Reactions of Perfluoroalkyl Nitriles. VI. Perfluoroacyl Imidates as Intermediates[1]

HENRY C. BROWN AND CHARLES R. WETZEL

The Department of Chemical Engineering and the Department of Chemistry, University of Florida, Gainesville, Florida

Received February 5, 1965

Alkyl perfluoroacyl imidates are useful intermediates for the formation of other fluorocarbon derivatives containing nitrogen. Methyl perfluoroacyl imidates produced perfluoroacyl amidines, amidoximes, or hydrazidines when allowed to react with ammonia, hydroxylamine, or hydrazine. Methyl perfluorobutyrimidate rearranged in the presence of boron trifluoride or phosphorus pentoxide to N-methyl perfluorobutyramide. 2-Perfluoroalkyl-Δ^2-oxazolines were prepared by cyclization of 2-chloroethyl perfluoroalkyl imidates; these perfluoroalkyl-substituted heterocyclesr earranged to N-vinylperfluoroalkylamides. 2-Perfluoroalkyl-Δ^2-imidazolines were prepared from ethylenediamine and methyl perfluoroacyl imidates. Evidence is presented for the formation of 2-perfluoroalkyl-Δ^2-imidazolin-4-ones.

The synthesis of perfluoroacyl imidates described in the previous paper[1b] has led to investigation of the use of these compounds as intermediates for synthesis of other fluorocarbon derivatives, particularly those containing nitrogen in the functional group or heterocyclic compounds having perfluoroalkyl substituents.

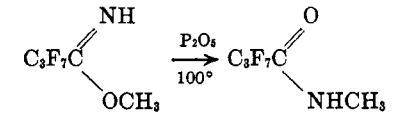
The formation of amidines from imidates is a simple illustration of a reaction which involves replacement of the alkoxy group of the imidate. Shriner and Neumann[2] have proposed a mechanism for this reaction similar to that suggested for the hydrolysis of esters. A similar reaction occurs between hydroxylamine and imidates to give amidoximes. Oberhummer[3] studied the reaction of aliphatic imidate hydrochlorides with anhydrous hydrazine and isolated products which arise from replacement of both imino and alkoxy groups; among these products were both heterocyclic and linear compounds.

Imidates have been used extensively in the preparation of many heterocyclic compounds, generally by the condensation of the imino and alkoxy groups of the imidate with another difunctional compound. For example, 2-imidazolines have been synthesized by heating 1,2-alkyldiamines with imidates[4]; similarly King and Acheson[5] have prepared benzimidazoles using *o*-phenylenediamine. Benzoxazoles[6] can be prepared by the condensation of *o*-aminophenol with imidates; β-hydroxy-N-alkylamines have been condensed with imidates to form 2-oxazolines.[7] Other heterocyclic systems which have been prepared using imidates include tetrazoles[8] and triazoles.[9]

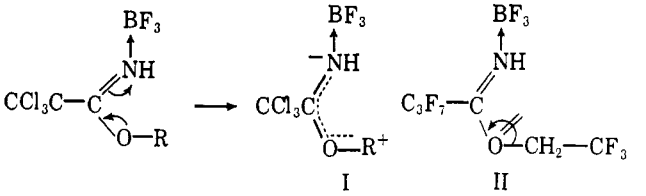
The instability of the perfluoroacyl imidate hydrochlorides, formed when hydrogen chloride was used as a catalyst for imidate preparation, was described in the previous paper.[1b] During the present study the hydrochloride of methyl perfluorobutyrimidate was prepared in the absence of a solvent and found to decompose relatively slowly. In one experiment decomposition required 8 hr. Although it would be desirable to be able to use the imidate hydrochlorides for the preparation of ortho esters, it was found that they decomposed immediately in the presence of alcohols. Thus, instability in polar solvents is a limitation on the usefulness of the hydrochlorides of perfluoroacyl imidates.

2,2,2-Trifluoroethyl perfluorobutyrimidate hydrochloride formed rapidly in diethyl ether but decomposed almost immediately. It is evident that the inductive effect of the trifluoroethyl group accelerated the decomposition as compared with the electron-releasing methyl group. Phenyl perfluorobutyrimidate did not form a stable hydrochloride; hydrogen chloride caused its decomposition and the formation of 2,4,6-tris(perfluoropropyl)-1,3,5-triazine.

Rearrangement of the alkyl perfluoroacyl imidates was promoted by Lewis acids. Phosphorus pentoxide caused the rearrangement of methyl perfluorobutyrimidate to N-methyl perfluorobutyramide at 100°.



Cramer[10] recently described the boron trifluoride catalyzed rearrangement of alkyl trichloroacetimidates to N-substituted amides. After a thorough study he proposed the reactive intermediate, I, which yielded



products that would result from both migration and elimination of the alkyl group; presumably, carbonium ion formation was involved.

Methyl perfluorobutyrimidate was found to rearrange readily to N-methylperfluorobutyramide on refluxing in benzene containing a catalytic amount of boron trifluoride etherate. The mechanism and intermediate proposed by Cramer seem applicable to this case. Additional evidence to support this mechanism was obtained from the reaction of trifluoroethyl perfluorobutyrimidate with boron trifluoride. A stable salt, II, was formed which did not rearrange, even on heating at 93° for 24 hr. The inductive effect of the

(1) (a) This investigation was supported by Public Health Service Research Grant CA-05083 from the National Cancer Institute. (b) For previous paper in this series, see H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3724 (1965).

(2) R. L. Shriner and F. W. Neuman, *Chem. Rev.*, **35**, 351 (1944).

(3) W. Oberhummer, *Monatsh. Chem.*, **63**, 285 (1933).

(4) R. J. Ferm and J. L. Riebsomer, *Chem. Rev.*, **54**, 593 (1954).

(5) F. E. King and R. M. Acheson, *J. Chem. Soc.*, 1396 (1949).

(6) H. L. Wheeler, *Am. Chem. J.*, **17**, 397 (1895).

(7) R. H. Wiley and L. L. Bennett, *Chem. Rev.*, **44**, 447 (1949).

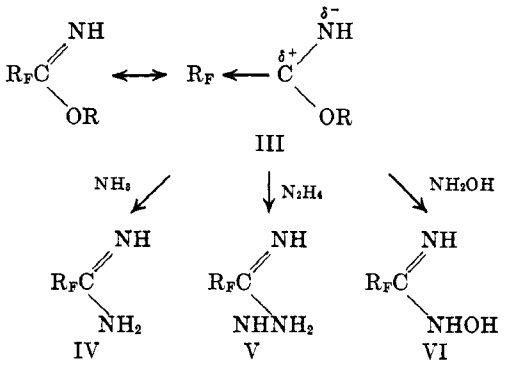
(8) C. Ainsworth, *J. Am. Chem. Soc.*, **75**, 5728 (1953).

(9) A. Pinner, *Ann.*, **298**, 1 (1897).

(10) F. Cramer and N. Hennrick, *Ber.*, **94**, 976 (1960).

trifluoroethyl group appears to prevent the electron displacement indicated in II, thus stabilizing the complex.

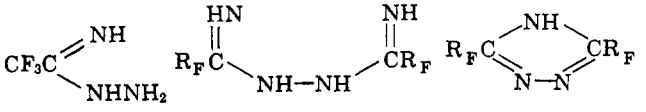
The alkyl perfluoroacyl imidates were readily attacked by nucleophilic reagents. Attack by nucleophiles or bases would be expected to occur at the electron-deficient carbon atom of structure III. Re-



placement of the imino group would not be expected, since, in order to break the strong double bond between the nitrogen atom and the electropositive carbon, the presence of a strong acid with the ability to protonate the nitrogen atom would be necessary. We have shown that most perfluoroacyl imidate acid salts are unstable.

The reactions of ammonia, hydroxylamine, and hydrazine with alkyl perfluoroacyl imidates were investigated. The expected products from these reactions would be the same as the addition products, previously studied in this laboratory, of these nitrogen bases to the perfluoroalkyl nitriles. Ammonia reacted readily with methyl perfluorobutyrimidate to give the corresponding amidine (IV) in good yield. Hydroxylamine, as the free base, reacted with methyl perfluorobutyrimidate to give the corresponding amidoxime (VI) in low yields. The perfluoroacyl imidates are inherently less reactive with nitrogen bases than the corresponding perfluoroalkyl nitriles; this factor and the low basicity of hydroxylamine may account for the lower yields of amidoxime.

Methyl perfluorobutyrimidate reacted with an equivalent amount of hydrazine and gave the corresponding perfluoroalkyl hydrazidine (V) in high yield. The reaction of methyl perfluoroacetimidate with hydrazine gave the unstable liquid perfluoroacethydrazidine (VII). This compound could not be isolated by

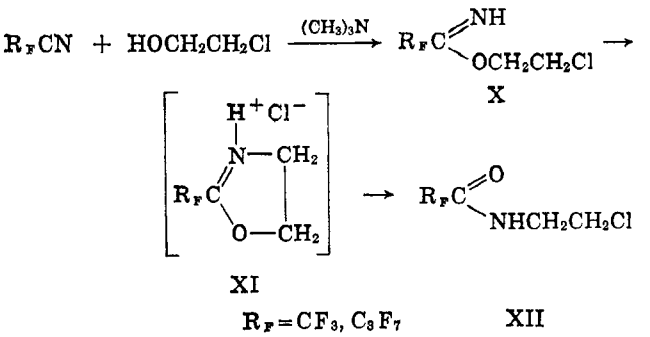


Brown and Pilipovich[11] in their study of the reaction of perfluoroacetonitrile with hydrazine. This previous work resulted in the isolation of a product assigned the 2,5-bis(perfluoromethyl)-4-N-amino-1,2,4,4-H-triazole structure. The present work produced an identical product by the reaction of perfluoroacethydrazidine with perfluoroacetonitrile; the reaction was apparently a simple addition to produce the structure VIIIa, N^2-(perfluoroacetimidoyl)perfluoroacethydrazidine. This structure was confirmed by its deammonation with anhydrous hydrogen chloride to 3,5-bis-(perfluoromethyl)-1,2,4-H-triazole (IXa), identical with an authentic sample.[12] The original assignment[11] of the N-aminotriazole structure was therefore incorrect. N^2-(Perfluoroacylimidoyl)perfluoroalkyl hydrazidines, VIII, were also prepared directly from the corresponding imidates by increasing the temperature of the reactions.

It is interesting to compare the simplicity of the reactions of perfluoroacylimidates with the complexities and multitudes of reaction products obtained from the reaction of nonfluorinated aliphatic imidates with hydrazine as described in the literature. The difference appears to be due to the resistance to replacement of the imino group in the perfluoroacylimidates.

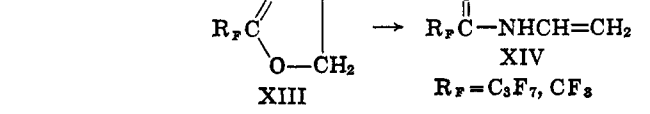
The first method chosen for synthesis of the 2-perfluoroalkyl-Δ^2-oxazolines followed the work of Gabriel and Neuman[13] who synthesized 2-oxazolines in fair yields by treating imidate salts derived from β-chloro alcohols with ethereal or alcoholic ammonia solutions.

2-Chloroethyl perfluoroacyl imidates X were prepared from 2-chloroethyl alcohol and perfluoroalkyl nitriles using trimethylamine as a catalyst. These



imidates were found to be unstable and rearranged slowly at room temperature (and rapidly above 90°) to the corresponding N-(2-chloroethyl)perfluoroalkyl amides (XII). 2-Perfluoropropyl-Δ^2-oxazoline hydrochloride (XI), shown as the probable intermediate, was isolated in small amounts from 2-chloroethyl perfluorobutyrimidate kept at room temperature. The cyclization of these imidates by the use of sodium carbonate or potassium hydroxide was not successful.

The 2-perfluoroalkyl-Δ^2-oxazolines were successfully prepared directly from the reaction of perfluoroalkyl nitriles with 2-chloroethyl alcohol in the presence of excess trimethylamine. The reaction involved the *in situ* formation of the imidate X and its cyclization in the presence of trimethylamine to the oxazoline XIII on heating. Control of reaction conditions was



critical in achieving yields of 60–70%, since the perfluoroalkyl-substituted 2-oxazolines were only slightly more stable than the imidates from which they were

(11) H. C. Brown and D. Pilipovich, *J. Am. Chem. Soc.*, **82**, 4700 (1960).

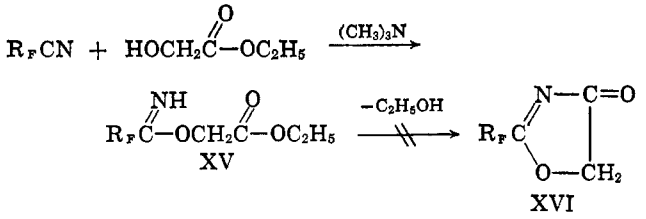
(12) H. C. Brown and M. T. Cheng, *J. Org. Chem.*, **27**, 3240 (1962).

(13) S. Gabriel and A. Neuman, *Ber.*, **25**, 2383 (1892).

prepared. 2-Perfluoropropyl-Δ^2-oxazoline was converted rapidly to N-vinylperfluorobutyramide (XIV) at its boiling point (131°) at atmospheric pressure but was sufficiently stable to be purified by fractionation at reduced pressure. 2-Perfluoromethyl-Δ^2-oxazoline rearranged completely within 3 weeks at room temperature to the corresponding vinyl amide.

The infrared spectra of the 2-perfluoroalkyl-Δ^2-oxazolines, which may be considered cyclic imidates, exhibited the typically strong C=N absorption at 5.97 μ. The infrared spectra of N-vinylperfluorobutyramide was examined as a mull in Halocarbon Oil 13–21 and also in solution in carbon tetrachloride. The solution showed N–H stretching at 2.88 μ (w); this band shifted to 3.00 μ in the solid state. C–H stretching appeared at 3.3–3.4 μ (vw) in solution; this feature was well defined in the mull at 3.22 (w), 3.37 (w), and 3.49 (vw) μ. C=O stretching produced a single band at 5.73 μ (s) in solution; in the solid state this was split into a triplet at 5.75 (s), 5.80 (s), and 5.88 (s) μ. A band at 6.50 (s) μ with a shoulder at 6.40 (m) for the solution was not assigned; this band appeared as a well-defined doublet in the solid at 6.40 (s) and 6.47 (s) μ. One might be tempted to assign this doublet to C=C stretching, shifted to longer wave lengths by p–π conjugation with N–H or conjugation with the tautomeric structure, $R_FC(OH)=N-CH=CH_2$. Strong absorption also appeared at 6.93 (solution) and 6.94 μ (solid).

An attempt was made to prepare 2-perfluoroalkyl-Δ^2-oxazolin-4-ones by preparation of the α-(carbethoxy)methyl perfluoroacyl imidates XV with subsequent intramolecular condensation and elimination of ethyl alcohol. The intermediate imidates XV were stable

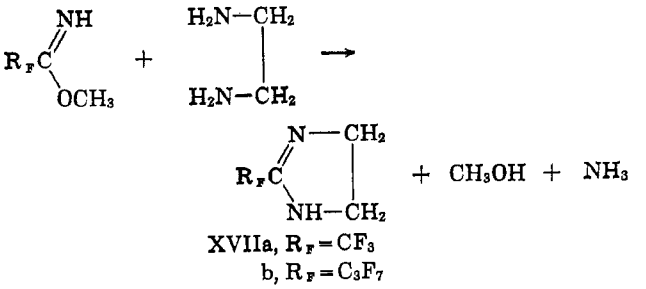


liquids readily purified by fractionation at reduced pressure. The infrared absorption spectra of these imidates gave the characteristic absorption band showing N–H stretching at 2.95 μ, C–H stretching at 3.33 μ, and C=N stretching at 5.92 μ; the band characteristic of the carbonyl group appeared at 5.70 μ.

Attempts to cyclize the α-(carbethoxy)methyl perfluoroacyl imidates by prolonged heating at 120° were unsuccessful. This behavior may be due to a lack of sufficient basicity of the imino group caused by the inductive effect of the perfluoroalkyl group.

The preparation of 2-perfluoromethyl-Δ^2-imidazoline was reported by Johnson and Woodburn[14] from the reaction of perfluoroacetonitrile with ethylenediamine. These authors noted the marked effect of methyl alcohol on this reaction and it was considered possible that methyl perfluoroacetimidate was present as an intermediate.

In the present work both methyl perfluoroacetimidate and methyl perfluorobutyrimidate were found to give good yields of the corresponding 2-perfluoroalkyl-Δ^2-

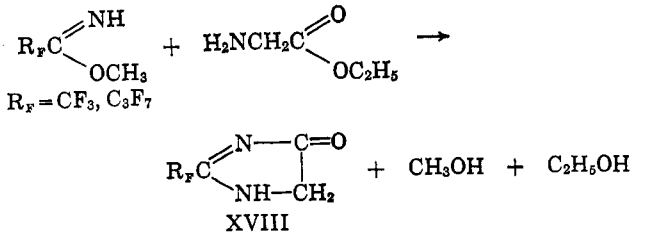


imidazolines (XVII). Solvents depressed the yield of product and the reaction was best carried out with no solvent. This reaction may be described as displacement of the alkoxy group of the imidate followed by the intramolecular elimination of ammonia. Although 2-perfluoromethyl-Δ^2-imidazoline formed at room temperature, its perfluoropropyl analog required refluxing of the reaction mixture for several days before elimination of ammonia was complete.

Although this work does not conclusively prove the methyl perfluoroacetimidate was an intermediate in the imidazoline synthesis of Johnson and Woodburn, the perfluoroacyl imidates were shown to be very useful for this type of reaction.

The infrared absorption spectra of the 2-perfluoroalkyl-Δ^2-imidazolines showed the expected N–H and C–H stretching bands at 3.10, 3.33, and 3.42 μ. Absorption due to C=N stretching appeared at 6.15 μ; a medium band at 6.45–6.48 μ was not assigned.

Preparation of 2-substituted Δ^2-imidazolin-4-ones from the reaction of imidates and α-amino esters was first described by Finger.[15] Kjaer[16] more recently prepared the unstable 2-phenyl-Δ^2-imidazolin-4-one by this method. In the present work the perfluoroacyl imidates were allowed to react with the ethyl ester of glycine and gave compounds in good yield that appear to be the 2-perfluoroalkyl-Δ^2-imidazolin-4-ones XVIII. However, the perfluoroalkyl group



apparently destabilized this ring even more than the phenyl group reported by Kjaer; the perfluoroalkyl-substituted compounds prepared by this method oxidized rapidly in air to black oils. Even those samples stored under vacuum became brown. Solutions in several different solvents became dark red, an effect which Kjaer also reported for the phenyl analog, presumably as a result of oxidation.

Owing to the instability of the 2-perfluoroalkyl-Δ^2-imidazolin-4-ones, elemental analyses were not obtained. The infrared spectra, however, support the postulated structure. Characteristic absorption maxima appeared at 2.80–2.85 (N–H stretching), 3.00–3.12 (N–H stretching, associated), 3.35–3.45 (C–H stretching), 5.78 (C=O stretching), 6.01–6.05 (C=N stretching), and 6.20–6.22 μ (N–H deformation).

(14) R. N. Johnson and H. M. Woodburn, *J. Org. Chem.*, **27**, 3958 (1962).

(15) H. Finger and W. Zeh, *J. prakt. Chem.*, **82**, 50 (1910).

(16) A. Kjaer, *Acta Chem. Scand.*, **7**, 1030 (1953).

Experimental Section

Reaction of Methyl Perfluorobutyrimidate with Hydrogen Chloride.—Freshly prepared methyl perfluorobutyrimidate (2.29 g., 0.010 mole) and hydrogen chloride (0.36 g., 0.010 mole) were accurately measured in a calibrated portion of the vacuum system and condensed in a 100-ml. flask cooled in liquid nitrogen. The flask was isolated from the vacuum system and warmed rapidly to room temperature. A white solid formed quickly; decrease in pressure in the flask indicated almost complete reaction of the imidate with hydrogen chloride. On standing at room temperature for 8 hr., the imidate hydrochloride evolved 0.0090 mole of gas identified by infrared spectra and molecular weight as methyl chloride. The white solid remaining in the flask, 1.9 g., was shown by melting point and infrared spectra to be perfluorobutyramide.

2,2,2-Trifluoroethyl perfluorobutyrimidate also reacted rapidly with hydrogen chloride. Attempts at preparing the hydrochloride in ether resulted in only the momentary formation of a white solid which decomposed immediately. Perfluorobutyramide was isolated from the solution.

Reaction of Methyl Perfluorobutyrimidate with Phosphorus Pentoxide.—Methyl perfluorobutyrimidate (7.26 g., 0.032 mole) and phosphorus pentoxide (3.0 g.) were sealed in a 125-cc. glass ampoule which had been pumped free of air. The ampoule was heated at 100° for 4 hr., cooled, and opened, and 2.1 g. of methyl perfluorobutyrimidate was recovered. Vacuum sublimation of the white solid remaining in the ampoule gave 4.9 g. of pure material shown by comparison with an authentic sample (prepared by the reaction of methyl perfluorobutyrate with methylamine) to be N-methyl perfluorobutyramide.

Reaction of Alkyl Perfluoroacyl Imidates with Boron Trifluoride Etherate.—2,2,2-Trifluoroethyl perfluorobutyrimidate (10.0 g.) was placed in a 10-ml. flask and 1 ml. of boron trifluoride etherate was added. A white precipitate formed immediately. The flask was fitted with a reflux condenser protected from atmospheric moisture and refluxed for 24 hr. No decomposition of the boron trifluoride complex was evident. Unreacted imidate was removed under reduced pressure to leave 0.7 g. of the white solid complex.

In contrast, N-methyl perfluorobutyramide was obtained from methyl perfluorobutyrimidate on refluxing in benzene solution with catalytic amounts of boron trifluoride etherate in excellent conversions.

Perfluorobutyramidine.—Methyl perfluorobutyrimidate (6.81 g., 0.030 mole) and 15 ml. of anhydrous methyl alcohol were placed in a 50-ml. three-necked flask equipped with magnetic stirrer, gas entry tube, ice bath, and Dry Ice–acetone cooled reflux condenser. The solution was saturated at 0° with ammonia and allowed to stand overnight at room temperature. Removal of the solvent and unreacted starting materials under reduced pressure left 5.9 g. (92%) of white solid perfluorobutyramidine. A small amount was purified by sublimation under reduced pressure to give a product melting at 51–52°.[17]

Perfluorobutyramidoxime.—Hydroxylamine hydrochloride (3.5 g., 0.050 mole) in 100 ml. of anhydrous methyl alcohol was added to 2.7 g. (0.050 mole) of sodium methoxide in 25 ml. of methyl alcohol. Methyl perfluorobutyrimidate (11.35 g., 0.050 mole) was added to the solution which was then stoppered and allowed to stand 24 hr. Solvent and unreacted starting materials were removed under reduced pressure and the solid product was dissolved in hot carbon tetrachloride and filtered to remove sodium chloride. On cooling the carbon tetrachloride filtrate, 4.0 g. (35%) of pure perfluorobutyramidoxime, m.p. 78°, crystallized. This product was identified by comparison with an authentic sample.[18]

Perfluoroacethydrazidine.—Methyl perfluoroacetimidate (12.7 g., 0.10 mole) and 5 ml. of dry methyl alcohol were placed in a flask cooled by an ice bath and 3.2 g. of hydrazine (95+%) in 5 ml. of dry methyl alcohol was added dropwise with stirring. After addition was completed, the reaction flask was left standing in an ice bath for 24 hr.; the unreacted starting materials and solvent were removed by lowering the pressure in the flask to 0.5 mm. for 12 hr. A clear viscous liquid, 1.8 g., n^{25} 1.4230, remained in the flask. This product was identified as perfluoroacethydrazidine (93%) by subsequent reactions (see below). The infrared spectra of perfluoroacethydrazidine showed absorption maxima at 2.96, 3.12, 5.95, and 7.05 μ.

Perfluoroacethydrazidine decomposed slowly with the evolution of a basic gas at room temperature; decomposition was rapid at temperatures above 60°. After storage at room temperature for 3 weeks, a sample was found to contain approximately 20% N^2-(perfluoroacetimidoyl)perfluoroacethydrazidine (see preparations below).

N^2-(Perfluoroacetimidoyl)perfluoroacethydrazidine.—Freshly prepared perfluoroacethydrazidine (6.35 g., 0.050 mole) and 2 ml. of anhydrous methyl alcohol were placed in a 30-cc. heavy-wall glass ampoule. The ampoule was cooled in liquid nitrogen and pumped free of air. Perfluoroacetonitrile (4.7 g., 0.050 mole) was condensed in the ampoule and the reaction mixture was allowed to stand 12 hr. at room temperature. Removal of the solvent under reduced pressure left 10.7 g. of white, solid product, m.p. 117–119°, which, after purification by sublimation at reduced pressure, had a melting point of 118.5–119°. The infrared spectrum of this product, N^2-(perfluoroacetimidoyl)perfluoroacethydrazidine, was identical with that of the product incorrectly reported by Brown and Pilipovich[11] as 2,5-bis(trifluoromethyl)-N-amino-1,3,4-triazole.

N^2-(Perfluoroacetimidoyl)perfluoroacethydrazidine was prepared directly from methyl perfluoroacetimidate by allowing 25.4 g. (0.20 mole) of the imidate to react with 3.2 g. (0.10 mole) of hydrazine (95+%) dissolved in 2 ml. of dry methyl alcohol. The reaction mixture was kept at 0° for 24 hr., then at room temperature for 24 hr. Solvent and unreacted starting materials were removed by reducing the pressure in the reaction flask to 0.1 mm. for 6 hr.; remaining in the flask was 20.8 g. (94%) of N^2-(perfluoroacetimidoyl)perfluoroacethydrazidine melting, after sublimation at reduced pressure, at 119–120°. The spectrum of this compound was identical with that of the other preparations described above, and the melting point of a mixture of this preparation with previous ones showed no depression.

3,5-Bis(perfluoromethyl)-1,2,4,4-H-triazole.—N^2-(Perfluoroacetamidoyl)perfluoroacethydrazidine hydrochloride (8.5 g., 0.033 mole) was placed in a 40-cc. glass ampoule which was pumped free of air and sealed. The ampoule was heated for 12 hr. at 140°. The crude product was washed with water to remove ammonium chloride and sublimed several times from phosphorus pentoxide to give pure 3,5-bis(perfluoromethyl)-1,2,4,4-H-triazole, m.p. 74–76°. The melting point of this product reported by Brown and Cheng[12] was 76–77°; the infrared spectrum of the present preparation was in agreement with that previously reported.

Perfluorobutyrhydrazidine.—Methyl perfluorobutyrimidate (11.35 g., 0.050 mole) was allowed to react with hydrazine (95+%, 1.6 g., 0.050 mole) in 2 ml. of dry methyl alcohol at 0°. The mixture was allowed to stand at room temperature for 24 hr. Solvent and unreacted starting materials were removed under reduced pressure to yield 10.2 g. (90%) of crude perfluorobutyrhydrazidine. A small amount of this product, after recrystallization from chloroform, gave a melting point of 70.5–71.5° (lit.[11] m.p. 69.5–70.0°). The infrared spectrum of this compound was identical with that of the product prepared by the method of Brown and Pilipovich.

N^2-(Perfluorobutyrimidoyl)perfluorobutyrhydrazidine.—Methyl perfluorobutyrimidate (11.35 g., 0.050 mole) was placed in a 50-ml. flask and cooled to 0°. Hydrazine (95+%, 0.80 g., 0.025 mole) in 4 ml. of dry methyl alcohol was added dropwise to the imidate with stirring. The flask was allowed to stand at room temperature for 6 hr. and heated to reflux for 6 hr. Solvent and unreacted starting materials were removed under reduced pressure to leave 8.3 g. (85%) of crude N^2-(perfluorobutyrimidoyl)perfluorobutyrhydrazidine. After recrystallization from carbon tetrachloride, this compound showed a melting point of 50.5–51.5°. The melting point of a mixture with an authentic sample[19] showed no depression; the infrared spectra of the two preparations were identical.

2-Chloroethyl Perfluorobutyrimidate.—2-Chloroethanol (4.0 g., 0.050 mole), perfluorobutyronitrile (9.7 g., 0.050 mole), and trimethylamine (0.59 g., 0.01 mole) were sealed in a previously evacuated heavy-wall glass ampoule and allowed to stand at room temperature for 12 hr. The reaction mixture was washed with two 100-ml. portions of water and dried over anhydrous cal-

(17) D. R. Husted [U. S. Patent 2,676,985 (1954)] reported m.p. 52° for $C_3F_7C(=NH)NH_2$.

(18) H. C. Brown and C. R. Wetzel, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963; Abstracts, p. 19M.

(19) N^2-(Perfluorobutyrimidoyl)perfluorobutyrhydrazidine was first prepared and characterized in this laboratory by R. Pater.

cium sulfate. Fractional distillation through a small packed column gave 11.2 g. (81%) of 2-chloroethyl perfluorobutyrimidate, a clear colorless liquid, b.p. 54.0–54.5° (27 mm.), n^{25} 1.3492. This compound was unstable at room temperature and after 24 hr. standing contained traces of a white, insoluble solid which gave the same melting point (with decomposition) as the hydrochloride of 2-perfluoropropyl-Δ^2-oxazoline.

Heating pure 2-chloroethyl perfluorobutyrimidate at 100° caused a rapid rearrangement to N-(2-chloroethyl)perfluorobutyramide, m.p. 48–49°.

Anal. Calcd. for $C_6H_5ClF_7NO$: N, 5.08. Found: N, 5.34.

2-Chloroethyl Perfluoroacetimidate.—This compound was prepared according to the procedure given above for the preparation of 2-chloroethyl perfluorobutyrimidate. Perfluoroacetonitrile (9.5 g., 0.10 mole), chloroethanol (8.0 g., 0.10 mole), and 0.59 g. of trimethylamine gave a crude yield of 17.1 g. Fractionation gave 15.2 g. (87%) of unstable, liquid 2-chloroethyl perfluoroacetimidate, b.p. 47–48° (52 mm.), n^{25} 1.3768. This compound was much less stable than its C_3F_7 analog.

Heating 2-chloroethyl perfluoroacetimidate in dry pyridine at 80° for 12 hr. caused its complete rearrangement to N-(2-chloroethyl) perfluoroacetamide.

2-Perfluoropropyl-Δ^2-oxazoline.—2-Chloroethanol (8.0 g., 0.10 mole) and 5 ml. of dry tetrahydrofuran were placed in a 80-cc. glass ampoule. The ampoule was cooled in liquid nitrogen and pumped free of air, and perfluorobutyronitrile (19.5 g., 0.10 mole) and trimethylamine (8.75 g., 0.15 mole) were condensed in the ampoule. The ampoule was sealed, allowed to stand 2 hr. at room temperature, then heated with agitation at 75° for 20 hr. The reaction mixture was washed with two 100-ml. portions of water and the water-insoluble layer was dried over anhydrous calcium sulfate. Fractionation yielded 14.30 g. (63%) of pure 2-perfluoropropyl-Δ^2-oxazoline, b.p. 61° (40 mm.), n^{25} 1.3459.

Anal. Calcd. for $C_6H_4F_7NO$: N, 5.86. Found: N, 6.00.

2-Perfluoromethyl-Δ^2-oxazoline.—This compound was prepared in a manner similar to that described for 2-perfluoropropyl-Δ^2-oxazoline. Perfluoroacetonitrile (19.0 g., 0.20 mole), 2-chloroethanol (16.0 g., 0.20 mole), and trimethylamine (14.7 g., 0.25 mole) were heated at 60–65° for 12 hr. Fractionation of the product gave 14.2 g. (51%) of 2-perfluoromethyl-Δ^2-oxazoline, b.p. 39.0–41.0 (55 mm.), n^{25} 1.3735.

This product decomposed at room temperature to N-vinylperfluoroacetamide, m.p. 56–58°.

N-Vinylperfluorobutyramide.—Freshly prepared 2-perfluoropropyl-Δ^2-oxazoline (8.0 g.) was placed in a 20-cc. glass ampoule which was then cooled in liquid nitrogen, pumped free of air, and sealed. After the ampoule had been heated at 90° for 14 hr., unreacted oxazoline (3.2 g.) was removed under reduced pressure. Sublimation of the remaining product under reduced pressure at 60° gave 4.5 g. of pure N-vinylperfluorobutyramide, m.p. 51–52°. The conversion was 56%.

Anal. Calcd. for $C_6H_4F_7NO$: N, 5.86. Found: N, 5.46.

This reaction was also run at a temperature of 120° for 12 hr. to give a conversion of 87%.

α-(Carbethoxy)methyl Perfluorobutyrimidate.—Freshly prepared ethyl glycolate (10.3 g., 0.10 mole) was placed in a 40-cc. glass ampoule which was cooled in liquid nitrogen and pumped free of air. Perfluorobutyronitrile (19.5 g., 0.10 mole) and triethylamine (0.59 g., 0.010 mole) were condensed in the ampoule which was sealed and allowed to stand at room temperature for 12 hr. Fractionation of the reaction mixture through a small packed column yielded 21.5 g. (72%) of clear, liquid α-(carbethoxy)methyl perfluorobutyrimidate, b.p. 63.0–63.5 (6 mm.), n^{25} 1.3570, d^{25} 1.413.

Anal. Calcd. for $C_8H_8F_7NO_3$: N, 4.68. Found: N, 4.95.

α-(Carbethoxy)methyl Perfluoroacetimidate.—In a manner similar to that described in the previous procedure, ethyl glycolate (10.3 g., 0.10 mole) was allowed to react with perfluoroacetonitrile (9.5 g., 0.10 mole) in the presence of 0.059 g. (0.010 mole) of trimethylamine. Fractional distillation through a small packed column gave 12.8 g. (65%) of pure α-(carbethoxy)-methyl perfluoroacetimidate, b.p. 60.0–60.8 (11 mm.), n^{25} 1.3955, d^{25} 1.290.

Anal. Calcd. for $C_6H_8F_3NO_3$: N, 7.04. Found: N, 7.16.

Cyclization of α-(carbethoxy)methyl perfluorobutyrimidate was attempted by heating 15.0 g. in a 100-ml. flask equipped with thermometer and reflux condenser, and connected to a manostat. The manostat was connected through a trap cooled in liquid nitrogen to a vacuum pump. The pressure in the system was adjusted so that the reflux temperature was a constant 120° and the compound was refluxed for 48 hr. The infrared spectra indicated no change in the compound and no ethyl alcohol was collected in the liquid nitrogen cooled trap.

2-Perfluoropropyl-Δ^2-imidazoline.—Methyl perfluorobutyrimidate (6.81 g., 0.030 mole) was placed in a 50-ml. flask and 1.8 g. (0.030 mole) of ethylenediamine in 4 ml. of dry methyl alcohol was added dropwise with stirring. The reaction mixture was allowed to stand at room temperature for 24 hr., then refluxed for 48 hr. The solution was added slowly to 200 ml. of ice water; the resulting white solid product was separated by filtration and dried in a desiccator over barium oxide to yield 7.0 g. (91%) of white, impure 2-perfluoropropyl-Δ^2-imidazoline. A small amount of product was sublimed at atmospheric pressure to give a sample for analysis, m.p. 76.0–77.2° (sealed tube).

Anal. Calcd. for $C_6H_5F_7N_2$: C, 30.26; H, 2.11; N, 11.77. Found: C, 30.65; H, 2.39; N, 11.92.

2-Perfluoromethyl-Δ^2-imidazoline.—Methyl perfluoroacetimidate (5.08 g., 0.040 mole) was placed in a small flask cooled in an ice bath and 2.4 g. (0.040 mole) of ethylenediamine in 3 ml. of dry methyl alcohol was added dropwise to the vigorously stirred solution. The flask was then allowed to stand 48 hr. at room temperature. Removal of the solvent under reduced pressure left 5.1 g. (80%) of 2-perfluoromethyl-Δ^2-imidazoline. Purification by sublimation gave crystals melting at 112–113° (lit.[14] m.p. 112°).

2-Perfluoropropyl-Δ^2-imidazolin-4-one.—Methyl perfluorobutyrimidate (22.7 g., 0.10 mole), 50 ml. of anhydrous ethyl ether, and 10.3 g. (0.10 mole) of the ethyl ester of glycine were placed in a 100-ml. flask which was tightly stoppered and allowed to stand at room temperature for 20 hr. Solvent was removed under reduced pressure to leave 20.1 g. of light brown solid product, which was easily purified by sublimation under reduced pressure at 60°. However, the white solid, in contact with the air, colored very quickly and became a black oil within 1 week. Samples stored under vacuum also acquired a brown coloration and elemental analyses were not obtained. The white solid, presumably 2-perfluoropropyl-Δ^2-imidazolin-4-one, melted at 70.5–71.5° with decomposition.

2-Perfluoromethyl-Δ^2-imidazolin-4-one.—Methyl perfluoroacetimidate (3.81 g., 0.030 mole) and 3.09 g. (0.030 mole) of the ethyl ester of glycine were placed in a 20-cc. glass ampoule. The ampoule was cooled in liquid nitrogen, pumped free of air, and allowed to stand at room temperature for 8 hr. after sealing. A black solution developed. Volatile material was removed under reduced pressure and the black solid remaining was purified by a vacuum sublimation. The resulting white product, however, immediately developed a pink coloration and rapidly became a black oil on standing in contact with the air. The infrared spectrum had the same characteristic absorption bands as that of the more stable perfluoropropyl analog.