

cm^{-1} region. This would tend to account for the high intensity of the (Hg–O) stretch and low intensity of the (Hg–C) stretch of CH_3HgOH . With the heterocyclic base coordinated, one mode would be expected to involve almost pure (Hg–C) stretching leading to an increase in its intensity. Such mixing, however, is not supported by the observation that the stretching frequency at 568 cm^{-1} does not shift in going from CH_3HgOH to CH_3HgOD .

A second possible explanation would involve a pre-resonance effect. Coordination of CH_3Hg^+ to Urd or Cyd shifts the absorption bands toward the visible.¹¹ Such a pre-resonance effect has been suggested as the explanation for marked changes in the Raman intensities of polynucleotides with changes in conformation.¹⁶ On the other hand, the absorption bands of the $\text{CH}_3\text{Hg}^{\text{II}}$ –Urd and –Cyd complexes are at *ca.* 265 and 280 nm, far removed from the 514.5-nm exciting line. In addition, such an effect would require substantial interaction between the electronic transition originally occurring in the heterocyclic base and the (Hg–C) vibration. This hyperchromism is being studied further.

Mansy, *et al.*,²⁰ observed a decrease in the scattering of Poly U at 1681 cm^{-1} with solutions containing *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ which is similar to the effect observed here upon binding of CH_3Hg^+ to Urd and Poly U. The decrease in the scattering at 1291 cm^{-1} of Poly C upon reaction with the two platinum ammine isomers also is similar to that observed upon binding of

CH_3Hg^+ to Cyd in H_2O at pH 7. It is probable that the platinum binds at the $\text{N}_{(3)}$ site of both of these bases too.

In summary, Raman spectroscopy and particularly Raman difference spectroscopy has been shown to be an effective technique for studying the interaction of heavy metals with nucleosides and establishing the binding site. The $\text{CH}_3\text{Hg}^{\text{II}}$ cation binds both to Urd and Cyd at pH 7, although binding to Urd is more nearly complete at that pH. This is consistent with the results of Simpson's uv spectrophotometric investigation.¹¹ The suggestion of Nandi, *et al.*,⁴² that Hg(II) binds to dThd at $\text{N}_{(3)}$ in AT rich DNA at pH 9 seems more likely than for coordination to occur at $\text{C}_4=\text{O}$.¹² The difference spectra of the complexes with the nucleosides exhibit bands characteristic of the metallated nucleoside. Consequently, this technique should be capable of establishing the binding sites in polynucleotides containing both the uracil and cytosine bases.

Supplementary Material Available. Raman spectra will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ($105 \times 148\text{ mm}$, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1762.

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Photochemistry of Perfluoroalkyl and Perfluoroacyl *N*-Chloramines. Reactions of *N*-Chloramines and *N*-Chlorimines in the Presence of Mercury

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Abstract: Photolysis of perfluoroalkyl(fluoroformyl) and bis(fluoroformyl) *N*-chloramines neat or with other similarly substituted chloramines resulted in the formation of a new family of hydrazines which includes $\text{CF}_3\text{-(FCO)NN(FCO)CF}_3$, $(\text{FCO})_2\text{NN(FCO)}_2$, $(\text{CF}_3)_2\text{NN(FCO)CF}_3$, $(\text{CF}_3)_2\text{NN(FCO)}_2$, and $\text{CF}_3\text{(FCO)NN(FCO)}_2$. With $\text{CF}_3\text{(FCO)NCl}$, CO and SO_2 inserted into the nitrogen-chlorine bond to give $\text{CF}_3\text{(FCO)NC(O)Cl}$ and the unstable $\text{CF}_3\text{(FCO)NSO}_2\text{Cl}$. Bis(fluoroformyl), trifluoromethylfluoroformyl, and bis(trifluoromethyl) *N*-chloramines and hexafluoroisopropylidene(*N*-chloro)imine were treated with CF_3SCl and $\text{CF}_3\text{C(O)Br}$ in the presence of mercury to form $(\text{FCO})_2\text{NSCF}_3$, $\text{CF}_3\text{(FCO)NSCF}_3$, $(\text{CF}_3)_2\text{NSCF}_3$, $(\text{CF}_3)_2\text{C}=\text{NSCF}_3$, and $(\text{CF}_3)_2\text{C}=\text{NC(O)CF}_3$ via the solid amido or imido mercuric chloride. Compounds which contain the fluoroformyl moiety tend to be less stable due to the ease of fluoride ion shift. Formation of chlorine pseudohalides when $(\text{CF}_3\text{S})_2\text{Hg}$ and AgNCO were treated with the *N*-chloramines argues for the positive nature of the chlorine in these compounds.

Fluorinated *N*-chloramines have been obtained from proton abstraction reactions of fluorinated amines with ClF^1 or Cl_2^{2-4} in the presence of alkali metal

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fluorides. More recently facile additions of ClF to fluoroalkylimines^{1,5-7} and fluoroalkyl or acyl isocyanates⁸ have resulted in a wide variety of *N*-chlor-

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amines. The polar character of the $>N^{\delta-}-Cl^{\delta+}$ bond has been suggested by the formation of elemental chlorine when the *N*-chloramine was treated with compounds which contained negative chlorine.⁸⁻¹⁰

In addition to metathesis reactions,^{11,12} under appropriate thermal or photolytic conditions, chloramines gave rise to hydrazines^{1,12} and chlorine or underwent insertion reactions with carbon monoxide to form $>NC(O)Cl$ ^{2,13} compounds. Photolysis studies have been limited to those chloramines which contain either perfluoroalkyl or fluorosulfonyl substituents. In the present study, photolysis of various combinations of $(CF_3)_2NCl$, $CF_3(FCO)NCl$, and $(FCO)_2NCl$ made it possible to generate a new series of substituted hydrazines $(CF_3)_{4-x}(FCO)_xN_2$ ($x = 0, 1, 2, 3, 4$) and also demonstrated that this route can be useful in cases where the intermediate radical $(R_f)_2N\cdot$ has even minimal stability.

Reactions of mercurial compounds, $((R_f)_2N)_2Hg$, traditionally have provided routes to the introduction of the $(R_f)_2N$ moiety into a variety of systems and the molecule where $R_f = CF_3$ has been used extensively as a synthetic reagent.¹⁴ We now have found that mercury readily inserted into the N-Cl bond of *N*-chloramines and imine chlorides to form very reactive mercurials ($>NHgCl$ and $=NHgCl$). Although these compounds had only moderate stability, their utility as synthetic reagents has been demonstrated.

Experimental Section

General Methods. Gases and volatile liquids were handled in a conventional Pyrex vacuum system equipped with a Heise-Bourdon tube gauge. Photolytic reactions were normally run in a Srinivasan-Griffin reaction that had a forced air cooling system maintained at 30° (The Southern New England Ultraviolet Co. RPR Model 100). Photolytic conditions were adjusted by the use of standard RPR (Rayonet photochemical reactor) 2537, 3000, or 3500 Å lamps and vessels of suitable composition. An alternate photolytic reactor was a 3.5-l. flask with a water cooled quartz finger using a 450-W Hanovia (679A36) lamp and appropriate filters. Purification of products was accomplished by fractional condensation or gas chromatography by using a 7-ft column of 20% Kel-F no. 3 oil on Chromosorb P. Infrared spectra were recorded at 4 Torr on a Perkin-Elmer Model 457 spectrometer with a 10-cm gas cell equipped with NaCl windows. A Hitachi Perkin-Elmer Model RMU-6E spectrometer operating at an ionization potential of 70 eV was used to obtain mass spectra. ¹⁹F nuclear magnetic resonance spectra were recorded on a Varian HA-100 spectrometer operating at 94.1 MHz. Either a 10% solution of the compound in Freon 11 (CCl_3F) or a mixture of 10% sample, 10% CF_3SSCF_3 , and 80% CH_2Cl_2 or CH_3CN solution was used for nmr measurements. In the latter case, the observed shift values were converted to ϕ values by adding 46.9, the chemical shift of CF_3SSCF_3 relative to CCl_3F . The method of Kellogg and Cady¹⁵ was used to obtain vapor pressure data, and PVT measurements were used for molecular weight determinations. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Materials. Methods reported in the literature were used to synthesize $(FCO)_2NCl$,⁸ $CF_3(FCO)NCl$,⁸ $CF_3C(O)(FCO)NCl$,⁸ $AgNCO$,¹⁶ $CF_3C(O)Br$,¹⁷ $CF_3SHgSCF_3$,¹⁸ CF_3SCl ,¹⁹ and $(CF_3)_2C=$

NCl .⁶ ClF readily adds to $CF_3N=CF_2$ under high pressure at 25° to yield 80% $(CF_3)_2NCl$. $CF_3N=CF_2$ was synthesized in a 20% yield by the fluorination of $ClCN$ with HgF_2 at 280° for 1 hr. ClF and HgF_2 were purchased from Ozark-Mahoning, $ClCN$ from K and K, CF_3SSCF_3 from PCR, and CCl_3SCl from Eastman-Kodak and were used without further purification.

Caution! Although we have had no difficulties with explosions with this research, nitrogen-fluorine-containing compounds are known to be unstable and should be handled with care.

Preparation of $(FCO)_2NSCF_3$. Two millimoles of $(FCO)_2NCl$ was condensed with 2.7 mmol of CF_3SCl onto 1.5 ml of Hg in a 3-ml Pyrex vessel fitted with a Teflon stopcock. The mixture was agitated mechanically for about 0.5 hr. The product, $(FCO)_2NSCF_3$ (1.3 mmol, 54%), was easily separated from the other products, CF_3SSCF_3 and $FC(O)NCO$, by fractional condensation. Purification was easier to achieve if the starting materials were pure and a large excess of mercury was used.

Preparation of $CF_3(FCO)NSCF_3$. To approximately 1 ml of mercury in a 3-ml thick-walled Pyrex vessel equipped with a Teflon stopcock were added 4.0 mmol of $CF_3(FCO)NCl$ and 7.0 mmol of CF_3SCl . The mixture was agitated with a mechanical shaker for 1 hr and separated by fractional condensation. Condensed in a -50° trap was $CF_3(FCO)NSCF_3$ (1.7 mmol, 42%), and, in colder traps, CF_3NCO and CF_3SSCF_3 were also found.

New Preparation of $CF_3SN(CF_3)_2$. $(CF_3)_2NCl$ (0.7 mmol) and CF_3SCl (1.0 mmol) were condensed into a 3-ml Pyrex vessel fitted with a Teflon stopcock which contained 1.5 ml of benzene and 0.5 ml of mercury. The mixture was warmed to 25° in a vertical position to prevent reactant contact with the mercury until diffusion into the benzene phase was completed. The mixture was then agitated for 1 hr and separated by fractional condensation. A mixture of $CF_3SN(CF_3)_2$ and CF_3SSCF_3 (0.8 mmol) was recovered in a -78° trap after passing a -52° trap. A portion of the mixture was purified by gas chromatography and a peak at m/e 253, the molecular ion of $CF_3SN(CF_3)_2$, was observed in the mass spectrum. The ¹⁹F nmr gave confirmatory evidence for the indicated product.²⁰ The yield of $CF_3SN(CF_3)_2$ was about 30%. $CF_3N=CF_2$ (0.3 mmol) was also found.

New Preparation of $CF_3C(O)N=C(CF_3)_2$. $(CF_3)_2C=NCl$ (0.4 ml) and $CF_3C(O)Br$ (0.4 mmol) were condensed into a 2-ml Pyrex vessel fitted with a Teflon stopcock which contained about 1 ml of mercury. The reaction mixture was agitated for 1.5 days. The volatile portion was removed and separated by fractional condensation to give 0.37 mmol (93%) of $CF_3C(O)N=C(CF_3)_2$ in a trap at -78°. Traces of $CF_3C(O)Br$ were also identified.

New Preparation of $CF_3SN=C(CF_3)_2$. $(CF_3)_2C=NCl$ (0.8 mmol) was treated with about 1 ml of mercury while shaking for 4 hr in a 2-ml Pyrex vessel fitted with a Teflon stopcock. The vessel was evacuated in order to remove any unreacted $(CF_3)_2C=NCl$ (0.1 mmol). CF_3SCl (1.1 mmol) was condensed on the remaining 0.7 mmol of imido mercuric chloride and mercury mixture and shaken for 1 hr. After fractional condensation, 0.7 mmol (100%) of $CF_3SN=C(CF_3)_2$ was isolated in a trap at -78°. CF_3SSCF_3 (0.2 mmol) and traces of $(CF_3)_2C=NCl$ were noted in the volatile products.

Preparation of $CF_3(FCO)NC(O)Cl$. A mixture of $CF_3(FCO)NCl$ (10 mmol) and CO (75 mmol, purified by passing through a "U" trap at -183°) in a 3.5-l. vessel was photolyzed for 10 hr with a lamp (450-W, Hanovia, 679A36) inserted into a water-cooled quartz finger equipped with a Pyrex filter (1 mm thick). After photolysis, the reaction mixture was removed, and the products were separated by fractional condensation. $CF_3(FCO)NC(O)Cl$ (6.8 mmol) was found in a trap at -78° after passing through a trap at -40°. Final purification was by gas chromatography. Other products included COF_2 , $COCl_2$, $COFCl$, CF_3NCO , and $CF_3(FCO)NH$ (an impurity in the starting chloramine).

Preparation of $CF_3(FCO)NN(FCO)CF_3$. $CF_3(FCO)NCl$ (5.0 mmol) was placed in the 3.5-l. vessel and was photolyzed through quartz with the 450-W medium-pressure lamp. After 12-14 hr, quantitative amounts of chlorine in addition to CF_3NCO (10%) and

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(13) J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **23**, 1576 (1958).

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(18) G. R. A. Brandt, R. N. Hazeldine, and H. J. Emelús, *J. Chem. Soc.*, 2198 (1952).

(19) C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

(20) B. W. Tattershall and H. J. Emelús, *J. Inorg. Nucl. Chem.*, **28**, 1832 (1966).

$\text{CF}_3(\text{FCO})\text{NNCF}_3(\text{FCO})$ resulted as volatile products. The hydrazine (1.9 mmol, 76%) was easily purified by fractional condensation (stopped in -56° trap after passing a trap at -40°).

Preparation of $(\text{FCO})_2\text{NN}(\text{FCO})_2$. About 16 Torr (1.5 mmol) of $(\text{FCO})_2\text{NCl}$ was placed in a 1.8-l. quartz vessel and photolyzed for 1 hr at 30° using 16 RPR 2537 Å low-pressure lamps. The product mixture was separated by fractional condensation and contained Cl_2 (100%), $\text{FC}(\text{O})\text{NCO}$, SiF_4 , and pure $(\text{FCO})_2\text{NN}(\text{FCO})_2$ (0.6 mmol, 85%) remained in a trap at -20° .

Preparation of $\text{CF}_3(\text{COF})\text{NN}(\text{FCO})_2$. About 16 Torr of $(\text{FCO})_2\text{NCl}$ (1.4 mmol) was expanded into a 1.6-l. quartz reactor. The total reactor pressure was increased to 32 Torr with $\text{CF}_3(\text{FCO})\text{NCl}$ (1.4 mmol). No liquid phase existed in the reaction vessel. The reactants were allowed to mix by diffusion for 1 hr and then were photolyzed for 1 hr at 30° using 16 RPR 2537 Å low-pressure lamps. The reaction mixture was then condensed onto mercury to remove the chlorine and any remaining chloramines. Careful fractional condensation of the remaining products resulted in $\text{CF}_3(\text{FCO})\text{NN}(\text{FCO})_2$ (0.6 mmol) and $\text{CF}_3(\text{FCO})\text{NNCF}_3(\text{FCO})$ (0.7 mmol) with traces of COF_2 , CF_3NCO , and $(\text{FCO})_2\text{NN}(\text{FCO})_2$. In the separation the trap at -30° contained $\text{CF}_3(\text{FCO})\text{NN}(\text{FCO})_2$ contaminated with $(\text{FCO})_2\text{NN}(\text{FCO})_2$, and the trap at -40° contained $\text{CF}_3(\text{FCO})\text{NN}(\text{FCO})_2$ contaminated with $\text{CF}_3(\text{FCO})\text{NNCF}_3(\text{FCO})$. The material in the trap at -30° was retrapped and the portion that passed the trap at -30° was relatively pure $\text{CF}_3(\text{FCO})\text{NN}(\text{FCO})_2$.

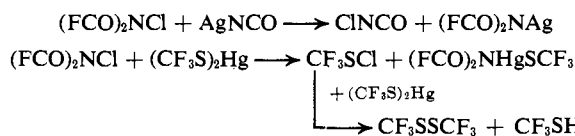
Preparation of $(\text{CF}_3)_2\text{NNCF}_3(\text{FCO})$. $\text{CF}_3(\text{FCO})\text{NCl}$ (1.3 mmol) and $(\text{CF}_3)_2\text{NCl}$ were condensed into a 1.6-l. quartz vessel. The reactants were allowed to mix by diffusion for 1 hr and then photolyzed at 30° with 16 RPR 2537 Å low-pressure sources for 1 hr. The product mixture (2.4 mmol) was condensed onto mercury to remove chlorine (1.1 mmol) and unreacted chloramines. The remaining mixture was separated by fractional condensation to give $(\text{CF}_3)_2\text{NNCF}_3(\text{FCO})$ (0.7 mmol) and $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ (0.6 mmol) with minor amounts of $\text{CF}_3(\text{FCO})\text{NNCF}_3(\text{FCO})$, CF_3NCO , $\text{CF}_3\text{N}=\text{CF}_2$, and $\text{CF}_3(\text{FCO})\text{NH}$ (a starting material impurity). Final purification was effected by stopping the product in a trap at -78° after it passed through a trap at -56° .

Preparation of $(\text{CF}_3)_2\text{NN}(\text{FCO})_2$. $(\text{FCO})_2\text{NCl}$ (1.1 mmol) (16 Torr) was expanded into a 1.2-l. quartz vessel. $(\text{CF}_3)_2\text{NCl}$ (1.1 mmol) was then added to the vessel and allowed to mix with the first amine for about 1 hr. The mixture was photolyzed 1 hr at 30° using 16 RPR 2537 Å sources. The product mixture (2.8 mmol) was condensed onto mercury to remove the chlorine (1.1 mmol) and unreacted chloramines. $(\text{CF}_3)_2\text{NN}(\text{FCO})_2$ (0.4 mmol) was purified by trapping at -60° after passing a -40° trap. Other volatile compounds included $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ (0.5 mmol) and minor amounts of $\text{FC}(\text{O})\text{NCO}$, $\text{CF}_3\text{N}=\text{CF}_2$, COFCl , COF_2 , SiF_4 , and $(\text{FCO})_2\text{NN}(\text{FCO})_2$.

Results and Discussion

In an earlier study of the chloramines, we obtained evidence for the positive character of the chlorine in the polar N-Cl bond of $\text{CF}_3(\text{FCO})\text{NCl}$ through reaction with a variety of molecules which contained negative chlorine (e.g., BCl_3 , Al_2Cl_6 , NaCl , and $(\text{CH}_3)_3\text{SiCl}$) to produce elemental chlorine. The proposed intermediate, $\text{CF}_3\text{N}(\text{M})\text{C}(\text{O})\text{F}$, was not isolated due to MF elimination accompanied by the formation of the isocyanate, CF_3NCO . However, under the conditions used, CF_3SCl , $\text{CF}_3\text{C}(\text{O})\text{Cl}$, and HgCl_2 did not react with the chloramines.⁸

In the present work further evidence was obtained for the positive character of the chlorine in the chloramines from reactions with metal pseudohalides, e.g.



in which the chlorine pseudohalide was eliminated. Only the volatile compounds were identified and the proposed silver and mercury salts were not.

Therefore, in an attempt to extend the reaction chem-

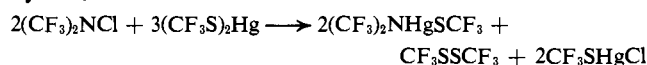
istry of the chloramines, it was found that mercury inserted into the N-Cl bond at 25° apparently to form the relatively stable solid amido mercuric chlorides which on standing evolved the respective isocyanate over a

$$\text{R}_f(\text{FCO})\text{NCl} + \text{Hg} \longrightarrow \text{R}_f(\text{FCO})\text{NHgCl} \longrightarrow \text{R}_f\text{NCO} + \text{HgClF}$$

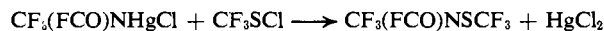
$$\text{R}_f = \text{CF}_3, \text{FCO}, \text{CF}_3\text{C}(\text{O})$$

period of a few days. In the $(\text{CF}_3)_2\text{NCl-Hg}$ system, a similar fluoride shift occurred to form $\text{CF}_3\text{N}=\text{CF}_2$. Very rapid evolution of the isocyanate was observed when a reactant or solvent was added to the solid material. However, if the chloramine, $\text{R}_f(\text{FCO})\text{NCl}$, and CF_3SCl were condensed simultaneously onto a large excess of mercury and the mixture was agitated vigorously for short time periods, trisubstituted amines, $\text{R}_f(\text{FCO})\text{NSCF}_3$, were isolated.

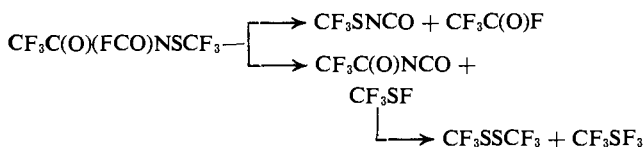
Trifluoromethylsulfonyl chloride reacts with mercury to form CF_3SSCF_3 and HgCl_2 .²¹ The reaction suggests initial formation of CF_3SHgCl which subsequently reacts with CF_3SCl to give CF_3SSCF_3 and HgCl_2 . Thus, the formation of the product amine could be the result of the reaction of the chloramine with CF_3SHgCl . However, considering the positive nature of chlorine in $\text{R}_f(\text{FCO})\text{NCl}$ and the previously reported similar case where chlorine is not displaced by CF_3S ¹¹



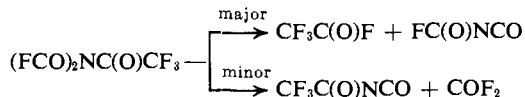
it is highly unlikely that the reaction in this case proceeds *via* CF_3SHgCl but rather



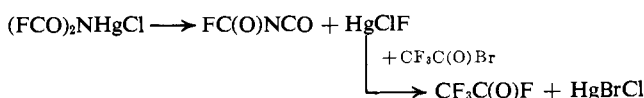
The amine, $\text{CF}_3\text{C}(\text{O})(\text{FCO})\text{NSCF}_3$, decomposed upon standing in glass or when transferred in the vacuum manifold. A fluoride ion shift from the fluoroformyl moiety to either CF_3S or $\text{CF}_3\text{C}(\text{O})$ is a likely step in the decomposition process and accounts for the decomposition products.



When $\text{R}_f(\text{FCO})\text{NCl}$ was agitated with Hg and $\text{CF}_3\text{C}(\text{O})\text{Cl}$ up to 60° where the $\text{R}_f(\text{FCO})\text{NHgCl}$ began to decompose rapidly, no reaction occurred and the $\text{CF}_3\text{C}(\text{O})\text{Cl}$ was recovered quantitatively. While reaction with $\text{CF}_3\text{C}(\text{O})\text{Br}$ at 25° resulted solely in the formation of $\text{CF}_3\text{C}(\text{O})\text{F}$ and R_fNCO , when $(\text{FCO})_2\text{NCl}$ was treated with $\text{CF}_3\text{C}(\text{O})\text{Br}$, the product apparently decomposed by two routes.



The fact that $\text{CF}_3\text{C}(\text{O})\text{NCO}$ and COF_2 resulted when $(\text{FCO})_2\text{NCl}$ was the reacting amine supports the above reaction and tends to discredit an alternate route which involved the initial decomposition of the amido mercuric chloride.



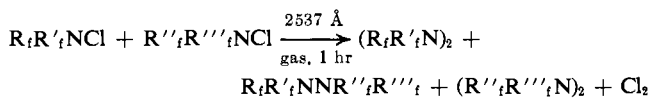
(21) R. N. Hazeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1966).

When a chloramine was mixed with $\text{CF}_3\text{C}(\text{O})\text{Br}$, a red-brown color (BrCl) appeared immediately. However, after 24 hr, the reaction was far from complete since the chloramine was recovered essentially quantitatively.

Other N-Cl systems were examined also. When the somewhat simpler $(\text{CF}_3)_2\text{NCl}$ was mixed with CF_3SCl and then agitated with mercury, only $\text{CF}_3\text{N}=\text{CF}_2$ and CF_3SSCF_3 were recovered. However, if the reactants were diluted with benzene, prior to shaking with Hg, moderate yields of $(\text{CF}_3)_2\text{NSCF}_3$ ¹¹ resulted.

The rate of reaction of $(\text{CF}_3)_2\text{C}=\text{NCl}$ with mercury was significantly slower than that of the chloramines; *i.e.*, complete reaction resulted after 4-5 hr compared to less than 0.5 hr. This slow formation of $(\text{CF}_3)_2\text{C}=\text{NHgCl}$ accounts for the failure of the reaction between Hg, CF_3SCl , and $(\text{CF}_3)_2\text{C}=\text{NCl}$ to produce $(\text{CF}_3)_2\text{C}=\text{NSCF}_3$ (in contrast to the $\text{CF}_3(\text{FCO})\text{NCl}$ system) with CF_3SSCF_3 found as the only volatile product. Some of the $(\text{CF}_3)_2\text{C}=\text{NCl}$ was consumed in $(\text{CF}_3)_2\text{C}=\text{N HgCl}$ formation. However, if CF_3SCl was added to a mixture of $(\text{CF}_3)_2\text{C}=\text{NHgCl}$ and Hg, formed from the reaction of $(\text{CF}_3)_2\text{C}=\text{NCl}$ and excess Hg, $(\text{CF}_3)_2\text{C}=\text{NSCF}_3$ ²² resulted readily. The fact that $(\text{CF}_3)_2\text{C}=\text{NC}(\text{O})\text{CF}_3$ ⁷ resulted when $\text{CF}_3\text{C}(\text{O})\text{Br}$, $(\text{CF}_3)_2\text{C}=\text{NCl}$, and Hg were agitated at 25° suggested that rates of reaction of the two halogen compounds with mercury are again different. In this case, the imine chloride reacted to form the imido mercuric chloride which in turn formed the final product with the less reactive $\text{CF}_3\text{C}(\text{O})\text{Br}$. The greater stability of $(\text{CF}_3)_2\text{C}=\text{NC}(\text{O})\text{CF}_3$ compared to $\text{CF}_3(\text{FCO})\text{NC}(\text{O})\text{CF}_3$ arises in part from the absence of a labile fluoride ion available to undergo a shift which would enhance the possibility of the formation of more stable simple molecules.

A new family of mixed perfluoroalkyl(fluoroformyl) and tetrakis(fluoroformyl) hydrazines resulted from the low-pressure photolysis of a substituted chloramine or mixtures of chloramines.



$\text{R}_i, \text{R}'_i, \text{R}''_i, \text{R}'''_i = \text{any combination of } \text{CF}_3 \text{ and/or } \text{FCO}$

While photolysis of bis(perfluoroalkyl)chloramines has been shown to form stable $(\text{R}_i)_2\text{N}\cdot$ radicals^{12,23} which dimerize to the respective hydrazines, careful photolysis conditions were required to preclude decomposition of the amino radical when the parent amine contained perfluoroacyl substituent groups. At wavelengths greater than 3000 Å, the $(\text{FCO})_2\text{N}-$ moiety decomposed to form COF_2 and $-\text{NCO}$, but the symmetric hydrazine formed in good yield at 2537 Å. The rate of decomposition of $\text{CF}_3(\text{FCO})\text{N}-$ to give COF_2 was much slower which permitted the use of a 450-W medium-pressure lamp to form the hydrazine as well as the insertion products described below. In contrast, it was not possible under the conditions used to prevent the complete decomposition of $\text{CF}_3\text{C}(\text{O})(\text{FCO})\text{N}-$ and therefore the isolation of its dimer was not realized.

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The problems associated with photolytic decomposition were minimized through the use of low-pressure sources with 80-90% of the radiation at 2537 Å.

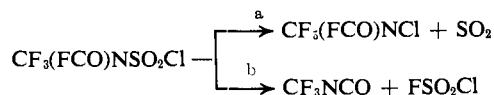
Since the equilibrium vapor pressures of these chloramines at 25° vary greatly, gas-phase photolysis reactions were required to ensure formation of the mixed hydrazines. When $(\text{CF}_3)_2\text{NCl}$ ($P_{25^\circ} > 1 \text{ atm}$) was photolyzed in a small quartz vessel with an equal amount of $(\text{FCO})_2\text{NCl}$ ($P_{25^\circ} = 16 \text{ Torr}$), only the symmetric hydrazines, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ and $(\text{FCO})_2\text{NN}(\text{FCO})_2$, were obtained. However, when these two chloramines in the gas phase were photolyzed under otherwise identical conditions, only a trace of $(\text{FCO})_2\text{NN}(\text{FCO})_2$ was found. Invariably the more volatile symmetric hydrazine was formed in large excess over the symmetric hydrazine of lower volatility.

Although all of the hydrazines in this study were stable in glass at 25° for extended periods, the least stable, $(\text{FCO})_2\text{NN}(\text{FCO})_2$, was 75% decomposed after 24 hr at 135° in glass. While $(\text{CF}_3)_2\text{NN}(\text{FCO})_2$ decomposed slowly over a period of days at 200°, its isomers, $\text{CF}_3(\text{FCO})\text{NN}(\text{FCO})\text{CF}_3$ and $(\text{CF}_3)_2\text{NN}(\text{FCO})\text{CF}_3$, were stable at 270° for 12 hr in stainless steel vessels. The possibility for fluorine transfer to form COF_2 and a stable isocyanate accounts for this lower stability compared to $((\text{CF}_3)_2\text{N})_2$ ²⁴ (stable to 325°) or $(\text{CF}_3\text{C}(\text{O}))_2\text{N}_2$ ²⁵ (stable to 350°). These new hydrazines, however, are much more stable than the parent chloramines⁸ due to the abnormally shortened and strong nitrogen-nitrogen bond. Support for this conclusion was obtained from the fact that insertions into the N-N bond by CO, for example, to form ureas, did not occur. Either no reaction or complete decomposition was observed.

Carbon monoxide inserted readily into the N-Cl bond of $\text{CF}_3(\text{FCO})\text{NCl}$ to form the stable acid chloride $\text{CF}_3(\text{FCO})\text{NC}(\text{O})\text{Cl}$. However, due to the inherent susceptibility of acyl groups to photolytic decomposition, it was not possible to obtain the analogous acid chloride *via* an insertion reaction with either $(\text{FCO})_2\text{NCl}$ or $\text{CF}_3\text{C}(\text{O})(\text{FCO})\text{NCl}$.

The $\text{CF}_3\text{C}(\text{O})$ functional group was susceptible to photolytic decomposition by elimination of $\text{CF}_3\cdot$. $\text{CF}_3\text{C}(\text{O})(\text{FCO})\text{NCl}$ decomposed photolytically in the presence of CO to $\text{FC}(\text{O})\text{NCO}$ and all possible combinations of $\text{CF}_3\cdot$, $\text{Cl}\cdot$, and CO. The $(\text{FCO})_2\text{N}-$ moiety was particularly unstable to photolysis at energies less than 3000 Å. $(\text{FCO})_2\text{NCl}$ in the presence of CO decomposed photolytically to COF_2 , COFCl , COCl_2 , $\text{FC}(\text{O})\text{NCO}$, and $\text{ClC}(\text{O})\text{NCO}$.

Sulfur dioxide was found to insert into the NCl bond of $\text{CF}_3(\text{FCO})\text{NCl}$ when conditions analogous to that of CO insertion were employed. However, the sulfuryl chloride $\text{CF}_3(\text{FCO})\text{NSO}_2\text{Cl}$, although isolated, was too unstable to be characterized. The observed decomposition products suggested decomposition *via* either SO_2 elimination (a) or a fluoride ion shift (b)



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Table I. Thermodynamic and Elemental Analyses Data

Compound	A ^a	B ^a	Bp, °C	ΔH_v , kcal/mol	ΔS_v , eu	% C	% F	% N	% S/Cl	Mol wt
CF ₃ (FCO)NSCF ₃	7.6659	1555.0	52	7.12	21.9	(15.58) ^b 15.52	(57.6) 57.9	(6.06) 5.99	(13.85) 13.94	(231) 228
(FCO) ₂ NSCF ₃	8.4988	2127.7	106	9.85	25.9	(17.22) 17.24	(45.5) 45.8	(6.70) 6.67	(15.31) 15.49	(209) 210
CF ₃ (FCO)NC(O)Cl	7.9955	1735.7	126	7.97	19.9	(18.62) 18.71	(39.3) 40.9	(7.23) 7.39	18.3 (17.3)	(193) 191
CF ₃ (FCO)NNCF ₃ (FCO)	8.0722	1734.9	61	7.99	23.9	(18.46) 18.38	(58.5) 58.6	(10.77) 10.84		(260) 263
(FCO) ₂ NN(FCO) ₂	8.5061	2180.2	115	9.98	25.8	(22.22) 22.32	(35.2) 35.4	(12.96) 13.07		(216) 212
CF ₃ (FCO)NN(FCO) ₂	8.4420	2006.9	89	9.19	25.4	(20.16) 20.14	(47.9) 48.0	(11.76) 11.82		(238) 233
(CF ₃) ₂ NNCF ₃ (FCO)	7.3520	1451.4	52	6.63	20.4	(17.02) 16.80	(67.4) 67.6	(9.93) 9.84		(282) 277
(CF ₃) ₂ NN(FCO) ₂	5.2815	1610.2	73	7.41	21.4	(18.46) 17.97	(58.5) 56.4	(10.77) 10.77		(260) 259

^a $\log P_{\text{Torr}} = A - B/T(^{\circ}\text{K})$. ^b Calculated value.

Table II. Infrared and ¹⁹F Nmr Spectra

Compound	Ir, cm ⁻¹	¹⁹ F Nmr ^a
CF ₃ (FCO)NC(O)Cl	1873 vs, 1810 vs, 1348 s, 1307 s, 1260 s, 1215 vs, 1035 w, 1003 m, 962 s, 755 m, 722 w	CF ₃ ^b = 57.95 (d) FCO = 7.63 (q) $J_{\text{F-F}} = 16.6$
CF ₃ (FCO)NSCF ₃	1878 s, 1315 s, 1282 s, 1230 br, 1182 s, 1122 s, 1015 w, 975 m, 752 m, 680 m	CF ₃ ^b = 57.71 (d of q) FCO = 5.52 (q of q) CF ₃ S = 51.96 (c) FCO ^b = -0.47 (q) CF ₃ S = 51.03 (t) $J_{\text{CF}_3\text{-FCO}} = 15.3$ $J_{\text{CF}_3\text{S-FCO}} = 3.1$ $J_{\text{CF}_3\text{S-CF}_3} = 3.0$ $J_{\text{FCO-CF}_3\text{S}} = 3.1$
(FCO) ₂ NSCF ₃	1918 m, 1879 s, 1289 m, 1233 vs, 1201 s, 758 w	CF ₃ S = 51.03 (t) $J_{\text{FCO-CF}_3\text{S}} = 3.1$
(CF ₃) ₂ NNCF ₃ (FCO)	1890 s, 1397 m, 1340 vs, 1315 vs, 1298 vs, 1230 s, 1200 br, 1040 m, 992 s, 912 w, 893 m, 744 m, 722 m, 700 m	(CF ₃) ₂ ^c = 61.40 (p) (CF ₃) ₁ = 61.96 (d, br) FCO = 12.31 (q, br) $J_{(\text{CF}_3)_1\text{-FCO}} = 13.5$ $J_{(\text{CF}_3)_2\text{-(CF}_3)_1} = 3.5$
(CF ₃) ₂ NN(FCO) ₂	1919 m, 1895 vs, 1871 s, 1389 s, 1382 vs, 1303 vs, 1264 vs, 1232 s, 1204 m, 1060 w, 1000 s, 922 w, 901 w, 760 m, 730 m, 698 m	FCO = 60.14 (t) FCO = 6.47 (h) $J_{\text{CF}_3\text{-FCO}} = 2.6$
CF ₃ (FCO)NNCF ₃ (FCO)	1887 vs, 1390 w, 1385 s, 1338 s, 1237 s, 1290 s, 1260 s, 1232 s, 1205 m, 1045 m, 998 m, 892 w, 740 m, 678 w	CF ₃ ^c = 61.32 (d) FCO = 14.31 (q) $J_{\text{CF}_3\text{-FCO}} = 15.2$
CF ₃ (FCO)NN(FCO) ₂	1932 w, 1898 vs, 1872 vs, 1393 m, 1331 s, 1310 s, 1268 s, 1240 s, 1057 m, 1009 w, 928 w, 909 w, 758 m, 748 m, 697 m	CF ₃ ^c = 60.38 (d) (FCO) ₂ = 7.36 (s, br) (FCO) ₁ = 13.11 (q) $J_{(\text{FCO})_1\text{-CF}_3} = 15.0$ $J_{(\text{FCO})_2\text{-CF}_3} = 1.5$ $J_{(\text{FCO})_2\text{-(FCO})_1} = (u)$
(FCO) ₂ NN(FCO) ₂	1905 s, 1865 vs, 1368 w, 1323 s, 1272 s, 1248 s, 1086 w, 1052 m, 843 m, 715 w	FCO ^c = 0.96 (s)

^a ϕ = MHz (CFCl₃), J = Hz, br = broad, c = complex, d = doublet, h = heptet, p = pentet, s = singlet, t = triplet, u = unresolved. Spectra obtained at 30°. ^c Spectra obtained at 70°. ^d -70°.

Table III. Mass Spectra (70 eV)

Compound	Significant fragments for structure confirmation
CF ₃ (FCO)NSCF ₃	M ⁺ 11.6 ^a , (M - F) ⁺ 3.1, (CF ₃ SNCO) ⁺ 9.3, (CF ₃ NCO) ⁺ 4.0
(FCO) ₂ NSCF ₃	M ⁺ 6.0, (CF ₃ SF) ⁺ 10.0, (CF ₃ SN) ⁺ 6.0, (CF ₃ S) ⁺ 14.7, (FC(O)NCO) ⁺ 27.0
CF ₃ (FCO)NC(O)Cl	(M - Cl) ⁺ 5.8, (CF ₂ NCO) ⁺ 15.2, (CF ₂ NCO) ⁺ 12.6, (C(O)NCO) ⁺ 9.1
(CF ₃) ₂ NNCF ₃ (FCO)	M ⁺ 2.3, (M - F) ⁺ 2.1, (M - COF ₂) ⁺ 3.1, (M - CF ₄) ⁺ 4.8, (M - CF ₃) ⁺ 8.3
(CF ₃) ₂ NN(FCO) ₂	M ⁺ 5.7, (M - F) ⁺ 1.5, (M - COF ₂) ⁺ 4.0
CF ₃ (FCO)NNCF ₃ (FCO)	M ⁺ 3.7, (M - F) ⁺ 1.2, (M - CF ₃) ⁺ 1.7, (M - CF ₄) ⁺ 7.0
CF ₃ (FCO)NN(FCO) ₂	M ⁺ 4.2, (M - COF ₂) ⁺ 10.8, (COF ₃) ⁺ , (SiF ₂) ⁺ 9.1
(FCO) ₂ NN(FCO) ₂	M ⁺ 1.6, (M - COF ₂) ⁺ 2.8, (COF ₃) ⁺ , (SiF ₂) ⁺ 7.9

^a Per cent relative abundance.

No attempts were made to introduce SO₂ into either CF₃C(O)(FCO)NCl or (FCO)₂NCl. The thermodynamic data, elemental analyses, ir spectra, and mass spectra of the new compounds are cited in Tables I, II, and III.

The mass spectra taken at an ionizing voltage of 70 eV confirm all of the new compounds. The molecular ion (M⁺) was observed for all of the compounds except for CF₃(FCO)NC(O)Cl where the largest m/e observed was (M - Cl)⁺. The second most intense peak in the spectrum of the latter compound was the C(O)-³⁵Cl (m/e 63). The associated C(O)³⁷Cl⁺ (m/e 65) exhibited the proper intensity ratios for the chlorine isotopes. All of the compounds had a base peak of m/e 69 (CF₃⁺) except (FCO)₄N₂ which exhibited a base peak of m/e 44 (CO₂⁺ and N₂O⁺). All of the hydra-

zines that contained the (FCO)₂N- moiety exhibited intense (m/e 44) peaks and the second largest m/e (M - COF₂)⁺. (M - F)⁺ ions were observed for each of the hydrazines which contained the CF₃(FCO)N- moiety.

The ¹⁹F nmr spectra of the amines were typical and are reported in Table II. The nmr spectra of the hydrazines were temperature dependent which implies conformer effects. The spectra indicate multiple conformer changes over the range of -70 to +70° which was dependent on the hydrazine concerned. From +70 to +120° various conformer effects seemed to disappear or were minimized. Therefore in Table I the nmr data were reported at 70°.

Conformer effects are the topic of continued research. The changes could involve hindered bond ro-

tation about the N-N bond²⁶⁻²⁹ inversion of the nitrogen atom,^{30,31} and the resonance effects of the non-

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bonded electrons of the nitrogen interacting with the fluoroformyl group resulting in hindered bond rotation about the carbonyl nitrogen bond.^{31,32} The number and location of the FCO group seem to determine the complexity of the variable temperature spectra; e.g., (CF₃)₄N₂ yields the simplest and CF₃(FCO)NNCF₃-(FCO) gave the most complex spectra of the entire hydrazine series. It should be noted that (CF₃C(O))₄N₂²⁵ and (CF₃FN)₂³² are reported to have incongruous nmr spectra.

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Activated Metals. IV. Preparation and Reactions of Highly Reactive Magnesium Metal¹

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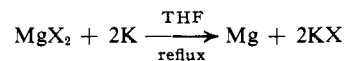
Abstract: The reduction of magnesium salts in ethereal solvents with potassium or sodium yields magnesium in the form of a fine black powder. This magnesium metal exhibits unusual reactivity toward alkyl and aryl halides. For example, bromobenzene reacts with the magnesium yielding phenylmagnesium bromide in a few minutes at -78°. The addition of potassium iodide and other inorganic salts prior to the reduction of the magnesium salt yields magnesium of even greater reactivity. Reactions of this magnesium with a variety of alkyl and aryl halides were studied as well as some of the physical properties of the black magnesium powders.

Grignard reagents represent one of the most important and versatile classes of organic intermediates known to the synthetic chemist. In spite of this, several types of Grignard reagents have not been readily available due to the lack of or slowness of reaction of certain types of halides with magnesium metal.

Previous to our studies, there were three basic modifications of the general procedure for the direct synthesis of difficultly formed Grignard reagents from the reaction of magnesium metal and an organic halide: (1) use of higher reaction temperatures by solvent variation, (2) use of a more strongly coordinating solvent, such as THF,³⁻⁷ and (3) activation of the magnesium metal.⁸⁻¹² The third method consists of activation of

the magnesium by reduction of the size of the metal particle¹¹ or by a chemical reaction. The Gilman catalyst,⁸ which involves the addition of iodine to activate the magnesium, is representative of this technique. Ethyl bromide and ethylene bromide have been employed in catalytic amounts to activate the metal surface and in molar quantities as entrainers.⁹ The use of certain transition metal halides has proven them to be useful catalysts.¹⁰ Ashby has recently combined the three techniques to prepare some alkylmagnesium fluorides.¹²

The initial studies of Rieke and Hudnall of the preparation of highly reactive magnesium metal have been reported.¹ We wish to report here further studies of activated magnesium prepared in a highly reactive state, finely divided, and free of metal oxides. The general technique is the reduction of a magnesium halide with alkali metal or other reducing agent, preferably in an ethereal solvent, and under an inert atmosphere. If



alkali metals are used, a solvent whose boiling point exceeds the melting point of the alkali metal is chosen. The reduction of magnesium halide yields a fine gray-black powder of magnesium metal. Usually, the Grignard reagents were prepared by simply adding the organic halide to the suspension of magnesium metal.

The studies reported here and preliminary investigations¹ show the reactivity of magnesium produced by our method is vastly superior to that of any of the methods described above.

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