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PHOSPHA-S-TRIAZINES. IX. CHLORO-SUBSTITUTED MONOPHOSPHA-S-TRIAZINES AND DERIVATIVES

K. J. L. PACIOREK, J. H. NAKAHARA, M. E. SMYTHE, D. H. HARRIS and R. H. KRATZER

Ultrasystems, Inc., 16845 Von Karman Avenue
Irvine, California 92714 (U.S.A.)

SUMMARY

1-Dichlorophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine and one of its perfluoroalkylether analogues were synthesized by interaction of phosphorus pentachloride with the respective imidoylamidines; subsequent replacement of the chloro- by azido groups proceeded readily. 1-Chloro(phenyl)-phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine was prepared by a parallel process using tetrachlorophenylphosphorane instead of phosphorus pentachloride; phenoxy and stearyloxy derivatives were formed without difficulty. All the compounds, with the exception of 1-stearyloxy(phenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, exhibited the characteristic mass spectral fragmentation patterns associated with the monophospha-s-triazine ring system.

INTRODUCTION

No monophospha-s-triazines substituted on the ring phosphorus by groups other than phenyl or pentafluorophenyl have been reported to date [1,2]. Since diphospha-s-triazines with a chloro group replacing one of the phenyls on each of the ring phosphorus atoms were successfully synthesized [3], it was only natural to extend this concept to the monophospha-s-triazines.

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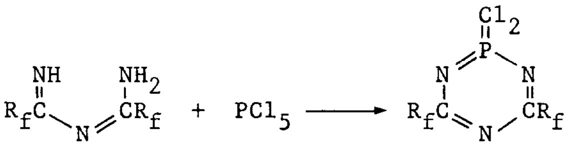
Douglas and Herring [4] did prepare geminally substituted dichlorotetraphenyl phosphazene trimer via interaction of imino-bis(aminophosphorane) with phosphorus pentachloride at elevated temperatures. Based on the similarities of the phospha-s-triazines and phosphazene trimers, one would expect a related approach to form the dichloromonophospha-s-triazines. These compounds, aside from their potential for introduction of a variety of substituents, were of particular interest with regard to mass spectral breakdown patterns to determine whether the characteristic fragmentations observed to date [5] were really ring-derived or were governed largely by the phenyl substituents on phosphorus.

RESULTS AND DISCUSSION

Synthesis

The novel dichloromonophospha-s-triazines were prepared by the interaction of an imidoylamidine with phosphorus pentachloride at 0°C in the presence of an acid acceptor.



I, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

II, $R_f = n\text{-}C_7F_{15}$

The yields realized of pure Compounds I and II, as evident from the Table 1 listing, are good compared to the phosphazenes [4]. Attempts to prepare a 4-ring compound by reaction of Compound II with perfluoro-n-octanoylamidine in a 1:1 ratio gave a product mix from which no pure substance could be isolated. On the other hand, the diazido-derivative was formed readily by an exchange with lithium azide. Although low melting, the perfluoroheptyl-substituted compounds were solids at room temperature, whereas the perfluoroalkylether-substituted material was a liquid, which is in agreement with what was found in the past [1,2].

TABLE 1

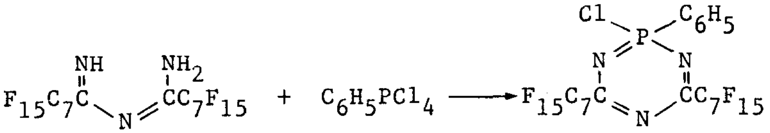
Chloromonophospha-s-triazines and derivatives

Compound	Mp °C	Bp °C	Yield %	IR bands $(cm^{-1})^a$
$[R_fCN]_2[Cl_2PN]^b$ (I)	-	73-74/0.001 mm Hg	45	1546 (vs), 1554 (sh)
$[n\text{-}C_7F_{15}CN]_2[Cl_2PN]$ (II)	30-31	88-89/0.001 mm Hg	61	1545 (vs), 1558 (sh)
$[n\text{-}C_7F_{15}CN]_2[(N_3)_2PN]$ (III)	35-36	∿85-90/0.001 mm Hg	64	2170 (vs) (ν, N_3) 1550 (vs), 1555 (sh)
$[n\text{-}C_7F_{15}CN]_2[C_6H_5(Cl)PN]$ (IV)	-	137-142/0.001 mm Hg	60	1495 (vs), 1510 (sh)
$[n\text{-}C_7F_{15}CN]_2[C_6H_5(OC_6H_5)PN]$ (V)	65-66	-	47	1565 (vs), 1590 (sh)
$[n\text{-}C_7F_{15}CN]_2[C_6H_5(OC_{18}H_{37})PN]$ (VI)	45-46	-	53	1570 (vs)

[a] Unless otherwise indicated, the absorption bands given are characteristic of phosphatriazine rings.

[b] $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-.

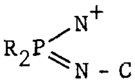
1-Chloro(phenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine was obtained from the interaction of tetrachlorophenylphosphorane and N'-(perfluorooctanoylimidoyl) perfluorooctanoylamidine, i.e.:



The product was admixed with ~10% of its fluoro-analogue. The origin of the latter is not readily apparent; however, its presence did not interfere with preparation of the phenoxy and stearyloxy derivatives.

Mass spectral data

The fragmentation patterns of the dichloro- and diazido-monophospha-s-triazines (I-III), as evident from the data given in Table 2, follow closely those reported for the phenyl-substituted analogues. The presence of high intensity (>80%) molecular ions in these compounds shows clearly that the stabilizing action of phenyl substituents on the ring is not necessary, which previously was believed to be the case [5]. The characteristic fragment



A

constituted the base peak in both of the perfluoro-n-heptyl-substituted materials, peaks at m/e 141 and 155 for the chloro and azido compounds, respectively. In the case of 1-dichlorophospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (Compound I), although not the base peak, the 141^+ ion corresponding to the fragment A was still a major intensity peak. This proves further that the observed breakdown pattern is not phenyl-substituent dependent, but is characteristic of the ring system itself.

TABLE 2

Ion fragments and intensities relative to base peak of 1-dichlorophospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (I), 1-dichlorophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (II), and 1-diazidophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (III)[a]

m/e	I	II	III	m/e	I	II	III	m/e	I	II	III
31	12.8	7.0	8.6	184		5.0		622	13.4		
36	6.1	6.1		191	53.2	25.8		718	37.3		
45			20.7	193	33.5	25.9		719	6.9		
47	11.8			195	8.5	5.7		720	26.5		
50	10.6	5.4	6.2	205			6.0	721	5.6		
66	10.2	12.5		214	5.3			784	28.8		
68		5.3		222		8.7		785	6.5		
69	92.4	49.2	69.5	224		6.5		786	22.7		
71	19.7	28.2	68.6	225	16.4			788	5.2		
76	8.9	9.7	17.1	227	5.3			868	10.5		
80		8.5		241	23.8	5.2		870		19.2	
85	15.4	21.4		243	16.9			871		6.2	
87	5.7	9.2		267		6.1		872		8.8	
92			14.8	269		5.2		877			13.4
93		5.1		286	9.3			884	30.5		
97	13.5			288	5.9			885	7.3		
100	23.4	18.0	12.0	313	6.3			886	23.5	46.9	
101	25.3	30.4		335	32.7			887		14.5	
103	17.3	25.9		391	6.2			888		34.9	
105		6.9		407	11.4			889		11.5	
106	8.8	12.2		409	7.8			890		10.4	
107			7.3	452	21.3			899		5.0	
108		5.8		454	13.6			900			46.5
114			9.1	475		5.1		901			15.4
115		5.5	6.3	491		8.8		905		81.4(M^+)	
119	38.5	26.6	27.9	493		6.3		906		28.2	
121			8.3	502	10.3			907		57.6	
125		9.2		504	6.9			909		21.0	
126	12.7		14.0	505			11.0	910		19.5	
127		6.4	5.6	520		6.1		911		5.9	
130		7.8		527			6.2	919			82.5(M^+)
131	6.9	28.4	22.7	536		90.1		920			32.5
132	5.7	10.3	7.0	537		21.9		921			5.6
139	5.7	8.8		538		70.5		950	12.8		
141	83.2	100.0		539		13.7		952	8.4		
142		7.8		540		17.5		1000	13.2		
143	53.9	83.9		550			44.7	1002	9.1		
144		5.5		551			11.3	1047	8.5		
145	12.9	26.1		586		33.4		1049	5.9		
147	15.6			587		8.0		1050	47.0		
150	13.7			588		28.1		1051	13.7		
155			100.0	589		6.3		1052	35.8		
156			12.8	590		7.2		1053	11.3		
165		7.6		596	5.2			1054	7.6		
167		5.5		600			5.9	1069	86.6^b(M^+)		
169	100.0	16.2	15.6	618	70.2			1070	16.1		
170	9.5			619	14.4			1071	52.8		
171			8.3	620	49.8			1072	11.0		
175	5.2	6.2		621	10.2			1073	9.4		
181		6.5									

[a] Peaks having intensities lower than 5% of the base peak are not reported.

[b] Relative intensities for ions above m/e=1066 were determined by comparative measurement of oscillograph peaks.

The loss of one of the perfluorinated side chains in all three members of the series proceeds from the molecular ion as shown by the metastables, e.g.,

I $1069^{+} \longrightarrow 618^{+} + 451[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$ m*, 357.3

II $905^{+} \longrightarrow 536^{+} + 369[C_7F_{15}]$ m*, 317.5

III $919^{+} \longrightarrow 550^{+} + 369[C_7F_{15}]$ m*, 329.2

In the case of the perfluoroalkylether-substituted triazine (I), stepwise fragmentation of the side chains governed by the oxygen presence is supported by the metastables at m/e 657.6 and 330.6, e.g.,

$784^{+} \longrightarrow 718^{+} + 66[COF_2]$ m*, 657.6

$618^{+} \longrightarrow 452^{+} + 166[CF_3CF_2COF]$ m*, 330.6

The influence of the oxygen is also evident from the relatively high abundance of the 241^{+} ion which is representative of the β-cleavage.

If one compares the breakdown patterns of the 1-diazido- versus 1-dichloro-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazines, the action of the azido-groups mirrors that of the chloro substituents which was not the case in the diphospha-s-triazine series [3]. One might have expected two azido groups present on one phosphorus atom, in the absence of the stabilizing action of the phenyl, to have had more influence on the fragmentation behavior.

The 1-phenyl(chloro)phospha- and 1-phenyl(phenoxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazines (Compounds IV and V, Table 3) exhibited very intense molecular ions, which, as discussed above, was found to be typical of the phospha-s-triazines in general. Actually, in both of these materials, the molecular ion constituted the base peak. This was not the case in the fragmentation of the stearyloxy derivative (Compound VI) where the molecular ion amounted to only 12% of the base peak.

TABLE 3

Ion fragments and intensities relative to base peak of 1-phenyl(chloro)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (IV), 1-phenyl(phenoxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (V), and 1-phenyl(stearyloxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (VI)[a]

m/e	IV	V	VI	m/e	IV	V	VI	m/e	IV	V	VI
41			17.8	111			6.0	534	5.3		
43			34.7	119	9.8			535	8.0		
50	5.8			122	7.2			578	26.3		
51	10.9	5.2		125			7.9	579	9.7		
54			6.8	127	13.1	8.2		580	14.5		
55			25.8	131	10.3		5.1	591		7.4	
56			9.6	138	5.0			636		13.0	
57			29.2	143	15.7	6.5	13.8	686		8.5	
67			8.6	145	8.9			910			5.0
68			8.3	147	8.0			912	26.3	14.8	6.3
69	29.6	10.1	29.7	165			17.3	914	9.9		
70			9.7	167	8.4	6.3	7.1	928	33.6		
71	8.2		14.9	169	8.9			930	32.6		100.0
76	6.3			170		17.8		931	9.2		41.4
77	29.1	26.6	11.5	183	72.6			933			11.9
78	5.7			184	21.6			947	100.0(M^+)		
81			9.2	185	48.2			948	39.0		
82			7.3	186	9.4			949	43.8		
83			15.9	199		9.1		950	19.9		
84			5.5	215		11.2		986		27.5	
85			8.6	233	10.2			987		13.0	
95			5.5	241		35.8		1004		76.5	
96			7.4	242		7.5		1005		100.0(M^+)	
97			13.5	467		5.5		1006		38.5	
100	7.2			517	17.7			1007		9.4	
107	11.3			518	5.4			1181			12.2(M^+)
108	7.7	8.2		533	17.8			1182			5.9

[a] Peaks having intensities lower than 5% of the base peak are not reported.

In all the monophospha-s-triazines synthesized to date, the ion corresponding to fragment A (or rather a loss of the perfluoro- side chain and the nitrile moiety) was either the 100% peak or one of the most intense peaks. Relatively high intensity peaks at m/e 183 and 241 in the mass spectra of chloro- and phenoxy-substituted materials are in agreement with these past results. No peak corresponding to fragment A was found in the breakdown pattern of the stearyloxy derivative (Compound VI). The 100% peak, m/e 930, is formed here from the molecular ion as shown by a metastable at m/e 732.3.

$1181^+ \longrightarrow 930^+ + 251[C_{18}H_{35}]$ m*, 732.3

The 930^+ ion contains most likely the POH_2^+ arrangement which will be expected to lead to ring breakdown and P=O formation. Accordingly, it can be deduced that this compound will exhibit a low thermal stability.

The two metastables at m/e 967.4 and 402.5 in the mass spectrum of the phenoxy-derivative (V) show that the intense ions at m/e 986 and 636 are formed from the molecular ion, i.e.

$1005^+ \longrightarrow 986^+ + 19[F]$ m*, 967.4

$1005^+ \longrightarrow 636^+ + 369[C_7F_{15}]$ m*, 402.5

Surprisingly, no metastable was observed for the formation of 912^+ ion which results from the loss of the phenoxy group.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air-sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian gas chromatograph Model 2700, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

1-Dichlorophospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (I)

Under nitrogen by-pass, to a stirred solution of phosphorus pentachloride (2.15 g, 10.32 mmol) in tetrachloroethane (60 ml) at 0°C, was added a solution of the imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)\text{-}N{=}C(NH_2)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (10.02 g, 10.32 mmol), and triethylamine (3.64 g, 35.97 mmol) in Freon-113 (30 ml), over a period of 1 hr. Stirring at 0°C was continued for an additional 30 min followed by 66 hr at room temperature. The bulk of the solvents were removed in vacuo, followed by addition of Freon-113 (60 ml) to precipitate triethylamine hydrochloride (4.45 g, 100%). Distillation in vacuo of the filtrate afforded 1-dichlorophospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (4.91 g, 44.5% yield), bp 73-74°C/0.001 mm Hg. Anal. calcd. for $C_{18}F_{34}Cl_2N_3O_4P$: C, 20.20; F, 60.37; Cl, 6.63; N, 3.93; O, 5.98; P, 2.89; MW, 1070.04. Found: C, 20.64; F, 57.47; Cl, 6.39; N, 4.32; P, 2.82; MW, 1090.

1-Dichlorophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (II)

Under nitrogen by-pass, a solution of N'-(perfluorooctanoylimidoyl)perfluorooctanoylamidine (14.40 g, 17.84 mmol) and triethylamine (5.45 g, 53.66 mmol) in Freon-113 (65 ml) was added to a stirred solution of phosphorus pentachloride (4.50 g, 21.61 mmol) in tetrachloroethane (80 ml) at 0°C over a period of 2 hr. Stirring at 0°C was continued for an additional hour, followed by 16 hr at room temperature. After addition of Freon-113 (50 ml), the precipitated triethylamine hydrochloride (6.35 g, 86% yield) was filtered off in an inert atmosphere enclosure. After solvent removal, distillation in vacuo gave 1-dichlorophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (9.81 g, 61% yield), mp 30-31°C, bp 88-89°C/0.001 mm Hg. Anal. calcd. for $C_{16}F_{30}N_3Cl_2P$: C, 21.21; F, 62.91; N, 4.64; Cl, 7.83; P, 3.42; MW, 906.02. Found: C, 21.27; F, 62.55; N, 4.79; Cl, 7.59; P, 3.41; MW, 910.

1-Diazidophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (III)

In an inert atmosphere enclosure, to a slurry of lithium azide (0.40 g, 8.17 mmol) in acetonitrile (10 ml) was added a mixture of 1-dichlorophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (2.00 g, 2.21 mmol) and acetonitrile (25 ml). The phosphatriazine was only partially soluble in the acetonitrile. After stirring at room temperature for 65 hr, a white precipitate (0.32 g) of lithium chloride and unreacted lithium azide was filtered off. Following the removal of solvents, the oily residue was redissolved in Freon-113 and purified by passing through a 1.0 x 4.0 cm column of neutral Woelm alumina. Distillation gave 1-diazidophospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine as a colorless liquid which solidified on cooling (1.30 g, 64% yield), bp ∿85-90°C/0.001 mm Hg; mp 35-36°C. Anal. calcd. for $C_{16}F_{30}N_9P$: C, 20.91; F, 62.01; N, 13.71; P, 3.37; MW, 919.16. Found: C, 20.37; F, 62.49; N, 12.99; P, 3.33; MW, 965.

1-Phenyl(chloro)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (IV)

Under nitrogen by-pass, to a stirred solution of tetrachlorophenylphosphorane (9.01 g, 36.05 mmol) in benzene (150 ml) was added at room temperature over a period of 2.5 hr a solution of N'-(perfluorooctanoylimidoyl)perfluorooctanoylamidine (29.10 g, 36.05 mmol) and triethylamine (11.35 g, 112.2 mmol) in Freon-113 (100 ml). Evolution of white fumes and the formation of a white precipitate was observed during the addition. Following the addition, stirring at room temperature was continued for 16 hr. Subsequent filtration, followed by the solid extraction with boiling Freon-113, gave 16.08 g of triethylamine hydrochloride admixed with an unidentified impurity. After solvent removal, vacuum distillation gave a product, bp 137-142°C/0.001 mm Hg (20.5 g, 60% yield), consisting of a mixture of chloro- and fluoro-1-phenyl(halo)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazines in a ratio of 8:1, as determined by combined gas chromatography and mass spectrometry.

1-Phenyl(phenoxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (V)

In an inert atmosphere enclosure, to a stirred slurry of sodium phenolate (prepared from phenol and sodium hydride; 0.35 g, 3.03 mmol) in tetrahydrofuran (40 ml), was added at room temperature a solution of 1-phenyl(halo)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (2.87 g, 3.03 mmol) in tetrahydrofuran (20 ml) over a period of 30 min. After stirring at room temperature for 18 hr, the reaction mixture was filtered from sodium chloride. The residue left after solvent removal, on recrystallization from hot pentane afforded white crystals of 1-phenyl(phenoxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (1.43 g, 47% yield), mp 65-66°C. Anal. calcd. for $C_{28}H_{10}F_{30}N_3OP$: C, 33.45; H, 1.00; F, 56.69; N, 4.18; P, 3.08; MW, 1005.34. Found: C, 34.69; H, 1.24; F, 56.82; N, 4.34; P, 3.05; MW, 1000.

1-Phenyl(stearyloxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (VI)

In an inert atmosphere enclosure, to a stirred slurry of the sodium salt of 1-octadecanol (2.09 g, 7.17 mmol) in tetrahydrofuran (20 ml) at room temperature, was added a solution of 1-phenyl(chloro)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (6.79 g, 7.16 mmol) in tetrahydrofuran (15 ml) over a period of 20 min. After stirring at room temperature for 18 hr, the reaction mixture was filtered from sodium chloride (0.40 g, 96% yield). The solid left on solvent removal was recrystallized from hot acetonitrile to give white crystals, 4.46 g (53% yield), of 1-phenyl(stearyloxy)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, mp 45-46°C. Anal. calcd. for $C_{40}H_{42}F_{30}N_3OP$: C, 40.66; H, 3.58; F, 48.23; P, 2.62; MW, 1181.72. Found: C, 40.30; H, 3.91; F, 48.98; P, 2.70; MW, 1170.

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