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REACTIONS OF PERFLUORONITRILES. I. INTERACTIONS WITH ANILINE

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SUMMARY

Perfluoro-n-octanonitrile was found to react with aniline both in the absence and presence of solvents. A spectrum of products was formed including tris(perfluoro-n-heptyl)-s-triazine, N-phenyl-perfluoro-n-octylamidine, and N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine, as well as the diphenyl analogues of the last two compounds. The reaction mechanisms, infrared and mass spectra are discussed.

INTRODUCTION

Early work by Grivas and Taurins [1,2] has shown that aniline and trifluoroacetonitrile react readily at room temperature in polar solvents; however, as reported by these authors and others [3], no reaction was found to occur in the absence of solvent. The only product mentioned was the amidine. No reports in the literature could be found regarding the formation of imidoylamidines from the amidines on further reaction with nitriles. It was thus of interest to determine whether these types of interactions are completely arrested or eliminated by the presence of the phenyl group. In the current investigations, perfluorooctanonitrile was employed since its relatively high boiling point permitted reactions to be carried out not exclusively in the sealed systems, which is necessary with trifluoroacetonitrile. Furthermore, a longer chain material is believed to be more representative of the perfluorinated nitriles than trifluoroacetonitrile.

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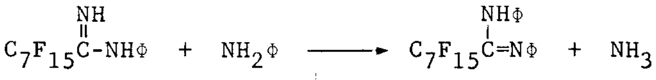
RESULTS AND DISCUSSION

Synthesis

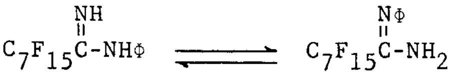
Interaction of perfluoro-n-octanonitrile with aniline in the absence of solvent at relatively high temperatures, 120-140°C, using a 2:1 perfluoro-n-octanonitrile to aniline ratio, gave the amidine (II), $C_7F_{15}C(NHC_6H_5)=NH$, in ∿77% yield based on the recovered aniline. The major product based on the consumed perfluoro-n-octanonitrile was tris(perfluoro-n-heptyl)-s-triazine (I); its formation from the nitrile was most likely catalyzed by ammonia [4,5] which was produced by the reaction of the N-phenyl-perfluoro-n-octylamidine (II) with aniline, i.e.:



$$C_7F_{15}\overset{NH}{\overset{\|}{C}}\text{-}NH\Phi \;+\; NH_2\Phi \longrightarrow C_7F_{15}\overset{NH\Phi}{\overset{|}{C}}{=}N\Phi \;+\; NH_3$$

II IV

The presence of the interaction product IV was shown by combined gas chromatography and mass spectrometry (GC/MS). Grivas and Taurins [1,2] have shown the N-aryltrifluoroacetamidines to exist in the imino form II shown above; however, for the aniline interaction to take place, the presence of the tautomeric form, i.e.,



$$C_7F_{15}\overset{NH}{\overset{\|}{C}}\text{-}NH\Phi \rightleftharpoons C_7F_{15}\overset{N\Phi}{\overset{\|}{C}}\text{-}NH_2$$

is mandatory. Infrared spectra of the amidine, II, and another product, the imidoylamidine, III, are given in Fig. 1 and 2, respectively.

Pure N-phenyl-perfluoro-n-octylamidine (II) was obtained in 26% yield by reacting aniline and the nitrile in acetonitrile/Freon-113 solvent mixture. Interaction of aniline and perfluoro-n-octanonitrile in 2:1 mole ratio over an extended period at 90-115°C gave a mixture of products listed in Table 1. The compounds were identified and quantitated by GC/MS.

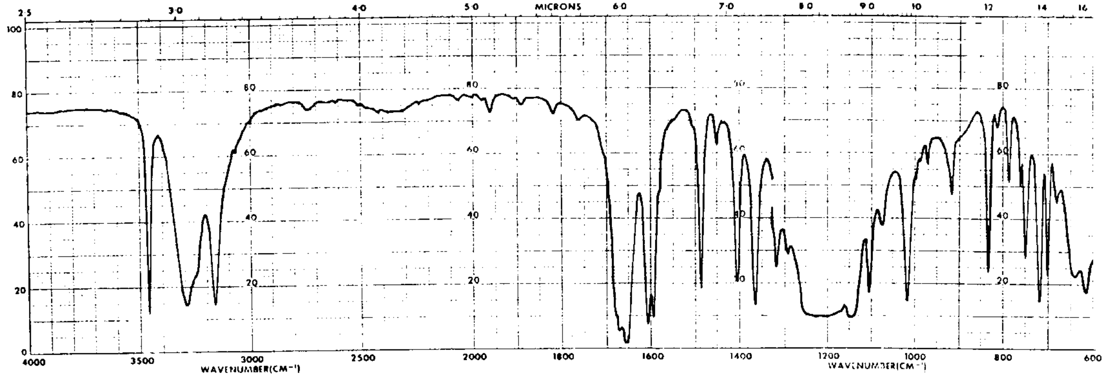


Fig. 1. Infrared spectrum of N-phenyl-perfluoro-n-octylamidine (II) (Kel-F/Nujol).

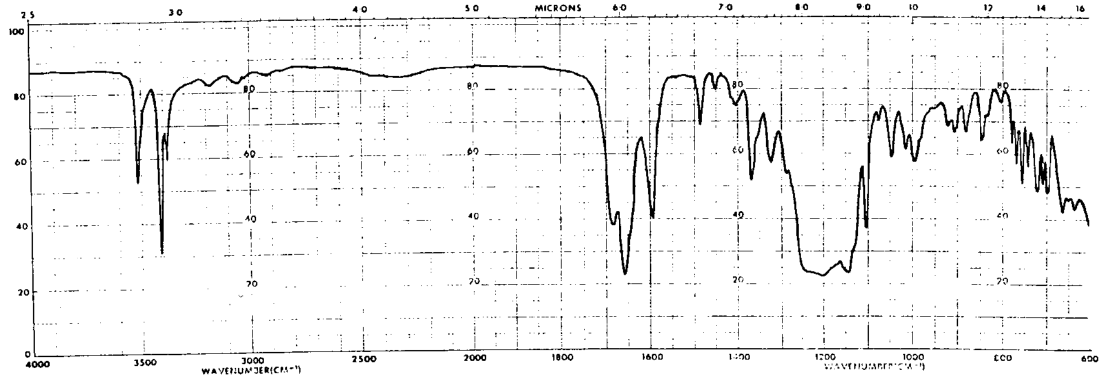


Fig. 2. Infrared spectrum of N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine (III) (Kel-F/Nujol).

TABLE 1

Products obtained from the interaction of aniline and perfluoro-n-octanonitrile in 2:1 mole ratio at 90-115°C

Compound	Percent of product mix
$[C_7F_{15}CN]_3$, I	44.0
$C_7F_{15}C(=NH)NH\Phi$, II	9.8
$C_7F_{15}C(=NH)N=C(NH\Phi)C_7F_{15}$, III	6.9
$C_7F_{15}C(=N\Phi)NH\Phi$, IV	7.5
$C_7F_{15}C(=N\Phi)-N=C(NH\Phi)C_7F_{15}$, V	7.7

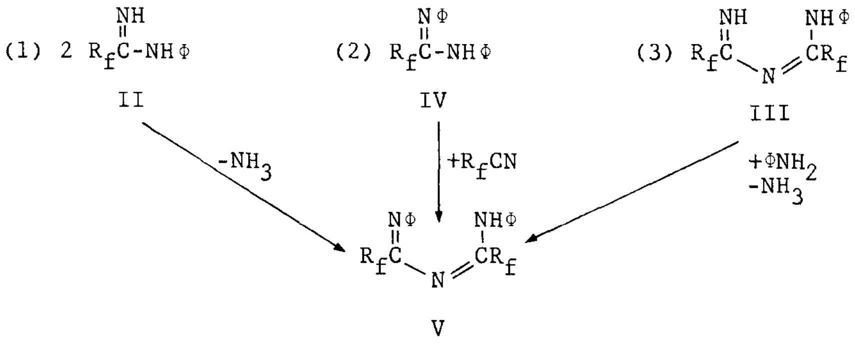
The origins of triazine (I), N-phenyl-perfluoro-n-octylamidine (II), and Compound IV have been discussed above. The imidoylamidine (III) must be produced by the addition of the nitrile to N-phenyl-perfluoro-n-octylamidine (II), *i.e.*:

$$C_7F_{15}\overset{NH}{\overset{\|}{C}}-NH\Phi + C_7F_{15}CN \longrightarrow C_7F_{15}\overset{NH}{\overset{\|}{C}}\diagdown_{N}\!\diagup\!\!\!\!\diagup\overset{NH\Phi}{\overset{|}{C}}C_7F_{15}$$

II III

This was verified by its preparation and isolation from the reaction of amidine (II) with perfluoro-n-octanonitrile. The occurrence of secondary reactions, even under these conditions, was evidenced by the presence of triazine (I). Such interconversions in systems containing or producing ammonia-nitrile-amidine and imidoylamidine were observed previously [6]. These processes would be expected to be more evident in reactions carried out at elevated temperatures for prolonged periods of time.

With respect to the product mix given in Table 1, there are three possible paths for the formation of the imidoylamidine V, *i.e.*:



The first process is unlikely since after exposure at 200°C for 15 hr the amidine was recovered unchanged. Having an excess of aniline would favor process 3 rather than reaction 2. It should be noted that in the presence of acetonitrile at 50°C, the production of the imidoylamidine, III, was enhanced; however, all the other products were also formed.

The only novel compounds, which could be isolated and fully characterized, were N-phenyl-perfluoro-n-octylamidine (II) and N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine (III). All the other compounds were identified by their mass spectral breakdown patterns which are compiled in Table 2.

Mass spectral data

The fragmentation patterns of the amidines and imidoylamidines, Compounds II-V, were closely related (Table 2). All the compounds showed a strong molecular ion and a fragment following a loss of fluorine. The ion corresponding to the loss of the perfluoroheptyl side chain constituted the base peak in all four compounds. Its formation from the molecular ion in the case of the two isolated compounds, N-phenyl-perfluoro-n-octylamidine, II, and N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine, III, is shown by the metastables at m/e 29 and 299.5, respectively, i.e.:

$$488^+ \text{ (M)} \longrightarrow 119^+ + 369[C_7F_{15}] \qquad m^* \; 29.0$$

$$883^+ \text{ (M)} \longrightarrow 514^+ + 369[C_7F_{15}] \qquad m^* \; 299.2$$

TABLE 2

Mass spectral breakdown patterns of $R_fC(=NH)NH\Phi$ (II), $R_fC(=NH)N=CR_f(NH\Phi)$ (III), $R_fC(=N\Phi)NH\Phi$ (IV), and $R_fC(=N\Phi)N=CR_f(NH\Phi)$ (V)[a]

m/e	II	III	IV	V	m/e	II	III	IV	V
31		4.0			257		4.0		
36		3.8			271				15.0
39	3.9		3.1		272				13.7
50	4.9	3.1	3.5		295				4.3
51	14.4	7.7	14.3	5.1	331			9.7	
60	4.8				332			3.4	
64	4.4				346			6.6	
65	7.1	3.1	8.5		452	3.0			
66	3.6				469	13.5	4.3		
69	14.5	26.7	12.0	14.5	470	3.0			
76	4.0	6.0	5.5	3.5	472		10.6	26.5	15.8
77	44.2	35.2	85.2	49.5	473			5.6	3.4
78	7.5	9.1	9.0	6.2	487	14.3	4.2		
91	5.4	6.6	3.7		488	38.8(M^+)	10.8		
92	5.6	8.7	25.9		489	8.6			
93	3.5		4.1		514		100.0		
100	3.9	7.1	3.9	3.9	515		24.8		
103		8.9	6.6	5.1	516		3.2		
104		3.8	3.3	3.7	545			15.6	
118	8.0	18.3	4.3	15.5	546			3.8	
119	100.0	54.4	6.5	7.2	562			4.9	
120	16.5	8.0			563			44.3	
127				3.5	564			60.8(M^+)	
131	6.0	7.5	3.3	4.9	565			17.7	
135				3.8	589				4.2
144		4.5			590				100.0
150	3.4				591				36.9
153				3.1	592				6.4
167		3.5	4.8		864		25.4		
168	8.3		7.4		865		8.6		
169		8.7		4.0	881		3.9		
181		3.1			882		3.8		
194			6.7		883		38.2(M^+)		
195		7.4	100.0		884		14.3		
196			23.6		940				34.8
207			4.4	4.5	941				12.2
224			3.0		958				7.0
243			6.2		959				67.8(M^+)
244			3.0		960				29.8
253			15.1		961				5.9
254			4.5						

[a] Peaks having intensities lower than 3% of the base peak are not reported.

The imidoylamidines, III and V, as well as the amidine, IV, had high intensity peaks at m/e 472^+ corresponding to the $C_7F_{15}C{=}N\Phi$ fragment. This ion was absent in the mass spectrum of N-phenyl-perfluoro-n-octylamidine, II.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. Gas chromatography was performed employing a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Interaction of perfluoro-n-octanonitrile with aniline

(a) In 2:1 ratio at 120-140°C in a sealed tube

A mixture of perfluoro-n-octanonitrile (3.07 g, 7.77 mmol) and aniline (263 mg, 2.82 mmol) was heated in an evacuated, sealed ampoule at 120-140°C for 13 hr. Vacuum line fractionation gave ammonia (11.8 mg) and aniline (60.1 mg, 23% recovery). The involatile residue consisted of perfluoro-n-heptyltriazine (I) and N-phenyl-perfluoro-n-octylamidine (II). A portion (470 mg) of the latter, mp 107-110°C, could be separated from the bulk of the triazine by recrystallization from hexane and repeated partitions in benzene.

(b) In a 1:2 mole ratio at 90-115°C under nitrogen by-pass

A stirred mixture of perfluoro-n-octanonitrile (3.00 g, 7.59 mmol) and aniline (1.25 g, 13.44 mmol) was heated at 92-115°C under nitrogen by-pass for 235 hr. Vacuum line fractionation gave aniline (1.07 g, 86% recovery) and perfluoro-n-octanonitrile (1.40 g, 47% recovery). The involatile residue, based on GC/MS, consisted of: $(C_7F_{15}CN)_3$, 44%; $C_7F_{15}C(=NH)N\Phi H$, 10%; $C_7F_{15}C(=NH)N=C(N\Phi H)C_7F_{15}$, 7%; $C_7F_{15}C(=N\Phi)N\Phi H$, 8%; and $C_7F_{15}C(=N\Phi)N=C(N\Phi H)C_7F_{15}$, 8%.

(c) Equimolar ratio in 1:1 acetonitrile/Freon-113 mixture at 50°C

A solution of perfluoro-n-octanonitrile (2.04 g, 5.16 mmol) and aniline (0.47 g, 5.05 mmol) in 10 ml of 1:1 acetonitrile/Freon-113 was stirred at room temperature for five days. The extent of reaction was very low as shown by GC. The rate at 50°C was higher by a factor of 5 as measured by the ratio of amidine to aniline. After 41 days at 50°C, the ratio of aniline:triazine:amidine:imidoylamidine was 1:0.5:2.9:1.2. Out of the reaction mixture, N-phenyl-perfluoro-n-octylamidine (II) n.c. (0.64 g, 26% yield), mp 111-112°C), crystallized out. Anal. calcd. for $C_{14}H_7F_{15}N_2$: C, 34.44; H, 1.45; F, 58.37; N, 5.74; MW, 488.20. Found: C, 33.75; H, 1.39; F, 58.69; N, 6.07; MW, 500.

Thermal treatment of N-phenyl-perfluoro-n-octylamidine

A 91.3 mg sample of N-phenyl-perfluoro-n-octylamidine in an evacuated ampoule was subjected to stepwise heat treatment: 16 hr at 120°C; 38 hr at 150°C; and 15 hr at 200°C. Unchanged starting material was recovered.

Preparation of N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine (III)

A solution of N-phenyl-perfluoro-n-octylamidine (II) (1.45 g, 2.97 mmol) and perfluoro-n-octanonitrile (2.44 g, 6.18 mmol) in Freon-112 (10 ml) was heated at 50-65°C for 19 days. Gas chromatography of the reaction mixture showed presence of nitrile, N-phenyl-perfluoro-n-octylamidine (II), and imidoylamidine (III) in the ratio 1:1.7:0.2. At that stage, additional nitrile (1.4 g) was added to the reaction mixture and the temperature was increased to 80°C; the reaction was then carried out for a further 21 days. At the end of this period, the ratio of nitrile:triazine:amidine:imidoylamidine was 1:0.3:0.6:0.9, giving the overall yield of the imidoylamidine as 55%. Subsequently, some of the unreacted amidine (0.17 g, 12%) crystallized out of solution and was filtered from the reaction mixture. After evaporation of the solvents, more of the amidine (0.25 g, 17%) was recovered from the residue upon addition of pentane, followed by filtration. The pentane was removed from the filtrate and the rest of the amidine was separated from the solid residue by sublimation. The sublimation residue was washed with pentane and the pale yellow solid which remained (0.31 g, 12% yield) was found to be pure N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine (III) n.c., mp 52-53°C. Anal. calcd. for $C_{22}H_7F_{30}N_3$: C, 29.92; H, 0.80; F, 64.53; N, 4.76; MW, 883.27. Found: C, 29.43; H, 0.78; F, 64.50; N, 5.33; MW, 880.

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REFERENCES

1 J. C. Grivas and A. Taurins, Can. J. Chem., 39, (1961) 414.

2 J. C. Grivas and A. Taurins, Can. J. Chem., 39, (1961) 761.

3 W. L. Reilly and H. C. Brown, J. Am. Chem. Soc., 78, (1956) 6032.

4 H. C. Brown, Synthesis of Semi-Inorganic Fluorine Polymers. Part III. Perfluoroalkyl-Triazine Polymers. Studies of Intermediate Polymer Formation, Mechanism of Polymerization, and Catalytic Trimerization of Perfluoroalkyl Nitriles, WADC TR-59-272, Part III, August 1961.

5 W. L. Reilly and H. C. Brown, J. Org. Chem., 22, (1957) 698.

6 R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., 13, (1979) 189.