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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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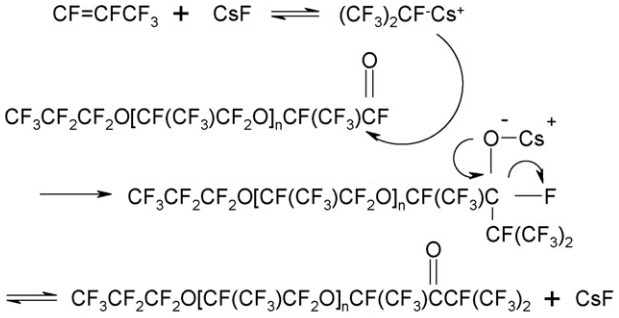
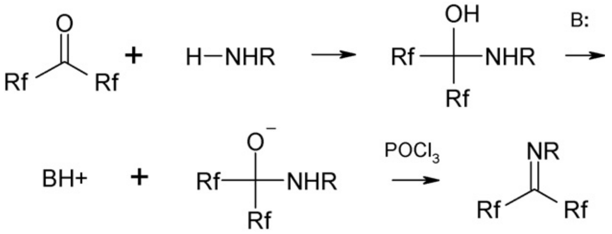


Scheme 1. Formation of poly(hexafluoropropylene oxide)perfluoroisopropyl ketone.

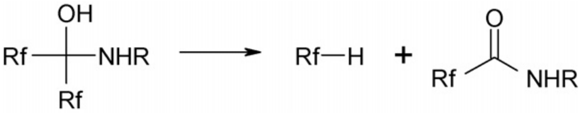


Scheme 2. Formation of the imine of a fluorinated ketone using base and $POCl_3$.

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				
$(CF_3)_2C\mathit{F}–$	−192.4	−189.8	−190.2	–
$(C\mathit{F}_3)_2CF–$	−75.6	−75.2	−75.1,	−75.4
$C\mathit{F}_3CF_2–$	−83.8	–	–	–
$CF_3C\mathit{F}_2–$	−122.4 (d)	–	–	–
$CF_3C\mathit{F}_2CF_2O–$	–	–	−146.0	−146.0