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OXADIAZOLES WITH NF_2-CONTAINING SUBSTITUENTS

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SUMMARY

Oxalyl chloride was reacted with sodium-5-(difluoroamino)-difluoromethyltetrazolate or sodium-5-pentafluoroethyltetrazolate to form $[R_f\overbrace{C{=}NN{=}C(O)}\dagger_2$ [R_f = NF_2CF_2 (**7**)], and with $F_2NCF_2C(NH_2){=}NOH$ to give $[F_2NCF_2C(NH_2){=}NOC(O)\dagger_2$ (**5**) which may be dehydrated to the 1,2,4-oxadiazole $[F_2NCF_2\overbrace{C{=}NOC{=}N}]_2$ (**6**). Both sodium salts can be reacted with perfluoroacyl acid chlorides to form 2,5-disubstituted 1,3,4-oxadiazoles, $R_f\overbrace{C{=}NN{=}C(R_f')O}$ where R_f' = NF_2CF_2 and R_f = CF_3 (**8**), C_2F_5 (**9**), or C_3F_7 (**10**); R_f' = C_2F_5 and R_f = CF_3 (**11**) or C_2F_5 (**12**).

INTRODUCTION

Compounds that contain NF_2, NCl_2, NClF and -N=N- moieties have been of considerable interest as candidates for high energy roles [1-4]. The oxidizing properties of substituted tetrazoles that contain the $-NF_2$ group when combined with possible fuels such as hydrazines have been examined [5]. Earlier we, and others, reported the high yield synthesis of (difluoroamino)difluoro-acetonitrile, NF_2CF_2CN, in our case by the reaction of tetra-fluorohydrazine with 1,1-difluoroethene in the presence of KF [3], and the subsequent synthesis of oxadiazoles [1] and tetrazolates [6,7], viz.

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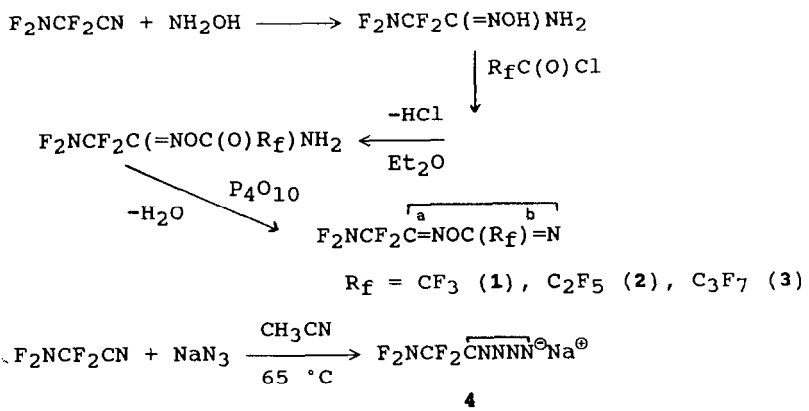
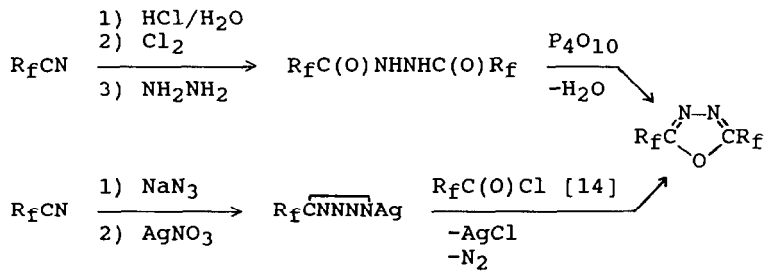


R_f = CF_3 (**1**), C_2F_5 (**2**), C_3F_7 (**3**)

4

In acetonitrile, sodium azide can be reacted smoothly with perfluorinated nitriles. This is as predicted based on the enhanced reactivity of the electropositive cyanocarbon towards nitrogen, oxygen and sulfur bases [8-12].

Both 3,5-perfluoroalkyl-1,2,4-oxadiazoles and their isomers, 2,5-perfluoroalkyl-1,3,4-oxadiazoles, can be synthesized by utilizing R_fCN. The former compounds were obtained previously by the dehydration of O-acylperfluoroalkylamidoximes [13], while the latter were produced by reaction with hydrazine as shown [14-16].



In this paper, the synthesis and characterization of isomeric oxadiazoles that contain the $-NF_2$ group are reported.

RESULTS AND DISCUSSION

We have previously reported the synthesis of 3-(difluoroamino)difluoromethyl-5-perfluoroalkyl-1,2,4-oxadiazoles [1]. Our continuing interest in these heterocyclic compounds that contain NF_2-substituted fluoroalkyls as ring substituents has

prompted the synthesis of several new doubly substituted 1,2,4-oxadiazoles by our earlier method.

$$ClC(O)C(O)Cl + F_2NCF_2C(NH_2)=NOH \longrightarrow [F_2NCF_2C(NH_2)=NOC(O)-]_2$$

5

$$\mathbf{5} + P_4O_{10} \xrightarrow{-H_2O} \left[\begin{array}{c} O\text{—}N_a \\ C \quad CCF_2NF_2 \\ {}_b N \end{array}\right]_2$$

6

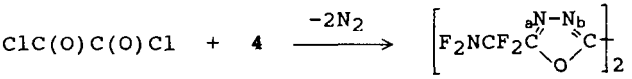
Compound **5**, O-oxalylbis[(difluoroamino)difluoroacetamidoxime], is a stable crystalline material that shows NH_2 asym, sym and def frequencies at 3510, 3330 and 1575 cm^{-1}, respectively, in the IR spectrum. Carbonyl and C=N stretching bands occur at 1760 and 1651 cm^{-1}. This compound is insoluble in $CDCl_3$ but is soluble in ether. In the ^{19}F NMR spectrum of **5** dissolved in ether, signals are observed at Ø 17.72 and -108.5 for NF_2 and CF_2, respectively. In the CI mass spectrum a molecular ion peak at m/e 376 is also observed.

On dehydration, **5** yields bis[3,3'-(difluoroaminodifluoromethyl)-1,2,4-oxadiazole] **6**. The infrared spectrum of **6** contains bands at 1534 and 1481 cm^{-1} indicating the presence of two types of C=N moieties. These absorption bands are shifted markedly from those observed for bis(perfluoroalkyl)-1,2,4-oxadiazoles (see Table I). Similar stretching frequencies occur at 1593 and 1515 cm^{-1} when the starting material is $ClC(O)CF_2C(O)Cl$ [1]. This shift towards lower frequency is apparently due to increased conjugation in **6** [13].

$$F_2NCF_2C\text{—}C\text{—}CCF_2NF_2 \longleftrightarrow F_2NCF_2C^{\oplus}\text{—}C\text{—}CCF_2NF_2$$

The usual C-F and N-F absorption bands are present between 1227-1155 and 1009-923 cm^{-1}, respectively. The ^{19}F NMR spectrum also has peaks at Ø 22.0 and -101.6 assigned to NF_2 and CF_2, respectively. The CI mass spectrum contains peaks assignable to M^++1 and M^+ at m/e 341 and 340. The accompanying fragmentation pattern supports the postulated structure for **6**.

The isomer of **6**, bis[2,2'-(difluoroaminodifluoromethyl)-1,3,4-oxadiazole], **7**, was synthesized according to



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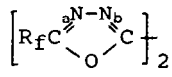
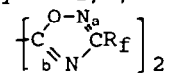
As expected, there is an appreciable change in $\nu_{C=N}$ in **7** relative to other 1,3,4-oxadiazoles.

TABLE I

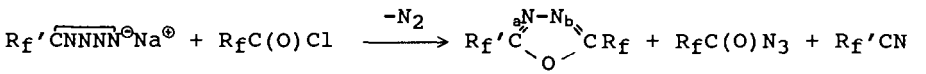
Infrared spectral stretching frequencies and ^{19}F NMR coupling constants for oxadiazoles

Compound	$\nu^{a}_{C=N}$	$\nu^{b}_{C=N}$	$J_{CF_2-NF_2}$, Hz
1[c]	1610	1530	2.44
2[c]	1599	1529,1515	2.56
3[c]	1597	1515	2.50
8[d]	1560	1515	4.70
9[d]	1568	1559	3.40
10[d]	1561	---	3.35
6[d]	1534	1481	2.44
$\{CF_2\overline{C=NC(CF_2NF_2)=NO}\}_2$[c]	1593	1515	2.07
$\overline{C(C_3F_7)=NOC(C_3F_7)=N}$[e]	1526	1475	--
7[d]	1567	1474	3.34
11[d,f]	1535	---	2.68 (CF_3CF_2)
12[d,f]	1570	---	2.57 (CF_3CF_2)

[a,b] Labels identifying position of C=N moiety in 1,3,4 and 1,2,4 oxadiazole rings,  and 

[c] Reference 1; [d] this work; [e] Reference 13; [f] References 15 and 16.

Several 2-(difluoroamino)difluoromethyl-5-perfluoroalkyl-1,3,4-oxadiazoles as well as some previously known 2,5-bis(perfluoroalkyl)-1,3,4-oxadiazoles were also synthesized. While silver tetrazolates were previously used in these syntheses [14], we find that the analogous sodium salts are equally effective precursors without the concomitant problems of shock sensitivity.

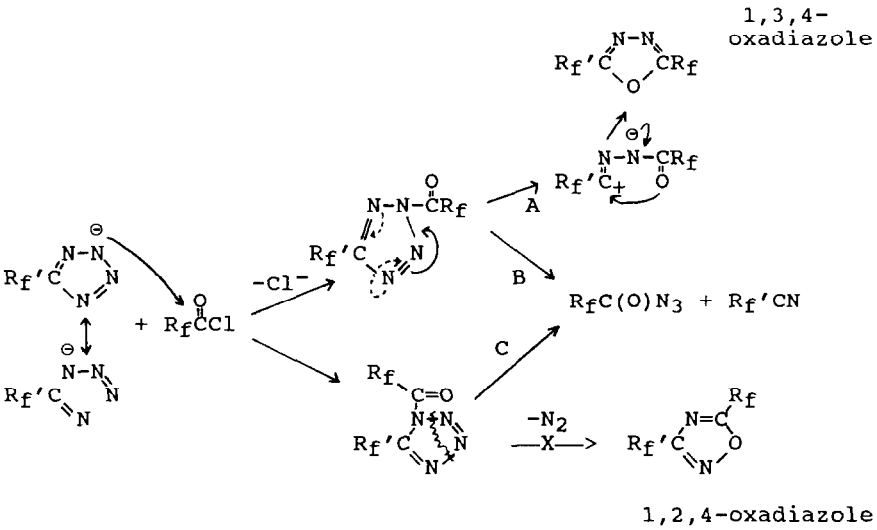


$R_f' = NF_2CF_2$; $R_f = CF_3$ (**8**), C_2F_5 (**9**), C_3F_7 (**10**)

$R_f' = C_2F_5$; $R_f = CF_3$ (**11**), C_2F_5 (**12**)

Compounds **8-12** are colorless, volatile stable liquids. These compounds have characteristic infrared absorption bands (Table I) assignable to $\nu_{C=N}$ that are greatly different from the 1,2,4-oxadiazole isomers (**1-3**) where the N-C=N band appears at a higher frequency than for O-C=N and thus $\Delta\nu$ is larger (compounds **8**, **9**, and **10** in Table I). It should be noted that the fluorine-fluorine coupling in the 1,3,4-oxadiazoles is invariably greater than in 1,2,4-oxadiazoles, **1-3**, e.g. $^{J}NF_2\text{-}R_f$ decreases in the order $R_f = CF_3 > C_2F_5 > C_3F_7$ (4.7, 3.40, 3.35 Hz) while for 1,2,4-oxadiazoles, $J < 2.6$ Hz (Table I). In the CI mass spectrum, for **8**, **9** and **10**, M^++1, M^+ and M^+-NF_2 occur at m/e 240, 239, 187; 290, 289, 237; 340, 339, 287, respectively.

In these reactions, the presence of $R_fC(O)N_3$ [17] and R_fCN as byproducts can be explained by the formation of two intermediate species that disproportionate by two different pathways, A and B or C [18-21]. Path A appears to be predominant since the major product is the 1,3,4-oxadiazole.



It is likely, based on earlier observations [21], that nucleophilic attack is predominantly by N-2 on the carbonyl carbon of $R_fC(O)Cl$. This would be favored sterically and electrostatically. The total absence of the 1,2,4-oxadiazole suggests that the contribution to the overall reaction by attack of N-1 must be small at best. This is supported by the presence of relatively small amounts (≤5%) of $R_fC(O)N_3$ and $R_f'CN$ which are the only feasible decomposition products of the N-1 intermediate (path C) and also are products of the decomposition of the N-2 intermediate (path B). The formation of the latter products would decrease formation of the 1,3,4-oxadiazole (path A) which, however, occurs in greater than 80% yield. These observations support N-2 as the attacking species and thus as a very major, if not sole, route to the observed product.

EXPERIMENTAL

Materials

Reagents were purchased or prepared as indicated: perfluorocarboxylic acid chlorides (PCR); hydroxylamine hydrochloride and sodium azide (J. T. Baker); difluoroaminodifluoroacetonitrile [3], sodium (difluoroamino)difluoromethyl-

tetrazolate [6,7] and (difluoroamino)difluoroacetamidoxime [1] by literature methods.

General Procedures

A Perkin-Elmer 1710 Fourier transform infrared spectrometer, a JEOL FX90Q Fourier transform NMR spectrometer and a VG 7070HS mass spectrometer were used to record the spectral data. Gases and volatile liquids were manipulated in a Pyrex vacuum system equipped with a Heise-Bourdon tube and Televac thermocouple pressure gauges. Elemental analyses were performed by Bellar Mikroanalytisches Laboratorium, Göttingen, FRG.

Reaction of (difluoroamino)difluoroacetamidoxime with oxalyl chloride

To (difluoroamino)difluoroacetamidoxime (1.5 mmol) in anhydrous Et_2O was added oxalyl chloride (0.75 mmol) at -196 °C. After the mixture was held at -20 °C for ~0.5 h and agitated at 25 °C for ~0.5 h, an essentially quantitative yield of **5** was obtained upon removal of HCl and the solvent. Spectral data obtained for **5** are: IR (KBr disk): 3510 w, 3330 w, 1760 vs, 1656 vs, 1651 vs, 1575 m, 1210 s, 1190 s, 1140 s, 985 vw, 970 w, 920 m, 730 w, cm^{-1}; NMR ^{19}F Ø 17.72 (NF_2, br), -108.5 (CF_2). EI MS [m/e (species) intensity]: 376 (M^+) 0.6; 306 ($C_6F_6N_4O_4^+$) 0.3; 288 ($C_6HF_5N_4O_4^+$) 0.4; 250 ($C_6HF_3N_4O_4^+$) 0.1; 216 ($C_6F_2N_3O_4^+$) 1.6; 161 ($C_2H_3F_4N_3O^+$) 40; 145 ($C_2HF_4N_2O^+$) 5.2; 123 ($C_2F_3N_3^+$) 6.1; 109 ($C_2F_3N_2^+$) 69.1; 92 ($C_2H_2F_2N_2^+$) 100; 78 ($C_2H_2F_2N^+$) 19.8; 66 ($C_2N_3^+$) 65.5.

Compound **6**

A Pyrex glass tube that contained a mixture of **5** (0.75 mmol) and P_4O_{10} was evacuated, sealed and heated to 160 °C for 48 h. The product was distilled at 60 °C under dynamic vacuum (68% yield) and retained in a trap at -10 °C. Spectral data obtained are: IR (thin film): 1534 vw, 1481 s, 1384 m, 1227 vs, 1121 vs, 1194 vs, 1155 s, 1117 m, 1009 s,

966 s, 944 vs, 932 vs, 794 m, 668 m, 625 w, cm^{-1}; NMR ^{19}F Ø 22.00 (NF_2, br), -101.6 (CF_2, tr, J = 2.44); CI MS [m/e (species) intensity]: 342 (M^++2) 3.1; 341 (M^++1) 45; 321 (M^+-F) 8.4; 303 (M^++1-2F) 12.3; 288(M^+-NF_2) 100; 265 (M^++1-4F) 2.7; 264 (M^+-4F) 0.32; 250 (M^+-NF_4) 16.4; 236 (M^+-N_2F_4) 9.1; 198 (M^+-N_2F_6) 2.8; 149 ($C_4F_3N_2O$) 7.6; 92 ($C_2F_2NO^+$) 56.7; 83 (CF_3N^+) 11.3; 69 (CF_3^+) 28.3; 57 (C_2FN^+) 20.7. Anal. Calcd for $C_6N_6F_8O_2$: C, 21.18. Found: C, 21.04.

Compound **7**

Sodium (difluoroamino)difluoromethyltetrazolate **4** (1 mmol) was mixed with oxalyl chloride (0.5 mmol) and the vessel evacuated at -196 °C. After warming to 25 °C, the mixture was stirred for 72 h, and then to ensure complete reaction, it was heated at 60 °C for 0.5 h. The product was sublimed onto a cold finger under vacuum (yield ~80%). Spectral data obtained are: IR (KBr disk) 1763 vw,br, 1587 vvw, 1474 s, 1446 vvw, 1419 vw, 1373 s, 1314 vw, 1235 vs, 1196 vs, 1150 vs, 1111 s, 1065 vvw, 1019 s, 1002 vw, 983 m, 969 s, 956 s, 946 s, 929 vs, 796 vw, 760 vvw, 678 vw, 669 vw, 627 vvw, 614 w, 538 m, cm^{-1}; NMR ^{19}F Ø 23.6 (NF_2, br), -100.5 (CF_2, tr, J = 3.3 Hz); CI MS [m/e (species) intensity]: 342 (M^++2) 8.8; 341 (M^++1) 100; 321 (M^+-F) 4.5; 303 (M^++1-2F) 26.7; 302 (M^+-2F) 0.1; 289 (M^++1-NF_2) 23.7; 288 (M^+-NF_2) 71.5; 238 (M^+-CF_2NF_2) 238; 219 (M^+-CF_3NF_2) 4.3; 200 (M^+-CNF_6) 19.7; 186 ($C_5F_2N_4O_2^+$) 5.7; 90 ($C_2N_2F_2^+$) 8.5; 69 ($C_2N_2OH^+$) 31.9; 68 ($C_2N_2O^+$) 2.2.

Synthesis of **8**, **9** and **10**

The general procedure is as follows: compound **4** (1-1.5 mmol) and the appropriate perfluoroalkylacetonitrile (1-1.5 mmol) were combined in an evacuated vessel at -196 °C. The temperature was raised slowly to 25 °C, and the mixture was stirred for 72-96 h in the dark. Separation was accomplished by using trap-to-trap distillation with the products found in traps at -40 to -50 °C. Small amounts (≤5%) of R_fCN and $R_fC(O)N_3$ were stopped in colder traps and identified by their infrared spectra. Further purification was done by fractional

evaporation. Typical yields were 50-70%. Spectral data obtained are: For **8**: IR (gas) 1568 vw, 1559 w, 1420 m, 1313 vs, 1236 vs, 1197 vs, 1141 vs, 1105 m, 1016 m, 988 w, 965 m, 934 s, 759 m, 670 w, 620 vw, cm^{-1}; NMR ^{19}F Ø 23.0 (NF_2, br), -64 (CF_3), -100.7 (CF_2, tr, J = 4.7 Hz); CI MS [m/e (species) intensity]: 240 (M^++1) 100; 239 (M^+) 0.1; 220 (M^+-F) 14.2; 201 (M^++1-2F) 27.6; 188 (M^++1-NF_2) 38.4; 187 (M^+-NF_2) 44.7; 168 (M^+-NF_3) 10.9; 137 (M^+-CNF_4) 12.0; 102 (CF_4N) 1.4; 97 ($C_2F_3O^+$) 11.0; 95 ($C_2F_3N^+$) 2.0; 78 ($C_2F_2O^+$) 84.7; 69 (CF_3+) 89.6. Anal. Calcd for $C_4F_7N_3O$: C, 20.08; N, 17.57. Found: C, 20.66; N, 17.54. For **9**: IR (gas): 1560 w, 1511 vw, 1411 s, 1343 vs, 1298 s, 1241 vs, 1188 s, 1149 vs, 1112 vs, 1042 s, 1006 s, 940 vs, 934 s, 796 w, 756 m, 731 vw, 671 vw, 622 m, cm^{-1}; NMR: ^{19}F Ø 32.17 (NF_2, br), -83.4 (CF_3, tr, J = 2.60 Hz), 100.83 (CF_2, tr, $^{J}CF_2$-NF_2 = 3.40 Hz), 115.5 (CF_2, q, $^{J}CF_3$-CF_2 = 2.60 Hz); CI MS [m/e (species) intensity]: 290 (M^++1) 100; 270 (M^+-F) 16.7; 252 (M^++1-2F) 36.0; 251 (M^+-2F) 1.33; 238 (M^++1-NF_2) 33.8; 237 (M^+-NF_2) 60.9; 218 (M^+-NF_3) 10.4; 214 (M^++1-4F) 14.1; 187 (M^+-CNF_4) 17.0. Anal. Calcd for $C_5F_9N_3O$: C, 20.76; N, 14.53. Found: C, 20.90; N, 14.53. For **10**: IR (gas): 1735 vvw, 1561 w, 1410 m, 1351 s, 1299 s, 1249 vs, 1232 vs, 1205 s, 1183 s, 1146 s, 1126 w, 1080 w, 1020 w, 993 w, 965 w, 925 m, 882 m, 795 vw, 752 vw, 728 vvw, 632 vvw, 538 vvw, 409 vvw, cm^{-1}. NMR: ^{19}F Ø 23.34 (NF_2, br), -80.33 (CF_3), -100.8 (CF_2-N), -113 (CF_2), -126 (CF_2); CI MS [m/e (species) intensity]: 340 (M^++1) 100; 339 (M^+) 1; 320 (M^+-F) 10; 287 (M^+-NF_2) 41; 268 (M^+-NF_3) 13; 237 (M^+-CNF_4) 12; 169 ($C_3F_7^+$) 45.9; 133 ($C_2F_5H^+$) 2.4; 131 ($C_3F_5^+$) 6.2; 119 ($C_2F_5^+$) 7; 100 ($C_2F_4^+$) 6.3; 69 (CF_3^+) 73.2, 68 ($C_2N_2O^+$) 0.7. Anal. Calcd for $C_6F_{11}N_3O$: C, 21.24; N, 12.39. Found: C, 21.72; N, 12.52.

Synthesis of **11** and **12**

Compounds **11** and **12** were obtained using sodium pentafluoroethyltetrazolate and trifluoroacetyl chloride or pentafluoropropionyl chloride, respectively. Each was characterized by obtaining IR, MS, NMR and elemental analysis data and compared with data cited in the literature [15-16].

Yields of **11** and **12** were >80%. The yields quoted in the literature were invariably less (~25-30%).

ACKNOWLEDGEMENT

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