR;  $4.80 \mu$  (C=C=N),  $6.59 \mu$  (C=N). PMR: 1.0 ppm (overlapping singlet, 18H). FMR: -80.88 ppm (singlet, 3H), -53.60 ppm (triplet,  $J = 6.0$  Hz, 3F), -114.42 ppm (quartet,  $J = 6.0$  Hz, 2F).

Anal: Calcd. for  $C_{14}H_{18}F_8N_2$ : C, 45.91; H, 4.95; F, 41.51; N, 7.64.

Found: C, 45.72; H, 5.09; F, 41.60; N, 7.88.

#### Reverse Order of Addition and Isolation of 12.

#### 3-(1,1-Dimethylethylamino)-4,4,5,5,5-pentafluoro-2-cyano-2-pentenenitrile (12) (nc)

The above reaction was repeated, but the order of addition was reversed. There was obtained 24% of 10, 46% of 9 and a higher boiling fraction (17.1 g) which crystallized and was recrystallized from hexane and then toluene to give 2 g of 12, mp  $56-58^\circ$ .

IR:  $4.45 \mu$  (C=N). PMR: 1.58 ppm (singlet, 9H) and 6.10 ppm (broad, 1H). FMR: -82.99 ppm (triplet,  $J = 5.0$  Hz, 3F) and -116.76 ppm (quartet,  $J = 5.0$  Hz, to doublet,  $J = 4.0$  Hz, 2F).

Anal: Calcd. for  $C_{10}H_{10}F_5N_3$ : C, 44.95; H, 3.77; F, 35.55; N, 15.73.

Found: C, 45.03; N, 3.82; F, 35.56; N, 15.75.

#### Higher Temperature Isolation of 11 and 13. 3-(1,1-Dimethylethylamino)-4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-2-pentene-nitrile (11) and 2-Cyano-3-(1,1-dimethylethylimino)-4,4,5,5,5-pentafluoropentanamide (13) (nc)

A solution of 150 g (0.5 m) of Dimer II in 100 ml ether was added dropwise with stirring and cooling (ca.  $30^\circ$ ) to 146 g. (2.0 m) of t-butylamine in 500 ml of ether. The mixture was refluxed for one hour after addition was complete, cooled and 750 ml water added.

The ether layer was washed twice with water, dried over  $\text{MgSO}_4$ , ether removed, and the residue distilled. There was recovered 25 g of a mixture of 9 and 10, 33 g of compound 11, bp  $52^\circ/0.6$  mm, mp  $62-3^\circ$  (pet. ether), and 20.5 g of pot residue from which 2.6 g of 13, mp  $119-121^\circ$ , was obtained by two recrystallizations from toluene.

For 11: Apparently two isomers (1,3-proton shift).

IR:  $4.50 \mu$  ( $\text{C}=\text{N}$ ). PMR: (for minor isomer) 1.41 ppm (singlet, 9H), (for major isomer) 1.58 ppm (singlet, 9H) and a broad peak for both isomers, 5.10 ppm (singlet, 1H). FMR: (for major isomer)  $-52.9$  ppm (multiplet, 3F),  $-81.1$  ppm (multiplet, 3F) and  $-116.0$  ppm (multiplet, 2F). (For minor isomer)  $-58.4$  ppm (doublet,  $J = 1$ , 2 Hz, 3F),  $-82.6$  ppm (triplet,  $J = 2.7$  Hz, 3F) and  $-112.9$  ppm (multiplet, 2F).

Anal: Calcd. for  $\text{C}_{10}\text{H}_{11}\text{F}_8\text{N}_2$ : C, 38.59; H, 3.56; F, 48.84; N, 9.00.  
Found: C, 38.65; H, 3.45; F, 48.83; N, 9.27.

Mass measurement: 311.08, Calcd. 311.21

For 13: IR:  $4.50 \mu$  ( $\text{C}\equiv\text{N}$ ). PMR: 1.39 (singlet 9H), 6.11 ppm (broad, 2H) and 10.0 ppm (broad, 1H). FMR:  $-83.93$  ppm (triplet,  $J = 2.2$  Hz, 3F) and  $-120.43$  ppm (multiplet, 2F).

Anal: Calcd. for  $\text{C}_{10}\text{H}_{12}\text{F}_5\text{N}_3\text{O}$ : C, 42.12; H, 4.24; F, 33.32; N, 14.74.  
Found: C, 42.16; H, 4.36; F, 32.88; N, 14.70.

Hydrolysis of 9 to 14. 3-Amino-4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-2-pentenenitrile (14) (nc)

Compound 9 (25 g) was stirred while adding dropwise 25 ml of conc.  $\text{H}_2\text{SO}_4$ . Ice was added to the resulting solution which was then extracted with ether. The ether extract was dried over  $\text{MgSO}_4$  and distilled. There was obtained an oil which crystallized. The crystals were washed with hexane and recrystallized three times from toluene to give 1.2 g of the aminonitrile 14, mp  $49-51^\circ$ .

IR: 4.54  $\mu$  (C $\equiv$ N). PMR: 5.95 ppm (broad, 2H). FMR: -59.76 ppm (multiplet, 3F); -83.99 ppm (triplet, J = 2.3 Hz, 3F) and -119.62 ppm (multiplet, 2F).

Anal: Calcd. for C<sub>6</sub>H<sub>2</sub>F<sub>8</sub>N<sub>2</sub>: C, 28.36; H, 0.79; F, 59.82; N, 11.02.

Found: C, 28.40; H, 1.06; F, 59.80; N, 10.46.

Hydrolysis of 13 with Sulfuric Acid to 15. 3-Amino-2-cyano-4,4,5,5,5-pentafluoro-2-pentenamide (15) (nc).

Compound 13 (ca. 10 g) was treated with 10 ml conc. H<sub>2</sub>SO<sub>4</sub> in the manner described above for compound 9. The recovered solid 15 recrystallized from nitromethane melted at 180-182°. It was identical to material isolated from sulfuric acid hydrolysis of 6 above.

Reaction of 4 with t-Butylamine. N, N'-[1,4,5,5,5-pentafluoro-2-(1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio)-4-(trifluoromethyl)-1,3-pentanediyldene] bis(1,1-dimethylethanamine) (16) (nc), N-[3,3,4,5,5,5-Hexafluoro-(1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethylthio)-4-(trifluoromethyl)-1-penten-1-ylidene] - 1,1-dimethylethanamine (17) (nc) and N, N'-[4,5,5,5-Tetrafluoro-2-(1,2,2,2-tetrafluoro-2-(trifluoromethyl)ethylthio)-1-pentene-1,3-diyldene] bis(1,1-dimethylethanamine) (18) (nc).

A solution of the perfluorovinylsulfide 4 (241 g, 0.5 m) in 100 ml ether was added dropwise to a stirred solution of 219 g (3.0 m) of t-butylamine in 500 ml ether keeping the temperature below -50° with a dry ice-acetone bath. Stirring was continued after removal of the cooling bath, and the reaction exothermed to ca. 40°. After standing overnight, cold water was added, and the ether layer was washed twice with water, dried with MgSO<sub>4</sub>, ether removed, and the residue distilled rapidly and then redistilled. There was separated 62 g (24%) of 17, bp ca. 50°/0.6 mm, n<sub>D</sub><sup>25</sup> 1.3717, 55 g (19%) of 16 bp ca. 63°/0.6 mm, n<sub>D</sub><sup>25</sup> 1.3838, and 53 g (19%) of 18, bp ca. 88°/0.6 mm, n<sub>D</sub><sup>25</sup> 1.3966.

For 17: IR:  $4.75 \mu$  (C=C=N). PMR: 1.23 ppm (singlet, 9H). FMR: -72.94 ppm (triplet,  $J = 11.0$  Hz to doublet,  $J = 6.5$  Hz, 6F); -75.23 ppm (triplet,  $J = 0.2$  Hz to doublet,  $J = 11.0$  Hz, 6F); -93.97 ppm (multiplet, 2F); -163.25 ppm (multiplet, 1F) and -182.81 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{13}H_9F_{16}NS$ : C, 30.30; H, 1.76; F, 59.00; N, 2.72; S, 6.22.

Found: C, 30.22; H, 1.95; F, 60.22; N, 3.17; S, 6.32.

Mass measurement: 515.021, Calcd. 515.020.

For 16: IR:  $6.00 \mu$  (C=N). PMR: 1.05 ppm (multiplet, 9H); 1.14 ppm (multiplet, 9H), and 3.37 ppm (singlet, 1H). FMR: -73.03 ppm (multiplet, 3F); -75.19 ppm (multiplet, 9F); -89.99 ppm (multiplet, 1F); 158.80 ppm (multiplet, 1F) and -183.39 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{17}H_{19}F_{15}N_2S$ : C, 35.92; H, 3.37; F, 50.14; N, 4.93; S, 5.64.

Found: C, 36.13; H, 3.55; F, 50.18; H, 5.21; S, 5.93.

For 18: IR:  $4.82 \mu$  (C=C=N). PMR: 1.16 ppm (singlet, 18H). FMR: -74.16 ppm (multiplet, 6F); -75.79 ppm (multiplet to doublet,  $J = 11$  Hz, 6F); -164.30 ppm (multiplet, 1F); and -172.44 ppm (multiplet 1F).

Anal: Calcd. for  $C_{17}H_{18}F_{14}N_2S$ : C, 37.23; H, 3.31; F, 48.50; N, 5.11; S, 5.85.

Found: C, 37.40; H, 3.42; F, 50.99; N, 5.85; S, 6.05.

Hydrolysis of 17. 3,4,5,5,5-Pentafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-2-pentenamide (19) (nc)

Compound 2 (50 g) was added slowly with stirring to 50 ml of conc.  $H_2SO_4$  and the resulting solution allowed to stand overnight. Ice was added, the organic material extracted with methylene chloride and quickly distilled (ca.  $105^\circ/4mm$ ). Recrystallization from chloroform gave 5.6 g of 19, mp  $106-108^\circ$ .

IR: 5.93  $\mu$  (C=O). PMR: 7.3 ppm (broad 2H). FMR: -74.64 ppm (multiplet, 12F), -96.87 ppm (multiplet, 1F), -157.83 ppm (multiplet, 1F) and -182.20 ppm (multiplet, 1F).

Anal: Calcd. for  $C_9H_2F_{15}NSO$ : C, 23.64; H, 0.44; F, 62.34; N, 3.06; S, 7.01.

Found: C, 23.83; H, 0.68; F, 62.07; N, 3.53; S, 7.05.

Mass measurement: 456.9629, Calcd.: 456.9617.

#### Hydrolysis of 18 to 7.

Compound 1 (4.8 g) was added slowly with stirring to 10 ml of conc.  $H_2SO_4$ . Ice was added to the resulting solution to give 3.4 g of 7, recrystallized from chloroform, mp 122-123°. This compound had been characterized above as the product obtained by reacting the perfluorovinylsulfide with ammonia.

#### Ultraviolet Irradiation of 18 to give 21. 3(1,1-dimethylethylimino)-4,5,5,5-tetrafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-pentanenitrile (21) (nc).

A mixture of 25 g of the ketenimine 18 and 30 g of hexafluoropropene (HFP) sealed in a quartz tube was irradiated with a low pressure mercury lamp in an ice-cooled water bath for one week. Distillation gave 21 g of a mixture, bp 65-95°/2.8 mm containing some of 18 (infrared). It crystallized on standing and was recrystallized from petroleum ether to give 10g of 21, mp 64-65°.

IR: 4.54  $\mu$  (C $\equiv$ N). PMR: 1.32 ppm (multiplet, 9H) and 4.89 ppm (broad, 1H). FMR: -72.46 ppm and -73.32 ppm (two multiplets perhaps due to two isomers by a 1,3-hydrogen shift, total 6F), -74.94 ppm (multiplet, 6F), -163.18 ppm (multiplet, 1F), and -171.8 ppm and -173.34 ppm (two multiplets, total 1F).

Anal: Calcd. for  $C_{13}H_{10}F_{14}N_2S$ : C, 31.71; H, 2.05; F, 54.03; N, 5.69; S, 6.51.

Found: C, 31.86; H, 2.31; F, 53.78; N, 5.97; S, 6.38.

Reaction of 4 with Aniline. N-Phenyl-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-3-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-quinolinamine (22) (nc) and N,N'-Diphenyl-3-(phenylamino)-4,5,5,5-tetrafluoro-4-(trifluoromethyl)-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)-ethylthio]-2-pentenimidamide (24) (nc).

The perfluorovinylsulfide 4 (24 g, 0.05 m) in 25 ml tetrahydrofuran (THF) was added dropwise to 56 g (0.6 m) aniline in 100 ml THF and refluxed for 90 minutes. The mixture was then poured into dilute HCl, extracted with ether, the extract dried over  $MgSO_4$  and the ether removed to give about 20 g of crystals. By fractional recrystallization from methanol it was possible to separate pure samples of 22, mp 102-103° and 24, mp 110-111°.

The reaction was repeated but with 61 g (0.6 m) triethylamine added to the aniline solution. The reaction exothermed to 40° and was not heated. After 3 hours, the workup yielded 24 g of nearly pure 24.

For 22: PMR: 6.87 ppm to 8.15 ppm (broad area of multiplets, 10H). FMR: -71.24 ppm (multiplet, 3F), -74.46 ppm (multiplet, 6F); -75.56 ppm (multiplet, 3F), -156.68 ppm (multiplet, 1F) and -174.38 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{21}H_{10}F_{14}N_2S$ : C, 42.87; H, 1.71; F, 45.21; N, 4.76; S, 5.45.

Found: C, 42.85; H, 1.89; F, 44.81; N, 4.74; S, 6.70.

Mass measurement: 588.0336, Calcd.: 588.0340.

For 24: PMR: 5.92 ppm to 7.05 ppm (broad area of multiplets, 17H). FMR: -73.56 ppm (multiplet, 6F), -75.45 ppm (multiplet, 6F), -163.60 ppm (multiplet, 1F) and -174.53 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{27}H_{17}F_{14}N_3S$ : C, 47.58; H, 2.51; F, 39.03; N, 6.17; S, 4.71.

Found: C, 48.06; H, 2.71; F, 38.92; N, 6.34; S, 4.67.

Mass measurement: 681.0941, Calcd: 681.0918.



Reaction of 4 with p-Toluidine. 6-Methyl-N-(4-methylphenyl)-2-[1, 2, 2, 2-tetrafluoro-1-(trifluoromethyl)ethyl]-3-[1, 2, 2, 2-tetrafluoro-1-(trifluoromethyl)-ethylthio]-4-quinolamine (23) (nc) and N,N'-di-4-methylphenyl-3-(4-methylphenylamino)-4, 5, 5, 5-tetrafluoro-4-(trifluoromethyl)-2-[1, 2, 2, 2-tetrafluoro-1-(trifluoromethyl)-ethylthio]-2-pentenimidamide (25) (nc).

A solution of 24 g (0.05 m) of the perfluorovinylsulfide 4 in 25 ml of THF was added dropwise to a solution of 37.5 g (0.35 m) p-toluidine in 100 ml THF with stirring. After standing overnight, the mixture was poured into dilute HCl and extracted with ether. The ether extract was dried over  $MgSO_4$  and the ether removed. The residue crystallized and by fractional recrystallization from methanol 10.2 g of 25 and 5.0 g of 23 were isolated. When pure, compound 25 melted at 122-124° and 23 at 96-98°. In one run, recrystallization of the crude product from nitromethane gave a small amount (1.4 g) of orange crystals, mp 186-187°, which may be an isomer (cis-trans) of 25. When the reaction was run in the presence of triethylamine about equal amounts of 23 and 25 were isolated. When the amine was added to the olefin, only 23 was isolated.

For 23: PMR: 2.24 ppm (singlet, 3H), 2.36 ppm (singlet, 3H), (In F-11 solvent. In acetone the two methyl peaks overlap at 2.34 ppm), 6.75 ppm to 8.16 ppm (multiplets, 8H). FMR: -70.48 ppm (multiplet, 3F), -73.69 ppm (multiplet, 6F), -75.13 ppm (multiplet, 3F), -157.43 ppm (multiplet, 1F) and -172.17 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{23}H_{14}F_{14}N_2S$ : C, 44.81; H, 2.29; F, 43.15; N, 4.55; S, 5.20.

Found: C, 45.10; H, 2.52; F, 42.90; N, 4.60; S, 5.35.

For 25: PMR: 2.10 ppm (singlet, 6H), 2.33 ppm (singlet, 3H) and 6.59 ppm to 7.37 ppm (multiplets, 14H). FMR: -72.80 ppm (multiplet, 3F), -74.84 ppm (multiplet, 3F), -163.86 ppm (multiplet, 1F) and -174.36 ppm (multiplet, 1F).

Anal: Calcd. for  $C_{30}H_{23}F_{14}N_3S$ : C, 49.79; H, 3.20; F, 36.76; N, 5.81.

Found: C, 50.04; H, 3.35; F, 37.21; N, 6.05.

orange isomer Found: C, 47.34; H, 3.42; F, 35.03; N, 5.91.

Reaction of 2 with Diethylamine. N,N-Diethyl-1,3,3,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-1-penten-1-amine (26)

Flowers et al [4] have reported this compound without experimental details. HFP dimer 2 (45 g, 0.15 m) was added dropwise to 27.4 g (0.375 m) of diethylamine in 100 ml THF with stirring. The reaction was slightly exothermic. After standing overnight, water was added and the mixture extracted with ether. The ether extract was washed with water, dried and distilled to give 37 g (70%) of 26, bp 56°/3 mm,  $n_D^{25} = 1.3613$ .

IR: 5.95  $\mu$  (C=C). PMR: 0.88 ppm (triplet,  $J = 7.0$  Hz, 6H) and 3.08 ppm (multiplet, 4H). FMR: -53.65 ppm (multiplet, 1F and 3F), -81.30 ppm (triplet,  $J = 11.0$  Hz, 3F), -103.04 ppm (multiplet, 2F) and -124.82 ppm (multiplet, 2F).

Anal: Calcd. for  $C_{10}H_{10}F_{11}N$ : C, 34.01; H, 2.85; F, 59.17; N, 3.97.

Found: C, 34.35; H, 3.22; F, 58.85; N, 3.96.

Hydrolysis of 26. N,N-Diethyl-3,3,4,4,5,5,5-heptafluoro-2-(trifluoromethyl)pentanamide (28)

Flowers, et al [4] have reported this hydrolysis product without experimental details. Compound 26 (10 g) was stirred while adding slowly 10 ml of conc.  $H_2SO_4$ . Ice was then added and the mixture allowed to stand overnight. The crystals which formed were recrystallized from petroleum ether to give 2 g of 28, mp 46-49°.

IR: 5.98  $\mu$  (C=O). PMR: 0.97 ppm (quartet,  $J = 7$  Hz, 6H), 3.21 ppm (multiplet, 4H) and 4.1 ppm (multiplet, 1H). FMR: -61.82 ppm (multiplet, 3F), -82.92 ppm (triplet,  $J = 5.8$  Hz, 3F), AB pattern at -108.93 ppm, -111.91 ppm, -113.36 ppm and -116.40 ppm (all multiplets, 2F) and -125.42 ppm (multiplet, 2F).

Anal: Calcd. for  $C_{10}H_{11}F_{10}NO$ : C, 34.20; H, 3.16; F, 54.10; N, 3.99.  
 Found: C, 32.72; H, 3.09; F, 54.19; N, 3.61.

Reaction of 4 with Diethylamine. N,N-Diethyl-1,3,3,4,5,5,5-heptafluoro-2-[1,2,2-tetrafluoro-1-(trifluoromethyl)-ethylthio]-4-(trifluoromethyl)-1-penten-1-amine (27) (nc).

The perfluorovinylsulfide 4 (48 g, 0.1 m) was added dropwise with stirring to a solution of 18.3 g (0.25 m) of diethylamine in 100 ml of THF with cooling to keep at ca 35°. The mixture was then refluxed for two hours. After standing overnight, it was poured into water, extracted with ether, and the ether extract washed with water, dried, and distilled to give 4.94 g (92%) of 27, bp 142°/140 mm,  $n_D^{25} = 1.3766$ .

IR: 6.17  $\mu$  (C=C). PMR: 1.02 ppm (triplet,  $J = 7.2$  Hz, 6H) and 3.33 ppm (multiplet, 1H). FMR: -47.4 ppm (doublet,  $J = 48$  Hz, to doublet,  $J = 32$  Hz, 1F), -73.4 ppm (multiplet, 6F), -74.6 ppm (multiplet 6F), AB pattern at -83.5 ppm, -86.5 ppm, -93.5 ppm and -96.5 ppm (multiplets, 2F), -163.5 ppm (multiplet, 1F) and -181.8 ppm (doublet,  $J = 48$  Hz to multiplet, 1F). In the absence of an asymmetric carbon, the AB pattern must be due to a conformational preference.

Anal: Calcd. for  $C_{13}H_{10}F_{17}NO$ : C, 29.17; H, 1.88; F, 60.34; N, 2.62.  
 Found: C, 29.47; H, 1.86; F, 60.44; N, 2.74.

Hydrolysis of 27. N,N-Diethyl-3,4,5,5,5-pentafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-2-pentenamide (29) (nc).

The enamine 27 (20 g) was stirred while adding slowly 30 ml conc.  $H_2SO_4$ . The mixture was warmed and stirred on a steam bath one hour and ice added. The organic layer was distilled to give 8.15 g of amide 29, bp  $61^\circ/0.5$  mm,  $n_D^{25} = 1.3723$ .

IR:  $5.98 \mu$  (C=O). PMR: 0.92 ppm (multiplet, 6H) and 3.15 ppm (multiplet, 4H). FMR:  $-74.67$  ppm (multiplet, 6F),  $-75.04$  ppm (multiplet, 6F),  $-96.43$  ppm (multiplet, 1F),  $-157.90$  ppm (multiplet, 1F) and  $-183.40$  ppm (multiplet, 1F).

Anal: Calcd. for  $C_{13}H_{10}F_{15}NSO$ : C, 30.42; H, 1.96; F, 55.52; N, 2.73; S, 6.25.

Found: C, 30.48; H, 2.08; F, 56.82; N, 3.02; S, 6.15.

Reaction of 2 with Piperidine. 1-[3,3,3-Trifluoro-1-(pentafluoroethyl)-2-(trifluoromethyl)-1-propenyl]-piperidine (30) and 1-[1,3,3,4,4,5,5,5-octafluoro-2-(trifluoromethyl)-1-pentenyl]piperidine (31) (nc).

Flowers, et al [4] reported without details only product 30 from this reaction, but we found this was the minor product along with compound 31 formed from the terminally unsaturated isomer 3.

To a stirred solution of 32.6 g (0.375 m) piperidine in 100 ml THF was added dropwise 45 g (0.15 m) of HFP dimer 2. After addition was complete (exothermic to  $35^\circ$ ), the mixture was stirred for 2 hours and then cold water was added. It was extracted with ether, the ether extract washed with water, dried over  $MgSO_4$ , ether removed, and the residue distilled to give 9.03 g (16.5%) of compound 30, bp  $33^\circ/0.5$  mm, and 18.71 g (34.1%) of 31, bp  $47^\circ/0.3$  mm.

For 30: PMR: 1.44 ppm (broad singlet, 6H) and 3.17 ppm (broad singlet, 4H). FMR:  $-54.87$  ppm (multiplet, 3F),  $-60.16$  ppm (quartet,  $J = 9.1$  Hz, 3F),  $-80.23$  ppm (quartet,  $J = 8.0$  Hz, 3F) and  $-110.17$  ppm (quartet,  $J = 18$  Hz, 2F).

Anal. Calcd. for  $C_{11}H_{10}F_{11}N$ : C, 36.18; H, 2.76; F, 57.22; N, 3.84.

Found: C, 36.03; H, 2.93, F, 56.94; N, 3.86.

For 31: PMR: 1.47 (broad singlet, 6H) and 3.18 ppm (broad singlet, 4H). FMR: -53.10 ppm (multiplet, 3F), -56.87 ppm (multiplet, 1F), -81.31 ppm (triplet,  $J = 10.8$  Hz, 3F), -103.04 ppm (multiplet, 2F) and -124.97 ppm (quartet,  $J = 7.7$  Hz to doublet,  $J = 26$  Hz, 2F).

Anal: Calcd. for  $C_{11}H_{10}F_{11}N$ : C, 36.18; H, 2.76; F, 57.22; N, 3.84.

Found: C, 36.10; H, 2.93; F, 57.28; N, 3.98.

Hydrolysis of 31. 3,3,4,4,5,5,5-Heptafluoro-1-(1-piperidiny)-2-(trifluoromethyl)-1-pentanone (33) (nc).

Compound 31 (10 g) was stirred while adding slowly 10 ml of conc.  $H_2SO_4$  and the mixture was then warmed for one hour on a steam bath. Ice was added and the solid formed was recrystallized from petroleum ether to give 5.48 g of the amide 33, mp 80-82°.

IR: 5.99  $\mu$  (C=O). PMR: 1.41 ppm (broad singlet, 6H), 3.30 ppm (multiplet, 4H) and 4.22 ppm (multiplet, 1H). FMR: -62.03 ppm (multiplet, 3F), -80.98 ppm (triplet,  $J = 11$  Hz, 3F), AB pattern at -108.38 ppm, -111.38 ppm, -113.60 ppm and -116.63 ppm (multiplets, 2F) and -125.57 ppm (multiplet, 2F).

Anal: Calcd. for  $C_{11}H_{11}F_{10}NO$ : C, 36.38; H, 3.05; F, 52.31; N, 3.86

Found: C, 36.63; H, 3.45; F, 52.26; N, 3.37.

Reaction of 4 with Piperidine. 1-[1,3,3,4,5,5,5-Heptafluoro-2-(1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio)-4-(trifluoromethyl)-1-pentenyl]piperidine (32) (nc)

To a stirred solution of 21.7 g (0.25 m) of piperidine in 100 ml THF was added dropwise 48.2 g (0.1 m) of the perfluoro-vinylsulfide 4. The mixture exothermed to 45°, was refluxed for 2-1/2 hours, cooled, poured into cold water, and extracted with ether.

The ether extract was washed with water, dried over  $\text{MgSO}_4$ , ether removed, and the residue distilled to give 37 g (63%) of 32, bp  $85^\circ/0.5$  mm, which solidified and was recrystallized from pet ether, mp  $36-37^\circ$ .

PMR: 1.67 ppm (broad singlet, 6H) and 3.38 ppm (multiplet, 4H). FMR: -46.88 ppm (doublet,  $J = 42$  Hz to doublet  $J = 32$  Hz to multiplet, 1F), -73.30 ppm (multiplet, 6F), -74.82 ppm (doublet,  $J = 11$  Hz to multiplet, 6F), AB pattern at -86.15 ppm, -89.09 ppm, -94.78 ppm and -97.76 ppm (multiplets, 2F), -164.22 ppm (multiplet, 1F) and -183.27 ppm (doublet,  $J = 42$  Hz to multiplet, 1F). In the absence of an asymmetric carbon atom the AB pattern must be due to a conformational preference in the molecule.

Anal: Calcd. for  $\text{C}_{14}\text{H}_{10}\text{F}_{17}\text{NS}$ : C, 30.72; H, 1.84; F, 59.02; N, 2.56.

Found: C, 30.89; H, 1.86; F, 59.25; N, 2.51.

Hydrolysis of 32. 3,4,5,5,5-Pentafluoro-1-(1-piperidinyl)-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-trifluoromethyl-2-penten-1-one (34) (nc)

A mixture of 10 g of 32 and 10 ml conc.  $\text{H}_2\text{SO}_4$  sealed in a Carius tube was heated in a steam bath overnight and then added to cold water. The solid product was recrystallized twice from chloroform to give 3.2 g of the amide 34, mp  $53-55^\circ$ .

IR:  $6.00 \mu$  to  $6.10 \mu$  (C=C and C=O). PMR: 1.46 ppm (broad singlet, 6H) and 3.23 ppm (doublet,  $J = 18$  Hz to multiplet, 4H). FMR: -74.88 ppm (multiplet, 6F), -75.23 ppm (multiplet, 6F), -96.70 ppm (multiplet, 1F), -158.30 ppm (multiplet, 1F) and -184.20 ppm (multiplet, 1F). Smaller peaks were probably due to a minor isomer (cis-trans).

Anal: Calcd. for  $\text{C}_{14}\text{F}_{15}\text{NSO}$ : C, 32.01; H, 1.92; F, 54.25; N, 2.67.

Found: C, 32.55; H, 2.12; F, 54.10; N, 2.82.

Reaction of 2 with Hydroxylamine. 1,1,1,4,4,5,5,5-Octafluoro-2-(trifluoromethyl)-3-pentanone Oxime (35) (nc)

A mixture of 18 g (0.25 m) hydroxylamine hydrochloride, 80 ml of 10% NaOH solution (0.2 m) and 30 g (0.1 m) of HFP dimer 2 was sealed in a Carius tube and heated in a steam bath for 60 hr. The heavy layer was separated, washed with conc.  $H_2SO_4$  and distilled to give 19 g (61%) of 35, bp  $50^\circ/32$  mm,  $n_D^{25}$  1.3080. Gas chromatography showed two compounds present in different amounts in the distilled fraction. Separation by prep. chromatography gave a fraction which checked as a 90-10 mixture, apparently an equilibrium mixture because it remained the same on attempted re-separation. A tautomeric equilibrium is proposed, but characterization by nmr was not definitive. Crystals which separated on standing showed the same nmr.

PMR: 7.28 ppm (broad, exchanges with  $D_2O$ , 1H), 2.85 ppm (broad, 1/2H), and 1.8 ppm (broad with probable septet,  $J = 7.5$  Hz, 1/2H).

Anal: Calcd. for  $C_6H_2F_{11}NO$ : C, 23.02; H, 0.64; F, 66.77; N, 4.48.  
Found: C, 23.06; H, 0.99; F, 66.89; N, 4.70.

Reaction of 4 with Hydroxylamine. 1,1,1,4,5,5,5-Heptafluoro-2-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethylthio]-4-(trifluoromethyl)-3-pentanone Oxime (36) (nc)

To a solution of 80 ml of 10% NaOH in 100 ml THF was added 18 g (0.26 m) of hydroxylamine hydrochloride. To this solution was added 48 g (0.1 m) of the perfluorovinylsulfide 4, and the mixture was refluxed for two hours. The organic layer was separated, washed with water, dried, and distilled to give 27 g, bp  $119^\circ/100$  mm, which partially crystallized on standing. The pure compound boiled at  $92^\circ/20$  mm, mp  $55-56^\circ$  ( $CHCl_3$ ).

PMR and FMR were consistent with a mixture of the above tautomers.

Anal: Calcd. for  $C_9H_2F_{17}NOS$ : C, 21.83; H, 0.41; F, 65.23;  
N, 2.83; S, 6.48.

Found: C, 21.68; H, 0.65; F, 64.96;  
N, 3.01; S, 6.65.

Reaction of 2 with Carbonyl Fluoride. 3,3,4,4,5,5,5-  
Heptafluoro-2,2-bis(trifluoromethyl)pentanoyl Fluoride (38) (nc)

A mixture of 0.5 g silver oxide, 5 ml diglyme, 11 g  $COF_2$  and 30 g HFP dimer 2 was sealed in a Carius tube and heated to  $150^\circ$  for 8 hr. There was recovered 16.1 g of impure 2 and 15.5 g (42.3%) of the above acid fluoride, bp  $82^\circ$ .

IR:  $5.38 \mu$  (COF). FMR: -44.1 ppm (multiplet, 1F),  
-82.8 ppm (triplet,  $J = 12.8$  Hz, 3F), -63.4 ppm (multiplet, 6F),  
-107.9 ppm (multiplet, 2F) and -124.7 ppm (multiplet, 2F).

Anal. Calcd. for  $C_7F_{14}O$ : C, 22.97; F, 72.68.

Found: C, 22.79; F, 72.59.

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