of the central atom is clear from the figures in Table III. Only the result for $BInW_{11}$ falls somewhat out of line, unless we postulate a significant distortion of the BO_4 central tetrahedron, extrapolating the results obtained for the less symmetric h-$BW_{12}O_{40}$ isomer to the even less symmetric $BW_{11}O_{39}$ anion.[21,22] This line of reasoning is corroborated by the relative order of stability exposed above. Rhodium(III) is the only outer heteroelement present in $M\overset{-}{\cdot\cdot}O$ form[2c] at pH 5 (but not at pH 2); at pH 5 $XRh(O)W_{11}$ polytungstates are less stable than the (aquo–) iron(III) and (aquo–) chromium(III) homologues but not at pH 2. Possible preferential solvation effects should not be discounted, however.[23] The inversion of the order of stability with change of pH for group 3A elements has been explained previously.[2c] Another possible reason for the small exchange constant values is the low degree of delocalization of the single d electron on V(IV) over the polyanion, due to unfavorable overlap with the bridging oxygens' 2p orbitals.[22,23] This effect is more pronounced in polytungstates than in polymolybdates.[23] The argument is subject to caution, however.[23] Data on the homologous heteropolymolybdates are needed to judge its validity.

Conclusions

Keggin- and Dawson-type heteropolytungstate anions are convenient pentadentate ligands for many transition and group 3A elements, whose octahedral coordination is completed by a single, usually aquo, ligand. Exchange of this "sixth" ligand can be studied with simple techniques. The coordination approximates that of the corresponding aquo ion. For $XFe^{III}(OH_2)W_{11}$ and $X_2Fe^{III}(OH_2)W_{17}$ anions the conditional equilibrium exchange constants are for several ligands generally similar to those found for the substitution of a single ligand on the aquo ion, inasfar as such figures are available. The stabilization of higher oxidation states of the metal heteroatom in polytungstates leads to the obtention of air-stable mono(sulfito)–iron(III) derivatives. The exchange equilibrium between a trivalent heteroatom and vanadium(IV) present as $VO^{2+}(aq)$ is slow to establish; reproducible results have been obtained for the $In^{3+} \rightleftarrows V^{4+}$ exchange only. The exchange constants are much smaller than those generally found for $M^{2+} \rightleftarrows M^{3+}$ exchange, for reasons that are not yet completely clear.

Registry No. $K_5SiFe^{III}(OH_2)W_{11}O_{39}$, 81553-20-0; $K_5GeFe^{III}(OH_2)W_{11}O_{39}$, 81553-10-8; $K_9SiFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-67-4; $K_9GeFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-69-6; $K_4PFe^{III}(OH_2)W_{11}O_{39}$, 81553-16-4; $K_8PFe^{III}[Fe^{II}(CN)_6]W_{11}O_{39}$, 84774-65-2; $K_{11}P_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}$, 84750-80-1; $K_{11}As_2Fe^{III}[Fe^{II}(CN)_6]W_{17}O_{61}$, 84774-63-0; $K_7P_2Fe^{III}(OH_2)W_{17}O_{61}$, 81553-24-4; $K_7As_2Fe^{III}(OH_2)W_{17}O_{61}$, 81552-73-0; $K_6SiFe^{III}(SCN)W_{11}O_{39}$, 84774-61-8; $K_6GeFe^{III}(SCN)W_{11}O_{39}$, 84774-60-7; $K_5PFe^{III}(SCN)W_{11}O_{39}$, 84750-81-2; $K_7BFe^{III}(SCN)W_{11}O_{39}$, 84750-78-7; $K_6BFe^{III}(OH_2)W_{11}O_{39}$, 81552-94-5; $K_8P_2Fe^{III}(SCN)W_{17}O_{61}$, 84835-84-7; $K_8As_2Fe^{III}(SCN)W_{17}O_{61}$, 84835-83-6; $(gua)_5AsFe^{III}(SCN)W_{11}O_{39}$, 84750-83-4; $(gua)_4AsFe^{III}(OH_2)W_{11}O_{39}$, 81571-91-7; $K_7SiFe^{III}(SO_3)W_{11}O_{39}$, 84809-55-2; $K_7GeFe^{III}(SO_3)W_{11}O_{39}$, 84809-54-1; $K_6PFe^{III}(SO_3)W_{11}O_{39}$, 84774-70-9; $K_8BFe^{III}(SO_3)W_{11}O_{39}$, 84774-59-4; $K_9P_2Fe^{III}(SO_3)W_{17}O_{61}$, 84848-77-1; $K_9As_2Fe^{III}(SO_3)W_{17}O_{61}$, 84835-82-5; $(gua)_6AsFe^{III}(SO_3)W_{11}O_{39}$, 84774-72-1; $K_5SiIn(OH_2)W_{11}O_{39}$, 81553-61-9; $K_5GeIn(OH_2)W_{11}O_{39}$, 81553-46-0; $K_6BIn(OH_2)W_{11}O_{39}$, 81553-00-6; $K_4PIn(OH_2)W_{11}O_{39}$, 81553-59-5; $K_7P_2In(OH_2)W_{17}O_{61}$, 81553-63-1; $K_7As_2In(OH_2)W_{17}O_{61}$, 81552-83-2; $K_4Fe(CN)_6$, 13943-58-3; KSCN, 333-20-0; $KHSO_3$, 7773-03-7; VO^{2+}, 20644-97-7.

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Trifluoroacetyl Derivatives of *N*,*N*-Dimethylhydrazine, Urea, and Thiourea. Reaction of Hexafluoroacetylacetone with *N*,*N*-Dimethylhydrazine

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Received April 21, 1982

Trifluoroacetyl chloride was reacted in the presence of CsF with $(CH_3)_2NNH_2$, $H_2NC(S)NH_2$, and $H_2NC(O)NH_2$ to give $CF_3C(O)NHN(CH_3)_2$, $CF_3C(O)NHC(S)NHC(O)CF_3$ and $CF_3C(O)NHC(S)NH_2$, and $CF_3C(O)NHC(O)NH_2$, respectively. With $(C_2H_5)_3N$ as base, $CF_3C(O)NHN(CH_3)_2$ was also formed with $(CH_3)_2NNH_2$. Hexafluoroacetylacetone gave $CF_3C(=NN(CH_3)_2)CH=C(OH)CF_3$ with $(CH_3)_2NNH_2$.

Introduction

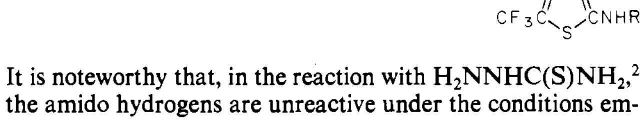
Studies of the reactions of trifluoroacetyl halides with amines[1] or substituted hydrazines[2,3] have shown that formation of the trifluoroacetamide derivative with concomitant loss of HX is the typical behavior.

$$CF_3C(O)X + RR'NH \xrightarrow{\text{solv}} CF_3C(O)NRR' + HX$$

$$R = R' = H;\ R = H,\ R' = \text{alkyl};$$
$$R = H,\ R' = H_2NNHC(S)$$

$$CF_3C(O)X + H_2NNHP_3N_3F_5 \rightarrow CF_3C(O)NHNHP_3N_3F_5 + HX$$

However, in some cases, elimination of HX occurs with subsequent intramolecular addition to the carbonyl function followed by elimination of water by heating in the presence of H_2SO_4 to form interesting heterocycles,[4,5] viz.



It is noteworthy that, in the reaction with $H_2NNHC(S)NH_2$,[2] the amido hydrogens are unreactive under the conditions employed. Thus, we were prompted to examine the reactions of $CF_3C(O)Cl$ with an unsubstituted amide ($NH_2C(O)NH_2$) and

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a thioamide ($NH_2C(S)NH_2$) as well as unsymmetric dimethylhydrazine ($(CH_3)_2NNH_2$) in order to compare the relative reactivities of the N–H bonds.

In contrast to trifluoroacetyl chloride, hexafluoroacetylacetone has been reacted with ammonia, primary amides, and hydrazine monohydrate to lose water to form imines, which may be cyclic.[6] Acyclic imine formation was noted here with unsymmetrical dimethylhydrazine.

Results and Discussion

The product isolated when $CF_3C(O)Cl$ and $(CH_3)_2NNH_2$ are reacted is independent of the base used. When triethylamine or CsF is used, the involatile white products that are formed are only partially soluble in diethyl ether. After evaporation of the ether solvent, a white solid that is readily sublimed at 27 °C (0.07 torr) was obtained. It was identified as $(CH_3)_2NNHC(O)CF_3$ (I).

$$CF_3C(O)Cl + (CH_3)_2NNH_2 \xrightarrow{(C_2H_5)_3N} \underset{\text{I}}{(CH_3)_2NNHC(O)CF_3}$$

An intense molecular ion (61% relative abundance at 17 eV) was observed in the mass spectrum.

In the ^1H NMR spectra of I resonance bands assigned to CH_3 occurred at δ 2.6 and 2.8. The area of the pair of peaks integrated to give the expected value relative to NH, i.e., 6:1. When a solution of I in $CDCl_3$ was heated to 50 °C, the resonance at δ 2.6 disappeared. It reappeared upon cooling to 25 °C. These results suggest that the presence of nonequivalent methyl groups must result from hindered rotation at nitrogen due to some double-bond character, which results from participation of the unshared pair of electrons on the nitrogen.

When slightly more than a 2-fold excess of $CF_3C(O)Cl$ was reacted with thiourea (11 mmol:5 mmol) in the presence of CsF, three compounds, $CF_3C(O)NHC(S)NH_2$ (II), $CF_3C(O)NHC(S)NHC(O)CF_3$ (III), and $(CF_3CO)_2NH$ (IV), were obtained. When the reaction time did not exceed 2–4 days, altering the stoichiometry did not change the relative amounts of products with IV invariably formed in the largest amounts. When the reaction was carried out in the presence of NaF, the reaction rate was slower and III and IV were the only products isolated.

A molecular ion is observed in the mass spectrum of the hygroscopic white solid, $CF_3C(O)NHC(S)NH_2$ (II). It is separated with difficulty from IV, and the elemental analyses data reflect this rather poor separation. *N*-(Trifluoroacetyl)thiourea was reported in a study of the leveling capacity of a copper-plating sulfate electrolyte.[7] However, no details of its synthesis or characterization were given. *N*,*N*′-Bis(trifluoroacetyl)thiourea (III) is an extremely hygroscopic yellow crystalline solid, which shows a molecular ion in its mass spectrum. When exposed to ambient air, III is rapidly hydrolyzed to $CF_3C(O)NHC(S)NH_2$ and $CF_3C(O)OH$, and after an exposure of about 2 days, only $H_2NC(S)NH_2$ was recovered.

Bis(trifluoroacetyl)amine (IV), was formed in small yields both with thiourea and urea. It is a feathery white solid, which has been well characterized.[8] It is interesting to note that, when $C_6F_5C(O)Cl$ was reacted with urea in the presence of pyridine,[9] $(C_6F_5CO)_2NH$ was the major product and $C_6F_5C(O)NHC(O)NHC(O)C_6F_5$ was a minor product.

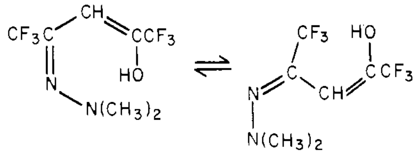
$$R_fC(O)Cl + H_2NC(E)NH_2 \rightarrow$$

$$E = O, S$$

$$[R_fC(O)NHC(E)NH_2] \xrightarrow{R_fC(O)Cl} [(R_fC(O))_2N^-] \rightarrow (R_fCO)_2NH$$

The compound $CF_3C(O)NHC(O)NH_2$ (V) had been prepared by the aqueous hydrolysis of fluorobis(trifluoromethyl)triazine.[10,11] However, the reaction of $CF_3C(O)Cl$ with urea in the presence of CsF provides a straightforward and nearly quantitative route to $CF_3C(O)NHC(O)NH_2$. The feathery white solid can be separated from the reaction mixture by sublimation at 60 °C. Small amounts of $(CF_3C(O))_2NH$ were also obtained. The substituted urea melts at 175–176 °C (lit. mp 189 °C). The degree of purity based on elemental analyses, a molecular ion in the mass spectrum, and the ^{19}F and ^1H NMR spectral data suggest that the lower melting point is the correct one for the pure compound. This compound is not hygroscopic.

When a small molar excess of hexafluoroacetylacetone was reacted with $(CH_3)_2NNH_2$ (11 mmol:10 mmol), colorless crystals and a very dense yellow liquid were formed. The former were sublimed at 50 °C under static vacuum and shown to be $CF_3C(=NN(CH_3)_2)CH=C(OH)CF_3$ (VI). Upon heating >80 °C, decomposition to a yellow liquid occurred. A molecular ion was observed in the mass spectrum of the solid. On the basis of ^{19}F and ^1H NMR spectral data, the syn and anti forms of the molecule appear to be present in a 4:1 ratio. The yellow liquid was not identified.



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The chemical shifts, relative areas, and assignments of resonance bands in the ^1H NMR spectrum were δ 15.8 (4, OH), 5.6 (4, CH), and 2.8 (24, CH_3) for the syn form and δ 10.6 (1, OH), 5.7 (1, CH), and 2.6 (6, CH_3) for the anti form. The band at δ 2.8 for the syn form is a doublet, which arises from coupling with the OH proton as is demonstrated by spin–spin decoupling experiments. This suggests through-space coupling between OH and CH_3, a phenomenon frequently observed in fluorinated compounds but more rarely in protonated ones. The bands in the ^{19}F NMR spectrum were ϕ −68.9 (4) and −72.9 (4) for the syn form and ϕ −66.6 (1) and −76.5 (1) for the anti form. In the anti form, the CF_3 resonance at ϕ −66.6 is a doublet arising from coupling with the OH proton.

Experimental Section

Materials. All reagents were used as received from commercial suppliers without further purification with the exception of hexafluoroacetylacetone, which was converted to the tetraol and then dehydrated. Sources were as follows: $CF_3C(O)Cl$, PCR Research Chemical Co., Inc.; $(CH_3)_2NNH_2$ and $H_2NC(S)NH_2$, Aldrich Chemical Co.; $H_2NC(O)NH_2$, Fisher Scientific Co.; $CF_3C(O)CH_2C(O)CF_3$, Columbia Organic Chemical Co.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex-glass vacuum manifold equipped with a Heise-Bourdon tube gauge and a Televac vacuum gauge, which were connected directly to the manifold. Gaseous materials were measured with the assumption of the ideal gas law. Involatile materials were weighed. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cm cell equipped with KBr windows for volatile compounds, and spectra of solids were recorded as KBr disks.

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^{19}F NMR spectra were obtained on a Varian EM-360 L spectrometer and a JEOL FX-90Q spectrometer operating at 54.6 and 84.26 MHz, respectively. ^{1}H NMR spectra were recorded on either a Varian EM-360 or EM-360L spectrometer operating at 60.0 MHz or a JEOL FX-90Q spectrometer at 89.56 MHz. All bands are reported relative to CCl_3F or Me_4Si. The usual solvents were $CDCl_3$ and/or CD_3SOCD_3. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, or at the University of Idaho.

Reaction of $CF_3C(O)Cl$ with $(CH_3)_2NNH_2$. A. Using $(C_2H_5)_3N$. Ten millimoles (0.60 g) of $(CH_3)_2NNH_2$ and approximately 10 mL of $(C_2H_5)_3N$ were mixed in a 250-mL Pyrex flask. After 8 mmol of $CF_3C(O)Cl$ was condensed onto the mixture at −196 °C, the flask was warmed to and maintained at 25 °C for 12 h. The volatile materials ($(CH_3)_2NNH_2$ and $(C_2H_5)_3N$) were distilled away under vacuum, and the white solid residue was extracted with ether. The material insoluble in ether was identified as $(C_2H_5)_3NH^+Cl^-$ by comparison of its infrared spectrum with that of an authentic sample. After the ether was evaporated, the white residue was sublimed at 27 °C (0.06 torr) to give pure $(CH_3)_2NNHC(O)CF_3$ (I). The white crystalline solid melts at 85–87 °C. The mass spectrum shows a molecular ion at *m/e* 156 in 61% relative abundance and other appropriate fragments. The infrared spectrum which was recorded as a KBr disk is as follows: 3030 (vs), 2840 (s), 2705 (m), 1630 (vs), 1480 (m), 1470 (m), 1460 (m), 1370 (s), 1210 (vs), 1175 (vs), 1150 (sh), 1100 (sh), 1000 (w), 950 (s), 780 (m), 730 (s), 600 (m), 555 (m), 445 (m), 405 (m) cm^{-1}. The ^{19}F NMR spectrum contains a single resonance at ϕ −75.5. The ^{1}H NMR spectrum contains bands at δ 2.6, 2.8 (CH_3 combined area ratio, 6), and 7.3–8.7 (NH, broad, 1).

Anal. Calcd for $C_4F_3N_2OH_7$: C, 30.78; H, 4.52; N, 17.95. Found: C, 30.73; H, 4.70; N, 17.95.

B. Using CsF. The reaction was carried out as in part A with CsF as base instead of $(C_2H_5)_3N$. The product was easily separable from the ether-insoluble residue.

Reaction of $CF_3C(O)Cl$ with $H_2NC(S)NH_2$. The reaction was carried out as above by using CsF as the base and 5 mmol of $H_2NC(S)NH_2$ with ~11 mmol of $CF_3C(O)Cl$. The reaction vessel contained a product mixture of yellow and white solids. When the mixture was sublimed at 40 °C, yellow crystals appeared on the cold finger and were identified as $CF_3C(O)NHC(S)NHC(O)CF_3$. Prolonged sublimation caused some white crystals to appear on the cold finger. These were identified as $CF_3C(O)NHC(S)NH_2$. When the stoichiometry was changed, e.g., smaller amounts of $CF_3C(O)Cl$ to encourage formation of $CF_3C(O)NHC(S)NH_2$, the disubstituted species was invariably the major product. When a larger excess of $CF_3C(O)Cl$ was used, a white featherlike crystal which sublimed easily at 25 °C in the vacuum manifold was obtained and identified as $(CF_3CO)_2NH$ on the basis of infrared and mass spectral analysis and elemental analysis data.[8]

$CF_3C(O)NHC(S)NH_2$ (II) is a hygroscopic white crystalline solid, which melts at 117–118 °C. The mass spectrum has the molecular ion (*m/e* 172) as the base peak. The infrared spectrum is as follows: 3375 (vs), 3350 (vs), 3235 (vs), 3175 (vs), 3140 (sh), 3060 (sh), 1735 (vs), 1720 (sh), 1600 (vs), 1545 (sh), 1535 (vs), 1440 (m), 1380 (m, br), 1320 (s), 1290 (s), 1210 (vs), 1170 (vs), 1135 (vs), 1105 (sh), 1100 (sh), 990 (s), 915 (m), 805 (m), 775 (w), 715 (s), 650 (s), 600 (m), 570 (s, br), 520 (w), 445 (w) cm^{-1}. The ^{19}F NMR spectrum contains a single resonance at ϕ −77.1 and the ^{1}H NMR spectrum has two broad peaks at δ 11.0 (1) and 9.0 (2).

Anal. Calcd for $C_3F_3OSN_2H_3$: C, 20.93; H, 1.74; N, 16.28. Found: C, 19.38, H, 2.44; N, 16.10.

$CF_3C(O)NHC(S)NHC(O)CF_3$ (III) is an extremely hygroscopic yellow crystalline solid, which melts at 42–44 °C. The mass spectrum has the molecular ion (*m/e* 268) as the base peak. The infrared spectrum is as follows: 3530 (sh), 3390 (sh), 3280 (s), 3180 (sh), 3050 (m), 1775 (s), 1735 (vs), 1700 (sh), 1600 (sh), 1580 (m), 1510 (vs, br), 1330 (sh), 1260 (vs), 1220 (vs), 1165 (vs), 1130 (s), 990 (w), 920 (m), 885 (w), 800 (w), 760 (w), 750 (m), 720 (m), 655 (w), 625 (m), 600 (w, br), 520 (w), 485 (w), 450 (sh) cm^{-1}. The ^{19}F NMR spectrum has a single resonance at ϕ −76.7, and the ^{1}H NMR spectrum has a single broad resonance at δ 11.0.

Anal. Calcd for $C_5F_6N_2O_2SH_2$: C, 22.39; H, 0.75; N, 10.45; F, 42.50. Found: C, 22.72; H, 0.98; N, 11.13; F, 41.50.

Reaction of $CF_3C(O)Cl$ with $H_2NC(O)NH_2$. A 10% molar excess of $CF_3C(O)Cl$ was added to a mixture of $H_2NC(O)NH_2$ and CsF as above. $CF_3C(O)F$ was recovered as the only volatile material. After sublimation of 60 °C for several hours, white crystalline $CF_3C(O)NHC(O)NH_2$ (V), which melts at 175–176 °C, was obtained (yield based on $H_2NC(O)NH_2$ ~99%). When a larger excess of $CF_3C(O)Cl$ was used, small amounts of $(CF_3CO)_2NH$ were obtained in addition to $CF_3C(O)NHC(O)NH_2$. The mass spectrum contains a molecular ion at *m/e* 156 with a relative abundance of 34%. The infrared spectrum is as follows: 3480 (vs), 3420 (vs), 3230 (s), 3020 (s), 1745 (vs), 1705 (vs), 1605 (s), 1500 (s), 1390 (vs), 1320 (s), 1220 (vs), 1190 (vs), 1165 (vs), 1100 (vs), 960 (s), 910 (w), 810 (w), 780 (w), 740 (m), 710 (m), 660 (m), 630 (m), 570 (w), 525 (w), 495 (w) cm^{-1}. The ^{19}F NMR spectrum has a single resonance at ϕ −77.5. The ^{1}H NMR spectrum measured in $CDCl_3/CD_3SOCD_3$ has bands at δ 7.6–7.2 (NH_2, br, 2) and at 11.4 (NH, 1).

Anal. Calcd for $C_3F_3O_2N_2H_3$: C, 23.08; H, 1.90; N, 17.95. Found: C, 22.76; H, 1.90; N, 18.22.

Reaction of $CF_3C(O)CH{=}C(OH)CF_3$ with $(CH_3)_2NNH_2$. Eleven millimoles of $CF_3C(O)CH{=}C(OH)CF_3$ was mixed with 10 mmol of $(CH_3)_2NNH_2$ in a 250-mL Pyrex glass vessel. After 2 days at 25 °C, the volatile material (unreacted $CF_3C(O)CH{=}C(OH)CF_3$) was removed under vacuum. Remaining in the reactor were colorless crystals and a very dense yellow liquid. The crystals, which sublimed at ~50 °C under static vacuum, were identified as $CF_3C({=}NN(CH_3)_2)CH{=}C(OH)CF_3$ (VI) (mp 65–66 °C). The mass spectrum contains a molecular ion at *m/e* 250 with a relative abundance of 72%. $(M - OH)^+$ is also a prominent peak. The infrared spectrum is as follows: 3120 (w, br), 3000 (w), 2970 (w), 2945 (w), 2900 (w), 2870 (w), 2830 (w), 2790 (w), 1645 (s), 1605 (vs), 1470 (w), 1455 (w), 1440 (m), 1350 (m), 1270 (vs), 1210 (vs), 1180 (vs), 1150 (vs), 1100 (m), 1040 (w), 1015 (w), 970 (m), 920 (w), 860 (w), 715 (w), 680 (m), 605 (m), 580 (w) cm^{-1}. The ^{19}F NMR spectrum contains four bands at ϕ −66.6 (d, 1), −68.9 (s, 4), −72.9 (s, 4), and −76.5 (s, 1). The ^{1}H NMR spectrum has bands at δ 15.8 (s, 4), 10.6 (s, 1), 5.7 (s, 1), 5.6 (s, 4), 2.8 (d, 24), and 2.6 (s, 6).

Anal. Calcd for $C_7F_6ON_2H_8$: C, 33.60; H, 3.20; N, 11.20. Found: C, 33.75; H, 3.17; N, 11.39.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-8100156) for support of this research. We thank Dr. Gary Knerr and Charles Barinaga for mass and ^{19}F NMR spectral data.

Registry No. I, 40348-34-3; II, 34067-44-2; III, 84802-75-5; V, 760-41-8; VI, 84802-76-6; $CF_3C(O)Cl$, 354-32-5; $(CH_3)_2NNH_2$, 57-14-7; $H_2NC(S)NH_2$, 62-56-6; $H_2NC(O)NH_2$, 57-13-6; $CF_3C(O)CH_2C(O)CF_3$, 1522-22-1; $(C_2H_5)_3N$, 121-44-8; CsF, 13400-13-0.