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SYNTHESIS OF ENERGETIC MATERIALS AT HIGH PRESSURES.(U)
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WORK REQUEST
N0001479WR90056

(9) Annual Technical Report for FY 1979

(6) SYNTHESIS OF ENERGETIC MATERIALS AT HIGH PRESSURES

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White Oak
Silver Spring, Maryland 20910

(11) March 1980

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A084800	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis of Energetic Materials at High Pressures	5. TYPE OF REPORT & PERIOD COVERED Annual Report for FY79
	6. PERFORMING ORG. REPORT NUMBER None
7. AUTHOR(s) W. M. Koppes and H. G. Adolph	8. CONTRACT OR GRANT NUMBER(s) N0001479WR90056
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center White Oak, Silver Spring, Maryland 20910	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N; RR02402; RR0240201; 9R11AA701
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Code 473 Arlington, VA 22217	12. REPORT DATE March 1980
	13. NUMBER OF PAGES 36
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

N/A

18. SUPPLEMENTARY NOTES

None

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

High Pressure Synthesis; Fluorodinitromethyl triazines; Fluorodinitroacetonitrile; Explosives

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The utility of a high-pressure technique to effect the trimerization of fluorodinitroacetonitrite to the corresponding triazine has been investigated. A Harwood Engineering Co. high-pressure apparatus, which had been assembled and debugged during last year's effort, was used throughout this work and was found to deliver with adequate reliability pressures of up to 1 GPa (10 Kbar) for 48-72 h periods. Whereas fluorodinitroacetonitrile had resisted previous ambient pressure attempts at trimerization with a variety of catalysts, it was

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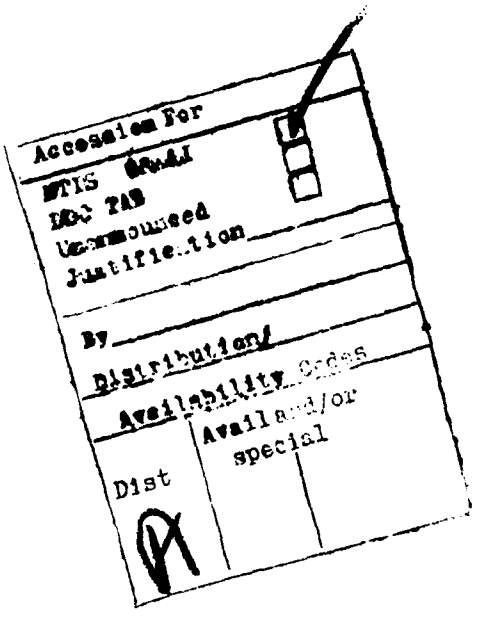
found to form triazines quite readily when subjected to 1 GPa pressures in the presence of certain primary alcohols and phenols. However, the triazines formed contained a mixture of fluorodinitromethyl and alkoxy or aryloxy substituents, apparently as a consequence of competition between $CF(NO_2^-)_2^-$ and ROH for elimination in the cyclization steps, or of nucleophilic displacement of $CF(NO_2^-)_2^-$ by ROH in the initial triazine product. A study was made of the effect of ROH acidity on product composition with the finding that mixed triazines formed in all cases in which reaction occurred. An alternative mechanism for triazine formation from nitriles was postulated to account for some novel observations made during this work. Our results indicate that tris (fluorodinitromethyl) triazine must be highly susceptible to nucleophilic attack with displacement of at least one $CF(NO_2^-)_2^-$ group, and would thus be subject to easy hydrolysis.

Table of Contents



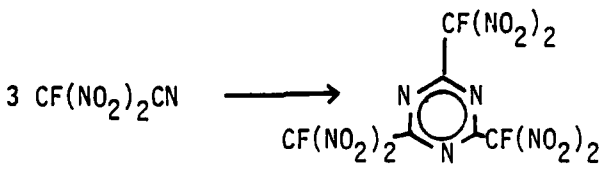
Summary

The utility of a high-pressure technique to effect the trimerization of fluorodinitroacetonitrile to the corresponding triazine has been investigated. A Harwood Engineering Co. high-pressure apparatus, which had been assembled and debugged during last year's effort, was used throughout this work and was found to deliver with adequate reliability pressures of up to 1 GPa (10 Kbar) for 48-72 h periods. Whereas fluorodinitroacetonitrile had resisted previous ambient pressure attempts at trimerization with a variety of catalysts, it was found to form triazines quite readily when subjected to 1 GPa pressures in the presence of certain primary alcohols and phenols. However, the triazines formed contained a mixture of fluorodinitromethyl and alkoxy or aryloxy substituents, apparently as a consequence of competition between $CF(NO_2)_2$ and ROH for elimination in the cyclization steps, or of nucleophilic displacement of $CF(NO_2)_2$ by ROH in the initial triazine product. A study was made of the effect of ROH acidity on product composition with the finding that mixed triazines formed in all cases in which reaction occurred. An alternative mechanism for triazine formation from nitriles was postulated to account for some novel observations made during this work. Our results indicate that tris (fluorodinitromethyl) triazine must be highly susceptible to nucleophilic attack with displacement of at least one $CF(NO_2)_2$ group, and would thus be subject to easy hydrolysis.

Foreword

The purpose of this work was to investigate the utility of high pressure techniques for the synthesis of new high energy compounds where the use of elevated temperatures as a tool to effect chemical reactions is often precluded because of thermal instability of product, reaction intermediates, or starting 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. 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 magnitude of the pressure effect varies with reaction type and is particularly large for addition reactions in which the number of moles of products is smaller than the number of moles of reactants (for a more detailed discussion, see G. Jenner, Angew. Chem. Internat. Edit., 1975, 137). Consequently, such a reaction type was chosen for study. A suitable reaction was identified in the cyclotrimerization of nitroacetonitriles to tris (nitromethyl) triazines, specifically that of fluorodinitroacetonitrile, which we had found to resist trimerization by conventional means.



The product which results from this trimerization of the latter compound is of great interest as a high energy material because of its high oxygen content and predicted high crystal density.

A partial account of this work has been given in the previous annual report (W. M. Koppes and H. G. Adolph, NSWC/WOL MP 78-22, December 1978). The results of this year's effort, which has brought to a conclusion the work on trimerization of fluorodinitroacetonitrile, are given in a manuscript prepared for publication, which constitutes the remainder of this report.

Pressure Induced Cyclotrimerization of Electron Deficient Nitriles. Catalysis by Acidic Alcohols and Phenols.

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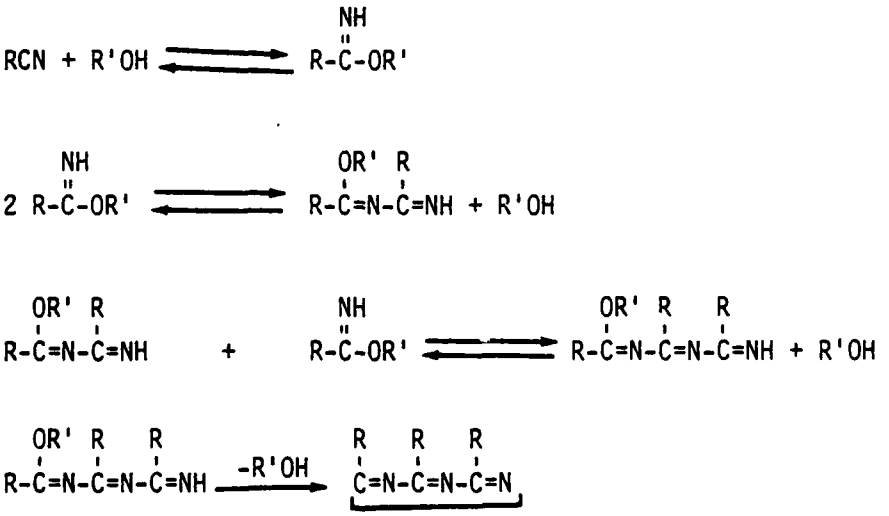
Fluorodinitroacetonitrile, 1, was pressurized at 1 GPa in the presence of a variety of ROH catalysts. Cyclotrimerization of 1 occurred in several cases but the observed triazines contained RO groups in place of one or several $CF(NO_2)_2$ groups. Some mechanistic aspects of this reaction are explored by comparison with the results of the pressurization of preformed fluorodinitroacetimidates.

INTRODUCTION

Nitriles differ considerably in their ability to undergo cyclotrimerization to 1, 3, 5-triazines under the influence of acidic or basic catalysts. Facile trimerization has been reported for some nitriles[1] (eg., CCl_3CN, 2-cyanonaphthalene but not 1-cyanonaphtalene with HCl/PCl_5[2]; F - alkyl nitriles with NH_3[3]) but in general the scope of this reaction has been limited. The use of high pressure, as first reported by Cairns[1a] allowed a larger variety of nitriles to be cyclotrimerized. Subsequently, Kurabayashi[4] et al., Korte[1b], and Zhulin[5] provided additional examples and showed that a probable mechanism is formation of imidate ester (or amidine) and its self condensation to triazine (Scheme 1).

Scheme 1



Among the nitriles which have resisted attempts at cyclotrimerization by conventional means are difluoronitro and fluorodinitroacetonitrile (1), the fact not withstanding that inductively electron withdrawing substituents normally facilitate this process. Thus, Bissel[6] found that the ammonia-catalyzed

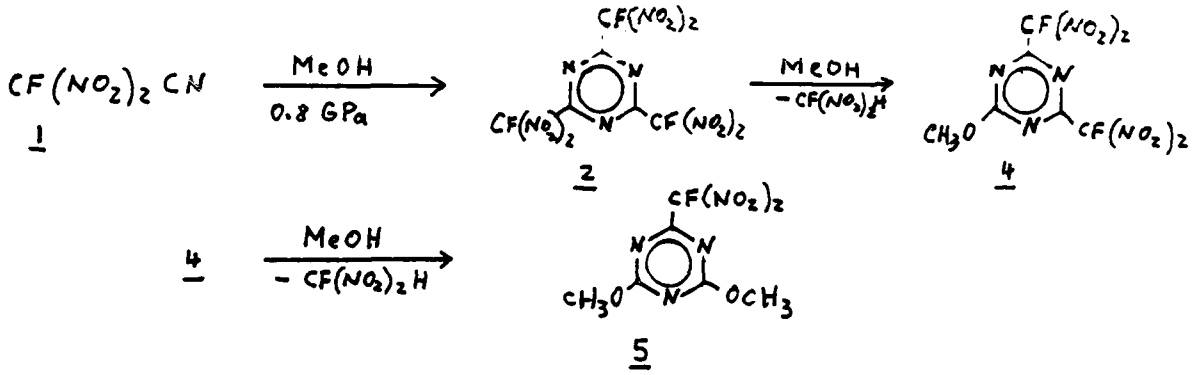
trimerization of F-alkyl nitriles, in which amidines are formed as intermediates, could not be extended to difluoronitroactonitrile because difluoronitroacetamidine on heating eliminates difluoronitromethane rather than ammonia. In fluorodinitroacetonitrile, the C-C bond should be cleaved by bases even easier, although the amidine can be prepared at low temperature[7]. Several attempts at acid-catalyzed trimerization of 1 were also not successful. Thus, with the catalyst PCl_5/HCl, 1 forms a homogeneous solution from which it can be recovered largely unchanged after heating for several weeks at 60^o without indication of any triazine formation. With chlorine fluorsulfate, $ClOSO_2F$,a 1:1 adduct is formed[8]. Since 1 begins to decompose near its boiling point (74^oC), the use of forcing conditions of temperature is precluded. In our efforts to effect the trimerization of 1 to tris(fluorodinitromethyl)triazine, $\{CF(NO_2)_2\}_3(CN)_3$, 2, we have investigated and report here on the application of the pressure method to this reaction.

RESULTS

The use of the usual catalyst, methanol, for the high pressure trimerization of 1 was first explored since the preparation of methyl fluorodinitroacetimidate, 3, in 50% yield from 1 and methanol had been reported[7]. In our experience, this reaction is strongly affected by the presence of water in the methanol which catalyses an unidentified exothermic process leading to the evolution of CO_2 and the destruction of 1; care is therefore required to ensure anhydrous conditions in reactions involving 1 and methanol. When a 3:1 mixture of 1 and methanol in dichloromethane was pressurized for 44 hours at 0.8 GPa and 60^oC, the resulting solution contained 3 and two new compounds in the ratio 70:30 (by GC peak areas) which were assigned structures 4 and 5, respectively, on the basis of GC/MS analysis. Mass spectra with base peaks at M+1 were obtained for 4 and 5 after GC separation. No evidence could be

found for the presence of 2 in the reaction mixture. The crude yields of triazines 4 and 5 were ca. 45% and 19%, respectively.

On the basis of the accepted mechanism (Scheme 1), the unexpected appearance of methoxy groups in the product could result from competition for elimination by fluorodinitromethane and methanol in the dimerization and trimerization steps of the initially formed 3. This seems unlikely, however, since a similar competition would be expected in the final cyclization step and would result in the formation of trimethoxy triazine, which was also not found among the products. A more probable explanation is that 2 was formed intitially, but that the methanol present in the system caused successive displacement of fluorodinitromethyl groups from the triazine ring[9]. Since the susceptibility to such nucleophilic displacement should decrease in the order 2>4>5, the observed product distribution is readily accounted for.



Without studying this reaction in greater detail it was decided to investigate more acidic alcohols as trimerization catalysts on the supposition that they would be less effective in displacing fluorodinitromethide in 2 and thus might permit its isolation. In an effort to minimize the amount of free alcohol in the system we also investigated the use of preformed imidate in place of the mixture of 1 and alcohol. These esters (Table 1) were prepared by the base catalyzed addition of the appropriate alcohol to 1. The use of potassium

carbonate generally gave better results than triethylamine.

Table 1. FLUORODINITROACETIMIDATES, $CF(NO_2)_2C(=NH)OR$, FROM 1 AND ROH.

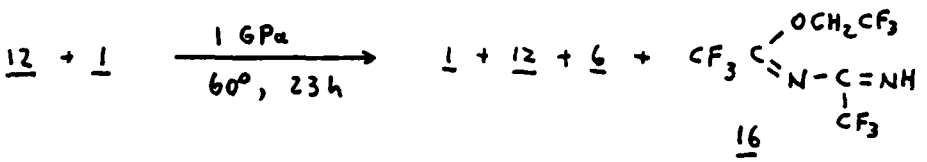
R	No.	Yield (%)	bp (kPa)	mp °C
CF_3CH_2	6	66	51-52 (7)	-
$CF(NO_2)_2CH_2$	7	34	68-69 (0.005)	27-28
C_6H_5	8	90 (crude)	70 (0.3)	38.5-41
C_6F_5	9	22	47-48 (0.01)	-
m-CF_3-C_6H_4	10	88	80 (0.009)	50-51.5
m-$NO_2C_6H_4$	11	93 (crude)	-	59.5-61

When dichloromethane solutions of preformed imidate were pressurized at ca. 1 GPa and 60°C, the results shown in Table 2 were obtained. Pressurization of trifluoroethyl trifluoroacetimidate 12 was included for comparison purposes. Noteworthy features of this set of reactions are: a) the absence of 2 among all of the reaction products; b) the drastic differences in reactivity between the various imidates; c) the effect of added 1 on the pressurization of 6 and of CF_3CH_2OH on that of 12 . As will be seen these observations are not readily explained by the mechanistic picture of Scheme 1.

TABLE 2. PRESSURIZATION OF TRIFLUORO- AND FLUORODINITROACETIMIDATES[10]

Imidate $RC(=NH)OR'$	Conditions	Products, %			
		Imidate Recovered	Dialkyltriazine $R_2(CN)_3OR'$	Dialkoxytriazine $R(CN)_3(OR')2$	Other
6; $R=CF(NO_2)_2$ $R'=CH_2CF_3$	CH_2Cl_2, 1GPa 65^o, 39h	95	0	0	No products by TLC, GC, IR
8; $R=CF(NO_2)_2$ $R'=C_6H_5$	CH_2Cl_2, 1GPa 40^o, 20h	0	0	0	Trace $(CN)_3(OR'_3)$; no other identifiable products
10; $R=CF(NO_2)_2$ $R'=m\text{-}CF_3C_6H_4$	CH_2Cl_2, 1GPa, 60^o, 68h	>99	0	0	$(CN)_3(OR')_3$, 0.5
12; $R=CF_3$ $R'=CH_2CF_3$	CH_2Cl_2, 1GPa 60^o, 65h	69	0	0	$R_3(CN)_3$, 6; $CF_3C(NH_2)(OCH_2CF_3)_2$, 15, 2-3
12 + CF_3CH_2OH $R = CF_3$ $R' + CH_2CF_3$	CF_3CH_2OH 1GPa, 60^o, 65h	not determined	0	0	$R_3(CN)_3$, 16; 15,2
6 + 1 $R = CF(NO_2)_2$ $R' = CH_2CF_3$	CH_2Cl_2, 1GPa 65^o, 23h	96	13, 2.7	14, 0.5	

When 12 was pressurized in the presence of 1, a more complex set of products was obtained:



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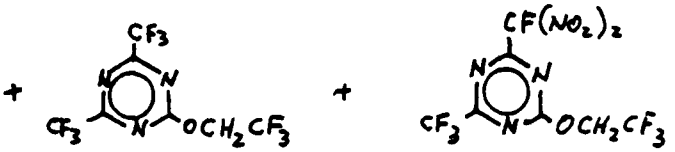

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In a second set of experiments, mixtures of 1 and alcohol or phenol were pressurized under similar conditions (Table 3). In general, the reactivity pattern observed for the different alcohols and phenols paralleled that of the imidates, i. e., no reaction past the imidate stage with the more acidic phenols (pK_a < ca. 8), and formation of alkoxy substituted triazines with alcohols and phenols of $pK_a \geq$ 8.4. The anticipated effect of catalyst acidity was clearly not observed, however, and no 2 was found in any of the reactions investigated.

In blank experiments, 1 and CF_3CH_2OH were heated at ambient pressure for 75h at 70°C with the result that there was no reaction detected. When a mixture of 6 and 1 was refluxed in $CH_2C\ell_2$, no reaction occurred.

DISCUSSION

The data in Tables 2 and 3 show that fluorodinitroacetimidates derived from acidic alcohols with inductively electron-withdrawing substituents are not able to participate in the addition-elimination sequence of Scheme 1 when pressurized alone. Presumably this is due to the lower basicity of the imine nitrogen in these compounds. That 8 is found to be much more reactive than 6, which derives

Table 3. Pressurization of 1 with Alcohols and Phenols in CH_2Cl_2 at ca. 1 GPa.[10]

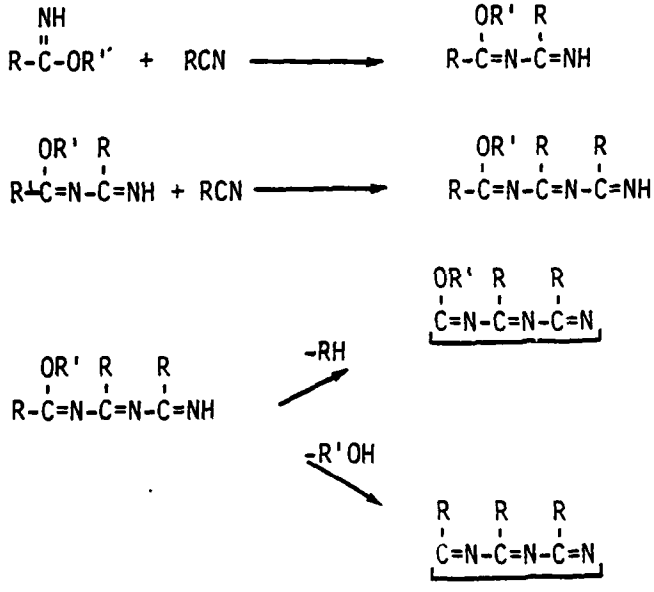
ROH (pK_a)	Mol ratio ROH/1	Conditions	Products, %				
			1	$CF(NO_2)_2C(NH)OR$	$[CF(NO_2)_2]_2(CN)_3OR$	$CF(NO_2)_2(CN)_3(OR)_2$	Other
CH_3OH (16)	1:3	60°, 44h	*	*	4, 45	5, 19	$CF(NO_2)_2H$
CF_3CH_2OH (12)	1:3	65°, 60h	*	45	13, ca. 6	14, ca. 17	Unidentified product with higher retention time
$(CF_3)_2CHOH$ (9.3)	1:3	60°, 45h	No Reaction				
C_6H_5OH (10)	1:2	65°, 40h	*	0	19, 68	0	$(C_6H_5O)_3(CN)_3$, 20, 4
m-O_2N-C_6H_4OH (8.4)	1:3.5	60°, 48h	48	*	0	21, 37	$(m\text{-}O_2N\text{-}C_6H_4O)_3(CN)_3$, 22, 2
m-CF_3-C_6H_4OH (9.0)[11]	1:3	60°, 50h	50	0	0	23, 45	$(m\text{-}CF_3\text{-}C_6H_4O)_3(CN)_3$, 24, 1
		60°, 4 h	62	*	0	23, 15	
C_6F_5OH (5.5)	1:3	60°, 50h	61	94	0	0	
p-O_2N-C_6H_4OH (7.2)	1:3.2	60°, 55h	62.5	100	0	0	

*present but yield not determined

from a less acidic ROH species, is compatible with this interpretation since the σ^* value for CF_3CH_2 is greater than that for C_6H_5 (0.92 vs. 0.60). The sensitivity of imidate di- and trimerization to relatively small inductive effects is further indicated by the drastic difference in reactivity between 8 and 10 (Table 2).

The effect of added 1 on the pressurization of 6 (Table 2) is best explained by the assumption of an alternative reaction pathway which involves initially addition of imidate to the more electrophilic nitrile 1, followed by an addition-elimination sequence which eventually leads to the observed triazines (Scheme 2).

Scheme 2



Whether this alternative mechanism is also operative when mixtures of 1 and acidic alcohols or phenols are pressurized (Table 3) is not clear because of the additional complication that the presence of ROH in the reaction mixture has an accelerating effect on at least some of the reactions (compare 6 + 1 (Table 2) with 1 + CF_3CH_2OH (Table 3), and the pressurizations of 12 with and without added CF_3CH_2OH (Table 2)). This accelerating effect may be operating on either of the

two mechanisms. It might involve activation of the imidate via a hydrogen-bonded complex, in analogy to the effect of acetic acid observed by Schaefer and Peters,[12] in the case of mechanism 1 (Scheme 1), and a similar activation of 1 or of an intermediate adduct in the case of mechanism 2 (Scheme 2). In most cases our data do not permit a clear distinction between these possibilities, since all of the products observed in the pressurizations with ROH present can be formed both ways. For example, one of the more complex products, 18, could result from the process, 12 + 1 + 1 (mechanism 2), but also from the sequence 12 + 6 + (6 or 1) (mechanism 1). In the reactions involving phenol as ROH component, more tris(aryloxy)triazine is formed than in the other cases. Here, in the pressurization of 8, mechanism 1 is operating; however, in the reaction of 1 with phenol 20 is probably also formed by this route, for if both 19 and 20 arose via mechanism 2, then an intermediate yield of the fluorodinitromethyldiphenoxy-triazine would certainly be expected, but none was found. The same argument precludes formation of both 19 and 20 by mechanism 1, and thus it is likely, that at least in this case, both mechanisms are operating simultaneously.

Another question pertinent to the purpose of this work concerns the mechanism of alkoxy and aryloxy introduction into the triazine ring. The mono-RO-triazines are best accounted for by mechanism 2 with either $CF(NO_2)_2H$ elimination in the final step, or ROH elimination followed by $CF(NO_2)_2$ displacement. If exclusive $CF(NO_2)_2H$ elimination occurred in the pressurization of 6 + 1, however, then there would be no ROH which is needed for the formation of 14. The presence of dialkoxytriazine in the product of this reaction thus gives indirect evidence for the initial formation of 2 to at least some extent. Substantial $CF(NO_2)_2H$ elimination is also unlikely if mechanism 1 applies, since it should occur to comparable extents in all 3 steps, and lead to more trialkoxy- or triaryloxytriazine than was found. The observed substantial variation in the mono-/di-RO-triazine ratios can be qualitatively understood in terms of a combination of factors which include: the pK_a and

nucleophilicity of ROH which determine its ability to displace $CF(NO_2)_2$ from the triazine ring, as well as the amount of more reactive RO^- present in the reaction mixture (this might account for the surprising results with the phenols, Table 3); the inductive effect of the RO group which determines the susceptibility of the mono-RO-triazine to nucleophilic attack; the ROH concentration ($\underline{6}$ + $\underline{1}$ vs $\underline{1}$ + CF_3CH_2OH).

The synthesis of $\underline{2}$ by the reaction studied here is prevented by either $CF(NO_2)_2H$ elimination in the ring closure step, or by the extreme lability of at least one $CF(NO_2)_2$ group in $\underline{2}$. The isolation of $(RO)_3(CN)_3$ in some cases shows that $CF(NO_2)_2H$ elimination is possible, but indirect evidence was also obtained for the initial formation of $\underline{2}$. That even the last $CF(NO_2)_2$ group in $\underline{14}$ is susceptible to nucleophilic attack was shown by its conversion to $(CF_3CH_2O)_3(CN)_3$ on reaction with KOH/CF_3CH_2OH at room temperature.

EXPERIMENTAL SECTION[13)]

Fluorodinitroethyl Fluorodinitroacetimidate, 7. The general procedure as described for the addition of $CF_2NO_2CH_2OH$ to 1 was followed.[7] A solution of $CF(NO_2)_2CH_2OH$ (5.60g, 36.4 mmol) and Et_3N (20 mg. 0.2 mmol) in 25 ml Et_2O was treated dropwise with a solution of 1 (3.58g, 24.0 mmol) in 5 mL Et_2O. The yellow solution was stirred for 2h, washed with water (2 x 50 mL) and saturated NaCℓ solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo to 6.94g of yellow oil. Short path distillation at 0.33 kPa gave 2.44g of recovered alcohol. Continuation at a lower pressure gave 2.44g (34%) of 7 with bp 68-69° (0.0050 kPa). Traces of $CF(NO_2)_2C(=O)NH_2$ which codistilled with the product were removed by extraction of the amide from a $CCℓ_4$ solution of the imidate ester with water. Pure 7 had the following properties: mp 27-28°; d^{20} 1.670; IR (film) 1700 (C=N), 3350 (N-H) cm^{-1}; ^1H NMR ($CCℓ_4$) δ 9.42 (s, 1, NH), 5.46 (d, 2, J = 17 Hz, CH_2); ^{19}F NMR φ* 102 ($CF(NO_2)_2C=NH$), 110 ($CF(NO_2)_2CH_2$). 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.

2,2,2-Trifluoroethyl Fluorodinitroacetimidate, 6. A solution of 5.2g (35 mmol) 1, 40.0g (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 27 kPa provided 1.9g of recovered 1. The pressure was reduced to 0.9 kPa whereupon 5.80g (66%) of 6 was collected: bp 51-52° (0.9 kPa); IR (film) 3350 (N-H), 1698 (C=N) cm^{-1} ; ^1H NMR ($CCℓ_4$) δ 9.16 (s, 1, NH), 4.74(q,2,J=8Hz,CH_2); ^{19}F NMR φ* 74.0(CF_3), 100.6($CF(NO_2)_2$); MS, m/z (rel intensity) 278 (M+29,1), 250 (M+1,8), 204(22), 101(100), 81(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.

2,2,2-Trifluoroethyl Trifluoroacetimidate, 12. Preparation according to a literature method[15)] gave material with: bp 58° (lit. 58-59°); IR (gas) 3380 (N-H), 1700 (C=N)

cm^{-1}; ^{19}F NMR($CD_2C\ell_2$) ϕ* 74.2 (t, J=8Hz, $CH_2\underline{CF_3}$), 74.6 (s, CF_3C=NH).

Phenyl Fluorodinitroacetimidate, 8. A stirred mixture of 4.90g (52.1 mmol) PhOH, 1.0g K_2CO_3, and 30 mL $CH_2C\ell_2$ was treated dropwise (30 min.) with 7.52g (51.1 mmol) 1. The orange solution was filtered and concentrated in vacuo (aspirator) to give 11.6g of residue. Removal of unreacted PhOH by distillation at 0.3 kPa (bp 52-56°) left 11.14g (90%) of 8 which was pure by TLC and identical to subsequently distilled material by IR. Distilled material was light yellow[16] and was a mixture of syn and anti isomers: bp 70°(0.032 kPa); mp 38.5-41.0°; IR (film) 3300 (N-H), 1692(C=N)cm^{-1}; ^1H NMR ($CC\ell_4$) δ 8.31 (s, NH), 7.24 (m, C_6H_5); ^{19}F NMR ($CC\ell_4$) ϕ* 102.4 (s, $CF(NO_2)_2$), 100.6 (s, $CF(NO_2)_2$, small amount); MS, m/z (rel intensity) 284 (M+41,2), 272(M+29,1), 244(M+1,), 244(M+1,62), 198(55), 168(88), 152(100), 151(51), 122(93), 93(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.

The following imidate esters were prepared in the same manner:

F - Phenyl Dinitroacetimidate, 9. A mixture of syn and anti isomers was obtained as a pale yellow liquid in 22% yield by distillation: bp 47-48° (0.010 kPa); IR (film) 3340 (N-H), 1700(C=N) cm^{-1}; ^{19}F NMR ($CC\ell_4$) ϕ* 98.4 (s, $CF(NO_2)_2$), 99.6 (s, $CF(NO_2)_2$, in lesser amount, 20/80 isomer composition indicated), 150-162 (m, C_6F_5); MS, m/z (rel intensity) 334 (M+1, 4), 288(1), 185(100), 168(2), 150(27), 132(30), 105(12). Anal. Calcd for $C_8HF_6N_3O_5$: C, 28.84; H, 0.30; F, 34.22; N, 12.61. Found: C, 28.81; H, 0.31; F, 33.92; N, 12.52.

m-(Trifluoromethyl)phenyl Fluorodinitroacetimidate, 10. Crude product (mp 45-49°) obtained in 98% yield by filtration and removal of solvent was purified by distillation to give 10 in 88% yield as a light yellow solid with the following properties: bp 80° (0.0093 kPa); mp 50-51.5°; IR (KBr) 1700 (C=N), 3300 (N-H) cm^{-1}; ^{19}F NMR ($CC\ell_4$) ϕ* 63.7 (s, CF_3), 100.8, 102.4 (s, $CF(NO_2)_2$, isomer ratio of 32/68). Anal. Calcd for $C_9H_5F_4N_3O_5$: C, 34.74; H, 1.62; F, 24.42; N, 13.50. Found: C, 34.71; H, 1.58;

F, 24.69; N, 13.49.

m - Nitrophenyl Fluorodinitroacetimidate, 11. The crude product (mp 50-55°) obtained after filtration of the reaction solution and evaporation of solvent represented a 93% yield and was identical by IR analysis to subsequently recrystallized ($CC\ell_4$) material. The light yellow solid had mp 59.5-61.0°; IR (KBr) 1701 (C=N), 3310 (N-H) cm^{-1}; ^{19}F NMR ($CD_2C\ell_2$) ϕ* 99.0, 101.2 (s, $CF(NO_2)_2$, isomer ratio of 40/60). Anal. Calcd for $C_8H_5FN_4O_7$: C, 33.34; H, 1.75; F, 6:59; N, 19.44. Found: C, 33.53; H, 1.79; F, 6.56; N, 19.19.

Pressurization of 6 at 1.0 GPa. A solution of 0.75g (3.0 mmol) of 6 in 3 mL $CH_2C\ell_2$ was held at 1.0 GPa and 65° for 39 h. Removal of solvent on a rotary evaporator gave 0.71g (95%) of recovered 6 which was pure by GC, IR, and TLC analyses.

Pressurization of 12 at 1.0 GPa. A. In $CH_2C\ell_2$: A solution of 0.19g (0.97 mmol) 12 in 2.6 mL $CH_2C\ell_2$ was held at 1.0 GPa and 60° for 65 h. GC analysis with $CC\ell_4$ internal standard showed a 69% recovery of 12. The triazine $(CF_3)_3(CN)_3$, obscured by the solvent peak in GC analysis was detected at ϕ* 71.9 in the ^{19}F spectrum. Analysis with $PhCF_3$ internal standard gave 0.019 mmol (6%) triazine. An additional product, $CF_3C(NH_2)(OCH_2CF_3)_2$, 15, which eluted immediately after the $CC\ell_4$ peak in the gas chromatogram, was not isolated. Its structure is supported by GC/MS and ^{19}F NMR data. The NMR analysis showed 0.031 mmol (3%): ^{19}F NMR ($CH_2C\ell_2$) ϕ* 77.5 (t, J=8Hz, CF_3CH_2), 83.2 (s, $CF_3C(NH_2)$); MS, m/z (rel intensity) 296 (M + 1, 2), 279 (4), 276(5), 256 (9), 196 (92), 101 (100), 81 (65).

B. In CF_3CH_2OH: After treatment at 1.0 GPa and 60° for 65 h, a solution of 0.18g (0.92 mmol) 12 in 2.6 mL CF_3CH_2OH was taken up in 3 mL $CH_2C\ell_2$, washed with water (4 x 10 mL), and dried ($MgSO_4$). ^{19}F NMR analysis with $PhCF_3$ standard showed 0.05 mmol (16%) $(CF_3)_3(CN)_3$. Prior to the aqueous workup GC analysis with $CC\ell_4$ standard indicated 0.015 mmol (2%) 15, assuming its relative response to $CC\ell_4$ to be the same as for 12[17].

Pressurization of 8 at 1.0 GPa. A solution of 1.22g (5.02 mmol) 8 in 10 mL $CH_2C\ell_2$ was held at 1.0 GPa and 40° for 20 h. Considerable gas pressure was vented as the Teflon reaction vessel was carefully opened. The dark reaction mixture contained 0.34g of insoluble black solid. TLC and GC analyses of the solution showed the absence of any 8 or 19. Small amounts of $CF(NO_2)_2H$ and 20 were detected. The black solid and a tacky brown solid (1.05g) left after evaporation of solvent were composed of polar material which remained at the origin on TLC analysis and showed strong absorptions at 3200-3400 cm^{-1} in the IR. Extensive decomposition had apparently occurred accompanied by the generation of nitrogen oxides.

Pressurization of 10 at 1.0 GPa. A solution of 0.36g (1.2 mmol) of 10 in 3 mL $CH_2C\ell_2$ was held at 1.0 GPa and 60° for 68 h. No gas pressure was noted when the reaction vessel was opened. Analysis by ^{19}F NMR with PhF added as a standard showed complete recovery of 10. A trace of $CF(NO_2)_2H$ was detected at ϕ^* 120, however, and HPLC analysis showed 1.1 mg (0.5%) of 23 (quantitated by addition of an authentic sample prepared from the phenol and cyanuric chloride, vide infra).

1 and CH_3OH at 0.8 GPa. A solution of 1.34g (9.0 mmol) 1, 0.0945g (3.0 mmol) CH_3OH, and 3 mL $CH_2C\ell_2$ was held at 0.8 GPa and 60° for 44 h. Gas pressure was carefully vented as the reaction vessel was opened. The yellow solution continued to effervesce on standing. GC analysis showed, in addition to a group of low retention peaks which included $CF(NO_2)_2H$, the following products in order of elution (uncorrected area %): 3 (64%), 5 (11%), 4 (25%). Removal of volatiles in vacuo gave 0.90g of liquid consisting of the above products. The imidate ester was removed by stirring the liquid at 20° and 0.007 kPa to give 0.63g of the 30/70 mixture of triazines, which represents approximate yields of 5 (19%) and 4 (45%). The triazine structures were confirmed by GC/MS analysis. 5 gave MS, m/z (rel intensity) 304 (M+41, 4), 292 (M+29, 2), 264 (M+1, 100), 245 (2), 218 (65), 188 (6), 173 (16), 61 (7). 4 gave MS, m/z (rel intensity) 396 (M+41, 5), 384 (M+29, 16), 356 (M+1, 100), 337 (3), 310 (11), 266 (5), 234 (1), 220 (1), 125 (1), 61 (1).

1 and CF_3CH_2OH at 1.0 GPa. A solution of 8.94 g (60 mmol) 1, 2.00 g (20 mmol) CF_3CH_2OH, and 25 mL CH_2Cl_2 was held at 1.0 GPa 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 1 together with the following products in order of elution (uncorrected area %): 6 (74%), 14 (18%), 13 (6%), unknown A (2%). Distillation at 0.93 kPa gave 2.0 g of 6 (bp 52°) and a 1.89 g residue composed of 12% residual 6 and 88% of products 13, 14, and unknown A (ca. 24% crude yield of triazine products). Continued distillation at 0.0016 kPa gave 0.94 g of 14 and a 0.56 g residue. GC/MS analysis of the residue identified the structure of 13 as $(CF(NO_2)_2)_2(CN)_3OCH_2CF_3$. The structure of unknown A, which by its position in the chromatogram, would be the next triazine in the series representing decreasing replacement of fluorodinitromethyl by alkoxy, could not be confirmed as 2 by the mass spectral data: 447 (M, not found), 357 (M-3NO,3), 317 (M-$2NO_2F$,25), 271 (317-NO_2,94), 241 (271-NO,100). Fragments at 226(23), 221(43), and 193(14) cannot be interpreted as logical fragments of the triazine 2.

The distillation residue was chromatographed on a silica gel column with 50/50 c-C_6H_{12}/CH_2Cl_2 to give an analytical sample of 14, but further elution with 100% CH_2Cl_2 failed to provide any 13 or unknown A.

14 had bp 80° (0.0016 kPa); IR (film) 1605 (broad, with 1550 cm^{-1} shoulder); ^1H NMR (CCl_4) δ 4.83 (q, J=8H_z,CH_2); ^{19}F NMR (CD_2Cl_2) ϕ* 99.0 (s, $CF(NO_2)_2$), 73.9 (t,J=7.4 Hz, CF_3); MS, m/z (rel intensity) 440 (M+41,6), 428 (M+29,9), 400 (M+1,100), 380 (9), 354(33). Anal. Calcd for $C_8H_4F_2N_5O_6$: 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.

13 had the following mass spectrum: m/z (rel intensity) 424 (M+1,2), 348 (20), 302 (12), 272 (100), 252 (23), 125 (66).

1 and PhOH at 1.0 GPa. A solution of 2.03 g (13.6 mmol) 1, 0.64 g (6.8 mmol) PhOH, and 1.92 g (1.4 mL) $CH_2C\ell_2$ was held at 1.0 GPa and 65° for 40 h. Gas pressure was carefully vented as the vessel was opened. Removal of volatiles in vacuo gave a viscous red liquid (2.21 g) which contained no PhOH or 19 by IR and GC analyses. The liquid was further subjected to 0.007 kPa and 120° to give a red-brown solid of 1.28 g. This material consisted of one major component by TLC and GC. The presence of a small amount of 20 was indicated by TLC. A portion of the solid was distilled in a short path apparatus at 0.007 kPa and 100-123° bath temperature. The viscous, yellow, liquid distillate was identical to the red-brown solid by IR analysis, and was identified by ^{19}F NMR and MS as $PhC(CN)_3\{CF(NO_2)_2\}_2$, 19. The 1.28 g of solid represents a 68% yield of this triazine with the following properties: IR (film) 1605 (strong, with shoulders at 1570 and 1542), 1462 (strong), 1385 (strong) cm^{-1}; ^{19}F NMR ($CDC\ell_3$) ϕ* 100 (s, broad, $CF(NO_2)_2$); MS, m/z (rel intensity) 458 (M+41, 2), 446 (M+29, 5), 418 (M+1, 43), 388 (19), 372 (11), 215 (79), 171 (11), 140 (100), 125 (28), 95 (65).

Chromatography of the 1.28 g of solid on silica gel with $c\text{-}C_6H_{12}/CH_2C\ell_2$ solvent gave 0.06 g (4%) of 20, which was identical by IR to an authentic sample. It was not possible to obtain an analytically pure sample of 19 by chromatography; contact with silica gel produced a new component which contaminated the isolated triazine.

1 and $m\text{-}CF_3C_6H_4OH$ at 1.0 GPa. A solution of 0.45 g (3.0 mmol) 1 and 0.16 g (1.0 mmol) $m\text{-}CF_3C_6H_4OH$ in 3 mL $CH_2C\ell_2$ was held at 1.0 GPa and 60° for 50 h. There was no darkening of the solution or buildup of gas pressure in the reaction vessel. Bulb to bulb transfer of volatiles at 0.007 kPa and 20° gave 0.28 g of liquid residue and a colorless distillate containing 0.22 g of recovered 1 by GC analysis with $CC\ell_4$ as internal standard. IR analysis of the residue indicated the absence of any phenol or imidate ester. ^{19}F NMR analysis with PhF added as a standard showed 0.45 mmol (45%) of 23 and 0.46 mmol $CF(NO_2)_2H$ [18]. HPLC analysis of the residue for 24 by the method of addition of an authentic sample showed 0.0082 mmol (0.8%) present. The triazine 23 had the following properties:

^{19}F NMR ($CC\ell_4$) ϕ* 63.7 (s, CF_3), 99.0 (s, $CF(NO_2)_2$); MS m/z (rel intensity) 524 (M+1, 1), 191 (13), 163 (72), 143 (100).

An identical solution was held at 1.0 GPa and 60° for only 4 h to check for extent of reaction during a short time period. In a similar workup 0.29 g of distillation residue was obtained together with a distillate that contained 0.28 g 1. The presence of unreacted phenol and imidate ester was evident by IR analysis of the residue. ^{19}F NMR analysis with added PhF as standard showed 0.15 mmol (15%) of 23.

1 and $(CF_3)_2CHOH$ at 1.0 GPa. A solution of 0.90 g (6.0 mmol) 1 and 0.34 g (2.0 mmol) $(CF_3)_2CHOH$ in 3 mL $CH_2C\ell_2$ was held at 1.0 GPa and 60° for 45 h. GC analysis showed only recovered nitrile and alcohol. Removal of volatiles in vacuo left 0.01 g of liquid which was identified by IR as $CF(NO_2)_2C(=O)NH_2$.

1 and m-$NO_2C_6H_4OH$ at 1.0 GPa. A solution of 5.22 g (35.0 mmol) 1, 1.39 g (10.0 mmol) m-$NO_2C_6H_4OH$, and 28 mL $CH_2C\ell_2$ was held at 1.0 GPa and 60° for 48 h. Only a slight gas pressure was noted when the vessel was opened. Volatiles were removed at 70° and 0.02 kPa to give 2.43 g of yellow, solid residue and a distillate which contained 2.52 g of recovered 1 and 0.70 g $CF(NO_2)_2H$ by GC analysis with $CC\ell_4$ as standard. IR analysis of the residue showed the presence of 11 and the absence of any phenol. 11 and a small amount of $CF(NO_2)_2C(=O)NH_2$ were removed by subjecting the residue to 110° at 0.005 kPa. HPLC analysis of the 2.04 g residue showed one major component and several minor contaminants. This material was identical by IR to subsequently recrystallized 21 and represents a 37% yield of this triazine. One of the minor impurities was isolated by chromatography on silica gel ($CH_2C\ell_2$) and, although still impure, was shown by mass spectral analysis to be 22 (ca. 2% yield). Recrystallization ($CH_2C\ell_2$) of 21 gave material with mp 159.5 - 160.5°; IR (KBr) 1610, 1530, 1460, 1385, 1350, 1260, 1200 cm^{-1}; ^{19}F NMR ($CD_2C\ell_2$) ϕ* 98.8 (s, $CF(NO_2)_2$); MS, m/z (rel intensity) 518 (M+41, 5), 506 (M+29, 13), 478 (M+1, 100), 433 (21), 140 (20), 61 (5). Anal. Calcd for $C_{16}H_8FN_7O_{10}$: C, 40.26; H, 1.69; F, 3.98; N, 20.54. Found: C, 39.98; H, 2.05; F, 4.24; N, 19.86.

22 had the following properties: IR (KBr) 1580, 1530, 1380, 1350, 1280, 1215 cm^{-1}; MS m/z (rel intensity) 533 (M+41, 3), 521 (M+29, 4), 493 (M+1, 100), 463 (5), 354 (9), 140 (16).

1 and $p\text{-}NO_2C_6H_4OH$ at 1.0 GPa. A solution of 0.48 g (3.2 mmol) 1, 0.14 g (1.0 mmol) $p\text{-}NO_2C_6H_4OH$, 2.6 mL CH_2Cl_2, and 0.4 mL Et_2O (added to enhance solubility of the phenol) was held at 1.0 GPa and 60° for 55 h. There was no gas pressure observed when the vessel was opened. Bulk to bulk transfer of volatiles at 0.007 kPA and 20° gave a yellow, solid residue of 0.31 g and a distillate which contained 0.30 g of recovered 1 by GC analysis with CCl_4 internal standard. IR analysis of the residue showed the absence of any phenol. The spectrum was identical to that of pure $p\text{-}NO_2\text{-}C_6H_4O\ C(=NH)CF(NO_2)_2$, obtained by recrystallization of the residue from CCl_4 (represents 100% yield of imidate ester); mp 100.5 - 101.0°; IR (KBr) 3290 (N-H), 1700 (C=N) cm^{-1}; MS, m/z (rel intensity) 289 (M+1, 1), 150 (4), 140 (100), 123 (5), 94 (3). Anal. Calcd for $C_8H_5FN_4O_7$: C, 33.34; H, 1.75; F, 6.59; N, 19.44. Found: C, 33.49; H, 1.79; F, 6.57; N, 19.27.

1 and C_6F_5OH at 0.9 GPa. A solution of 0.46 g (3.1 mmol) 1, 0.20 g (1.1 mmol) C_6F_5OH, and 2.7 mL CH_2Cl_2 was held at 0.9 GPa and 60° for 50 h. No gas pressure was noted on opening the vessel. Bulb to bulb transfer of volatiles at 20° gave a light yellow liquid residue of 0.35 g and a distillate which contained 0.28 g of recovered 1 by GC analysis with CCl_4 standard. The residue was pure $CF(NO_2)_2\text{-}C(=NH)OC_6F_5$ by comparison of its IR spectrum to that of an authentic sample and represents a 94% yield of the imidate ester.

1 and CF_3CH_2OH at 70°. A sealed tube containing 0.20 g (2.0 mmol) CF_3CH_2OH, 0.90 g (6.0 mmol) 1, and 2 mL CH_2Cl_2 was heated at 70° for 75 h. No evidence for 6 or any triazine products was detected by GC and TLC analyses.

1 and 6 at 1.0 PGa. A solution of 1.49 g (10.0 mmol) 1, 0.63 g (2.5 mmol) 6, and 2.5 mL CH_2Cl_2 was held at 1.0 GPa and 65° for 23 h. The solution was concentrated in vacuo to 0.84 g of liquid with the following composition by GC

analysis (uncorrected area %): 6 (96.4%), 14 (0.5%), 13 (2.7%), and an unknown with long retention time (0.4%). The ratio of 14:13 changed from 75:25 obtained in pressurization of 1 and CF_3CH_2OH in CH_2Cl_2 to 15:85 in this experiment.

1 and 12 at 1.0 GPa. A solution of 4.55 g (30.5 mmol) 1, 1.95 g (10.0 mmol) 12, and 24 mL CH_2Cl_2 was held at 1.0 GPa and 60° for 23 h. A small amount of gas pressure was vented as the reaction vessel was opened. Bulb to bulb transfer at 20° gave 0.83 g of liquid residue and a distillate which contained 1.00 g of 12 and 3.50 g of 1. A trace of $(CF_3)_3(CN)_3$ was also found in the distillate by ^{19}F NMR. The residue was analyzed by GC with $(CF_3CH_2O)_3(CN)_3$ added as an internal standard, on the assumption that its response would be similar to the triazine products in the product mixture. Its relative response to $CF(NO_2)_2H$ and 6 was measured. A GC/MS analysis of the product mixture was used to assign structures to peaks in the chromatogram. The five major product peaks in order of elution were as follows (mmol): $CF(NO_2)_2H$ (0.23), 17 (0.12), 16 (0.23), 6 (0.41) 18 (0.37). MS of 17: m/z (rel intensity) 356 (M+41, 1), 344 (M+29, 1.5), 316 (M+1, 24), 296 (2), 113 (92), 101 (6), 85 (17), 71 (100), 69 (16). MS of 16: m/z (rel intensity) 331 (M+41, 0.1), 319 (M+29, 0.2), 291 (M+1, 3), 209 (34), 119 (34), 114 (99), 101 (100), 81 (41). MS of 18: m/z (rel intensity) 410 (M+41, 4), 398 (M+29, 8), 370 (M+1, 100), 350 (3), 324 (22), 273 (10), 240 (13), 144 (11), 101 (3), 69 (6).

$(m\text{-}CF_3C_6H_4O)_3(CN)_3$, 23. A solution of 1.72g of (30.7 mmol) KOH in 5 mL $m\text{-}CF_3C_6H_4OH$ was treated with 1.88 g (10.2 mmol) $Cl_3(CN)_3$. After a short period a vigorous reaction ensued causing the solution to boil. Cooling the flask in a water bath caused the mixture to solidify. An additional 2 mL of phenol was added to liquify the mass which was then held at 100°C overnight. The cooled mixture was extracted with water (3 x 30 mL) and then 25 mL CH_2Cl_2. The phenol was removed by distillation (bp 56° at 0.7 kPa) to leave a residue of 0.40 g (7%) of crude triazine. Recrystallization from CCl_4 gave material with mp 158 - 160°; IR (KBr) 1570 (sh 1585, 1598), 1382, 1320, 1180 cm^{-1}; MS, m/z (rel intensity) 602 (M+41, 7), 590 (M+29, 28), 562 (M+1, 100), 542 (89), 512 (12), 163 (36), 143 (56).

$(CF_3CH_2O)_3(CN)_3$. This compound was prepared in 61% yield by a literature method[19] involving reaction of cyanuric chloride with CF_3CH_2OH and KOH. Material recrystallized from hexane had mp 55 - 57° (lit mp 45 - 46°); IR (KBr) 1592 cm^{-1} (C=N); ^1H NMR ($CC\ell_4$) δ 4.76 (q, J = 8 Hz).

Reaction of 14 with $KOCH_2CF_3$. To a stirred solution of 0.11 g 14 in 2.5 CF_3CH_2OH was added a 0.18 g KOH pellet. An initially formed yellow precipitate disappeared in ca 30 min to give a colorless solution. GC analysis showed complete consumption of 14 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 was treated with $CH_2C\ell_2/H_2O$; the material in the $CH_2C\ell_2$ was identical to the known triazine by IR.

Acknowledgment. This work was supported by the Office of Naval Research, Code 473.

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10. Yields were determined by chromatography (HPLC or GC) by use of internal standards and in a few instances by isolation of the products (cf. Experimental). Yields are based on the amount of starting material and are not corrected for recovered material.
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13. 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 6 x 1 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. Corrugated Teflon tubes (Penntube Plastics Co.), plugged at the ends with Teflon rod held in place with Taper-Tite Kel-F nuts (Chemplast, Inc.), were also used. GC analysis was done on a 120 x 0.3 cm column of 5% UC W-982 silicone rubber/Chrom P at 65 mL/min He flow with a TC detector. TLC analyses were done on precoated plastic plates (0.25 mm layer of silica gel) with fluorescent binder 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 (specific for nitro groups): (1) 50% KOH in MeOH, followed by oven drying, and (2) dilute solution of Ph_2NH in 50% H_2SO_4. HPLC analyses were performed on a 300 x 4 mm column loaded with C_{18}-coated silica gel (10 μ) with a 1.5 mL/min flow of 30/70 H_2O/CH_3CN and a UV detector (254 nm). NMR chemical shift data are reported in positive ppm units (δ) downfield from Me_4Si (int. std.) and in positive ppm units (ϕ^*) upfield from $CFCl_3$ (int. std.). Spectra were obtained in this laboratory and at Biomeasure, Inc. 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. CH_2Cl_2 and CF_3CH_2OH were distilled from P_2O_5, and MeOH from $Mg(OCH_3)_2$. $CF(NO_2)_2CN$ was obtained by the literature method[14]; bp 52 - 53° (27 Pa), d^{20} 1.49.

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16. This material turned brown and partially liquified on storage for 1 week at room temperature in a stoppered flask. Within 2 months extensive decomposition had occurred (gas evolution).

17. In part A this assumption gave 1.4% 15 as compared to 3.2% by ^{19}F NMR.

18. Not all of the $CF(NO_2)_2H$ is represented by this analysis since it is volatile enough (bp 125°C) to codistill with the $CH_2C\ell_2$ during bulb to bulb transfer.

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