Journal of Fluorine Chemistry, *28* (1985) 387–398

Received: October 30, 1984; accepted: November 28, 1984

PHOSPHA-S-TRIAZINES. VIII. CHLORO-SUBSTITUTED DIPHOSPHA-S-TRIAZINES

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

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

SUMMARY

1,3-Bis(phenylchlorophospha)-5-perfluoroalkyl-2,4,6-triazine and the corresponding perfluoroalkylether analogue were synthesized by interaction of equimolar amounts of the respective amidines and imido-diphenyl-diphosphinic acid pentachloride. With additional quantities of amidine, 1,3-bis(phenylperfluoro-n-octanoylamidinophospha)-5-perfluoro-n-heptyl-2,4,6-triazine was obtained. The replacement of the chloro- by azido-groups in 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine proceeded readily. The mass spectral breakdown patterns of the chloro- and the amidino-substituted compounds were directly comparable to those of the bis(diphenylphospha)-s-triazines.

INTRODUCTION

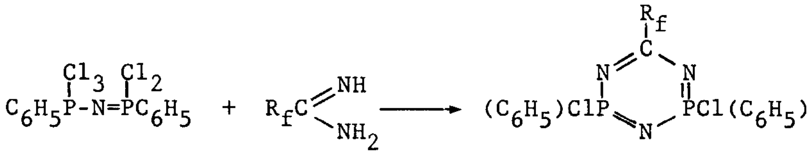
All the diphospha-s-triazines and diphosphatetraazacyclooctatetraenes reported to date [1-3] contained phenyl groups on the ring phosphorus atoms. Even partial replacement of the phenyls by a reactive moiety such as chlorine would permit introduction of other ring substituents and evaluation of their effect on the ring. Having the chloro compounds would also allow reactivity comparisons with those of similarly

0022-1139/85/$3.30

substituted cyclic phosphazenes [4,5]. In addition, difunctional material with the chlorines situated on two different ring atoms would be expected to undergo condensation polymerization with suitable co-monomers. It is believed that in a potential polymer derived from this type of a precursor the presence of the phenyl groups would provide thermal stability, whereas the '*meta*' arrangement and the perfluoroalkylether chain on the carbon ring atom would impart low Tg characteristics.

RESULTS AND DISCUSSION

1,3-Bis(phenylchlorophospha)-s-triazines were obtained by interaction of amidines with imido-diphenyl-diphosphinic acid pentachloride, *i.e.*:



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

II, R_f = *n*-C_7F_{15}

The compounds synthesized are listed in Table 1. The lower yield of the perfluoroalkylether-substituted analogue, as compared to the perfluoro-*n*-heptyl group containing material, is due to the unavoidable presence of imidoylamidine in the amidine [1] resulting in the formation of octatetraene [3] which was separated by distillation. Inasmuch as pure 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine was obtained in high yield (79%), it is obvious that the two chlorines on the ring phosphorus atoms are relatively unreactive towards the amidine. Yet, in the presence of an excess of amidine, the substitution of the two chlorines took place on a one-to-one basis; two isomers were obtained, one melting at 54-56°C and the other at 103-106°C (Table 1). The lower melting compound could be transformed into the higher melting material on treatment with hot benzene. Whether the two isomers can be represented by the arrangements IIIa and

TABLE 1

Dichlorodiphospha-s-triazines and derivatives

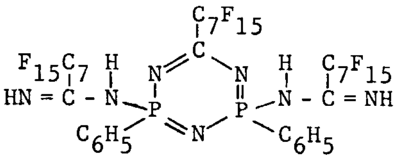
Compound	Mp °C	Bp °C	Yield %	IR bands $(cm^{-1})^a$
$[R_fCN][C_6H_5(Cl)PN]_2^b$ (I) n.c.	-	130-135/0.001 mm Hg	60	1494(vs),1501(sh)
$[n\text{-}C_7F_{15}CN][C_6H_5(Cl)PN]_2$ (II) n.c.	59-62	153-162/0.001 mm Hg	79	1490(vs),1508(sh)
$[n\text{-}C_7F_{15}CN][C_6H_5(Am)PN]_2^c$ (III) n.c.	54-56 103-106	-	72	1510(vs) 1500(vs),1505(sh)
$[n\text{-}C_7F_{15}CN][C_6H_5(N_3)PN]_2$ (IV) n.c.	-	148-150/0.001 mm Hg	71	2140(vs) (ν, N_3) 1497(vs),1503(sh)
$[n\text{-}C_7F_{15}CN][C_6H_5(N{=}P(C_6H_5)_3)PN]_2$ (V) n.c.	59-65	-	71	1514(vs)

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

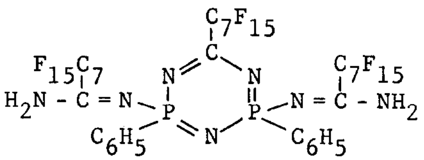
[b] $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-.

[c] Am = $-N{=}C(NH_2)\text{-}\underline{n}\text{-}C_7F_{15}$.

IIIb, or whether one is dealing with *cis-trans* isomerism, which was found to occur in the cyclic phosphazenes [4,5], has not been determined.

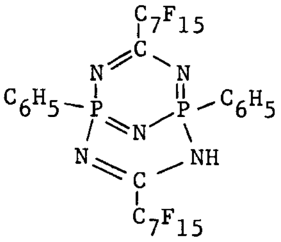


IIIa



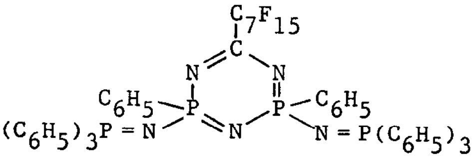
IIIb

When the reaction was carried out using a 1:1 phospha-s-triazine to amidine mole ratio, no bridged, VI, or singly-substituted product was isolated. The only compounds identified by gas chromatography were 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine and the di-amidino derivative.



VI

Replacement of the chlorines in the diphospha-s-triazine Compound II, by azido-groups proceeded readily which was also found to be the case in the corresponding cyclic phosphazenes [6]. 1,3-Bis(phenylazidophospha)-5-perfluoro-*n*-heptyl-2,4,6-triazine was further characterized by the preparation of the triphenylphosphine derivative, compound V.



V

The diazido derivative was surprisingly thermally stable to permit its distillation above 150°C.

TABLE 2

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

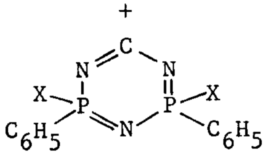
m/e	I	II	III	IV	m/e	I	II	III	IV	m/e	I	II	III	IV
43			100.0		169	11.5		16.2		655			45.7	
44			12.1		170	6.1	11.1			656			12.3	
46			6.8	6.2	171	6.6	9.9			674		20.0		
50		11.3	20.7		178	7.6	16.9			675		7.1		
51	10.9	27.5	10.3	14.3	180	6.0	12.5			676		9.1		
58			9.2		181			13.3		680			80.2	
69	19.7	21.6	78.3	15.3	183	15.1	24.7		17.1	681			28.6	100.0
70			6.6		185	6.6	9.0		24.1	682				34.2
76		6.2	9.2		198		8.9		13.9	683				9.2
77		33.6	18.0	37.7	199				16.1	690		19.4		
78		8.4	9.1	7.5	212				6.4	691		7.5		
81		6.2	7.9		213				31.8	692		13.2		
86			30.2		214				7.6	700			10.2	
91				8.5	223		6.1			704				10.3
93			10.8		225				16.5	709		39.7		
96			31.2		226		6.9			710		17.9(M^+)		
100		7.6	45.6		228	10.9	23.0			711		31.9		
101			10.0		230		9.2			712		14.8		
107	7.8	18.1	8.8	15.6	231			9.5		713		11.7		
108		7.1		17.0	253				6.8	722			6.5	
109				6.4	264		9.1			723				41.5(M^+)
119		8.1	32.5	6.5	270				7.6	724				16.8
122	10.3	26.4	16.2	42.1	285			12.9		730.5			10.2(M^{++})	
123				8.3	304		11.5			756	7.1			
124			10.8		335			6.9		772	9.5			
127			8.3	9.7	340	100.0	100.0			774	6.8			
131		8.1	49.1		341	27.1	14.1			791	27.7(M^+)			
136				8.0	342	70.4	63.0			792	11.2			
138			16.4		343	20.2	6.2			793	23.1			
139			7.0		344	24.1	9.5			794	7.3			
143	12.4	29.3	11.4		354				34.4	795	6.6			
145	6.0	13.5			355				12.0	954			9.4	
146		6.5			361			7.8		974			47.2	
147		7.0		6.6	366			6.1		975			12.6	
150			6.4		424	8.5				1048			8.1	
153		6.5			440	13.5				1049			25.2	
156				7.2	442	10.2				1050			63.0	
157		15.1			533			11.6		1051			24.3	
158		14.3			562				8.0	1052			6.2	
162				12.0	604			11.3		1066			6.9	
164			22.0		608				13.8	1092			(99.9)[b]	
167			8.1	14.6	642				9.4					

---

[a] Peaks having intensities lower than 6% 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 mass spectral breakdown patterns of the diphospha-s-triazines, wherein one of the phenyls on each of the ring phosphorus atoms has been replaced by another group, follow closely those reported for the bis(diphenylphospha)-analogues [1] as evident from the data given in Table 2. For both of the dichloro members of the series, compounds I and II, the fragment A



A

(m/e = 340; X = Cl) was found to constitute the 100% peak. A very weak metastable at m/e 163 for the perfluoro-n-heptyl-substituted material indicates that this ion is formed at least in part from the molecular ion:

709^+ (M) $\longrightarrow 340^+ + 369[C_7F_{15}]$

The relatively high intensity of the molecular ions 709^+ and 791^+ for compounds I and II, respectively, shows that the replacement of two of the phenyl groups by chlorines did not affect the ring stability to electron impact. Strong metastables at m/e 640.7 and 271.8 show that the two processes depicted below are responsible for the 674^+ and 304^+ ions in 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (II).

709^+ (M) $\longrightarrow 674^+ + 35[Cl]$

$340^+ \longrightarrow 304^+ + 36[HCl]$

Only the second process was found to take place in the perfluoroalkylether analogue, compound I, as evidenced by the metastable at m/e 271.8.

In the amidino derivative, compound III, due to instrument limitation, no molecular ion was recorded. The ion 1092^+ corresponds to the fragment A; however, it can also arise by the loss of the C_7F_{15} group from the amidine side chain. The 1092^+ ion can lose both the whole amidine side chain together with an extra hydrogen atom, as shown by the metastable at 423.4, i.e.,

$$1092^+ \longrightarrow 680^+ \quad + \quad 412[C_7F_{15}C(=NH)NH_2]$$

as well as only the amidine function, $C(NH)_2$. The latter path is confirmed by the presence of the metastable at m/e 1009.6, i.e.,

$$1092^+ \longrightarrow 1050^+ \quad + \quad 42[C(NH)_2]$$

The first process points to structure A for the 1092^+ ion, whereas the second breakdown proves initial loss of C_7F_{15} from the amidine side chain followed by subsequent scission next to the phosphorus atom. This would imply that both arrangements are responsible for the 1092^+ ion. The high intensity ion at 974 originates most likely from the subsequent loss of a phenyl group and the amidine side chain (minus hydrogen). The presence of the doubly charged parent ion 730.5^{++} has not been encountered to date in the diphospha-s-triazines, although the octatetraenes have been found to produce this type of an ion [3].

In all the compounds discussed above, including the bis(diphenylphospha)- series, the ion corresponding to the loss of the perfluoroalkyl or perfluoroalkylether group was the most intense peak. This, however, is not true for 1,3-bis(phenylazidophospha)-5-perfluoro-n-heptyl-2,4,6-triazine where the base peak corresponds to a loss of an azido group. This ion, 681^+, is formed from the molecular ion as shown by the metastable at 641.4, i.e.,

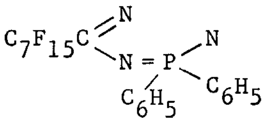
$$723^+ \longrightarrow 681^+ \quad + \quad 42[N_3]$$

Further breakdown of the 681^+ ion leads to the formation of the 653^+ and 608^+ ions shown by the presence of metastables at m/e 626.2 and m/e 542.8, respectively, corresponding to the processes delineated below.

$$681^+ \longrightarrow 653^+ \quad + \quad 28[N_2]$$

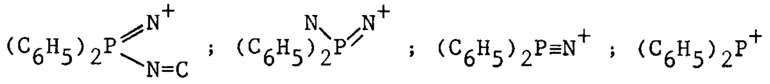
$$681^+ \longrightarrow 608^+ \quad + \quad 73[N_3 + P]$$

This breakdown is unusual for the diphospha-s-triazine system since it must involve a rearrangement followed by ring breakdown. In all the other members of this series, the loss of a perfluorinated group from the ring carbon atom constituted the major cleavage. The ion corresponding to this fragmentation is present also here, m/e 354^+, however, at a relatively low abundance, 34%. One is tempted to speculate that in the ion 608^+ both of the phenyl groups are situated on the remaining phosphorus atom, i.e.,



608^+

The validity of this postulation is based on the presence in the mass spectrum of several prominent ions which most likely do have this arrangement, e.g.,



225^+ (16.5%) ; 213^+ (31.8%); 199^+ (16.1%); 185^+ (24.1%)

It is noteworthy that the 225^+ ion is characteristic of the diphenylmonophospha-s-triazine series [7].

Based on the infrared and mass spectral data, it is apparent that the ring stability is not significantly affected by replacing a phenyl substituent, in bis(diphenylphospha)-triazine, by a chloro, perfluoroalkylamino, or an azido group. Although the latter seems to promote rearrangement in agreement with its known thermal instability.

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 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.

1,3-Bis(phenylchlorophospha)-5-perfluoroalkylether-2,4,6-triazine (I)

In an inert atmosphere enclosure to imido-diphenyldiphosphinic acid pentachloride (8.08 g, 19.80 mmol (prepared following the procedure of Fluck and Reinisch [8] with the exception that purification was effected by crystallization from cold chloroform by addition of benzene) in tetrachloroethane (40 ml) was slowly added at room temperature a solution of perfluoroalkyletheramidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$ (9.80 g, 19.80 mmol), and triethylamine (6.02 g, 59.50 mmol) in Freon-113 (25 ml). After stirring at room temperature for 65 hr, a white precipitate (7.60 g, 93%) of triethylamine hydrochloride was isolated by filtration. Removal of solvents in vacuo, initially at room temperature, then at 50°C, gave a pale yellow viscous liquid which was redissolved in Freon-113 and purified by filtration through a 1.5 x 4.0 cm column of neutral Woelm alumina. After solvent removal, distillation gave 1,3-bis(phenylchlorophospha)-5-perfluoroalkylether-2,4,6-triazine (9.41 g, 60% yield), bp 130-135°C/0.001 mm Hg. Anal. calcd. for $C_{21}H_{10}F_{17}Cl_2N_3O_2P_2$: C, 31.84; H, 1.27; F, 40.77; Cl, 8.95; N, 5.30; P, 7.82; MW, 792.16. Found: C, 31.90; H, 1.51; F, 41.06; Cl, 8.72; N, 5.21; P, 7.83; MW, 810.

1,3-Bis(phenylchlorophospha)-5-perfluoro-*n*-heptyl-2,4,6-triazine (II)

In an inert atmosphere enclosure to imido-diphenyldiphosphinic acid pentachloride (14.83 g, 36.40 mmol) in tetrachloroethane (50 ml) was slowly added at room temperature a solution of perfluorooctanoylamidine (15.00 g, 36.40 mmol) and triethylamine (11.05 g, 109.2 mmol) in Freon-113 (120 ml). After stirring at room temperature for 71 hr, a precipitate (13.64 g of triethylamine hydrochloride) was filtered off. Subsequently, the solvents were removed *in vacuo*, initially at room temperature, then at 40°C. The residue was redissolved in Freon-113 and an additional 0.70 g of triethylamine hydrochloride precipitated, bringing the total to 14.34 g (91%). The filtrate was then passed through a 1.5 x 3 cm column of neutral Woelm alumina and distilled giving 1,3-bis(phenylchlorophospha)-5-perfluoro-*n*-heptyl-2,4,6-triazine (20.53 g, 79% yield), bp 153-162°C/0.001 mm Hg; mp 59-62°C. Anal. calcd. for $C_{20}H_{10}F_{15}N_3Cl_2P_2$: C, 33.83; H, 1.42; F, 40.13; N, 5.92; Cl, 9.99; P, 8.72; MW, 710.15. Found: C, 33.84; H, 1.66; F, 39.89; N, 5.93; Cl, 9.70; P, 8.74; MW, 747.

1,3-Bis(phenylperfluoro-n-octanoylamidinophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (III)

To a stirred solution of 1,3-bis(phenylchlorophospha)-5-perfluoro-*n*-heptyl-2,4,6-triazine (1.0 g, 1.41 mmol) in Freon-113 (10 ml) at 0°C under nitrogen by-pass was added a solution of perfluoro-*n*-octanoylamidine (1.16 g, 2.81 mmol) and triethylamine (0.29 g, 2.87 mmol) in Freon-113 (40 ml), over a period of 1 hr. The reaction was allowed to warm to room temperature and then stirred for 16 hr. Filtration, in an inert atmosphere enclosure, afforded triethylamine hydrochloride (0.30 g, 77%). Removal of solvents from the colorless filtrate *in vacuo*, followed by extraction with Freon-113 (20 ml) and filtration, resulted in the separation of additional triethylamine hydrochloride (90 mg, 23%). Removal of Freon-113 from the colorless filtrate gave a gum-like solid which, after repeated recrystallizations from Freon-113/hexane, afforded a white solid (1.48 g, 72% yield), mp 54-56°C. Calcd. for $C_{36}H_{14}F_{45}N_7P_2$: MW, 1461.43. Found: MW, 1450. A portion of the above product was recrystallized from benzene to give white crystalline 1,3-bis(phenylperfluoro-n-octanoylamidinophospha)-5-perfluoro-n-heptyl-2,4,6-triazine, mp 103-106°C. Anal. calcd. for $C_{36}H_{14}F_{45}N_7P_2$: C, 29.59; H, 0.97; F, 58.50; N, 6.71; P, 4.24; MW, 1461.43. Found: C, 29.68; H, 1.18; F, 57.90; N, 6.62; P, 4.24; MW, 1490.

1,3-Bis(phenylazidophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (IV)

In an inert atmosphere enclosure, to a slurry of lithium azide (1.00 g, 20.43 mmol) in acetonitrile (10 ml) was added a solution of 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (5.00 g, 7.04 mmol) in acetonitrile (40 ml). After stirring at room temperature for 40 hr, the reaction mixture was filtered to afford a white precipitate of lithium chloride and excess lithium azide, and a pale yellow filtrate which gave a moderately viscous yellow liquid on removal of solvents in vacuo. The oil was redissolved in Freon-113 and was passed through a 1.0 x 5.0 cm column of neutral Woelm alumina. Distillation gave 1,3-bis(azidophenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine as a colorless liquid (3.61 g, 71% yield), bp 148-150°C/0.001 mm Hg. Anal. calcd. for $C_{20}H_{10}F_{15}N_9P_2$: C, 33.21; H, 1.39; F, 39.40; N, 17.43; P, 8.56; MW, 723.28. Found: C, 33.32; H, 1.61; F, 40.07; N, 17.02; P, 8.56; MW, 760.

1,3-Bis(phenyltriphenylphosphineiminophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (V)

In an inert atmosphere enclosure, to a solution of 1,3-bis(phenylazidophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (1.25 g, 1.73 mmol) in benzene (10 ml) was added a solution of freshly sublimed triphenylphosphine (1.10 g, 4.19 mmol) in benzene (5 ml). After stirring at room temperature for 20 hr, the mixture was heated at reflux temperature under nitrogen by-pass for 45 hr. Solvents were removed in vacuo at room temperature; this was followed by heating at 70-90°C for 10 hr to remove, by sublimation, the excess triphenylphosphine. The solid product was redissolved in a minimum of Freon-113 and passed through a 1.0 x 4.0 cm column of neutral Woelm alumina. Removal of volatiles in vacuo afforded 1,3-bis(phenyltriphenylphosphineiminophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (1.46 g, 71% yield) as a white solid, mp 59-65°C. Anal. calcd. for $C_{56}H_{40}F_{15}N_5P_4$: C, 56.44; H, 3.38; F, 23.91; N, 5.88; P, 10.40; MW, 1191.84. Found: C, 56.57; H, 3.61; F, 22.83; N, 5.72; P, 9.74; MW, 1210.

ACKNOWLEDGEMENTS

Research was sponsored by the Air Force Office of Scientifi Research (AFSC), United States Air Force, under Contract F49620-82-C-0021. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon. The authors are indebted to Dr. A. J. Matuszko for helpful discussions and suggestions.

REFERENCES

1 R. H. Kratzer, K. J. L. Paciorek, J. Kaufman, T. I. Ito, and J. H. Nakahara, J. Fluorine Chem., 13, 189 (1979).
2 K. J. L. Paciorek, T. I. Ito, and R. H. Kratzer, J. Fluorine Chem., 15, 327 (1980).
3 K. J. L. Paciorek, T. I. Ito, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., 16, 431 (1980).
4 R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, Chem. Rev., 62, 247 (1962).
5 H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, 1972.
6 C. M. Sharts, A. J. Bilbo, and D. R. Gentry, Inorg. Chem., 5, 2140 (1966).
7 K. J. L. Paciorek, J. H. Nakahara, and R. H. Kratzer, J. Fluorine Chem., 11, 537 (1978).
8 E. Fluck and R. M. Reinisch, Ber., 96, 3085 (1963).