

for 24 hr. before carbonation by decantation. The tan carbonation mixture yielded 14.1 g. of acidic material and 24.7 g. of neutral material after work-up in the manner described above. The acidic material was suspended in 650 ml. of boiling water²⁴ and filtered hot to give 1.2 g. of triphenylacrylic acid, m.p. 219.5–220° after three recrystallizations from ethanol (lit.²⁸ m.p. 216–217.5°), mixture melting point with an authentic sample, 216–218°.

The neutral fraction was distilled to give 23 g. of a mixture, b.p. 100–125 (0.6 mm.), $\nu_{\text{max}}^{\text{C}^{14}}$ 1667 cm^{-1} , which probably consists of diphenylacetylene and benzophenone (lit.²⁵ $\nu_{\text{max}}^{\text{C}^{14}}$ for benzophenone 1664 cm^{-1}). The undistilled portion was recrystallized from ethanol to give 8.2% (based on phenyllithium) of triphenylcarbinol.

Oxidative Cleavage of Dideuterated *trans*- α -*n*-Butylstilbene (II). The procedure was that of Pappo, Allen, Lemieux, and Johnson.¹⁶ A solution of 9.0 g. (0.038 mole) of II and 0.193 g. (0.00076 mole) of osmium tetroxide in 150 ml. of purified dioxane and 50 ml. of water was stirred for 5 min. during which time the solution became purple in color. While maintaining a temperature of 24–26°, a total of 34.2 g. (0.16 mole) of sodium metaperiodate was added over a period of 1 hr. The purple solution was stirred at room temperature for 60 hr. with little change in color. Heating for 15 min. at 60° resulted in a color change to pale yellow. The mixture

(24) Curtin and Richardson²⁸ separated benzoic acid and triphenylacrylic acid by employing the difference in solubilities in boiling water. Benzoic acid is soluble in water to the extent of 2.2 g./100 ml. at 75°. Triphenylacrylic acid dissolves in boiling water to the extent of 2.8 mg./ml. of water. Therefore 650 ml. of boiling water will dissolve 1.82 g. of triphenylacrylic acid but 14.3 g. of benzoic acid. The total yield (11%) of triphenylacrylic acid is then 3.02 g., 1.2 g. isolated and 1.82 g. lost due to solubility in boiling water.

(25) N. Fuson, M. L. Josein, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

was extracted with diethyl ether, and the combined organic layer (about 600 ml.) was filtered through anhydrous sodium sulfate. The solution was concentrated to 150 ml. and a calculated slight excess of saturated aqueous sodium bisulfite was added. The precipitate was collected on a filter, acidified with dilute hydrochloric acid, extracted with diethyl ether, dried over sodium sulfate, and distilled to yield 3.21 g. (79%) of benzaldehyde- α -*d*, pure by v.p.c. No aldehydic hydrogen appeared in the low-field area of the n.m.r. spectrum. *Anal.* Calcd. for $\text{C}_7\text{H}_5\text{DO}$: D, 16.67 atom %. Found: D, 16.15 atom %.

A portion of benzaldehyde- α -*d* was oxidized with sodium hydroxide-potassium permanganate²⁶ to give benzoic acid (identical with an authentic sample) which contained 0.00 atom % deuterium. Other workers have shown that under these conditions deuterium bound to the aryl ring would not be exchanged.²⁷

The remaining solution, after the sodium bisulfite treatment was distilled through a Vigreux column to yield 4.34 g. (71%) of valero-phenone-*o*-*d*, b.p. 78–80° (0.4 mm.), pure by v.p.c. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{13}\text{DO}$: D, 7.14 atom %. Found: D, 6.60 atom %.

In addition to having the correct infrared and n.m.r. spectra (see Discussion), a 2,4-dinitrophenylhydrazone of the product had m.p. 169.0–169.5° (lit.²⁶ m.p. 166°).

Acknowledgment. It is a pleasure to thank the Socony-Mobil Oil Company and the Air Force Office of Scientific Research, Grant No. AF-AFOSR 270-65, for support of this research.

(26) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 397.

(27) F. Jones, M. Zinn, and C. Hauser, *J. Org. Chem.*, **28**, 663 (1963)

Fluorocarbon Nitroxides

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Contribution from Texaco, Inc., Beacon, New York. Received October 1, 1965

Abstract: Nitroxides with fluorocarbon substituents have been found to form isolable, stable free radicals. Bis(2-chlorotetrafluoroethyl) nitroxide has been synthesized and characterized successfully. Evidence is presented for the existence of additional stable nitroxides containing fluorinated alkyl substituents. Nitroxide radicals with two difluoromethylene groups bonded to the nitrogen atom are believed to form a general class of stable radical species. The electron spin resonance spectra of these radicals is discussed.

Nitroxide radicals (R_2NO) stabilized by fluorocarbon substituents have been known for a very short time with the first example, bis(trifluoromethyl) nitroxide, being reported in 1965.¹ The corresponding hydrocarbon radical $((\text{CH}_3)_2\text{NO})$ as well as other nitroxides having hydrogen on the carbon adjacent to the nitrogen have never been isolated. Dimethyl nitroxide and its deuterated analog were observed as major fragments in the mass cracking pattern of a mass spectroscopic study of the reaction of methyl and deuteriomethyl radicals with nitric oxide.² Although it was not detected, $(\text{CH}_3)_2\text{NO}$ was proposed as the intermediate in the formation of the trimethylhydroxylamine. Stable nitroxide radicals containing hydrocarbon substituents require a tertiary carbon atom adjacent to the nitrogen (α -carbon) such as in the case of di-*t*-butyl nitroxide³ or aromatic substituents such as in diphenyl

nitroxide.⁴ A number of such radicals has been made. The stabilizing factors in these cases are reported to be resonance delocalization in the aromatic substituents and steric effects in the case of the alkyl substituents. Three-electron bond formation in compounds containing the N–O linkage has also been considered to lend stability to the radical structures.⁵

Paramagnetic species have been detected in liquid nitroso fluorocarbons by electron spin resonance (e.s.r.) spectroscopy.⁶ The spectra obtained were reported to be consistent with fluorocarbon nitroxides which were postulated to be reactive intermediates in the copolymerization of nitroso fluorocarbons and tetrafluoroethylene. The subsequent synthesis and isolation of $(\text{CF}_3)_2\text{NO}$ indicated that fluorocarbon nitroxides

(3) A. K. Hoffmann and A. T. Henderson, *ibid.*, **83**, 4671 (1961).

(4) H. Wieland and M. Offenbacher, *Ber.*, **47**, 211 (1914).

(5) R. B. Briere, H. Lemaire, and A. Rassat, *Tetrahedron Letters*, 1775 (1964).

(6) L. H. Piette and G. H. Crawford, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962, Abstracts, p. 10N.

(1) W. D. Blackley and R. R. Reinhard, *J. Am. Chem. Soc.*, **87**, 802 (1965).

(2) A. Maschke, B. Shapiro, and F. W. Lampe, *ibid.*, **86**, 1929 (1964).

were stable, isolable compounds. In view of the difficulty of isolating or even detecting nitroxides with normal alkyl hydrocarbon substituents, the perfluoroalkyl groups were believed to be the major factor in the stabilization of the fluorocarbon nitroxide structure. The object of this work was, firstly, to determine if $(CF_3)_2NO$ is a unique species or whether fluorocarbon nitroxides are a more general class of stable radical compounds and, secondly, to determine the stabilizing effect of the α -fluorine atoms by replacing some of these atoms with other groups.

Some cases involving a delocalization of electrons by fluorine have been reported to account for the apparent anomalies of fluorocarbon compounds relative to their hydrocarbon analogs. Trifluoronitrosomethane contains more ionic character than would be expected to result from the removal of electrons by the trifluoromethyl group based on electronegativity alone.⁷ This would tend to indicate that the fluorine might be introducing additional electron delocalization. The order of stability of perfluoroalkyl carbanions is reported by Andreades⁸ to be in the order tertiary > secondary > primary due to the "no bond" resonance and charge delocalization by the β -fluorine atoms. In addition, fluorine atoms are reported to stabilize certain radical species.⁹ Supported by the existence of $(CF_3)_2NO$ and the above reports, it seems reasonable that nitroxides with two fluorines attached to each α -carbon should be stabilized by these electron delocalization effects but to a lesser degree than $(CF_3)_2NO$.

In this report, the synthesis of a second stable nitroxide radical, bis(2-chlorotetrafluoroethyl) nitroxide is described. This radical was isolated as a relatively stable purple liquid. Evidence also was obtained for other stable higher fluorocarbon analogs of $(CF_3)_2NO$ by electron spin resonance.

Experimental Section

Reaction of ClNO and C_2F_4 . Tetrafluoroethylene (10 g., 0.1 mole) and nitrosyl chloride (6.5 g., 0.1 mole) were condensed into an evacuated Pyrex bulb (5-l.) which had an attached cold finger and vacuum connections. The cold finger was cooled in a wet ice bath as the bulb was irradiated with sunlight for approximately 5 days, during which time the color of the gases changed from brown to blue to greenish brown and a dark brown liquid collected in the cold finger. The contents of the bulb then was vacuum fractionated by trap-to-trap distillation. On the basis of infrared and gas chromatographic analyses, the low-boiling products were COF_2 , C_2F_4 , acid fluorides, and a few other minor components. The brown liquid (8.5 g., 50% average crude yield) was somewhat unstable, fumed in air, and contained strong infrared absorptions at 1835, 1775, 1610, 1200, 1120, 993, 955, 935, 820, and 760 cm^{-1} . The gas chromatographic (g.c.) analysis of the brown liquid indicated at least six components. Trapping of the larger peaks from a g.c. fractionation gave a first fraction which was a blue liquid at low temperature and was identified as $ClCF_2CF_2NO$. The second fraction was a white solid at low temperature and gave infrared absorptions in the gas phase at 1610, 1200, 1150, 955, 910, and 815 cm^{-1} . In later runs this material was tentatively identified as $(ClCF_2CF_2)_2NNO_2$. The third fraction was a brown liquid with the strong absorption in the infrared at 1835 cm^{-1} similar to the N-O absorption of the dimer of CF_3NO . This material was identified as $(ClCF_2CF_2)_2NONO$. The brown liquid reacted vigorously with methanol generating methyl nitrite which was identified on the basis of infrared and mass spectroscopic analyses. Attempts to

purify the brown liquid by distillation were not successful. Electron spin resonance analysis of the brown liquid before thermal decomposition indicated a low concentration of radical species. The radical forming reaction occurred in the thermal decomposition of the $(ClCF_2CF_2)_2NONO$ described below.

Synthesis of $(ClCF_2CF_2)_2NO$. The crude dimer, $(ClCF_2CF_2)_2NONO$ (54 g.), was heated slowly in a Teflon¹⁰ (FEP) reactor attached to a Dry Ice cooled Teflon trap. The system was open to the atmosphere during heating. A brown gas (NO_2 on the basis of infrared analysis) was evolved at 55° and continued to evolve as the temperature was gradually increased to a maximum of 100°. Volatile products and the brown gases were condensed in the Dry Ice cooled trap and the material in the reactor gradually turned to a purple-colored liquid. The volatile liquids (11.6 g.) were composed of two major components which were separated by g.c. fractionation. One was identified as 1,5-dichloroheptafluoro-3-azapentene-2, $ClCF_2CF_2N=CFCF_2Cl$, by infrared (absorptions at 1775, 1300, 1200, 1110, 990, 955, 930, 818, 758, and 690 cm^{-1}), mass spectroscopy, and nuclear magnetic resonance analyses (four ¹⁹F peaks were obtained in approximately a 2:2:2:1 ratio at +20.6, -2.81, -12.4, and -46.3 p.p.m. from CF_3COOH). The other component tentatively was identified as bis(2-chlorotetrafluoroethyl)nitramine, $(ClCF_2CF_2)_2NNO_2$, based on the infrared analysis (strong absorption at 1610 cm^{-1}) and its mass cracking pattern which contained a large fragment at 46 (NO_2^+) in addition to the fragments expected from the proposed structure. The purple liquid remaining in the reactor (40.3 g.) was composed of three major components. Two of these products were the same as those identified above, that is, $ClCF_2CF_2N=CFCF_2Cl$ and $(ClCF_2CF_2)_2NNO_2$, while the third was a purple liquid as trapped from a g.c. fractionation. It was a liquid at room temperature and a purple solid when frozen at liquid nitrogen temperatures. The crude material was distilled under atmospheric pressure in air through a Pyrex column (0.5 × 6 in.) packed with 1/8-in. glass beads. Gas chromatographic analysis indicated the purple fraction, which distilled from the glass column at 92°, was 69% radical material. Radical samples of over 95% purity were obtained by trapping from a g.c. fractionation. The impurity was $ClCF_2CF_2N=CFCF_2Cl$. When the above thermal decomposition was run in Pyrex, the yield of the azapentene appeared greater, whereas, in a Teflon reaction system, the second by-product, the nitramine, was obtained in higher yields. E.s.r. confirmed the presence of free radicals in the purple liquid.

Characterization of $(ClCF_2CF_2)_2NO$. A. Electron spin resonance spectra were obtained on a Varian X-band spectrometer with a 100-kc. field modulation using a Harvey-Wells 12-in. electromagnet. A concentrated solution of the radical material in carbon tetrachloride gave a broad single line pattern having a g value of 2.0074. On further dilution the single line split into a symmetrical seven-line pattern with 10.2-gauss splitting and relative peak heights of 1:4.3:8.2:9.2:8.3:4.3:1 (Figure 1). The average line width of each of the seven lines was 4.5 gauss. Further dilution and degassing did not produce additional hyperfine splitting. No loss in signal intensity was observed in a sample sealed and stored at room temperature in a quartz e.s.r. tube for over 1 year. Dilution of the sample with Freon 11 ($CFCl_3$) (Figure 2) also gave seven major lines but considerable additional splitting appeared. The separation of the larger peaks was 10.3 gauss. The two outer peaks appeared to be split into quintuplets with about 1 gauss separation and the central peaks also showed additional structure with the major peak being split into seven equally spaced lines having a 1-gauss separation. The values of a_F and a_N were calculated from the spectrum data to be 10.1 and 9.3 gauss, respectively.

Diluting a carbon tetrachloride solution of the radical or the radical alone with ether gave a very complex pattern on analysis by e.s.r.

B. Reaction with NO. Crude radical material (0.998 g.) was placed in an ampoule attached to the vacuum system and condensed with liquid nitrogen and degassed. Nitric oxide (4.6 mmoles) was introduced over the radical solution with stirring. The purple color of the solution rapidly changed to brown with a loss of 0.83 mmole of NO as indicated by the pressure drop in the system of known volume. The resulting brown liquid gave a strong absorption at 1835 cm^{-1} in the infrared spectrum, characteristic of $(ClCF_2CF_2)_2NONO$. This loss in NO corresponded to a solution containing 25% radical material.

(7) J. E. Boggs, D. Coffey, and J. C. Davis, *J. Phys. Chem.*, **68**, 2383 (1964).

(8) S. Andreades, *J. Org. Chem.*, **27**, 4157 (1962).

(9) M. Stacey, J. C. Tatlow, and A. G. Sharpe, *Advan. Fluorine Chem.*, **1**, 144 (1960).

(10) Trademark of the E. I. du Pont de Nemours and Co.

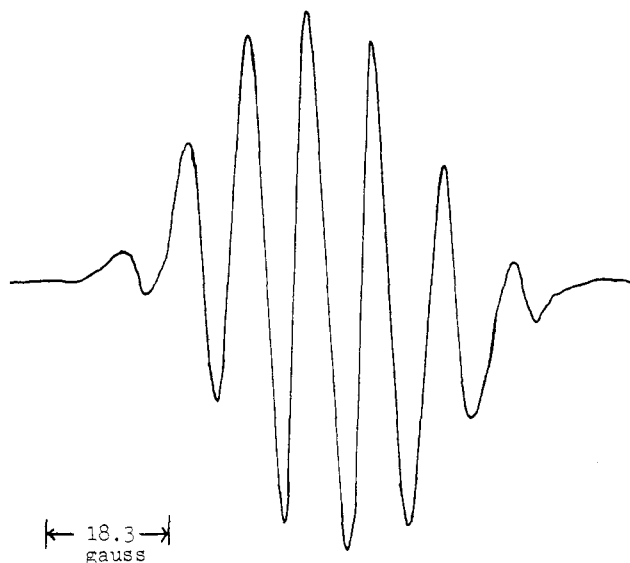


Figure 1. Electron spin resonance spectrum of $(\text{ClCF}_2\text{CF}_2)_2\text{NO}$ in carbon tetrachloride solution.

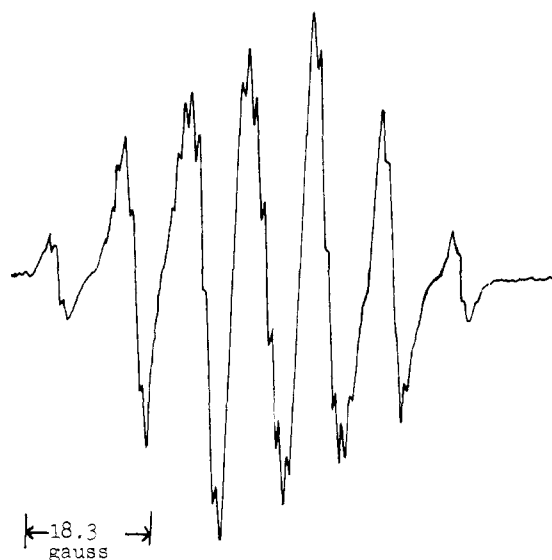


Figure 2. Electron spin resonance spectrum of $(\text{ClCF}_2\text{CF}_2)_2\text{NO}$ in chlorotrifluoromethane solution.

C. Mass Cracking Pattern. The mass cracking pattern of a g.c.-purified fraction gave parent peaks at 302 and 300 in agreement with values expected from a structure containing the naturally occurring isotopes of chlorine, that is, ^{37}Cl and ^{35}Cl . The fragments observed in decreasing order of intensity were 85, 135, 30, 87, 137, 69, 180, 31, 100, 50, 116, 66, 114, 47, 165, 230, 130, 76, 118, 119, 167, 232, 95, 265, 280, 300, 246, 132, 302, and 248.

D. Molecular Weight. The molecular weight was determined by the Regnault method at the vapor pressure of the liquid in a 133-cc. Pyrex bulb fitted with a Fisher-Porter greaseless stopcock. Four determinations gave values of 302.5, 309, 302, and 300.5 for an average molecular weight of 303.5. The calculated value for $(\text{ClCF}_2\text{CF}_2)_2\text{NO}$ is 301. The vapors of the radical appeared to dissolve in Fluorolube, Kel-F, and Silicone greases and reacted with Spectrovac and Lubriseal greases which is the reason the greaseless stopcock was necessary.

E. Gas Chromatography. Best chromatographic results were obtained on a 3 ft. \times 0.25 in. copper column packed with 33% FC-43¹¹ on Chromosorb P at room temperatures. All g.c. frac-

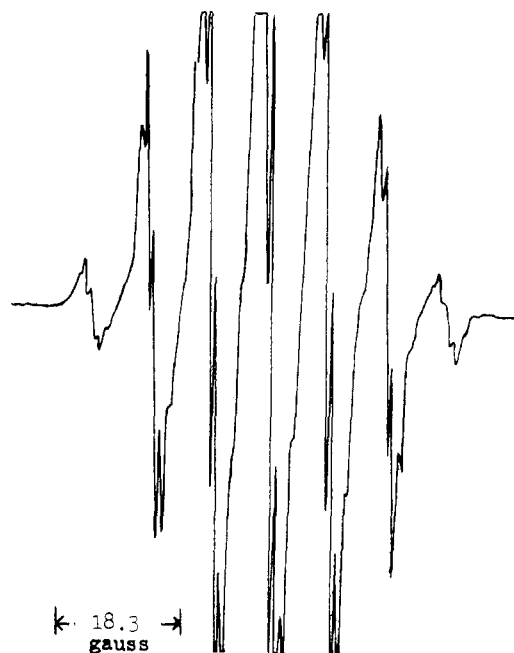


Figure 3. Electron spin resonance spectrum of $(\text{C}_7\text{F}_{15})_2\text{NO}$.

tions were made on this system. Fluorine analysis of a purified fraction gave 49.9% vs. a theoretical value of 50.5%.

F. Reaction with Nitrogen Dioxide. Excess nitrogen dioxide was introduced over distilled radical material. The purple color disappeared with stirring but on removal of the excess NO_2 , the solution evolved a brown gas and the color of the solution returned to the original purple color. Loss of the purple color to brown also was observed when NO_2 was bubbled through a solution of 2.0 g. of radical material in carbon tetrachloride. On removal of excess NO_2 , the CCl_4 solution remained brown in color. New absorptions appeared in the infrared spectrum of this solution at 1725 and 1250 cm^{-1} . Heating resulted in the evolution of a brown gas and the liquid solution again became purple in color. Shaking the brown solution with mercury followed by infrared analysis showed the presence of absorptions at 1835 cm^{-1} , characteristic of $(\text{ClCF}_2\text{CF}_2)_2\text{NONO}$. Nitrogen dioxide in CCl_4 gave absorptions in the infrared at 1725 and 1245 cm^{-1} but lost these with no new bands forming when it was shaken with mercury.

Reaction of $(\text{ClCF}_2\text{CF}_2)_2\text{NONO}$ with Methanol. The brown liquid (5.0 g.) was magnetically stirred in a flask fitted with a dropping funnel and a water condenser and Dry Ice cooled trap in series. A vigorous evolution of gas resulted when methanol was added slowly from the dropping funnel. The Dry Ice trap collected a volatile product identified as CH_3ONO by infrared and mass spectroscopic analyses. The infrared spectrum of the solution contained absorptions at 3650 cm^{-1} which is characteristic of the hydroxyl absorptions of the perfluoroalkylhydroxylamines.

Synthesis of $\text{C}_7\text{F}_{15}\text{COONO}$. Perfluorooctanoic acid (100 g.) (Peninsular Chem Research) was dissolved in acetone (200 ml.) and excess silver oxide (27 g.) was added slowly. The mixture was stirred for 15 min. and filtered. Evaporation of the acetone left a white solid (118 g.). The silver salt (60 g.) was allowed to react with nitrosyl chloride at -22° (CCl_4 slush) for about 2 hr. Distillation from the reaction flask under vacuum produced the expected yellow oil (45 g.).¹²

Reactions of $\text{C}_7\text{F}_{15}\text{COONO}$. The perfluorooctanoyl nitrite (8 g.) was thermally decomposed at 160° for 6–8 hr. A second sample (5.0 g.) was irradiated with ultraviolet light for 24 hr. The crude reaction mixture from each of the above reactions was analyzed by electron spin resonance spectroscopy. Both samples contained free-radical species having the same electron spin resonance pattern. The spectra obtained are represented by the pattern shown in Figure 3. The radical concentration from these reactions was low in all cases studied but was stable for extended periods of time (several weeks gave no detectable change) in contact with the

(11) Perfluorotri-*n*-butylamine made by Minnesota Mining and Manufacturing.

(12) C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, **27**, 1064 (1962).

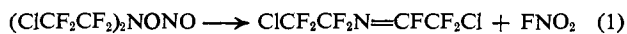
atmosphere. The e.s.r. pattern consisted of seven peaks, 1:4.6:10:12.5:10:4.7:1 relative peak heights, and an average splitting of 9.6 gauss, each split into five additional lines with relative heights of 1:3.9:6:5:1.5 and an average separation of 1 gauss. The line width was 0.6 gauss. Identical e.s.r. results were obtained from the product mixture in the reaction of $C_7H_{15}I$ (0.01 mole) and NO (0.01 mole) on irradiation in a glass apparatus for 12 hr.

Discussion

The reactions of nitrosyl chloride and tetrafluoroethylene,¹³ nitric oxide, and tetrafluoroethylene in the presence of ferric chloride,¹⁴ and the reaction of chlorine, nitric oxide, and tetrafluoroethylene¹⁵ have been investigated with the reported formation of $CICF_2CF_2NO_2$, $CICF_2CF_2NO$, $CICF_2CF_2Cl$, an oxazetidine, and a copolymer as major products depending on the conditions of the reaction. The "azapentene derivative," $CICF_2CF_2N=CFCF_2Cl$, has been reported¹⁵ previously as one of the products obtained from the thermal reaction of $CICF_2CF_2NO$. Other compounds having the $CF=N$ linkage have been reported to result from the decomposition of $(CF_3)_2NONO$,¹⁶ $(CF_3)_2CFNO$,¹⁷ and C_2F_5NO ¹⁷ so the formation of the "azapentene" in this work was not too surprising. These "aza" compounds also form on pyrolysis of the copolymers of perfluoroalkylnitroso compounds and the fluoroolefins.

When an ice-water-cooled cold finger was used to trap out the products during the irradiation of the $CINO-C_2F_4$ mixture, a dark brown liquid containing a good yield of $(CICF_2CF_2)_2NONO$ collected in the cold finger. With no means of removing the above product from the reaction, the "azapentene" derivative and other decomposition products became the only products, indicating that the $(CICF_2CF_2)_2NONO$ was unstable to light or other reaction conditions employed. The brown liquid could be transferred in a vacuum system with no significant change. Volatilization of the $(CICF_2CF_2)_2NONO$ through a hot tube *in vacuo* resulted in some decomposition, primarily to $CICF_2CF_2N=CFCF_2Cl$, but much of the $(CICF_2CF_2)_2NONO$ was recovered. This may very well have been a dissociation into the radicals $(CICF_2CF_2)_2NO$ and NO which then merely recombine outside the heated reactor tube. The "azapentene" may have resulted from a dissociation of the $(CICF_2CF_2)_2NONO$ at the $N-ONO$ bond to produce NO_2 radicals (reaction 1) accompanied by the loss of a fluorine at the α -carbon. Heating $(CICF_2CF_2)_2N_2ONO$ in the presence of air or oxygen resulted in the production of NO_2 and the formation of $CICF_2CF_2N=CFCF_2Cl$, $(CICF_2CF_2)_2NNO_2$, and $(CICF_2CF_2)_2NO$ with complete loss of the $(CICF_2CF_2)_2NONO$. The amounts of the two major by-products varied depending on whether the reaction was run in Teflon or Pyrex vessels. The Pyrex vessel produced more of the "azapentene," whereas, in a Teflon apparatus the amount of $(CICF_2CF_2)_2NNO_2$ produced was greater. The Pyrex apparently destroyed the FNO_2 producing NO_2 and SiF_4 leaving the $CICF_2-$

$CF_2N=CFCF_2Cl$ product. On the other hand, in Teflon, the FNO_2 is not destroyed and can recombine with the "azapentene" and form the nitramine, $(CICF_2CF_2)_2NNO_2$ (reaction 2).



O-Nitrosobis(trifluoromethyl)hydroxylamine undergoes a reaction¹⁶ analogous to reaction 1 above and reactions analogous to reaction 2 also have been reported.^{16,17} Finally, the FNO_2 is known to react with glass.¹⁸ The radical-forming reaction may result from a cleavage at the $NO-NO$ bond to produce the nitroxide and nitric oxide (reaction 3). The nitric oxide in the presence of oxygen then reacts to form NO_2 which is evolved at room temperature since it forms a thermally unstable compound with the nitroxide. The reaction between the radical and nitrogen dioxide appears to be reversible and is favored by low temperatures and excess NO_2 . These competing reactions are proposed to account for the major products observed.



The direct oxidation of $(R_F)_2NONO$ to $(R_F)_2NNO_2$ cannot be eliminated completely as a possible mechanism.

In carbon tetrachloride solution (Figure 1), the electron spin resonance pattern consisted of the seven-line pattern expected from a radical having four equivalent fluorine atoms on two carbon atoms adjacent to nitrogen, $(RCF_2)_2NO$, where the fluorine and nitrogen splittings are equal. On the basis of the e.s.r. results of $(CF_3)_2NO$, the splittings of the fluorine attached to the carbon adjacent to the nitrogen (α -fluorine) and the nitrogen would be expected to be close but not equal, so that additional splitting of the central peaks was expected. In carbon tetrachloride solution the relative heights of the seven lines were 1:4.3:8.2:9.3:8.3:4.3:1 which is not in exact agreement with the calculated intensities of 1:5:11:14:11:5:1 for the model system, $(RCF_2)_2NO$, on the basis of equal fluorine and nitrogen hyperfine coupling constants. The large line width (4.5 gauss) would tend to obscure the additional splittings expected from the differences in the fluorine and nitrogen coupling and the low intensity of the central peaks is expected from the resultant inhomogeneous line broadening. No additional splitting could be obtained in carbon tetrachloride solution although attempts to obtain it included low radical concentrations and extreme care in degassing the e.s.r. samples. The additional structure expected was observed when the radical material was diluted with Freon 11 ($CFCl_3$), as is shown in Figure 2. The four outside peaks appeared to split into quintuplets of about 1-gauss separation and approximately 1:4:6:4:1 relative intensity. This splitting was attributed to the four equivalent fluorine atoms attached to the second carbon in the fluoroalkyl chain (the β -fluorine). The central major peak was split into seven additional lines with about 1-gauss separation. The 1-gauss splitting of the β -fluorine is about the same as the expected difference in the α -fluorine and nitrogen splittings. Therefore, assuming the β -fluorine splitting and the difference

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(14) J. D. Park, A. P. Stefani, and J. R. Lacher, *J. Org. Chem.*, **26**, 3319 (1961).

(15) W. A. Ginsburg, N. F. Priwieszewa, W. A. Schpanski, N. P. Rodionowa, S. S. Dubow, A. M. Chochlowa, S. P. Makarow, and A. J. Jakubowitsch, *J. Gen. Chem. USSR*, **30**, 2409 (1960); *Chem. Zentr.*, **134**, 4320 (1963).

(16) J. Mason, *J. Chem. Soc.*, 4537 (1963).

(17) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

between the α -fluorine and nitrogen splittings are both 1 gauss, one would expect to see seven additional lines of 1:5.5:13:17:13:5.5:1 relative intensity. The measured heights of the seven observed lines on the central peak were 1:4.7:7.2:8.3:7.3:5.2:1.2. The low values for these peaks again may be due to the inhomogeneous line broadening because of inequality of the above splittings. In fluorocarbon nitroxides, the fluorine bonded to the β -carbon are believed to give splittings of about 1 gauss, while the nitrogen and fluorine bonded to the α -carbon give about equal splitting and can be expected to be in the 8–11-gauss range.

The α -fluorine and nitrogen splitting in $(C_7F_{15})_2NO$ appear to be much closer than they are in $(ClCF_2CF_2)_2NO$, based on the rather close agreement of the measured peak heights in the e.s.r. spectra to the expected values. In addition, five equally spaced lines of slightly less than 1-gauss separation were observed on all seven major peaks and were attributed to the interactions of the four equivalent β -fluorine atoms. The relative peak heights of the five peaks are in good agreement with the expected values. The e.s.r. spectra furnish good evidence for the existence of stable higher nitroxides containing perfluoroalkyl substituents.

The complex spectra obtained on the addition of any of the radicals to ether was believed to result from the

formation of a new radical species and not a solvent effect.

The e.s.r. data, mass spectroscopic analysis, molecular weight, fluorine analysis, and reaction with nitric oxide establish the structure of the first radical material as that proposed, bis(2-chlorotetrafluoroethyl) nitroxide. The e.s.r. results indicate the existence of other stable nitroxides containing fluorocarbon substituents with up to 7 carbons in the chain. It is believed that fluorocarbon nitroxides are a stable class of free-radical species. The loss of a fluorine from each of the α -carbons and replacement with a fluorocarbon group did not significantly affect the stability of the nitroxide. As the fluorine is replaced by larger fluoroalkyl groups, any loss in stabilization by decreased electron delocalization may be balanced by an increase in the stabilization by steric effects. The radical $(ClCF_2CF_2)_2NO$ did not appear to dimerize on cooling, as $(CF_3)_2NO$ did, indicating possible steric repulsions by the larger chlorotetrafluoroethyl groups.

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Synthesis of Functionally Substituted Alkylboronic Acids, Hydroboration of N-Alkenylureas and -carbamates¹

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Abstract: In contrast with terminal hydrocarbon olefins, the hydroboration of certain N-alkenylureas and N-alkenylcarbamates ceases to an appreciable extent at the monoalkylborane stage. This is indicated by the hydrolysis of these intermediate organoboranes to the corresponding substituted aminoalkylboronic acids.

The preparation of a variety of functionally substituted alkylboronic acids has been limited as a result of the incompatibility between the previous synthetic methods for introducing the boronic acid moiety and the desired functional groups. To circumvent this difficulty, Matteson³ introduced functional groups into ethylenic and acetylenic boronic acids esters by radical additions. Recently the application of the hydroboration reaction to functionally substituted olefins has led to the synthesis of several substituted alkylborons,⁴ some novel boron hetero-

cycles,⁵ and alcohols resulting from the oxidation of borane intermediates.⁶ This latter work has demonstrated the feasibility of this reaction in the presence of certain functional groups including some that are normally reduced by diborane. However, the extreme reactivity of unhindered monoalkylboranes to undergo further hydroboration to trialkylborons⁴ appeared to preclude the general synthesis of boronic acids by this method, though the utility of this reaction for the synthesis of such compounds had been indicated.⁷

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