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F-Ethylamine and F-Ethylimine

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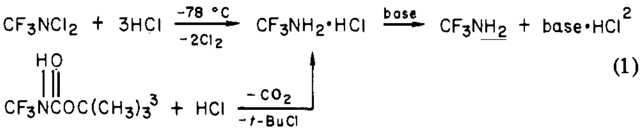
Abstract: The new compounds *F*-ethylamine, $C_2F_5NH_2$, and *F*-ethylimine, $CF_3CF{=}NH$, are readily prepared by the reaction of *N*,*N*-dichloro-*F*-ethylamine with trimethylsilane at -45 or -25 °C, respectively. Both compounds are subject to dehydrofluorination. Thus, $CF_3CF{=}NH$ may be obtained by the loss of a single HF molecule from $CF_3CF_2NH_2$ at -25 °C. $CF_3CF_2NH_2$ will react with SF_4 to form $CF_3CF_2N{=}SF_2$. Similarly, $CF_3CF{=}NH$ forms $CF_3CF{=}NCl$ with ClF in the presence of CsF.

Compounds containing fluorine and (non-carbon-bonded) hydrogen in a geminal or vicinal neighborhood have long raised the interest of synthetic chemists because of their inherent instability toward the facile loss of HF under ambient conditions. However, through the use of appropriate experimental conditions many of these compounds have been isolated recently, characterized, and, in some instances, used as reaction precursors. A case in point is the synthesis of HOF which was predicted, on the basis of thermodynamic arguments, to be stable in a low-temperature matrix only, but is, in fact, now a well-studied compound.[1] Additionally, the fluorinated alcohols, CF_3OH[2] and SF_5OH[2], as well as *F*-methylamine, CF_3NH_2,[2,3] have been described. The general method for the amine is



$$CF_3NCl_2 + 3HCl \xrightarrow[-2Cl_2]{-78\ °C} CF_3NH_2{\cdot}HCl \xrightarrow{base} \underline{CF_3NH_2} + base{\cdot}HCl^{2}$$

$$CF_3N(H)C(=O)OC(CH_3)_3{}^{3} + HCl \xrightarrow[-t\text{-}BuCl]{-CO_2} CF_3NH_2{\cdot}HCl \qquad (1)$$

In this paper, we describe a route to the new compounds *F*-ethylamine, $C_2F_5NH_2$, and *F*-ethylimine, $CF_3CF{=}NH$, which, although resulting in somewhat lower yields, is more straightforward than those utilized in the case of CF_3NH_2[2,3] and is generally applicable. A direct synthesis of $CF_3CF{=}NCl$ is now possible.

Results and Discussion

F-Ethylamine was formed at -45 °C and was stable in Pyrex glass at that temperature for an extended period. The reaction of *N*,*N*-dichloro-*F*-ethylamine with trimethylsilane produced *F*-ethylamine in yields of 40% (eq 2) and has the advantage that

$$CF_3CF_2NCl_2 + 2(CH_3)_3SiH \xrightarrow{-45\ °C} CF_3CF_2NH_2 + 2(CH_3)_3SiCl \qquad (2)$$

the pure amine can be removed at -95 °C under dynamic vacuum. Because CF_3NH_2 exhibits some basic character, in the literature methods,[2,3] both of which utilize HCl as one of the reactants, it must be freed from its hydrochloride by the addition of a base.

The infrared spectrum which can be obtained in a Pyrex gas cell at 25 °C has the features appropriate to an *F*-alkylamine, i.e., asymmetric and symmetric N-H stetching bands at 3465 and 3385 cm^{-1} and a relatively intense N-H deformation band at 1605 cm^{-1}. Stretching and deformation modes are observed for the carbon-fluorine bonds in the molecule. A molecule ion is not observed in the mass spectrum. The highest *m/e* 115 arises from loss of HF to form the *F*-alkylimine, $CF_3CF{=}NH^+$. However, the ^{19}F NMR spectrum clearly shows two chemically different types of fluorine in the ratio of 3:2. There is no fluorine-fluorine coupling but the amine hydrogens do couple with both the CF_3 and CF_2 fluorine atoms, giving triplets ($^4J_{F-H}$ = 3.0 Hz; $^3J_{F-H}$ = 9.0 Hz). The ^1H NMR spectrum consists of a very broad peak at δ 5.10.

When equimolar amounts of $CF_3CF_2NH_2$ and SF_4 were allowed to warm slowly from -196 to 25 °C in the presence of excess CsF, it was possible to isolate $CF_3CF_2N{=}SF_2$[4] in 40% yield (see eq 3). Additional evidence for the existence of $CF_3CF_2NH_2$ arises

$$CF_3CF_2NH_2 + SF_4 \xrightarrow[-196\ to\ +25\ °C]{CsF} CF_3CF_2N{=}SF_2 + CsF{\cdot}nHF \qquad (3)$$

from the fact that it is possible to observe the decomposition of $CF_3CF_2NH_2$ to $CF_3CF{=}NH$ in a period of about 3 min by monitoring the diminution of the bands assigned to ν_{NH_2} and the concomitant growth of bands at 3325 and 1680 cm^{-1} which can be assigned to ν_{NH} and $\nu_{C=N}$ of the imine (see eq 4). During this

$$CF_3CF_2NH_2 \xrightarrow{25\ °C} CF_3CF{=}NH + HF \qquad (4)$$

period $\nu_{C\equiv N}$ of CF_3CN is not observed. The imine can be prepared in good yield from allowing reaction 5 to occur at -25 °C. At

$$CF_3CF_2NCl_2 + (CH_3)_3SiH \xrightarrow{-25\ °C} CF_3CF_2NH_2 + (CH_3)_3SiCl \qquad (5)$$

$$CF_3CF_2NH_2 \rightarrow CF_3CF{=}NH + HF$$

$$HF + (CH_3)_3SiCl \rightarrow (CH_3)_3SiF + HCl$$

-25 °C, $CF_3CF{=}NH$ is stable with respect to dehydrofluorination, and although it probably arises because of the thermal instability of the $CF_3CF_2NH_2$ formed initially, it can be isolated from this reaction mixture.

A molecular ion *m/e* 115 was observed in the mass spectrum, and the ^{19}F NMR showed a doublet (CF_3) at ϕ -71.8 and a quartet (CF) at ϕ -42.5 (J_{F-F} = 5.3 Hz). No fluorine-hydrogen coupling occurred, and the ^1H NMR is a broad singlet at δ 5.49.

Although $CF_3CF{=}NH$ is also unstable with respect to dehydrofluorination when retained at 25 °C for more than a few minutes, it can be reacted with ClF in the presence of CsF at -78 °C. This provides an easy direct route to *N*-chloro-*F*-ethylimine.[5] The chlorimine is thermally stable.

This new route to $CF_3CF_2NH_2$ and $CF_3CF{=}NH$ is more convenient, requiring less manipulation of the product mixture than those described earlier. It is easily possible to synthesize sufficient quantities of these two rather unstable materials and to store them at low temperatures for long periods, which makes studying their reaction chemistry attractive.

Experimental Section

Materials. *F*-Acetonitrile (PCR, Inc.), chlorine monofluoride (Ozark-Mahoning), and trimethylsilane (PCR, Inc.) were used as received. *N*,*N*-Dichloro-*F*-ethylamine was prepared by using the literature method.[6]

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General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube gauge. Volatile starting materials and products were measured quantitatively by PVT techniques. Known products were confirmed on the basis of spectral data of authentic samples.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer with a 5-cm gas cell fitted with KBr windows. The ^{19}F NMR spectra were obtained by using a Varian HA-100 with CCl_3F as an internal reference. The ^1H NMR spectra were measured with a Varian EM-360 spectrometer with $(CH_3)_4Si$ as an internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV. All nuclear magnetic resonance shifts are assigned negative values for positions upfield from the reference.

***F*-Ethylamine.** *N*,*N*-Dichloro-*F*-ethylamine, $CF_3CF_2NCl_2$ (1 mmol) and $(CH_3)_3SiH$ (2 mmol) were condensed into a Pyrex glass reaction vessel at −196 °C. The mixture was allowed to warm slowly to −45 °C and was maintained at this temperature for 1.5 h. At −95 °C, the *F*-ethylamine, $CF_3CF_2NH_2$, was removed from the reaction vessel under dynamic vacuum and transferred into a tube at −196 °C. The yield was approximately 40%. Trimethylsilyl chloride, unreacted trimethylsilane, and *N*,*N*-dichloro-*F*-ethylamine remained in the trap at −95 °C. The new amine melted at ~−38 to −40 °C. Although $CF_3CF_2NH_2$ decomposes rapidly at room temperature, it is possible to obtain a gas-phase infrared spectrum with bands at 3465 (m) ($\nu_{as}(NH_2)$), 3385 m ($\nu_s(NH_2)$), 1605 (s) (δ (NH_2)), 1250 (sh), 1220 (vs, br), 1070 (s), 990 (w), 900 (vs), 845 (vs), 748 (s), 630 (w), 475 (s) cm^{-1}. A molecular ion is not observed in the mass spectrum but peaks at *m/e* 115 (CF_3CFNH^+, 18%), 114 ($C_2F_4N^+$, 18%), 95 ($C_2F_3N^+$, 58%), and 69 (CF_3^+, 100%) are present. The ^{19}F NMR spectrum showed a triplet at ϕ −87.0 ($^4J_{F-H}$ = 3 Hz) and a triplet at ϕ −86.1 ($^3J_{F-H}$ = 9 Hz). No CF_3–CF_2 coupling occurs. The formation of $CF_3CF{=}NH$ can be observed as $CF_3CF_2NH_2$ decomposes in the IR gas cell. The $\nu(NH_2)$ features rapidly decrease in intensity with the concomitant appearance of new $\nu(NH)$ bands. After 3 min, the decomposition to imine is complete.

Reaction of $CF_3CF_2NH_2$ with SF_4. Equimolar amounts (0.6 mmol) of *F*-ethylamine and SF_4 were condensed into a Pyrex glass reactor at −196 °C which contained an excess of CsF. The mixture was warmed slowly to −45 °C and then to 25 °C over 8 h. After trap-to-trap distillation, $CF_3CF_2N{=}SF_2$ (40%), which was collected in a trap at −78 °C, was identified by its infrared spectrum.[4]

***F*-Ethylimine.** If the mixture of $CF_3CF_2NCl_2$ and $(CH_3)_3SiH$ was maintained at −25 °C for 1 h, no $CF_3CF_2NH_2$ was obtained but rather $CF_3CF{=}NH$. The product mixture was held at −78 °C and the volatile materials were removed under dynamic vacuum. After trap-to-trap separation, $CF_3CF{=}NH$ (60% yield), $(CH_3)_3SiF$, and small amounts of HCl were recovered. The gas-phase IR spectrum has bands at 3325 (m) ($\nu(NH)$), 1680 (s) ($\nu(C{=}N)$), 1300 (s), 1225 (vs), 1190 (vs), 1140 (vs), 1065 (w br), 875 (s), 735 (s) cm^{-1}. A molecular ion is observed at *m/e* 115 (M^+, 20%) in the mass spectrum. In addition, other peaks at *m/e* 114 ($C_2F_4N^+$, 22%), 95 ($C_2F_3N^+$, 61%), and 69 (CF_3^+, 100%) are present. The ^{19}F NMR spectrum measured at ambient temperature showed a doublet at ϕ −71.8 and a quartet at ϕ −42.5 (J_{F-F} = 5.3 Hz). The ^1H spectrum consisted of a broad singlet at δ 5.49. After about 12 min in the infrared cell at ambient temperature, decomposition of the imine to nitrile, CF_3CN, is complete.

***N*-Chloro-*F*-ethylimine.** Equimolar amounts (0.7 mmol) of $CF_3CF{=}NH$ and ClF were condensed at −196 °C into a Pyrex tube which contained an excess of CsF. The mixture was allowed to warm slowly to −78 °C and finally to 25 °C overnight. It was separated by trap-to-trap distillation and $CF_3CF{=}NCl$ was isolated in a trap at −78 °C. It was identified from its infrared spectrum.[5]

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π-Arene Complexes of Nickel(II). Synthesis (from Metal Atoms) of (π-Arene)bis(pentafluorophenyl)nickel(II). Properties, π-Arene Lability, and Chemistry

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Abstract: A new series of transition-metal–π-arene complexes has been prepared by a metal atom synthetic method. The deposition of Ni vapor, C_6F_5Br, and arenes has produced high yields of $(C_6F_5)_2Ni$–π-arene complexes. A variety of π-arene ligands are η^6 bound by the $(C_6F_5)_2Ni$ moiety, resulting in soluble highly labile materials, where the π-arene ligand is exchangeable at room temperature. These complexes have not been isolable when σ-bonding ligands other than C_6F_5 have been employed. The formation of the π-toluene complex proceeds through a pseudostable C_6F_5NiBr species that can be trapped at −80 °C with R_3P but decomposes by reductive elimination of C_6F_5–C_6F_5 in the absence of R_3P or electron-rich arenes. It is likely that C_6F_5NiBr–π-arene is formed initially, which then disproportionates to $(C_6F_5)_2Ni$–π-arene and $NiBr_2$. Due to the high lability of the π-arene ligand, these complexes possess a rich chemistry. Displacement of the π-arene ligand can be carried out cleanly and in high yield by $P(Et)_3$, 1,5-cyclooctadiene, and THF to form $(C_6F_5)_2NiL_2$. Treatment of (π-toluene)bis(pentafluorophenyl)nickel (**1**) with norbornadiene at 0 °C causes the formation of a high polymer of norbornadiene as well as (π-norbornadiene)bis(pentafluorophenyl)nickel, which appears to be either the active polymerization catalyst or its precursor. Similarly, treatment of **1** with 1,3-butadiene at 25 °C and <1 atm causes the formation of a new organometallic compound and the production of cyclic tetramers of 1,3-butadiene. When **1** was treated with cyclopentadiene at 0 °C, a rapid production of C_6F_5H was observed with the subsequent formation of a dimeric nickel complex $(C_6F_5)_2(Cp)_2Ni_2(C_5H_6)$ where the Ni atoms appear to be bound together through a mutually π-bonded cyclopentadiene (C_5H_6) ligand. Reductive elimination reactions have also been induced under mild conditions by addition of CO or C_2H_4. With CO a nearly quantitative production of $C_6F_5C_6F_5$ and $Ni(CO)_4$ took place. Lastly, **1** served as a short-lived arene hydrogenation catalyst at room temperature.

Introduction

π-Arene complexes of the group 8 transition metals have been of considerable interest in recent years.[2] This interest is probably due to the high reactivity these complexes possess both chemically[2] and catalytically.[3] This high reactivity is manifested in the lability of the π-arene bond and the fact that arenes can bind to these metals in η^6-, η^4-, or η^2-coordination.

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(2) See R. G. Gastinger and K. J. Klabunde, *Transition Met. Chem.*, **4**, 1 (1979), a review of this area.

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