

recorded on a Perkin-Elmer Model 337 spectrophotometer, a Cary Model 14 spectrophotometer, a Varian Model A-60 spectrometer, and a GE Monopole mass spectrometer (mass range 600), respectively. Gas chromatographic analyses were carried out on an F & M Model 700 vapor fractometer with a 4-ft 10% Apiezon L on Chromosorb W column.

Oxidation of 2,6-Di-*t*-butyl-*p*-cresol (I) in Methanol with Cuprous Chloride-Amine Catalyst. A. Conditions for the Isolation of III, IV, VII, and VIII.—A suspension of 0.544 g (0.0055 mol) of cuprous chloride and 6 g of anhydrous magnesium sulfate in a solution of 0.646 g (0.0055 mol) of tetramethylethylenediamine (TMEDA) and 0.59 g (0.01 mol, 7.5 ml) of a solution of trimethylamine in toluene (0.078 g/ml) of trimethylamine in 125 ml of anhydrous methanol was prepared. A stream of oxygen (flow rate, 1 ft³/hr) was bubbled through the stirred suspension for 10 min. While oxygen was continuously bubbled through the blue suspension, a solution of 22 g (0.1 mol) of I in 125 ml of methanol was then added to this mixture over a 0.5-hr period. The temperature of the reaction mixture was kept at 25° with cold-water bath. The reaction was continued for an additional 3.83 hr. The yellow-green reaction mixture was filtered and the filtrate evaporated to an oil. The oil was extracted with 200 ml of hot hexane and the hexane extract decanted from the residue. The volume of the extract was reduced to 50 ml and refrigeration of the resulting solution at 0° for 12 hr provided 0.66 g (3%) of VIII: mp 154–156°; $\lambda_{\text{max}}^{\text{CCl}_4}$ (cm⁻¹), 3640, 1660, and 1640; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ (m μ) 237 (ϵ 21,188), 274 (2150); nmr, τ (CCl₄) 8.77 (18 H), 8.60 (18 H), 8.41 (3 H), 4.88 (1 H, exchanged in D₂O), 3.45 (2 H), and 2.95 (2 H); mass spectrum, m/e 424 (M)⁺.

A second crop of crystals was obtained upon cooling the filtrate, 0.012 g (0.05%) of III, mp 246° (lit.^{2b} mp 246°). The infrared spectrum of this product was identical with that of authentic 3,5,3',5'-tetra-*t*-butyl-4,4'-diphenoquinone.

Preparative thin layer chromatography of the filtrate from III on 1-mm thickness silica gel (Stahl GF 254) 8 × 8 in. plates using benzene-carbon tetrachloride (1.7:1) as solvent provided two isolable crystalline fractions: (1) 2,6-di-*t*-butyl-*p*-benzoquinone (IV), mp 55–58° (lit.^{2b} mp 67°), and (2) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII), mp 180–183° (lit.^{2b} mp 187°). The infrared spectra of both of these products were identical with those of authentic samples.

B. Conditions for Quantitative Analysis of Products.—A suspension of 0.544 g (0.0054 mol) of cuprous chloride and 6 g of magnesium sulfate in 125 ml of methanol containing 0.646 g (0.0055 mol) of TMEDA and 0.59 g (0.01 mol) of trimethylamine (7.5 ml of a solution of trimethylamine in toluene, 0.078 g/ml) was stirred at 25° while a stream of oxygen was bubbled through the mixture (flow rate, 1 ft³/hr) for 10 min. A solution of 22 g (0.1 mol) of I in 125 ml of methanol was then added dropwise during a 0.5-hr period to the blue reaction mixture maintaining the same oxygen flow rate. After the addition was complete, the mixture was oxygenated for an additional 3.83 hr. During the reaction, the temperature rose to 45° and gradually returned to 25°. The yellow-green reaction mixture was filtered and evaporated to a dark oil. This oil was dissolved in 250 ml of ethyl acetate and this solution was washed with 150 ml of cold 3% aqueous hydrochloric acid. The ethyl acetate layer was washed with water several times until the washings were neutral. The organic layer was dried (MgSO₄), filtered, and evaporated to a liquid which contained some solid. Filtration of the mixture gave 1.79 g of a solid, mp 180–183°, which was identical with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. The filtrate (21.2 g) was then analyzed by gas chromatography. This analysis provided the following percentage composition of this mixture: (1) III (5%); (2) IV (27%); (3) V (14%); (4) VI (14%); (5) VII (12%);¹⁰ and (6) VIII (2%).

Oxidation of VIII in Methanol with Cuprous Chloride-Amine Catalyst.—A mixture of 0.490 g (0.0011 mol) of VIII, 0.0059 g (5.9 × 10⁻⁵ mol) of cuprous chloride, 0.0071 g (6 × 10⁻⁵ mol) of TMEDA, 0.0065 g (1.1 × 10⁻⁴ mol) of trimethylamine, and 0.066 g of magnesium sulfate in 12 ml of methanol was oxygenated for 4.5 hr and worked up as previously described for I (part B). Gas chromatographic analysis of the reaction product (0.383 g) showed the following components: (1) VIII, 0.333 g (67% recovered); (2) 2,6-di-*t*-butyl-*p*-benzoquinone, (IV, 22%);¹¹ (3) 2,6-di-*t*-butyl-4-methyl-4-hydroxy-2,5-cyclohexadien-1-one (V, 0.9%).¹¹

(10) This per cent yield includes the 1.79 g of VII which was isolated.

(11) Yield based upon the number of moles of VIII which reacted (3.7 × 10⁻⁴).

Oxidation of IX¹² in Methanol with Cuprous Chloride-Amine Catalyst.—A mixture of 1.0 g (0.004 mol) of IX, 0.022 g (2.2 × 10⁻⁴ mol) of cuprous chloride, 0.24 g of magnesium sulfate, 0.025 g (2.2 × 10⁻⁴ mol) of TMEDA, and 0.0236 g (4 × 10⁻⁴ mol) of trimethylamine was oxygenated for 4.5 hr and worked up as previously described. Gas chromatographic analysis of the reaction product (0.743 g) indicated the following components: (1) III, 5%; (2) IV, 2%; (3) V, 58%; (4) VIII, 2%.

Oxidation of V in Methanol with Cuprous Chloride-Amine Catalyst.—A mixture of 2.0 g (0.0084 mol) of V, 0.045 g (4.5 × 10⁻⁴ mol) of cuprous chloride, 0.054 g (4.6 × 10⁻⁴ mol) of TMEDA, and 0.049 g (8 × 10⁻⁴ mol) of trimethylamine in 21 ml of methanol was oxygenated for 4.5 hr and worked up as previously described. A quantitative recovery of V was obtained.

Registry No.—I, 128-37-0; VIII, 14387-13-4; oxygen, 7782-44-7.

(12) Prepared according to the method described in ref 2.

The Photolysis of Perfluoro-2,3-diazabuta-1,3-diene and Perfluoroacyl Fluorides

PAUL H. OGDEN

Contribution No. 494 from the Central Research Laboratories,
Minnesota Mining and Manufacturing Company,
St. Paul, Minnesota 55101

Received November 29, 1967

The generation of the difluoromethylenimino radical from the photolysis of perfluoro-2,3-diazabuta-1,3-diene has been reported recently.¹ The apparent stability of this radical and the ease with which it adds to fluoro olefins² suggested that the photolysis of perfluoro-2,3-diazabuta-1,3-diene in the presence of photolytic sources of fluoroalkyl radicals would be a convenient route to the synthesis of azomethines. Heretofore, the only method of preparing these compounds was from the pyrolysis of oxazetidines³ since it has recently been shown that the pyrolysis of tertiary perfluoroamines produces isomers of azomethines.^{4,5}

Although several photolytic sources of fluoroalkyl radicals are available it was decided to use perfluoroacyl fluorides in this study. These materials were readily available and have been shown to produce both fluoroalkyl and fluoroformyl radicals upon photolysis.⁶ Few reactions of the fluoroformyl radical have been described previously although the formation of difluoroamino carbonyl fluoride, NF₂C(O)F, from the photolysis of tetrafluorohydrazine and carbon monoxide, is thought to involve a combination of difluoroamino and fluoroformyl radicals.⁷

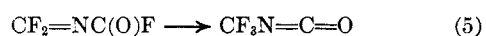
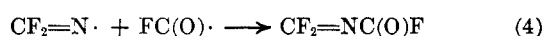
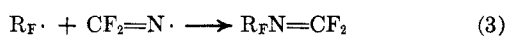
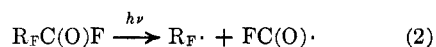
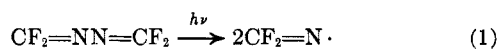
Results and Discussion

The photolysis of monofunctional perfluoroacyl fluorides in the presence of perfluoro-2,3-diazabuta-1,3-

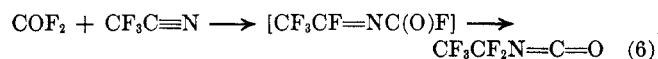
- (1) R. A. Mitsch and P. H. Ogden, *Chem. Commun.*, 59 (1967).
- (2) P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, **89**, 3868 (1967).
- (3) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955); 3461 (1955). D. A. Barr, R. N. Haszeldine, and C. J. Willis, *ibid.*, 1351 (1961).
- (4) W. H. Pearlson and L. J. Hals, U. S. Patent 2,643,267.
- (5) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965).
- (6) J. F. Harris, *J. Org. Chem.*, **30**, 2182 (1965).
- (7) G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).

diene produces trifluoromethyl isocyanate and the predicted azomethine together with carbonyl fluoride and some noncondensable material. The noncondensable, which was not characterized, is presumably carbon monoxide and/or nitrogen, since these are known products from the photolytic decomposition of the above compounds.^{1,6}

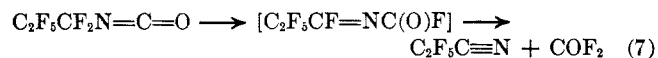
The products obtained may be rationalized using the reaction scheme in eq 1-5.



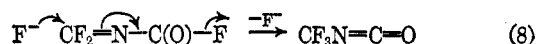
That N-difluoromethylene carbamyl fluoride, $\text{CF}_2=\text{NC}(\text{O})\text{F}$, should rearrange is not surprising since such compounds have been postulated as intermediates which isomerize in the presence of fluoride ion. Fawcett and his coworkers⁸ suggest that the formation of pentafluoroethyl isocyanate from the addition of carbonyl fluoride to trifluoroacetonitrile involves such a rearrangement (eq 6).



In addition, Banks and his coworkers⁵ suggest that isomerization of this type of intermediate is responsible for the formation of pentafluoropropionitrile and carbonyl fluoride from heptafluoro-*n*-propyl isocyanate during the pyrolysis of trisheptafluoro-*n*-propylhydroxylamine (eq 7).



The mechanism of isomerization (eq 5) has not been investigated but it is probably initiated by nucleophilic attack at the terminal azomethine group by fluoride ion (eq 8), trace quantities of which could be generated by



the presence of adventitious moisture on the glass. That the carbamyl fluoride should isomerize under conditions which do not cause the azomethine to isomerize also is not surprising since the nature of the groups adjacent to the azomethine moiety affects the ease with which isomerization of the $\text{C}=\text{N}$ bond occurs, as will be shown later.

Yields of azomethine and trifluoromethyl isocyanate after purification by gas-liquid partition chromatography are summarized in Table I.

The data contained in Table I indicates that the photolysis of perfluoro-2,3-diazabuta-1,3-diene in the presence of a photolytic source of fluoroalkyl radicals is a potentially useful route to azomethines. The detrimental affect on the yield of azomethine caused by the formation of isocyanate could be avoided by using an alternative source of fluoroalkyl radicals, *i.e.*, azo compounds, etc.

(8) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 4275 (1962).

TABLE I
YIELD OF PRODUCTS FROM THE PHOTOLYSIS OF $\text{CF}_2=\text{NN}=\text{CF}_2$
WITH VARIOUS PERFLUOROACYL FLUORIDES

Acyl fluoride	Ratio of acyl fluoride to azine	Product	% yield	T_r^a
$\text{C}_3\text{F}_7\text{C}(\text{O})\text{F}$	5:1	$\text{CF}_3\text{N}=\text{C}=\text{O}$	36	46
		$\text{C}_3\text{F}_7\text{N}=\text{CF}_2$	24	
$(\text{CF}_3)_2\text{CFC}(\text{O})\text{F}$	5:1	$\text{CF}_3\text{N}=\text{C}=\text{O}$	20	40
		$(\text{CF}_3)_2\text{CFN}=\text{CF}_2$	35	
$\text{C}_4\text{F}_9\text{C}(\text{O})\text{F}$	3:1	$\text{CF}_3\text{N}=\text{C}=\text{O}$	25	145
		$\text{C}_4\text{F}_9\text{N}=\text{CF}_2$	25	

^a T_r = relative retention time = $(T_{\text{compd}} - T_{\text{air}})/(T_{\text{CFCl}_3} - T_{\text{air}}) \times 100$.

Isomerization of Azomethines.—Perfluoro-2-azapentene-1 has been shown to isomerize at 250° in the presence of anhydrous potassium fluoride producing perfluoro-2-azapentene-2 in 55% yield.⁵ In the presence of cesium fluoride, both perfluoro-2-azapentene-1 ($\text{C}_3\text{F}_7\text{N}=\text{CF}_2$) and perfluoro-2-azahexene-1 ($\text{C}_4\text{F}_9\text{N}=\text{CF}_2$) isomerize quantitatively at room temperature; however, the isomeric azomethine, perfluoro-3-methyl-2-azabutene-1 [$(\text{CF}_3)_2\text{CFN}=\text{CF}_2$] did not, even when heated to 200°. This observation is in agreement with the relative rates with which the $\text{CF}_2=\text{N}$ moiety isomerizes in perfluoro α , ω -bisazomethines.⁹

Spectral Properties.—The spectral properties of the materials described above are summarized in Table II.

TABLE II
SPECTRAL DATA

Compd	Registry no.	Infrared, μ ($>\text{C}=\text{N}-$)	F ¹⁹ nmr	
			$\phi^* \text{ }^a$	Group
$(\text{CF}_3)_2\text{CFN}=\text{CF}_2$	16200-40-1	5.51	33.7	$\text{CF}_2=\text{N}^b$
			42.7	
2 1 $\text{CF}_3\text{CF}_2\text{CF}_2\text{N}=\text{CF}_2$	378-00-7	5.55 ^c	80.7	CF_2^c
			155.5	CF^d
			28.9	$\text{CF}_2=\text{N}^f$
			44.7	
			93.7	$\text{CF}_2(1)^d$
			129.7	$\text{CF}_2(2)^d$
3 2 1 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{N}=\text{CF}_2$	424-32-8	5.56	81.5	CF_2^g
			28.4	$\text{CF}_2=\text{N}^h$
			44.5	
			92.7	$\text{CF}_2(1)^d$
			ca. 126.2	$\text{CF}_2(2)^d$
			ca. 126.4	$\text{CF}_2(3)^d$
$\text{CF}_3\text{CF}_2\text{CF}=\text{NCF}_3$	680-23-9	5.61	81.8	CF_3^i
			2.64	CF^d
			57.7	CF_3N^j
			121.4	CF_2^k
			83.5	CF_3C^l
			2 1 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}=\text{NCF}_3$	559-93-3
57.8	CF_3-N^n			
119.0	$\text{CF}_2(1)^n$			
127.0	$\text{CF}_2(2)^n$			
81.7	CF_3-C^n			

^a G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). ^b Broad AB. ^c Doublet ($J = 4.1$ cps) of triplets ($J = 1.5$ cps). ^d Complex. ^e Lit.^{3a} 5.51. ^f AB pattern ($J = 80$ cps). ^g Triplet ($J = 8.9$ cps). ^h AB pattern ($J = 86$ cps). ⁱ Triplet ($J = 9.0$ cps) of triplets ($J = 1.8$ cps). ^j Doublet ($J = 13.4$ cps). ^k Doublet ($J = 13.3$ cps). ^l Doublet ($J = 5.0$ cps). ^m R. E. Banks, W. M. Cheng, and R. N. Haszeldine [*J. Chem. Soc.*, 3407 (1962)] report 5.63. ⁿ For J values see ref *m*.

All of the azomethines show a characteristic infrared absorption at about 5.5 μ corresponding to the $\text{C}=\text{N}$ bond. Isomerization to the internal azaalkene causes a small shift to longer wavelength; however, the shift is

(9) P. H. Ogden and R. A. Mitsch, *ibid.*, **87**, 5007 (1967).

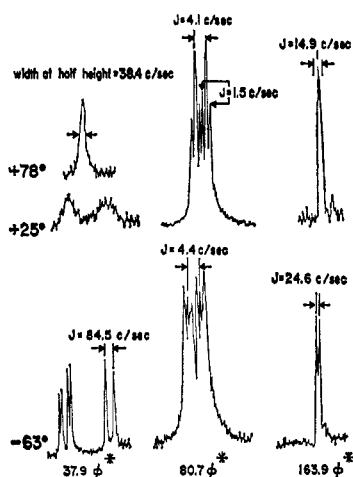


Figure 1.— F^{19} nmr spectrum of $(CF_3)_2CFN=CF_2$ at $+78$, $+25$, and -63° .

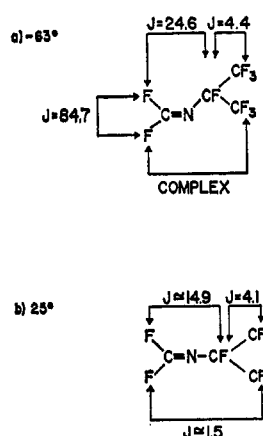


Figure 2.—Structures assigned to $(CF_3)_2CFN=CF_2$ at -63 and $+25^\circ$.

not so large as that observed previously when perfluoro-bisazomethines isomerize.⁹

The F^{19} nmr spectra show an AB pattern characteristic of the $CF_2=N-$ group. In the case of $(CF_3)_2CFN=CF_2$, the pattern is broadened into two humps. F^{19} nmr measurements at various temperatures show that this effect, which appears to be characteristic of the $CF_2=N-$ group when adjacent to a branched fluorocarbon chain, *i. e.*, $CF_2=NCF(CF_3)_2$, $CF_2=NCF(CF_3)CF_2N=CF_2$, or $CF_2=N(CF_2CF_3)_2N=CF_2$,² is caused by stereoisomerization about the $C=N$ bond.¹⁰ The F^{19} nmr spectrum of $(CF_3)_2CFN=CF_2$ at different temperatures is summarized in Figures 1 and 2.

Experimental Section

Infrared spectra were measured on a Perkin-Elmer Model 21 double-beam instrument using a 2.5-cm gas cell fitted with NaCl windows. Nuclear magnetic resonance measurements were made with a Varian V-4300-2 instrument operating at 40.0 Mc and utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts. The values reported are ϕ^* values¹¹ at a dilution of 10–25%. Trifluoroacetic acid is ϕ^* 76.5 on this scale. Mass spectra were measured utilizing a C.E.C. 21-103c instrument with an inlet temperature of 30° , ion chamber temperature of 250° , ion voltage of 70 V, and ion current of 10 μA . Molecular weights where quoted were determined by effusion. Peaks reported are the most significant ones and are described by *m/e*

(relative intensity) assigned ion. Vapor phase chromatographic separations were made using a 2 m \times 0.5 in. Kel-F 8126 column, and by condensing the products from the effluent gas at -196° in a trap filled with glass beads. The recovery of products from the vpc apparatus was unfortunately rather low and the actual yields obtained are probably considerably higher.

Perfluorobutyryl Fluoride.—Perfluoro-2,3-diazabuta-1,3-diene (5.5 mmol) and perfluorobutyryl fluoride (22.0 mmol, 4 molar excess) were condensed at -196° into a silica tube of 200-cc capacity fitted with a Fischer & Porter polytetrafluoroethylene valve. After warming to room temperature, the tube was irradiated with ultraviolet light from a water-cooled Hanovia 450-W lamp for 24 hr. Trifluoromethylisocyanate (4.0 mmol, 36% conversion of $CF_2=NN=CF_2$) and perfluoro-2-azapentene-1 (2.7 mmol, 24% conversion of $CF_2=NN=CF_2$) were then separated from unreacted starting material and by-products by vapor phase chromatography. They were identified by comparison of their infrared spectra with those of authentic samples. The spectral properties of $C_3F_7N=CF_2$ are summarized in Table II. The mass spectral pattern is summarized as follows: 31(29.9) CF, 43(2.4) C_2F , 50(19.7) CF_2 , 69(91.2) CF_3 , 76(5.2) C_2F_2N , 95(4.6) C_2F_3N , 100(6.7) C_2F_4 , 114(100) C_2F_4N , 119(6.3) C_2F_5 , 164(16.7) C_3F_5N , 169(5.9) C_3F_7 , and 214(13.7) C_4F_5N .

Calcd for C_4F_5N : mol wt, 233. Found: mol wt, 232.

Perfluorovaleryl fluoride was prepared from perfluorovaleric acid by treatment with phosphorus pentachloride followed by potassium fluoride. Tetrafluoro-2,3-diazabuta-1,3-diene (3.1 mmol) and perfluorovaleryl fluoride (9.0 mmol, 3 molar excess) were photolyzed together in the manner described previously. Trifluoromethyl isocyanate (1.6 mmol, 25% conversion of $CF_2=NN=CF_2$) and perfluoro-2-azahexene-1 (1.6 mmol, 25% conversion of $CF_2=NN=CF_2$) were isolated by vapor phase chromatography. Perfluoro-2-azahexene-1, $CF_3CF_2CF_2CF_2N=CF_2$, was characterized by its molecular weight and infrared, F^{19} nmr, (see Table II), and mass spectra. The mass spectrum is summarized as follows: 31(20.3) CF, 50(12.6) CF_2 , 69(100) CF_3 , 76(3.7) C_2F_2N , 95(3.9) C_2F_3N , 100(9.5) C_2F_4 , 114(67.9) C_2F_4N , 119(9.9) C_2F_5 , 126(2.5) C_2F_6N , 131(3.3) C_2F_7 , 145(3.0) C_3F_5N , 164(4.3) C_3F_6N , 176(3.1) C_4F_5N , 214(5.8) C_4F_5N , and 264(9.9) $C_6F_{10}N$.

Calcd for $C_6F_{10}N$: mol wt, 283. Found: mol wt, 289.

Perfluoroisobutyryl Fluoride.—Tetrafluoro-2,3-diazabuta-1,3-diene (5.5 mmol) and perfluoroisobutyryl fluoride (25 mmol, 4.5 molar excess) were photolyzed together in the manner described previously. Trifluoromethyl isocyanate (2.2 mmol, 20% conversion of $CF_2=NN=CF_2$) and perfluoro-3-methyl-2-azabutene-1 (3.8 mmol, 35% conversion of $CF_2=NN=CF_2$) were isolated by vapor phase chromatography. Perfluoro-3-methyl-2-azabutene-1, $(CF_3)_2CFN=CF_2$, was characterized by its infrared, mass, and F^{19} nmr spectra. The mass spectrum is summarized as follows: 31(34.1) CF, 50(26.0) CF_2 , 69(95.0) CF_3 , 76(12.6) C_2F_2N , 95(7.8) C_2F_3N , 100(4.4) C_2F_4 , 114(84.0) C_2F_4N , 119(3.6) C_2F_5 , 164(100) C_3F_5N , and 214(22.6) C_4F_5N . The F^{19} nmr spectrum is described in Figures 1 and 2.

Anal. Calcd for C_4F_5N : C, 20.6; N, 6.0; F, 71.4; mol wt, 233. Found: C, 20.6; N, 5.8; F, 72.3; mol wt, 232.

Isomerization of Azomethines.—Perfluoro-2-azapentene-1 (2.0 mmol) and trichlorofluoromethane (8.0 mmol) were condensed under vacuum at -196° into an nmr tube containing dried cesium fluoride (0.2 g). The cesium fluoride was dried immediately before use by heating it at 250° for 5 min under vacuum. The F^{19} nmr spectrum of the sample, which is summarized in Table II, indicated that isomerization was complete almost immediately. After removal of $CFCl_3$, the infrared spectrum of the product, perfluoro-2-azapentene-2, was shown to be identical with that of the major product from the pyrolysis of perfluoro tertiary *n*-propylamine.⁴

Perfluoro-2-azahexene-1 (2.0 mmol) and trichlorofluoromethane (8.0 mmol) were condensed under vacuum into a tube containing dried ferric fluoride (0.1 g). After heating at 100° for 30 min, no evidence of isomerization was observed from infrared measurements. The volatile material was then transferred to an nmr tube containing dried cesium fluoride (0.1 g). Infrared and F^{19} nmr spectral observations indicated that isomerization occurred almost immediately. The F^{19} nmr spectrum was shown to be identical with that reported by Banks, *et al.*,¹² for perfluoro-2-azahexene-2, $CF_3CF_2CF_2CF=NCF_3$. After removal of $CFCl_3$,

(10) P. H. Ogden and G. V. D. Tiers, *Chem. Commun.*, 5217 (1967).

(11) See Table II, ref a.

(12) See Table II, footnote m.

the infrared spectrum was also shown to be identical with that of an authentic sample of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}=\text{NCF}_3$.

Perfluoro-3-methyl-2-azabutene-1 did not isomerize when heated at 200° in the presence of dried cesium fluoride for 12 hr.

Registry No.—Perfluoro-2,3-diazabuta-1,3-diene, 692-73-9.

Acknowledgment.—The author wishes to express his gratitude to Dr. J. J. McBrady for infrared and F^{19} nmr spectra, to Mr. S. Kulver for mass spectra, and to Mr. P. B. Olson for elemental analysis.

The Synthesis of Saturated and Unsaturated α -Difluoramino Ethers

D. D. ROSENFELD, J. R. LOVETT, and E. SCHMALL

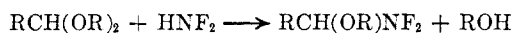
Special Projects Unit,
Esso Research and Engineering Company,
Linden, New Jersey

Received December 27, 1967

In recent years, the syntheses of a variety of organic compounds containing the difluoramino grouping have been reported. Included are acyl difluoramines,¹ alkyl difluoramines,² perfluoroalkyldifluoramines,³ and difluorourea.⁴ In addition, the properties of a *vic*-difluoramino compound, 1,2-bisdifluoramino-4-methylpentane,⁵ have been reported. Several review articles⁶ emphasizing inorganic difluoramino compounds have also appeared.

For the most part the synthesis of difluoramino-containing molecules had been accomplished *via* fluorination of amines and thermal or photochemical reactions of tetrafluorohydrazine. A more recent publication⁷ has disclosed the alkylation of difluoramino by various carbonium ions. As one of several reactions, Graham and Freeman reported the preparation of α -difluoramino-pyran by reaction of dihydropyran and HNF_2 at room temperature. This appears to be the first indication that HNF_2 had any synthetically useful nucleophilic properties.

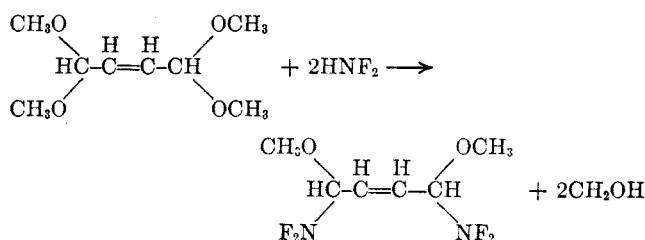
We now wish to report an additional synthetic utility of difluoramino. The reaction of acetals with HNF_2 now provides a new method for preparing α -difluoramino ethers. This reaction probably represents a fairly general mode of attack in that it occurs with saturated and unsaturated mono- and diacetals such as dimethyl acetal, acrolein acetal, tetra-



methoxypropane, tetramethoxybutene-2, and tetraethoxybutyne-2.⁸ The only acetals tried that failed to react were two ketene acetals, specifically, the parent compound and dicyano ketene acetal. In all other

examples, one alkoxide from each acetal grouping was replaced by $-\text{NF}_2$.

The reaction conditions varied according to the starting material used. All reactions were carried out under an excess pressure of HNF_2 at temperatures ranging from ambient to 100° using standard vacuum line techniques. The appropriate alcohol (1 molar equiv) was isolated in each case and identified *via* infrared and gc. Tetramethoxypropane and tetraethoxybutyne-2 reacted similarly in that under the milder reaction conditions a mixture of the mono- and bisdifluoramino ether was isolated. On recycling this material with additional HNF_2 at a higher temperature the corresponding 1,3 or 1,4 product formed. On the other hand, tetramethoxybutene-2 reacted at room temperature in CCl_4 to give a nearly quantitative yield of high purity (92%) 1,4-bisdifluoramino ether. The



integrated area ratio of 3:1:1 for methoxy, vinyl, and tertiary hydrogens and the nmr results listed in Table I are consistent with the proposed difluoramino ether. The reaction was also run in the absence of solvent (excess HNF_2) without affecting either the yield or purity of the bis ether. The work-up of the reaction mixture was greatly facilitated in the latter case.

TABLE I

F^{19}	H^1
$\phi -25.5$ (d) [$-\text{CH}(\text{OR})\text{NF}_2$]	τ 3.91 (m) ($-\text{CH}=\text{C}$)
$J_{\text{HF}} \sim 18.5$ cps	τ 5.21 (dt) (tertiary H)
	$J_{\text{HF}} \sim 18.5$ cps
	τ 6.43 (s) ($-\text{OCH}_3$)

Experimental Section

Caution: Difluoramino should be handled with care. Explosions have occurred when HNF_2 was condensed at -196° .

Apparatus.—A heavy-wall glass pressure reactor⁹ (15-ml capacity) fitted with a Teflon¹⁰ valve was used in this experiment.

1,4-Bisdifluoramino-1,4-dimethoxybutene-2.—Tetramethoxybutene-2 (0.5 g, 0.0029 mol) was dissolved in 0.5 ml of CCl_4 and charged *via* a drawn-out medicine dropper to the bulb of the reactor. The reactor was then degassed three times and 0.700 g (0.013 mol) of HNF_2 was condensed in using a -126° bath (Freon-21 and liquid N_2). The reactor was allowed to warm to room temperature. Stirring (*via* magnetic stirrer) was continued for 24 hr. The volatile products were passed through a -78° (trichloroethylene-Dry Ice) and a -126° trap. The desired product remained behind as a colorless liquid. Bulb-to-bulb distillation of this liquid at 75° (0.5 mm) gave 0.607 g (98%) of the bis- α -difluoramino ether.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2\text{F}_4$: C, 33.0; N, 12.85; F, 34.9; mol wt, 218. Found: C, 32.85; N, 13.02; F, 34.6; mol wt, 214.

1,4-Bisdifluoramino-1,4-diethoxybutyne-2.—The tetraethoxybutyne-2 (0.59 g, 0.0026 mol) was charged neat into a glass pressure reactor. The reactor was then degassed three times. The HNF_2 (0.50 g, 0.009 mol) was condensed in using a -126° bath. After reaching room temperature the reaction was stirred for 24 hr. Work-up in the usual manner (see reaction above)

(9) R. P. Rhodes, *J. Chem. Educ.*, **40**, 423 (1963).

(10) Available from Fischer & Porter, Warminster, Pa., Catalog No. 795-609.

(1) R. Petry and J. Freeman, *J. Amer. Chem. Soc.*, **83**, 3912 (1961).

(2) J. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

(3) R. Haszeldine, *J. Amer. Chem. Soc.*, **72**, 1638 (1950); R. Pearson and R. Dresdner, *ibid.*, **84**, 4743 (1962).

(4) E. Lawton and J. Weber, *ibid.*, **81**, 4755 (1959).

(5) W. Good, D. Doussin, and J. McCullough, *J. Phys. Chem.*, **67**, 1312 (1963).

(6) A. V. Pankratov, *Russ. Chem. Rev.*, **32**, 157 (1963); C. Hoffman and R. Neville, *Chem. Rev.*, **62**, 1 (1962).

(7) W. Graham and J. Freeman, *J. Amer. Chem. Soc.*, **89**, 716 (1967).

(8) D. D. Rosenfeld, *J. Org. Chem.*, **28**, 2900 (1963).