

Fluoroalkyl-*s*-triazines

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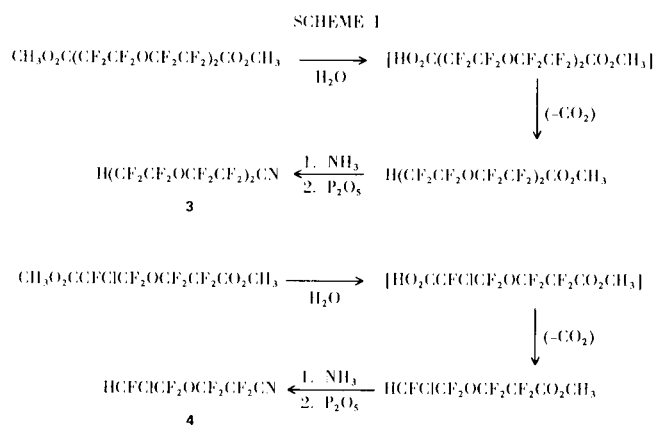
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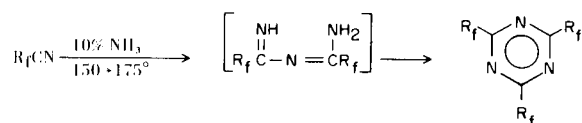
A series of symmetrically and unsymmetrically substituted *s*-triazines was synthesized by condensation of fluorocarbon nitriles (Scheme II, compounds **1a-c**) and by cyclodehydration of a fluorocarbon imidoylamidine utilizing a fluorocarbon anhydride (Scheme III, compounds **2a-e**). Among the new nitriles prepared for incorporation in these reaction paths were 11-*H*-4,9-dioxahexadecylfluoroundecanenitrile (**3**) and 6-chloro-6-*H*-4-oxaheptafluorohexanenitrile (**4**), prepared by Scheme I.

A recent review by Young (1) has summarized the literature pertaining to the synthesis of fluoroalkyl-*s*-triazines. Early studies on the trisubstituted *s*-triazines described fully halogenated substituents, but recent research has emphasized the incorporation of hetero-atoms, such as oxygen, as a flexible unit (2). This paper reports on the synthesis of triazine compounds with pendent fluorocycloalkyl groups and fluoroalkyl and fluorocycloalkyl groups containing hetero-atoms.

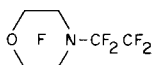
The synthesis of the symmetrical triazines required the preparation of a number of previously unreported fluoroalkyl nitriles. Scheme I depicts the reaction sequences utilized to prepare 11-*H*-4,9-dioxahexadecylfluoroundecanenitrile, compound **3**, from methyl-4,9-dioxahexadecylfluorododecanedioate (**3**) and 6-chloro-6-*H*-4-oxaheptafluorohexanenitrile, compound **4**, from methyl-2-



SCHEME II

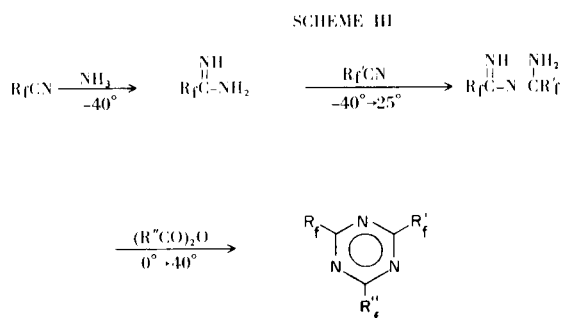


Triazine

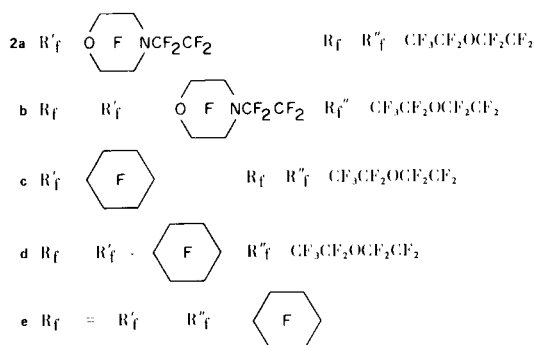
**1a** R<sub>f</sub> H(CF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>**1b** R<sub>f</sub> **1c** R<sub>f</sub> HCFCFCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>

chloro-4-oxaheptafluoroheptanedioate (**4a**). Modification of a reported decarboxylation technique (5) afforded the mono-esters and subsequent formation of the amides from these esters, followed by dehydration with phosphorus pentoxide, produced the necessary nitriles. 3-Octafluoromorpholinotetrafluoropropanenitrile (**7**) was obtained by a similar procedure from the corresponding acid (6). Scheme II summarizes the employment of these nitriles in the formation of triazines (**1a-c**) through the catalytic action of ammonia (7).

The desired unsymmetrical triazines were prepared by a cyclodehydration technique (8) in which a *N'*-(perfluoroacylimidoyl)perfluoroalkylamidine, here abbreviated to imidoylamidine, was cyclized with a fluorocarbon anhydride as described in Scheme III for the synthesis



Triazine



of **2a-e**. The application of known procedures to the available starting materials, undecylfluorocyclohexane carboxylic acid (9) and 4-oxanonafluorohexanoic acid

(10), led to the necessary intermediate fluoroalkyl nitriles and anhydrides. When the synthesis of tris(undecylfluorocyclohexyl)-s-triazine (**2e**) proved to be difficult by catalytic trimerization of the nitrile, the use of the cyclodehydration technique gave the desired material.

An analysis of the physical property data obtained for these triazines with varied fluorinated substituents provided guidelines for synthesis of new materials for use as high temperature fluids (2h).

## EXPERIMENTAL

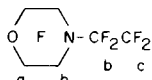
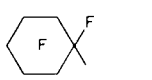
Infrared spectra were measured on a Perkin-Elmer Model 21 spectrophotometer. The  $^{19}F$  nuclear magnetic resonance measurements were taken at  $34^\circ$  with a Varian V-4300-2 instrument operating at 40.0 MHz and utilizing an internal standard of fluorotrichloromethane for the determination of chemical shifts, reported as  $\phi^*$  values (11). Due to the repetitive nature of the fluorocarbon substituents of the triazine products, their  $^{19}F$  nmr data are condensed into Table I. Finally, proton nmr values were obtained from a Varian Model A-60 instrument with fluorotrichloromethane as solvent and tetramethylsilane as reference (12). The differential thermoanalysis spectra were obtained with a rate of rise of  $30^\circ/\text{minute}$  and  $T_b$  taken as an indication of the boiling point. Short path distillations were carried out at less than 1 mm pressure.

11-11-4,9-dioxahexadecylfluoroundecanenitrile (**3**).

A 50 g. sample of methyl-4,9-dioxahexadecylfluorododecanoate (**3**) was refluxed overnight with 5 ml. of 5% sodium

TABLE I

 $^{19}F$  NMR Spectra for Triazines

Compounds	Group	$\phi^*$
<b>1a</b>	HCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub>	CF <sub>2</sub> (a)
	a b c d e f	CF <sub>2</sub> (b)
		CF <sub>2</sub> (c)
		CF <sub>2</sub> (d)
		CF <sub>2</sub> (e)
		CF <sub>2</sub> (f)
<b>1b; 2a,b</b>		CF <sub>2</sub> (a)
	a b b c	CF <sub>2</sub> (b)
		CF <sub>2</sub> (c)
<b>2c,d,e</b>		CF
		CF <sub>2</sub>
<b>2a,b,c,d</b>	CF <sub>3</sub> CF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub>	CF <sub>3</sub>
	a b c	CF <sub>2</sub> (a)
		CF <sub>2</sub> (b)
		CF <sub>2</sub> (c)
<b>1c</b>	HCFClCF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub>	CF
	a a b	CF <sub>2</sub> (a)
		CF <sub>2</sub> (b)

Note: The limits for the  $\phi^*$  values represent the range for that fluorocarbon substituent in the different triazine products and are not the standard deviations of measurement.

hydroxide, after which 0.2 g. of morpholine was added and the mixture heated to 285°. The product was collected by a short path distillation and redistilled to give a recovery of 27 g. of starting material and 1.5 g. of 1,10-di-*H*-3,8-dioxaheptadecylfluorodecane: nmr (chlorotrifluoromethane): 4.23  $\tau$  (t, t,  $J = 52.4$ , 2.5,  $HCF_2$ ), 138.0  $\phi^*$  (d, t,  $J = 52.4$ , 4.2,  $HCF_2$ ), 88.9  $\phi^*$  (d, t,  $J = 2.5$ , 4.2,  $HCF_2CF_2$ ) 83.5  $\phi^*$  ( $HCF_2CF_2OCF_2$ ), 126.3  $\phi^*$  ( $HCF_2CF_2OCF_2CF_2$ ).

Anal. Calcd. for  $C_8H_{12}F_{16}O_2$ : C, 22.1; F, 70.0. Found: C, 22.5; F, 69.1.

Also collected was 12 g. of methyl-11-*H*-4,9-dioxaheptadecylfluoroundecanoate (**5**): ir 5.5  $\mu$  (C=O); nmr (chlorotrifluoromethane): 4.23  $\tau$  (t, t,  $J = 52.6$ , 2.9,  $HCF_2$ ), 6.07  $\tau$  (s,  $CO_2CH_3$ ), 138.0  $\phi^*$  (d, t,  $J = 52.6$ , 4.2,  $HCF_2$ ), 89.0  $\phi^*$  (d, t,  $J = 2.9$ , 4.2,  $HCF_2CF_2$ ), 83.8  $\phi^*$  ( $HCF_2CF_2OCF_2$  and  $CF_2OCF_2CF_2CO_2CH_3$ ), 126.3  $\phi^*$  ( $HCF_2CF_2OCF_2CF_2CF_2$ ), 86.2  $\phi^*$  ( $CF_2CF_2CO_2CH_3$ ), 122.0  $\phi^*$  ( $CF_2CO_2CH_3$ ).

Anal. Calcd. for  $C_{10}H_{14}F_{16}O_4$ : C, 24.4; F, 61.8. Found: C, 24.8; F, 61.4.

Ammonia was bubbled into a diethyl ether solution of **5** until the ir indicated complete amide formation. Without isolation of the amide, 6.5 g. of phosphorus pentoxide (in sand) was added and the mixture heated to 210° as ether was removed and 2.2 g. of the title compound collected: ir 4.4  $\mu$  (CN); nmr (fluorotrichloromethane): 4.23  $\tau$  (t, t,  $J = 52.5$ , 2.7,  $HCF_2$ ), 138.0  $\phi^*$  (d, t,  $J = 52.5$ , 4.0,  $HCF_2$ ), 88.9  $\phi^*$  (d, t,  $J = 4.0$ , 2.7,  $HCF_2CF_2$ ), 83.6  $\phi^*$  ( $HCF_2CF_2OCF_2$  and  $CF_2OCF_2CF_2CN$ ), 126.1  $\phi^*$  ( $HCF_2CF_2OCF_2CF_2CF_2$ ), 87.4  $\phi^*$  (t,  $J = 4.7$ ,  $CF_2CF_2CN$ ), 109.2  $\phi^*$  (t,  $J = 4.7$ ,  $CF_2CN$ ).

Anal. Calcd. for  $C_9H_{16}F_{16}NO_2$ : C, 23.5; F, 66.2. Found: C, 23.9; F, 66.6.

#### 2,4,6-Tris(10-*H*-3,8-dioxaheptadecylfluorodecyl)-s-triazine (**1a**).

Utilizing a thick walled glass reactor, equipped with a Fisher-Porter valve, 1.8 g. of **3** and 0.007 g. of ammonia were heated at 165° for 16 hours and 175° for 4 hours. A short path distillation under vacuum gave 1.6 g. of **1a**:  $T_b$  (dta) 281°; ir 6.44  $\mu$  ( $C_3N_3$ ).

Anal. Calcd. for  $C_{27}H_{34}F_{48}N_3O_6$ : C, 23.5; H, 0.2; F, 66.2. Found: C, 23.6; H, 0.3; F, 66.0.

#### 6-Chloro-6-*H*-4-oxaheptafluorohexanenitrile (**4**).

A 3% sodium hydroxide solution (3 to 1 molar excess) was refluxed with 52 g. of methyl-2-chloro-2-oxaheptafluoroheptanedioate (**4a**) for 16 hours. Addition of 0.2 g. of morpholine was followed by heating to 250°, the products being collected by a short path distillation. Redistillation gave 18 g. of starting material: ir 5.6  $\mu$  (C=O); nmr ( $CFCl_3$ ), 6.06  $\tau$  (s,  $CH_3$ ), 122.3  $\phi^*$  (t,  $J = 3.4$ ,  $CH_3O_2CCF_2$ ), 86.8  $\phi^*$  (complex,  $CH_3O_2CCF_2CF_2$ ), 80.4 and 84.2  $\phi^*$  (AB,  $J = 140$ ,  $CF_2CFCl$ ), 131.3  $\phi^*$  ( $CFCl$ ).

Found also was 2.6 g. of 1-chloro-1,5-di-*H*-3-oxaheptafluoropentane: nmr (fluorotrichloromethane): 3.90  $\tau$  (d, t,  $J = 47.5$ , 4.2,  $HCFCl$ ), 155.1  $\phi^*$  (d, t,  $J = 47.5$ , 11.0,  $HCFCl$ ), 84.7  $\phi^*$  (complex,  $HCFClCF_2$ ), 89.3  $\phi^*$  (complex,  $CF_2CF_2H$ ), 137.9  $\phi^*$  (d, t,  $J = 53.0$ , 4.6,  $CF_2H$ ), 4.25  $\tau$  (t, t,  $J = 53.0$ , 2.8,  $CF_2H$ ).

Also isolated was 12 g. of methyl-6-chloro-6-*H*-4-oxaheptafluorohexanoate (**6**): ir 5.52  $\mu$  (C=O); nmr (fluorotrichloromethane): 3.87  $\tau$  (d, t,  $J = 48.2$ , 4.2,  $HCFCl$ ), 155.3  $\phi^*$  (d, t,  $J = 48.2$ , 10.2,  $CHCl$ ), 85.0  $\phi^*$  (complex,  $CHClCF_2$ ), 86.4  $\phi^*$  (complex,  $CHClCF_2OCF_2$ ), 122.1  $\phi^*$  (t,  $J = 2.6$ ,  $CF_2CO_2CH_3$ ), 6.06  $\tau$  (s,  $CH_3$ ).

Anal. Calcd. for  $C_6H_4ClF_7O_3$ : C, 24.6; H, 1.4; F, 45.4. Found: C, 24.7; H, 1.6; F, 45.5.

Ammonia was bubbled into an ether solution of 12 g. of **6** until the reaction was complete by ir. Then 34 g. of phosphorus pentoxide (in sand) was added and the mixture heated gradually to 250°; with 6 g. of **4** collected by distillation: ir 4.43  $\mu$  (CN); nmr (fluorotrichloromethane): 3.86  $\tau$  (d, t,  $J = 47.7$ , 4.1,  $HCFCl$ ), 155.5  $\phi^*$  (d, t,  $J = 47.7$ , 11.2,  $CHCl$ ), 85.5  $\phi^*$  (complex,  $HCFClCF_2$ ), 87.7  $\phi^*$  (complex,  $HCFClCF_2OCF_2$ ), 109.2  $\phi^*$  (t,  $J = 4.9$ ,  $CF_2CN$ ).

Anal. Calcd. for  $C_5HClF_7NO$ : C, 23.1; F, 51.2. Found: C, 23.3; F, 51.0.

#### 2,4,6-Tris(5-chloro-5-*H*-3-oxaheptafluoropentyl)-s-triazine (**1c**).

Heating 6 g. of **4** with 0.01 g. of ammonia in a thick walled glass reactor to 150° for 19 hours led to 5 g. of **1c** by a short path distillation: ir 6.42  $\mu$  ( $C_3N_3$ ).

Anal. Calcd. for  $C_{15}H_3Cl_3F_{21}N_3O_3$ : C, 23.1; F, 51.3; N, 5.4. Found: C, 23.3; F, 51.4; N, 5.4.

#### 3-Octafluoromorpholinotetrafluoropropanenitrile (**7**).

Dehydration of the amide of the corresponding acid (**6**) with phosphorus pentoxide as previously described led to the title compound: ir 4.44  $\mu$  (CN); nmr (fluorotrichloromethane): 87.6  $\phi^*$  ( $CF_2OCF_2$ ), 92.6  $\phi^*$  ( $CF_2NCF_2$ ), 106.8  $\phi^*$  ( $CF_2CN$ ).

Anal. Calcd. for  $C_7F_{12}N_2O$ : C, 23.6; F, 64.0. Found: C, 23.7; F, 64.3.

#### 2,4,6-Tris(2-octafluoromorpholinotetrafluoroethyl)-s-triazine (**1b**).

A thick walled glass reactor containing 17 g. of **7** and 0.085 g. of ammonia was heated to 150° for 14 hours. A short path distillation under vacuum gave 15 g. of **1b**:  $T_b$  (dta) 301°; ir 6.44  $\mu$  ( $C_3N_3$ ).

Anal. Calcd. for  $C_{21}F_{36}N_6O_3$ : C, 23.6; F, 64.0; N, 7.9. Found: C, 23.5; F, 64.1; N, 7.8.

#### 4-Oxanonfluorohexanoic Anhydride (**8**).

The title compound (**4c**) was prepared by heating 28 g. of the corresponding acid (**10**) with a two molar excess of phosphorus pentoxide at 130° for 4 hours. Distillation gave 24 g. of **8**, b.p. 121-124° (730 mm); ir 5.35 and 5.54  $\mu$  (C=O); nmr (fluorotrichloromethane): 87.5  $\phi^*$  ( $CF_3$ ), 88.9  $\phi^*$  ( $CF_3CF_2$ ), 85.4  $\phi^*$  ( $C_2F_5OCF_2$ ), 121.8  $\phi^*$  ( $C_2F_5OCF_2CF_2$ ).

Anal. Calcd. for  $C_{10}F_{18}O_5$ : C, 22.2; F, 63.1. Found: C, 22.2; F, 62.9.

#### 4-Oxanonfluorohexanenitrile (**9**).

Preparation was carried out as before by dehydrating the amide of the corresponding acid (**10**) with phosphorus pentoxide to yield **9** (**4c**), b.p. 27-30° (730 mm); ir 4.43  $\mu$  (CN); nmr (fluorotrichloromethane): 87.3  $\phi^*$  ( $CF_3$ ), 88.9  $\phi^*$  ( $CF_3CF_2$ ), 87.4  $\phi^*$  ( $C_2F_5OCF_2$ ), 109.0  $\phi^*$  ( $C_2F_5OCF_2CF_2$ ).

Anal. Calcd. for  $C_5F_9NO$ : C, 23.0; F, 65.6. Found: C, 23.1; F, 65.0.

#### 2,4-Di(3-oxanonfluoropentyl)-6-(2-octafluoromorpholinotetrafluoroethyl)-s-triazine (**2a**).

Excess ammonia was condensed with 8.3 g. of **9** frozen with liquid nitrogen and this mixture stirred at -40° for 2 hours. The excess ammonia was then removed under vacuum at 25° to leave the amidine [ir 5.96  $\mu$  (C=N)], dry Freon 113 (duPont inert fluid) added, and at -40°, a rapid addition of 10.7 g. of **7** in F-113 gave the intermediate imidoylamidine. After having stirred the reaction mixture for 6 hours at 25°, this solution was added dropwise to 34 g. of **8** in F-113 at 0°. A short path distillation

under vacuum after stirring overnight at 25°, gave 17 g. of **2a**,  $T_b$  (dta) 235°; ir 6.41  $\mu$  ( $C_3N_3$ ).

*Anal.* Calcd. for  $C_{17}F_{30}O_3N_4$ : C, 23.2; F, 64.9; N, 6.4. Found: C, 23.2; F, 64.5; N, 6.6.

2,4-Di(2-octafluoromorpholinotetrafluoroethyl)-6-(3-oxanonylfluoropentyl)-s-triazine (**2b**).

A mixture of 10.7 g. of **7** and excess ammonia was stirred at 40° for two hours, the excess removed at 25°, and F-113 added as solvent. The amidine solution [ir 5.96  $\mu$  (C=N)] was cooled to -20°, 10.7 g. of **7** added rapidly, and the resulting imidoamidine stirred overnight at 25°. This solution was then added dropwise to 34 g. of **8** in F-113 and after having been stirred overnight at 40° the product was isolated by short path distillation under vacuum to yield 15.5 g. of **2b**,  $T_b$  (dta) 270°; ir 6.42  $\mu$  ( $C_3N_3$ ).

*Anal.* Calcd. for  $C_{19}F_{33}O_3N_5$ : C, 23.4; F, 64.4; N, 7.2. Found: C, 23.6; F, 64.3; N, 7.3.

Undecylfluorocyclohexanecarbonitrile (**10**).

Dehydration with phosphorus pentoxide of the amide of the corresponding acid (**9**) led to the title compound (**10**): ir 4.40  $\mu$  (CN); nmr (fluorotrichloromethane): 176.2  $\phi^*$  (CF), 110 to 145  $\phi^*$  (complex, cyclo  $CF_2$ ).

*Anal.* Calcd. for  $C_7F_{11}N$ : C, 27.4; F, 68.1. Found: C, 27.9; F, 66.9.

Undecylfluorocyclohexanecarboxylic Anhydride (**11**).

Again, dehydration of the acid with phosphorus pentoxide gave the desired compound: ir 5.39 and 5.58  $\mu$  (C=O); nmr (fluorotrichloromethane), 178.8  $\phi^*$  (CF), 112 to 147  $\phi^*$  (complex, cyclo  $CF_2$ ).

*Anal.* Calcd. for  $C_{14}F_{22}O_3$ : C, 26.5; F, 65.9. Found: C, 26.3; F, 65.9.

2,4-Di(3-oxanonylfluoropentyl)-6-(undecylfluorocyclohexyl)-s-triazine (**2c**).

The amidine of **9** was prepared as described previously and 9.2 g. of **10** in F-113 added at 25°. This solution of imidoamidine was stirred overnight at 25°, then added dropwise to 40 g. of **8** in F-113 at 0°. Short path distillation under vacuum, after stirring overnight at 40°, gave 11 g. of **2c**,  $T_b$  (dta) 225°; ir 6.41  $\mu$  ( $C_3N_3$ ).

*Anal.* Calcd. for  $C_{17}F_{29}O_2N_3$ : C, 24.7; F, 66.6; N, 5.1. Found: C, 24.7; F, 65.7; N, 5.0.

2,4-Di(undecylfluorocyclohexyl)-6-(3-oxanonylfluoropentyl)-s-triazine (**2d**).

Excess ammonia was condensed with 7.7 g. of **10** at -20° to yield the solid amidine [ir 5.96  $\mu$  (C=N)] after removal of the excess ammonia. F-113 was added, the mixture cooled to -20°, and 7.7 g. of **10** added. After having been stirred overnight, the resulting imidoamidine was added dropwise to 34 g. of **8** in F-113 at 0°. As before, the resulting mixture was stirred overnight at 40° and a short-path distillation under vacuum gave 14 g. of **2d**,  $T_b$  (dta) 250°; ir 6.43  $\mu$  ( $C_3N_3$ ).

*Anal.* Calcd. for  $C_{19}F_{31}ON_3$ : C, 26.1; F, 67.3; N, 4.8. Found: C, 25.9; F, 66.9; N, 4.8.

2,4,6-Tris(undecylfluorocyclohexyl)-s-triazine (**2e**).

The imidoamidine from **10** prepared as described above was added dropwise to 38 g. of **11** in F-113 at 0°. After having been heated at 40° overnight, a short path distillation under vacuum led to 8 g. of **2e**, m.p. 95-97°; ir 6.42  $\mu$  ( $C_3N_3$ ).

*Anal.* Calcd. for  $C_{21}F_{33}N_3$ : C, 27.4; F, 68.1; N, 4.6. Found: C, 27.5; F, 67.9; N, 4.5.

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