$(OEOEO)_2E$·D-$C_6H_5CH(CO_2CH_3)NH_3ClO_4$ complex was prepared. Into separate ^1H NMR tubes were placed 10-mg samples of each of the above complexes to which were added 500 μL of 0.45 mol fraction solution of CD_3CN in $CDCl_3$. The ^1H NMR spectra were taken on these four solutions at ambient temperature on a Bruker WP 200 spectrometer.

Registry No. (*S*)-**2** (A = CH_2OH), 55516-00-2; (*S*)-**2** (A = CH_2Cl), 55516-09-1; (*S*)-**2** (A = CHO), 75684-68-3; (*R*)-**3**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75684-70-7; (*R*)-**3**·L-$PhCH(CO_2CH_3)NH_3ClO_4$, 75684-71-8; **3**·NH_4^+·picrate, 75640-37-8; **3**·$CH_3NH_3^+$·picrate, 75640-38-9; **3**·*t*-$BuNH_3^+$·picrate, 75640-39-0; (*R*)-**4**, 75684-72-9; (*R*)-**4**·D-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75684-73-0; **4**·$NH_4^+$·picrate, 75640-40-3; **4**·$CH_3NH_3^+$·picrate, 75640-41-4; **4**·*t*-$BuNH_3^+$·picrate, 75640-42-5; (*S*)-**5**, 75640-43-6; (*S*)-**5**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-45-8; (*S*)-**6**, 75640-46-9; (*S*)-**6**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-47-0; (*S*)-**6**·L-$PhCH(CO_2CH_3)NH_3ClO_4$, 75640-48-1; (*S*)-**7**, 75640-49-2; (*S*)-**7**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-50-5; (*S*)-**8**, 75640-51-6; (*S*)-**8**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-52-7; (*S*)-**9**, 75640-53-8; (*S*)-**9**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-54-9; (*S*)-**10**, 75640-55-0; (*S*)-**10**·L-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75640-56-1; (*R,S*)-**11**, 75640-57-2; (*R*)-**11**, 75684-74-1; (*S*)-**11**, 75684-75-2; (*R*)-**11**·D-$C_6H_5CH(CO_2H)NH_3ClO_4$, 75684-76-3; (*R*)-**11**·D-$(CH_3)_2CHCH(CO_2CH_3)NH_3ClO_4$, 75684-77-4; (*R*)-**11**·D-$C_6H_5CH(CO_2CH_3)NH_3ClO_4$, 75684-78-5; (*R*)-**11**·D-$(CH_3)_2CHCH(CO_2H)NH_3ClO_4$, 75684-80-9; (*R*)-**11**·D-$C_8H_6NCH_2CH(CO_2CH_3)NH_3ClO_4$, 75684-82-1; (*R*)-**11**·D-$C_8H_6NCH_2CH(CO_2H)NH_3ClO_4$, 75684-84-3; (*R*)-**11**·D-$C_6H_5CH_2CH(CO_2CH_3)NH_3ClO_4$, 75684-85-4; (*S*)-**11**·L-$C_6H_5CH_2CH(CO_2H)NH_3ClO_4$, 75684-86-5; (*R*)-**11**·D-$CH_3SCH_2CH_2CH(CO_2CH_3)NH_3ClO_4$, 75684-88-7; (*R*)-**11**·D-$CH_3SCH_2CH_2CH(CO_2H)NH_3ClO_4$, 75684-90-1; (*R*)-**11**·D-$CH_3CH(CO_2CH_3)NH_3ClO_4$, 75714-58-8; (*R*)-**11**·D-$CH_3CH(CO_2H)NH_3ClO_4$, 75684-91-2; **11**·NH_4^+·picrate, 75640-59-4; **11**·$CH_3NH_3^+$·picrate, 75640-60-7; **11**·*t*-$BuNH_3^+$·picrate, 75640-61-8; (*S*)-**12**, 75640-62-9; (*S*)-**12**·L-$C_6H_5CH(CO_2CH_3)NH_3ClO_4$, 75640-63-0; **12**·$NH_4^+$·picrate, 75640-65-2; **12**·$CH_3NH_3^+$·picrate, 75640-66-3; **12**·*t*-$BuNH_3^+$·picrate, 75640-67-4; (*S*)-**13**, 75684-92-3; (*S*)-**14**, 75640-68-5; (*R,S*)-**15**, 75640-69-6; (*R*)-**15**, 75714-59-9; (*S*)-**15**, 75714-60-2; (*R,S*)-**17**, 75640-70-9; (*R*)-**17**, 75684-93-4; (*S*)-L-**19** ($R^1 = CH_3$), 75684-94-5; (*S*)-L-**19** (R^1 = H), 75684-95-6; (*S*)-D-**19** ($R^1 = CH_3$), 75684-96-7; (*S*)-D-**19** (R^1 = H), 75684-97-8; L-$C_6H_5CH(CO_2H)NH_3ClO_4$, 74292-06-1; D-$C_6H_5CH(CO_2H)NH_3ClO_4$, 74345-75-8; (*S*)-$[C_6(CH_3)_5]_2D(OH)_2$, 75640-71-0; $Nap(OEOEO)_2E$·NH_4^+·picrate, 64916-33-2; $Nap(OEOEO)_2E$·$CH_3NH_3^+$·picrate, 75640-72-1; $Nap(OEOEO)_2E$·*t*-$BuNH_3^+$·picrate, 64916-32-1; $P(OEOEO)_2E$·NH_4^+·picrate, 75640-73-2; $P(OEOEO)_2E$·$CH_3NH_3^+$·picrate, 75640-74-3; $P(OEOEO)_2E$·*t*-$BuNH_3^+$·picrate, 75640-75-4; $D(OEOEO)_2D$·NH_4^+·picrate, 75640-76-5; $D(OEOEO)_2D$·$CH_3NH_3^+$·picrate, 75640-77-6; $D(OEOEO)_2D$·*t*-$BuNH_3^+$·picrate, 75640-78-7; $(CH_3)_2D(OEOEO)_2P$·NH_4^+·picrate, 75640-80-1; $(CH_3)_2D(OEOEO)_2P$·$CH_3NH_3^+$·picrate, 75640-81-2; $(CH_3)_2D(OEOEO)_2P$·*t*-$BuNH_3^+$·picrate, 75640-82-3; $(CH_3)_2D(OEOEO)_2D$·NH_4^+·picrate, 75640-83-4; $(CH_3)_2D(OEOEO)_2D$·$CH_3NH_3^+$·picrate, 75640-84-5; $(CH_3)_2D(OEOEO)_2D$·*t*-$BuNH_3^+$·picrate, 75640-85-6; $(CH_3)_2D(OEOEO)_2D(CH_3)_2$·$NH_4^+$·picrate, 75684-99-0; $(CH_3)_2D(OEOEO)_2D(CH_3)_2$·$CH_3NH_3^+$·picrate, 75685-00-6; $(CH_3)_2D(OEOEO)_2D(CH_3)_2$·*t*-$BuNH_3^+$·picrate, 75685-93-7; D-$C_6H_5CH(CO_2CH_3)NH_3Cl$, 19883-41-1; L-$(CH_3)_2CHCH(CO_2CH_3)NH_3Cl$, 6306-52-1; L-$(CH_3)_2CHCH(CO_2H)NH_3ClO_4$, 74292-12-9; L-$C_8H_6NCH_2CH(CO_2CH_3)NH_3Cl$, 7524-52-9; L-$C_8H_6NCH_2CH(CO_2H)NH_3ClO_4$, 74292-14-1; L-$C_6H_5CH_2CH(CO_2CH_3)NH_3Cl$, 7524-50-7; L-$C_6H_5CH_2CH(CO_2H)NH_3ClO_4$, 74292-10-7; L-$CH_3SCH_2CH_2CH(CO_2CH_3)NH_3Cl$, 2491-18-1; L-$CH_3SCH_2CH_2CH(CO_2H)NH_3ClO_4$, 74292-16-3; D-$CH_3CH(CO_2CH_3)NH_3Cl$, 14316-06-4; D-$CH_3CH(CO_2H)NH_3ClO_4$, 75640-86-7; (*R*)-3,3′-dimethyl-2,2′-dihydroxy-1,1′-dinaphthyl, 55515-98-5; pentaethylene glycol ditosylate, 41024-91-3; iodomethane, 74-88-4; phenol, 108-95-2; *p*-methoxyphenol, 150-76-5; thiophenol, 108-98-5; benzyl mercaptan, 100-53-8; benzoyl chloride, 98-88-4; (*R*)-2,2′-dimethoxy-1,1′-dinaphthyl, 35294-28-1; (*S*)-2,2′-dimethoxy-1,1′-dinaphthyl, 75640-87-8; (*R*)-2,2′-dihydroxy-1,1′-dinaphthyl, 18531-94-7; (*S*)-2,2′-dihydroxy-1,1′-dinaphthyl, 18531-99-2; (*R,S*)-2,2′-dimethoxy-1,1′-dinaphthyl, 75685-01-7; phenyl bromide, 108-86-1; pentamethylbromobenzene, 5153-40-2; DL-valine methyl ester perchlorate, 75640-88-9; DL-tryptophane methyl ester perchlorate, 75640-89-0; DL-methionine methyl ester perchlorate, 75640-90-3.

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

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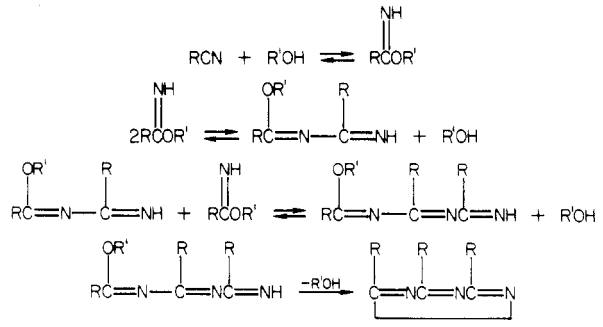
Fluorodinitroacetonitrile (1) was pressurized at 1 GPa in the presence of a variety of ROH catalysts. Cyclotrimerization of 1 occurred in several cases, but the observed triazines contained RO groups in place of one or several $CF(NO_2)_2$ groups. Some mechanistic aspects of this reaction are explored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

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] (e.g., CCl_3CN and 2-cyanonaphthalene but not 1-cyanonaphthalene 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. This pressure effect is probably a consequence of the negative volume of activation of addition reactions in general and of cycloadditions in particular.[4] Subsequently, Kurabayashi[5a] et al., Korte,[1b] and Zhulin[5b] provided additional examples and showed that a probable mechanism is formation of imidate ester (or amidine) and its self-condensation to triazine (Scheme I).

Scheme I



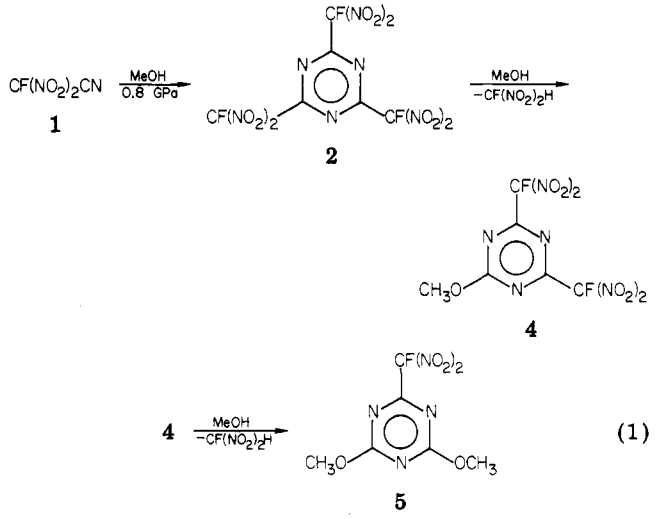
Triazines derived from nitro- and polynitroacetonitriles have been sought as high-energy compounds for some time, but several representative nitriles, difluoronitro- and fluorodinitroacetonitrile (1), have resisted attempts at

(1) For leading references see: (a) Cairns, T. L.; Larchar, A. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1952**, *74*, 5633; (b) Jarre, W.; Bienik, D.; Korte, F. *Tetrahedron* **1975**, *31*, 619.
(2) Yanagida, S.; et al. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 306.
(3) Brown, H. C.; Reilly, W. L. *J. Org. Chem.* **1957**, *22*, 698.
(4) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.
(5) (a) Kurabayashi, M.; Yanagiya, K.; Yasumoto M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3413. (b) Zhulin, V. M.; Volchek, S. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1295.

cyclotrimerization by conventional means, although inductively electron-withdrawing substituents normally facilitate this process. Thus, Bissell[6] found that the ammonia-catalyzed trimerization of *F*-alkyl nitriles, in which amidines are formed as intermediates, could not be extended to difluoronitroacetonitrile because difluoronitroacetamidine on being heated 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 being heated for several weeks at 60 °C 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 °C), 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 catalyzes an unidentified exothermic process leading to the evolution of some 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 h at 0.8 GPa and 60 °C, 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** (eq 1), respectively,



(1)

on the basis of gas chromatographic/mass spectral 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 I), the unexpected appearance of methoxy groups in the product could result from competititon 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 trimethoxytriazine, which was also not found among the products. A more probable explanation is that **2** was formed initially 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.

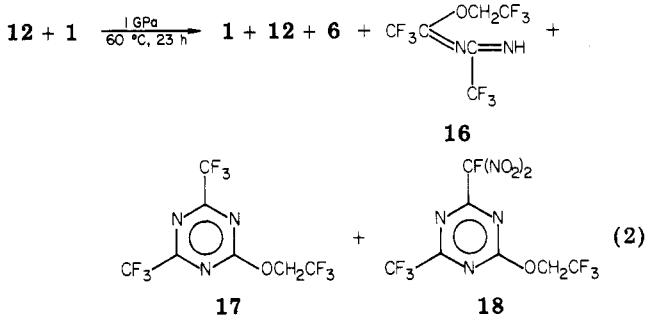
Without studying this reaction in greater detail, it was decided to investigate more acidic alcohols as trimerization catalysts on the supposition that they would be less effective in displacing fluorodinitromethide in **2** and thus might permit its isolation. In an effort to minimize the amount of 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 I) 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 I. Fluorodinitroacetimidates, $CF(NO_2)_2C(NH)OR$, from 1 and ROH

R	no.	yield, %	bp, °C (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-$CF_3C_6H_4$	**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 II 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, and (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 I.

When **12** was pressurized in the presence of **1**, a more complex set of products was obtained (eq 2).



(2)

(6) Bissell, E. R. *J. Org. Chem.* **1963**, 28, 1717.
(7) Fokin, A. V.; et al. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 456.
(8) Fokin, A. V.; et al. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 489.

(9) Fluorodinitromethide is not as good a leaving group as are other dinitromethides (see, for example: Adolph, H. G.; Kamlet, M. J. *J. Org. Chem.* **1969**, *34*, 45), but its displacement from sp^3 and sp^2 carbon and from nitrogen has been observed previously: Kamlet, M. J.; Adolph, H. G. *J. Org. Chem.* **1968**, *33*, 3073; also the paper cited above.
(10) Yields are determined by chromatography (high-pressure LC or GC) by use of internal standards and in a few instances by isolation of the products (cf. Experimental Section). Yields are based on the amount of starting material and are not corrected for recovered material.
(11) Determined by D. J. Glover of the Naval Surface Weapons Center.

Table II. Pressurization of Trifluoro- and Fluorodinitroacetimidates[10]

imidate, RC(NH)OR′	conditions	% products: imidate recovd	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, 1 GPa, 65 °C, 39 h	95	0	0	no products by TLC, GC, IR
8; R = $CF(NO_2)_2$, R′ = C_6H_5	CH_2Cl_2, 1 GPa, 40 °C, 20 h	0	0	0	trace $(CN)_3(OR'_3)$; no other identifiable products
10; R = $CF(NO_2)_2$, R′ = *m*-$CF_3C_6H_4$	CH_2Cl_2, 1 GPa, 60 °C, 68 h	>99	0	0	$(CN)_3(OR')_3$, 0.5
12; R = CF_3, R′ = CH_2CF_3	CH_2Cl_2, 1 GPa, 60 °C, 65 h	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, 1 GPa, 60 °C,	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, 1 GPa, 65 °C, 23 h	96	2.7 (**13**)	0.5 (**14**)	

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

ROH (pK_a)	molar ratio of 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 °C, 44 h	*a*	*a*	45 (**4**)	19 (**5**)	$CF(NO_2)_2H$
CF_3CH_2OH (12)	1:3	65 °C, 60 h	*a*	45	~6 (**13**)	~17 (**14**)	unidentified product with higher retention time
$(CF_3)_2CHOH$ (9.3)	1:3	60 °C, 45 h	no reaction				
C_6H_5OH (10)	1:2	65 °C, 40 h	*a*	0	68 (**19**)	0	$(C_6H_5O)_3(CN)_3$ (**20**), 4
m-O_2N-C_6H_4OH (8.4)	1:3.5	60 °C, 48 h	48	*a*	0	37 (**21**)	(*m*-O_2N-$C_6H_4O)_3(CN)_3$ (**22**), 2
m-CF_3-C_6H_4OH (9.0)[11]	1:3	60 °C, 50 h	50	0	0	45 (**23**)	(*m*-CF_3-$C_6H_4O)_3(CN)_3$ (**24**), 1
		60 °C, 4 h	62	*a*	0	15 (**23**)	
C_6F_5OH (5.5)	1:3	60 °C, 50 h	61	94	0	0	
p-O_2N-C_6H_4OH (7.2)	1:3.2	60 °C, 55 h	62.5	100	0	0	

[a] Present but yield not determined.

In a second set of experiments, mixtures of **1** and alcohol or phenol were pressurized under similar conditions (Table III). 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 75 h at 70 °C with the result that there was no reaction detected. When a mixture of **6** and **1** was refluxed in CH_2Cl_2, no reaction occurred.

Discussion

The data in Tables II and III show that fluorodinitroacetimidates derived from acidic alcohols with inductively electron-withdrawing substituents are not able to participate in the addition–elimination sequence of Scheme I 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 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 II).

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

Whether this alternative mechanism is also operative when mixtures of **1** and acidic alcohols or phenols are pressurized (Table III) 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** in Table II with **1** + CF_3CH_2OH in Table III) and the pressurizations of **12** with and without added CF_3CH_2OH in Table II). 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 I), and a similar activation of **1** or of an intermediate adduct in the case of mechanism 2 (Scheme II). 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 not only 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 the 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 (fluorodinitromethyl)diphenoxytriazine 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

(12) Schaefer, F. C.; Peters, G. A. *J. Org. Chem.* **1961**, *26*, 2778.

that, at least in this case, both mechanisms are operating simultaneously.

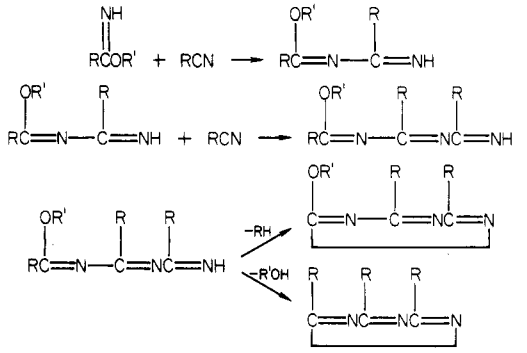
Another question pertinent to the purpose of this work concerns the mechanism of alkoxy and aryloxy introduction into the triazine ring. The mono-RO-substituted triazines are best accounted for by mechanism 2 with either $CF(NO_2)_2H$ elimination in the final step or ROH elimination followed by $CF(NO_2)_2$ 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 three steps and lead to more trialkoxy- or tris(aryloxy)triazine than was found. The observed substantial variation in the mono-RO/di-RO-substituted ratios can be qualitatively understood in terms of a combination of factors which include the following: 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 III); the inductive effect of the RO group which determines the susceptibility of the mono-RO-substituted triazine to nucleophilic attack; the ROH concentration (6 + 1 vs. 1 + CF_3CH_2OH).

The synthesis of 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 2. The isolation of $(RO)_3(CN)_3$ in some cases shows that $CF(NO_2)_2$ elimination is possible, but indirect evidence was also obtained for the initial formation of 2. That even the last $CF(NO_2)_2$ group in 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]

Caution. Many materials described here are explosives, and appropriate care should be taken in their handling. A number of fluorodinitromethyl compounds also show varying degrees of toxicity. Fluorodinitromethane and particularly fluorodinitroethanol may cause painful burns on the skin.

Scheme II



Fluorodinitroethyl Fluorodinitroacetamidate (7). The general procedure as described for the addition of $CF_2NO_2CH_2OH$ to 1 was followed.[7] A solution of $CF(NO_2)_2CH_2OH$ (5.60 g, 36.4 mmol) and Et_3N (20 mg, 0.2 mmol) in 25 mL of Et_2O was treated dropwise with a solution of 1 (3.58 g, 24.0 mmol) in 5 mL of Et_2O. The yellow solution was stirred for 2 h, washed with water (2 × 50 mL) and saturated NaCl solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo to give 6.94 g of yellow oil. Short-path distillation at 0.33 kPa gave 2.44 g of recovered alcohol. Continuation of the distillation at a lower pressure gave 2.44 g (34%) of 7, bp 68–69 °C (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 °C; d^{20} 1.670; IR (film) 1700 (C=N), 3350 (NH) 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 5.2 g (35 mmol) of 1, 40.0 g (40 mmol) of CF_3CH_2OH, and 20 μL of Et_3N in 6 mL of CH_2Cl_2 was stirred at 20 °C for 1 h, washed with four equal volumes of water, dried ($MgSO_4$), and heated to 60 °C to distill off the solvent. Continued distillation at 27 kPa provided 1.9 g of recovered 1. The pressure was reduced to 0.9 kPa, whereupon 5.80 g (66%) of 6 was collected: bp 51–52 °C (0.9 kPa); IR (film) 3350 (NH), 1698 (C=N) cm^{-1}; ^1H NMR (CCl_4) δ 9.16 (s, 1, NH), 4.74 (q, 2, J = 8 Hz, CH_2); ^{19}F NMR ϕ^* 74.0 (CF_3), 100.6 ($CF(NO_2)_2$); mass spectrum, m/z (relative 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 the following: bp 58 °C (lit. bp 58–59 °C); IR (gas) 3380 (NH), 1700 (C=N) cm^{-1}; ^{19}F NMR (CD_2Cl_2) ϕ^* 74.2 (t, J = 8 Hz, CH_2CF_3), 74.6 (s, CF_3C=NH).

Phenyl Fluorodinitroacetimidate (8). A stirred mixture of 4.90 g (52.1 mmol) of PhOH, 1.0 g of K_2CO_3, and 30 mL of CH_2Cl_2 was treated dropwise (30 min) with 7.52 g (51.1 mmol) of 1. The orange solution was filtered and concentrated in vacuo (aspirator) to give 11.6 g of residue. Removal of unreacted PhOH by distillation at 0.3 kPa (bp 52–56 °C) left 11.14 g (90%) of 8 which was pure by TLC and identical with subsequently distilled material by IR. Distilled material was light yellow[16] and was a mixture of syn and anti isomers: bp 70 °C (0.032 kPa); mp 38.5–41.0 °C; IR (film) 3300 (NH), 1692 (C=N) cm^{-1}; ^1H NMR (CCl_4) δ 8.31 (s, NH), 7.24 (m, C_6H_5); ^{19}F NMR (CCl_4) ϕ^* 102.4 (s, $CF(NO_2)_2$), 100.6 (s, $CF(NO_2)_2$, small amount); mass spectrum, m/z (relative 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

(13) High-pressure experiments were done with a standard 200 000-psi pressure-generating panel from Harwood Engineering Co., Inc. The apparatus delivered a high-pressure fluid composed of 50/50 ethylene glycol/water to a Harwood bomb with a 6 × 1 in. 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 the tubes were filled to capacity with solution, and subjected to hydrostatic pressure in the bomb. Corrugated Teflon tubes (Penntube Plastics Co.), plugged at the ends with Teflon rods held in place with Taper-Tite Kel-F nuts (Chemplast, Inc.), were also used. GC analysis was done on a 120 × 0.3 cm column of 5% UC W-982 silicone rubber/Chrom P at 65 mL/min of 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 of silica gel) with 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. High-pressure LC analyses were performed on a 300 × 4 mm column loaded with C_{18}-coated silica gel (10 μm) 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 parts per million units (δ) downfield from Me_4Si (internal standard) and in positive parts per million units (ϕ^*) upfield from $CFCl_3$ (internal standard). 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 was distilled from Mg $(OCH_3)_2$. $CF(NO_2)_2CN$ was obtained by the literature method:[14] bp 52–53 °C (27 kPa); d^{20} 1.49.

(14) Wiesboeck, R. A.; Russ, J. K. *J. Org. Chem.* **1968**, *33*, 1257.

(15) Brown, H. C.; Wetzel, C. R. *J. Org. Chem.* **1965**, *30*, 3724.

(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).

(93), 93 (98). Anal. Calcd for $C_8H_6FN_3O_6$: 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 °C (0.010 kPa); IR (film) 3340 (NH), 1700 (C=N) cm^{-1}; ^{19}F NMR (CCl_4) ϕ^* 98.4 (s, $CF(NO_2)_2$), 99.6 (s, $CF(NO_2)_2$, in a lesser amount a 20/80 isomer composition was indicated), 150–162 (m, C_6F_5); mass spectrum, m/z (relative 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 °C) 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 °C (0.0093 kPa); mp 50–51.5 °C; IR (KBr) 1700 (C=N), 3300 (NH) cm^{-1}; ^{19}F NMR (CCl_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 °C) obtained after filtration of the reaction solution and evaporation of solvent represented a 93% yield and was identical by IR analysis with subsequently recrystallized (CCl_4) material. The light yellow solid had the following: mp 59.5–61.0 °C; IR (KBr) 1701 (C=N), 3310 (NH) cm^{-1}; ^{19}F NMR (CD_2Cl_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 0.75 g (3.0 mmol) of **6** in 3 mL of CH_2Cl_2 was held at 1.0 GPa and 65 °C for 39 h. Removal of the solvent on a rotary evaporator gave 0.71 g (95%) of recovered **6** which was pure by GC, IR, and TLC analyses.

Pressurization of 12 at 1.0 GPa. (A) In CH_2Cl_2. A solution of 0.19 g (0.97 mmol) **12** in 2.6 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C for 65 h. GC analysis with CCl_4 as an 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 $PhCF_3$ as an internal standard gave 0.019 mmol (6%) of triazine. An additional product, $CF_3C(NH_2)(OCH_2CF_3)_2$ (**15**), which eluted immediately after the CCl_4 peak in the gas chromatogram was not isolated. Its structure is supported by gas chromatographic/mass spectral and ^{19}F NMR data. The NMR analysis showed a yield of 0.031 mmol (3%): ^{19}F NMR (CH_2Cl_2) ϕ^* 77.5 (t, J = 8 Hz, CF_3CH_2), 83.2 (s, $CF_3C(NH_2)$); mass spectrum, m/z (relative 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 °C for 65 h, a solution of 0.18 g (0.92 mmol) of **12** in 2.6 mL of CF_3CH_2OH was taken up in 3 mL of CH_2Cl_2, washed with water (4 × 10 mL), and dried ($MgSO_4$). ^{19}F NMR analysis with $PhCF_3$ as the standard showed 0.05 mmol (16%) of $(CF_3)_3(CN)_3$. Prior to the aqueous workup, GC analysis with CCl_4 as the standard indicated 0.015 mmol (2%) of **15**, assuming its relative response to CCl_4 to be the same as that for **12**.[17]

Pressurization of 8 at 1.0 GPa. A solution of 1.22 g (5.02 mmol) of **8** in 10 mL of CH_2Cl_2 was held at 1.0 GPa and 40 °C for 20 h. Considerable gas pressure was vented as the Teflon reaction vessel was carefully opened. The dark reaction mixture contained 0.34 g 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 tacky brown solid (1.05 g) 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 0.36 g (1.2 mmol) of **10** in 3 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C 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 high-pressure LC analysis showed 1.1 mg (0.5%) of **24** (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 1.34 g (9.0 mmol) of **1**, 0.0945 g (3.0 mmol) of CH_3OH and 3 mL of CH_2Cl_2 was held at 0.8 GPa and 60 °C for 44 h. Gas pressure was carefully vented as the reaction vessel was opened. The yellow solution continued to effervesce on being allowed to stand. 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 0.90 g of liquid consisting of the above products. The imidate ester was removed by stirring of the liquid at 20 °C and 0.007 kPa to give 0.63 g of a 30/70 mixture of triazines, which represents the approximate yields of **5** (19%) and **4** (45%). The triazine structures were confirmed by gas chromatographic/mass spectral analysis. Compound **5** gave the following: mass spectrum, m/z (relative intensity) 304 (M + 41, 4), 292 (M + 29, 2), 264 (M + 1, 100), 245 (2), 218 (65), 188 (6), 173 (16), 61 (7). Compound **4** gave the following: mass spectrum, m/z (relative 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) of **1**, 2.00 g (20 mmol) of CF_3CH_2OH, and 25 mL of CH_2Cl_2 was held at 1.0 GPa and 65 °C for 60 h. GC analysis of a light yellow residual liquid (6.55 g) left after rotary evaporation of the 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 °C) and a 1.89 g of 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. Gas chromatographic/mass spectral 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: m/z (relative intensity) 447 (M, not found), 357 (M − 3 NO, 3), 317 (M − 2 NO_2F, 25), 271 (317 − NO_2, 94), 241 (271 − NO, 100). Fragments at m/z (relative intensity) 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.

For **14**: bp 80 °C (0.0016 kPa); IR (film) 1605 (br, with a 1550-cm^{-1} shoulder); ^1H NMR (CCl_4) δ 4.83 (q, J = 8 Hz, 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); mass spectrum, m/z (relative 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.

Compound **13** had the following mass spectrum: m/z (relative intensity) 424 (M + 1, 2), 348 (20), 302 (12), 272 (100), 252 (28), 125 (66).

1 and PhOH at 1.0 GPa. A solution of 2.03 g (13.6 mmol) of **1**, 0.64 g (6.8 mmol) of PhOH, and 1.92 g (1.4 mL) of CH_2Cl_2 was held at 1.0 GPa and 65 °C 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 °C 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 °C (bath temperature). The viscous, yellow, liquid distillate was identical with the red-brown solid by IR analysis and was identified by ^{19}F NMR and mass spectroscopy as $PhO(CN)_3[CF(NO_2)_2]_2$ (**19**). The 1.28 g of solid represents a 68% yield of this triazine with the following properties: IR (film) 1605 (s, with shoulders at 1570 and 1542), 1462 (s), 1385 (s) cm^{-1}; ^{19}F NMR ($CDCl_3$) ϕ^* 100 (br s, $CF(NO_2)_2$); mass spectrum, m/z (relative

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

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-C_6H_{12}/CH_2Cl_2 as solvent gave 0.06 g (4%) of **20**, which was identical by IR with 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*-$CF_3C_6H_4OH$ at 1.0 GPa. A solution of 0.45 g (3.0 mmol) of 1 and 0.16 g (1.0 mmol) of *m*-$CF_3C_6H_4OH$ in 3 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C 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 °C gave 0.28 g of liquid residue and a colorless distillate containing 0.22 g of recovered 1 by GC analysis with CCl_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 of $CF(NO_2)_2H$.[18] High-pressure LC analysis of the residue for **24** by the method of addition of an authentic sample showed that 0.0082 mmol (0.8%) of **24** was present. The triazine **23** had the following properties: ^{19}F NMR (CCl_4) ϕ^* 63.7 (s, CF_3), 99.0 (s, $CF(NO_2)_2$); mass spectrum, *m/z* (relative intensity) 524 (M + 1, 1), 191 (13), 163 (72), 143 (100).

An identical solution was held at 1.0 GPa and 60 °C for only 4 h to check for the 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 of **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 a 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) of 1 and 0.34 g (2.0 mmol) of $(CF_3)_2CHOH$ in 3 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C 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) of 1, 1.39 g (10.0 mmol) of *m*-$NO_2C_6H_4OH$, and 28 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C for 48 h. Only a slight gas pressure was noted when the vessel was opened. Volatiles were removed at 70 °C 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 of $CF(NO_2)_2H$ by GC analysis with CCl_4 as the standard. IR analysis of the residue showed the presence of **11** and the absence of any phenol. Compound **11** and a small amount of $CF(NO_2)_2C(O)NH_2$ were removed by subjecting the residue to 110 °C at 0.005 kPa. High-pressure LC analysis of the 2.04-g residue showed one major component and several minor contaminants. This material was identical by IR with subsequently recrystallized **21** and represents a 37% yield of this triazine. One of the minor impurities was isolated by chromatography on silica gel (CH_2Cl_2) and, although still impure, was shown by mass spectral analysis to be **22** (ca. 2% yield). Recrystallization (CH_2Cl_2) of **21** gave material: mp 159.5–160.5 °C; IR (KBr) 1610, 1530, 1460, 1385, 1350, 1260, 1200 cm^{-1}; ^{19}F NMR (CD_2Cl_2) ϕ^* 98.8 (s, $CF(NO_2)_2$); mass spectrum, *m/z* (relative 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.

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

1 and *p*-$NO_2C_6H_4OH$ at 1.0 GPa. A solution of 0.48 g (3.2 mmol) of 1, 0.14 g (1.0 mmol) of *p*-$NO_2C_6H_4OH$, 2.6 mL of CH_2Cl_2, and 0.4 mL of Et_2O (added to enhance the solubility of the phenol) was held at 1.0 GPa and 60 °C for 55 h. There was no gas pressure observed when the vessel was opened. Bulb to bulb transfer of volatiles at 0.007 kPA and 20 °C 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 as the internal standard. IR analysis of the residue showed the absence of any phenol. The spectrum was identical with that of pure *p*-$NO_2C_6H_4OC(NH)CF(NO_2)_2$, obtained by recrystallization of the residue from CCl_4 (represents 100% yield of imidate ester): mp 100.5–101.0 °C; IR (KBr) 3290 (NH), 1700 (C=N) cm^{-1}; mass spectrum, *m/z* (relative 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) of 1, 0.20 g (1.1 mmol) of C_6F_5OH, and 2.7 mL of CH_2Cl_2 was held at 0.9 GPa and 60 °C for 50 h. No gas pressure was noted when the vessel was opened. Bulb to bulb transfer of volatiles at 20 °C 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 as the standard. The residue was pure $CF(NO_2)_2C(NH)OC_6F_5$ by comparison of its IR spectrum with that of an authentic sample and represents a 94% yield of the imidate ester.

1 and CF_3CH_2OH at 70 °C. A sealed tube containing 0.20 g (2.0 mmol) of CF_3CH_2OH, 0.90 g (6.0 mmol) of 1, and 2 mL of CH_2Cl_2 was heated at 70 °C 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) of 1, 0.63 g (2.5 mmol) of **6**, and 2.5 mL of CH_2Cl_2 was held at 1.0 GPa and 65 °C 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 a long retention time (0.4%). The ratio of **14** to **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) of **1**, 1.95 g (10.0 mmol) of **12**, and 24 mL of CH_2Cl_2 was held at 1.0 GPa and 60 °C for 23 h. A small amount of gas pressure was vented as the reaction vessel was opened. Bulb to bulb transfer at 20 °C 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 gas chromatographic/mass spectral 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 (mmoles): $CF(NO_2)_2H$ (0.23), **17** (0.12), **16** (0.23), **6** (0.41), **18** (0.37). Mass spectrum of **17**, *m/z* (relative 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). Mass spectrum of **16**, *m/z* (relative 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). Mass spectrum of **18**, *m/z* (relative 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*-$CF_3C_6H_4O)_3(CN)_3$ (24). A solution of 1.72 g of (30.7 mmol) KOH in 5 mL of *m*-$CF_3C_6H_4OH$ was treated with 1.88 g (10.2 mmol) of $Cl_3(CN)_3$. 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 liquefy the mass which was then held at 100 °C overnight. The cooled mixture was extracted with water (3 × 30 mL) and then 25 mL of CH_2Cl_2. The phenol was removed by distillation [bp 56 °C (0.7 kPa)] to leave a residue of 0.40 g (7%) of crude triazine. Recrystallization from CCl_4 gave material with the following: mp 158–160 °C; IR (KBr) 1570 (sh 1585, 1598), 1382, 1320, 1180 cm^{-1}; mass spectrum, *m/z* (relative 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 the following: mp 55–57 °C (lit. mp 45–46 °C); IR (KBr) 1592 cm^{-1} (C=N); ^1H NMR (CCl_4) δ 4.76 (q, J = 8 Hz).

Reaction of 14 with $KOCH_2CF_3$. To a stirred solution of 0.11 g of **14** in 2.5 mL of CF_3CH_2OH was added a 0.18-g KOH pellet. An initially formed yellow precipitate disappeared in ca. 30 min

(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_2Cl_2 during bulb to bulb transfer.

(19) Matuszko, A. J.; Chang, M. S. *J. Org. Chem.* **1965**, *30*, 3724.

to give a colorless solution. GC analysis showed complete consumption of 14 and the appearance of a new compound with a 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_2Cl_2/H_2O; the material in the CH_2Cl_2 was identical with the known triazine by IR.

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Registry No. 1, 15562-09-1; 3, 52801-29-3; 4, 75780-65-3; 5, 75767-45-2; 6, 75767-46-3; 7, 75767-47-4; 8, 75767-48-5; 9, 75767-49-6; 10, 75767-50-9; 11, 75767-51-0; 12, 4134-43-4; 13, 75767-52-1; 14, 75767-53-2; 15, 75767-54-3; 16, 75767-55-4; 17, 75767-56-5; 18, 75767-57-6; 19, 75767-58-7; 20, 1919-48-8; 21, 75767-59-8; 22, 75767-60-1; 23, 75767-61-2; 24, 54416-56-7; methanol, 67-56-1; 2,2,2-trifluoroethanol, 75-89-8; 1,1,1,3,3,3-hexafluoro-2-propanol, 920-66-1; phenol, 108-95-2; 3-nitrophenol, 554-84-7; 3-(trifluoromethyl)phenol, 98-17-9; pentafluorophenol, 771-61-9; 4-nitrophenol, 100-02-7; 2,2-dinitro-2-fluoroethanol, 17003-75-7; 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, 368-66-1; 2,2-dinitro-2-fluoroacetamide, 15562-10-4; *p*-nitrophenyl fluorodinitroacetimidate, 75767-62-3; 2,4,6-trichloro-1,3,5-triazine, 108-77-0; 2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine, 1547-96-2; fluorodinitromethane, 7182-87-8.

Primary and Secondary Kinetic Isotope Effects in the Acid-Catalyzed Dehydration of 1,1'-Diadamantylmethylcarbinol in Aqueous Acetic Acid

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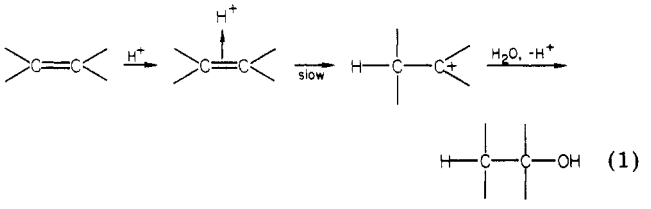
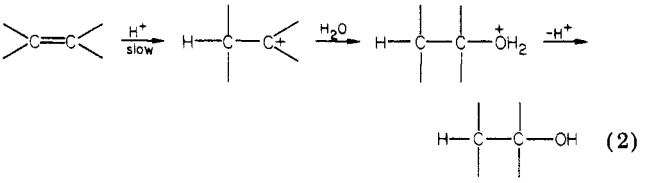
The sulfuric acid catalyzed dehydration of 1,1'-diadamantylmethylcarbinol in anhydrous acetic acid proceeds exclusively to 1,1-bis(1-adamantyl)ethylene. The secondary deuterium isotope effect of 1.32 found for this reaction shows that carbonium ion formation from the protonated alcohol is rate determining. In the presence of water, however, capture of the carbonium ion competes with deprotonation, introducing a primary isotope effect. Consequently, the overall KIE rises, reaching 3.18 for 80% aqueous acetic acid. Analysis of the KIE for 80–100% aqueous acetic acid is consistent with a simple classical mechanism involving reversible formation of the intermediate carbonium ion. The primary isotope effect upon deprotonation is at the most 2.98, indicative of an asymmetric transition state close to the carbonium ion.

It is generally agreed that the acid-catalyzed hydration of olefins proceeds via protonation, reaction of the resulting carbonium ion with water, and final deprotonation of the oxonium ion to alcohol. Nevertheless, the finer details of this mechanism remained controversial for many years.[1] Various kinetic criteria, formerly believed to support rate-determining collapse of a π-complex intermediate to a carbonium ion (eq 1), did not rule out an A-S_E2 mech-



(1)

anism where protonation of the olefin is rate determining (eq 2). The finding of general acid catalysis in the case

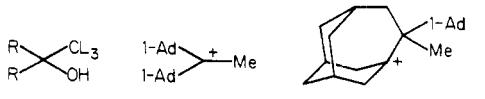


(2)

of simple olefins,[1c] following unsuccessful attempts,[2] finally established this latter mechanism, already adopted for functionally substituted olefins. As a consequence of microscopic reversibility, the rate-determing step of alcohol dehydration must then be carbonium ion deprotonation, as has been shown directly in the case of 1,2-diphenylethanols.[3]

As to the mechanism of alcohol dehydration in *nonaqueous media*, little is known. Rocek's assertion that in 85% to 100% aqueous acetic acid heterolysis of the protonated alcohol is rate determining, based as it is on the interpretation of an acidity function correlation,[4] cannot be taken as conclusive. However, we have shown that the isotope effects on the kinetics and products of the dehydration of di-*tert*-butylmethylcarbinol, **1**, in anhydrous acetic acid are consistent with rate-determining heterolysis.[5] This reaction is unfortunately complicated by the fact that the intermediate di-*tert*-butylmethylcarbonium ion can rearrange to the triptylidimethylcarbonium ion and that, consequently, only small kinetic isotope effects would be observed even if deprotonation were rate determining. It was of interest therefore to seek a system where no such rearrangement was likely to occur.

1,1'-Diadamantylmethylcarbinol, **2**, was chosen on the grounds that rearrangement of the corresponding carbonium ion, **3**, would lead to formation of the homoadamantyl system, **4**. Homoadamantane is, according to



1, R = *t*-Bu
2, R = 1-Ad
h, L = H;
d, L = D

3

4

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