Fluorocarbon Nitro Alcohols and α-Hydroxycarboxylic Acids. The Reaction of Dinitrogen Tetroxide with 2*H*-Polyfluoro-1-alkenes

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Fluoroölefins possessing the structure $—CF_2CH{=}CF_2$ have been found to undergo reaction with dinitrogen tetroxide with formation (after hydrolysis) of the novel nitro alcohols $—CF_2CHOHCF_2NO_2$ and α-hydroxycarboxylic acids $—CF_2CHOHCOOH$. From $C_3F_7CH{=}CF_2$ and $C_3F_7CH_2CF_2CH{=}CF_2$ there were obtained $C_3F_7CHOHCF_2NO_2$ plus $C_3F_7CHOHCOOH$ and $C_3F_7CH_2CF_2CHOHCF_2NO_2$ plus $C_3F_7CH_2CF_2CHOHCOOH$, respectively. From 2*H*-pentafluoropropene there was obtained 2*H*-pentafluoro-1-nitro-2-propanol (which formed a stable addition compound with ethyl ether, $3CF_3CHOHCF_2NO_2{\cdot}C_2H_5OC_2H_5$) as well as trifluorolactic acid.

The addition of dinitrogen tetroxide to hydrocarbon olefins which usually yields *vic* dinitroalkanes, nitronitrites (often hydrolyzed to nitro alcohols), and nitronitrates has been well investigated.[1,2]

The addition of dinitrogen tetroxide to the perhaloolefins has been reported to produce the dinitro adduct with tetrachloroethylene,[3,4] tetrabromoethylene,[3] tetrafluoroethylene,[5–8a,9] chlorotrifluoroethylene,[5,7,9] dichlorodifluoroethylene,[5,7] and hexafluoropropene.[8a] Bissel[9] also reported the production of 1-chloro-2-nitrotrifluoroethyl nitrite from chlorotrifluoroethylene, while Knunyants[8a] reported the formation of nitronitrites of the perfluoro-olefins, tetrafluoroethylene, hexafluoropropene, and octafluoroisobutylene, which on hydrolysis gave the nitrocarboxylic acid NO_2CF_2COOH, $CF_3CF(NO_2)COOH$, and $(CF_3)_2C(NO_2)COOH$, respectively. Due to the hydrolytic instability of $—CFOH$[8b] or $—CF_2OH$ groups, nitro alcohols are not obtained in these reactions.

The ready availability of highly fluorinated olefins of the type $R_fCH{=}CF_2$ and $R_f(CH_2CF_2)_nCH{=}CF_2$,[10] where R_f = perfluoroalkyl, prompted us to study the reaction of these olefins with dinitrogen tetroxide in the hope of synthesizing fluorocarbon nitro alcohols, a new class of compounds.[11] It was indeed of much interest to find that the major product of the reaction (after hydrolysis) was the desired nitro alcohol and that the principal byproduct was the novel fluorocarbon α-hydroxy acids.

Thus, terminal olefins of the structure $R_fCH{=}CF_2$, where R_f = CF_3, C_3F_7, or $C_3F_7CH_2CF_2$, have reacted with dinitrogen tetroxide[12] at temperatures of about 100° and in the presence of a halogenated solvent to produce N_2O_4 addition products that on hydrolysis yield the nitro alcohol $R_fCH_2OHCF_2NO_2$, derived from the nitronitrite,[13] $R_fCHONOCF_2NO_2$, and the α-hydroxy acid $R_fCHOHCOOH$, probably derived from the dinitrite, $R_fCHONOCF_2ONO$[13,14] and its unstable hydrolysis intermediate, *i.e.*, $R_fCHOHCF_2OH \xrightarrow{-HF} R_fCHOHCOF \xrightarrow{H_2O} R_fCHOHCOOH$.

In contrast to nitro alcohols possessing the $—CHOHCH_2NO_2$ group, the fluorocarbon nitro alcohols such as $C_3F_7CHOHCF_2NO_2$ are stable to both strong acid and base. Thus, 2*H*-nonafluoro-1-nitro-2-pentanol was stable to boiling concentrated sulfuric acid and hot 20% potassium hydroxide solution. These properties unequivocally eliminated the remote possibility that the structure had a nitrite group in place of the nitro group. The presence of a nitrite group was also ruled out by the infrared and ultraviolet spectra (see below). Incidentally, the intermediate nitronitrite could not have been the isomer resulting from reverse addition, *i.e.*, $R_fCHNO_2CF_2ONO$, because the nitro alcohol and not the nitro acid, *i.e.*, $R_fCHNO_2CF_2OH \rightarrow R_fCHNO_2COF \rightarrow R_fCHNO_2COOH$, was the hydrolysis product isolated.

The infrared spectrum of $C_3F_7CHOHCF_2NO_2$ showed OH stretching absorption at 2.88 μ and had bands at 6.25 and 7.42 μ, corresponding to the asymmetric and symmetric NO_2 stretching vibrations for a $—CF_2NO_2$ group. The ultraviolet spectrum showed the characteristic nitro absorption at 283 mμ.[15,16] The spectra of nitrites, *e.g.*, 2,2,2-trifluoroethyl nitrite, shows a strong band at 221 mμ and multiple weak absorption bands in the 315–380-mμ region of the ultraviolet and at 5.8 μ in the infrared.[15] On the other hand, the compound $ICH_2CF_2NO_2$ shows bands at 6.28 and 7.40 μ corresponding to the asymmetric and symmetric NO_2 stretching absorptions, while the isomer $ICF_2CH_2NO_2$ has corresponding peaks at 6.37 and 7.31 μ[16]; $CF_3CH_2NO_2$

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[1] H. Schechter and F. Conrad, *J. Am. Chem. Soc.*, **75**, 5610 (1953), and references therein.

[2] H. Schechter, J. J. Gardikes, and A. H. Pagono, *ibid.*, **81**, 5420 (1959), and references therein.

[3] H. Blitz, *Ber.*, **35**, 1528 (1902).

[4] W. L. Argo, E. M. James, and J. L. Donnelly, *J. Phys. Chem.*, **23**, 578 (1919).

[5] H. B. Haas and A. C. Whitaker, U.S. Patent 2,447,504.

[6] D. D. Coffman, M. S. Raasch, G. W. Ribgy, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949).

[7] R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953).

[8] (a) I. L. Knunyants and A. V. Fokin, *Dokl. Akad. Nauk SSSR*, **111**, 1035 (1956); **112**, 67 (1957); (b) The first example of a perfluorinated α-fluoro alcohol, heptafluorocyclobutanol, reasonably stable in the absence of moisture, was reported by S. Andreades and D. C. England, *J. Am. Chem. Soc.*, **83**, 4670 (1961).

[9] E. R. Bissell, *J. Org. Chem.*, **26**, 5100 (1961).

[10] M. Hauptschein and R. E. Oesterling, *J. Am. Chem. Soc.*, **82**, 2868 (1960).

[11] D. J. Cook, O. R. Pierce, and E. T. McBee, *ibid.*, **76**, 83 (1954), prepared the first (and only) examples of aliphatic fluorine-containing nitro alcohols by condensation of nitroalkanes with fluoral and heptafluorobutyral hydrates. These compounds, *e.g.*, $C_3H_7CHOHCH_2NO_2$ and $C_3F_7CHOHCH(C_2H_5)NO_2$, contain hydrocarbon moieties alpha to the nitro group.

[12] Dinitrogen tetroxide is, of course, an equilibrium mixture with other nitrogen oxides, particularly nitrogen dioxide. The composition is dependent on temperature with the monomolecular form predominating at higher temperatures; J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

[13] It should be understood that, due to the oxidative reaction conditions, the intermediates could also be nitronitrates and dinitrates, respectively.

[14] It is of interest to note that J. L. Reibsomer, *Chem. Rev.*, **36**, 197 (1945), indicated that there had been no instance in which it was shown clearly that the dinitrite is a product of the reaction of an olefin with dinitrogen tetroxide. On the other hand, a usual product, the dinitroalkane was not isolated from the present reactions, although the lack of a quantitative accounting of products does not preclude the possibility that some dinitro compounds were formed.

[15] R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); R. N. Haszeldine and B. J. H. Mattinson, *ibid.*, 4172 (1955).

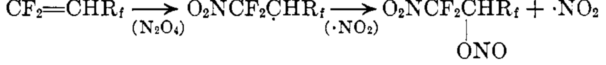
[16] M. Hauptschein, R. E. Oesterling, M. Braid, E. A. Tyczkowski, and D. M. Gardner, *J. Org. Chem.*, **28**, 1281 (1963). Also, M. Hauptschein and R. E. Oesterling, unpublished work.

has corresponding bands at 6.34 and 7.33 μ[16] (all infrared spectra are of liquid phase). Thus, all of the spectral data support the formulation of a $—CF_2NO_2$ compounds as distinct from any isomeric nitrite.

The nitro alcohols were also characterized as either the N-phenyl carbamate or the cyanurate. The compound tris(2*H*, 4*H*, 4*H*-undecafluoro-1-nitro-2-heptyl) cyanurate did not decompose at temperatures up to 340°.

2*H*-Pentafluoro-1-nitro-2-propanol was isolated as the stable etherate, $3CF_3CHOHCF_2NO_2 \cdot C_2H_5OC_2H_5$. This nitro alcohol, like the perfluoro fatty acids,[17] is sufficiently acidic to form stable addition compounds with ethers in other than 1:1 molar ratios.

The formation of the nitronitrite addition compound probably proceeds by a homolytic process[2] involving attack of nitrogen dioxide (or dinitrogen tetroxide) at the terminal olefin carbon to form a nitroalkyl radical, which then chain transfers (homolytic exchange) with dinitrogen tetroxide or couples with a nitrogen dioxide radical.



$$CF_2{=}CHR_f \xrightarrow[(N_2O_4)]{\cdot NO_2} O_2NCF_2\dot{C}HR_f \xrightarrow[(\cdot NO_2)]{(N_2O_4)} O_2NCF_2\underset{\displaystyle ONO}{\underset{|}{C}}HR_f + \cdot NO_2$$

If the above mechanism is correct, we have in this case an example where the direction of attack of a $\cdot NO_2$ radical is opposite to that of a $CF_3\cdot$ radical.[18,19]

Experimental

Reaction of 2-*H*-Nonafluoro-1-pentene with Dinitrogen Tetroxide.—A 46.4-g. portion (0.2 mole) of 2*H*-nonafluoro-1-pentene[10] was added to 100 ml. of 1,1,2-trichlorotrifluoroethane and the resulting solution was cooled to 0°. Into this solution there was condensed 27.6 g. (0.3 mole) of dinitrogen tetroxide and the mixture then was dried over phosphorus pentoxide at 0° for 2 to 3 hr. The solution was filtered into a 300-ml. stainless steel autoclave chilled to −10°, which then was sealed and heated at 100° for 16 hr. with agitation. The autoclave was cooled in an ice bath and the contents transferred to a 200-ml. Vigreux still. The excess dinitrogen tetroxide and trichlorotrifluoroethane solvent was distilled from the product leaving 40 g. of a yellow oil.

This crude product was stirred with 200 ml. of water and then with excess sodium carbonate. An immiscible pale yellow oil was separated, and the water layer was extracted twice with 40-ml. portions of ether. The ether extracts were combined with the separated oil, dried over anhydrous magnesium sulfate, and subsequently evaporated to provide 24 g. (40%) of 2*H*-nonafluoro-1-nitro-2-pentanol, $CF_3CF_2CF_2CHOHCF_2NO_2$. Distillation gave the pure nitro alcohol, b.p. 62° (44 mm.), $n^{25}D$ 1.3240.

Anal. Calcd. for $C_5F_9H_2NO_3$: C, 20.35; H, 0.68; N, 4.75. Found: C, 20.56; H, 0.86; N, 4.99.

The infrared spectrum of the liquid showed the typical asymmetric and symmetric NO_2 stretching vibrations in compounds containing the $-CF_2NO_2$ group[15,16] at 6.25 and 7.42 μ, respectively. A typical hydroxyl absorption band was present at 2.88 μ. The ultraviolet spectrum in 95% ethanol showed the expected maximum at 283 mμ.[15,16]

The N-phenyl carbamate derivative of 2*H*-nonafluoro-1-nitro-2-pentanol was prepared by refluxing for 30 min. 6 g. of the nitro alcohol dissolved in 20 ml. of carbon tetrachloride with 3.6 g. of phenyl isocyanate together with 3 drops of triethylamine. On cooling, a heavy precipitate was formed, which after filtering and drying yielded 6.8 g. of a pale yellow solid. Recrystallization from a benzene–light petroleum ether solvent gave colorless needles of pure 2*H*-nonafluoro-1-nitro-2-amyl carbanilate, $C_3F_7CH(O_2CNHC_6H_5)CF_2NO_2$, m.p. 88–89°.

Anal. Calcd. for $C_{12}F_9H_7N_2O_4$: C, 34.79; H, 1.70; N, 6.76. Found: C, 34.65; H, 2.17; N, 6.57.

The alkaline (sodium carbonate) aqueous layer remaining after ether extraction of the nitro alcohol in the original reaction was acidified with dilute hydrochloric acid and extracted three times with 40-ml. portions of diethyl ether. The ether extract was dried over anhydrous magnesium sulfate and evaporated to give 10 g. (20% yield) of a pale yellow oil which crystallized on standing overnight. Recrystallization from a benzene–light petroleum ether solvent gave colorless needles of pure 2*H*-pentafluoro-2-hydroxypentanoic acid, $CF_3CF_2CF_2CHOHCOOH$, m.p. 68–69°, the infrared spectrum of which showed the characteristic—OH and —COOH absorptions at 2.9 and 5.8 μ, respectively.

Anal. Calcd. for $C_5F_7H_3O_3$: C, 24.60; H, 1.24; F, 54.49; neut. equiv., 244. Found: C, 24.38, 24.44; H, 1.43, 1.65; F, 54.90, 54.87; neut. equiv., 241, 246, 246.

Reaction of 2*H*,4*H*,4*H*-Undecafluoro-1-heptene with Dinitrogen Tetroxide.—A 50-g. portion (0.17 mole) of 2*H*,4*H*,4*H*-undecafluoro-1-heptene[10] was allowed to react with 23 g. (0.25 mole) of dinitrogen tetroxide in 100 ml. of trichlorotrifluoroethane at 100° for 15 hr. according to the previous procedure. There was obtained 61 g. of a crude liquid product that after hydrolysis in aqueous sodium carbonate gave 35 g. (58%) of the water insoluble nitro alcohol. Distillation gave the pure colorless oil, 2*H*,4*H*,4*H*-undecafluoro-1-nitro-2-heptanol, $CF_3CF_2CF_2CH_2CF_2CHOHCF_2NO_2$, b.p. 72° (4 mm.), $n^{25}D$ 1.3347.

Anal. Calcd. for $C_7F_{11}H_4NO_3$: C, 23.41; H, 1.12; N, 3.90. Found: C, 23.79; H, 1.20; N, 3.86.

The infrared spectrum of the liquid showed the typical asymmetric and symmetric NO_2 stretching vibrations in compounds containing the $—CF_2NO_2$ group at 6.25 and 7.39 μ, respectively; an —OH band was at 2.86 μ. The ultraviolet spectrum in 95% ethanol showed a maximum at 284 mμ.

The aqueous alkaline layer from the above reaction was acidified with dilute hydrochloric acid and extracted with diethyl ether to give 10 g. (19%) of a pale yellow oil which crystallized on standing. Recrystallization from benzene–light petroleum ether gave colorless needles of pure 2*H*,4*H*,4*H*-nonafluoro-2-hydroxyheptanoic acid, $C_3F_7CH_2CF_2CHOHCOOH$, m.p. 82–83°, the infrared spectrum of which showed the characteristic —OH and —COOH absorptions at 2.88 and 5.8 μ, respectively.

Anal. Calcd. for $C_7F_9H_5O_3$: C, 27.28; H, 1.63. Found: C, 27.00; H, 1.69.

Reaction of 2*H*,4*H*,4*H*-Undecafluoro-1-nitro-2-heptanol with Cyanuric Chloride.—A 7.2-g. sample of $C_3F_7CH_2CF_2CHOHCF_2NO_2$ was converted to the sodium salt by treating with 0.6 g. of sodium hydride in 40 ml. of anhydrous diethyl ether. There was then added slowly 1.1 g. of cyanuric chloride (heat of reaction caused ether to reflux) and the mixture was then stirred for 1 hr. at room temperature. The reaction mixture was poured into an ice slush and the ether layer was separated, dried, and evaporated to give 7.5 g. of a dense yellow oil. Distillation *in vacuo* gave a pale yellow viscous oil, b.p. 175–185° (0.1 mm.). The infrared spectrum of the liquid is consistent with a tris(polyfluoronitroalkyl)cyanurate having bands at 5.77, 6.05 sh, 6.20, 6.30 sh, 6.77, 6.99 sh, 7.18, and 12.24 μ; *cf.*, tris-2,2,2-trifluoroethyl cyanurate (Nujol mull) bands at 5.82, 6.27, 6.36, 6.86, 7.01, 7.19, and 12.41 μ.[16]

These bands are generally associated with a triazine ring structure.[20] The strongest of these absorptions in the nitro-cyanurate derivative is at 6.2 μ enhanced, of course, by the intense NO_2 asymmetric stretching vibration. The spectrum of the nitroalkyl cyanurate showed no —OH absorption, as expected.

Anal. Calcd. for $C_{24}F_{33}H_9N_6O_9$: N, 7.29. Found: N, 7.27.

Reaction of 2*H*-Pentafluoropropene with Dinitrogen Tetroxide.—To a solution of 27.6 g. (0.3 mole) of dinitrogen tetroxide in 100 ml. of $CF_2ClCFCl_2$ in a 300-ml. stainless steel autoclave was added by vacuum transfer 26.4 g. (0.2 mole) of 2*H*-pentafluoropropene.[10,21] After heating at 90–100° for 1/ hr. while

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(17) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 5139 (1951).

(18) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3005 (1955). These authors noted, however, that the HBr adduct had the structure $CF_3CH_2CF_2Br$, representing attack of a Br· on the CF_2 group if the mechanism was free radical, which their experimental evidence suggested. They preferred to leave open the issue as to whether a bromine atom behaves differently from a trifluoromethyl radical in that instance.

(19) Although not isolated the formation of small amounts of R_fCHNO_2COOH by hydrolysis of $R_fCHNO_2CF_2ONO$ (which represents attack of $\cdot NO_2$ on the CH group) is not unequivocally eliminated.

(20) W. M. Padgett, II, and W. F. Hamner, *J. Am. Chem. Soc.*, **80**, 803 (1958).

(21) A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

shaking, the autoclave was cooled to room temperature; upon venting 2.5 g. of unchanged olefin was collected. The liquid product from the autoclave was stirred with 100 ml. of water and then made slightly alkaline with sodium bicarbonate. The water insoluble layer was separated, dried, and the solvent was removed by evaporation. The water layer was extracted three times with diethyl ether; the ether extract was dried and the ether removed by evaporation. The pale yellow oil residues were combined to provide 16 g. of a product that was vacuum distilled to give a colorless liquid, the constant boiling etherate of the nitro alcohol, $3CF_3CHOHCF_2NO_2 \cdot C_2H_5OC_2H_5$, b.p. 70° (100 mm.), $n^{29}D$ 1.335.

Anal. Calcd. for $C_{13}F_{15}H_{16}N_3O_{10}$: C, 23.7; H, 2.44; F, 43.2; N, 6.37; ethoxyl, 6.84. Found: C, 24.4; H, 2.78; F, 43.0; N, 6.35; ethoxyl, 6.92.

The infrared spectrum of this etherate showed strong bonded —OH in the 3-μ region, and a strong asymmetrical and symmetrical NO_2 stretching band at 6.25 and 7.33 μ, respectively.

The N-phenyl carbamate derivative of 2*H*-pentafluoro-1-nitro-2-propanol was prepared by treating the etherate of this nitro alcohol with an equimolar amount of freshly distilled phenyl isocyanate and a small amount of triethylamine as a catalyst. The reaction mixture was warmed for a few minutes on a steam bath and then cooled in ice to solidify the product. Recrystallization from petroleum ether gave $C_6H_5NHCO_2CH(CF_3)CF_2NO_2$, white needles, m.p. 88–89°.

Anal. Calcd. for $C_{10}F_5H_7N_2O_4$: C, 38.24; H, 2.25; N, 8.92. Found: C, 38.05; H, 2.27; N, 8.38.

The aqueous alkaline layer remaining after ether extraction of the nitro alcohol was acidified with dilute hydrochloric acid and extracted three times with diethyl ether. This ether extract was dried over magnesium sulfate and evaporated to give 15 g. of a base soluble oil consisting mainly of a hydrate of 3,3,3-trifluorolactic acid, $CF_3CHOHCOOH$, b.p. 57° (123 mm.)

Anal. Calcd. for $CF_3CHOHCOOH$: F, 39.6; neut. equiv., 144; calcd. for $CF_3CHOHCOOH \cdot H_2O$: F, 35.2; neut. equiv., 162. Found: F, 36.15; neut. equiv., 154.

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The Reaction of 1,1-Difluoroethylene with Mixtures of Dinitrogen Tetroxide and Iodine. Difluoroiodonitroethanes and 1,1-Difluoro-1-alkoxynitroethanes

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The reaction of 1,1-difluoroethylene with a mixture of dinitrogen tetroxide and iodine has been found to give the two novel isomeric adducts, 1,1-difluoro-1-iodo-2-nitroethane (predominantly) and 1,1-difluoro-2-iodo-1-nitroethane. The unusual facile reaction of the former isomer with alkanols to yield the novel fluoronitro ethers $ROCF_2CH_2NO_2$, where R = CH_3- or CH_3CH_2-, is described. 1,1,1-Trifluoro-2-nitroethane was produced in good yield by the reaction of anhydrous sodium fluoride in tetramethylene sulfone with 1,1-difluoro-1-iodo-2-nitroethane.

The reaction of olefins with mixtures of dinitrogen tetroxide and iodine has been reported to produce either β-iodoalkyl nitrates or β-nitroalkyl iodides, depending on the olefin used and on the reaction conditions.[1–3]

As part of our studies on the chemistry of the olefin 1,1-difluoroethylene,[4,5] we wished to investigate the synthesis and reactivity of the nitroiodides of 1,1-difluoroethylene. Of the theoretically possible adducts, $ICF_2CH_2NO_2$, $ICH_2CF_2NO_2$, ICH_2CF_2ONO (ICH_2COOH after hydrolysis), and ICF_2CH_2ONO (ICF_2CH_2OH after hydrolysis), the first three were obtained from the reaction of a mixture of dinitrogen tetroxide and excess iodine with 1,1-difluoroethylene using methylene chloride as the solvent.

The predominant nitroiodide isomer produced was 1,1-difluoro-1-iodo-2-nitroethane, whether the olefin was added to a mixture of dinitrogen tetroxide and iodine or whether dinitrogen tetroxide was added slowly to the other reactants. The latter procedure minimized the formation of iodonitrite (or iodonitrate), which after hydrolysis gave iodoacetic acid, *i.e.*, $ICH_2CF_2ONO \rightarrow [ICH_2CF_2OH] \rightarrow ICH_2COOH$. The mechanism of formation of the nitroiodides probably

$$N_2O_4 \rightleftharpoons 2NO_2\cdot$$

$$\begin{tikzcd} \cdot NO_2 + CH_2{=}CF_2 \arrow[r] & NO_2CH_2CF_2\cdot \arrow[d, "I_2"] & + & NO_2CF_2CH_2\cdot \arrow[d, "I_2"] \\ & NO_2CH_2CF_2I + I\cdot & & NO_2CF_2CH_2I + I\cdot \end{tikzcd}$$

involves the trapping of an intermediate β-nitroalkyl radical with iodine.

The nitro radical preferentially, but not exclusively, attacked the CH_2 group of 1,1-difluoroethylene to give predominantly $ICF_2CH_2NO_2$. This finding is similar to the attack of a perfluoralkyl radical, *e.g.*, $C_3F_7\cdot$ from C_3F_7I, on 1,1-difluoroethylene, which gave 95% of $C_3F_7CH_2CF_2I$ and only 5% of $C_3F_7CF_2CH_2I$.[6]

The main isomer $ICF_2CH_2NO_2$ was found to react readily with dry sodium fluoride in tetramethylene sulfone to give a good yield of 1,1,1-trifluoro-2-nitroethane, $CF_3CH_2NO_2$, demonstrating that the iodine atom was attached to the —CF_2 group. The infrared and ultraviolet spectra of both of these compounds were consistent with the presence of a —CH_2NO_2 group (see Experimental) and with a —CF_2I group for the former, *i.e.*, λ_{max} at 270 mμ in the ultraviolet.

The isomer 1,1-difluoro-1-iodo-2-nitroethane is unstable in basic aqueous solution, and has been found

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(1) G. B. Bachman and T. J. Logan, *J. Org. Chem.*, **21**, 1467 (1956).

(2) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

(3) G. B. Bachman, T. J. Logan, K. R. Hill, and N. W. Standish, *J. Org. Chem.*, **25**, 1312 (1960).

(4) M. Hauptschein, A. H. Fainberg, and M. Braid, *ibid.*, **23**, 322 (1958).

(5) M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Am. Chem. Soc.*, **80**, 846 (1958).

(6) (a) M. Hauptschein and R. E. Oesterling, *ibid.*, **82**, 2868 (1960); (b) We favor this explanation for the principal mode of formation of the isomer 1,1-difluoro-2-iodo-1-nitroethane over alternative interpretations involving ionic species (*e.g.*, NO_2^-, I^+) or iodine atom attack.