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New methods for the preparation of perfluoroalkyl- and perfluoroalkylether-s-triazines

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Abstract

Two new single-step processes are provided for the preparation of 2,4,6-tris(perfluoroalkyl) and (perfluoroalkylether)-1,3,5-triazines. One method involves the nucleophilic substitution of cyanuric fluoride with (perfluoroalkyl) and (perfluoroalkylether)trimethylsilanes in the presence of cesium fluoride. Substituted s-triazines, 2,4,6-$(R_f)_3C_3N_3$ (**IIa–d**) {**IIa**, $R_f = n\text{-}C_8F_{17}$; **IIb**, $R_f = (CF_3)_2CFO(CF_2)_4$; **IIc**, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$; **IId**, $R_f = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$}, with either primary or secondary carbon atoms next to the ring can be produced by this method in reasonable yields, 41–77%. Using the second method, substituted triazines, **IIa** and **IIb**, are prepared by the cross-coupling reactions of cyanuric chloride with perfluoroalkyl and perfluoroalkylether iodides in the presence of copper powder. This method can only produce substituted triazines with primary carbon atoms adjacent to the ring. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Triazine; Cyanuric fluoride; Nucleophilic substitution

1. Introduction

Known processes for producing perfluoroalkyl and perfluoroalkylether substituted s-triazines are extensively described in the literature. They include thermal cyclotrimerization of nitriles at elevated pressures [1], as well as cyclotrimerization in the presence of a variety of catalysts [2–5]. Methods are also known where a nitrile is condensed with ammonia to obtain an amidine, which reacts with another molecule of a nitrile to yield an imidoylamidine and which in turn is cyclized with an acid anhydride to form the trisubstituted s-triazine [6–9]. The starting nitrile used in all the above methods are normally prepared from an acid halide, its conversion to an amide followed by dehydration of the amide. Thus, these processes are multiple-step processes and have the usual limitations and inefficiencies associated with such processes.

Single-step processes for the production of perfluoroalkyl-s-triazines from low-molecular weight perfluoroolefins and cyanuric fluoride are also known which involve reaction of carbanions generated *in situ* from perfluoroolefin and fluoride ions with cyanuric fluoride [10,11]. The yields of the trisubstituted s-triazines are relatively low. It is thus desirable to have efficient and improved single-step synthesis procedures to obtain these useful classes of materials starting from cyanuric fluoride or preferably the less expensive cyanuric chloride.

2. Experimental details

All reactions were carried out in oven-dried glassware under an atmosphere of dry nitrogen. Copper bronze was purchased from Gralled Schlesinger Chemical, New York, and was used without activation. Cyanuric fluoride ($C_3N_3F_3$) and cyanuric chloride ($C_3N_3Cl_3$) were from Lancaster Synthesis, CsF, $ClSiMe_3$, $n\text{-}C_8F_{17}I$ and $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F$ ($n = 1, 2$) were from PCR, $(CF_3)_2CFO(CF_2)_4I$ was obtained from Allied Chemical. The solvents used were purchased from Aldrich Chemical and were anhydrous. The secondary perfluoroalkylether iodides, $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)I$ ($n = 1, 2$), were prepared by a modification of known methods [12–14]. (Perfluoroalkyl)- and (perfluoroalkylether)-trimethylsilanes, R_fSiMe_3 {Ia, $R_f = n\text{-}C_8F_{17}$; Ib, $R_f = (CF_3)_2CFO(CF_2)_4$; Ic, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$; Id, $Rf = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$}, were prepared by reported procedures [15]. GC analyses were performed on a Perkin-Elmer Sigma 1 using a six foot stainless steel column (1/4 in o.d.) packed with 10% SP-2100 on 80–100 mesh supelcoport. The

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Table 1
Reaction of $C_3N_3F_3$[a] and R_fSiMe_3 at ~0°C[b] in the presence of CsF

Experiment	Reagent, R_fSiMe_3, R_f	Molar Ratio $C_3N_3F_3$:R_fSiMe_3:CsF	Solvent	Time (h)	Product $(R_f)_3C_3N_3$, Isolated yield, %
1	n-C_8F_{17}	1:3.3:1	CH_3CN	4	**IIa**, 41
2	$(CF_3)_2CFO(CF_2)_4$	1:3.3:1	CH_3CN	4	**IIb**, 59
3	n-C_8F_{17}	1:3.7:1.4	Et_2O/CH_3CN[c]	22[d]	**IIa**, 57
4	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	1:3.1:1.1	CH_3CN	1.5	**IIc**, 70
5[e]	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	1:3.4:1.2	CH_3CN	1.0	**IIc**, 60
6	$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$	1:3.1:1.1	CH_3CN	1.5	**IId**, 69
7	$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$	1:3.2:1.3	Et_2O/CH_3CN[c]	2[f]	**IId**, 77

[a] $C_3N_3F_3$: cyanuric fluoride.
[b] Cooling with salt-ice bath, temperature range from −5 to 0°C.
[c] Et_2O/CH_3CN: 4/1 ratio by volume.
[d] Also at r.t. 1 h.
[e] R_fSiMe_3 was used without purification.
[f] Also at r.t. 2 h.

GC-MS analyses were performed on a Finnigan 4021 mass spectrometer in the electron impact mode. IR specta were recorded on a Perkin-Elmer 683 spectrometer. NMR spectra were obtained on an NT-300 spectrometer. All boiling points and melting points are uncorrected.

2.1. Preparation of $C_3N_3(R_f)_3$ (IId) from R_fSiMe_3 and $C_3N_3F_3$, $R_f = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$ in CH_3CN

An acetonitrile (20 ml) solution of cyanuryl fluoride (0.69 g, 5.11 mmol) and R_fSiMe_3 (11.0 g, 15.9 mmol) was cooled to ~ −5°C. To this solution was added CsF (0.84 g, 5.53 mmol) slowly over 20 min. An exothermic reaction was noted immediately on addition of CsF and a yellow color developed. The mixture was periodically analyzed by GC for the completion of the reaction. After stirring at 0°C for ~ 1.5 h, the reaction mixture was diluted with H_2O (20 ml). The lower organic layer was separated and washed with H_2O (3×10 ml). The crude product (9.45 g) was distilled to yield 2,4,6-tris[perfluoro(1′,4′,7′-trimethyl-2′,5′,8′-trioxaundecyl)]-1,3,5-triazine (**IId**) (6.79 g, 69% yield, 99% purity).

Compound **IIc** was prepared by the same procedure as compound **IId**. Compounds **IIa** and **IIb** were prepared in a similar manner as described above for **IId** except the reaction time and work-up procedure were different. It took 4 h to complete the reactions for **IIa**,**IIb**. They were worked up without adding H_2O. From the reaction mixture solvent was removed by distillation at reduced pressure. The crude product residue obtained was extracted with 1,1,2-trichlorotrifluoroethane, the solvent was removed and the product was distilled to yield the pure compound. The experimental conditions and the results are listed in Table 1.

2.2. Preparation of $C_3N_3(n\text{-}C_8F_{17})_3$ (IIa) from $C_8F_{17}SiMe_3$ and $C_3N_3F_3$ in Et_2O/CH_3CN

Cyanuric fluoride (0.51 g, 3.78 mmol) and perfluoro-*n*-octyltrimethyl silane (6.81 g, 13.84 mmol) were dissolved in a mixture of anhydrous diethyl ether (8.0 ml) and anhydrous acetonitrile (2.0 ml), taken in a 25-ml round-bottomed flask maintained under an atmosphere of dry nitrogen. The flask was cooled to −5°C and anhydrous CsF (0.78 g, 5.13 mmol) was added. After stirring the reaction mixture for 22 h at 0°C and then 1 h at room temperature, the reaction mixture was distilled under reduced pressure to remove solvents. The crude product residue obtained was extracted with 1,1,2-trichlorotrifluoroethane, the solvent was removed and the product was distilled at reduced pressure. Pure 2,4,6-tris(perfluoro-*n*-octyl)-1,3,5-triazine (**IIa**) (2.88 g, 57% yield) was obtained as a colorless liquid boiling at 142°C/0.3 mm Hg. On cooling, it solidified into a white solid melting at 52–53°C.

Following the same general procedure set forth above, cyanuric fluoride (0.31 g, 2.30 mmol) and $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)SiMe_3$ (Id) (5.15 g, 7.46 mmol) were dissolved in a mixture of dry acetonitrile (2.0 ml) and anhydrous diethyl ether (8.0 ml), and the mixture was cooled to about −5°C under a nitrogen atmosphere. Anhydrous CsF (0.45 g, 2.96 mmol) was added to the reaction mixture in small lots. After stirring the reaction mixture at about 0°C for 2 h, the temperature was allowed to rise to ambient and the mixture was stirred for an additional 2 h. The reaction mixture was then diluted with water (15 ml) and the lower layer was separated and washed with water (3×5 ml). The crude product obtained was distilled under reduced pressure to obtain 2,4,6-tris[perfluoro(1′,4′,7′-trimethyl-2′,5′,8′-trioxaundecyl)]-1,3,5-triazine (**IId**) (3.40 g, 77% yield) as a colorless liquid boiling at 143°C/0.03 mm Hg.

2.3. Preparation of $C_3N_3(R_f)_3$ (IIc) from R_fI, Me_3SiCl, $C_3N_3F_3$, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

A benzonitrile (4.5 ml) solution of R_fI (5.50 g, 9.52 mmol) and Me_3SiCl (0.98 g, 9.03 mmol) was cooled to ~ −5°C. To this solution was added $(Et_3N)_3P$ solution (2.28 g in 2 ml C_6H_5CN, 9.22 mmol) dropwise during a 10 min period. After stirring at ~0°C for an additional hour, the bottom layer (4.47 g, 84 GC area % of R_fSiMe_3) was separated. It was used without further purification in the subsequent reaction. A CH_3CN (5 ml) solution of $C_3N_3F_3$ (0.30 g, 2.22 mmol) and crude product R_fSiMe_3 was added to CsF (0.39 g, 2.57 mmol) slowly over 10 min. After stirring at 0°C for 1 h, the bottom layer was washed with H_2O (3×3 ml). The crude product (3.05 g) was distilled to yield 2,4,6-tris[perfluoro(1′,4′-dimethyl-2′5′-dioxaoctyl)]-1,3,5-triazine (**IIc**) (1.91 g, 60% yield base on $C_3N_3F_3$).

2.4. Preparation of $C_3N_3(n\text{-}C_8F_{17})_3$ (IIa) from n-$C_8F_{17}I$ and $C_3N_3Cl_3$

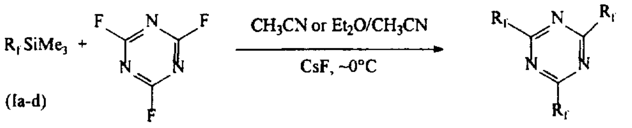
Cyanuric chloride (1.3 g, 7.05 mmol), n-$C_8F_{17}I$ (15.4 g, 28.2 mmol), copper bronze (3.95 g, 62 mmol), 2,2′-bipyridine (0.31 g, 1.97 mmol) and hexafluorobenzene (40 ml) were in a 100-ml round-bottom flask, under a nitrogen atmosphere. With efficient stirring of the contents, the flask was heated to about 85°C so as to reflux the reaction mixture. The reaction was continued at 85°C for a period of 4 days. After the reaction, the contents were allowed to cool to room temperature, filtered and the brown solid was extracted with 1,1,2-trichlorotrifluoroethane. This extract was combined with the filtrate and was distilled to remove the solvents. The liquid residue obtained was distilled under reduced pressure to obtain 2,4,6-tris(perfluorooctyl)-1,3,5-triazine (**IIa**) (3.32 g, 34% yield). The physical properties and the spectral data of this material were identical to those of the sample obtained from the reaction of $C_8F_{17}SiMe_3$ and $C_3N_3F_3$. Compound **IIb** was also synthesized by the same procedure. The yield was 37%.

The secondary perfluoroalkylether iodide, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)I$, was used to react with cyanuric chloride under the similar conditions. No desired product **IIc** was formed.

3. Results and discussion

Trisubstituted s-triazines, 2,4,6-$(R_f)_3C_3N_3$ (**IIa–d**) were synthesized by two new single-step processes as follows:

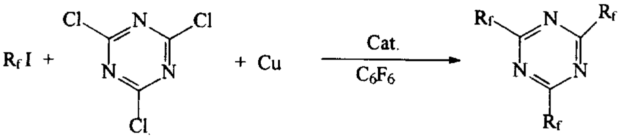
Method A: Cyanuric fluoride route



(IIa-d)

Ia, **IIa**: $R_f = n\text{-}C_8F_{17}$
Ib, **IIb**: $R_f = (CF_3)_2CFO(CF_2)_4$
Ic, **IIc**: $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
Id, **IId**: $R_f = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$

Method B: Cyanuric chloride route



(IIa,b)

Cat.: 2,2′-bipyridine
IIa: $R_f = n\text{-}C_8F_{17}$
IIb: $R_f = (CF_3)_2CFO(CF_2)_4$

Compounds **IIa–d** were synthesized by method A, the reaction of the corresponding R_fSiMe_3, cyanuric fluoride and cesium fluoride in CH_3CN or Et_2O/CH_3CN mixture (4:1 by volume) at −5 to 0°C in reasonable yields, ranging from 41 to 77%. The reaction time can vary depending on the structure of the silane reagent used as well as other reaction conditions and is best determined by following the extent of reaction by GC analysis of the reaction mixture. (Perfluoroalkyl)- and (perfluoroalkylether)-trimethylsilanes (**Ia–d**) used in this study were prepared by reported procedures [15]. Compounds **Ic**,**d** prepared by a modified procedure of Ruppert et al. [16], Pawelke [17], and Krishnamurti et al. [18] can also be used without purification (Table 1, exp. 5).

Compounds **IIa**,**b** were also prepared by Method B by the reaction of the corresponding (perfluoroalkyl)- and (perfluoroalkylether)-iodides (R_fI) with cyanuric chloride in the presence of copper powder in hexafluorobenzene using 2,2′-bipyridine as catalyst at refluxing temperature (~85°C). The isolated yields of **IIa**,**b** are low, 34 and 37%, respectively. In an attempt to improve the yield, dimethyl sulfoxide (DMSO) was used in the reaction to form the complexing ligand for the organocopper intermediates as in a previous report [14]. Due to the stability of cyanuric chloride in DMSO, the reaction was unsuccessful. The secondary perfluoroalkylether iodide was allowed to react with cyanuric chloride using the same experimental condition as above. After 4 days of reaction, no substitution product was obtained except some decomposition products of secondary iodide. However, considering the low cost of cyanuric chloride compared to cyanuric fluoride or the additional reaction step involved in converting cyanuric chloride to cyanuric fluoride [19,20] and perfluoroalkyl or perfluoroalkylether iodides to trimethylsilyl compounds (**Ia-d**), method B is also efficient and viable.

Following the reaction period, the product is isolated in method A, by diluting the reaction mixture with water and distilling the lower layer after it is separated. When the product is a triazine with a primary carbon atom adjacent to the triazine ring (**IIa**, **IIb**), the water treatment is avoided, as such triazines in general have low hydrolytic stability. Instead, the reaction mixture is usually filtered or centrifuged, and the solid part is extracted with 1,1,2-trichlorotrifluoroethane, combined with the liquid part and distilled to remove the solvent. The residual product obtained is distilled under reduced pressure to isolate the pure triazine. In method B, the product is isolated by cooling the reaction mixture, followed

Table 2
Characterization of 2,4,6-tris(perfluoroalkyl) and (perfluoroalkylether)-1,3,5-triazines

Compounds	B.P. (°C/mm Hg) [m.p., (°C)]	Elemental analysis (Calc./Found)			MS/EI (m/z)[a]
		%C	%N	%F	
IIa	142/0.3	24.29	3.15	72.57	966 $(M-C_7F_{15})^+$
	[52–53]	24.09	3.45	70.85	
IIb	108/0.1	23.38	3.41	69.33	948 $(M-C_3F_7OC_2F_4)^+$
		23.20	4.16	67.83	
IIc[b]	95/0.02	22.66	2.94	67.70	914 $(M-C_3F_7OC_3F_6OCF_2\text{-}C_2F_4O)^+$
		21.91	3.48	67.40	
IId[b]	143/0.03	22.41	2.18	67.95	–
		22.19	2.69	68.97	

[a] Molecular ion of compounds (> 1000) were beyond the mass limit of the spectrometer.
[b] Known compounds [7,8].

Table 3
NMR spectra of 2,4,6-tris(perfluoroalkyl) and (perfluoroalkylether)-1,3,5-triazines[a]

Compounds, 2,4,6-$(R_f)_3C_3N_3$ R_f	^{19}F NMR δ (ppm)
IIa, n-C_8F_{17}	−81.7 (tt, CF_3); −116.8 (t, CF_2); −121.5 (b, CF_2); −122.3 (b, $2CF_2$); −122.5 (b, CF_2); −123.3 (b, CF_2); −126.8 (b, CF_2 next to CF_3)
IIb, $(CF_3)_2CFO(CF_2)_4$	−81.2 (b, CF_2O); −81.5 (om, $2CF_3$); −116.8 (t, CF_2); −122.4 (m, CF_2); −125.0 (m, CF_2); −145.0 (t, CF)
IIc, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$[b]	−78.0 (m, part of CF_2O); −80.9 (tp, CF_3); −82.3 (m, $2CF_3$ and CF_2O); −130.4 (s, CF_2 next to CF_3); −134.0 (tm, CF next to ring); −145.0 to −145.5 (tm, CF in chain)
IId, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$[b]	−79.0 (um, part of CF_2O); −81.2 and −82.7 (b, $4CF_3$ and $2CF_2O$); −130.4 (s, CF_2 next to CF_3); −134.0 (tm, CF next to CF_3); −145 to −146 (tm, 2CF in chain)

[a] ^{19}F NMR (282.3 MHz); b = broad, m = multiplet, om = overlapping multiplets, s = singlet, t = triplet, tm = two overlapping multiplets, tp = two peaks, tt = tripled triplet, um = unresolved multiplet. Solvent: $CDCl_3$; reference: $CF_2ClCFCl_2$.
[b] Known compounds [7,8].

by filtering to remove solids. The solid part is extracted with 1,1,2-trichlorotrifluoroethane and combined with the filtrate. Distillation to remove the solvents followed by distillation under reduced pressure lead to isolation of pure triazine. The results in Table 1 indicate that the mixture of Et_2O/CH_3CN is preferable for higher yield than CH_3CN only. In two cases, Table 1, exp. 1 and 3, exp. 6 and 7, the yields are increased from 41 to 57% and 69 to 77%, respectively.

The physical properties, mass spectral data and elemental analysis of compounds **IIa–d** are given in Table 2. All the parent ion peaks of compounds (> 1000) were beyond the limit of the spectrometer used. However, the fragmentation peaks were consistent with the assigned structure. The infrared spectra of all compounds showed a strong absorption near 1560 cm^{-1} due to the triazine ring and strong absorption bands between 1380 and 1110 cm^{-1} due to C–F bonds. The ^{19}F NMR data of the compounds are presented in Table 3. All NMR data are in agreement with structural assignments.

Based on the results the following conclusions can be drawn. A primary R_f group in R_fSiMe_3 (**Ia,b**) exhibits less reactivity toward cyanuric fluoride than a secondary R_f group in R_fSiMe_3 (**Ic,d**). Primary $(R_f)_3C_3N_3$ is less hydrolytically stable under these reaction conditions than secondary $(R_f)_3C_3N_3$. A mixture of Et_2O/CH_3CN is preferable for higher yield than CH_3CN only. The yield of product by the cross-coupling reaction is lower than that in the nucleophilic displacement reaction. But the low cost of cyanuric chloride makes this method attractive. Cross-coupling reaction can only produce $(R_f)_3C_3N_3$ with primary carbon atoms adjacent to the ring under the experimental conditions used.

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