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Iron(0) Oxidation by Hydrogen Chloride in Tetrahydrofuran: a Simple Way to Anhydrous Iron(II) Chloride

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Anhydrous iron(II) chloride is prepared by reaction of iron powder with dry HCl at high temperature.[1] Its preparation under milder conditions has received considerable attention; e.g., attempts to obtain $FeCl_2$ by heating the tetrahydrate under nitrogen[2] or in vacuo afforded a product often contaminated with Fe(III). Azeotropic distillation of the water from the tetrahydrate using benzene–methanol (or other mixtures) gave the dihydrate.[3] Recently Winter[4] reported that the reaction of HCl with Fe(0) in hot methanol affords $FeCl_2·6CH_3OH$. Subsequent prolonged heating in vacuo of the methanol-solvated species affords $FeCl_2$.

We have carried out the reaction of iron powder with anhydrous HCl in tetrahydrofuran (THF) at low temperature (5 °C) and we have obtained a pearly microcrystalline compound which analyzes for $FeCl_2·1.5THF$ (I).

It is sparingly soluble in THF and in nonpolar solvents but soluble in coordinating solvents such as alcohols, dimethylformamide, and dimethyl sulfoxide and very soluble in water. Compound I suspended in THF readily undergoes replacement of the coordinated THF by a number of ligands (phosphines, amines, sulfides); therefore I represents a convenient starting material for the preparation of iron(II) compounds where acidic species such as water and alcohols must be excluded.

The IR spectrum of I (4000–200 cm^{-1}, Nujol mull) shows bands at 1071 (vs), 918 (w), and 886 (vs) cm^{-1} attributable to coordinated THF and bands at 345 (s), 288 (m), 279(s), and 238 (s) cm^{-1} due to ν(Fe–Cl) and diagnostic of a polymeric structure.

Careful heating of I in vacuo (or under nitrogen) at 80–85 °C for 1 h gives off THF leaving colorless $FeCl_2$.

We have investigated the influence of the temperature on the reaction of Fe with HCl in THF and we have found that when the reaction was carried in a thermostated bath at 5 °C no other products were formed beside I, even with excess HCl. When the reaction was run at room temperature (20 °C) without temperature control, as long as iron powder was present in the system, the temperature increased only moderately (up to 25 °C). After Fe(0) completed oxidation, an increase in the temperature was recorded (up to 45 °C), while the solid $FeCl_2·1.5THF$ passed into solution, which assumed a syrupy consistency. From this solution 4-chloro-1-butanol (cb) (80% yield based on the starting THF) and $FeCl_2·cb$ (96% based on iron) were isolated.

It is known that THF can undergo nucleophilic and acid-catalyzed ring-opening reactions. Examples of the former reaction are provided by the cleavage by tritylmagnesium bromide,[5] by lithium aluminum hydride with $AlCl_3$,[6] and by diborane[7] or diborane in the presence of iodine[8] to give 4-R-1-butanol.

The acid-catalyzed ring-opening reaction in the presence of $TiCl_4$[9] and the reaction with HCl in the presence of $ZnCl_2$, under reflux,[10] afford 1,4-dichlorobutane.

In our case it can be inferred that iron(0) oxidation by the tetrahydrofuranium ion is energetically favored with respect to the ring-opening reaction which can take place only when all of the iron has been oxidized.

Experimental Section

All of the reactions were carried out in the absence of air and moisture. THF was dried and distilled under nitrogen. Anhydrous HCl was prepared as reported in ref 11. IR spectra were recorded with a Perkin-Elmer 557 spectrometer and ^1H NMR spectra with a Varian HA 100 spectrometer.

Preparation of $FeCl_2·1.5THF$. Anhydrous HCl was bubbled slowly (30 drops/min) through a stirred suspension of hydrogen-reduced iron powder (1.0 g) in THF (50 cm^3) at 5 °C. A white microcrystalline solid began to separate after 30 min and the reaction was complete in 2 h. Dry nitrogen was bubbled through the slurry cooled at 0 °C in order to eliminate the excess HCl and the solid filtered by vacuum-line technique, washed with anhydrous THF, and dried in vacuo at room temperature.

This compound is very sensitive to moisture and must be stored under dry nitrogen.

Anal. Calcd for $FeCl_2·1.5C_4H_8O$: C, 30.7; H, 5.15; Cl, 30.2; Fe, 23.8. Found: C, 30.5; H, 5.1; Cl, 30.4; Fe, 23.7.

Preparation of $FeCl_2$. Compound I was heated under vacuum at 80–85 °C for 1 h with absolute exclusion of oxygen and moisture. It converted to a light, white compound. The THF could be eliminated as well by heating I at the same temperature in a pure, dry nitrogen flow.

Anal. Calcd for $FeCl_2$: Cl, 55.94; Fe, 44.06. Found: Cl, 56.1; Fe, 43.8.

Identification of the Ring-Opening Reaction Products. (i) Isolation of $FeCl_2·HO(CH_2)_4Cl$. The reaction of HCl with iron powder was allowed to run without temperature control starting from 20 °C. A moderate temperature increase was recorded during the iron oxidation process (up to 25 °C). When this reaction was complete, compound I separated.[12] The temperature began to rise reaching a maximum of 45 °C in 1 h, while I passed slowly into solution which assumed a syrupy consistency. HCl was bubbled for a further 30 min and then nitrogen was passed through the solution cooled at 0 °C until excess HCl was eliminated. The residual THF was evaporated, in vacuo, at room temperature and addition of toluene–pentane (1:1) caused precipitation of a white solid which was filtered out, washed with toluene and pentane, and dried in vacuo; yield 96% based on iron.

Anal. Calcd for $FeCl_2·HO(CH_2)_4Cl$: C, 20.3; H, 3.85; Cl, 45.4; Fe, 23.6. Found: C, 20.4; H, 3.90; Cl, 45.4; Fe, 23.5.

(ii) Isolation of 4-Chloro-1-butanol. The reaction syrup was distilled in vacuo to give 35 g of a colorless, fruit-smelling liquid boiling at 52.5 °C (1.5 mmHg); $n^{20}{}_D$ 1.4519 (lit.[13] $n^{20}{}_D$ 1.4518). ^1H NMR (in C_6D_6, TMS as internal standard):[14] τ 6.65 (2 H, H^1, triplet, J_{1-2} = 6.0 Hz), 6.78 (3 H, H^4 + OH, broadened triplet, J_{3-4} = 6.0 Hz; OH proton masked by the central peak of the triplet), 8.48 (4 H, H^2 + H^3, multiplet).

Anal. Calcd for C_4H_9ClO: C, 44.25; H, 8.36; Cl, 32.65. Found: C, 44.3; H, 8.37; Cl, 32.63.

Registry No. I, 12562-70-8; $FeCl_2$, 7758-94-3; $FeCl_2·HO(CH_2)_4Cl$, 62521-10-2; 4-chloro-1-butanol, 928-51-8.

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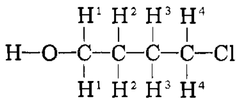
(14) Protons are numbered as follows



$$\mathrm{H{-}O{-}\overset{H^1}{\underset{H^1}{C}}{-}\overset{H^2}{\underset{H^2}{C}}{-}\overset{H^3}{\underset{H^3}{C}}{-}\overset{H^4}{\underset{H^4}{C}}{-}Cl}$$

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Hydrolysis of $CF_3SF_2Cl{=}NCF(CF_3)_2$. Preparation of $CF_3(S{=})(O)[N{=}C(CF_3)_2]$-Containing Compounds

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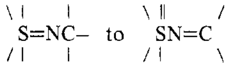
Hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$ results in the formation of (trifluoromethyl)(hexafluoroisopropylidenimino)sulfuroxydifluoride, $CF_3S(O)F_2[N{=}C(CF_3)_2]$, which is a ready precursor to $CF_3S(O)({=}NCH_3)[N{=}C(CF_3)_2]$, $CF_3S(O)[{=}NCF(CF_3)_2][N{=}C(CF_3)_2]$, and $CF_3S(O)({=}NH)[N{=}C(CF_3)_2]$. The latter compound can be reacted with $CF_3C(O)F$, $(CH_3)_3SiCl$, and Ag_2O to form $CF_3S(O)[{=}NC(O)CF_3][N{=}C(CF_3)_2]$, $CF_3S(O)[{=}NSi(CH_3)_3][N{=}C(CF_3)_2]$, and $CF_3S(O)({=}NAg)[N{=}C(CF_3)_2]$.

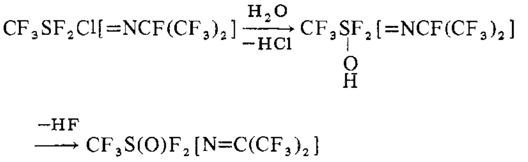
Substituted sulfur(VI)oxydifluorides, $RN{=}S(O)F_2$ (R = alkyl, FSO_2), are stable compounds which result either from the reaction of primary amines, RNH_2, with sulfinyl tetrafluoride or from the photolysis of RNSO with fluorine.[1] Earlier we reported the synthesis of bis(perfluoroalkyl)sulfuroxydifluorides via the oxidative fluorination of bis(perfluoroalkyl) sulfoxides with chlorine monofluoride at −78 °C.[2] We now find that it is possible to form a new, reactive member of this family, (trifluoromethyl)(hexafluoroisopropylidenimino)sulfuroxydifluoride, $[CF_3S(O)F_2[N{=}C(CF_3)_2]$, by the hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$[3] which is accompanied by a concomitant double-bond shift



The sulfur is susceptible to attack by nucleophiles, e.g., CH_3NH_2, NH_3, and $LiN{=}C(CF_3)_2$, to form $CF_3S(O)({=}NR)[N{=}C(CF_3)_2]$. Further reactions of the latter, where R = H, lead to additional new sulfoximides.

Results and Discussion

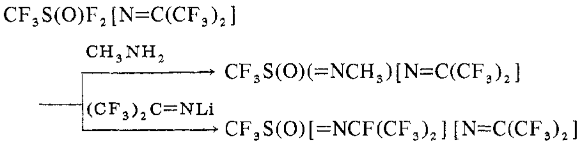
The hydrolysis of $CF_3SF_2Cl[{=}NCF(CF_3)_2]$ provides a direct route to the preparation of $CF_3S(O)F_2[N{=}C(CF_3)_2]$



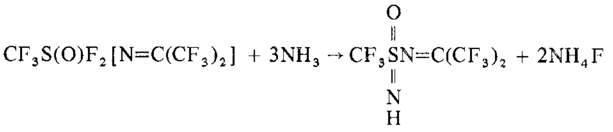
$$CF_3SF_2Cl[{=}NCF(CF_3)_2] \xrightarrow[-HCl]{H_2O} CF_3\underset{\underset{H}{O}}{S}F_2[{=}NCF(CF_3)_2] \xrightarrow{-HF} CF_3S(O)F_2[N{=}C(CF_3)_2]$$

Elucidation of the structure of this compound is facilitated by the presence of bands in the infrared spectrum which are assigned to $\nu_{S=O}$ (1335 cm^{-1}) and asymmetric and symmetric ν_{S-F} (800, 538 cm^{-1}). These regions are typical for analogous stretching frequencies for axial S—F bonds in similar compounds, e.g., OSF_4.[4] The ^{19}F nuclear magnetic resonance spectrum contains resonances typical of fluorine atoms in environments consistent with the proposed structure,[2] e.g.: CF_3S, ϕ^* 66.2; S–F, ϕ^* −70.8; $C(CF_3)$, ϕ^* 67.1, 68.6. The magnetic nonequivalence of the two trifluoromethyl groups in the hexafluoroisopropylidenimino group is well established.[5-8]

Subsequent nucleophilic displacement reactions of $CF_3S(O)F_2[N{=}C(CF_3)_2]$ with CH_3NH_2 and $(CF_3)_2C{=}NLi$ result in the formation of sulf- and carbodiimides. In the latter case, fluorine migration occurs to give the diimide.[3,9-11]

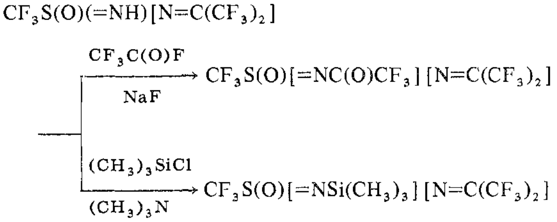


Previous work in this laboratory resulted in the preparation of bis(perfluoroalkyl)sulfoximides.[12] In a similar manner, $CF_3S(O)F_2[N{=}C(CF_3)_2]$ undergoes reaction with ammonia to produce the (trifluoromethyl)(hexafluoroisopropylidenimino)sulfoximide.



$$CF_3S(O)F_2[N{=}C(CF_3)_2] + 3NH_3 \rightarrow CF_3\overset{\overset{O}{\|}}{\underset{\underset{H}{\underset{N}{\|}}}{S}}N{=}C(CF_3)_2 + 2NH_4F$$

In the infrared spectrum, the absorption band at 3445 cm^{-1} is assigned to ν_{N-H}. This sulfoximide is a useful precursor to new substituted oximides. In the cases examined, bases were used to enhance the loss of HX.



The silver salt of bis(trifluoromethyl)sulfoximide is formed by the reaction of $(CF_3)_2S(O)({=}NH)$ and Ag_2O in benzene.[12-14] In an analogous manner, $CF_3S(O)({=}NAg)[N{=}C(CF_3)_2]$ is formed quantitatively. The existence of this salt was demonstrated by reacting it with methyl iodide to yield $CF_3S(O)({=}NCH_3)[N{=}C(CF_3)_2]$ which was formed in the reaction between CH_3NH_2 and the sulfoximide above.

$$CF_3S(O)({=}NH)[N{=}C(CF_3)_2] + Ag_2O$$
$$\xrightarrow{PhH} CF_3S(O)({=}NAg)[N{=}C(CF_3)_2]$$
$$\xrightarrow{CH_3I} CF_3S(O)({=}NCH_3)[N{=}C(CF_3)_2]$$

Experimental Section

Materials. Methods in the literature were used to prepare $CF_3SF_2Cl[{=}NCF(CF_3)_2]$[3] and $LiN{=}C(CF_3)_2$.[5] Commercially available materials, $CF_3C(O)F$, CH_3NH_2, NH_3, and $(CH_3)_3SiCl$, were used without further purification.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus and measured using standard *PVT* techniques. Infrared spectra were recorded by a Perkin-Elmer Model 457 spectrometer. The ^{19}F and ^1H nuclear