Reactions of Perfluoroalkyl Nitriles. VII. Perfluoroacyl Amidoximes and 3,5-Bis(perfluoroalkyl)-1,2,4-oxadiazoles[1]

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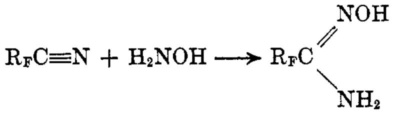
Perfluoroacyl amidoximes, $R_FC(=NOH)NH_2$, where R_F is CF_3, C_2F_5, C_3F_7, or C_7F_{15}, were prepared by the addition of hydroxylamine to the corresponding perfluoroalkyl nitrile. Acylation by perfluoroacyl chlorides produced stable O-perfluoroacyl perfluoroacyl amidoximes, $R_FC(NH_2)=N-O-C(=O)R_F$; these compounds were cyclized by dehydration with phosphorus pentoxide to give 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles. Acylation of perfluoroacyl amidoximes with phosgene gave the isolable O-chloroformyl perfluorobutyramidoxime, which was cyclized with elimination of hydrogen chloride to 3-perfluoropropyl-1,2,4-oxadiazolin-5-one. Acylation of 2 molar equiv. of perfluorobutyramidoxime with oxalyl chloride produced an intermediate that was cyclized to 3,3′-bis(perfluoropropyl)-1,2,4-bioxadiazole.

The addition of ammonia,[2] hydrazine,[3] hydrogen sulfide,[4] alcohols,[5] and active methylene compounds[6] to the exceptionally reactive cyano group of the perfluoroalkyl nitriles has led to many useful intermediate compounds for the synthesis of a variety of heterocycles with perfluoroalkyl-substituent groups. Because of the strong electronegative effect of the perfluoroalkyl group many of these heterocycles possess interesting and unusual properties.

This paper describes the addition of hydroxylamine to some perfluoroalkyl nitriles to give the perfluoroacyl amidoximes and includes the study of these reactive intermediates for the preparation of 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles and related compounds.

The perfluoroacyl amidoximes were prepared by a modification of the classical method of Tiemann and Kruger.[7] Free hydroxylamine was generated from its hydrochloride in methanol by the addition of equivalent amounts of an alcoholic solution of sodium methoxide. All the perfluoroalkyl nitriles used reacted rapidly at room temperature; removal of the solvent gave the perfluoroacyl amidoximes in yields ranging from 60 to 97%.



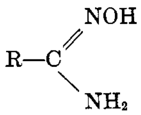
$$R_FC\equiv N + H_2NOH \longrightarrow R_FC(=NOH)NH_2$$

The reactivity of the perfluoroalkyl nitriles toward hydroxylamine and other nitrogen bases is probably a consequence of the increased positive character of the carbon of the cyano group caused by the inductive effect of the perfluoroalkyl group. In contrast to their perfluoroalkyl analogs, the hydrocarbon nitriles[8] require considerably higher reaction temperatures and longer reaction times in order to obtain comparable yields. Perfluoroglutaronitrile was found to be exceptionally reactive, adding hydroxylamine rapidly at 0° to give almost quantitative yields of the corresponding diamidoxime. The perfluoroacyl amidoximes prepared are listed in Table I.

The perfluoroacyl amidoximes are colorless, crystalline solids which are soluble in most polar and nonpolar organic solvents; in general, solubility decreases with increasing fluorocarbon chain length. These compounds have the amphoteric nature common to other amidoximes, as indicated by their solubility in dilute mineral acids and in aqueous alkaline solutions. However, the basic nature of the amino group appears to be significantly affected by the fluorocarbon group; the perfluoroacyl amidoximes, unlike their hydrocarbon analogs, do not form stable hydrochlorides. Furthermore, the perfluoroacyl amidoximes formed insoluble, green cupric salts rather than the usual metal chelates[9] formed by nonfluorinated aliphatic and aromatic amidoximes. Perfluorobutyramidoxime was hydrolyzed by heating in dilute alkaline solution to give perfluorobutyramide.

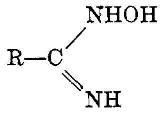
The perfluoroacyl amidoximes are quite stable thermally, in contrast to their aliphatic analogs, which usually decompose at their melting points. They more closely resemble aromatic amidoximes[10] in this respect. The decomposition of perfluoropropionamidoxime in air is slow at 170°; 24-hr. heating was required for decomposition of 60–70% of the sample. The only decomposition product identified was 3,5-bis(perfluoroethyl)-1,2,4-oxadiazole, in yields of 30–40%. At a pyrolysis temperature of 250°, etching of the apparatus occurred, indicating rupture of the C–F bond of the fluorocarbon group.

Amidoximes may exist in either of two tautomeric forms. Although Ungnade and Kissinger[11] have



$$R-C(=NOH)NH_2$$

I



$$R-C(NHOH)=NH$$

II

favored II, most authors[12] have concluded that I, the "amino oxime" form, best represents the structure of the amidoximes. Table II shows the principal infrared absorption bands between 2.5 and 7.0 μ of the perfluoroacyl amidoximes; the simplicity of the spectra would appear to rule out the presence of a

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[1] This work was supported by Public Health Service Research Grant CA-05083 from the National Cancer Institute. Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963. For preceding paper in this series, see H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3729 (1965).

[2] D. Husted, U. S. Patent 2,676,985 (1954).

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

[4] W. L. Reilly and H. C. Brown, *ibid.*, **78**, 6032 (1956).

[5] H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3724 (1965).

[6] A. D. Josey, *ibid.*, **29**, 707 (1964).

[7] F. Tiemann and P. Kruger, *Ber.*, **17**, 1685 (1884).

[8] For a recent review of the amidoximes, see F. Eloy and R. Lenaers, *Chem. Rev.*, **62**, 155 (1962).

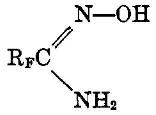
[9] A. Werner, *Ber.*, **41**, 1062 (1908). Many amidoximes have been used as reagents for various cations.

[10] G. Leandri and P. Rebora, *Ann. chim.* (Rome), **46**, 953 (1956).

[11] H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **23**, 1112 (1958).

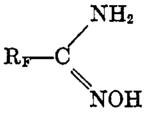
[12] C. L. Bell, C. N. V. Nambury, and L. Bauer, *ibid.*, **29**, 2873 (1964), and references therein.

TABLE I
PERFLUOROACYL AMIDOXIMES



R_F	M.p., °C.	Yield, %	Calcd., % C	Calcd., % H	Calcd., % F	Calcd., % N	Found, % C	Found, % H	Found, % F	Found, % N
CF_3	27.5–29.0	65	18.75	2.42	44.50	21.87	18.85	2.26	44.34	21.71
C_2F_5	55.0–56.0	76	20.23	1.70	53.35	15.73	20.33	1.64	53.67	15.90
C_3F_7	78.0–79.0	80	21.07	1.32	58.33	12.28	21.39	1.46	58.36	12.00
C_7F_{15}	121.0–122.5	70	22.44	0.71	66.57	6.54	22.70	0.68	66.28	6.33
$-(CF_2)_3-$	212.0–213.0	97	22.40	2.25	42.51	20.90	22.58	2.39	42.18	21.03

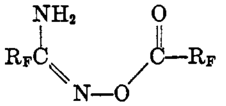
TABLE II
INFRARED ABSORPTION[a] OF PERFLUOROACYL AMIDOXIMES (2.5–7.0 μ)



R_F	NH_2 Assym. str.	NH_2 Sym. str.	OH, assocd.	ND_2 Assym. str.	ND_2 Sym. str.	OD, assocd.	C=N, str.	C=N, str. (deut.)	NH, def.
C_2F_5	2.85 (m)	2.95 (s)	3.40 (w)	3.73 (m)	4.00 (m)	4.40	5.93 (s)	5.93 (s)	6.24 6.30 (s)
C_3F_7	2.85 (m)	2.95 (s)	3.40 (w)	...	...	...	5.92 (s)	...	6.23 6.30
CF_3	2.90 (s)	3.00 (s)	3.42 (w)	...	...	...	5.97 (s)	...	6.33

[a] In microns.

TABLE III
O-PERFLUOROACYL PERFLUOROALKYL AMIDOXIMES



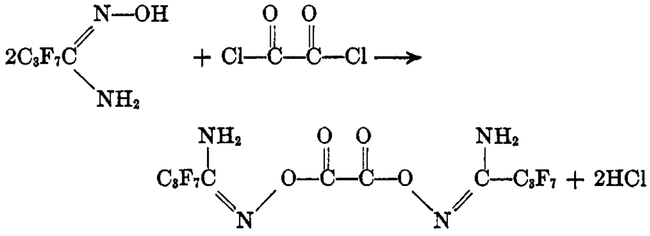
R_F	M.p., °C.	Calcd., % C	Calcd., % H	Calcd., % F	Calcd., % N	Found, % C	Found, % H	Found, % F	Found, % N
CF_3	Unstable	...	...	...	...	...	...	...	...
C_2F_5	57.0–58.0	22.24	0.62	58.64	8.64	22.14	0.45	58.60	8.62
C_3F_7	86.2–87.6	22.65	0.47	62.71	6.60	22.52	0.59	62.47	6.77
C_7F_{15}	90.0[a]	23.31	0.24	69.15	3.39	23.10	0.52	...	3.61

[a] Sublimes.

mixture of tautomers. Deuteration clearly identified the C=N stretching by causing the NH_2 bending vibrations to shift into the region of the strong C–F stretching absorption, where they cannot be seen. Comparison of the spectra with those of representative aromatic and aliphatic amidoximes[13] shows a definite shift of the C=N stretching to a shorter wave length and also a considerable decrease in intensity of absorptions attributable to associated OH and NH stretching bands, presumably as a consequence of the decreased basicity of the amino group which lessens the normally highly associated nature of the amidoximes.

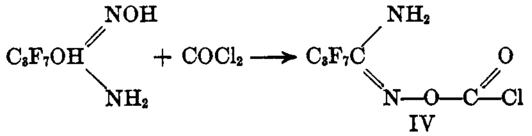
Acylation of the perfluoroacyl amidoximes with perfluoroacyl chlorides at room temperature was rapid and gave almost quantitative yields of the monoacylated derivative. The compounds prepared are shown in Table III. All of the acyl amidoximes prepared were stable, colorless, crystalline solids with the exception of $CF_3C(NH_2){=}N{-}O{-}C({=}O)CF_3$, which was extremely susceptible to hydrolysis by atmospheric moisture.

Oxalyl chloride also was used successfully as an acylating agent for perfluorobutyramidoxime in ether at 0°. Yields of 75% were realized of the high-melting (195–196°) compound III.



III

Perfluorobutyramidoxime was allowed to react with phosgene to give a new[14] and unique amidoxime derivative, O-chloroformyl perfluorobutyramidoxime (IV).



IV

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[13] J. Barrous, R. Mathie-Noel, and F. Mathis, *Compt. rend.*, **245**, 419 (1957).

[14] Both active chlorine atoms of phosgene are usually displaced in reactions with amidoximes: See E. Falck, *Ber.*, **19**, 1481 (1886).

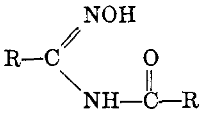
TABLE IV

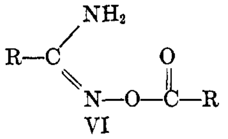
INFRARED ABSORPTION SPECTRA ASSIGNMENTS IN THE 2.5–6.2-μ REGION

Compd.	Group	N-H str., μ	C=O str., μ	C=N str., μ
$C_3F_7\overset{\overset{O}{\|}}{C}-OCH_3$	$-\overset{\overset{O}{\|}}{C}-O-$	. . .	5.60 (s)	. . .
$C_3F_7\overset{\overset{O}{\|}}{C}-NH-CH_3$	$-\overset{\overset{O}{\|}}{C}-N-$	. . .	5.81 (s)	. . .
$C_3F_7\overset{\overset{NH_2}{\|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-C_3F_7$	$-\overset{\overset{O}{\|}}{C}-O-$	2.77 (w), 2.90 (s)	5.58 (s)	6.07 (s)
$C_3F_7\overset{\overset{NH_2}{\|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-Cl$	$-\overset{\overset{O}{\|}}{C}-O-$	2.70 (m), (2.85) (s)	5.56 (s)	6.00 (s)
$(C_3F_7\overset{\overset{NH_2}{\|}}{C}=N-O-\overset{\overset{O}{\|}}{C}-)_2$	$-\overset{\overset{O}{\|}}{C}-O-$	2.82 (m), 2.97 (s)	5.68 (s)	6.10 (s)

This reaction was carried out at −20 to 5°, using a large excess of phosgene to produce an almost quantitative yield of the stable, crystalline acylated compound. The structure of the compound was confirmed by elemental analysis and infrared spectra. The acyl chloride group of IV reacted readily with a silver nitrate solution to give a precipitate of silver chloride.

Amidoximes have two possible points of acylation, one of which would produce an N-acyl (V) and the other an O-acyl (VI) amidoxime.[15] Although most of the acyl derivatives of amidoximes are reported as

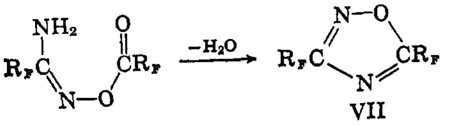

V


VI

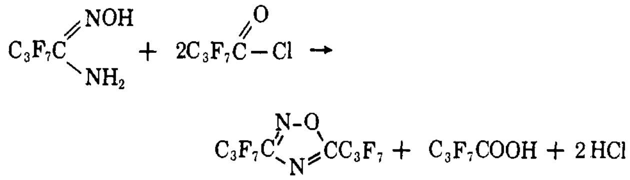
having the O-acyl structure, Steinkopf and Borhmann,[16] who studied the halogenated acetamidoximes, claimed that their acylation occurred on the amino nitrogen; reinvestigation of this early work by Eloy[17] indicated that these were O-acyl derivatives also.

Comparison of the position of carbonyl bands in the infrared absorption spectra of the acylated perfluoroacyl amidoximes with those of amides and esters (Table IV) shows clearly that these compounds have the $-C(=O)-O-$ structure rather than $-C(=O)-NH-$. In addition, the associated OH band of the perfluoroacyl amidoximes has completely disappeared from these spectra.

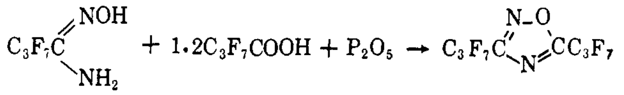
The O-perfluoroacyl perfluoroacyl amidoximes were easily dehydrated by heating with phosphorus pentoxide to give the 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles VII. The reaction occurred at 200–300° and gave yields ranging from 50 to 80%. Table V lists the compounds prepared.


VII

Two additional modifications of this method were found for the preparation of 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles whereby acylation and dehydration were accomplished in a single step. In the first perfluorobutyryl chloride functioned both as an acylating and dehydrating agent. This reaction, when carried



out at 200° in a sealed ampoule, gave quantitative yields. The second modification involved merely the mixing of perfluorobutyramidoxime and phosphorus pentoxide with perfluorobutyric acid and refluxing for several hours and gave yields of 80%. The reaction probably involves initial formation of perfluorobutyric anhydride, which acylates the perfluoro-



butyramidoxime, and, with phosphorus pentoxide, also acts as a dehydrating agent.

The 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles are stable colorless liquids, having no ultraviolet absorption maxima above 220 mμ but having characteristic infrared absorption bands between 6.22–6.27 and 6.55–6.60 μ. With 3,5-CF_3 substituents these bands are slightly shifted to 6.17 and 6.47 μ. These bands are presumably due to C=N stretching of the two distinct C=N groups of the 1,2,4-oxadiazole ring.

The thermal stability of the 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles is high. No decomposition was evident on heating 3,5-bis(perfluoropropyl)-1,2,4-oxadiazole in a sealed tube at 400° for 1 hr.

The chemical passivity of 3,5-disubstituted-1,2,4-oxadiazoles[18] does not seem to have been altered by the introduction of the perfluoroalkyl group. The compounds prepared were stable in dilute and concentrated acid and, somewhat surprisingly, also in most alkaline solutions tested. Facile nucleophilic attack has been observed, however, with nitrogen bases having a particular structure. This subject will be treated in a forthcoming publication.

Phosphorus pentoxide was used to dehydrate III to yield 3,3′-bis(perfluoropropyl)-1,2,4-bioxadiazole (VIII) in 61% yield. Unlike the other disubstituted

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[15] A third possible acylation product is RC(=NH)N(OH)C(=O)R. This structure is not considered since all perfluoroalkylamidoximes could be dehydrated with cyclization to the corresponding 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazole.

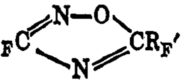
[16] W. Steinkopf and L. Borhmann, *Ber.*, **40**, 1633 (1907).

[17] F. Eloy, R. Lenaers, and R. Buyle, *Bull. soc. chim. Belges*, **73**, 518 (1964).

[18] Monosubstituted and unsubstituted 1,2,4-oxadiazoles are more reactive: see C. Moussebois and F. Eloy, *Helv. Chim. Acta*, **47**, 838 (1964).

TABLE V

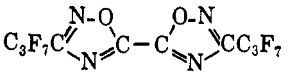
3,5-BIS(PERFLUOROALKYL)-1,2,4-OXADIAZOLES



R_F	R_F'	Yield, %	B.p., °C. (mm.)	n^{25}	Calcd., % C	Calcd., % F	Calcd., % N	Found, % C	Found, % F	Found, % N
CF_3	CF_3	75	46.0	1.2895	23.31	55.32	13.59	23.59	55.44	13.40
C_2F_5	C_2F_5	76	80.5	1.2918	23.54	62.07	9.15	23.68	61.80	9.00
C_3F_7	CF_3	..	86.0	1.2942[a]	...	...	9.15	...	...	9.91
C_3F_7	C_3F_7	72	118.5	1.2958	23.66	65.50	6.90	23.80	65.48	6.90
C_7F_{15}	C_7F_{15}	70	118.0–120.0 (7)[b]	...	23.84	...	3.48	23.95	...	3.62
$-(CF_2)_3-$	C_2F_5	..	90.0–92.0 (12)	...	...	...	10.69	...	...	10.53
$-(CF_2)_3-$	C_3F_7	49	96.0–97.0 (7)	1.3270	25.00	61.00	8.97	25.25	60.86	8.88

[a] At 25.2°. [b] M.p. 25–27°.

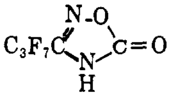
1,2,4-oxadiazoles prepared, this compound had an ultraviolet absorption maxima [λ_{max} 232 mμ in isopropyl alcohol (log ϵ_{max} 4.04)]. This absorption is probably due to the increased conjugation in the compound, specifically the –N=C–N=C–C=N–C=N–group.[19] The infrared spectra showed characteristic bands at 6.55 and 6.78 μ, a considerable shift from those of the perfluoroalkyl-disubstituted 1,2,4-oxadiazoles.



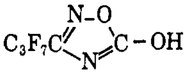
VIII

The attempted dehydration of O-(chloroformyl)-perfluorobutyramidoxime (IV) with phosphorus pentoxide, phosphorus pentachloride, or phosphorus trichloride to form 3-perfluoropropyl-5-chloro-1,2,4-oxadiazole was unsuccessful.

On heating above 100°, O-(chloroformyl)perfluorobutyramidoxime (IV) gradually evolved hydrogen chloride to give IX, 3-perfluoropropyl-1,2,4-4H-oxadiazolin-5-one.[20] Infrared spectra of this compound indicated that IXa rather than its tautomeric form IXb, 3-perfluoropropyl-5-hydroxy-1,2,4-oxadiazole, was the correct structural representation; the presence of a strong, strained-ring lactone C=O was indicated by a band at 5.47 μ. This spectra also showed a broad associated N–H band between 3.0 and 3.5 μ and an absence of any O–H stretching band.



IXa



IXb

Experimental Section[21]

Materials.—All perfluoroalkyl nitriles were prepared by standard methods from the corresponding acids obtained from Columbia Organic Chemicals Co. Sodium methoxide–methanol solutions used were freshly prepared from clean sodium metal and contained, on the average, 1.0 g. of sodium methoxide/5.0 ml. of methanol.

Perfluoroacyl Amidoximes. General Procedure.—Hydroxylamine hydrochloride, a 10% excess of 0.1 molar equiv., was dissolved in 125 ml. of dry methanol and added to a 250-ml. flask equipped with a dropping funnel, magnetic stirring bar, and Dry Ice cooled reflux condenser. Sodium methoxide (0.1 molar equiv.) in methanol solution was added slowly to the stirred solution. Perfluoroalkyl nitrile (0.1 molar equiv.) was admitted slowly to the side arm of the reflux condenser and dropped into the stirred solution. Reaction temperature was maintained at 25° by external cooling. When addition was complete, the flask was allowed to stand for 1 hr., the precipitated sodium chloride was removed by filtration, and solvent from the filtrate was removed under reduced pressure. Perfluoropropio-, perfluorobutyr-, and perfluorocaprylamidoximes were obtained as colorless crystalline solids, and were purified by recrystallization from chloroform or carbon tetrachloride after filtration of the hot solution to remove traces of sodium chloride. Perfluoroglutarodiamidoxime was recrystallized from water. Perfluoroacetamidoxime was obtained as a viscous liquid; purification was effected by vacuum distillation, b.p. 85–87° (30 mm.), n^{25} 1.4889. On standing, perfluoroacetamidoxime solidified into a low-melting solid. Those perfluoroacyl amidoximes prepared are listed in Table I with some of their physical properties and analyses. Important infrared adsorption bands are shown in Table II.

O-Perfluoroacyl Perfluoroacyl Amidoximes. General Procedure.—Perfluoroacyl amidoxime (0.1 molar equiv.) was dissolved in anhydrous ether (with perfluorocaprylamidoxime, tetrahydrofuran was used as a solvent) and placed in a 250-ml. flask equipped with an ice bath, magnetic stirring bar, and Dry Ice–acetone condenser. Perfluoroacyl chloride (0.1 molar equiv.) was passed through a side arm of the Dry Ice–acetone condenser and condensed into the stirred solution (perfluorobutyryl chloride and perfluorooctanoyl chloride are liquids at room temperature and were introduced into the reaction flask with a dropping funnel). After the addition was complete, the ice bath was removed and the solution was allowed to stand for 1 hr. at room temperature. Removal of the solvent under reduced pressure left crystalline solids. Lower molecular weight perfluoroacyl perfluoroacyl amidoximes were readily purified by recrystallization from chloroform or carbon tetrachloride. Acyl derivatives of perfluorocaprylamidoxime were recrystallized from xylene or toluene. O-Perfluoroacyl perfluoroacyl amidoximes prepared are listed in Table III with some physical properties and analyses.

O-(Perfluoroacetyl)perfluoroacetamidoxime was prepared in good yield by the above method, using thoroughly dry reagents and apparatus. However, the compound darkened rapidly on exposure to the atmosphere and rapidly hydrolyzed. When

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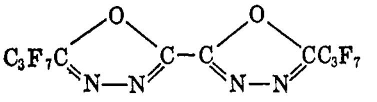
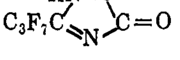
[19] A very similar system is found in the following compound. It had λ_{max} 234 mμ (isopropyl alcohol) (log ε 4.09), infrared absorption maxima at 6.35 and 6.81 μ: R. J. Kassal, Ph.D. Dissertation, University of Florida, Dec. 1963.



[20] Another tautomeric form is possible. However, 3-aryl- and 3-alkyl-1,2,4-oxadiazoline-5-ones gave 4-methyl derivatives on methylation: G. d'Alo, M. Perghem, and P. Gruenanger, *Ann. chim.* (Rome), **53** (10), 1405 (1963), and references therein.



[21] Microanalyses are by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Capillary melting points were measured in a Thomas-Hoover apparatus. Infrared absorption spectra were measured with either a Perkin-Elmer Infracord or a Beckman IR-4 spectrophotometer using the neat liquid or Kel F oil mull. Ultraviolet absorption spectra were measured with a Beckman DK-2 recording spectrophotometer.

freshly prepared, the compound could be dehydrated to the corresponding oxadiazole in good yields.

3,5-Bis(perfluoroalkyl)-1,2,4-oxadiazoles. Method A. General Procedure.—The O-perfluoroacyl perfluoroacyl amidoxime was thoroughly mixed with a large excess of phosphorus pentoxide and placed in a 250-ml. flask equipped with a heating mantle and connected to a Dry Ice–acetone cooled trap protected from atmospheric moisture. The flask was heated at 250–300° for 12–24 hr. The trap was then connected to a vacuum line and cooled by liquid nitrogen, and the pressure in the system was reduced to less than 3 mm. The crude product collected in the trap. (The preparation of 3,5-bis(perfluoroheptyl)-1,2,4-oxadiazole required, because of its high boiling point, that the reaction flask and connecting line to the trap be heated with the pressure at less than 0.5 mm. for transfer of the material into the trap.) The crude product was washed with water several times and fractionated from a pot containing a small amount of phosphorus pentoxide. The 3,5-bis(perfluoroalkyl)-1,2,4-oxadiazoles prepared are listed in Table V with some physical properties and analyses. 1,3-Bis(5,5′-perfluoroalkyl-1,2,4-oxadiazolyl)perfluoropropanes were prepared by dehydration of the O-(perfluoroacyl)perfluoroglutarodiamidoxime in a similar manner to that described above. The compounds are listed in Table V with some physical properties and analyses.

3,5-Bis(perfluoropropyl)-1,2,4-oxadiazole. Method B.—Perfluorobutyramidoxime (3.64 g., 0.016 mole) was placed in a heavy-walled Pyrex glass tube of approximately 100-ml. capacity which had been previously constricted for sealing. The tube was connected to a vacuum system, pumped free of air, and cooled in liquid nitrogen. Perfluorobutyryl chloride (7.50 g., 0.032 mole) was condensed into the tube which was sealed and warmed to room temperature. The tube was placed in a furnace, heated at 150° for 4 hr., and allowed to cool. After cooling in liquid nitrogen, the tube was opened and its contents were washed with water. After drying over calcium sulfate and fractionation through a small packed column, an almost quantitative yield of 3,5-bis(perfluoropropyl)-1,2,4-oxadiazole, b.p. 118.5°, was obtained. The infrared spectrum of this compound was identical with that prepared by method A.

Method C.—Perfluorobutyramidoxime (11.8 g., 0.05 mole) was dissolved in 15 ml. of perfluorobutyric acid and placed in a 50-ml. flask with approximately 10 g. of phosphorus pentoxide. The flask was fitted with heating mantle and reflux condenser. The solution was refluxed for 6 hr., then cooled and added to ice–water. After separation and washing with another small portion of water, the liquid was dried over calcium sulfate. Fractionation in a small packed column gave 16.0 g. of 3,5-bis(perfluoropropyl)-1,2,4-oxadiazole, b.p. 118°, identical with material prepared by methods A and B.

Reaction of Perfluorobutyramidoxime with Oxalyl Chloride.—Perfluorobutyramidoxime (16.0 g., 0.07 mole) in 75 ml. of dry ethyl ether was placed in a 250-ml. flask equipped with a stirring bar; the flask was cooled in liquid nitrogen and pumped free of air. Oxalyl chloride (4.5 g., 0.035 mole) was condensed in the flask; the reaction mixture was warmed slowly to room temperature with vigorous stirring and allowed to stand 0.5 hr. Solvent was removed under reduced pressure to leave a white solid product. Recrystallization from xylene gave III, 13.50 g. (75%), m.p. 195–196 dec.

Anal. Calcd. for $C_{10}H_4F_{14}N_4O_4$: C, 23.54; H, 0.79; N, 10.98. Found: C, 23.00; H, 1.46; N, 10.67.

3,3′-Bis(perfluoropropyl)-1,2,4-bioxadiazole (VIII).—The product from the reaction of perfluorobutyramidoxime and oxalyl chloride (III, 5.10 g., 0.010 mole) was mixed thoroughly with 10.0 g. of phosphorus pentoxide, placed in a 12-in. glass tube fitted with a water-cooled cold-finger condenser and having a side arm near to the top to which a drying tube was attached, and heated to 200° for 3 hr. The apparatus was then connected to a vacuum line, and under reduced pressure, a white solid collected on the cold finger. Recrystallization from dry ether at −78° gave 2.90 g. (61%) of pure 3,3′-bis(perfluoropropyl)-1,2,4-bioxadiazole, m.p. 84–85°.

Anal. Calcd. for $C_{10}F_{14}N_4O_2$: C, 25.33; F, 56.10; N, 11.81. Found: C, 25.12; F, 55.81; N, 11.93.

The infrared spectrum showed two bands, at 6.55 and 6.78 μ, assigned to C=N stretching. The ultraviolet spectrum showed one maximum at 232 mμ (isopropyl alcohol) (log ϵ 4.04).

O-(Chloroformyl)perfluorobutyramidoxime (IV).—A three-neck 100-ml. flask equipped with a Dry Ice–acetone reflux condenser, a 25-ml. dropping funnel, and a magnetic stirring bar was placed in an acetone–Dry Ice bath and cooled to −15°. Phosgene gas was passed into the flask through a side arm of the Dry Ice–acetone condenser. After approximately 10 ml. of liquid phosgene had accumulated, the phosgene inlet was closed and 2.90 g. (0.0128 mole) of perfluorobutyramidoxime dissolved in 15 ml. of dry ethyl ether was added slowly with rapid stirring of the reaction mixture. After addition was complete, cooling was discontinued and the mixture was allowed to stand 1 hr. Removal of solvent under reduced pressure (*caution*—use appropriate measures for the disposal of excess phosgene) gave a white solid, O-(chloroformyl)perfluorobutyramidoxime, in quantitative yield. Recrystallization from CCl_4 gave a product melting at 68.0–69.0°.

Anal. Calcd. for $C_5H_2ClF_7N_2O_2$: C, 20.61; H, 0.69; Cl, 12.23; F, 45.90; N, 9.65. Found: C, 20.85; H, 0.76; Cl, 12.09; F, 46.06; N, 9.62.

3-Perfluoropropyl-1,2,4-4H-oxadiazolin-5-one (X).—O-(Chloroformyl)perfluorobutyramidoxime (3.0 g.) was placed in a stoppered 8-in. test tube with a side arm near the top to which an anhydrous calcium sulfate drying tube was attached. The tube was placed in an oil bath and the temperature was brought slowly up to 125°. Evolution of hydrogen chloride was essentially complete after 3 hr. After cooling the product, recrystallization from carbon tetrachloride gave a quantitative yield of 3-perfluoropropyl-1,2,4-4H-oxadiazolin-5-one, m.p. 80.0–81.0°.

Anal. Calcd. for $C_5HF_7N_2O_2$: C, 23.65; H, 0.38; F, 52.34; N, 11.04. Found: C, 23.77; H, 0.50; F, 52.06; N, 11.22.

The infrared spectra showed bands at 3.1–3.5 (associated N—H stretching), 5.47 (broad, C=O stretching), and 6.23 μ (C=N stretching).