transfer spectrum is from $(N{=}O)^-$ to cobalt, just as are the charge-transfer bands in the halogen complexes of cobalt(III).[17]

The pentacoordinate complex, $[CoNO(das)_2][ClO_4]_2$, again deserves special consideration. The reflectance spectrum of the complex is quite different from that of the other nitrosyl complexes of this series, having no absorption bands below 19,000 cm.$^{-1}$. There are two bands at 25,000 cm.$^{-1}$, which are probably due to d–d transitions. Although it is not yet clear what the formal oxidation state of cobalt is in this five-coordinate nitrosyl, it probably consists of NO coordinated to Co(II) with spin pairing between the odd electron on the NO ligand and the Co(II), thus accounting for the observed diamagnetism of the compound. Further study is needed before drawing any final conclusions about the bonding in this five-coordinate complex.

Summary

With the exception of $[CoNO(das)_2][ClO_4]_2$, the properties of the mononitrosyl compounds of cobalt reported above can be described in terms of a model which consists of a Co(III) ion coordinated to $(N{=}O)^-$ and five other ligands. This model is capable of correlating such diverse observations as: (1) the observed NO stretching frequencies (typical of double bonds); (2) the presence of *cis* and *trans* isomers typical of Co(III); and (3) the ligand field and charge-transfer spectra, which are typical of those observed for other six-coordinate Co(III) compounds containing ligands other than NO. Further experiments are in progress to test the implications of such a model for other metal complexes containing NO groups with low NO stretching frequencies (1550 cm.$^{-1}$).

(17) H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

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Fluorophosphine Ligands. I. The Preparation and Characterization of Difluorophosphine

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From a reaction involving equal amounts of HI and PF_2I in the presence of free mercury, difluorophosphine has been isolated and characterized. The physical properties and spectral data for PHF_2 are compared to those of PH_3 and PF_3; they indicate that PHF_2 (a) is monomeric in the vapor, (b) is associated in the liquid, and (c) probably has a pyramidal structure. Basic hydrolysis of difluorophosphine yields hydrogen, indicative of its reducing properties.

Introduction

Nitrogen has been known to form haloamines for some time.[1-3] The literature also mentions an attempted characterization of halophosphines, but no real halophosphines were ever isolated.[4] We wish to report the preparation and characterization of difluorophosphine, PHF_2.

Difluorophosphine was prepared by a reaction involving equal amounts of PF_2I[5] and HI in the presence of free mercury. The equation is

$$PF_2I + HI + 2Hg \longrightarrow PHF_2 + Hg_2I_2$$

A typical experiment resulted in a 55% yield of the fluorophosphine based on the amount of PF_2I taken.

Experimental

Apparatus.—Standard high-vacuum techniques were used throughout.

Materials.—Phosphorus(III) iododifluoride was prepared by the action of hydrogen iodide on dimethylamidophosphorous difluoride.[6] Hydrogen iodide was prepared by standard methods.[7]

Preparation of Difluorophosphine.—A 2.0-cc. sample of triply distilled mercury was placed in a 70-cc. reaction tube which was equipped with a stopcock and a standard taper joint. The tube was evacuated and 3.36 mmoles of PF_2I and 3.36 mmoles of HI were condensed into the tube at −196°. After warming to 25° the tube was shaken for 1.5 hr. The tube was then opened to the Toepler system through two −196° traps and 0.17 mmole of H_2 (identified by gas density) was recovered. The products condensable at −196° were passed through traps at −140, −160, and −196°. A 0.72-mmole sample of PF_3 was trapped at −196° and a 0.47-mmole sample of an unstable compound assumed to be $PHF_2{\cdot}HI$ was retained at −140°. This compound decomposed at room temperature to yield PF_3, SiF_4, and yellow solids which contained iodine.[8]

A 1.85-mmole sample of the desired PHF_2 was retained in the trap at −160°. A second run using 1.52 mmoles of each reagent gave 0.84 mmole of PHF_2, 0.30 mmole of PF_3, 0.10 mmole of H_2,

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(1) A. Kennedy and C. B. Colburn, *J. Am. Chem. Soc.*, **81**, 2906 (1959).

(2) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(3) R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929).

(4) P. Royen and K. Hill, *Z. anorg. allgem. Chem.*, **229**, 112 (1936).

(5) Phosphorus(III) iododifluoride was originally reported by R. G. Cavell, *J. Chem. Soc.*, **1992** (1964), to be unstable and disproportionate rapidly to PF_3 and PI_3. Experiments in this laboratory indicate that PF_2I is reasonably stable. Complete characterization of this ligand and more of its chemistry will be presented in a future publication.

(6) This method for the preparation of pure phosphorus(III) monohalodifluorides was developed in this laboratory by (a) Sr. M. A. Fleming, Doctoral Dissertation, University of Michigan, 1963; (b) A. Moyé, unpublished results, University of Michigan, 1961, and reported independently by Cavell (ref. 5).

(7) C. J. Hoffman and E. A. Heintz, *Inorg. Syn.*, **7**, 180 (1963).

(8) In a separate experiment an equimolar mixture of PF_2H and HI decomposed to give PF_3, SiF_4, and yellow solids which contained iodine.

and 0.18 mmole of the unstable species retained at −140° as products.[9]

The X-ray powder pattern of the gray solids formed during the reaction was consistent with that of Hg_2I_2.

Hydrolysis of PHF_2.—Difluorophosphine (0.49 mmole) was condensed into a tube containing 10 ml. of 40% NaOH and then the tube was sealed off and held at 100° for 2 hr. After opening the tube 0.44 mmole of H_2 was recovered. In a separate experiment, water vapor (0.32 mmole) was allowed to mix with PHF_2 vapor (0.43 mmole) at 25°. After about 5 min., liquids began to form on the walls of the reaction tube. The only volatile recovered from the tube was silicon tetrafluoride (0.17 mmole).

Analysis.—A sample of difluorophosphine was pyrolyzed over chunks of uranium metal. The hydrogen evolved was identified by gas density and measured with a Toepler system. *Anal.* Calcd. for PHF_2: H, 1.43. Found: H, 1.46. Difficulties were encountered in obtaining satisfactory phosphorus and fluorine analysis; however, all other experimental and physical data leave no reasonable alternative to the formula PHF_2.

Characterization of Difluorophosphine

The formula PHF_2 is supported unequivocally by the hydrogen analysis, by the vapor density molecular weight value of 70.8 g./mole (*calcd.* for PHF_2: 70.0 g./mole), by the mass spectrum shown in Table I, and by both proton and fluorine n.m.r. spectra.

The proton spectrum, presented in Figure 1, shows a doublet, due to P–H spin–spin coupling, with each member of the doublet split into a 1:2:1 triplet by spin–spin coupling of the hydrogen with two equivalent fluorines. The P–H coupling constant of 182.4 c.p.s. is very close to the value of 183 c.p.s. reported for PH_3.[10] The F–H coupling constant is 41.7 c.p.s.

The fluorine n.m.r. resonance signal (Figure 2) is also split into a doublet by spin–spin coupling with phosphorus, and each member of the original doublet is again split into a doublet by coupling with the proton attached to phosphorus. The P–F coupling constant of 1134 ± 4 c.p.s. is somewhat lower than the value of 1400 c.p.s. found in PF_3,[10] but is in the range of substituted fluorophosphines. The J_{F-H} value of 40 ± 4 c.p.s. is consistent with the value of 41.7 c.p.s. found in the proton n.m.r. spectrum.

Table I

Mass Spectrum of PHF_2[a]

m/e	Relative peak height	Assignment	m/e	Relative peak height	Assignment
70	100.00	PF_2H^+	25.5	1.0	PFH^{2+}
69	52.4	PF_2^+	25	3.0	PF^{2+}
51	84.3	PFH^+	20	0.6	FH^+
50	27.5	PF^+	19	4.6	F^+
34.5	0.8	PF_2^{2+}	16	1.2	PH^{2+}
32	3.9	PH^+	15.5	2.3	P^{2+}
31	16.0	P^+			

[a] The spectrum was obtained on a Consolidated Electrodynamics Model 21-103B mass spectrometer at 70 e.v.; the spectrum was not investigated below *m/e* 14.

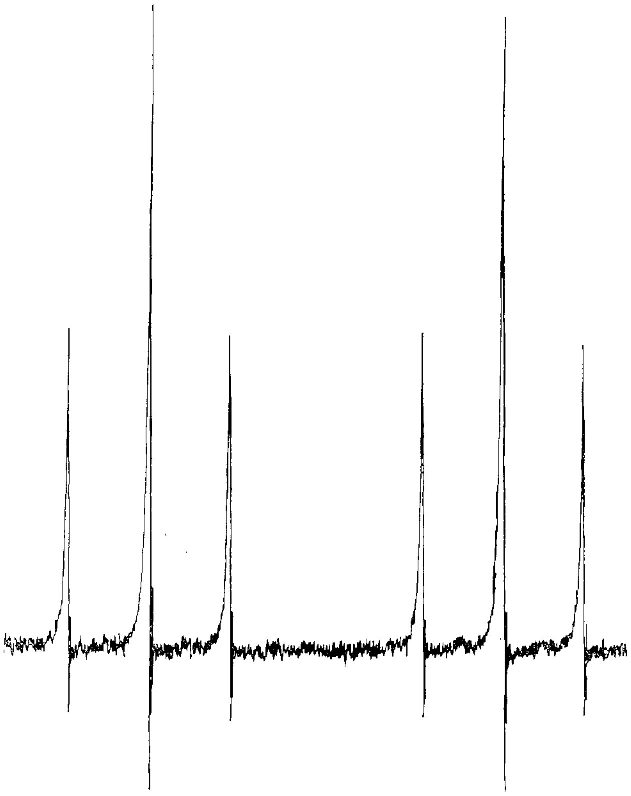

Figure 1.—^1H n.m.r. spectrum of $PHF_2(l)$ at −20°.

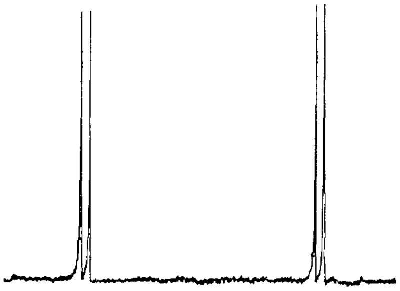

Figure 2.—^{19}F n.m.r. spectrum of $PHF_2(l)$ at −20°.

The molecular weight determination was confirmed by the mass spectrum (Table I), which is consistent with the fragmentation pattern expected for PHF_2.

General Chemical Characteristics.—Difluorophosphine is a stable colorless gas which can be maintained at room temperature and saturation pressure for 5 hr. with less than 5% decomposition. At lower pressures and temperatures PHF_2 is more stable, and, unlike difluoramine, we have never experienced violent disproportionation when difluorophosphine is condensed to the liquid or solid states.

The basic hydrolysis of PHF_2 is consistent with the equation

$$PHF_2 + H_2O \longrightarrow PF_2OH + H_2$$

However, less than 100% yields of H_2 indicate that a secondary reaction occurs. This secondary hydrolysis is $PHF_2 + 2H_2O \rightarrow HP(OH)_2 + 2HF$, followed by HF + (glass walls of tube) → SiF_4 as indicated in the hydrolysis of PHF_2 by water vapor. This behavior is similar to that observed for hydridic M–H linkages.

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[9] A satisfactory mass balance is obtained for each run if one assumes that PF_3 was formed by $3PF_2I \rightarrow 2PF_3 + PI_3$ and that the unstable material stopped at −140° was $PHF_2 \cdot HI$. Run 1: mmoles in: P, 3.36; F, 6.72; H, 3.36; mmoles out: P, 3.40; F, 6.80; H, 3.13. Run 2: mmoles in: P, 1.52; F, 3.04; H, 1.52; mmoles out: P, 1.47; F, 2.94; H, 1.40.

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 196.

It is also interesting to note that PHF_2 reduces water in basic solution whereas PH_3 can be prepared by the reaction of white phosphorus with a concentrated alkaline solution.

Although the elucidation of its chemistry is still in the preliminary stages, one might expect difluorophosphine to be similar in many respects to difluoramine, which is probably best described as amphoteric.[11-13]

Physical and Spectral Properties.—Vapor pressure data for PHF_2 ($-129.4°$, 2.7 mm.; $-112.0°$, 20.6 mm.; $-100.9°$, 56.4 mm.; $-84.4°$, 206.0 mm.; $-78.5°$, 308.2 mm.) are summarized by the equation

$$\log p \text{ (mm.)} = -1126/T + 8.280$$

The Trouton constant is 24.7 cal. deg.$^{-1}$ mole^{-1}, b.p. (extrapolated by vapor pressure equation) $-64.6°$, f.p. (sealed tube) -124.2 to $-123.6°$. Vapor density studies gave a molecular weight of 70.8 g./mole for PHF_2 (calcd. 70.0 g./mole).

The above data indicate that difluorophosphine is associated in the condensed phase and monomeric in the vapor. For comparison one should note that PHF_2 freezes and boils at higher temperatures than either PH_3 or PF_3; likewise, it has a higher entropy of vaporization (PH_3: b.p. $-87.8°$, f.p. $-133.8°$, Trouton constant 18.8 cal. deg.$^{-1}$ mole^{-1}; PF_3: b.p. $-101.8°$, f.p. $-151.5°$, Trouton constant 23.1 cal. deg.$^{-1}$ mole^{-1}).[14]

Corroborative evidence for association in the liquid is provided in the ^1H n.m.r. chemical shifts (Table II).

TABLE II

^1H AND ^{19}F N.M.R. DATA[a]

	PHF_2(l)		PHF_2 (g)	PH_3 (l)	PH_3 (g)	PF_3
	^1H	^{19}F	^1H	^1H	^1H	^{19}F
δ, p.p.m.	7.65^b	...	1.3^b	1.1^e	1.3^e	...
J_{PH}, c.p.s.	182.4	...	*d*	183^f	...	...
J_{FH}, c.p.s.	41.7	40 ± 4^c	*d*	...	...	...
J_{PF}, c.p.s.	...	1134 ± 4^c	*d*	...	...	1400^f

[a] The proton and fluorine n.m.r. spectra of liquid PHF_2 at $-20°$ were determined with Varian Associates A-60 and HR-100 (operating at 91.4 Mc.) n.m.r. spectrometers, respectively. The proton spectrum of difluorophosphine vapor was determined with the HR-100 at the ambient temperature of the instrument. [b] Shift downfield from TMS internal standard. [c] Measured by side-band technique. [d] Complex. [e] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958). Their value relative to cyclopentane. Tabulated value for liquid PH_3 adjusted to TMS at $-20°$; value for PH_3 gas adjusted to TMS at room temperature. $\delta_{liq} - \delta_{gas} \neq 0.78$ p.p.m. as given by S. B. and P. since bulk susceptibility corrections not applied. [f] Reference 10.

The large difference observed in the chemical shifts of PHF_2 vapor and PHF_2 liquid is indicative of association. It is yet to be determined whether this is a $>P-F--H--P<$ or a $>P-H--P<$ type bonding.[15] Since the chemical shift of liquid difluorophosphine is probably predominantly affected by association, it is difficult to compare with that of PH_3 as a measure of the acidity of the free P–H linkage. In fact, the gas phase proton chemical shifts of phosphine and difluorophosphine appear to be nearly identical (Table II).

The infrared spectrum (4000–200 cm.$^{-1}$) of PHF_2 vapor[16] shows absorption at (cm.$^{-1}$; tentative assignments included in parentheses): 2251 (R) br, m, 2240.5 (Q) vs, 2233 (P) br, m (ν_s P–H); 1015.7 s (δ_s P–H); 1008 br, m (δ_{as} P–H); 851.4 vs (ν_s P–F); 838.3 s, 825.3 m (ν_{as} P–F); 367 (R) br, w, 348 (P) br, w (δ_s F–P–F).[17] When compared with the P–H stretching frequencies of phosphine [ν_s (PH) = 2327 cm.$^{-1}$, ν_{as} (PH) = 2421 cm.$^{-1}$],[18] the P–H stretching frequency observed for difluorophosphine indicates that the P–H bond is probably more labile in difluorophosphine.

The infrared spectrum (4000–200 cm.$^{-1}$) of solid PHF_2[19] shows absorption at (cm.$^{-1}$): 2317.0 s, 1008.5 s, 968.0 m, 825.7 m, 782.8 vs, 371.3 s. When comparing the infrared spectra of solid and gaseous PHF_2, it is interesting to note the pronounced shift of the P–H stretching motion to a *higher* frequency in the solid, contrary to what would be expected if hydrogen bonding occurred in the solid. It should also be noticed that the P–F stretching motions are shifted to lower frequencies. The magnitudes of the changes in the P–F frequencies are comparable to those observed for PF_3 and other related compounds.[20] The lowering of the P–F stretching frequency in the solid is indicative of interaction through the fluorine atoms resulting in a diminution of the inductive effect of fluorine and a concomitant strengthening of the P–H bond so that the P–H stretching frequency approaches that usually observed in phosphines.

Some physical properties relating to the N–H and P–H bonds of NHF_2 and PHF_2 are similar when compared to those of NH_3 and PH_3. The proton n.m.r. chemical shift (δ *ca.* 7.4 p.p.m.[21]) and N–H stretching frequency (ν (N–H) 3193 cm.$^{-1}$)[22] observed for difluoramine are shifted relative to ammonia (δ 4.8 p.p.m.,[23] ν_s (NH) 3336, 3338 cm.$^{-1}$, ν_{as} (NH)[24] 3414 cm.$^{-1}$) in the same manner as the corresponding values for difluorophosphine are shifted relative to phosphine. It

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(11) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc*, **85**, 3595 (1963).

(12) A. D. Craig, *Inorg. Chem.*, **3**, 1628 (1964).

(13) E. A. Lawton, D. Pilipovich, and R. D. Wilson, *ibid.*, **4**, 118 (1965).

(14) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, New York, N. Y., 1958, p. 185.

(15) The ^1H n.m.r. of PHF_2 vapor may provide an answer to this question. The spectrum consists of a complex multiplet centered approximately 1.3 p.p.m. downfield from TMS; however, resolution of the spectrum is plagued by the low "proton" concentration in the vapor and saturation of the signal by the radiofrequency field.

(16) Determined with a Beckman IR-12 in a 75-mm. gas cell (p = 3 to 20 mm.) equipped with CsI windows.

(17) br, broad; vs, very strong; s, strong; m, medium; w, weak; and P, Q, R, refer to rotation–vibration bands. A complete vibrational study of PHF_2 including band assignments and force constant calculations is now under way in this laboratory.

(18) E. Lee and C. K. Wu, *Trans. Faraday Soc.*, **35**, 1366 (1939).

(19) Determined as a thin film at $-196°$ on a CsI window.

(20) R. C. Taylor, University of Michigan, private communication.

(21) The n.m.r. data for NHF_2 (footnote 1) are very qualitative; however, from the data of A. K. and C. B. C. we estimate δ (downfield from TMS) = approximately the shift of benzene = 7.4 p.p.m.

(22) J. J. Comeford, D. E. Mann, L. J. Schoen, and D. R. Lide, Jr., *J. Chem. Phys.*, **38**, 461 (1963).

(23) H. S. Gutowsky and S. Fujiwara, *J. Chem. Phys.*, **22**, 1782 (1954); their value adjusted for shift downfield from TMS.

(24) H. Y. Sheng, E. F. Barker, and D. M. Dennison, *Phys. Rev.*, **60**, 786 (1941).

will be interesting to observe how well the chemistry of the N–H and P–H bonds in difluoramine and difluorophosphine parallel one another.

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Pentafluorosulfur and Trifluoromethyl Oxydifluoramines. Preparations and Properties[1]

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Tetrafluorohydrazine reacts with pentafluorosulfur hypofluorite and trifluoromethyl hypofluorite to form SOF_4, SF_6, FNO, NF_3, and SF_5ONF_2 and COF_2, CF_4, FNO, NF_3, and CF_3ONF_2, respectively. The new difluoramines are colorless, do not react with glass or mercury at room temperature, and have normal boiling points of −10.0 and −60°, respectively, for the pentafluorosulfur and trifluoromethyl oxydifluoramines. The molecular compositions have been proved by physical methods and the reaction schemes for the formation and thermal decomposition of the compounds are given.

Tetrafluorohydrazine is known to exist in equilibrium with NF_2 radicals at room temperature.[2] Many studies, with and without ultraviolet light, have shown that N_2F_4 is an efficient reagent for the introduction of the NF_2 group into organic and inorganic substrates.[3–11]

Since SF_5OF[12] and CF_3OF[13] have been reported to give small amounts of F_5SO and F_3CO radicals upon irradiation with ultraviolet light, it was thought that N_2F_4 should react with SF_5OF and CF_3OF to give SF_5ONF_2 and CF_3ONF_2, respectively. The experiments described below confirm their discovery and characterization.

Experimental

Materials.—Pentafluorosulfur hypofluorite and trifluoromethyl hypofluorite were prepared by the methods of Dudley[14] and Kellogg,[15] respectively. The crude SF_5OF was purified by fractional codistillation[16] and pure SF_5OF was identified by its molecular weight and infrared spectrum. The crude CF_3OF was placed over water for 3 days to remove the COF_2. The gaseous mixture was then led through a trap at −95° and into a trap at −183° where a white solid was collected. The infrared spectrum of this material was identical with the literature spectrum of CF_3OF,[17] although it is possible that some CO_2 was present. A previous report states that CF_3OF is a liquid at −183°.[15] Tetrafluorohydrazine from E. I. du Pont de Nemours and Co. was sufficiently pure to use without additional purification.

Reaction of SF_5OF with N_2F_4.—The gases for this and all other reactions were handled in a vacuum line system with its stopcocks lubricated by No. 90 Kel-F grease. The appropriate quantities of the two reactant gases were condensed in zones in the cold finger of a 1-l. Pyrex glass vessel and then were allowed to warm to room temperature.

The reaction products were separated by means of fractional codistillation[16] and were identified by their molecular weights and characteristic infrared spectra.

Reaction 1.—Pyrex glass vessel at room temperature with initial pressures of 80 mm. for each reactant. The vessel was allowed to stand 17 hr., 8 of which were in the dark. Products found were NF_3, NO, SiF_4, SF_6, SO_2F_2, SOF_4, SF_5ONF_2, and NO_2. The yield of SF_5ONF_2 was 40 mole % with respect to the reactant, SF_5OF, and all of the SF_5OF and N_2F_4 was consumed.

Reaction 2.—Pyrex glass vessel at room temperature with initial pressures of 41 mm. for each reactant. The vessel was allowed to stand for 23 hr., 12 of which were in the dark. All the SF_5OF and N_2F_4 was consumed, but no SF_5ONF_2 was produced. Products observed were NF_3, NO, SiF_4, SF_6, SO_2F_2, SOF_4, and NO_2.

Reaction 3.—The vessel used was a prefluorinated 0.25-in. o.d. closed-end nickel tube fitted with a No. 327 Hoke valve (Teflon seal on stem). The initial pressure of each reactant in the vessel was 4 atm. After 24 hr. at room temperature, no SF_5ONF_2 was observed; 80% of each reactant was recovered unreacted. The remainder of the gas did not contain NO_2 until the gas had contacted the glass vacuum system. This behavior is indicative of the production of FNO as a primary reaction product. Gases present other than SF_5OF, N_2F_4, and NO_2 were NF_3, SiF_4, SF_6, SO_2F_2, and SOF_4.

Reaction 4.—Pyrex glass vessel at room temperature with initial pressures of 140 mm. for each reactant. Ultraviolet irradiation for 21 hr. by a General Electric Type H100-A4/T lamp produced a 60 mole % yield of SF_5ONF_2 (based on the reactant,

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(1) (a) This report is taken from the Ph.D. thesis of W. H. Hale and was presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965. (b) After this paper had been submitted for publication, the authors learned that G. H. Cady and L. C. Duncan had prepared CF_3ONF_2 several years ago, but because of governmental classification they did not report it or continue its characterization.

(2) (a) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **82**, 2400 (1960); (b) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

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