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# SYNTHESES AND DEGRADATIONS OF FLUORINATED HETEROCYCLICS. IV. IMIDOYLAMIDOXIMES, 1,2,4-OXADIAZOLE PRECURSORS

K.J.L. PACIOREK, T.I.ITO, J.H. NAKAHARA, J. KAUFMAN, R.H. KRATZER and R.W. ROSSER

Ultrasystems, Inc., 2400 Michelson Drive
Irvine, Calif. 92715 (U.S.A.)

## SUMMARY

Perfluoroalkylether amidoximes free from amide-contamination were prepared from imidate esters. The amidoximes were stable at 110°C; at ~170°C partial decomposition to 1,2,4-oxadiazoles, admixed with other compounds, took place. Interactions between nitriles and amidoximes at 50°C resulted in the formation of imidoylamidoximes; these dissociated readily into their constituents when subjected to higher temperatures. At 70°C and above, in the presence of excess nitrile or other ammonia acceptors, the imidoylamidoximes afforded high yields of the corresponding 1,2,4-oxadiazoles.

## INTRODUCTION

It has been established that perfluoroalkylether substituted 1,2,4-oxadiazoles exhibit excellent thermal, thermal oxidative, and hydrolytic stabilities [1]. Thus, the 1,2,4-oxadiazole ring system would seem to offer an attractive linkage for chain extending polyperfluoroalkylethers. The main

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*National Aeronautics & Space Administration, Ames Research Center, Moffett Field, Calif. 94035 U.S.A.

problem with this approach, especially for practical applications, is that the conventional reaction sequence leading to 1,2,4-oxadiazoles requires the interaction of a moisture sensitive acyl halide with an amidoxime followed by high temperature phosphorus pentoxide dehydration [1,2].

Consequently, the objective of the current study was to explore other synthetic routes more suitable for the formation of polymeric materials in high yields under practical conditions.

## RESULTS AND DISCUSSION

An amidoxime with its C-N-O arrangement is a logical starting material for the preparation of 1,2,4-oxadiazoles. It has been found, however, that the formation of perfluoroalkylether amidoximes from the respective nitriles, regardless of reaction conditions, solvent, and reagent purification procedures, resulted in the production of 15-20% amide as determined by gas chromatography and infrared spectral analysis. Utilizing the imidate ester instead of the nitrile in the reaction with hydroxylamine gave an amide-free amidoxime.

Perfluoroalkyl substituted amidoximes were found [2] to decompose at ~170°C to yield 30-40% of the corresponding 1,2,4-oxadiazoles. A perfluoroalkylether amidoxime, namely $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$, was recovered unchanged after being heated at 110°C for 24 hr. At higher temperatures, a spectrum of products was observed; these are listed in Table 1. Based on the amidoxime recovered, it is apparent that in the experiments conducted in sealed ampoules, a relatively low degree of decomposition took place, most likely due to an inhibiting action of the volatile pyrolysis products, e.g.,water, nitrous oxide and ammonia. When these were permitted to escape as soon as formed,by performing the reaction under nitrogen by-pass, a higher conversion to oxadiazole was observed. It is interesting that in all instances 1,2,4-oxadiazoles substituted by perfluoroalkylether chains shorter than those present in the original amidoxime were isolated. This finding indicates that the pyrolysis of amidoximes to form oxadiazoles is not a simple process and cannot be adequately described by the elimination of one mole each of hydroxylamine and ammonia for every two moles of amidoxime undergoing decomposition.

TABLE 1

Product distribution: thermal treatment of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$

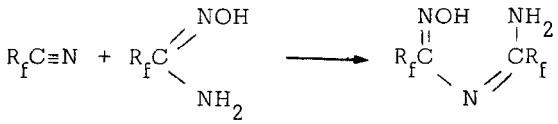
| Compounds | Conditions | | |
|---|---|---|---|
| | 180°C, 40 hr[a] | 204°C, 24 hr[a] | 204°C, 24 hr[b] |
| $N_2O$ | 0.2[c] | 0.4 | - |
| $NH_3$ | ? | 0.05 | - |
| $C_3F_7OCF(CF_3)H$ | 0.7 | 0.2 | - |
| $C_3F_7OCF(CF_3)CF_2H$ | 0.05 | 0.5 | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$ | 0.7 | 0.5 | - |
| $CF_3[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 5.2 | 3.9 | 0.7 |
| $C_3F_7OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 9.1 | 8.1 | 7.3 |
| $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_2[C_2N_2O]$ | 18.8 | 27.8 | 62.6 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH_2$ | 2.8 | 6.1 | 0.4 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ | 62.5 | 52.5 | 22.9 |
| $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_3$ | - | - | 0.8 |

a) This test was performed in an evacuated, sealed pyrex ampoule.

b) This test was performed in an inert atmosphere enclosure.

c) The products are given in weight percent based on the relative GC areas assuming all the compounds to have the same GC response per unit weight.

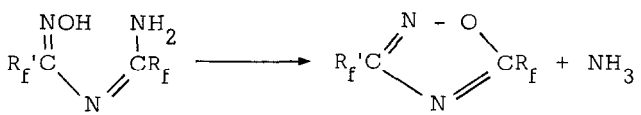
The structure of an amidoxime is basically identical with that of an amidine with the exception that here a NOH moiety replaces the NH group in an amidine. Perfluorinated amidines, when treated with an excess of perfluoroalkyl or perfluoroalkylether nitriles, form imidoylamidines [3]. In an analogous fashion, one would expect the interaction of an amidoxime with a nitrile to yield the corresponding imidoylamidoxime, i.e.,



As can be seen from Table 2, at room temperature only a small quantity of the imidoylamidoxime was formed, as determined by nitrile consumed and mass spectral analysis of the involatile residue. At 50°C, the reaction was quantitative; the imidoylamidoxime produced was free of impurities as shown by gas chromatography. The imidoylamidoxime derived from the short chain nitrile exhibited a mass spectral breakdown pattern consistent with its structure characterized by its parent peak m/e 821 (100%). Due to mass spectrometer limitations, no parent peak could be observed for the imidoyl-amidoxime containing the $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$ side chain.

Conducting the reaction at 110°C failed to result in the isolation of an imidoylamidoxime. Instead, the mixture of products listed in Table 3 was afforded.

The unsymmetrical 1,2,4-oxadiazole, which could have originated only from the imidoylamidoxime precursor, together with the nitrile derived imidoylamidine were the two major products formed. This finding would imply that the excess of the nitrile employed in Test No. 4 reacted with the ammonia evolved in the ring closing process, i.e.



giving the imidoylamidine found.

TABLE 2

Amidoxime-nitrile interactions

| Test No. | Reagents Used | | Temp °C | Time hr | $R_f'CN$ Consmd : $R_fC(=NOH)NH_2$ Employed | Yield % |
|---|---|---|---|---|---|---|
| | $R_f'CN$[a] mmol | $R_fC(=NOH)NH_2$[b] mmol | | | | |
| 1 | 1.86 | 0.96 | 23 | 16 | 0.15 : 1 | 8 |
| 2 | 4.82 | 1.97 | 50 | 89 | 1.02 : 1 | 100 |
| 3 | 2.43 | 0.92 | 50 | 41 | 0.92 : 1 | 86 |
| 4 | 1.70 | 0.72 | 110 | 72 | 2.00 : 1 | 0 |

a) In tests No. 1, 2, and 4, the $R_f'$ group was $C_3F_7OCF(CF_3)$; in test No. 3, the $R_f'$ group was $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$.

b) The amidoxime employed in all the tests was $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-$C(=NOH)NH_2$.

TABLE 3

Product distribution: interaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ and $C_3F_7OCF(CF_3)CN$ at 110°C for 72 hr in a sealed system

| Compounds | Percent |
|---|---|
| $C_3F_7OCF(CF_3)CN$ | 14.9[a] |
| $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_2[C_2N_2O]$ | 5.2[b] |
| $C_3F_7OCF(CF_3)C(O)NH_2$ | 3.6[a] |
| $C_3F_7OCF(CF_3)C(=NH)N=C(NH_2)CF(CF_3)OC_3F_7$ | 56.7[a] |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ | 20.1[b] |
| $C_3F_7OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 68.7[b] |

a) The yield is given with respect to $C_3F_7OCF(CF_3)CN$ originally employed.

b) The yield is given with respect to $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ consumed.

To determine whether the ring closure occurs indeed in the vicinity of 110°C, pure imidoylamidoxime was subjected to the heat treatment. Based on the data given in Table 4,

TABLE 4

Product distribution: heat treatment of imidoylamidoxime, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)-N=C(NH_2)CF(CF_3)[OCF_2CF(CF_3)]_2OC_3F_7$, at 110°C for 18 hr [a]

| Products | %[b] |
|---|---|
| $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN$ | 17.3 |
| $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 16.2 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ | 44.4 |
| imidoylamidoxime | 9.6 |
| $[C_3F_7O(CF(CF_3)CF_2O)_2CF(CF_3)]_2C(=NH)-N=C(NH_2)$ | 12.4 |

a) The quantity of the imidoylamidoxime used was 210 mg; although a reflux condenser was employed, only 150 mg were present at the end of the reaction. Based on the product distribution given, it is obvious that the observed weight loss was due to the volatilization of the nitrile, $C_3F_7O[CF(CF_3)CF_2O]_2-CF(CF_3)CN$.

b) These are weight percent based on the relative GC areas assuming all the compounds to have the same GC response per unit weight.

It is apparent that at 110°C the dissociation of the imidoylamidoxime is the predominant process; furthermore, it would seem that an ammonia acceptor is necessary to promote the desired ring closure. In a closed system, the excess of nitrile fulfilled this function as evident from the results listed in Table 3, where a ~69% yield of the unsymmetrical oxadiazole was obtained. However, for the preparation of a polyoxadiazole, this type of ammonia scavenging is not suitable due to the simultaneous formation of imidoyl-amidine as a by-product which at elevated temperatures, ~200°C, would be transformed into triazine.

Accordingly, a series of experiments was carried out to evaluate the efficiency of different organic and inorganic acids as promoters of the imidoylamidoxime cyclization. The results of these investigations are given in Tables 5 and 6. Examination of these tabulations shows that the longer chain perfluoroalkyl acids, as represented by n-perfluorooctanoic acid, afford the best yield of the desired unsymmetrical oxadiazole. However, some interaction of the acid with either imidoylamidoxime or the liberated amidoxime must also occur as indicated by the production of the perfluoroalkylether, perfluoro-n-heptyl-1,2,4-oxadiazole. The presence of amidoxime itself shows that even at 50°C, some dissociation of the imidoylamidoxime does take place. Due to the procedures used for the workup of the reaction mixtures, the evolved perfluoroalkylether nitrile is not included in the analyses. In certain instances, very poor separation of the amidoxime and imidoylamidoxime was achieved and in these cases, the two values were combined. The perfluoroalkylether acid, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2H$, in view of the inherent steric hindrance of the carboxyl function attached to a tertiary carbon atom [4], was found to be a less effective ring closing agent than n-perfluorooctanoic acid. On the other hand, due to the steric hindrance, only a trace of the 1,2,4-oxadiazole incorporating the acid was formed. Of the mineral acids, the main reaction of sulfuric acid was hydrolysis of the nitrile portion of the imidoylamidoxime molecule. Phosphoric acid and phosphorus pentoxide in their action were comparable to the perfluorinated acids, although longer reaction times were required to achieve a comparable extent of transformation.

## EXPERIMENTAL

### General

Infrared spectra were recorded using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. The oxadiazoles listed in Tables 1 and 5 have not been isolated as such; these compounds were identified by GC-MS. The identifications were made based on the

TABLE 5

Product distribution: interaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)-N=C(NH_2)CF(CF_3)OC_3F_7$ with perfluorinated acids

| Compound | $n-C_7F_{15}CO_2H$ | | $CF_3CO_2H$ | | | $R_fOR_fCO_2H$[b] | |
|---|---|---|---|---|---|---|---|
| | 70°C 19 hr | 101°C 17 hr | 23°C 48 hr | 50°C 22 hr | 70°C 20 hr | 50°C 24 hr | 70°C 24 hr |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF(CF_3)OC_3F_7$ | 71.0[a] | 48.7 | 15.7 | 19.9 | 25.1 | 13.1 | 48.5 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 1.1 | 1.3 | - | - | - | - | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]C_7F_{15}$ | 6.2 | 37.1 | - | - | - | - | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]C_2F_5$ | - | - | - | - | - | 0.1 | 0.2 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF_3$ | - | - | 5.4 | 6.0 | 5.0 | - | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)[C_2N_2O]CF(CF_3)[OCF_2CF(CF_3)]_2OC_3F_7$ | - | - | - | - | - | - | T[c] |
| $n-C_7F_{15}CONH_2$ | - | 1.8 | - | - | - | - | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH_2$ | - | 1.8 | 0.7 | 0.8 | 5.6 | - | 0.1 |
| $C_3F_7OCF(CF_3)CONH_2$ | 3.3 | 4.0 | 0.9 | 0.7 | 1.4 | 2.6 | 2.2 |
| $C_3F_7OCF(CF_3)C(=NH)NH_2$ | - | - | - | - | - | 3.3 | 7.4 |
| $C_3F_7OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OC_3F_7$ | - | - | - | - | - | 0.3 | - |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ | 18.5 | 5.4 | 72.7 | 67.0 | 46.3 | 55.7 | 40.2 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)-N=C(NH_2)CF(CF_3)OC_3F_7$ | - | - | | | 16.4 | 24.7 | 0.8 |

a) These are weight percent based on the relative GC areas assuming all the compounds to have the same GC response per unit weight.

b) The specific acid employed here was $C_3F_7O[CF(CF_3)CF_2O]_2CO_2H$.

c) Trace.

TABLE 6

Product distribution: interaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)-N=C(NH_2)CF(CF_3)OC_3F_7$ with inorganic acids

| Compound | $H_2SO_4$ 70°C 22 hr | $H_3PO_4$ 70°C 24 hr | $H_3PO_4$ 70°C 90 hr | $P_2O_5$ 70°C 91 hr |
|---|---|---|---|---|
| $C_3F_7OCF(CF_3)[C_2N_2O]CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ | 12.9[a] | 12.1 | 52.1 | 46.4 |
| $C_3F_7OCF(CF_3)CONH_2$ | 40.9 | 5.1 | 5.4 | 5.1 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CONH_2$ | 3.1 | 0.5 | 0.5 | 0.2 |
| $C_3F_7OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OC_3F_7$ | - | | - | |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$ | 33.7 | 79.2 | 40.9 | 43.3 |
| $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)-N=C(NH_2)CF(CF_3)OC_3F_7$ | 7.9 | | 0.4 | 3.5 |

a) These are weight percent based on the relative GC areas assuming all the compounds to have the same GC response per unit weight.

comparison of the GC retention times and fragmentation patterns with the homologues previously reported [1,6]. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of the amidoxime, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NOH)NH_2$

In an inert atmosphere enclosure to a stirred solution of hydroxylamine hydrochloride (0.28 g, 4.03 mmol) in methanol (8 ml) was added sodium methoxide prepared by dissolving sodium (0.09 g, 3.9 mg atom) in methanol (3 ml). To this mixture was added slowly at room temperature $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)OCH_3$ [5] (2.01 g, 3.95 mmol) and stirring was continued for 72 hr at this temperature before evaporating the solution in vacuo. A solid-liquid mixture resulted; it was taken up in Freon-113 and the solid, NaCl, was filtered off. The material obtained on evaporation of Freon-113 was amide-free as shown by infrared spectral analysis and gas chromatography. It was purified from residual imidate ester by distillation giving 1.42 g (71% yield) of pure product, bp 75-76°C at 2.1 mm Hg. The material solidified on standing; based on differential thermal analysis, mp 26°C, bp 212°C. Anal. Calcd. for $C_9H_3F_{17}N_2O_3$: C, 21.19; H, 0.59; N, 5.49. Found: C, 21.54; H, 0.84; N, 5.30.

Pyrolysis reactions, Tables 1 and 4

All the pyrolysis reactions were performed on 0.2 to 0.5 g samples either in vacuo in sealed ampoules or under nitrogen by-pass. In the former case after the selected heat treatment, the ampoule was opened to the vacuum line and the contents separated into room temperature volatile and involatile components. The volatile materials, if applicable, were further separated into liquid nitrogen condensible and non-condensible products. Each fraction was then weighed or, in the case of the non-condensibles, measured and examined by infrared spectroscopy and GC-MS analysis.

Imidoylamidoxime preparations, Table 2

In vacuo onto a given quantity of perfluoroalkylether amidoxime was condensed the denoted quantity of perfluoroalkylether nitrile. Subsequently, the ampoule was sealed and subjected to the selected heat treatment. At the conclusion of the test, the ampoule was opened to the vacuum line and the components were separated and analyzed as described above for the pyrolysis reactions. The room temperature involatile fraction obtained in Test No. 2 was found by GC-MS to consist of pure imidoylamidoxime, $C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)C(=NOH)N=C(NH_2)CF(CF_3)OC_3F_7$ (n.c.): ir 2.85, 3.0 (N-H); 3.15 (OH); 5.95 (C=N) and 7.25-9.0μ (C-F); mass spectrum m/e 821 (100%) M; m/e 802 (21%) M-F; m/e 536 (11.3%) M-$CF(CF_3)OC_3F_7$; m/e 370 (19.0%) M-$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$. This material could not be distilled due to its thermal instability. Anal. Calcd. for $C_{15}H_3F_{28}N_3O_4$: C, 21.94; H, 0.37; N, 5.12; MW, 821.15. Found: C, 22.40; H, 0.67; N, 5.10; MW, 858.

Evaluations of ammonia acceptors, Tables 5 and 6

All the tests were carried out in the absence of solvent under nitrogen by-pass; the quantity of imidoylamidoxime employed varied between 0.3 and 0.5 g. In all instances, an equimolar quantity of the ammonia acceptor was utilized. After the conclusion of an experiment, the reaction mixture was taken up in Freon-113, filtered to remove the ammonium salt, and the filtrate was subjected to GC-MS analysis.

CONCLUSIONS

Perfluoroalkylether amidoximes, in a manner analogous to that exhibited by amidines, were found to combine with perfluoroalkylether nitriles to yield

[redacted]

than the corresponding imidoylamidines. The imidoylamidoximes can be transformed at moderate temperatures in relatively high yields into 1,2,4-oxadiazoles. This ring closure process requires the presence of ammonia acceptors.

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