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PHOSPHA-S-TRIAZINES. VII. PHENYL-BRIDGED PHOSPHA-S-TRIAZINES

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SUMMARY

1,4-Bis(phenyltrichlorophosphino)benzene was synthesized by a 4-step process in an overall 58% yield. Interaction of the bis(trichlorophosphorane) with the appropriate imidoylamidines afforded the novel 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino]benzene and 1,4-bis[1-phenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazino]benzene. Electron impact fragmentation patterns of these compounds could be correlated with those of the single ring analogues. The thermal and thermal oxidative stability of the phenyl-bridged dumbbells was lower than that of the corresponding monomeric mono- and diphospha-s-triazines. These materials were found to be effective in arresting the degradation of perfluoroalkylether fluids in oxidizing atmospheres in the presence of metals.

INTRODUCTION

Poly(monophospha-s-triazines) prepared to date were linked by perfluoroalkyl and perfluoroalkylether groups [1,2]. The thermal and thermal oxidative stabilities of the dumbbell materials were found to correspond closely to those observed for the analogously substituted monocyclic

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compounds [2,3]. In the phenyl-bridged bicyclics conjugation can exist between the two rings via the bridging group. One would thus expect this bonding to impart increased thermal stability and to be reflected in the spectral characteristics of these systems. These compounds have not been prepared to date due to the unavailability of the required bis(trichlorophosphoranes).

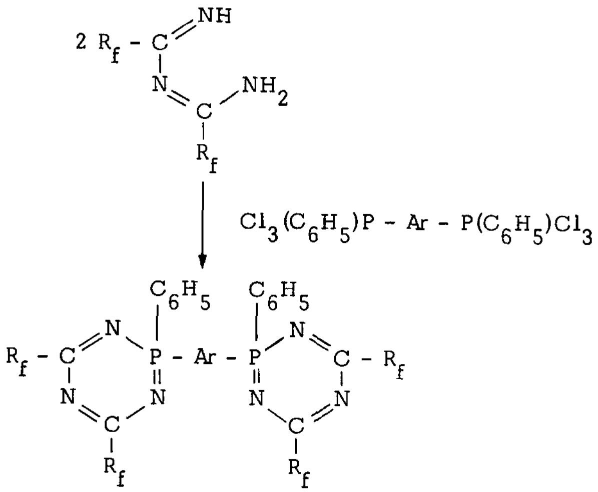
RESULTS AND DISCUSSION

The major aspect of the concept to form the aryl-linked poly(monophospha-s-triazines) was the feasibility of the synthesis of bis(trichlorophosphorane), $Cl_3(C_6H_5)P-C_6H_4-P(C_6H_5)Cl_3$. In the early sixties, Evleth et al. [4] were able to prepare $ClCH_3P-C_6H_4-PCH_3Cl$; based on this work, the sequence leading to the required bis(trichlorophosphorane) was developed, i.e.,

$$\begin{tikzcd}
(C_6H_5)PCl_2 \arrow[r, "(CH_3)_2NH"] & Cl(C_6H_5)PN(CH_3)_2 \arrow[d, "p\text{-}Li\text{-}C_6H_4\text{-}Li"] \\
 & (CH_3)_2N(C_6H_5)P - C_6H_4 - P(C_6H_5)N(CH_3)_2 \arrow[d, "HCl"] \\
 & Cl(C_6H_5)P - C_6H_4 - P(C_6H_5)Cl \arrow[d, "Cl_2"] \\
 & Cl_3(C_6H_5)P - C_6H_4 - P(C_6H_5)Cl_3
\end{tikzcd}$$

Phenyldichlorophosphine is available commercially, dimethylaminophenylchlorophosphine was prepared by Evleth et al. [4], the next three compounds have not been described in the literature. In the current study, dimethylaminophenylchlorophosphine was obtained in 93% yield; the subsequent intermediate was afforded in an essentially quantitative yield. The next two steps proceeded in 97% and 64% yields, respectively, resulting in an overall process yield from phenyldichlorophosphine to the bis(trichlorophosphorane) of 58%.

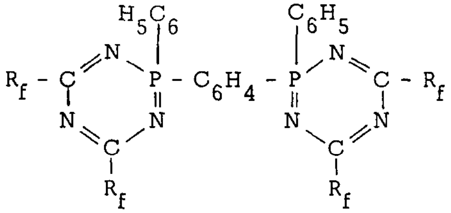
Interaction of the bis(trichlorophosphorane) with imidoylamidines gave the phenyl-bridged dumbbell monophospha-s-triazines.



The properties of the perfluoroalkyl and perfluoroalkylether substituted representative members of the series are given in Table 1.

TABLE 1

Phenyl-bridged dumbbell monophospha-s-triazines



R_f	Yield %	MW	mp ^oC
$CF_3(CF_2)_6$-	30	1900	125-126.5
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-	65	2228	liquid

TABLE 2

Ion fragments and intensities relative to base peak of 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino]benzene[a]

m/e	% of base peak	m/e	% of base peak	m/e	% of base peak
31	6.5	93	4.4	219	3.9
32	12.5	95	5.0	228	3.2
39	4.6	96	4.0	247	4.3
41	10.0	97	8.1	259	11.8
43	10.2	100	16.0	261	3.6
44	32.2	102	4.7	278	5.0
50	10.6	107	3.9	281	3.0
51	8.9	109	3.1	303	16.2
52	9.2	113	3.6	304	3.3
53	3.0	116	3.2	305	19.6
55	9.8	119	32.0	309	3.0
56	5.3	127	3.3	447	5.2
57	9.4	128	5.7	497	97.4
67	5.8	131	33.4	498	23.5
69	100.0	132	4.5	512	5.6
70	6.3	147	17.4	547	3.1
71	7.2	149	10.3	797	25.2
75	10.8	150	4.2	798	5.1
76	9.1	152	5.8	816	19.2
77	14.1	159	6.2	817	4.8
78	33.1	167	3.1	1023	2.1
79	3.4	169	18.3	1050	2.0
81	8.5	178	10.9	1066	3.7
82	6.6	181	8.0	1067	7.8
83	5.9	183	3.3	1068	5.8
85	3.9	197	24.2	1069	7.6
87	3.9	209	9.4		

[a] Peaks having intensities less than 3% of the base peak are not reported.

TABLE 3

Ion fragments and intensities relative to base peak of 1,4-bis[1-phenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazino]benzene[a,b]

m/e	% of base peak	m/e	% of base peak
31	22.4	107	5.6
32	3.3	119	56.9
41	6.3	126	12.3
43	10.1	127	5.7
44	3.6	131	4.7
47	24.9	147	10.2
50	24.1	149	4.5
51	9.4	150	10.5
55	8.3	151	3.9
56	3.3	165	5.3
57	10.3	167	3.6
60	3.1	169	48.2
66	11.0	170	3.3
67	3.9	183	4.2
69	100.0	186	18.5
70	7.3	187	4.4
71	6.8	211	3.6
76	7.1	236	7.2
77	6.9	243	3.3
78	9.0	259	3.9
81	9.4	281	3.1
82	4.3	303	5.8
83	4.9	305	6.2
85	4.3	351	3.3
93	3.4	650	3.8
95	4.7	968	1.4
96	9.1	1114	3.1
97	22.9	1135	1.6
100	24.4	1136	0.6
101	4.0	1241	0.5

[a] The perfluoroalkylether group, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

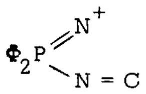
[b] Peaks having intensities less than 3% of the base peak below m/e, 900 are not reported.

In good agreement with previous findings [5,6], the material where R_f = n-C_7F_{15} was a solid, whereas the compound where $R_f = C_3F_7OCF(CF_3)$-$CF_2OCF(CF_3)$ was a liquid at room temperature. Phenyl-bridging, apparently, does not effect the ring bonding since the infrared spectra of the dumbbell compounds show the characteristic ring band at the same position, 1580 cm^{-1}, as that registered by the monocyclic monophospha-s-triazines [5]. The mass spectra of 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino]benzene and the perfluoroalkylether analogue are given in Tables 2 and 3, respectively. Due to instrument limitations, the parent ions, if any, could not be recorded.

The breakdown pattern of 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino]benzene follows essentially the path found to be operative in the single ring monophospha-s-triazine series [7], i.e.,

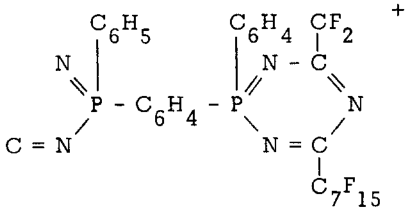
$$816^+ \longrightarrow M - 369(C_7F_{15}) - 395(C_7F_{15}CN) - 319(C_6F_{13}) - 1(H)$$

The major fragment in the monophospha-s-triazine series was:



225^+

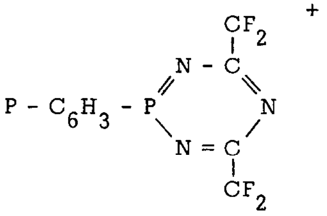
Accordingly, it would seem reasonable that the 816^+ ion has the structure given below wherein one of the rings is open, i.e.,



Again, in analogy with the 225^+ ion, it is believed that the hydrogen loss occurs on the phenyl group attached to the intact ring. The other prominent ions, 797^+ and 497^+, most likely originate from the 816^+ ion, i.e.,

$$797^+ \longrightarrow 816^+ - 19(F)$$
$$497^+ \longrightarrow 816^+ - 319(C_6F_{13})$$

It is quite probable that the 305^+ and 197^+ ions are then derived from the 497^+ ion. The possible arrangement for the 305^+ ion is given below:

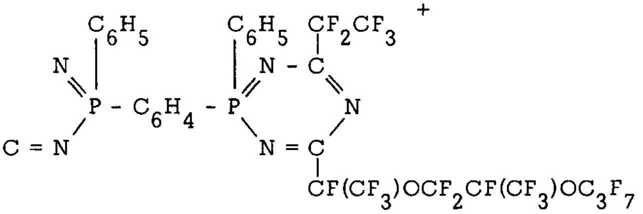


The loss of the fragment C_6H_3-P would then afford the 197^+ ion.

The mass spectrum of 1,4-bis[1-phenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazino]benzene (Table 3) does not contain many prominent ions in the high mass region. As noted, due to the instrument limitation, the parent peak, if any, could not be recorded. The ion at m/e = 1114 is the doubly charged parent ion, 2228^{++}. The 968^+ ion, in analogy with the simple monophospha-s-triazines and 1,4-bis[1-phenylphospha-3,5-bis-(perfluoro-n-heptyl)-2,4,6-triazino]benzene, is most likely derived by the process:

$$968^+ \longrightarrow M - 477[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN] - 451[C_3F_7OCF(CF_3)CF_2OCF(CF_3)] - 332[C_3F_7OCF(CF_3)COF]$$

giving the arrangement:



Contrary to the expectations, the thermal and thermal oxidative stabilities of the phenyl-bridged materials, as evident from the data given in Table 4, are significantly lower than those of the analogously-substituted monophospha-s-triazines [3]. This is especially evident in the case of the perfluoro-n-heptyl substituted compound (Test Nos. 7 and 8). In particular, the high extent of degradation of 1,4-bis[1-phenylphospha-3,5-bis-(perfluoro-n-heptyl)-2,4,6-triazino]benzene at 316°C in nitrogen is most

TABLE 4

Degradations of phenyl-bridged dumbbell monophospha-s-triazines

					Starting materials		Oxygen consumed		Volatile products				
									Total formed		Type		
Test No.	Material[a]	Duration hr	Temp °C	Atm	Used mg	Recov %[b]	mg	%[c]	mg	%[b]	CO %[b]	R_fCN %[b]	C_6H_6 %[b]
2	$Ar[(R_fCN)_2(\Phi PN)]_2$	24	235	Air	305.3	94	0.14	2.1	4.1	1.3	0.00	1.2	0.00
1	$Ar[(R_fCN)_2(\Phi PN)]_2$	24	316	N_2	302.5	74	-	-	19.6	6.5	0.02	5.6	0.01
6	$Ar[(R_fCN)_2(\Phi PN)]_2$	24	316	Air	344.9	75	1.33	21.0	30.3	8.8	0.02	6.5	0.02
3	$Ar[(R_fCN)_2(\Phi PN)]_2$	18	316	O_2	335.2	82	1.07	3.6	21.6	6.4	0.04	4.8	0.00
7	$Ar[(R_f'CN)_2(\Phi PN)]_2$	24	235	Air	313.2	85	0.69	10.9	10.0	3.2	0.00	3.0	?
8	$Ar[(R_f'CN)_2(\Phi PN)]_2$	24	316	N_2	400.2	14	-	-	135.4	33.8	0.00	31.4	?

[a] $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$; $R_f' = n\text{-}C_7F_{15}$; $Ar = C_6H_4$; $\Phi = C_6H_5$. [b] Weight percent of starting material. [c] Percent of oxygen available.

surprising. Inasmuch as the major volatile product of the degradation was perfluoro-n-octanonitrile, it would appear that dissociation was the predominant process. Whether this reaction was followed by phosphazene ring formation has not been established.

The phenyl-bridged materials did exhibit antioxidant and anticorrosive properties when used as additives in perfluoroalkylether fluids as evident from the data given in Table 5.

It should be noted that in both of the tests involving the additive, the pe fluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, constituted 75% of the products formed. Based on these data, the suppression of the fluid degradation is even more pronounced than that indicated by direct product weight comparisons between the experiments where the additive was present and those performed in its absence.

TABLE 5

Effect of 1,4-bis[1-phenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazino]benzene on perfluoroalkylether fluids in the presence of M-50 alloy at elevated temperatures in oxygen over a 24 hr period[a]

Fluid	g	Additive	Temp °C	Oxygen consumed %[b]	Oxygen consumed mg/g[c]	Products formed mg	Products formed mg/g[d]
Krytox[f]	12.13	None	316	24.6	5.8	576.7	47.5
Krytox[f]	4.83	1%[e] $Ar(C_2PN_3)_2$	316	0.0	0.0	6.3	1.3
Fomblin Z[g]	3.34	None	288	13.6	12.1	1117.1	421.6
Fomblin Z[g]	4.14	1% $Ar(C_2PN_3)_2$	288	0.0	0.0	7.9	1.9

[a] The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the products were collected and measured. [b] Percent of oxygen available. [c] Oxygen consumed in mg/g fluid employed. [d] Products formed in mg/g of fluid employed. [e] The percent is weight percent of additive per weight of fluid. [f] Du Pont trade name, $F-[CF(CF_3)-CF_2O]_n-C_2F_5$ fluid. [g] Montedison trade name, linear perfluoroalkylethers.

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 Du Pont 21-491B double focusing mass spectrometer attached to a Varian gas chromatograph Model 2700, equipped with a flame ionization detector, and a Du Pont 21-094 data acquisition and processing system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Stability investigations

The degradations were performed in sealed ampoules of ~ 50 ml volume over a period of 24 hr at the specified temperatures. The media studied were nitrogen and air; the gas pressures used were ~ 350 mm Hg at room temperature. The samples were introduced into the ampoules as Freon-113 solutions. The solvent was removed in vacuo and the sample dried at 50°C or above. At the conclusion of the experiment, the ampoules were cooled in liquid nitrogen and opened into the vacuum system. The liquid nitrogen noncondensibles were measured and analyzed by gas chromatography. The liquid nitrogen condensibles were fractionated from a warming trap through -23--78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed, and analyzed by infrared spectroscopy, batch mass spectrometry, and GC-MS. The involatile residues were handled in an inert atmosphere enclosure to avoid any interferences from subsequent hydrolysis or oxidations in the case of purely thermal degradations. The residue itself was weighed, analyzed by infrared spectral analysis and subjected to gas chromatography. The starting material recovery is based on the latter determination.

Preparation of dimethylaminophenylchlorophosphine, $(CH_3)_2NP(Cl)C_6H_5$

Following the procedure of Evleth et al. [4], dimethylamine (26.46 g, 0.59 mol) in ether (100 ml) was added dropwise over a period of 25 min at $0^{\circ}C$ to phenyldichlorophosphine (50.92 g, 0.28 mol) in ether (200 ml). The resulting mixture was stirred an additional 1.5 hr then filtered in an inert atmosphere enclosure. The residual oil that remained following solvent removal was distilled under reduced pressure to give the desired product, dimethylaminophenylchlorophosphine (49.54 g, 92.8%), bp $72-76^{\circ}C/1.8-1.5$ mm Hg ($78^{\circ}C/2$ mm Hg [4]).

Preparation of 1,4-bis(dimethylaminophenylphosphino)benzene, $1,4\text{-}C_6H_4\text{-}[(CH_3)_2NPC_6H_5]_2$

The procedure followed was essentially that described by Baldwin and Cheng [8]. Thus, to 1,4-dibromobenzene (30.47 g, 0.13 mol) in ether (250 ml) at $0-5^{\circ}C$ was introduced 0.51 mol of n-butyllithium (223.0 ml of 2.3M soln in hexane; diluted with additional hexane to a total of 308 ml) over a period of 2.1 hr. This was followed by refluxing for 3 hr during which period a solid appeared. Subsequently, the mixture was cooled in an ice bath and a solution of dimethylaminophenylchlorophosphine (47.98 g, 0.26 mol) in ether (50 ml) was added over a period of 1.3 hr. After stirring overnight at ambient temperature and a 2-hr reflux, the cool mixture was filtered in an inert atmosphere enclosure. Removal of solvent yielded a semi-solid product, 48.50 g (99.7%). A portion of this material was purified by precipitation from tetrahydrofuran-n-heptane: mp $87.5-89^{\circ}C$. Anal. Calcd. for $C_{22}H_{26}N_2P_2$: C, 69.46; H, 6.89; N, 7.36; P, 16.28. Found: C, 69.38; H, 7.19; N, 7.46; P, 15.86.

Preparation of 1,4-bis(phenylchlorophosphino)benzene, 1,4-$C_6H_4(C_6H_5PCl)_2$

The procedure followed was essentially that of Evleth et al. [4]. Thus, to 1,4-bis(dimethylaminophenylphosphino)benzene (28.82 g, 75.76 mmol) in ether (400 ml) at -70°C was added hydrogen chloride gas (21.07 g, 577.88 mmol). The resulting mixture was allowed to warm to ambient temperature, then filtered in an inert atmosphere enclosure. The solvent was removed in vacuo and the residue purified by precipitation from benzene by n-heptane. Filtration of the mixture followed by solvent removal under reduced pressure yielded 1,4-bis(phenylchlorophosphino)benzene as a green-yellow oil (16.85 g, 66.7%).

Preparation of 1,4-bis(phenyltrichlorophosphino)benzene, 1,4-$C_6H_4(C_6H_5$-$PCl_3)_2$

Chlorine gas (22.09 g, 311.52 mmol) was added to a stirred solution of 1,4-bis(phenylchlorophosphino)benzene (19.21 g, 52.90 mmol) in carbon tetrachloride (130 ml) at -18 to -23°C over a period of 50 min. A solid formed during the addition. After warming to ambient temperature, the solvent was removed in vacuo. The tan insoluble solid obtained after treatment of the residue with hot benzene (4 x 250 ml) was dried in vacuo giving 17.06 g (63.9%) of 1,4-bis(phenyltrichlorophosphino)benzene: mp 204-205.5 °C. Anal. Calcd. for $C_{18}H_{14}Cl_6P_2$: C, 42.81; H, 2.80; Cl, 42.12; P, 12.27. Found: C, 42.94; H, 2.99; Cl, 42.72.

Preparation of 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino]benzene

A solution of the imidoylamidine n-$C_7F_{15}C(=NH)N=C(NH_2)$n-C_7F_{15} (5.00 g, 6.19 mmol) and triethylamine (2.78 ml, 19.96 mmol) in Freon-113 (20 ml) was added over a period of 1.1 hr to a mixture of 1,4-bis(phenyltrichlorophosphino)benzene (1.56 g, 3.09 mmol) in benzene (15 ml) kept at 50°C. The mixture was stirred and heated at 50°C for 96 hr. After removal of solvents under reduced pressure, the residue was treated with Freon-113 (5 x 20 ml); each portion was filtered through a 1.5 x 3 cm column of neutral Woelm alumina. Subsequently, the solvent was removed in vacuo and the residue dried at 88°C for 4 hr to give a white solid (1.75 g, 29.7%); mp 125-126.5°C. Anal. Calcd. for $C_{50}H_{14}F_{60}N_6P_2$: C, 31.60; H, 0.74; F, 59.98; N, 4.42; P, 3.26; MW, 1900.53. Found: C, 31.14; H, 0.94; F, 60.84; P, 3.26; MW, 1950.

Preparation of 1,4-bis[1-phenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazino]benzene

A solution of the imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)N=C(NH_2)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (4.00 g, 4.12 mmol) and triethylamine (1.85 ml, 13.30 mmol) in Freon-113 (12 ml) was added over a period of 55 min to a mixture of 1,4-bis(phenyltrichlorophosphino)benzene (1.04 g, 2.06 mmol) in 1,1,2,2-tetrachloroethane kept at 50°C. The mixture was stirred and heated at 50°C for 72 hr. After removal of the solvents, the residue was treated with Freon-113 (6 x 20 ml); each portion was filtered through a 1.5 x 3 cm column of neutral Woelm alumina. Subsequently, the solvent was removed under reduced pressure and the viscous residue dried at 135°C for 5.5 hr to afford a slightly opaque liquid (2.97 g, 64.7%). Anal. Calcd. for $C_{54}H_{14}F_{68}N_6O_8P_2$: C, 29.10; H, 0.63; F, 57.97; N, 3.77; O, 5.74; P, 2.78; MW, 2228.55. Found: C, 29.10; H, 0.81; F, 58.93; N, 4.16; P, 2.80; MW, 2250.

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