Reactions of Nitrogen Dioxide with Organic Halogen Compounds. II.[1] Synthesis of Nitrofluoro Alkanes from Fluorocarboxylic Acids

RICHARD M. SCRIBNER

Contribution No. 862 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

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Fluorocarboxylic acids react with nitrogen dioxide at elevated temperatures to give 1-nitrofluoro alkanes in small yields (5–30%).

Silver salts of fluorocarboxylic acids readily undergo the Hunsdiecker reaction[2] with halogens, at temperatures generally below 100°, to afford fluoroalkyl halides in excellent yields. Analogous to this is the reaction of perfluorocarboxylic acids, rather than their silver salts, with bromine at high temperatures[3] to give perfluoroalkyl halides.

$$C_2F_5CO_2H + Br_2 \xrightarrow[80\%]{350°} C_2F_5Br + CO_2 + HBr$$

Silver perfluorobutyrate has been reported by Banus[4] to react with nitrogen dioxide in a sealed tube at 200° to afford a small yield of what is probably 1-nitroperfluoropropane, although no evidence for the structure of the product was given. Silver trifluoroacetate was found by Haszeldine and Jander[5] to react in the cold with nitrosyl chloride to form what was apparently trifluoroacetyl nitrite, decomposition of which by gentle heating gave a mixture of nitroso- and nitrotrifluoromethane. Superficially, at least,[6] both of these reactions appear similar to the Hunsdiecker reaction.

TABLE I

PREPARATION OF 1-NITROFLUORO ALKANES FROM FLUOROCARBOXYLIC ACIDS

Acid	Moles NO_2 per mole of acid	Temp., °C.	Time, hr.	Product	Yield, %	B.p., °C.[a]	Analysis, % N Calcd.	Analysis, % N Found
CF_3CO_2H	6	200	6	CF_3NO_2[b]	30[c]			
$ClCFHCF_2CO_2H$[d]	3	180	4	$ClCFH{-}CF_2NO_2$[e]	5	63–64	8.72	8.57
$H(CF_2)_4CO_2H$	5	160	6	$H(CF_2)_4NO_2$	30	80	5.67	5.48
$H(CF_2)_6CO_2H$	8	160	6	$H(CF_2)_6NO_2$	15	111	4.08	3.99
$F_3C(CF_2)_6CO_2H$	7	150	2	$F_3C(CF_2)_6NO_2$	10–15	121–122	3.38	2.99

[a] Ref. 13. [b] Identified by mass spectroscopic analysis and by comparison with the infrared spectrum reported by Haszeldine and Jander (ref. 5). [c] Approximate yield based on mass spectroscopy. [d] D. C. England, R. V. Lindsey, L. R. Melby, *J. Am. Chem. Soc.*, **80**, 6442 (1952). [e] The vapors of this nitro compound are extremely irritating to the nostrils.

Now, completing the two sets of analogies, we have found that fluorocarboxylic acids themselves react with nitrogen dioxide at elevated temperatures to give nitrofluoroalkanes in small yields.

$$RCF_2CO_2H \xrightarrow{NO_2} RCF_2NO_2 + CO_2$$

The reaction is carried out conveniently by heating a mixture of a fluorocarboxylic acid and excess nitrogen dioxide in an autoclave for several hours at 150–200°. Table I lists 1-nitrofluoro alkanes that have been prepared in this manner.

Passage of fluorocarboxylic acids and a mixture of nitric oxide (excess) and air through a reaction tube packed with glass helices and heated at 300° also produces 1-nitrofluoro alkanes,[1] but yields tend to be smaller, and the procedure is less convenient compared to the autoclave method.

Assignment of structure to these nitro compounds is based primarily on infrared spectroscopic evidence. Whereas simple nitro paraffins generally exhibit asymmetric and symmetric stretching vibrations at 6.38–6.49 and 7.26–7.45 μ, respectively, a powerful electron-withdrawing group attached directly to the nitro group shifts these bands to shorter and longer wave lengths, respectively.[7] Haszeldine,[8] for example, reports that 2-chlorotetrafluoro-1-nitroethane shows strong absorption bands at 6.18 and 7.85 μ. This is in good agreement with the band positions observed for our 1-nitrofluoro alkanes (Table II). To distinguish further our compounds from the isomeric nitrites (or nitrates), our compounds were shown to be unaffected by prolonged shaking with concentrated sulfuric acid or with 5% aqueous sodium hydroxide.

Although the reaction of fluorocarboxylic acids with nitrogen dioxide is undoubtedly quite complex, formation of 1-nitrofluoro alkanes can be rationalized, at least superficially, by the following radical reactions, exemplified by 7*H*-dodecafluoroheptanoic acid. Although eq. 1 implies nothing about the mechanism of formation of fluoroalkyl radical, there is ample ground

$$H(CF_2)_5CF_2CO_2H \xrightarrow{NO_2} H(CF_2)_5CF_2\cdot \qquad (1)$$

$$H(CF_2)_5CF_2\cdot + NO_2 \longrightarrow H(CF_2)_5CF_2NO_2 \qquad (2)$$

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(1) Part I in this series, *J. Org. Chem.*, **29**, 279 (1964).

(2) R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 250 (1956); C. V. Wilson, *Org. Reactions*, **11**, 332 (1957).

(3) J. D. LaZerte, W. H. Pearlson, and E. A. Kouck, U. S. Patent 2,647,933 (1953). Fluorine, however, reacts with perfluorocarboxylic acids at approximately 25° to give perfluoroacyl hypofluorites. *Cf.* G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953), and A. Meneffee and G. H. Cady, *ibid.*, **76**, 2020 (1954).

(4) J. Banus, *J. Chem. Soc.*, 3755 (1953). The preparation of $C_3F_7NO_2$ by irradiation of C_3F_7I and nitrogen dioxide in the presence of mercury also was reported.

(5) R. N. Haszeldine and J. Jander, *ibid.*, 4172 (1953).

(6) Both the Hunsdiecker reaction and the reaction of Haszeldine and Jander appear to involve generation of free radicals by decomposition of RCO·OX where X is halide or NO.

(7) J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(8) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

TABLE II

INFRARED ABSORPTION BANDS OF 1-NITROFLUORO ALKANES

Compound	NO_2 asym. stretch, μ	NO_2 sym. stretch, μ
CF_3NO_2	6.13, 6.18	7.78
$ClCFHCF_2NO_2$	6.24	7.33
$H(CF_2)_4NO_2$	6.18	7.40
$H(CF_2)_6NO_2$	6.16	7.40
$F_3C(CF_2)_7NO_2$	6.15	7.40

for its rationalization. It may progress through an acylnitrate intermediate, $H(CF_2)_5CF_2CO \cdot ONO_2$, akin to the nitrite intermediate proposed by Haszeldine and Jander[5] and analogous to the hypohalite intermediates, $RCO \cdot OX$, strongly implicated as precursors to the free radicals involved in the Hunsdiecker reaction.[2] Another possibility is that the fluorocarboxylic acid decarboxylates at the temperature of this reaction without participation of nitrogen dioxide.[9] Equation 2 represents reaction of the fluoroalkyl radical with the radical NO_2 to give a nitro compound.

Isolation of a waxy solid, m.p. 80°, having the structure $H(CF_2)_xH$ (x = unknown) from the reaction of 7*H*-dodecafluoroheptanoic acid and nitrogen dioxide supports the hypothesis that fluoroalkyl radicals participate in this reaction.

However, reflecting the over-all complexity of this reaction, a series of homologous 1-nitrofluoro alkanes is also found among the products.[10] Thus, fractional distillation of the liquid products from reaction of 7*H*-dodecafluoroheptanoic acid with nitrogen dioxide, after washing with base to remove possible nitrite esters, gave five fractions of colorless liquid boiling over the temperature range 79–111°. The highest boiling fraction was shown by gas chromatography to be 98% pure; by elemental analysis and n.m.r. and infrared analysis it clearly had the structure $H(CF_2)_6NO_2$. Spectral and gas chromatographic analysis of the lower fractions indicated that they were a mixture of homologous nitro compounds, $H(CF_2)_nNO_2$, one fraction of which appeared to be $H(CF_2)_4NO_2$, identical with the major product obtained from the reaction of 5*H*-octafluoropentanoic acid with nitrogen dioxide.

Experimental[13]

1-Nitrofluoro Alkanes from Fluorocarboxylic Acids.[14] Reactions in an Autoclave.—Table I summarizes conditions employed for the reaction of nitrogen dioxide with fluorocarboxylic acids. The following experiments are typical.

A 400-ml. stainless-steel autoclave (Hastelloy-C) charged with 20 g. (0.06 mole) of 7*H*-dodecafluoroheptanoic acid and 20 g. (0.25 mole) of dinitrogen tetroxide was heated gradually to 160° over an 8-hr. period at a rate of about 20° per hr. and then maintained at 160° for 6 hr. The autoclave was cooled to room temperature and vented slowly; a liquid residue was obtained. After washing with aqueous sodium bicarbonate, the liquid product (5.5 g.) was distilled through a Nester[15] 8-in. spinning-band column to give the following fractions: (1) b.p. 78–79°, 0.3 ml.; (2) 89–111°, 0.5 ml.; (3) 111°, 0.6 ml.; (4) 111°, 0.5 ml.; (5) 111°, 0.5 ml. A nondistillable residue was obtained which after crystallization from benzene melted at 80° and weighed 1.0 g. Fractions 2 through 5 were shown by gas chromatography[16] to be mixtures of five components in common. Fractions 4 and 5 were 98% pure and contained about 1.5% of the major component of fraction 2. The proton magnetic resonance spectrum of fraction 4 consisted of a single triplet (J = 51 c.p.s.) at τ 3.25 split further into triplets (J = 5 c.p.s.) (HCF_2CF_2–). The infrared absorption spectra for fractions 4 and 5 showed, in addition to strong C–F absorption in the 9–10-μ region, strong bands at 6.16 and 7.40 μ ($\lambda_{CF_2NO_2}$).

Anal. Calcd. for $C_6HF_{12}NO_2$: F, 65.8; N, 4.08. Found for fraction 4: F, 65.9; N, 3.99.

Fraction 2 was shown by g.c. to be 92% pure and to contain about 6% of the major component of fraction 4. Significantly, the retention time of the major component of fraction 2 was within about 4% (10 sec.) of the retention time observed, in another experiment, for $H(CF_2)_4NO_2$ (b.p. 80°) prepared from 1*H*-octafluoropentanoic acid. The p.m.r. spectrum was similar to that of fraction 4, and the infrared absorption spectrum showed bands characteristic of fluoronitro alkane at 6.16–6.18 and 7.40 μ.

Infrared analysis of the whole solie, m.p. 80°, described before showed the absence of bands ascribable to carbonyl, carboxyl, or nitro groups. The p.m.r. spectrum was difficult to interpret because of low signal strength, but it appeared to consist of a weak triplet at about τ 3.2. In spite of a low fluorine analysis, an α,ω-dihydrofluorocarbon structure is proposed for this compound.

Anal. Calcd. for $C_nH_2F_{2n}$: F, 75.8; N, 0.0. Found: F, 74.0; N, nil.

In another experiment, 20 g. (0.05 mole) of perfluorooctanoic acid and 15 g. (0.33 mole) of nitrogen dioxide were heated in a 200-ml. Hastelloy-lined autoclave, the temperature being raised at the rate of 20° per hr. to 150° and held at 150° for 2 hr. The vessel was cooled to room temperature and slowly vented, leaving about 7 g. of liquid and a trace of green nickel salt. The liquid was washed with three 50-ml. portions of saturated aqueous sodium bicarbonate, then dried over magnesium sulfate, giving about 3 g. of a colorless, mobile liquid that was distilled through a 4-in. micro spinning-band[15] column. The following fractions were obtained: (1) b.p. 82°, 0.1 ml. (N, 3.78); (2) b.p. 82–100°, 0.2 ml. (*Anal.* Calcd. for $C_6F_{13}NO_2$: N, 3.84. Found: N, 3.65.); (3) b.p. 100–103°, 0.3 ml. (N, 3.50); (4) 103–113°, 0.5 ml. (N, 3.42); (5) b.p. 115–121°, 0.5 ml. (N, 3.31); (6) b.p. 121–122°, 0.6 ml. (N, 3.25); (7) 122°, 0.2 ml. (*Anal.* Calcd. for $C_7F_{15}NO_2$: N, 3.38. Found: N, 2.99.).

As shown by gas chromatographic analysis, each of the seven fractions was a mixture of 4–5 components. The major (90%) component of fraction 7 was also the major component of frac-

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(9) Sodium salts of perfluorocarboxylic acids undergo thermal decomposition at 165–270° (to give perfluoro olefins). *Cf.* M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan Co., New York, N. Y., 1961, p. 270 ff.

(10) A tempting explanation for the formation of homologous nitrofluoro alkanes would be as follows. Combination of the fluoroalkyl radical produced by reaction 1 with the "ambidentate" radical NO_2 could give an unstable fluoroalkyl nitrite (reaction 2a). Homolytic dissociation[11] of this nitrite would give a fluoroalkoxy radical (reaction 3).

$$H(CF_2)_5CF_2\cdot + NO_2 \longrightarrow H(CF_2)_5CF_2ONO \qquad (2a)$$

$$H(CF_2)_5CF_2ONO \longrightarrow H(CF_2)_5CF_2O\cdot + NO \qquad (3)$$

$$H(CF_2)_5CF_2O\cdot \longrightarrow H(CF_2)_4CF_2\cdot + CF_2O \qquad (4)$$

$$H(CF_2)_4CF_2\cdot + NO_2 \longrightarrow H(CF_2)_4CF_2NO_2 \qquad (5)$$

$$H(CF_2)_4CF_2\cdot + NO_2 \longrightarrow H(CF_2)_4CF_2ONO \qquad (5a)$$

Haszeldine and Francis[12] have shown that such radicals, produced by photolysis of a fluoroalkyl iodide in the presence of oxygen, decompose by loss of carbonyl fluoride and formation of a fluorocarbon radical containing one less CF_2 group (reaction 4). This new radical could then undergo a similar cycle of reactions (5 and 5a) yielding a homologous 1-nitrofluoroalkane and, by way of the nitrite, more carbonyl fluoride, etc.

As reasonable as this reaction sequence may appear, it must at present be discounted on the basis of the fact that infrared and mass spectroscopic analysis of the gaseous products from the reaction of $H(CF_2)_6CO_2H$ and NO_2 at 160° for 6 hr. failed to detect the presence of even traces of COF_2. The major gaseous reaction product was instead carbon dioxide, accompanied by traces of several fluoro olefins. In another experiment it was shown that COF_2 is recovered unchanged after 8 hr. at 160° in the presence of a large excess of nitrogen dioxide. We are indebted to two referees who suggested that the validity of the reaction mechanism represented by equations 2a through 5a may be tested by analysis for carbonyl fluoride.

(11) For a summary of recent literature on pyrolysis of nitrites, *cf.* P. Gray, P. Rathbone, and A. Williams, *J. Chem. Soc.*, 3932 (1960), and A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 48 (1962).

(12) R. N. Haszeldine and W. C. Francis, *J. Chem. Soc.*, 2125 (1955).

(13) Boiling points are uncorrected.

(14) R. M. Scribner, U. S. Patent 3,057,931 (1962).

(15) R. G. Nester, U. S. Patent 2,712,520.

(16) Gas chromatographic analyses were carried out on a column packed with Dow Corning DC-200 silicon oil (30 parts) on powdered firebrick (70 parts) and operated at 140°.

tions 5 (63%) and 4 (60%). Fraction 2 was composed of about 80% of another component. Infrared analysis of all the fractions showed strong bands characteristic of nitro groups (6.15–6.18 and 7.50 μ). That none of the 4–5 components was an olefin or nitrite ester was demonstrated by the fact that the gas chromatogram of fraction 5 was not changed either qualitatively or quantitatively by prolonged (24 hr.) shaking with aqueous potassium permanganate or concentrated sulfuric acid.

Reactions in a Hot Tube.—Passage of excess nitric oxide (2.5 ml./sec.) and 5*H*-octafluoropentanoic acid through a quartz-packed tube (described in ref. 1) at temperatures from 200–390° gave, at lower temperatures, mainly gaseous degradation products boiling below 0°. From 7*H*-dodecafluoroheptanoic acid and excess nitric oxide at 360°, a trace of $H(CF_2)_4CF{=}CF_2$ was isolated.

When 7*H*-dodecafluoroheptanoic acid and a nitric oxide–air mixture[1] were passed through a reaction tube packed with quartz-chips and heated at 350°, there was obtained a 10% yield of 6*H*-1-nitrododecafluorohexane. The infrared absorption spectrum and g.c. retention time of this compound were essentially identical with those observed for the same nitrofluoro alkane obtained by synthesis in an autoclave.

Autoxidation of 2-Alkenyldioxolanes and 2-Alkenyl-1,3-dioxanes

C. K. IKEDA,[1] R. A. BRAUN, AND B. E. SORENSON

Marshall Laboratory, Fabrics and Finishes Department, E. I. du Pont de Nemours and Company, Philadelphia 46, Pennsylvania

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Eleven 2-alkenyldioxolanes and two 2-alkenyl-1,3-dioxanes were autoxidized under different conditions. Terminal products, such as peroxides, hydroperoxides, spirocyclic peroxides, α,β-unsaturated esters, and polymers, were isolated and identified. A mechanism which accounts for these products is presented.[2]

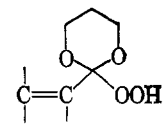
This paper describes the autoxidation of 2-alkenyldioxolanes and 2-alkenyl-1,3-dioxanes. While the literature on the autoxidation of hydrocarbons is voluminous[3–5] little has been reported on the autoxidation of acetals. Criegee[6] and Lederer oxidized 2-methyldioxolane with molecular oxygen and isolated di(2-methyldioxolan-2-yl) peroxide. Rieche, *et al.*,[7] autoxidized 2-phenyldioxolane and obtained 2-hydroperoxy-2-phenyldioxolane. No work on the autoxidation of 2-alkenyl-1,3-cyclic acetals has been reported in the literature.

We wish to report our findings on the autoxidation of a number of 2-alkenyl-1,3-cyclic acetals. The cyclic acetals (Table I) were autoxidized with (1) oxygen alone, (2) oxygen + a trace of Co(II), and (3) oxygen + a trace of *p*-toluenesulfonic acid. Five types of products were isolated and identified (a–e, col. 2).

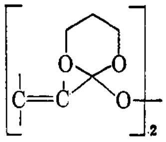
The principal product or products obtained from autoxidation of the cyclic acetals of Table I are summarized in Table II. Oxidations conducted in the absence of additives gave either hydroperoxides or spirocyclic peroxides. In the presence of Co(II) the products were generally α,β-unsaturated ester and polymer; in a few cases spirocyclic peroxide was the main product. Two oxidations conducted in the presence of *p*-toluenesulfonic acid also gave spirocyclic peroxides.

Thus, oxidation of 2-vinyl-4-methyldioxolane (I) in the absence of additives gave 2-hydroperoxy-2-vinyl-4-methyl dioxolane (XIV) and di(2-vinyl-4-methyldioxolan-2-yl) peroxide (XV). When the oxidation was conducted in the presence of a catalytic amount of cobaltous ion the products were 2-hydroxypropyl acrylate (XXV) and polymer XXVI.[8] Oxidation of I in the presence of toluenesulfonic acid gave the spirocyclic peroxide, 2-methyl-1,4,6,7-tetraoxaspiro-[4.4]nonane (XXXV), as the major product.

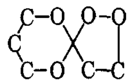
(a) Hydroperoxide



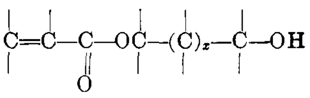
(b) Peroxide



(c) Spirocyclic peroxide

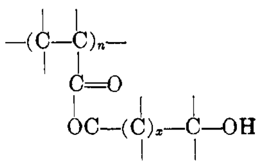


(d) α,β-Unsaturated esters



$$\mathrm{C{=}C{-}C({=}O){-}OC{-}(C)_x{-}C{-}OH}$$

(e) Complex polymers of α,β-unsaturated esters (where x = 0 or 1)



The reaction scheme (see eq. 1–5) accounts for the formation of the observed products in the case of 2-vinyl-4-methyldioxolane (I) (p. 287).

Reactions 2, 3, and 4 of this scheme comprise the free-radical sequence accounting for the formation of the hydroperoxide (XIV). Coupling reactions 5 and 6

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(1) To whom any correspondence should be addressed.

(2) E. J. Burrell, Radiation Physics Laboratory, Engineering Department, E. I. du Pont de Nemours and Co., Wilmington, Del., has examined the kinetics and has measured the absolute reaction rate constants for every significant step for the cobalt-catalyzed autoxidation of 2-vinyl-4(4-hydroxybutyl)dioxolane using pulse radiolysis. His work is summarized in another paper which has been submitted to the *Journal of Chemical Physics*.

(3) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(4) W. A. Waters, *Progr. Org. Chem.*, **5**, 1 (1961).

(5) F. R. Mayo, *Ind. Eng. Chem.*, **52**, 614 (1960).

(6) R. Criegee, "Methoden der Organische Chemie," Vol. III, 4th Ed., Georg Thieme Verlag, Stuttgart, 1952, p. 23.

(7) A. Rieche, E. Schmitz, and E. Beyer, *Ber.*, **91**, 1935 (1958).

(8) Fractionation of polymer XXVI by gradient elution through acid-washed alumina with benzene, ether, and finally ethanol gave five fractions with molecular weights ranging from 530 to 1050. The structure of the polymer is much more complex than one would suspect from the infrared spectra of the fractions which were all substantially the same as poly(2-hydroxypropyl acrylate). Elemental analyses (C, H, and O) and functional group determinations (OH and ester equivalent), although close, do not correspond to the values for poly(2-hydroxypropyl acrylate). The presence of such groups as hydroperoxy, peroxy, and dioxolanyl in the various fractions were demonstrated by qualitative tests.