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Contribution from Rocketdyne,
A Division of Rockwell International Corporation, Canoga Park, California 91304

Synthesis of *N*,*N*-Difluoro-*O*-perfluoroalkylhydroxylamines. 1. Reaction of Perfluoroalkyl Hypofluorites with Difluoramine

WALTER MAYA,[1a] DONALD PILIPOVICH,[1b] MICHAEL G. WARNER,[1c] RICHARD D. WILSON, and KARL O. CHRISTE*

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Perfluoroalkyl hypofluorites react with difluoramine in the presence of alkali-metal fluorides to produce the corresponding $-ONF_2$-substituted perfluoroalkanes. This method was used to prepare the prototype compounds CF_3ONF_2, $(CF_3)_2CFONF_2$, $CF_2(ONF_2)_2$, and $FOCF_2ONF_2$. Physical and spectroscopic properties are reported for these compounds including vibrational assignments for CF_3ONF_2, the simplest member of this class of compounds.

Introduction

Although the existence of NF_3O has been known for more than 20 years,[2] only a few $RONF_2$ compounds have been reported, e.g. CF_3ONF_2, $FC(O)ONF_2$, SF_5ONF_2, and FSO_2ONF_2, usually prepared by the combination of NF_2 and RO radicals generated from N_2F_4 and the corresponding peroxides or hypohalites, respectively.[3] In 1964 studies at Rocketdyne showed that the low-temperature reaction of alkali-metal fluoride–difluoramine adducts with fluorocarbon hypofluorites provides a new synthetic route to $-ONF_2$-substituted fluorocarbons. However, except for a brief and incomplete description of some of the results in a U.S. patent,[4] these data remained unpublished. In this paper, we present a full account of this and some subsequent work in our laboratory.

Experimental Section

Caution! Difluoramine is highly explosive,[5] and protective shielding should be used during handling operations. The compound was always condensed at -142 °C, and the use of a -196 °C bath for condensing HNF_2 should be avoided.[6] Furthermore, the $CsF{\cdot}HNF_2$ adduct invariably explodes before reaching 0 °C.[7]

Materials and Apparatus. Volatile materials, except for HNF_2, were manipulated in a passivated (with ClF_3) stainless-steel vacuum line equipped with Teflon FEP U-traps and 316 stainless-steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Difluoramine was handled in either a Pyrex glass or an all-Teflon PFA vacuum system. The hypofluorites CF_3OF, $(CF_3)_2CFOF$, and $CF_2(OF)_2$[8,9] and difluoramine[6] were prepared by literature methods. The alkali-metal fluorides were dried by fusion in a platinum crucible and then cooled and powdered in the dry N_2 atmosphere of a glovebox.

Table I. Reaction of Perfluoroalkyl Hypofluorites with HNF_2 in the Presence of KF[a]

starting materials (mole ratio)	product	yield, %
CF_3OF, HNF_2 (1:1)	CF_3ONF_2	10
$(CF_3)_2CFOF$, HNF_2 (1:1)	$(CF_3)_2CFONF_2$	10
$CF_2(OF)_2$, HNF_2 (1:2)	$CF_2(ONF_2)_2$	10-20
	$CF_2(OF)ONF_2$	5-10
$CF_2(OF)ONF_2$, HNF_2 (1:2.5)	$CF_2(ONF_2)_2$	20-100[b]

[a] In all reactions, except for that indicated in footnote *b*, $HNF_2{\cdot}KF$ was performed at -78 °C with use of using a large excess of KF; the perfluoroalkyl hypofluorites were added at -126 or -142 °C, and the mixtures were allowed to warm slowly to -80 °C over a period of several hours. [b] The quantitative yield of $CF_2(ONF_2)_2$ was achieved by cocondensation of the starting materials over KF (see text).

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points,[10,11] and the reported frequencies are believed to be accurate to ±2 cm^{-1}. The spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The spectra of matrix-isolated CF_3ONF_2 were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ar (Matheson) was used as a matrix material in a mole ratio of 300:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser and a Claassen filter[12] for the elimination of plasma lines. Quartz tubes (3-mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described[13] device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.[12]

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the $CFCl_3$ solvent with positive shifts being downfield from $CFCl_3$.[14]

Mass spectra were recorded with a CEC21-103C mass spectrometer modified with a metal inlet system, CEC Part No. 285400.

Syntheses of R_fONF_2 Compounds. Most reactions between the perfluoroalkyl hypofluorites and HNF_2 were carried out according to the following general procedure. Finely powdered dry KF (2 g) was loaded in the drybox into a 300-mL Pyrex reactor. Difluoramine (4 mmol) was added from the glass or Teflon line to the reactor at -142 °C. The mixture was warmed briefly to -78 °C and then recooled to -142 °C. The reactor was transferred to the metal line, and a slightly less than stoichiometric amount of perfluoroalkyl hypofluorite was added at -142 °C. The mixture was allowed to warm slowly over several hours to -78 °C. The volatile products were separated by fractional condensation through a series of cold traps kept at appropriate temperatures. The amounts of material were determined by *PVT* measurements and identified by spectroscopic techniques. Typical reaction conditions and yields are summarized in Table I.

Synthesis of $F_2C(ONF_2)_2$ in a Flow System. In a vacuum line, a U-trap filled with glass beads coated with KF was kept at -112 °C;

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(1) Present addresses: (a) Department of Chemistry, California State Polytechnic University, Pomona, CA 91768; (b) MVT, Microcomputer Systems, Inc., Westlake Village, CA 91361; (c) Jacobs Engineering Group, Inc., Pasadena, CA 91101.

(2) NF_3O was independently discovered in 1961 at Rocketdyne (Maya, W. U.S. Patent 3320147, 1962) and Allied Chemical (Fox, W. B.; MacKenzie, J. S.; Vaanderkooi, N.; Sukornick, B.; Wamser, C. A.; Holmes, J. R.; Eibeck, R. E.; Stewart, B. B. *J. Am. Chem. Soc.* **1966**, *88*, 2604) and in 1965 at the University of British Columbia, Vancouver (Bartlett, N.; Passmore, J.; Wells, E. J. *Chem. Commun.* **1966**, 213).

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on either side, U-traps were kept at −142 °C to condense products. A mixture of $F_2C(OF)_2$ (6.70 mmol) and HNF_2 (6.70 mmol) was passed through the system. The reactants were condensed at −142 °C allowed to pass through the cold traps and KF trap by warming, and recondensed at −142 °C. The operation was repeated several times. The products were separated by fractional condensation through traps kept at −142 and −196 °C. The −142 °C trap contained 0.45 mmol of a mixture of $F_2C(ONF_2)_2$ and $FOCF_2ONF_2$. In the −196 °C trap, there was left 6.52 mmol of a mixture of $F_2C(OF)_2$, N_2F_4, and NF_3.

Results and Discussion

Syntheses of R_fONF_2 Compounds. Perfluoroalkyl hypofluorites react with alkali-metal fluoride–HNF_2 adducts at low temperatures to produce the corresponding $-ONF_2$-substituted perfluoroalkanes:

$$R_fOF + MF\cdot HNF_2 \xrightarrow{-142\text{ to }-78\text{ °C}} R_fONF_2 + MF\cdot HF$$

The generality of this reaction was demonstrated by the synthesis of a primary (CF_3ONF_2), a secondary [$(CF_3)_2CFONF_2$], a geminal bis-substituted [$CF_2(ONF_2)_2$], and a geminal $-OF$-substituted ($FOCF_2ONF$) *N*,*N*-difluoro-*O*-perfluoroalkylhydroxylamine. It was found important to preform the alkali-metal fluoride–difluoramine adduct because in the absence of alkali-metal fluorides most of these hypofluorites react uncontrollably and sometimes explosively with HNF_2 to give zero yields of the desired $-ONF_2$-substituted products. A study of the effect of different alkali-metal fluorides showed that KF–, RbF–, and KF–NaF mixtures were all equivalent; CsF afforded only traces of the desired compounds and is also less desirable because of the tendency of its HNF_2 adduct to explode before reaching 0 °C.[7] Sodium fluoride alone and LiF were not examined because they do not form an adduct with HNF_2.[7]

The yields of R_fONF_2 in these reactions were generally low and were in the 10–20% range, except for the reaction of $CF_2(OF)ONF_2$ with HNF_2. When this reaction was carried out with preformed $KF\cdot HNF_2$, the yield of $CF_2(ONF_2)_2$ was low, but it was found that $CF_2(OF)ONF_2$ and HNF_2 could be premixed without reaction and after cocondensation over KF at −142 °C and slow warm-up to −78 °C produced $CF_2(ONF_2)_2$ in quantitative yield. The generally low yields and the nature of the main products (COF_2, CF_3CFO, CF_3COCF_3, CF_4, N_2F_4, NF_3, etc.) suggest a free-radical mechanism for these reactions. For $CF_2(OF)_2$ and HNF_2 a flow reaction was also studied by repeatedly passing an equimolar mixture of the starting materials over KF at −112 °C. Although $CF_2(ONF_2)_2$ and $CF_2(OF)ONF_2$ were formed, their yields were considerably lower than those obtained in a static system.

Since for CF_3ONF_2 the synthesis from CF_3OF and N_2F_4 under the influence of UV radiation[15,16] is clearly superior to the method reported here, we examined the analogous reaction between $CF_2(OF)_2$ and N_2F_4 under the influence of water-filtered UV radiation. However, no evidence could be obtained for the formation of either $CF_2(OF)ONF_2$ or $CF_2(ONF_2)_2$. The only $-ONF_2$ compound formed was a small amount of CF_3ONF_2, with COF_2 and FNO being the major products. Therefore, the KF-catalyzed reaction of HNF_2 with $CF_2(OF)_2$ represents, presently, the only known method for the syntheses of $CF_2(OF)ONF_2$ and $CF_2(ONF_2)_2$.

Table II. Vibrational Spectra of CF_3ONF_2

Obsd freq, cm^{-1}, and intens[a] Infrared gas	Infrared Ar Matrix	Raman liquid	Assignment in point group C_s
2605 vw			$2\nu_1$
2530 vw			$\nu_1 + \nu_2$
2485 vw			$2\nu_{12}$
2433 vw			$2\nu_2$
2340 vvw			$\nu_1 + \nu_3$
2280 vvw			$\nu_3 + \nu_{12}$
2245 vw			$\nu_2 + \nu_3$
2180 sh			$\nu_1 + \nu_5$
2157 w			$\nu_2 + \nu_4$
2020 vw			$\nu_1 + \nu_6$
1975 sh			$\nu_3 + \nu_4$ or $\nu_6 + \nu_{12}$
1936 w			$\nu_1 + \nu_{14}$ or $\nu_2 + \nu_6$ or $\nu_3 + \nu_{13}$
1905 sh			$\nu_3 + \nu_5$
1842 vvw			$\nu_4 + \nu_{13}$
1808 vw			$2\nu_{13}$ or $\nu_4 + \nu_5$
1792 sh			$\nu_1 + \nu_{15}$
1739 vw			$2\nu_5$ or $\nu_2 + \nu_8$
1661 vvw			$\nu_1 + \nu_{10}$ or $\nu_3 + \nu_{14}$ or $\nu_4 + \nu_6$
1568 vw			$\nu_2 + \nu_{10}$ or $\nu_4 + \nu_{14}$
1502 vw			$\nu_4 + \nu_7$ or $\nu_1 + \nu_{11}$
1420 vw			$\nu_2 + \nu_{11}$ or $\nu_4 + \nu_{15}$ or $\nu_8 + \nu_{13}$
1340 sh	1341 mw		$\nu_5 + \nu_{15}$ or $\nu_6 + \nu_{14}$
1303 vs	1302 vs	1308 (0.2)p	ν_1
	1292 mw		$\nu_4 + \nu_{10}$ or $\nu_6 + \nu_7$
	1268 w		$\nu_{10} + \nu_{13}$
	1251 w		$2\nu_{14}$
1247 vs	1242 vs	1248 (0+)	ν_{12}
	1230 w		$\nu_5 + \nu_{16}$
1221 vs	1218 vs	1214 (0+)	ν_2
	1216 sh		$\nu_5 + \nu_{10}$
	1207 sh		$\nu_6 + \nu_9$
	1186 w		$\nu_7 + \nu_{14}$
1076 mw		1060 sh	$\nu_5 + \nu_{11}$ or $\nu_6 + \nu_{10}$
1034 ms	1035 m	1032 (10)p	ν_3
942 ms	942 ms	939 (1.4)p	ν_4
901 s	908 s	906 (1.2)dp	ν_{13}
870 vs	866 vs	860 (1.2)p	ν_5
	853 vw		$\nu_{15} + \nu_{16}$
718 m	722 s	718 (9.6)p	ν_6
	710 vw	708 (0.7)p	$2\nu_{10}$
628 mw	629 mw	625 (1.3) dp	ν_{14}
579 w	568 w	566 (4.2)p	ν_7
528 vw	514 w	510 (0+)p	ν_8
480 w	480 mw	476 (0.2)dp	ν_9, ν_{15}
		368 (2.3)dp	ν_{16}
		351 (7.3)p	ν_{10}
		201 (1.8)p	ν_{11}
		75 (0+)	ν_{17}, ν_{18}

(a) Uncorrected Raman intensities representing relative peak height.

Properties of CF_3ONF_2. This compound is well-known and has been well characterized,[15,16] and the properties observed in this study were in good agreement with the literature data. However, since CF_3ONF_2 is the simplest member of the class of *N*,*N*-difluoro-*O*-perfluoroalkylhydroxylamines and since only a partial infrared spectrum had previously been reported,[15,16] it was desirable to obtain complete vibrational spectra (see Figure 1 and Table II). Assignments were made for CF_3ONF_2 by assuming symmetry C_s with the F–C–O–N part of the molecule being located in the symmetry plane. These assignments are summarized in Table III and were made by comparison with the spectra of similar molecules such as CF_3OF,[17] CF_3NO,[18] CF_3N_3,[19] CF_3NF_2,[20] SF_5ONF_2,[16] and

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Table III. Vibrational Assignments of CF_3ONF_2 Compared to Those of Similar Molecules

assignt in point group C_s		approx descripn of mode for CF_3ONF_2	obsd freq, cm^{-1}							
			CF_3ONF_2	CF_3N_3[a]	CF_3OF[b]	CF_3NO[c]	CF_3NF_2[d]	NF_2[e]	HNF_2[f]	SF_5ONF_2[g]
a′	ν_1	$\nu_s(CF_3)$[h]	1303	1284	1294	1291	1290			
	ν_2	$\nu_{as}(CF_3)$[h]	1218	1168	1222	1175	1221			
	ν_3	$\nu_s(NF_2)$	1034				1018	1070	972	1029
	ν_4	$\nu(C-O)$	942		947					
	ν_5	$\nu(O-N)$	866							858
	ν_6	$\delta_s(CF_3)$	720	730	678	730	721			
	ν_7	$\delta_{as}(CF_3)$	567	513	585	533	576			
	ν_8	$\delta(NF_2)$	512				525	573	500	
	ν_9	$\delta_{rock}(CF_3)$	478	402	429	428				
	ν_{10}	$\delta_{rock}(NF_2)$	351							
	ν_{11}	$\delta(CON)$	205	179	278					
a″	ν_{12}	$\nu_{as}(CF_3)$[h]	1245	1254	1261	1230	1240			
	ν_{13}	$\nu_{as}(NF_2)$	907				951	931	888	928
	ν_{14}	$\delta_{as}(CF_3)$	627	556	607	551	600			
	ν_{15}	$\delta_{rock}(CF_3)$	478	450	431	428				
	ν_{16}	$\delta_{rock}(NF_2)$	368							
	ν_{17}	$\tau(C-O)$	75		127	[50]				
	ν_{18}	$\tau(O-N)$								

[a] Reference 19. [b] Reference 17. [c] Reference 18. [d] Reference 20; the potential energy distribution of the fundamentals assigned to the CF_3, NF_2, and CN stretching modes indicates strong mixing of the corresponding symmetry coordinates. [e] Harmony, M. D.; Myers, R. J. *J. Chem. Phys.* 1962, *37*, 636. [f] Comeford, J. J.; Mann, D. E.; Schoen, L. J.; Lide, D. R. *Ibid.* 1963, *38*, 461. [g] Reference 16. [h] The assignments given in this table for the CF_3 stretching modes are tentative.

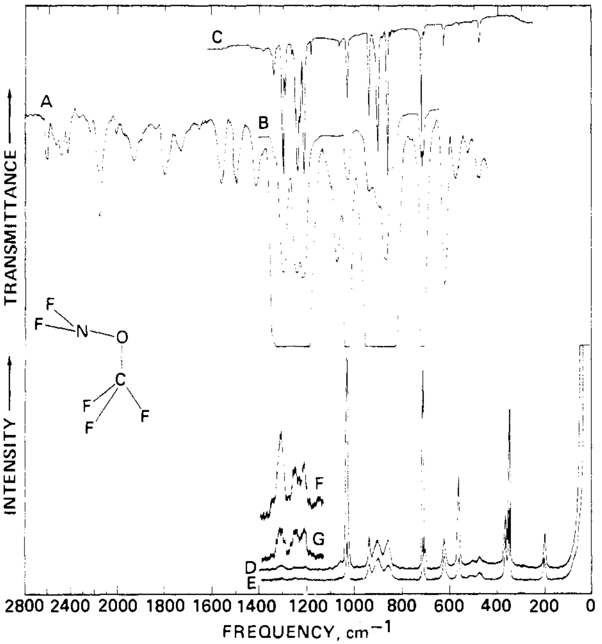
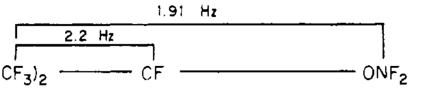


Figure 1. Vibrational spectra of CF_3ONF_2: traces A and B, infrared spectra of the gas recorded in a 5-cm path length cell with AgCl windows at pressures of 300 and 8 torr, respectively; trace C, infrared spectrum of Ar-matrix-isolated CF_3ONF_2 (mole ratio 300) at 6 K; traces D, E, and F, G, Raman spectra of the liquid in a quartz tube at −80 °C recorded at two different sensitivities with incident polarization parallel and perpendicular.

other $-ONF_2$-substituted perfluoroalkanes.[21] Most stretching modes and the ν_6, ν_7, and ν_{14} deformation modes can be assigned with confidence. The assignment for the remaining six deformation modes and for the CF_3 stretching modes are more or less tentative. In all the $\gt CONF_2$ compounds studied in this laboratory, the $\gt CONF_2$ group exhibits a very characteristic band pattern at about 860, 910, 940, and 1030 cm^{-1} of almost constant frequencies and intensities and therefore is well suited for the identification of a $\gt CONF_2$ group. In particular, the symmetric NF_2 stretching mode at about 1030 cm^{-1} is very useful for diagnostic purposes due to its high Raman intensity and the absence of other bands in this frequency region.

Properties of $(CF_3)_2CFONF_2$. This compound had previously been prepared by the reaction of $(CF_3)_2CO$ with N_2F_4 and N_2F_2 in a platinum tube at 100 °C and 1000 atm external pressure and identified by its infrared and mass spectrum.[22] The infrared spectrum of our product (frequency (cm^{-1}), intensity: 1327, s; 1264, vs; 1215, w; 1176 s; 1121, s; 1064, ms; 985, s; 910, ms; 849, s; 804, vw; 740, m; 725, m) was identical with that previously reported.[22] The identity of the compound was confirmed by its ^{19}F NMR spectrum, which showed the following shifts, multiplicities, coupling constants, and area ratios:



	$(CF_3)_2$	CF	ONF_2
	doublet of triplets	septet	broad triplet with partially resolved NF spin-spin coupling
φ	−79	−140	+131
area	6 :	1 :	2

Properties of $CF_2(ONF_2)_2$. $CF_2(ONF_2)_2$ is the first known example of geminal $(ONF_2)_2$-substituted compound. It is colorless as a solid, liquid, and gas. A sharp melting point was not observed for $CF_2(ONF_2)_2$ due to its tendency to form a glass at low temperature. The liquid boils at −9 °C. The vapor slowly passes through a −112 °C trap but stops at −126 °C. Vapor density measurements (M_r found 187, calcd 186) showed that in the gas phase the compound is not associated. The compound is completely stable at ambient temperature. Drop-weight tests performed on the liquid at about 0 °C were

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Table IV. Vibrational Spectra of $CF_2(ONF_2)_2$

obsd freq, cm^{-1}, and intens		
IR gas	Raman liquid, −80 °C	assignt
1306 m	1310 (0+)	$\nu_{as}(CF_2)$ and combination bands in Fermi resonance
1274 s	1274 (0+)	
1250 s	1248 (0+)	
1226 ms	1223 (0+)	
1189 vs	1185 (0+)	$\nu_s(CF_2)$
	1042 sh p	$\nu_s(NF_2)$
1038 ms	1035 (10) p	
949 mw	949 (0.4) p	ν(C-O)
916 s	909 (1) dp	$\nu_{as}(NF_2)$
877 s	870 (1) p	ν(N-O)
849 vs	835 (1)	
752 mw	749 (0.7)	
729 mw		
669 w	670 (7) p	
624 w	621 (0.5)	
571 vw	570 (7) p	
517 vw		
	458 (0.4)	
	391 (2.5) p	
	358 (2.2) p	
	341 (1.9) p	
	317 (2.5) p	
	270 (0.6) p	
	260 (3.2) p	
	241 (1.6) dp	
	217 (2) p	
	166 (0.6) dp	

Table V. Mass Spectrum[a] of $CF_2(ONF_2)_2$

m/e	abund	ion	*m/e*	abund	ion
118	21.5	$CF_2ONF_2^+$	50	2.2	CF_2^+
99	1	CF_2ONF^+ and $CFONF_2^+$	47	44.3	CFO^+
69	0.64	CF_3^+	33	14.7	NF^+
68	1	NF_2O^+	31	<0.5	CF^+
66	<0.5	CF_2O^+	30	70.5	NO^+
52	100	NF_2^+	28	<0.5	CO^+

[a] Recorded at 70 eV.

all negative at the 115 cm kg level, compared to a 50% point at 6.1 cm kg for ethyl nitrate. These tests indicate that $CF_2(ONF_2)_2$ is surprisingly stable and is much less sensitive than the analogous CNF_2 derivative, $CF_2(NF_2)_2$, which under the same conditions gave a positive test at 23 cm kg.

The structure of $CF_2(ONF_2)_2$ was established by its vibrational (see Figure 2, Table IV), mass (see Table V), and ^{19}F NMR spectra. The latter showed the following parameters:

2.3 Hz

	CF_2	$(ONF_2)_2$
	quintet	broad partially resolved triplet
ϕ	−69.3	+124.6
area	1 :	2

As expected, $CF_2(ONF_2)_2$ is an oxidizer liberating iodine from a KI solution. Unlike fluorocarbon ethers, $CF_2(ONF_2)_2$ does not readily hydrolyze in concentrated H_2SO_4 at 25 °C. After a 40-h contact time with agitation, 95% of the $CF_2(ONF_2)_2$ was recovered unchanged. In CH_3OH after 40 h at 25 °C, 90% of $CF_2(ONF_2)_2$ was recovered; however, in 1 M sodium methoxide in methanol, slow reaction was observed. Similarly, it slowly reacted with acetic acid. The nature of the reaction products was not investigated.

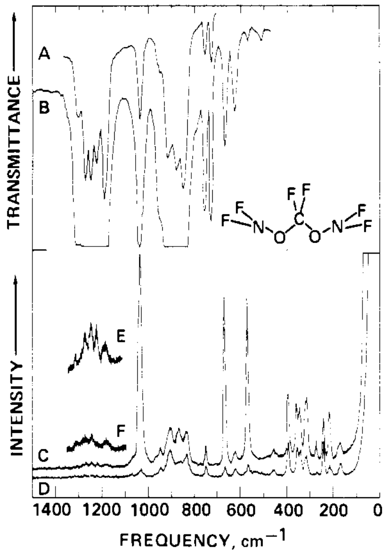


Figure 2. Vibrational spectra of $CF_2(ONF_2)_2$: traces A and B, infrared spectra of the gas in a 5-cm path length cell at 60 and 7 torr, respectively; traces C, E and D, F, Raman spectra of the liquid at −80 °C at two different sensitivities with incident polarization parallel and perpendicular.

Table VI. Vibrational Spectra of $CF_2(OF)ONF_2$

obsd freq, cm^{-1}, and intens		
IR gas	Raman liquid, −100 °C	assignt
1305 m	1305 (0.2)	$\nu_{as}(CF_2)$ and combination bands in Fermi resonance
1279 s	1279 (0.3) p	
1251 s	1249 (0+)	
1220 s	1216 (0.3) p	
1182 vs	1184 sh	
	1171 (1.1) p	$\nu_s(CF_2)$
1050 sh	1045 sh	$\nu_s(NF_2)$
1031 ms	1031 (10) p	
944 m	950 (3) p	ν(C-OF)
	939 (7.3) p	$\nu(C\text{-}ONF_2)$
914 s	917 (3) dp	$\nu_{as}(NF_2)$
895 sh	891 (7.5) p	ν(OF)
854 vs	855 sh	ν(ON)
	845 (3.5) p	
753 m	751 (2.5) p	$\delta(CF_2)$
689 mw	690 (8.2) p	
668 vw	667 (4.4) p	
601 w	601 (4.2) p	
563 vw	561 (6.8) p	
	520 (0.6) dp	
	463 (0.5) dp	
	450 (1.2) p	
	371 (3.3) dp	
	359 (7.3) p	
	348 (8.8) p	
	296 (2.8) p	
	258 (3.2) p	
	199 (3.1) p	
	146 (2) dp	
	131 (2.2) dp	

Properties of $CF_2(OF)ONF_2$. Like $CF_2(ONF_2)_2$, this compound had not been prepared previously. It is colorless as a solid, liquid, and gas and also shows a tendency to form a glass at low temperature. From experimental data (temperature (°C), vapor pressure (mm): −94.8, 11; −78.4, 41; −64, 101; −57.5, 141; −47, 228), the vapor pressure-temperature relationship was found to be

$$\log [P\ (\text{mm})] = 7.31997 - 1116.029/[T\ (\text{K})]$$

with an index of correlation of 0.9997. During fractional condensation, the compound slowly passes through a −126 °C trap but stops at −142 °C. The extrapolated boiling point is −21.8 °C, and the derived heat of vaporization is ΔH_{vap} = 5105

814 *Inorg. Chem.* **1983**, *22*, 814–818

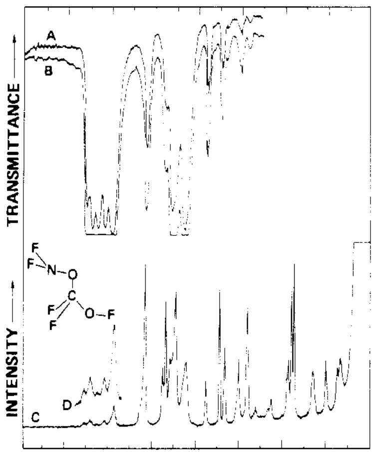
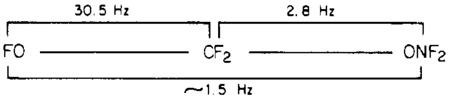


Figure 3. Vibrational spectra of $CF_2(OF)ONF_2$: traces A and B, infrared spectra of the gas recorded in a 5-cm path length cell with AgCl windows at pressures of 42 and 15 torr, respectively; traces C and D, Raman spectra of liquid $CF_2(OF)ONF_2$ at −100 °C recorded at two different sensitivities.

cal mol^{-1}. The Trouton constant (20.3) and the molecular weight of the gas M_r found 153, calcd 153) indicate little or no association in both the liquid and the gas phases.

The structure of the compound was established by vibrational (see Figure 3, Table VI) and ^{19}F NMR spectroscopy:



	triplet of triplets	doublet of triplets	broad triplet
			$J_{^{14}N-^{19}F} \approx 110$ Hz
φ	+156.6	−79	+125
area		: 2	: 2

The compound is stable at ambient temperature and liberates iodine from KI solution.

Conclusion. Complexing of HNF_2 with alkali-metal fluoride has successfully been used to moderate the otherwise explosive reaction of HNF_2 with hypofluorites. The general applicability of this method for the syntheses of *N,N*-difluoro-*O*-perfluoroalkylhydroxylamines has been demonstrated, and $CF_2(ONF_2)_2$, the first known example of a geminal-disubstituted $-ONF_2$ compound, has been prepared by this method.

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Registry No. CF_3OF, 373-91-1; $(CF_3)_2CFOF$, 3848-93-9; $CF_2(OF)_2$, 16282-67-0; $CF_2(OF)ONF_2$, 36781-60-9; HNF_2, 10405-27-3; CF_3ONF_2, 4217-93-0; $(CF_3)_2CFONF_2$, 84194-25-2; $CF_2(ONF_2)_2$, 36781-59-6; KF, 7789-23-3.

Contribution from the Department of Chemistry,
Texas Christian University, Fort Worth, Texas 76129

Synthesis of (Silylamino)phosphines with P–H Bonds[1]

H. RANDY O'NEAL and ROBERT H. NEILSON*

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The reactions of several [bis(trimethylsilyl)amino]chlorophosphines, $(Me_3Si)_2NP(R)Cl$, with *i*-PrMgCl generally yield mixtures of the isopropyl substitution products $(Me_3Si)_2NP(R)(i\text{-}Pr)$ and the unexpected reduction products $(Me_3Si)_2NP(R)H$ (R = *i*-Pr, *t*-Bu, CH_2SiMe_3, $N(SiMe_3)_2$, and Ph). The P–H phosphines appear to be formed by a process in which *i*-PrMgCl acts as a reducing agent with elimination of propylene. The reaction is catalyzed by magnesium salts, and the relative yield of reduced product increases with the steric bulk of the phosphorus substituents. In a more direct synthesis, these P–H substituted phosphines are prepared by the reduction of the chlorophosphines with $LiAlH_4$ in ether. Proton, ^{13}C, and ^{31}P NMR data are reported for both series of new phosphines.

Introduction

Silicon–nitrogen–phosphorus compounds, especially the (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$, are becoming increasingly important as synthetic reagents. Areas of active investigation include their use as precursors to new classes of phosphazene polymers[2,3] as well as novel organic[4–6] and organometallic[7–10] phosphorus compounds. Many of the most useful (silylamino)phosphines are prepared from commercially available reagents by a simple "one-pot" synthesis (eq 1) first utilized by Wilburn.[11,12] The complete preparative details of this process have recently been reported.[13]

$$(Me_3Si)_2NH \xrightarrow[(2)\ PCl_3]{(1)\ n\text{-BuLi}} \{(Me_3Si)_2NPCl_2\} \xrightarrow{2RMgX} (Me_3Si)_2NPR_2 \quad (1)$$

In attempting to further generalize this useful synthetic method, however, we find that reduced (P–H) or coupled (P–P) products are sometimes obtained. We report here the isolation and characterization of several new (silylamino)phosphines containing P–H bonds from such reactions. An independent, high-yield synthesis of the same series of compounds is also described.

Results and Discussion

Initially, we were interested in using the Wilburn method (eq 1) to prepare (silylamino)phosphines containing bulky alkyl

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