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SYNTHESIS OF ENERGETIC MATERIALS AT HIGH PRESSURES

BY WILLIAM M. KOPPES HORST G. ADOLPH

RESEARCH AND TECHNOLOGY DEPARTMENT

21 DECEMBER 1978

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Fluorodinitroacetonitrile (FDAN) has been trimerized to the 1,3,5-triazine structure at 10 kbar pressure with the use of acidic alcohol catalysts. The pseudohalogen character of the $CF(NO_2)_2$ group, however, makes it subject to displacement from the triazine ring by the alcohol catalyst. As a result the major triazine products bear alkoxy substituents. In the case of CF_3CH_2OH as catalyst the chief triazine product is →

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$(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$. Reaction of preformed imidic ester with the nitrile can diminish this side reaction to the point where $CF_3CH_2O(CN)_3(CF(NO_2)_2)_2$ is the chief triazine product. There is evidence that the FDAN cylotrimer is formed in low yield with CF_3CH_2OH as catalyst but the compound has not been isolated.

The use of the more acidic PhOH as catalyst gives $PhO(CN)_3(CF(NO_2)_2)_2$ as the chief product but the tris (fluorodinitromethyl) triazine still remains as a minor product, if present at all.

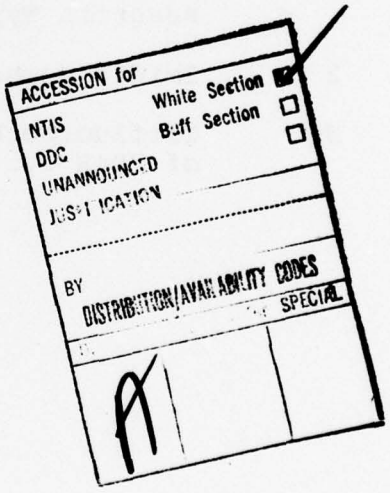
Two mechanisms of cyclotrimerization appear operative, depending on the structure of the imidic ester intermediate.

FOREWORD

This report describes an effort aimed at the utilization of very high pressures as a synthesis tool in the preparation of new and otherwise inaccessible high energy compounds. The work was performed under ONR work request N0001478WR80116 to the Naval Surface Weapons Center, Dahlgren, Virginia, during the period of 1 November 1977 through 31 October 1978. Dr. Richard S. Miller, ONR Code 473, is the scientific monitor of this effort.

Julius W. Enig

JULIUS W. ENIG
By direction



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INTRODUCTION

The purpose of this work is to investigate the utility of the effects of high pressure on chemical reactions in the synthesis of new high energy materials. Equilibria and rates of chemical reactions are affected by pressure when the quantities, ΔV (the difference of the partial molal volumes of products and reactants) and $\Delta V^{\ddagger}$ (the "activation volume", difference of partial molal volume of transition state and reactants) are not equal to zero. When ΔV and $\Delta V^{\ddagger}$ are negative, products are favored and reactions are accelerated, respectively, by application of pressure[1]. For condensed phase reactions, ΔV and $\Delta V^{\ddagger}$ are generally small, and substantial pressures -- in the kbar range -- are required to produce noticeable effects.

The quantitative relationship describing the pressure dependance of chemical reaction rates is given in equation (1).

$$(1) \qquad \left(\frac{\partial \ln(k_p/k_i)}{\partial p}\right)_T = - \frac{\Delta V^{\ddagger}}{RT}$$

where k_p/k_i = ratio of rate constants at elevated and ambient pressures, and $\Delta V^{\ddagger}$ = volume of activation. The magnitude of the pressure effect varies with reaction type (Table 1).

TABLE 1. PRESSURE SENSITIVITY OF DIFFERENT REACTION TYPES[1]

Reaction	Type	$\Delta V^{\ddagger}$ cm^3/mol
Radical Decomposition	A → B + C	0 to +15
Molecular Rearrangement	A → B	-8 to -15
Polymerization	nA → (A)n	-10 to -25
Bimolecular Addition Reaction	A + B → C	-25 to -50
Ionization	A → B^+ + C^-	-15 to -45
N-Quaternization	A + B → C^+ + D^-	-20 to -40

1) G. Jenner, Angew. Chem. Internat. Edit., 137, (1975).

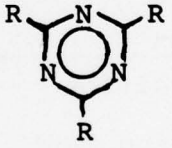
Some relative reaction rates as a function of pressure for two different $\Delta V^{\ddagger}$ are as follows (Temperature 25°C)[2].

	Relative Rate at Pressure		
$\Delta V^{\ddagger}$	1 Kbar	5 Kbar	10 Kbar
-30	3	240	58,000
-10	1.4	6	40

In practice, because $\Delta V^{\ddagger}$ is not pressure independent, the rate accelerations are smaller, but highly useful rate enhancements still occur for pressures up to 20-25 kbar (at higher pressures the $\ln(k_p/k_i)$ curves level off for many reactions, and further pressure increase serves no useful purpose).

It is seen from Table 1 that addition reactions of the type A + B → C are particularly susceptible to acceleration by pressure; consequently, such a reaction was chosen for initial studies

During recent years, the scope of the nitrile cyclotrimerization has been extended from a few examples at ambient pressure to include a large variety of differently substituted substrates that can be trimerized at elevated pressures (equation (2))[3].

(2) $3R\text{-}CN \xrightarrow[80\text{-}100^{\circ}C]{R'OH,\ 8\text{-}10\ Kbar}$ 

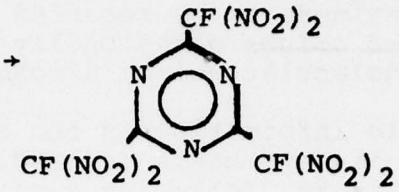
In company with many other aryl and alkyl nitriles, fluorodinitroacetonitrile (FDAN), difluoronitroacetonitrile (DFTAN), and trinitroacetonitrile (TAN) have resisted attempts at cyclotrimerization to the corresponding triazines under conventional conditions. The triazines derived from FDAN and TAN are of considerable interest as high energy materials because of their high oxygen content and "predicted" crystal densities[4] of ca. 2 g/cm^3. For these reasons the cyclotrimerization of FDAN and TAN appeared ideally suited for study at elevated pressures, and this report describes work in progress on the

2) W. G. Dauben, presented at the 100th Meeting of the American Chemical Society, New York, N.Y., 1976.

3) W. Jarre, D. Bienik, and F. Korte, Tetrahedron, 31, 619 (1975).

4) Using the method of J. Holden, NSWC, White Oak.

synthesis of tris (fluorodinitromethyl)-s- triazine by the cyclotrimerization of $CF(NO_2)_2CN$, FDAN (equation (3)).

(3) $3\ CF(NO_2)_2CN \rightarrow$ 

DISCUSSION AND RESULTS

A. Background and Ambient Pressure Chemistry of FDAN

There is a wide range of reactivity of nitriles in their cyclization to triazines. Trimerization of some nitriles has been accomplished at ambient temperature and pressure by the use of acid catalysts. Facile trimerization of CCl_3CN has been reported with the strong acid catalyst PCl_5/HCl.[5)]

(4) $$CCl_3CN \xrightarrow[20^o,240h]{PCl_5/HCl} (CCl_3)_3(CN)_3 \quad 82\%$$

With the same catalyst β-cyanonaphthalene gave a 22% yield of triazine at 100°/120h, while α-cyanonaphthalene was recovered unchanged. Conversion of C_3F_7CN to $C_3F_7C(=NH)OPh$ by reaction with phenol has led to formation of $(C_3F_7)_3(CN)_3$ by storage of the imidic ester at room temperature[6)]. Basic catalysis of trimerization has also been reported for F-alkylnitriles. Reaction of the nitriles with NH_3 gave the corresponding amidines which decomposed above their melting points with evolution of NH_3 to form 2,4,6-tris (F-alkyl)-1,3,5-triazines[7)]. It is of interest that when $CF_2NO_2C(=NH)NH_2$ is heated, however, there is no triazine formed and CF_2NO_2H is liberated in 61% yield.[8)] Examples of trimerization of nitriles under mild conditions appear to be limited to CCl_3CN and certain F-alkylnitriles. In general the use of high temperatures and pressures are required.

5) S. Yanagida, et al., Bull. Chem. Soc. Jap., 46, 306 (1973).

6) H. C. Brown and C. R. Wetzel, J. Org. Chem., 30, 3724 (1965).

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

8) E. R. Bissell, J. Org. Chem., 28, 1717 (1963).

Synthesis of triazines at high pressure (7-8 kbar) was first reported by Cairns in 1952 with methanol as catalyst[9]. This method continues to be reported in the literature with small amounts of amines occasionally added as cocatalyst. The use of higher molecular weight alcohols results in lower yields.

Very little information on the chemistry of FDAN has been reported since its synthesis in 1968. Its known reactions are summarized in the following equations.[10 a-c]

(5) $CF(NO_2)_2CN + H_2O \xrightarrow[Et_2O]{HCl} CF(NO_2)_2\,C(=O)NH_2$

(6) $CF(NO_2)_2CN + CF_2NO_2CH_2OH \xrightarrow[Et_2O]{Et_3N} CF(NO_2)_2\,C(=NH)OCH_2CF_2NO_2$

(7) $CF(NO_2)_2CN + NH_3 \xrightarrow[Et_2O]{-105^\circ} \xrightarrow{HCl} CF(NO_2)_2\,C(=NH)NH_2 \cdot HCl$

(8) $CF(NO_2)_2CN + ClOSO_2F \xrightarrow[CF_2ClCFCl_2]{-20^\circ} CF(NO_2)_2\,C(=NCl)OSO_2F$

The nitrile decomposes slowly near its boiling point (74°).

In exploring methods to trimerize FDAN the effect of acid and base catalysts at ambient pressure was tested. The nitrile was incompatible with bases such as Et_3N and KF; decomposition occurred with the release of NO_2. It forms a homogeneous solution with PCl_5/HCl from which it can be mostly recovered without evidence of triazine formation after heating for several weeks at 60°. Although FDAN has in common with the readily cyclized nitriles CCl_3CN and R_FCN an electronegative alkyl group attached to the nitrile function, it bears two α-nitro groups which provide more steric hindrance to attack by nucleophiles at the nitrile carbon. The weakly basic imino compounds formed as intermediates in acid catalyzed reactions would thus encounter more resistance in their addition to the nitrile.

9) T. L. Cairns, A. W. Larchar, and B. C. McKusick, J. Am. Chem. Soc., 74, 5633 (1952).

10a) R. A. Wiesboeck and J. K. Russ, J. Org. Chem., 33, 1257 (1968).

b) A. V. Fokin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 456 (1974).

c) A. V. Fokin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 489 (1976).

The use of high pressure to effect cyclotrimerization of FDAN seems particularly well suited in consideration of the steric requirements and thermal sensitivity of the nitrile. Pressurization of the nitrile with alcohols was chosen as the first area of study based on the literature reports of trimerizations catalyzed by methanol. Previously unexplored methods such as pressurization with inorganic and organic acids or with metal catalysts (carbonyls, oxides, organometallics) may be tried as the results with alcohols dictate.

The use of methanol as catalyst for high pressure trimerization of FDAN was first considered, but it was discovered that mixtures of these compounds at ambient pressure and temperature evolved heat after an initial quiescent period, followed by boiling and release of CO_2. This observation conflicts with a report by Russian workers that methyl fluorodinitroacetimidate can be prepared in 40% yield by reaction of FDAN with methanol in Et_2O.[10b] Without analyzing this reaction in detail, it was decided to investigate more acidic alcohols on the supposition that a less basic alcohol or imidic ester might diminish the undesired side reactions. This was found to be the case, and a group of imidic esters was synthesized by base catalyzed (Et_3N or K_2CO_3) addition of acidic alcohols to FDAN. Isolated yields and properties of the imidic esters are given in Table 2.

TABLE 2. IMIDIC ESTERS OF FDAN

$$CF(NO_2)_2CN + ROH \xrightarrow{\text{base}} CF(NO_2)_2\,\overset{NH}{\overset{\|}{C}}\text{-OR}$$

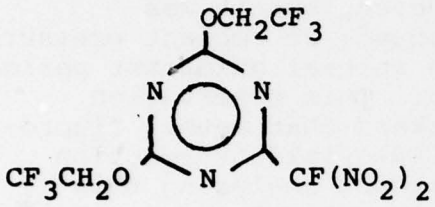
R	Yield(%)	bp(mm)	mp
CH_2CF_3	66	51-52°(7)	-
$CH_2CF(NO_2)_2$	34	68-69°(0.038)	27-28°
C_6H_5	27	66-67°(0.32)	38.5-41.0°

10b) A. V. Fokin, et al., Izv. Akad. Nauk SSSR, Ser. Khim, 456 (1974).

B. FDAN Pressurization with trifluoroethanol catalysis.

When CF_3CH_2OH and FDAN were subjected to 10 kbar pressure in CH_2Cl_2, the chief product in the reaction solution was the corresponding imidic ester. Trimerization of the nitrile occurred to the extent of 20-25% to give unsymmetrical 1,3,5-triazines bearing a mixture of alkyl and alkoxy substituents.

(9) $CF(NO_2)_2CN + CF_3CH_2OH \xrightarrow{10\ kbar} CF(NO_2)_2C(=NH)OCH_2CF_3 +$



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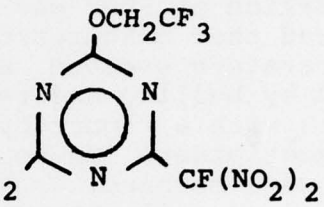

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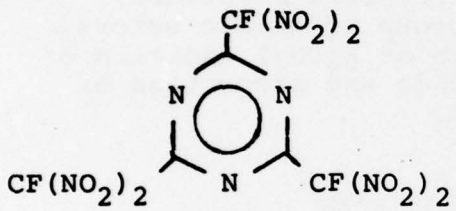


III

The incorporation of the alcohol catalyst into the triazine ring was accompanied by the formation of $CF(NO_2)_2H$.

The structure of I, the triazine formed in largest amount, was established by chemical ionization (CH_4) mass spectral data (parent ion base peak), elemental analysis, and ^1H and ^{19}F nmr data. The presence of a triazine ring was confirmed by conversion of I to the known tris(alkoxy) compound.

(10) $I + CF_3CH_2OH \xrightarrow{KOH} (CF_3CH_2O)_3(CN)_3 + K\ CF(NO_2)_2$

The structure of compound II is based on GC/MS data and is consistent with its observed reactivity. In the mass spectrum a parent ion (2%) peak was observed and a base peak corresponding to loss of N_2O_3 from each of the $CF(NO_2)_2$ groups.

Compound III is the least volatile product and is formed in less than 5% yield. Its structure is assigned as the FDAN

cyclotrimer based on the following data. III is at the end of a progression of four peaks on the GC chromatogram occurring at ca. one minute intervals on a 30°/min program beginning with $(CF_3CH_2O)_3(CN)_3$ (added as a spike to the reaction solution) and followed by I, II, and III. The successive substitution of CF_3CH_2O with $CF(NO_2)_2$ on the triazine ring causes a fairly regular increase in retention time and III occurs at the position on the chromatogram expected for complete substitution with $CF(NO_2)_2$ groups. The molecular ion for the FDAN trimer (MW 447) is not seen in the GS/MS data for III. The largest fragment, at 357 (3%), corresponds to loss of NO from each of the $CF(NO_2)_2$ groups. A peak at 271 (94%) is consistent with loss of three NO_2 groups and two fluorines from the trimer. The base peak (241, 100%) is derived from further loss of NO. There are peaks at 226 (23%) and 221 (43%) which do not seem to be logical fragments of the trimer. A possible explanation is that the column temperature necessary to elute III may be high enough to cause decomposition during the GC/MS analysis. It elutes at 200° on a 30°/min temperature program as a more broad and tailing peak as compared to sharp peaks at 150° and 170° for I and II.

The effects of temperature and time of reaction have not been carefully studied for the CF_3CH_2OH catalyzed trimerization of FDAN. A temperature limit of 65° to 70° is imposed by the stability of the nitrile. A practical consideration of frequency of equipment breakdown at 10 kbar imposes a limitation on reaction time. Data from the pressurization of the alcohol and nitrile at 10 kbar are presented in Table 3. An increase in solvent polarity (Exp. C) had a positive effect on the formation of imidic ester, but the yield of triazines remained unchanged. These experiments demonstrate that CF_3CH_2OH promotes trimerization of FDAN under

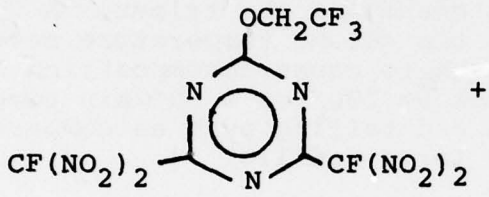
TABLE 3. TRIFLUOROETHANOL CATALYZED TRIMERIZATION OF FDAN

Exp.	Mole Ratio ROH:FDAN	Solvent	Reaction Time,h	Temp °C	Imidic Ester,%	Triazines, %
A	1:2	CH_2Cl_2	35	40	46	21
B	1:3	CH_2Cl_2	60	65	40	24
C	1:2	CH_2Cl_2/CH_3CN (50/50)	24	60	63	21

pressure to give a 1,3,5-triazine structure in ca. 20% yields. The alcohol, however, does not function as a regenerable catalyst and is incorporated in the triazine product. The composition of the triazine product mixture of I, II, and III in experiment B by GC analysis was 69, 23, and 8 percent.

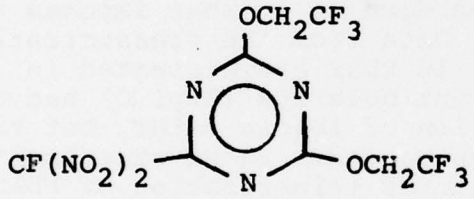
On the assumption that the alkoxy substituted triazines resulted from displacement of $CF(NO_2)_2$ by CF_3CH_2OH, preformed imidic ester (1 mol) was pressurized with FDAN (4 mol). The only free alcohol present would presumably arise from cyclotrimerization to form III. An excess of FDAN was made available to compete with III and II for liberated alcohol by its reaction to form imidic ester. Under these conditions the yield of III still remained small relative to I and II, but the ratio of I:II of 75:25 in experiment B changed to 15:85 in this experiment. Indirect evidence is thus provided that I is derived from II by reaction with CF_3CH_2OH. The displacement reaction by the weakly nucleophilic alcohol is probably enhanced by its ionization under the influence of pressure.

(11)



$+ CF_3CH_2OH \xrightarrow[CH_2Cl_2]{10\ kbar}$

II



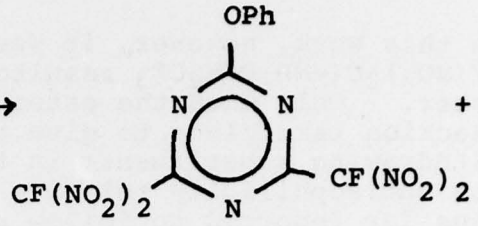
$+ CF(NO_2)_2H$

I

C. FDAN Pressurization with phenol catalysis.

The use of PhOH as catalyst for the trimerization was explored in anticipation that it would be less nucleophilic than CF_3CH_2OH by virtue of its being a more acidic alcohol. The objective of suppressing formation of a bis(aryloxy) triazine was achieved and the monoaryloxy triazine was formed as the main product.

(12) 2 $CF(NO_2)_2CN$ + PhOH $\xrightarrow[65°,40h]{10\ kbar}$



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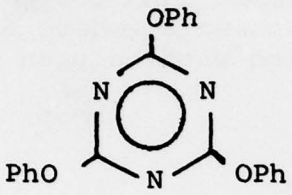
65%



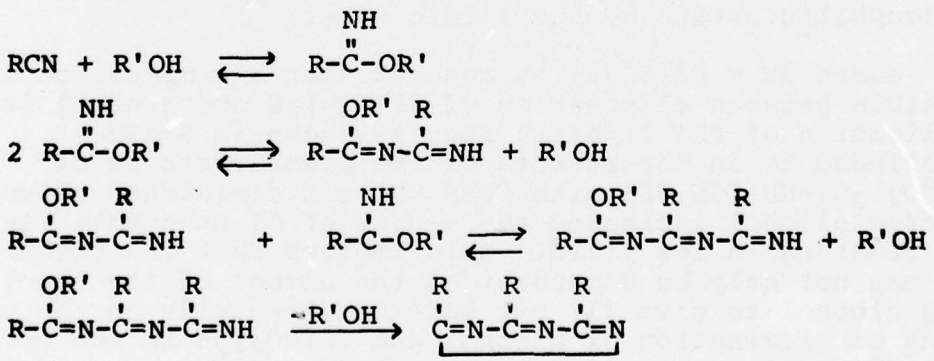
4%

A significantly higher yield of triazine products was obtained as compared to catalysis with CF_3CH_2OH. Two minor products were detected by GC with retention times in the region previously found for III, but neither appeared to coincide with III.

D. Mechanism.

The mechanism reported for alcohol catalysis of nitrile trimerization at high pressure involves initial formation of an imidic ester followed by dimerization of the imidic ester in a slow step and then further reaction of the dimer with another ester molecule and cyclization[11a-d] (Scheme 1).

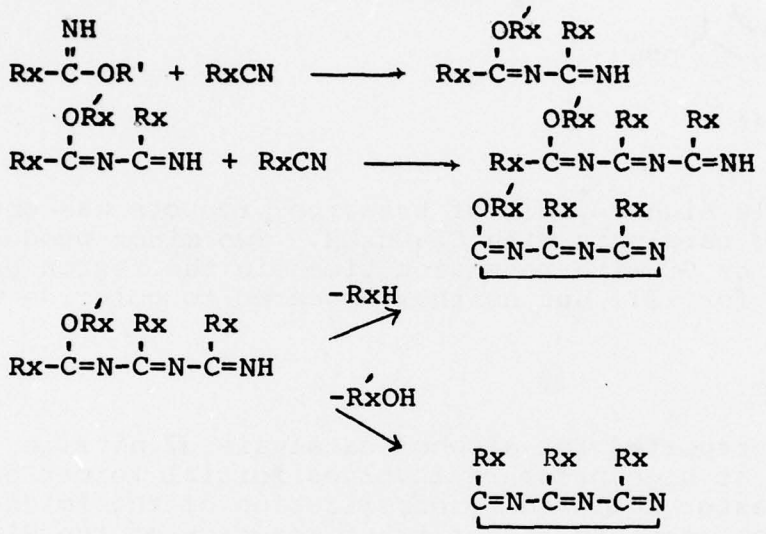
Scheme 1



11a) K. Yanagiya, M. Yasumoto, and M. Kurabayashi, Bull. Chem. Soc. Jap., 46, 2804 (1973)
b) M. Kurabayaski, K. Yanagiya, and M. Yasumoto, Bull. Chem. Soc. Jap., 44, 3413 (1971)
c) V. M. Zhulin and S. I. Volchek, Izv. Akad. Nauk SSSR, 1295 (1977)
d) W. Jarre, D. Bienik, and F. Korte, Tetrahedron, 31, 619 (1975)

In this work, however, it was found that pressurization of $CF(NO_2)_2C(=NH)OCH_2CF_3$ resulted in recovery of unchanged imidic ester. Only when the ester was pressurized with FDAN, did reaction take place to give triazine products. The electron withdrawing substituents in this imidic ester would decrease its nucleophilicity relative to those hydrocarbon esters thus far reported to follow an imidic ester dimerization mechanism. An alternate pathway is proposed then for weakly nucleophilic imidic esters as shown in Scheme 2, where Rx denotes an alkyl group heavily substituted with halogen or nitro groups.

Scheme 2



The negatively substituted Rx that contributes toward making the imidic ester unreactive in a dimerization reaction at the same time enhances reactivity of the nitrile toward nucleophilic attack by the imidic ester.

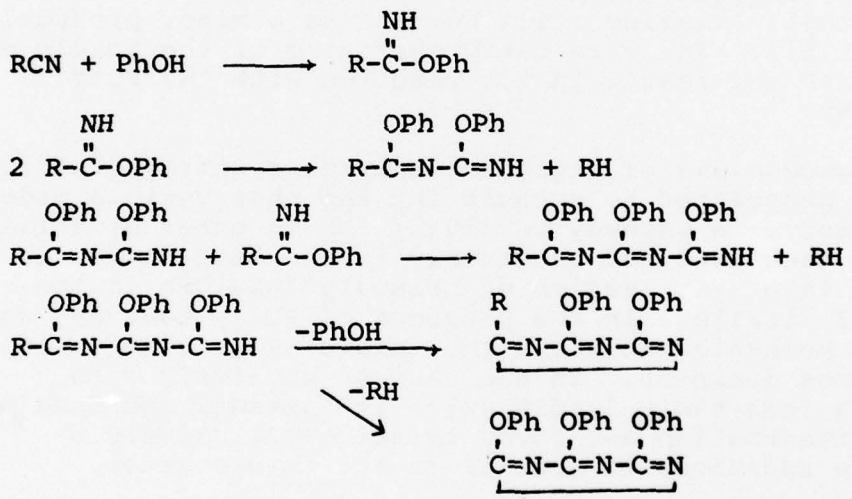
Where Rx = $CF(NO_2)_2$ it appears that a competition is possible between elimination of $CF(NO_2)_2H$ and alcohol in the cyclization of the linear trimer as shown in Scheme 2. This is alluded to in the results of the pressurization of $CF(NO_2)_2C(=NH)OCH_2CF_3$ with FDAN where a diminished amount of free alcohol increased the amount of II substantially while III remained in low yield. This implies that the yield of III may not only be dependent on the extent of its reaction with alcohol to give II, but more fundamentally on the relative rates of elimination of alcohol and $CF(NO_2)_2H$ in the cyclization of the linear trimer.

It is worth noting that in the imidic ester-FDAN experiment, if exclusive elimination of $CF(NO_2)_2H$ takes place in the cyclization to give II, there would be no free alcohol to account for formation of I. The presence of I thus gives indirect evidence of cyclization of the linear trimer to III.

The formation of a small amount of a tris(aryloxy) triazine in the phenol catalyzed experiment is in contrast to no trace of $(CF_3CH_2O)_3(CN)_3$ detected in experiments with CF_3CH_2OH. The formation of the completely substituted triazine $(RO)_3(CN)_3$ in the case where a more acidic alcohol is used cannot be explained unless it is derived by a process other than substitution. Furthermore, if 4% of $(PhO)_3(CN)_3$ is formed, then a higher yield of $(PhO)_2(CN)_3CF(NO_2)_2$ would certainly be expected. The bis(aryloxy) triazine has not been identified in the reaction mixture as yet, but TLC and IR evidence indicate that, if present, it is in very small amount.

These data suggest that trimerization is occurring by two different pathways in the case of phenol catalysis. The major pathway is according to Scheme 2 to give $PhO(CN)_3(CF(NO_2)_2)_2$. To a minor extent a process similar to Scheme 1 is followed to give $(PhO)_3(CN)_3$. This involves an imidic ester dimerization, but with the modification, now, that RH competes with PhOH for elimination (Scheme 3).

Scheme 3



The increased reactivity of $CF(NO_2)_2C(=NH)OPh$ accounts for its ability to dimerize with itself in competition with reacting with the nitrile. In the pressurization of phenol with nitrile the reaction with nitrile is dominant. Pressurization of the imidic ester in the absence of nitrile resulted in almost complete consumption of ester in contrast to no reaction found with pressurization $CF(NO_2)_2C(=NH)OCH_2CF_3$. The principal product was $(PhO)_3(CN)_3$, and there was no trace of $PhO(CN)_3(CF(NO_2)_2)_2$. These results are consistent with an imidic ester dimerization pathway in the absence of nitrile.

SUMMARY

Fluorodinitroacetonitrile (FDAN) has been trimerized to the 1,3,5-triazine structure at 10 kbar pressure with the use of acidic alcohol catalysts. The pseudohalogen character of the $CF(NO_2)_2$ group, however, makes it subject to displacement from the triazine ring by the alcohol catalyst. As a result the major triazine products bear alkoxy substituents. In the case of CF_3CH_2OH as catalyst the chief triazine product is $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$. Reaction of preformed imidic ester with the nitrile can diminish this side reaction to the point where $CF_3CH_2O(CN)_3(CF(NO_2)_2)_2$ is the chief triazine product. The monoalkoxy product is probably not derived by reaction of initially formed FDAN trimer with alcohol, but results mainly from a competition between elimination of CF_3CH_2OH or $CF(NO_2)_2H$ in the cyclization of the linear trimer precursor to the triazine. There is evidence that the FDAN cyclotrimer is formed in low yield with CF_3CH_2OH as catalyst, but the compound has not been isolated.

The use of the more acidic PhOH as catalyst gives $PhO(CN)_3(CF(NO_2)_2)_2$ as the chief product, but the tris(fluorodinitromethyl) triazine still remains as a minor product, if present at all. The more basic character of the imidic ester in this case may result in its reaction with the FDAN cyclotrimer.

Two mechanisms of alcohol-catalyzed cycotrimerization have been postulated to account for the observations made in this study. A pathway involving imidic ester dimerization, which has been reported previously in the literature, is operative in pressurization of $CF(NO_2)_2C(=NH)OPh$ in the absence of nitrile. In the presence of FDAN, however, an alternate mechanism in which the imidic ester reacts with FDAN becomes dominant. In the case of catalysis with CF_3CH_2OH a less basic imidic ester is formed which does not undergo dimerization and forms triazine exclusively by successive additions of nitrile to the imidic ester.

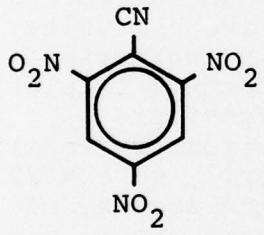
DIRECTION OF FUTURE WORK

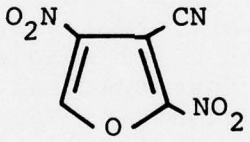
Use of the acidic alcohols CF_3CH_2OH and PhOH as catalysts in the cyclotrimerization of FDAN has provided valuable mechanistic information about this process. It is apparent that in choosing an alcohol consideration must be given to its pKa insofar as it is predictive of the tendency of the alcohol to displace $CF(NO_2)_2$ from the triazine. In substituting PhOH (pKa10) for CF_3CH_2OH (pKa12) a decrease

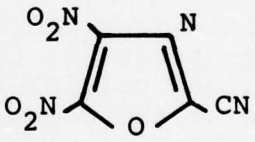
in $CF(NO_2)_2$ displacement occurred.[12] At the same time an increase in triazine yield was observed. A negatively substituted phenol appears at this point to offer the best opportunity to minimize displacement while at the same time not diminishing the nucleophilic properties of the imidic ester to the extent that would be expected if a comparably acidic aliphatic alcohol were used.

The problem of competition between elimination of $CF(NO_2)_2H$(pKa7.7) and the alcohol catalyst in the cyclization step may also be addressed by choice of a phenol with a pKa comparable to or less than that of the methane. Future work will thus be directed towards utilization of phenols such as p-$O_2NC_6H_4OH$(pKa7.2) and C_6F_5OH(pKa5.5). It is hoped that this will lead to the formation of tris(fluorodinitromethyl) triazine in yields sufficient to make its isolation and characterization feasible.

Other plans include the investigation of the trimerization of nitroaromatic and nitrosubstituted heterocyclic nitriles which are expected to form high-density energetic triazines.







12) This may also be due in part to a decrease in reactivity of the triazine ring in $RO(CN)_3(CF(NO_2)_2)_2$ towards nucleophiles with R=Ph vs. nucleophiles with R=CH_2CF_3.

EXPERIMENTAL

High pressure experiments were done with a standard 200,000 psi pressure generating panel from Harwood Engineering Company, Inc. The apparatus delivered a high pressure fluid composed of 50/50 ethylene glycol/water to a Harwood bomb with a 6x1 inch bore for containment of sample vessels. The bomb was heated with an external wrap of heating tape and the fluid pressure inside was measured with a bulk modulus cell connected by a "T" to the inlet pipe. Sample tubes of teflon (3.5 ml capacity) and copper (nickel plated copper bellows tubing, 32 ml) were sealed with threaded caps, after filling the tubes to capacity with solution, and subjected to hydrostatic pressure in the bomb. GC analysis was done on a 4'x1/8" column of 5% UC W-982 silicone rubber/chrom P at 65 ml/min He flow with a TC detector. Normalized areas reported herein are not corrected for relative thermal responses. TLC analyses were done on precoated plastic plates with fluorescent binder (0.25 mm layer of silica gel) and precoated glass plates (0.25 mm silica gel) using toluene as solvent. Triazine products containing no phenyl groups were best analyzed on the glass plates with the use of the following sequential sprays for visualization: 1) 50% KOH in MeOH, and 2) dilute solution of Ph_2NH in 50% H_2SO_4. NMR chemical shift data are reported in positive ppm units (δ) downfield from Me_4S (int. std.) and in positive ppm units (ϕ*) upfield from $CFCl_3$ (int. std.). Splitting patterns are designated s, q, t, and m for singlet, quartet, triplet, and undefined multiplet. Mass spectral analyses were performed at the Cornell University Mass Spectrometry Facility with CH_4 chemical ionization. Samples frequently gave M+29 and M+41 peaks in addition to the usual M+1 ion because of addition of C_2H_5 and C_3H_5 to the molecule. Data are presented as the fragment mass and, in parenthesis, its presumed structure and relative abundance.

A. Fluorodinitroacetonitrile

The preparation of FDAN (bp 74°) by aqueous fluorination of $NaC(NO_2)_2CN$ has been described.[10a] A solution of the products from this reaction obtained by extraction with CF_2ClCCl_2F (Freon 113, bp 48°) contained ca. 10% by weight FDAN.[13] Preliminary distillations were done at one atmosphere and then at 360 mm[14] with a Vigreux column. Nonvolatile side products (13% by weight of isolated FDAN) were then removed by flash distillation at 20°/0.01 mm.

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13) This product solution was purchased from Fluorochem, Inc.
14) Attempted fractionation of concentrated product solution at atmospheric pressure resulted in decomposition as evidenced by evolution of brown fumes.

Final distillation at 200 mm gave pure nitrile with bp 52-53° (d^{20} 1.49) and a residue (18% by weight of isolated FDAN)of nitrile, $CF(NO_2)_2H$, and unidentified impurity.

B. Fluorodinitroethyl Fluorodinitroacetimidate

The general procedure as described for the addition of $CF_2NO_2CH_2OH$ to FDAN was followed.[10b] A solution of $CF(NO_2)_2CH_2OH$ (5.60 g, 36.4 mmol) and Et_3N (20 mg, 0.2 mmol) in 25 ml Et_2O was treated dropwise during a 30 min. period with a solution of FDAN (3.58 g, 24.0 mmol) in 5 ml Et_2O. The resultant yellow solution was stirred for two hours and then washed with water (2x50 ml) and saturated NaCl solution (50 ml). The dried ($MgSO_4$) solution was concentrated on a rotary evaporator to 6.94 g of yellow oil. Short path distillation at 2.5 mm gave 2.44 g of $(CF(NO_2)_2CH_2OH$. Continuation of the distillation at a lower pressure gave 2.44 g (34%) of $CF(NO_2)_2C(=NH)OCH_2CF(NO_2)_2$ with bp 68-69°/ 0.038. Traces of $CF(NO_2)_2C(=O)NH_2$ codistilled with the product could be removed by extraction of the amide from a CCl_4 solution of the imidic ester with water. The pure material had the following properties: mp 27-28°; d^{20} 1.670; ir (film) 1700 (C=N) and 3350 cm^{-1} (N-H); ^1H nmr (CCl_4) δ 9.42 (s,1,NH) and 5.46 (d,2,J=17Hz, CH_2) ppm; ^{19}F nmr ϕ* 102 ($CF(NO_2)_2C=NH$) and 110 ($CF(NO_2)_2CH_2$) ppm.

Anal

Calcd for $C_4H_3F_2N_5O_9$: C, 15.85; H, 1.00; F, 12.54; N, 23.11

Found: C, 16.11; H, 0.95; F, 12.50; N, 22.85

In a test of its moisture sensitivity the imidic ester was spread on an open dish and exposed to 80% R.H. at room temperature for five weeks without any hydrolysis detected by NMR analysis for $CF(NO_2)_2CH_2OH$. Hydrolysis did occur in a homogeneous solution of imidic ester (0.37 mmol), D_2O (5.56 mmol), and 0.25 ml CH_3CN. Measurement of methylene areas due to imidic ester (δ 5.58) and alcohol (δ 4.59) showed 0, 4.6, 18.1, and 19.6 percent hydrolysis for 2,6,74 and 116 h. A sample exposed to 100° under vacuum[15] gave an initial 30 min. surge of 2.96 cc/g of gas, and during the next 48 h evolved 4.39 cc/g. The recovered material had a trace of suspended white solid, but its IR spectrum was identical to that of pure imidic ester.

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15) Simmons, H. T., Sr., "The Vacuum Thermal Stability Test for Explosives," NOLTR 70-142, 28 Oct 1970.

C. Trifluoroethyl Fluorodinitroacetimidate

A solution of 5.2 g (35 mmol) FDAN, 4.0 g (40 mmol) CF_3CH_2OH, and 20 µl Et_3N in 6 ml CH_2Cl_2 was stirred at 20° for one hour and then washed with four equal volumes of water, dried ($MgSO_4$), and heated to 60° to distill off solvent. Continued distillation at 200 mm provided 1.9 g of recovered FDAN. The pressure was then decreased to 7 mm whereupon 5.80 g (66%) of imidic ester was collected: bp 51-52°/7 mm; ir (film) 3350 (N-H) and 1698 cm^{-1} (C=N); ^1H nmr (CCl_4) δ 9.16 (s,1,NH) and 4.74 (q,2,J=8 Hz, CH_2) ppm; ^{19}F nmr φ* 56.4 (CF_3) and 76.4 ppm ($CF(NO_2)_2$); ms 278 (M+29,1), 250 (M+1,8), 204 (M+1-NO_2,22), 101 ($CF_3CH_2OH_2$,100), 81 (CF_2=$CHOH_2$,78).

Anal

Calcd for $C_4H_3F_4N_3O_5$: C, 19.29; H, 1.21; F, 30.51;N, 16.87
Found: C, 19.27; H, 1.22; F, 30.62; N, 17.14

D. Phenyl Fluorodinitroacetimidate

FDAN (4.47 g, 30.0 mmol) was added dropwise over a 10 min. period to a stirred slurry of PhOH (2.71 g, 28.8 mmol) and K_2CO_3 (0.5 g, 4 mmol) in 20 ml CH_2Cl_2. The solution turned orange and a slight warming was noted. After three hours at 20° the solution was refluxed for one hour then filtered and concentrated on a rotary evaporator to give 6.71 g of red liquid. Short path distillation at 2 mm provided 1.26 g of pure phenol (bp 50-52°). Some phenol and FDAN also collected in a cold trap. The 1.92 g of residue was homogeneous by GC and TLC (trace of origin material) and represents a 27% yield of $CF(NO_2)_2C(=NH)OPh$. Continued distillation gave 1.07 g of a light yellow liquid with the following properties: bp 66-67°/0.32 mm; mp 38.5-41.0°; ir (film) 3300 (N-H) and 1692 cm^{-1} (C=N); ^1H nmr (CCl_4) δ 8.31 (s, NH) and 7.24 (m, C_6H_5); ^{19}F nmr φ* 101 ppm; ms 284 (m+41,2), 272 (M+29,1), 244 (M+1,62), 198 (M+1-NO_2,55), 168 (M+1-N_2O_3,88), 152 (198-NO_2,100), 151 (M+1-OPh,51), 122 ($OCF(NO_2)CHO$,93), and 93 (PhO,98).

Anal

Calcd for $C_8H_6FN_3O_5$: C, 39.51; H, 2.49; F, 7.81; N, 17.28
Found: C, 39.48; H, 2.39; F, 7.63; N, 17.29

E. Tris(trifluoroethoxy)-1,3,5-triazine

This compound was prepared in 61% yield by a literature method involving reaction of cyanuric chloride with the

potassium salt of CF_3CH_2OH. Material recrystallized from hexane had mp 55-57° (lit[16] mp 45-46°). Previously unreported spectral data are presented here: ir (KBr) 1592 cm^{-1} (C=N); ^1H nmr (CCl_4) δ 4.76 (q, J=8.3 Hz) ppm; ^{19}F nmr ϕ* 56.4 ppm.

F. FDAN and CF_3CH_2OH at Ambient Pressure. Control Experiment

A solution of 0.46 g (3.1 mmol) FDAN and 0.15 g (1.5 mmol) CF_3CH_2OH in 4 ml CH_2Cl_2 was refluxed for 30 h. Removal of volatiles on a rotary evaporator gave 0.229 g of colorless liquid, which by GC, IR, and NMR analyses was pure $CF(NO_2)_2C(=NH)OCH_2CF_3$ (61% yield). None of the triazene products observed at high pressure were observed in this experiment.

G. FDAN and $CF(NO_2)_2C(=NH)OCH_2CF_3$ at Ambient Pressure. Control Experiment

A flask equipped with a condenser and drying tube and containing 0.63 g (2.53 mmol) imidic ester and 1.49 g (10.0 mmol) FDAN was heated in a 67° oil bath for 40 h. Analysis by IR, GC, and TLC showed only recovered starting materials and no evidence for the products observed at high pressure.

H. Pressurization of $CF(NO_2)_2C(=NH)OCH_2CF_3$ in CH_2Cl_2

A solution of 0.75 g (3.0 mmol) of imidic ester in 3 ml CH_2Cl_2 was held in a teflon vessel at 10.3 kbar and 65° for 39 h. Removal of solvent on a rotary evaporator gave 0.71 g (95%) of recovered ester which was pure by GC, IR, and TLC analyses.

I. Pressurization of FDAN and CF_3CH_2OH in CH_2Cl_2 at 40°

A solution of 0.46 g (3.1 mmol) FDAN, 0.15 g (1.5 mmol) CF_3CH_2OH, and 3 ml CH_2Cl_2 contained in a teflon vessel was subjected to 10.5 kbar at 40° for 35 h. Rotary evaporation gave 0.49 g residue of colorless liquid. IR analysis indicated $CF(NO_2)_2C(=NH)OCH_2CF_3$ for an apparent yield of 67%. There were, however, two extraneous weak bands at 1500 and 1390 cm^{-1}. The presence of an impurity was confirmed by NMR analysis where the expected singlet (NH) and quartet (CH_2) were observed, but the area ratio was 1/3.5. There was also a small amount of $CF(NO_2)_2H$ present at δ 6.74 with J=50 Hz. Data from subsequent experiments showed the excess area in the methylene region to be due to the overlapping quartet of $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$. The imino hydrogen area was used to calculate the amount of methylene area due

16) A. J. Matuszko and M. S. Chang, J. Org. Chem., 27, 677 (1962).

to triazine. A composition of 76% imidic ester and 24% triazine was thus calculated. The 0.249 g residue contained then 0.69 mmol (46% yield based on CF_3CH_2OH) of imidic ester and 0.22 mmol (21% yield based on FDAN) triazine.

J. Pressurization of FDAN and CF_3CH_2OH in CH_2Cl_2 at 65°

A solution of 8.94 g (60 mmol) FDAN, 2.00 g (20 mmol) CF_3CH_2OH, and 25 ml CH_2Cl_2 contained in metal bellows tube was held at 10.3 kbar and 65° for 60 h. GC analysis of a light yellow residual liquid (6.55 g) left after rotary evaporation of volatiles showed residual CH_2Cl_2 and FDAN together with products of the following composition: $CF(NO_2)_2C(=NH)OCH_2CF_3$ (74%), I (18%), II (6%), and III (2%). Compared to the imidic ester which eluted rapidly at 75°, the unknowns eluted in a cluster of three peaks at 150°, 170°, and 200° on a 30°/min temperature program. Distillation at 7 mm gave 2.0 g of imidic ester (bp 52°) and a 1.89 g residue composed of 12% residual ester and 88% unknowns by GC analysis (24% crude yield of triazine products). Continued short path distillation at 0.012 mm gave 0.94 g of I, identified as $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$, and a residue of 0.56 g. The triazine had the following properties: bp 80°/0.012 mm; ir (film) 1605 (broad) with 1550 cm^{-1} shoulder; ^1H nmr (CCl_4) δ 4.83 (q, J=7.7 Hz, CH_2) ppm; ^{19}F nmr ϕ* 56.4 (OCH_2CF_3) and 77.2 ($CF(NO_2)_2$) ppm; ms 440 (M+41, 6), 428 (M+29, 9), 400 (M+1, 100), 380 (M-F, 9), and 354 ($M+1-NO_2$, 33).

The 0.56 g of residue contained some $CF(NO_2)_2C(=O)NH_2$ by IR analysis. The amide was a minor contaminant of distilled I also. It was removed by water extraction of a CCl_4 solution of I. GC analysis of the 0.56 g residue showed a mixture of I (36%), II (42%), and III (22%). TLC analysis showed I with R_f 0.70 as compared to 0.52 for the imidic ester. Other spots occurred at 0.20 and 0.14. An origin spot occurred and would be expected for the amide. A GC/MS analysis of the residue gave data for II consistent with the triazine $(CF(NO_2)_2)_2(CN)_3OCH_2CF_3$: 424 (M+1, 2), 348 ($M+1-N_2O_3$), 302 ($M+1-N_2O_3$, NO_2; 12), 272 ($M+L-(N_2O_3)_2$, 100), 272-HF, 28), and 125 ($(CN)_3CFO$, 66) The peak for III in the same chromatogram gave the following data consistent with $(CN)_3(CF(NO_2)_2)_3$: 357 (M-3NO, 3), 317 ($M-2NO_2F$, 25), 271 ($317-NO_2$, 94), 241 (271-NO, 100). Fragments also occurred, however, at 226 (23), 221 (43), and 193 (14). These could not be interpreted as logical fragments of the triazine, and may represent an overlapping impurity in the chromatogram or are evidence that the GC peak is due to a compound of different structure.

The residue was chromatographed on a silica gel column with 50/50 cyclohexane/CH_2Cl_2 to give an analytical sample of I.

Anal

Calcd for $C_8H_4F_7N_5O_6$: C, 24.07; H, 1.01; F, 33.32; N, 17.55
Found: C, 23.79; H, 1.04; F, 33.15; N, 17.80

Compounds II and III did not elute with 100% CH_2Cl_2 and they appear to have reacted with the silica gel.

K. $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$ and $KOCH_2CF_3$

The triazine structure of I was confirmed by its conversion to the known $(CF_3CH_2O)_3(CN)_3$. A solution of 0.11 g I in 2.5 ml CF_3CH_2OH was treated with a 0.18 g pellet of KOH. A yellow color developed immediately on the surface of the pellet. As the solution was swirled to dissolve the pellet a slight warming occurred and the solution filled with a suspension of bright yellow precipitate. The precipitate disappeared in ca. 30 min. to give a colorless solution. GC analysis showed complete consumption of I and the appearance of a new compound with shorter retention time. This was shown to be $(CF_3CH_2O)_3(CN)_3$ by spiking the solution with an authentic sample. A sample of the product isolated by extraction with CH_2Cl_2/H_2O gave an IR spectrum identical to that of the known triazine.

L. Pressurization of FDAN and CF_3CH_2OH in CH_2Cl_2/CH_3CN

A teflon vessel containing 0.92 g (6.2 mmol) FDAN, 0.31 g (3.1 mmol) CF_3CH_2OH, and 3 ml of a 50/50 mixture of CH_2Cl_2 and CH_3CN was held at 10.5 kbar and 60° for 24 h. The solution had turned yellow and there was some release of gas on opening the vessel. The CH_2Cl_2 was first distilled off at 1 atm and then a mixture of FDAN and CH_3CN was distilled at 200 mm. The residue of 0.88 g appeared to be mainly $CF(NO_2)_2C(=NH)OCH_2CF_3$ by IR and would represent a 114% yield if pure. GC and TLC analysis showed the presence of $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$, however. An aliquot of the residue was analyzed by NMR with respect to an internal standard of benzene to show the following components: imidic ester (1.95 mmol, 63% based on CF_3CH_2OH), $(CF_3CH_2O)_2(CN)_3CF(NO_2)_2$ (0.44 mmol, 21% based on FDAN), and $CF(NO_2)_2H$ (0.92 mmol).

M. Pressurization of FDAN and $CF(NO_2)_2C(=NH)OCH_2CF_3$ in CH_2Cl_2

A teflon vessel containing 1.49 g (10.0 mmol) FDAN, 0.63 g (2.53 mmol) $CF(NO_2)_2C(=NH)OCH_2CF_3$, and 2 ml CH_2Cl_2

was held at 10.3 kbar and 65° for 23 h. The solution was concentrated on a rotary evaporator to a light yellow liquid of 0.84 g. GC analysis showed the following area percent composition: $CF(NO_2)_2C(=NH)OCH_2CF_3$ (96.4%), I (0.5%), II (2.7%), III (trace), and unknown of long retention time (0.4%). The ratio of I:II changed from 75:25 obtained in pressurization of FDAN and alcohol in CH_2Cl_2 to 15:85 in this experiment. TLC analysis showed a noticeable increase in the intensity of a spot at R_f=0.15 as compared to this spot in the analysis of the FDAN-alcohol reaction. Spots were thus assigned as follows: I (0.69), imidic ester (0.50), II (0.15), unknown (0.08), and origin spot. The spot with R_f 0.08 may be due to III. The much slower migration of II on the plate as compared to I is probably due to its hydrolysis to $CF(NO_2)_2(OH)(CN)_3OCH_2CF_3$ on contact with the silica gel. After several weeks storage of the rotary evaporator residue, GC analysis revealed a considerable decrease in II, presumably due to hydrolysis.

N. Pressurization of FDAN with PhOH in CH_2Cl_2

A teflon vessel loaded with 2.03 g (13.6 mmol) FDAN, 0.64 g (6.8 mmol) PhOH, and 1.92 g (1.4 ml) CH_2Cl_2 was held at 10.1 kbar and 65° for 40 h. Gas pressure was vented as the vessel was opened. The red solution was concentrated on a rotary evaporator to a viscous red liquid of 2.21 g. IR and GC analysis showed the absence of PhOH and $CF(NO_2)_2C(=NH)OPh$. The residue was subjected to 0.05 mm in a 120° bath to give a red-brown solid of 1.28 g. Most of the volatiles removed under these conditions did not condense in the receiver and were swept into a cold trap. Small amounts of a solid (C=O at 1774 cm^{-1}) and a liquid (C=O at 1800 cm^{-1}) condensed in the distillation head. TLC analysis of the 1.28 g residue showed small components at R_f=0.0, 0.11, 0.18, 0.21, and 0.32 with fluorescent visualization. The major spot occurred at 0.71. The 0.21 spot had the same R_f value as $(PhO)_3(CN)_3$. Visualization with a spray specific for nitro compounds revealed spots at 0.0, 0.15, 0.28 (faint), and a large 0.74 spot. GC analysis at a 30°/min program rate from 80° to 200° showed the following components (area %): 1) peak eluting at 185° (10.8%), 2) peak eluting 1 min after 200° limit reached (7.6%), and 3) peak eluting 8 min after 200° limit (81.6%). The major component was distilled from a portion of the 1.28 g residue in a short path apparatus at 0.056 mm and 100-123° bath temperature. The IR of this material was the same as that of the 1.28 g residue material. Its structure was assigned as $PhO(CN)_3CF(NO_2)_2$. The 1.28 g residue represents a 68% yield of this triazine. The viscous yellow liquid had the following properties: ir (film) 1605 (strong, with shoulders at 1570 and 1542), 1462 (strong), and 1385 (strong) cm^{-1};

'H nmr ($CDCl_3$) δ 7.24 (m, C_6H_5); ^{19}F nmr ϕ* 100 (s, broad, $CF(NO_2)_2$); ms 458 (M+41, 2), 446 (M+29, 5), 418 (M+1, 43) 388 (M+1-NO, 19), 372 (M+1-NO_2, 11), 215 (M+1-N_2O_4, F; 79), 171 ($PhO(CN)_3$, 11), 140 ($(CF)_2(CN)_3$, 100), 125 ($(CN)_3CFO$, 28), 95 ($(CN)_3OH$ or $PhOH_2$, 65).

The $(PhO)_3(CN)_3$ product was isolated from the 1.28 g residue by column chromatography on silica gel with CH_2Cl_2/ cyclohexane solvent to give 0.06 g (4% yield based on FDAN).

O. Pressurization of $CF(NO_2)_2C(=NH)OPh$ in CH_2Cl_2

A teflon vessel with 0.73 g of $CF(NO_2)_2C(=NH)OPh$ in 3 ml CH_2Cl_2 was held at 10.3 kbar and 65° for 44 h. Gas pressure was vented as the vessel was opened and a brown solution mixed with fine particles of black solid was poured from the vessel. Analysis by GC showed almost complete comsumption of imidic ester and a single major product peak in low yield at 185° on the 30°/min temperature program used in previous analyses. This peak corresponds to the 185° peak in the nitrile-phenol reaction. There was no trace of $PhO(CN)_3(CF(NO_2)_2)_2$ by GC analysis. TLC analysis showed $(PhO)_3(CN)_3$ and origin material as the major components of the mixture. A quantitative analysis of this experiment was not complete as of this writing.

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