iodides, that is, alkyl amines > alcohols > ethers > aromatics > alkanes. The low solubility of the pyridinium salts in poorly solvating liquids requires indirect methods for the assignment of Z values to the very soft donors. By contrast, iodine is particularly attractive as a reference soft acid for determining comparative softness of nonpolar and aprotic donors.

Experimental Section

The 4-carbomethoxy-1-ethylpyridinium iodide (Eastman Organic Chemicals) was recrystallized by dissolving the solid in warm chloroform containing a minimum of added absolute methanol. The filtered solution was allowed to concentrate and crystallize at room temperature, giving yellow-orange crystals (mp 114°). Acetone[5] was not as suitable as a solvent, since it was quite difficult to free the solid product completely from adsorbed solvent, and the solute tended to separate as an oil.

All donor solvents were Spectro-Analyzed reagents with the exception of the amines (Eastman White Label). Solvent Z values were obtained by the procedure of Kosower.[5] However, those for pure *p*-dioxane and tetrahydrofuran were graphically extrapolated from Z *vs.* v/v fraction in binary mixtures with water. Experimental values for chloroform and the amines were measured in binary solutions with added methanol (20% v/v), because of the low solubility of the pyridinium salt. Absorption maxima were determined on a Beckman DU spectrophotometer.

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Preparation of Chlorodifluoramine, $ClNF_2$

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The synthesis of $ClNF_2$ was first reported in 1960 by Petry.[1] Since then, numerous papers dealing with the preparation of this interesting compound have been published.[2-9] The majority of these preparations are based on the reaction of HNF_2 with chlorine or chlorine-containing compounds.[1,4-6,9] With the exception of the reactions between HNF_2 and ClF[9] or inorganic hypochlorites,[6] the yields of $ClNF_2$ (based on HNF_2) are only about 50% or lower. The remaining methods based on N_2F_4,[7,8] NaN_3,[3] or NH_4^+-containing salts[2] result in only moderate yields of $ClNF_2$ or are hard to control. This paper reports a new, more convenient synthesis of $ClNF_2$ from HNF_2 and *t*-butyl hypochlorite.

This reaction produces $ClNF_2$ in quantitative yield (based on HNF_2). In contrast to the reaction between HNF_2 and ClF,[9] it does not require the use of a metal–Teflon vacuum system but can be carried out in a standard all-glass vacuum line. Aqueous solutions of inorganic hypochlorites have previously been used[6] to convert NHF_2 into $ClNF_2$. However, in aqueous solutions proper control of the pH value and use of a flow reactor are essential to suppress the competing reaction resulting in the formation of N_2F_4.

Experimental Section

Caution! Difluoramine is highly explosive[4] and protective shielding should be used during handling operations. The compound was always condensed at −142° and the use of a −196° bath should be avoided.[4]

Materials and Apparatus.—Difluoramine was prepared from difluorourea as reported by Lawton, *et al.*[10] *t*-Butyl hypochlorite was prepared from *t*-butyl alcohol.[11] Both compounds were purified by fractional condensation and their purity was determined by infrared spectroscopy. All reactions were carried out in a Pyrex high-vacuum line having stopcocks lubricated with Halocarbon grease (from Halocarbon Products Corp.). Infrared spectra were taken on a Perkin-Elmer Model 337 spectrophotometer using a 5-cm Pyrex cell fitted with AgCl windows.

Preparation of $ClNF_2$.—Difluoramine (1.06 mmol) and *t*-butyl hypochlorite (1.08 mmol) were combined at −142° in a U trap. The mixture was allowed to warm to room temperature and a smooth reaction took place. After 90 min the mixture was separated by fractional condensation at −54, −95, −142, and −196°. An infrared spectrum of the material trapped at −196 and −142° showed the presence of only $ClNF_2$ (1.06 mmol). The large bulk of the organic material was trapped at −54°.

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A Crystalline Molybdenum(V)–Histidine Complex

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Interest in the implication of molybdenum in enzyme function has prompted recent research on the coordination chemistry of molybdenum ions with α-amino acids, notably cysteine and its esters.[1-3] With respect to other α-amino acids Spence and Lee[4] carried out spectrophotometric, electron paramagnetic resonance, and

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