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SYNTHESIS OF FLUORO-CONTAINING SUBSTITUTED 1,3,5-TRIAZINES

T. K. Shmel'kova, A. V. Ignatenko,
S. P. Krukovskii, and V. A. Ponomarenko

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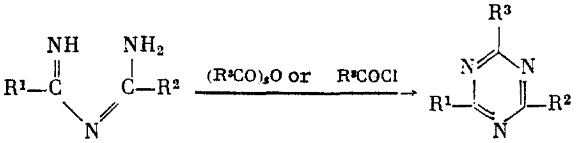
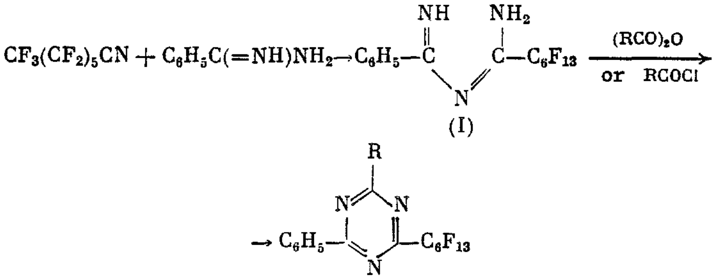
The synthesis and properties of triazines with identical substituents have been studied in detail: trisalkyltriazines [1, 2], trisperfluoroalkyltriazines [3, 4], and trisaryltriazines [1, 5]. The synthesis and properties of triazines with three different substituents have hardly been studied. Earlier, thermally stable 2-phenyl-4,6-perfluoroalkyl-1,3,5-triazines were prepared by cotrimerization of perfluoroalkanenitriles with benzonitrile [6] and also by reaction of the latter with tris-perfluoroalkyl-s-triazines [7].

For the synthesis of s-triazines with three different substituents R^1, R^2, and R^3, of which R^1 = phenyl and R^2 = perfluoroalkyl, the most useful method is acylation—cyclodehydration of N'-(perfluoroalkanimidoyl)benzamidines (imidoylamidines)* with anhydrides and acid halides of carboxylic acids because this makes it possible to prepare triazines with exactly determined positions of the substituents at the ring.



This article describes the synthesis of novel s-triazines by the method mentioned above. As starting compounds we used imidoylamidines (I) and (III), and bisimidoylamidine (II), prepared by reaction of mono- and dinitriles of perfluorocarboxylic acids with benzamidine. Subsequent cyclization of imidoylamidines (I)-(III) led to triazines (IV)-(VI).



(IVa-e)

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*Imidoylamidines are also called 1,3,5-triaza-1,3-pentadienes with indication of the specific substituents at the 2 and 4 positions.

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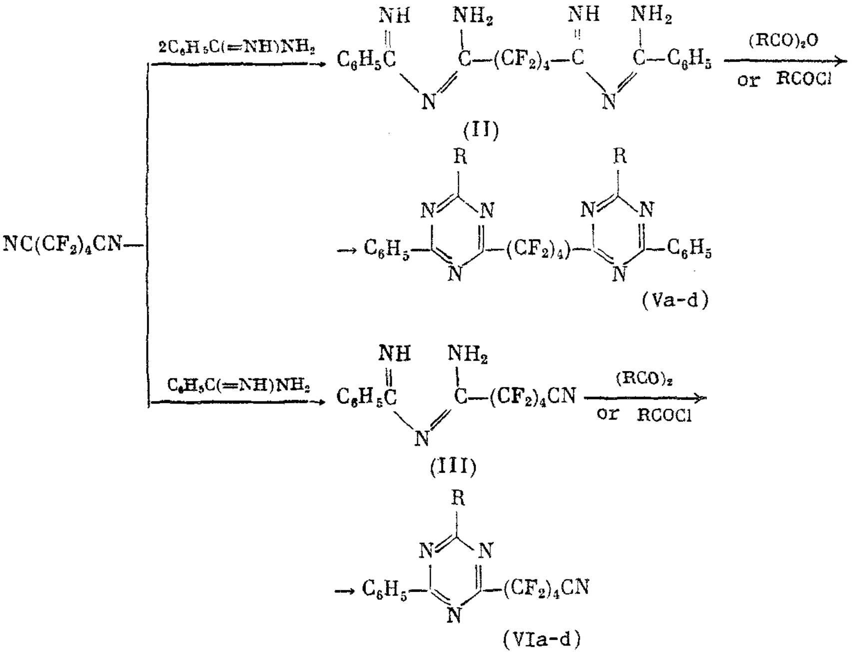

$R = CF_3$ (a), CH_3 (b), $CH{=}CH_2$ (c), $C(CH_3){=}CH_2$ (d), $CHBr{-}CH_2Br$ (e)

s-Triazines with one aryl and two perfluoroalkyl substituents were prepared earlier by a different method [6, 7], but they are also easily produced by acylation—cyclodehydration of imidoylamidines (I)-(III) with trifluoroacetic anhydride [(IVa)-(VIa)].

Anhydrides of perfluorinated acids are weaker acylating agents, but on using Ac_2O and also anhydrides and acid chlorides of acrylic and methacrylic acids we succeeded in preparing triazines (IVb-d) and (VIb-d) with three different substituents.

Imidoylamidine (III) is unstable at 20-25°C and therefore its synthesis was carried out at $\leq -50^\circ$ C. Attempts to prepare imidoylamidine (III) at higher temperatures led to the formation of bis-imidoylamidine (II), of which the occurrence apparently is the result of the known [8] exchange reactions between the imidoylamidine and nitrile groups.

EXPERIMENTAL

^{19}F NMR and PMR spectra were recorded on a PC-56M (SKBIOKh) spectrometer operating at 56.4 and 60 MHz, respectively, from $CDCl_3$ solutions relative to the external standard $CFCl_3$ and the internal standard TMS. IR spectra were taken on a UR-10 spectrometer and UV spectra on a Specord UV-VIS spectrometer.

Preparation of Imidoylamidines (I)-(III). Equimolar amounts of benzamidine and the nitrile of heptanoic acid in THF were gradually mixed at ~20°C, the mixture was allowed to stand for 1.5 h, and the solvent was evaporated to give (I) in quantitative yield. In much the same way bis-imidoylamidine (II) was prepared by reacting benzamidine with the dinitrile of perfluoroadipic acid. The IR spectra of the prepared compounds contain absorption bands of the nitrile group. In the UV spectra maximums at 245 and 284 nm are found.

To an excess of the dinitrile of perfluoroadipic acid was gradually added with stirring at −50°C a solution of benzamidine, and the mixture was kept at −50°C for 1.5 h. Compound (III) produced was immediately used in the acylation—dehydration reaction.

Preparation of Triazines (IV)-(VI). To a threefold excess of the appropriate anhydride of the carboxyl acid was gradually added at ~20°C a solution of imidoylamidine (I) or (II) and the mixture was kept at 30-50°C for 1.5-2 h. The yields of triazines (IV) and (V) are 30-75%. During the preparation of (VI) the temperature of the reaction mixture is kept at −15 to −10°C. Yields of triazines (VIa-d) are up to 50%.

When carboxylic acid chlorides are used as cyclizing agents, the reactions were carried out in the presence of pyridine or Et_3N. The anhydrides of acrylic and methacrylic acid were stabilized with hydroquinone (1-2%). The pure triazines (IV)-(VI) were isolated by preparative column chromatography over silica gel LL 40/100 (Czechoslovakia) with benzene—hexane as eluent.

TABLE 1. Spectral Data and Elemental Analysis of Triazines (IV)-(VI)

Compound	s-Triazine	Found/Calculated, %				Mp, °C	PMR spectrum, δ, ppm, J, Hz	IR spectrum, ν, cm^{-1}
		C	H	F	N			
(IVa)	2-Trifluoromethyl-4-perfluorohexyl-6-phenyl-s-triazine	35,21/35,37	1,12/0,93	56,28/55,96	7,38/7,74	52–53	8,85 m (2H, o-H), 7,80m (3H, m,p-H)	1560 (C=N in the triazine ring)
(IVb)	2-Methyl-4-perfluorohexyl-6-phenyl-s-triazine	39.01/39,28	1,89/1,65	51,02/50,48	8.39/8,59	66	2,78 s (3H, CH_3), 8,55m (2H, o-H), 7,50 m (3H, m,p-H)	1560
(IVc)	2-Vinyl-4-perfluorohexyl-6-phenyl-s-triazine	40,82/40,73	1,34/1,61	49,64/49,27	8,17/8,39	–	8,60m (2H, o-H), 7,55 m (3H, m,p-H). Protons at the double bond, ABX spectrum: δ_A=6,96; δ_B=7,12; δ_X=6,10. J_{AB}=17,2, J_{AX}=10,2, J_{BX}=1,6	1560 1640 (C=C)
(IVd)	2-Isopropenyl-4-perfluorohexyl-6-phenyl-s-triazine	42,74/41,95	1,96/1,95	48,19/47,95	8,04/8,16	63	8,60 m (2H, o-H), 7,55 m (3H, m,p-H), 7,92 d.q (1H, H_A, J_{AB}=1,5, $J_{H_A-CH_3}$=1,0), 5,85 q (1H, H_B, J_{BA}=$J_{H_B=CH_3}$=1,5), 2,30 dd (3H, =CH_3), $J_{CH_3-H_A}$=1,0, $J_{CH_3-H_B}$=1,5)	1560 1640 (C=C) 2960 (CH_3)
(IVe)	2-α,β-Dibromoethyl-4-perfluorohexyl-6-phenyl-s-triazine	31,02/30,88	1,22/1,22	37,54/37,36	6,23/6,36	62	8,65 m (2H, o-H), 7,60 (3H, m,p-H), 5.32 dd 1H, H_X, J_{XA}=11,5, J_{XB}=4,25), 4,50 dd (1H, H_A, J_{AB}=9,6, J_{AX}=11,5), 4,03 dd (1H, H_B, J_{BA}=9,6, J_{BX}=4,25)	1560
(Va)	α,ω-Di-(2-trifluoromethyl-4-phenyl-s-triazinyl-6) perfluorobutane	44,64/44,46	1,54/1,55	40,78/41,02	12,91/12,97	142–143	8,80 m (2H, o-H), 7,85 (3H, m,p-H)	1560

TABLE 1 (continued)

Compound	s-Triazine	Found/Calculated, %				Mp, °C	PMR spectrum, δ, ppm, J, Hz	IR spectrum, ν, cm^{-1}
		C	H	F	N			
(V b)	α,ω-Di-(2-methyl-4-phenyl-s-triazinyl-6) perfluorobutane	53,07 / 53,34	2,93 / 2,98	28,79 / 28,12	15,62 / 15,55	160–161	8,45 m (2H, o-H), 7,45 (3H, m,p-H), 2,66 s (3H, CH_3)	1560
(Vc)	α,ω-Di-(2-vinyl-4-phenyl-s-triazinyl-6) perfluorobutane	55,35 / 55,33	2,76 / 2,85	26,46 / 26,93	14,63 / 14,89	–	8,65 m (2H, o-H), 7,60 m (3H, m,p-H). Protons at the double bond, ABX spectrum: $\delta_A=6,97$, $\delta_B=7,12$, $\delta_X=6,15$; $J_{AB}=17,1$, $J_{AX}=10,1$, $J_{BX}=1,5$	1560 1640 ($C=C$)
(V d)	α,ω-Di-(2-isopropenyl-4-phenyl-s-triazinyl-6) perfluorobutane	56,48 / 55,76	3,42 / 3,40	25,78 / 25,65	14,26 / 14,13	153–154	8,62 m (2H, o-H), 7,55 m (3H, m,p-H), 7,94 (1H, H_A), 5,86 m (1H, H_B), 2,32 m (3H, CH_3)	1560 1640 ($C=C$) 2960 (CH_3)
(VI a)	2-Trifluoromethyl-4-ω-cyanoperfluorobutyl-6-phenyl-s-triazine	40,81 / 40,01	1,12 / 1,12	46,14 / 46,42	12,51 / 12,45	35	8,90 (2H, o-H), 7,90 m (3H, m,p-H)	1560 2270 ($C\equiv N$)
(VI b)	2-Methyl-4-ω-cyanoperfluorobutyl-6-phenyl-s-triazine	45,64 / 45,46	2,08 / 2,04	38,08 / 38,36	14,21 / 14,14	41	8,55 m (2H, o-H); 7,60 m (3H, m,p-H) 2,75 s (3H, CH_3)	1560 2270 ($C\equiv N$)
(VI c)	2-Vinyl-4-ω-cyanoperfluorobutyl-6-phenyl-s-triazine	47,31 / 47,07	1,96 / 1,97	37,01 / 37,23	13,80 / 13,73	–	8,60 m (2H, o-H), 7,56 (3H, m,p-H). Protons at the double bond, ABX spectrum $\delta_A=6,95$, $\delta_B=7,10$, $\delta_X=6,12$, $J_{AB}=17,2$, $J_{AX}=10,2$, $J_{BX}=1,6$	1560 1640 ($C=C$) 2270 ($C\equiv N$)
(VI d)	2-Isopropenyl-4-ω-cyanoperfluorobutyl-6-phenyl-s-triazine	48,54 / 48,35	2,38 / 2,39	35,77 / 35,33	13,33 / 13,27	138–139	8,61 (2H, o-H), 7,53 (3H, m,p-H), 7,92 m (1H, H_A), 5,85 m (1H, H_B), 2,30 m (3H, CH_3)	1560 1640 ($C=C$) 2270 ($C\equiv N$) 2960 (CH_3)

TABLE 2. ^{19}F NMR Spectra of Triazines (IV)-(VI)

s-Triazine	^{19}F (δ_{CFCl_3}, ppm)				
	F^1	F^2	F^3	F^4	F^5
$PhTr^{*}(\overset{1}{C}F_3)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{4}{C}F_2\overset{5}{C}F_3$ (IVa)	72.3 s	115,0 m	120.0 m	125.0 m	82.25 m
$PhTr(CH_3)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{4}{C}F_2\overset{5}{C}F_3$ (IVb)	–	115,2 m	120,0 m	124.6 m	82.3 m
$PhTr(CH{=}CH_2)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{4}{C}F_2\overset{5}{C}F_3$ (IVc)	–	115.3 m	120,2 m	124.8 m	82,4 m
$PhTr(CH_3C{=}CH_2)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{4}{C}F_2\overset{5}{C}F_3$ (IVd)	–	115,1 t	120,0 m	124.4 m	82,4 t
$PhTr(CHBrCH_2Br)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{4}{C}F_2\overset{5}{C}F_3$ (IVe)	–	115,3 t	120,1 m	124, 5 m	82.5 t
$PhTr(\overset{1}{C}F_3)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{2}{C}F_2(\overset{1}{C}F_3)TrPh$ (Va)	71,5 s	115,3 m	119,4	–	–
$PhTr(CH_3)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{2}{C}F_2(CH_3)TrPh$ (Vb)	–	115,1 m	119,2 m	–	–
$PhTr(CH{=}CH_2)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{2}{C}F_2(CH_2{=}CH)TrPh$ (Vc)	–	114,7m	120,2 m	–	–
$PhTr(CH_3C{=}CH_2)\overset{2}{C}F_2(\overset{3}{C}F_2)_3\overset{2}{C}F_2(CH_2{=}CCH_3)TrPh$ (Vd)	–	115,0m	119,1 m	–	–
$PhTr(CF_3)\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2C{\equiv}N$ (VIa)**	71,2 s	115,0 m	120.0 m	119,0m	104.0 m
$PhTr(CH_3)\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2C{\equiv}N$ (VIb)**	–	114,5 m	119.8 m	118,9m	103,8 m
$PhTr(CH{=}CH_2)\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2C{\equiv}N$ (VIc)**	–	114.8 m	119.4 m	118.2 m	104,0 m
$PhTr(CH_3C{=}CH_2)\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_2C{\equiv}N$ (VId)**	–	114.2 m	119.3 m	118.3 m	103.5 m

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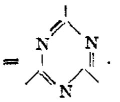
* Tr = .

**Assignment of the F^3 and F^4 signals was done on the basis of an increment scheme.

Spectral data, melting points, and elemental analysis of the isolated triazines are summarized in Tables 1 and 2.

CONCLUSIONS

By the method of acylation–cyclodehydration of imidoylamidines we have prepared 1,3,5-triazines with three different substituents, among them reactive unsaturated and nitrile groups.

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