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Reactions of poly(hexafluoropropylene oxide) perfluoroisopropyl ketone with various amines

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Abstract

The reaction of poly(hexafluoropropylene oxide) perfluoroisopropyl ketone, perfluoroethyl perfluoroisopropyl, or bis-perfluoroisopropyl ketone with various amines has been studied and the products identified. A comparison of the reactivity of the ketones with different amines is made and identified by mass spectroscopy. The reaction of diethyl amine with all three ketones leads to two unexpected products and the mechanism of their formation is considered.

Keywords: Poly(hexafluoropropylene oxide); Fluorinated ketones; Amines

1. Introduction

Poly(hexafluoropropylene oxide), poly(HFPO), is a member of an important class of compounds, perfluoropolyethers (PFPEs), which function as thermally and chemically stable lubricants, greases and fluids for corrosive environments. Since the polymer was first reported in the 1960s [1,2] many modifications have been made to the acyl fluoride terminated intermediate, opening up a wide variety of new chemistries.

Among the possible terminal groups observed in poly(HFPO) is a perfluoroketone, for example poly(HFPO) perfluoroisopropyl ketone. This ketone can be manufactured (see Scheme 1) through the reaction of poly(HFPO) acid fluoride with hexafluoropropylene (HFP) in the presence of a suitable catalyst such as cesium fluoride [3,4].

Simple fluorinated ketones such as hexafluoroacetone, add to nucleophiles such as amines easily. The intermediate hemiaminal is more stable than its alkyl counterpart and the equilibrium favors its formation [5,6]. This is, in part, due to the increased positive charge on the carbonyl group caused by the electron withdrawing effect of the fluorine atoms. As the fluorinated hemiaminal is a stable species, its dehydration to the imine does not occur readily. However, it is possible to induce the hemiaminal to dehydrate. Middleton and Krespan outlined a synthesis that takes advantage of the relative acidity of the hydroxyl group whereby pyridine is added (see Scheme 2) to remove the hydroxyl proton and $POCl_3$ is added to bring about the dehydration [6].

Although fluorinated hemiaminals are relatively stable, it has been reported that over long periods of time they decompose into an amide and a hydrofluorocarbon [5]. Heat (see Scheme 3) accelerates the decomposition [6].

Hexafluoroacetone has been the focus of the majority of the reported studies between fluorinated ketones and amines. However, when either trifluoromethyl group of the hexafluoroacetone is replaced with a branched perfluorinated moiety, alternative chemistries ensue. Smith, Fawcett and Coffman outline the synthesis of branched bis-(perfluoroisopropyl) ketone [3]. They report that with the addition of nucleophilic reagents such as ammonia the ketone immediately cleaves into 2-hydroheptafluoropropane and perfluoroisobutanamide.

Lindner and Lemal discuss the effect of steric bulk on the stability of various hydrates and hemiketals of highly fluorinated ketones [7]. They found that as the steric crowding was reduced, the hydrate or hemiketal became more stable. We thought that this trend seen in the addition of water or alcohol to a fluoroketone might extend to addition of amines.

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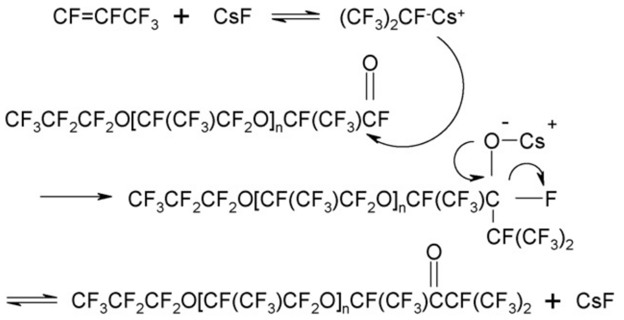
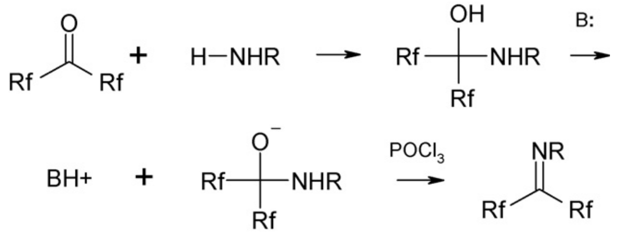


Scheme 1. Formation of poly(hexafluoropropylene oxide)perfluoroisopropyl ketone.

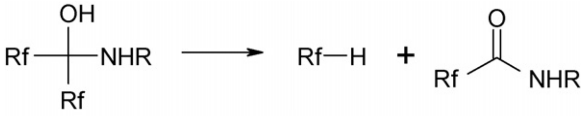


Scheme 2. Formation of the imine of a fluorinated ketone using base and $POCl_3$.

Poly(HFPO) perfluoroisopropyl ketone is highly hindered so its reactions with amines might be expected to react in a fashion similar to bis-(perfluoroisopropyl) ketone. The reactions of poly(HFPO) ketone with various amines were conducted to see how they compare to fluorinated ketones in the literature. Additionally, the same reactions were carried out with both a linear-branched and a bis-branched ketone, perfluoroethylisopropyl ketone and perfluorobis-isopropyl ketone, respectively.

Since the reaction between poly(HFPO)methyl esters and amines are known [8], a sample of poly(HFPO) methyl ester ($F(CF(CF_3)CF_2O)_3CF(CF_3)C(O)OCH_3$) was reacted with *n*-butylamine, pyrrolidine, and diethylamine. A study of these reaction products should provide an insight to the chemistries obtained from the reactions of the same amines with poly(HFPO) perfluoroisopropyl ketone.

Table 1 shows a summary of spectral and physical characterization of the starting reactants and Scheme 4 shows their synthesis.



Scheme 3. Decomposition of a hemiaminal into a fluoroalkane and a fluoroamide.

2. Results

2.1. Reactions of methyl ester with amines (pyrrolidine, n-butyl, and diethylamine)

The poly(HFPO) methyl ester was shown to produce poly(HFPO)-based amides in the presence of pyrrolidine and *n*-butylamine: $F(CF(CF_3)CF_2O)_3CF(CF_3)\text{-}C(O)N(CH_2)_3CH_3$ and $F(CF(CF_3)CF_2O)_3CF(CF_3)C(O)NHC_4H_9$, respectively. However, when mixed with diethylamine, the methyl ester decomposes to $F(CF(CF_3)CF_2O)_3CFHCF_3$. The decomposition of the methyl ester is highly unusual, however not without precedence [9].

2.2. Perfluoroethylisopropyl ketone reactions with amines (n-butyl, pyrrolidine, and diethylamine)

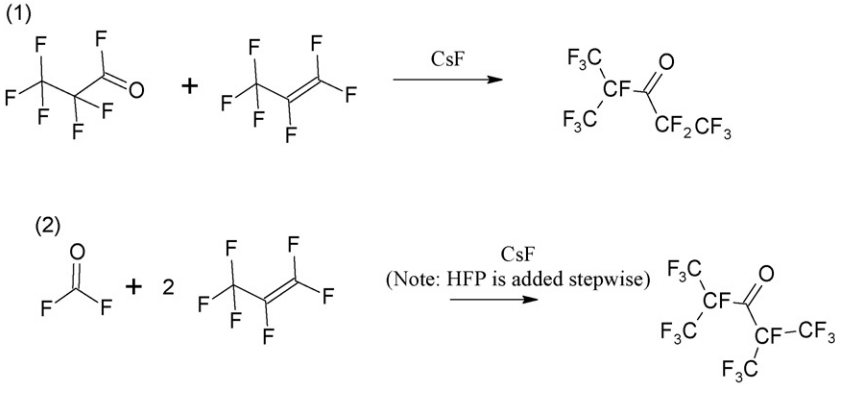
The reactions of the least sterically hindered perfluoroketone of this study with amines resulted in ketone decomposition, and did not form a hemiaminal. The reaction of the perfluoroethylisopropyl with *n*-butylamine and pyrrolidine, produced CF_3CFHCF_3 and the corresponding amide $CF_3CF_2C(O)NH(CH_2)_3CH_3$ and $CF_3CF_2C(O)NC_4H_8$, respectively. In the case of diethylamine, the reaction proceeded much more slowly, taking a few days to go to completion. As in the case for the other amines, $(CF_3)_2CFH$ is found, but additionally, $R_fC(O)NHCH_2CH_3$ and $R_fC(O)CH{=}CHN(CH_2CH_3)_2$ (where $R_f = CF_3CF_2–$) are formed.

2.3. Perfluorobis-isopropyl ketone reactions with amines (n-butyl, pyrrolidine, and diethylamine)

Similar to perfluoroethylisopropyl ketone, the perfluorobis-isopropyl did not form the hemiaminal. The reaction of the perfluorobis-isopropyl with *n*-butylamine and pyrrolidine produced CF_3CFHCF_3 and the corresponding amides $(CF_3)_2CFC(O)NH(CH_2)_3CH_3$ and $(CF_3)_2CFC(O)NC_4H_8$),

Table 1
Starting material general characteristics

	Ethylisopropylketone	Bisisopropyl ketone	Poly(HFPO)$_4$ isopropyl ketone	Poly(HFPO) methyl ester
MW	316	366	814	676
CI (MS)	317 ($M + H^+$)	367 ($M + H^+$)	463 (M − 2HFPO + F)	N/A
EI (MS)	69, 119, 197	69, 169, 197	147, 169, 197	59, 131, 169
^{19}F NMR				
$(CF_3)_2CF$–	−192.4	−189.8	−190.2	–
$(CF_3)_2CF$–	−75.6	−75.2	−75.1,	−75.4
CF_3CF_2–	−83.8	–	–	–
CF_3CF_2–	−122.4 (d)	–	–	–
$CF_3CF_2CF_2O$–	–	–	−146.0	−146.0



Scheme 4. Formation of the perfluoroketone.

respectively. In the case of diethylamine, again the reaction took several days and produced $(CF_3)_2CFH$, $R_fC(O)NHCH_2CH_3$ and $R_fC(O)CH{=}CHN(CH_2CH_3)_2$ (where $R_f = (CF_3)_2CF{-}$).

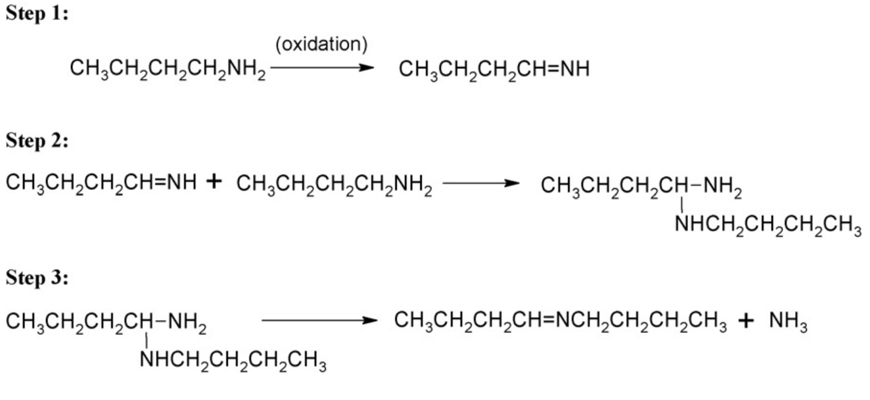
2.4. Poly(hexafluoropropylene oxide) perfluoroisopropyl ketone reactions with amines (n-butyl, pyrrolidine, and diethylamine)

The reactions of the poly(HFPO)perfluoroketone with *n*-butylamine gave the primary products of $(CF_3)_2CFH$ and $F[CF(CF_3)CF_2O]_3\ CF(CF_3)C(O)NH(CH_2)_3CH_3$ with trace amounts of $(CF_3)_2CFC(O)NH(CH_2)_3CH_3$, $F[CF(CF_3)CF_2O]_3\ CFHCF_3$, $C_3H_7CH{=}NC_4H_9$ and poly(HFPO)$_n$CF(CF$_3$)-C(O)NH$_2$. The reaction with pyrrolidine produced $(CF_3)_2CFH$ and $F[CF(CF_3)CF_2O]_3CF(CF_3)CONC_4H_8$ with trace amounts of $(CF_3)_2CFCONC_4H_8$, $F(CF(CF_3)CF_2O)_3CFHCF_3$ and a speculated, non-isolated, oligomer of pyrrolidine. When the poly(HFPO)perfluoroisopropyl ketone was reacted with diethylamine $F(CF(CF_3)CF_2O)_3CFHCF_3$ was formed, along with two products, $F[CF(CF_3)CF_2O]_3CF(CF_3)C(O)NHCH_2CH_3$ and $F[CF(CF_3)CF_2O]_3CF(CF_3)C(O){-}CH{=}CHNCH_2CH_3$, respectively. The hemiaminal did not form.

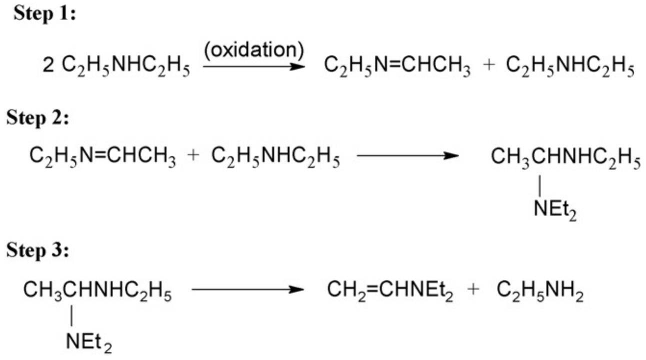
3. Discussion

The products from the reactions of perfluorinated ketones with amines, are dictated by two factors; the formation of the insipient negative charge on the leaving group and the amine steric bulk. The evidence of the influence of the first factor can be found in the products of the reaction of perfluorinated ketones with the three amines. In all cases the CF_3CFHCF_3 is the principal leaving group. We speculate the initial step in the reaction is the formation of the non-isolatable thermally unstable hemiaminal. The leaving perfluoroisopropyl better stabilizes the forming carbanioic center and thus primarily CF_3CFHCF_3 is observed. Another example of this effect is seen in the reaction of poly(HFPO) methyl ester with diethylamine. The product poly(HFPO)-CFHCF$_3$, is formed due to the ability of the poly(HFPO) segment to better stabilize the carbanioic center than the methoxy group [9].

Thus, with the exception of diethyl amine, in the case of the ketones and the methyl ester, the resulting co-products are the perfluoroisobutanamide or the *N*-tetramethylene amide. Another unusual finding in the case of the *n*-butylamine and pyrrodine $C_3H_7CH{=}NC_4H_9$ or what appears to be an oligomer of pyrrolidine were observed, respectively. We suspect the formation of the imine, $C_3H_7CH{=}NC_4H_9$, follows the synthesis found in Scheme 5. The polymer of pyrrolidine could be formed in a similar manner. Unexpectedly, the amines appear to be in an oxidizing atmosphere where the first intermediate must be the simple imine. A reason for the imine formation could be due to the electron-deficient carbonyl carbon attracting a hydride from the amine, followed by a proton loss from the nitrogen. This imine then further reacts with another equivalent of amine leading to free ammonia and the alkyl-substituted



Scheme 5. Formation of imine using butyl amine.

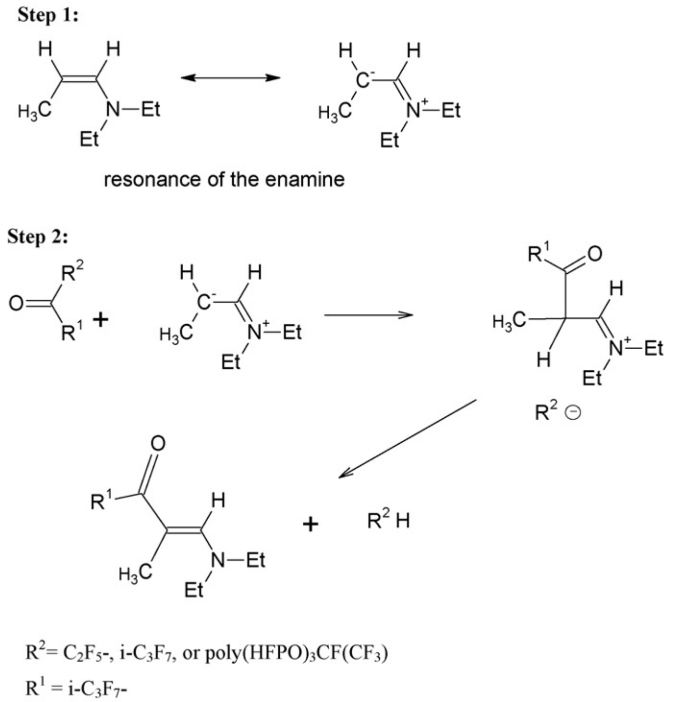


Scheme 6. Formation of imine and enamine using diethyl amine.

imine. Evidence of free ammonia is observed in the case of the poly(HFPO) perfluoroisopropyl ketone where the simple amide (–C(O)NH_2) was observed.

Unlike the reaction of the ketones with *n*-butylamine and pyrrolidine, the products formed during the reaction of the ketones with diethylamine are less intuitive. Instead of the expected *N*,*N*-diethylamide, two unexpected compounds, $R_fC(O)NHCH_2CH_3$ and $R_fC(O)CH{=}CHN(CH_2CH_3)_2$, are found. It can be speculated that the formation of these compounds arise from two new compounds, ethylamine and *N*,*N*-diethylaminoethylene, created in the reaction mixture (excess diethylamine). This reaction environment also appears to be in an oxidative in nature. The genesis of these two new compounds is outlined above in Scheme 6.

Ethylamine, reacts like *n*-butylamine with methyl ester, or *n*-butylamine with the various ketones producing the observed *N*-ethylamide. The *N*,*N*-diethylaminoethylene can act as a nucleophile and react with the various ketones to produce the observed *N*,*N*-diethylaminoethylene perfluoroalkyl(ether) ketone (Scheme 7).



Scheme 7. Formation of perfluoroalkyl(ether) *N*,*N*-diethylaminoethylene ketone.

While pyrrolidine and diethylamine have similar basicities [10], the steric bulk of diethyl amine slows precipitously from a few hours to a few days. This rate reduction allows time for the secondary reaction of diethyl amine to form ethylamine and *N*,*N*-diethylaminoethylene.

4. Conclusions

The original premise of the work was to prepare new fluorinated imines from perfluorinated ketones. Although, no new perfluoro imines were observed, a rich variety of chemistries was observed in reacting different amines with perfluoroisopropyl perfluoroketones. In each case the perfluoroisopropyl group is lost preferentially, the trend being branched side chains are lost in preference to normal side chains and perfluoroisopropyl in preference to poly(HFPO) (both branched). In these reactions where excess amine is incorporated, enamines from imine–enamine tautomerism can form and gives rise to perfluorinated vinyl ketone amines (see Schemes 5–7).

The reactions of the amines with poly(HFPO) methyl ester to form the appropriate amide was helpful in understanding the reactions of the amines with ketones. But in the case of diethylamine only $F[CF(CF_3)CF_2O]_3CFHCF_3$ was observed.

5. Experimental

General. All analysis were carried out using a 5890N Gas Chromatograph with a 5973N Mass Selective Detector with either CI (Methane) or EI detectors. The Gas Chromatograph was equipped with a 30 m × 0.250 mm, 0.25 μm df, DB-1 column. The initial temperature of 60 °C was held for 2 min and then increased at 10 °C/min to 250 °C and held for 15 min. A 1:50 split was used. Only those peaks characteristic of the compound in question or high in intensity are reported for the mass spectral data. The characteristic fragments of poly(HFPO) are: 69 (CF_3^+); 100 ($C_2F_4^+$); 119 ($C_2F_5^+$); 169 ($CF_3CF_2CF_2^+$).

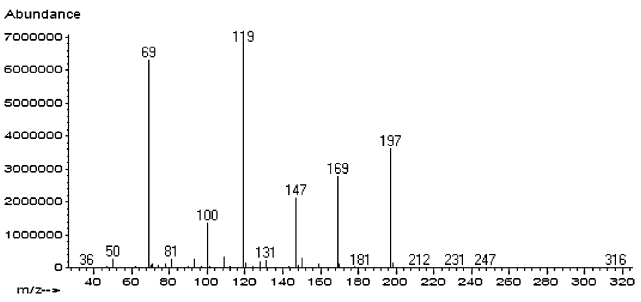
NMR analysis of some of the products was conducted on a Bruker DRX 400 MHz spectrometer. The experimental procedures for the reactions with *n*-butylamine, diethylamine, and pyrrolidine are all similar so a generic procedure is given. *n*-Butylamine, diethylamine and pyrrolide were purchased from Aldrich and used as received.

5.1. Starting materials characterization

Perfluoroethylisopropyl ketone $(CF_3CF_2C(O)CF(CF_3)_2$. GC/EI/MS (70 eV) retention time, *m/z* (fragment): 1.605 min, 69 (CF_3^+), 100 ($C_2F_4^+$), 119 ($CF_3CF_2^+$), 147 ($CF_3CF_2C(O)^+$), 169 ($(CF_3)_2CF^+$), 197 ($(CF_3)_2CFC(O)^+$) (see Fig. 1).

Perfluorobis-isopropyl ketone $((CF_3)_2CFC(O)CF(CF_3)_2$. GC/EI/MS (70 eV) retention time, *m/z* (fragment): 1.668 min, 69 (CF_3^+), 100 ($C_2F_4^+$), 119 ($CF_3CF_2^+$), 169 ($(CF_3)_2CF^+$), 197 ($(CF_3)_2CFC(O)^+$) (see Fig. 1).

(A) perfluoroethylisopropyl ketone



(B) perfluorodiisopropyl ketone

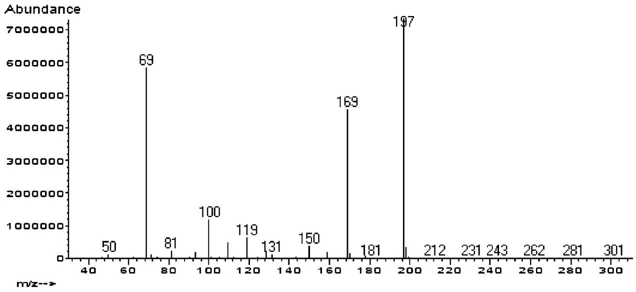


Fig. 1. EI/MS of fluorinated ketones: (A) perfluoroethylisopropyl ketone and (B) perfluorodiisopropyl ketone.

Poly(HFPO) perfluoroisopropyl ketone ($F[CF(CF_3)CF_2]_3CF(CF_3)C(O)\text{-}CF(CF_3)_2$). The poly(HFPO) perfluoroisopropyl ketone was obtained by adding cesium fluoride to hexafluoropropene and then introducing the poly(HFPO) acid fluoride. GC/EI/MS (70 eV) retention time, *m/z* (fragment): 3.936 min, 147 ($C(CF_3)CF_2O^+$), 197 ($(CF_3)_2CFC(O)^+$), 285 ($CF_3CF_2CF_2OCF(CF_3)^+$), 335 ($CF_3CF_2CF_2OCF(CF_3)CF_2^+$), 463 ($CF(CF_3)CF_2OCF(CF_3)\text{–}C(O)CF(CF_3)_2^+$) (see Fig. 2).

Poly(HFPO) methyl ester ($(F[CF(CF_3)CF_2]_nCF(CF_3)C(O)OCH_3$). where $n = 4, 5, 6$. The poly(HFPO) methyl ester was made from a low molecular weight cut of poly(HFPO) acid fluoride, where $n = 4, 5, 6$, by methanolysis of the acyl fluoride.

GC/EI/MS (70 eV) retention time, *m/z* (fragment): 6.447 min, 59 ($C(O)CH_3^+$), 131 ($CF_3CF_2C^+$), 150 ($CF_3CF_2CF^+$, 27), 325 ($CF(CF_3)CF_2OCF(CF_3)\text{–}C(O)OCH_3^+$) (see Fig. 2).

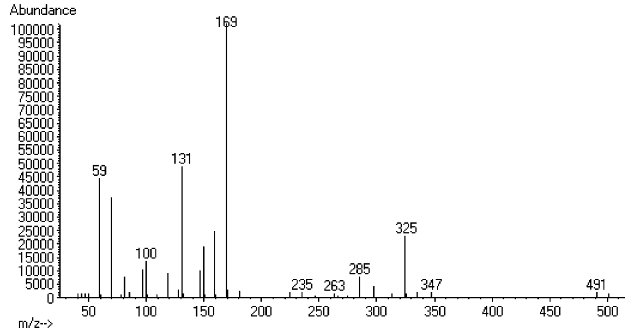
General procedure. Approximately, 0.25 g of the starting material was added to a 2 mL GC sample vial at room temperature. 0.75 g of Freon 11 ($CFCl_3$) was added to the vial. The vial was shaken. A fivefold molar excess of the amine was added to the vial, carefully so as not to mix the two layers. The vial was capped and then shaken. The reaction is exothermic in the case with *n*-butylamine and pyrrolidine. The contents of the vial were analyzed by GC/MS within 3–5 min of shaking. Further analysis by GC/MS was done until the reaction came to completion.

5.2. Reactions of perfluoro ketones with n-butylamine

5.2.1. Reaction of the perfluoroethylisopropyl ketone with n-butylamine

The reaction between the ketone and *n*-butylamine goes to completion immediately and is exothermic. The primary products of these reactions are $(CF_3)_2CFH$, $C_3H_7CH{=}NC_4H_9$, and the corresponding amide $CF_3CF_2C(O)NH(CH_2)_3CH_3$.

(A) poly(HFPO) methyl ester



(B) poly(HFPO) perfluoroisopropylketone

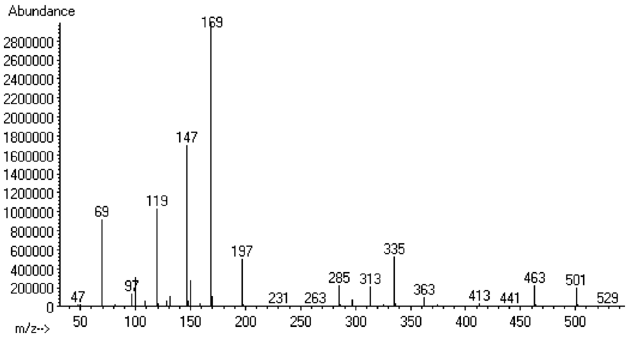


Fig. 2. EI/MS of poly(HFPO) derivatives: (A) MS of poly(HFPO) methyl ester and (B) MS.

$C_3H_7CH{=}NC_4H_9$ (*N*-butylidene-1-butanamine) GC/EI/MS (70 eV,) retention time, *m/z* (fragment): 8.604 min, 42 ($CH_3CH_2CH^+$); 56 ($CH_3CH_2CH_2CH^+$); 57 ($CH_3CH_2CH_2CH_2^+$); 70 ($CH_3CH_2CH_2CH{=}N^+$); 84 ($CH_3CH_2CH_2CH{=}NCH_2^+$); 99 ($CH_3CH_2CH_2CH{=}NCH_2\text{-}CH_2^+ + H^+$); 112 ($CH_3CH_2\text{–}CH_2CH{=}NCH_2CH_2CH_2^+$); 126 ($CH_3CH_2CH_2CH{=}NCH_2CH_2\text{–}CH_2CH_3^+ - H^+$).

CF_3CFHCF_3. GC/EI/MS (70 eV,) retention time, *m/z* (fragment): 1.513 min, 69 (CF_3^+); 82 (CF_3CH^+); 101 (CF_3CFH^+); 151 ($(CF_3)_2CF + H^+$). ^{19}F NMR (376 MHz; $CF_2ClCFCl_2$) δ (ppm): 7.62 (dm, 1H, $J^2_{HF} = 45$ Hz and $J^3_{HF} = 6$ Hz).

$C_2F_5C(O)NHC_4H_9$. GC/CI(methane)/MS (70 eV,) retention time, *m/z* (fragment): 8.043 min, 41 ($C_2H_3N^+$), 100 ($H_9C_4HNC(O)^+$); 119 ($C_2F_5^+$); 177 ($C_2F_5C(O)NHCH_2^+ + H^+$); 190 ($C_2F_5C(O)NHCH_2CH_2^+$); 220 ($M + H^+$).

5.2.2. Reaction of the perfluorobis-isopropyl ketone with n-butylamine

The reaction between the ketone and *n*-butylamine goes to completion immediately and is exothermic. The primary products of these reactions are $(CF_3)_2CFH$, $C_3H_7CH{=}NC_4H_9$, and the corresponding amide $(CF_3)_2CFC(O)\text{–}NH(CH_2)_3CH_3$.

$(CF_3)_2CFC(O)NH(CH_2)_3CH_3$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 8.056 min, 41 ($C_2H_3N^+$), 57 ($C_4H_9^+$); 71 ($NC_4H_9^+$); 100 ($C(O)NHC_4H_9^+$); 169 ($C_3F_7^+$); 250 ($M - F$); 270 ($M + H^+$).

5.2.3. Reaction of poly(HFPO) methyl ester with n-butylamine

Reaction with *n*-butylamine causes the poly(HFPO) methyl ester to immediately decompose into Hydrogen-Endcap (1.851 and 2.530 min) and *N*-*n*-butylpoly(HFPO) amide (10.355, 12.041 and 13.464 min). A small peak due to *N*-butylidene-1-butanamine (8.157 min) is also present.

$F(HFPO)_3CF(CF_3)C(O)NHC_4H_9$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 12.041 min, 41 ($\mathrm{C_2H_3N^+}$), 57 ($\mathrm{C_4H_9^+}$); 100 ($\mathrm{H_9C_4HNC(O)^+}$); 200 ($\mathrm{H_9C_4HNC(O)CF(CF_3)^+}$); 366 ($\mathrm{C_4H_9NHC(O)CF(CF_3)OCF_2CF(CF_3)^+}$); 432 ($\mathrm{C_4H_9NHC(O)CF(CF_3)OCF_2CF(CF_3)OCF_2^+}$); 532 ($\mathrm{C_4H_9NHC(O)CF(CF_3)OCF_2CF{–}(CF_3)OCF_2CF(CF_3)^+}$); 598 ($\mathrm{C_4H_9NH{–}C(O)CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OCF_2^+}$).

5.2.4. Reaction of the poly(HFPO) perfluoroisopropyl ketone with n-butylamine

The reaction between the ketone and *n*-butylamine goes to completion immediately and is exothermic. The primary products of these reactions are $\mathrm{(CF_3)_2CFH}$, $\mathrm{C_3H_7CH{=}NC4H9}$, $\mathrm{F[CF(CF_3)CF_2{–}O]_nCF(CF_3)C(O)NH(CH_2)_3CH_3}$. Over time $\mathrm{F[CF(CF_3)CF_2O]_nCFHCF_3}$, and the corresponding amide $\mathrm{(CF_3)_2CFC(O)NH(CH_2)_3CH_3}$ are produced.

$F(HFPO)_3CF(CF_3)C(O)NHC_4H_9$ (*N-n-butylpoly(HFPO) amide*). GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 12.056 min, 41 ($\mathrm{C_2H_3N^+}$), 57 ($\mathrm{C_4H_9^+}$); 69 ($\mathrm{CF_3^+}$); 100 ($\mathrm{C(O)NHC_4H_9^+}$); 169 ($\mathrm{CF_3CF_2CF_2^+}$); 200 ($\mathrm{H_9C_4HN{–}C(O)CF(CF_3)^+}$); 366 ($\mathrm{C_4H_9NHC(O)CF(CF_3)OCF_2CF(CF_3)^+}$); 432 ($\mathrm{C_4H_9NHC(O){–}CF(CF_3)OCF_2CF(CF_3){–}OCF_2^+}$); 532 ($\mathrm{C_4H_9NHC(O)CF(CF_3)OCF_2CF(CF_3)OCF_2CF{–}(CF_3)^+}$); 598 ($\mathrm{C_4H_9NHC(O){–}CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OCF_2^+}$).

$F(HFPO)_3CFHCF_3$ (*Hydrogen-Endcap*). GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 2.500 min, 69 ($\mathrm{CF_3^+}$, 100), 100 ($\mathrm{C_2F_4^+}$, 21), 101 ($\mathrm{CFHCF_3^+}$); 119 ($\mathrm{CF_3CF_2^+}$); 147 ($\mathrm{C(CF_3)CF_2O^+}$); 169 ($\mathrm{CF_3CF_2{–}CF_2^+}$); 267 ($\mathrm{CF(CF_3)CF_2OCFHCF_3^+}$); 335 ($\mathrm{CF_3CF_2CF_2OCF(CF_3)CF_2^+}$); 433 ($\mathrm{(CF(CF_3){–}CF_2O)_2CFHCF_3^+}$); 501 ($\mathrm{CF_3CF_2CF_2O{–}CF(CF_3)CF_2OCF(CF_3)CF_2^+}$); 599 ($\mathrm{CF_3CF_2CF_2O(CF(CF_3)CF_2O)_2CFHCF_3 + H^+{–}HF}$).

5.3. Reactions of perfluoro ketones with pyrrolidine

5.3.1. Reaction of the perfluoroethylisopropyl ketone with pyrrolidine

The reaction with pyrrolidine is exothermic immediately reacting with the ketone within seconds. The primary products of these reactions are $\mathrm{(CF_3)_2CFH}$, and the corresponding amide $\mathrm{CF_3CF_2C(O)NH(CH_2)_3CH_3}$.

$C_2F_5C(O)NC_4H_8$ (*N*-tetramethyleneperfluoropropanamide). GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 9.824 min, 98 ($\mathrm{C(O)NC_4H_8^+}$); 198 ($M - \mathrm{F}$); 218 ($M + \mathrm{H^+}$).

5.3.2. Reaction of the perfluorobis-isopropyl ketone with pyrrolidine

The reaction with pyrrolidine is exothermic immediately reacting with the ketone within seconds. The primary products of these reactions are $\mathrm{(CF_3)_2CFH}$, and the corresponding amide $\mathrm{(CF_3)_2CFC(O)NH(CH_2)_3CH_3}$.

$(CF_3)_2CFC(O)NC_4H_8$ (*N*-tetramethyleneperfluoroisobutanamide). GC/CI(Methane) /MS (70 eV,) retention time, *m/z* (fragment): 9.624 min, 98 ($\mathrm{C(O)NC_4H_8^+}$); 198 ($\mathrm{CF_2CF_2C(O)NC_4H_8^+}$); 248 ($M - \mathrm{F}$); 268 ($M + \mathrm{H^+}$).

5.3.3. Reaction of poly(HFPO) methyl ester with pyrrolidine

The reaction with pyrrolidine causes the poly(HFPO) methyl ester to immediately decompose into Hydrogen-Endcap (min) and *N*-tetramethylenepoly(HFPO)amide (13.265 min).

$F(HFPO)_3CF(CF_3)C(O)NC_4H_8$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 13.265 min, 55 ($\mathrm{C_4H_7^+}$); 98 ($\mathrm{C(O)NC_4H_8^+}$); 198 ($\mathrm{(CF_3)_2CFC(O)NC_4H_8^+}$); 264 ($\mathrm{CF_2OCF(CF_3)C(O)NC_4H_8^+}$); 364 ($\mathrm{CF(CF_3)CF_2OCF(CF_3)C(O)NC_4H_8^+}$); 430 ($\mathrm{CF_2O{–}CF(CF_3)CF_2OCF(CF_3)C(O)NC_4H_8^+}$); 530 ($\mathrm{(CF(CF_3)CF_2O)_2CF(CF_3)C(O)NC_4H_8^+}$); 596 ($\mathrm{CF_2O(CF(CF_3)CF_2O)_2CF(CF_3)C(O)NC_4H_8^+}$).

5.3.4. Reaction of the poly(HFPO) perfluoroisopropyl ketone with pyrrolidine

The reaction with pyrrolidine is exothermic immediately reacting with the ketone within seconds. The primary products of these reactions are $\mathrm{(CF_3)_2CFH}$, and the corresponding amide $\mathrm{F[CF(CF_3)CF_2O]_3CF(CF_3)C(O)NHC_4H_8}$.

$F(HFPO)_3CF(CF_3)C(O)NC_4H_8$ (*N-tetramethylenepoly(HFPO)amide*). GC/CI (Methane)/MS (70 eV,) retention time, *m/z* (fragment): 13.216 min, 69 ($\mathrm{CF_3^+}$); 98 ($\mathrm{C(O)NC_4H_8^+}$); 198 ($\mathrm{(CF_3)_2CFC(O)NC_4H_8^+}$); 264 ($\mathrm{CF_2OCF(CF_3)C(O)NC_4H_8^+}$); 364 ($\mathrm{CF(CF_3)CF_2OCF{–}(CF_3)C(O)NC_4H_8^+}$); 430 ($\mathrm{CF_2OCF(CF_3)CF_2OCF(CF_3)C(O)NC_4H_8^+}$); 530 ($\mathrm{(CF(CF_3){–}CF_2O)_2CF(CF_3)C(O)NC_4H_8^+}$); 596 ($\mathrm{CF_2O(CF(CF_3)CF_2O)_2CF(CF_3)C(O){–}NC_4H_8^+}$); 696 ($\mathrm{(CF(CF_3)CF_2)_3CF(CF_3)C(O)NC_4H_8^+}$).

5.4. Reactions of perfluoro ketones with diethylamine

5.4.1. Reaction of the perfluoroethylisopropyl ketone with diethylamine

Diethylamine reacts relatively slowly with the ketone, taking a few days to go to completion. The primary products of these reactions are $\mathrm{(CF_3)_2CFH}$, $\mathrm{CF_3CF_2C(O)NHCH_2CH_3}$, $\mathrm{CF_3CF_2C(O)N(CH_2CH_3)_2}$ and $\mathrm{CF_3CF_2C(O)CH{=}CHNEt_2}$.

$CF_3CF_2C(O)NHC_2H_5$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 4.756 min, 41 ($\mathrm{C_2H_3N^+}$), 72 ($\mathrm{H_5C_2HNC(O)^+}$); 172 ($M - \mathrm{F}$); 192 ($M + \mathrm{H^+}$).

$C_2F_5C(O)N(C_2H_5)_2$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 7.126 min MS (CI) (*m/z*): 41 ($\mathrm{C_2H_3N^+}$), 100($\mathrm{Et_2NC(O)^+}$); 200 ($M - \mathrm{F}$); 220 ($M + \mathrm{H^+}$)

trans-$C_2F_5C(O)CH{=}CHN(C_2H_5)_2$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 14.669 min, 41 ($\mathrm{C_2H_3N^+}$), 126 ($\mathrm{(Et)_2NCH{=}CHC(O)^+}$); 226 ($M - \mathrm{F}$); 246 ($M + \mathrm{H^+}$); 274 ($M + \mathrm{H^+} + 29$).

5.4.2. Reaction of the perfluorobis-isopropyl ketone with diethylamine

Diethylamine reacts relatively slowly with the ketones, taking a few days to go to completion. The primary products of these reactions are $(CF_3)_2CFH$, $(CF_3)_2CFC(O)NHEt$ and $(CF_3)_2CF\ C(O)CH{=}CHNEt_2$.

$(CF_3)_2CFC(O)NHC_2H_5$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 4.896 min, 41 ($C_2H_3N^+$) 72 ($EtHNC(O)^+$); 222 ($M-F$); 242 ($M+H^+$).

trans-$(CF_3)_2CFC(O)CH{=}CHNEt_2$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 14.674 min, 126 ($Et_2NCH{=}CHC(O)^+$); 276 ($M+H^+-F$); 296 ($M+H^+$); 324 ($M+29$).

5.4.3. Reaction of poly(HFPO) methyl ester with diethylamine

Poly(HFPO) methyl ester with diethylamine gives complete decomposition of the methyl ester into $F[CF(CF_3)CF_2O]_3CFHCF_3$.

5.4.4. Reaction of the poly(HFPO) perfluoroisopropyl ketone with diethylamine

Diethylamine reacts relatively slowly with the ketones, taking a few days to go to completion. $(CF_3)_2CFH$, was observed along with some unexpected products: $F[CF(CF_3)CF_2O]_3CF(CF_3)C(O)NHCH_2CH_3$ and $F[CF(CF_3)CF_2O]_3CF(CF_3)C(O)\text{-}CH{=}CHNEt_2$, and $F[CF(CF_3)CF_2O]_3CFHCF_3$.

$F[CF(CF_3)CF_2O]_3CF(CF_3)C(O)NHCH_2CH_3$, *N-ethylpoly(HFPO)amide*. GC/CI (Methane)/MS (70 eV,) retention time, *m/z* (fragment): 9.855 min, 670 ($F(HFPO)_3CF(CF_3)\text{-}C(O)NHCH_2CH_3 + H^+\text{–}HF$), 690 ($F(HFPO)_3CF(CF_3)C(O)NHCH2\text{-}CH_3 + H^+$).

trans-$F(HFPO)_3CF(CF_3)C(O)CH{=}CHN(Et)_2$. GC/CI(Methane)/MS (70 eV,) retention time, *m/z* (fragment): 17.189 min, 41 ($C_2H_3N^+$), 126 ($(Et)_2NCH{=}CHC(O)^+$); 392 ($(Et)_2NCH{=}CHC(O)CF(CF_3)OCF_2CF(CF_3)^+$); 558 ($(Et)_2NCH{=}CHC(O)CF(CF_3)\text{–}(HFPO)_2^+$); 696 ($M+H^+-F-C_2H_5$).

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