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Synthesis of (*E*)- and (*Z*)-1-*H*-Difluoromethanimine

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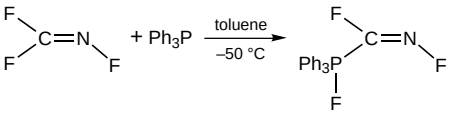
The kinetic stabilization affected by substitution of fluorine for hydrogen in many small molecules is well-known. Although the simplest imine, methanimine CH_2═NH, is unstable to polymerization even at low pressures,[1] the fluorinated analogue CF_2═NF is stable over a wide range of conditions.[2] Perfluoromethanimine is reactive towards nucleophiles and strong electrophiles and a range of interesting chemistry has been demonstrated for fluoride promoted reactions.[3]

In contrast other simple fluorinated methanimines, $CH_xF_{3-x}N$ (x = 1,2) have been of theoretical interest,[4] but only CF_2═NH has been isolated.[5] 1,1-Difluoromethanimine has low stability and readily undergoes a net disproportionation to FCN and CF_3NH_2. Calculations preduct higher stability for increasing fluorine substitution in methanimines and the *E* (**1**) and *Z* (**2**) isomers of CFH═NF are of interest. For the latter, a 1,2-elimination of HF may be less favorable than in CF_2═NH.

A possible route to CFH═NF is suggested by the reactions of 1,1-difluoroalkenes with tributylphosphine which inserts into the C−F bond forming a fluorophosphorane.[6] The latter are not easily isolated but can be converted stereoselectively to the respective (*E*)- or (*Z*)-1-*H*-alkenes by reaction with water. With 1,1-difluoro-2-azaalkenes, reactions with triphenylphosphine lead to α-defluorination and the respective isonitrile, indicating the probable formation of a related intermediate fluorosphosphorane.[7] We reasoned that CF_2═NF might react with triphenylphosphine forming a phosphorane that could lead to CHF═NF by hydrolysis or to the highly desirable but unknown C≡NF by α-elimination.

The reaction of CF_2═NF with triphenylphosphine produces a moderately stable intermediate fluorophosphane, (*Z*)-$FPPh_3$-CF═NF (**3**).



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The stereochemisry of **3** was established by low temperature ^{19}F and ^{31}P NMR spectroscopy. The *trans* orientation of the two fluorine atoms of the imine group is clearly indicated by the large coupling constant ($^3J_{FF}$ = 189 Hz) which is usually observed for *trans* fluorine atoms in alkenes and related compounds.[8] With the exception of the phenyl hydrogen atoms and the missing $^3J_{PF}$ coupling between the phosphorus and the N−F atoms, all abundant $I_{1/2}$ nuclei couple noticeably in the ^{19}F spectrum, generating sets of doublets in the NMR.

In addition to **3**, the other major product in this reaction is Ph_3PF_2 in about 60% by ^{19}F NMR.[9] This probably results from an α-elimination of fluorine forming C≡N−F or its isomer F−C≡N by a 1,2-fluoride elimination. We saw no evidence for C≡N−F but $(FCN)_3$ was observed by NMR in several reactions, suggesting that a 1,2-elimination was operative. Support for this was obtained by reaction of CF_3CF═NF under similar conditions: CF_3CN and Ph_3PF_2 were formed in high yield with no evidence for the intermediate phosphorane.

Even under very dry conditions, ^{19}F NMR experiments with **3** showed the presence of two multiplets at δ −111 and −47 whose intensity varied considerably for different trials. When toluene which had not been dried was used, the intensity of the multiplets increased considerably. From the coupling constants for the peak at −111 (J = 211 and 89 Hz) we believed that (*E*)-CHF═NF (**1**) had been formed by reaction of **3** with H_2O. This was confirmed by adding H_2O to **3** at −35 °C followed by distillation to isolate pure **1**. The source of **1** was further

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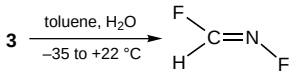

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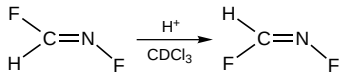
confirmed by reaction of **3** with D_2O. This gave exclusively (*E*)-CFD═NF (**4**) with $^2J_{D-F} = 12.4$ Hz compared to $^2J_{H-F} = 89$ Hz for **1**.

Compound **1** is remarkably stable and at 90 Torr in glass, it was recovered unchanged after 14 h at 100 °C. It is unaffected by NaF or KF at 25 °C. Perfluoromethanimine undergoes rapid dimerization to $CF_3N(F)CF{=}NF$ with KF at 25 °C,[3a] indicating a lower reactivity of **1** with nucleophiles as expected. A sample of **1** was irreversibly absorbed by dry $(CH_3)_4NF$ over a few hours but no dimer was found and the identity of the solid product was not determined. However **1** is affected by acids and traces of HF or other acids result in the isomerization of **1** to *Z*-CHF═NF (**2**). The isomerization of pure **1** into **2** could



1 **2**

be followed easily by ^{19}F or ^1H NMR in $CDCl_3$. The $CDCl_3$ is sufficiently acidic to catalyze the isomerization. Compound **2** exhibits large chemical shift differences (see experimental) compared to **1** and $^3J_{F-F}$ decreases to 45 Hz from 211 Hz in **1**. Other *J* values of **2** are comparable to **1**. In two experiments covering 7 d, pure **1** was converted to a ca. 5:95 mixture of **1** to **2** in $CDCl_3$ based on integration of the ^{19}F NMR. This ratio appeared to represent an equilibrium and additional time at 22 °C did not alter the ratio of **1** to **2**. If this is indeed the chemical equilibrium for this system, this represents a free energy difference between **1** and **2** on the order of 1.5 kcal/mol. This value is between earlier theoretical estimates of 0.6−0.8 kcal/mol[4d,e] and 2.6 kcal/mol.[4a] Efforts to obtain a pure sample of **2** via synthesis or by separation have so far been unsuccessful.

Experimental Data. In a typical reaction, 1.0 mL of 0.99 M PPh_3 in toluene was added via syringe to a 50 mL glass reactor equipped with a magnetic stirring bar and a Teflon-glass valve. The reactor was cooled to −196 °C and evacuated, and a 1.0 mmol sample of $CF_2{=}NF$ was added via vacuum transfer. The reactor was warmed to −75 °C and allowed to warm to −35 °C over 1 h. A small aliquot of water (0.1 mL) was then added, and the reaction was warmed from 0 to 20 °C over 1 h. The volatile products were then distilled under vacuum through a −110 into a −196 °C trap to remove all toluene. Pure **1** (0.4 mmol, 40%) was obtained at −141 °C from the contents of the −196 °C trap by fractional vacuum condensation through traps at −115, −141 and −196 °C. Hydrogen cyanide was identified (0.1 mmol) in the −115 °C trap and ca. 0.1 mmol of material was found in the −196 °C trap containing some $CF_2{=}NF$. Compound **4** was similarly isolated using D_2O.

1: Mp −101 to −102 °C; bp ca. −25 to −35 °C; IR (8 Torr, KCl) 3092 (vw), 2148 (vw), 2162 (vw), 1803 (vw), 1654 (s), 1638 (s), 1307 (m), 1299 (m), 1216 (vs), 1194 (vs), 965 (s), 950 (s), 906 (vw), 706 (vw) cm^{-1}; ^{19}F NMR (188 MHz, 25 °C, $CDCl_3$) (*E*)-$HF^XC{=}NF^A$ δ(A) −46.9 (br d), δ(X) −111.0 (d,d); $^3J_{A-X} = 211$, $^2J_{H-X} = 89$ Hz; ^1H NMR (200 MHz, TMS, 25 °C, $CDCl_3$) δ 8.65 (d, d); MS (CI, CH_4) *m*/*z* 66 (M + 1); MS (EI) 65 (M^+), 46 $(M - F)^+$, 45 $(M - HF)^+$.

2: ^{19}F NMR (*Z*)-$HF^XC{=}NF^A$ δ(A) −31.9 (br s), δ(X) = 78.5 (d, d), $^3J_{A-X} = 45$, $^2J_{H-A} = 84$, $^3J_{H-X} = 28$ Hz; ^1H NMR δ 7.3 (d, d).

Compound **3** could only be identified by NMR. **3** was prepared in a 5 mm NMR tube fitted with a glass−Teflon valve. The tube containing $CDCl_3$ was cooled to −196 °C and $CF_2{=}NF$ (0.1 mmol) was added by vacuum transfer. After warming and recooling of the NMR tube to −196 °C, 0.1 mL of Ph_3P in toluene (0.99 M) was added via syringe. The valve was removed by sealing with a torch, and the NMR tube was warmed to −50 °C and the ^{19}F NMR recorded at this temperature.

The ^{31}P NMR was similarly obtained at −25 °C by reacting $CF_2{=}NF$ with Ph_3P in toluene. The spectrum was recorded by placing the 5 mm tube inside a 10 mm tube containing CD_3CN (lock) and H_3PO_4.

3: ^{19}F NMR (*Z*)-$PPh_3F^ACF^X{=}NF^M$ (188 Mhz, −50 °C, $CDCl_3$/toluene) δ(A) = 0.0 (d, d, d), δ(M) = −39.5 (d, d) δ(X) = −69.0 (d, d, d); $^1J_{P-A} = 661$, $^2J_{P-X} < 5$, $J_{M-X} = 189$, $J_{A-X} = 31$ Hz, $J_{A-M} = 17$ Hz; ^{31}P (81 MHz, −25 °C, toluene) δ(P) −57.9 (d, d); $^1J_{P-X} = 671$, $^2J_{P-X} = 6.0$ Hz.

4: ^{19}F NMR (*E*)-$DF^XC{=}NF^A$ δ(A) (ppm) = −46.9 (br d), δ(X) = −111.1 (br, d) $J_{A-X} = 211$, $J_{D-X} = 12.4$, $J_{D-A} < 2$ Hz; IR (6 Torr, 2000−700 cm^{-1} only) 1656 (s), 1632 (s), 1232 (vs), 1216 (vs), 984 (s), 966 (s), 918 (vw), 848 (w), 742 (w) cm^{-1}; MS (CI, CH_4) *m*/*z* 67 $(M + 1)^+$, 66 (M^+), 47 $(M - F)^+$, 46 $(M + H - DF)^+$, 45 $(M - DF)^+$; EI 66 (M^+), 47 $(M - F)^+$, 46 $(M + H - DF)^+$.

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