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PHOSPHA-s-TRIAZINES. I. SYNTHESES AND PROPERTIES OF MONO(DIARYLPHOSPHA)-s-TRIAZINES[+]

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SUMMARY

A series of monophospha-s-triazines, namely 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis[C_3F_7-[$OCF(CF_3)CF_2]_xOCF(CF_3)$]-2,4,6-triazine ($x = 1$ and 2), and the pentafluorophenyl-substituted analogues were prepared, in yields of 50-75%, from the respective imidoylamidines and trichlorophosphoranes. The physical properties of the corresponding phenyl and pentafluorophenyl monophospha-s-triazines did not differ significantly; the perfluoroalkyl-substituted materials were low melting solids whereas the perfluoroalkylether-containing compositions were liquids. Preliminary degradative studies showed these compounds to be thermally and oxidatively stable. The 1-diphenylphospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine was found to be an effective anti-corrosion additive for perfluoroalkylether type fluids.

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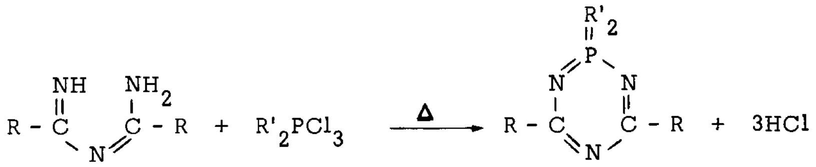
INTRODUCTION

Symmetrical triazines [1] and their triphospha analogues, the trimeric phosphazenes [2-5], have been studied extensively. A few examples of the intermediate diphospha-s-triazines have only relatively recently been reported [6], whereas monophospha-s-triazines apparently are so far unknown. Aside from the close structural similarities s-triazines and the trimeric phosphazenes have several other features in common. These include both methods of formation as well as physical properties. For example, the fully phenylated derivatives, triphenyl-s-triazine and diphenylphosphazene trimer, can be produced by very similar types of processes, for example the trimerization of benzonitrile [7] and the "trimerization" of diphenylphosphinous azide [8], respectively. Both compounds are known to exhibit high thermal [9] and oxidative [10] stabilities and practically identical melting points [1,11] (233 and 234°C, respectively). Interestingly, pentaphenyldiphospha-s-triazine melts in the same temperature region (239°C) [6], which may be taken as evidence that the replacement of carbon in the s-triazine ring system by phosphorus does not alter to any significant degree the bonding characteristics of this heterocyclic ring system.

Perfluoroalkyl- and perfluoroalkylether-substituted s-triazines have been shown to possess excellent thermal and thermal oxidative characteristics [12] and the latter, due to their low pour points and low vapor pressures at elevated temperatures, have been identified as promising candidates for high temperature fluids applications [13]. On the other hand, several phosphorus containing compositions are known to increase the lubricity of fluids and some have been found to reduce corrosion of metals exposed at elevated temperatures to perfluorinated fluids. Based on these observations a suitably substituted monophospha-s-triazine thus may combine the desirable stability characteristics of the triazine ring system with the lubricating and corrosion inhibiting properties of the phosphorus component within one and the same material.

RESULTS AND DISCUSSION

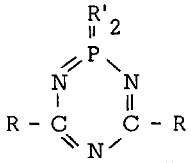
Douglas and Herring [14] described the synthesis of phosphazene trimers utilizing the reaction of an imino-bis(aminophosphorane) with a trihalophosphorane. It was of interest to determine whether this process can be extended to the synthesis of phospha-triazine ring systems. Although non-fluorinated imidoylamidines, as analogues to the above imino-bis(aminophosphoranes), do not appear to exist, perfluoroalkyl- and perfluoroalkylether-substituted imidoylamidines are well known and readily prepared [15]. The interaction of these materials with trichlorophosphoranes, using the general reaction given below



afforded good yields of the novel monophospha-s-triazines. The compounds prepared to date are listed in Table I.

TABLE I

Monophospha-s-triazines

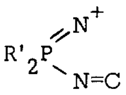


R	R'	Yield %	MW	m.p. °C	b.p. °C
$CF_3(CF_2)_6$, (I)	C_6H_5	61	989	73-74.5	380
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$, (II)	C_6H_5	73	1153	-	355
$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)$, (III)	C_6H_5	52	1485	-	385
$CF_3(CF_2)_6$, (IV)	C_6F_5	66	1169	74-75	345
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$, (V)	C_6F_5	74	1333	-	325

The perfluoroheptyl substituted monophospha-s-triazines were low melting solids, whereas the perfluoroalkylether group containing analogues were liquids. This is unexpected if one considers that the cyclic diphenylphosphazene trimer is a high melting solid [2]. As can be seen the physical characteristics of the phenyl and pentafluorophenyl derivatives are almost identical. All the compounds could be analyzed readily by gas chromatography which attests to their relative volatility and stability.

The infrared spectra of perfluoroalkyl and perfluoroalkylether-s-triazines show a characteristic band at 6.42 μ. It is noteworthy that each of the monophospha-s-triazines synthesized, Compounds I-V, exhibited a strong absorption at 6.3 μ, regardless of the substituents. Thus it must be concluded that this band is due to the monophospha-s-triazine ring arrangement.

The mass spectral breakdown patterns of the monophospha-s-triazines differ from those of the s-triazines and show characteristic ions specific to this ring system; these will be discussed in detail elsewhere [16]. However, it should be noted that each of the compounds synthesized gave as the base peak the ion



R' = C_6H_5; m/e = 225

R' = C_6F_5; m/e = 405

Preliminary thermal and thermal oxidative investigations performed on Compound II showed the monophospha-s-triazines to exhibit good stabilities as shown by the recovery of 96.5 and 97% of the unchanged starting material, after 24 hr heat treatment at 325° in nitrogen and 24 hr at 235°C in air, respectively.

The 1-diphenylphospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine, Compound II, was found to effectively inhibit oxidation of Krytox fluids (DuPont trade name, $F-[CF(CF_3)CF_2O]_n-C_2F_5$) and to prevent corrosion of M-50 ball bearing alloy by these fluids. A 1% by weight solution of this monophospha-s-triazine in Krytox decreased oxygen consumption and volatile products formation by a factor of over 60 during a 24 hr exposure to oxygen at 600°F as compared to an identical treatment of the fluid in the absence of the additive. In addition, the M-50 coupon surface in the presence of the additive appeared unchanged whereas in the absence of any additive, under otherwise identical conditions, the surface became covered with deeply colored irregular deposits. These data are summarized below in Table II.

TABLE II

Degradation of Krytox fluid in the presence of M-50 alloy coupon at 600°F in oxygen for 24 hr [a]

Fluid Used g	Additive	Oxygen Consumed Total mg	%[b]	mg/g[c]	Total Products Formed mg	mg/g[d]
12.13	none	70.8	24.6	5.84	576.7	47.54
8.59	1%[e] Compound II	1.0	0.35	0.12	6.1	0.71

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 oxygen was measured and the products were collected and measured.

b) Percent of oxygen available.

c) Oxygen consumed in mg/g Krytox employed.

d) Products formed in mg/g Krytox employed.

e) The percent is weight percent of additive per weight of Krytox fluid.

CONCLUSIONS

The monophospha-s-triazine arrangement as based on its mode of synthesis and general properties would appear to combine the characteristics of both the parent ring systems namely fluorinated s-triazines and the phosphazene trimer. On the other hand the observed corrosion inhibition is specific to monophospha-s-triazines since neither of the "parents" show this action. It is believed that investigations of these and related "hybrid" heterocyclics will result in further development of materials with a combination of unique properties.

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 21. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were obtained employing a CEC Model 21-620 instrument and a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, 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.

Preparation of Bis(pentafluorophenyl)chlorophosphine

Pentafluorophenylmagnesium bromide was prepared by Grignard exchange between bromopentafluorobenzene and ethylmagnesium bromide following essentially the procedure of Tamborski and Moore [17] with the exception that ether instead of tetrahydrofuran was employed.

The interaction of pentafluorophenylmagnesium bromide with phosphorus trichloride was performed using the procedure of Tesi, et al.[18], resulting in 56.5% yield of bis(pentafluorophenyl)chlorophosphine, bp, 98-100°C/ 0.001 mm Hg.

Preparation of Bis(pentafluorophenyl)trichlorophosphorane

The procedure used was a modification of that employed for the synthesis of diphenyltrichlorophosphorane. The synthesis of diphenyltrichlorophosphorane was accomplished by treatment of a carbon tetrachloride solution of diphenylchlorophosphine with chlorine at -22 to -18°C which resulted in the formation of the desired product as an insoluble precipitate. Crystallization from benzene following the method of Douglas and Herring [14] gave the diphenyltrichlorophosphorane in a 78% yield. In the case of the perfluorophenyl analogue, the use of higher temperatures was required (otherwise unreacted phosphine was recovered) and the product was soluble in carbon tetrachloride. In a typical preparation, 10.06 g (25.12 mmol) of bis(pentafluorophenyl)chlorophosphine was treated with gaseous chlorine (7.3 g) at -20 to -18°C for 3-1/2 hr. This was followed by passing into the solution an additional 2 g of chlorine at 0°C over a period of 2 hr. Subsequently the clear orange solution was stirred at room temperature for 1 hr. The pure phosphorane, mp, 112-115°C (lit. mp, 110°C [19]), was obtained in quantitative yield after removal of the solvent in vacuo at room temperature.

Preparation of 1-Diphenylphospha-3,5-bis(perfluoroheptyl)-2,4,6-triazine (I)

A mixture of N'-(perfluorooctanoylimidoyl)perfluorooctanoylamidine (1.76 g, 2.18 mmol) and diphenyltrichlorophosphorane (0.65 g, 2.23 mmol) was heated under nitrogen by-pass for 12 hr at 97-100°C. The resulting product was boiled with heptane and filtered hot, giving on cooling 1.32 g (61.1% yield) of 1-diphenylphospha-3,5-bis(perfluoroheptyl)-2,4,6-triazine, mp, 73-74.5°C. Anal. Calcd. for $C_{28}H_{10}F_{30}N_3P$: C, 33.99; H, 1.02;

F, 57.61; N, 4.25; P, 3.13; MW, 989.33. Found: C, 34.53; H, 1.16; F, 56.63; N, 4.52; P, 3.17; MW, 970.

Preparation of 1-Diphenylphospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine (II)

A mixture of the perfluoroalkylether-substituted imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)-N=C(NH_2)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (3.13 g, 3.22 mmol) and diphenyltrichlorophosphorane (1.02 g, 3.50 mmol) was heated under nitrogen by-pass for 12 hr at 104-110°C. The resulting product was distilled in vacuo giving 1-diphenylphospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine, 2.69 g (72.6% yield), bp, 108-111°C/0.001 mm Hg (bp = 355°C at 760 mm Hg; from DTA scan). Anal. Calcd. for $C_{30}H_{10}F_{34}N_3O_4P$: C, 31.24; H, 0.87; F, 56.01; N, 3.64; P, 2.69; MW, 1153.35. Found: C, 31.56; H, 0.99; F, 56.84; N, 3.43; P, 2.51; MW, 1150.

Preparation of 1-Diphenylphospha-3,5-bis[$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)$]--2,4,6-triazine (III)

A mixture of the perfluoroalkylether-substituted imidoylamidine $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)C(=NH)-N=C(NH_2)CF(CF_3)O[CF_2CF(CF_3)O]_2-C_3F_7$ (4.11 g, 3.15 mmol) and diphenyltrichlorophosphorane (1.07 g, 3.67 mmol) was heated under nitrogen by-pass for 26 hr at 100-105°C, 48 hr at 120°C, and 72 hr at 140°C. The resulting product was distilled in vacuo giving 1-diphenylphospha-3,5-bis[$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)$]--2,4,6-triazine, 2.44 g (52.1% yield), bp, 142-148°C/0.001 mm Hg (bp = 383°C at 760 mm Hg; from DTA scan). Anal. Calcd. for $C_{36}H_{10}F_{46}N_3O_6P$: C, 29.11; H, 0.68; F, 58.83; N, 2.83; P, 2.09; O, 6.46; MW, 1485.37. Found: C, 30.10; H, 0.98; F, 59.20; N, 2.82; P, 2.04; MW, 1500.

Preparation of 1-Bis(pentafluorophenyl)phospha-3,5-bis(perfluoroheptyl)-2,4,6-triazine (IV)

A mixture of the perfluoroalkyl-substituted imidoylamidine, $C_7F_{15}C$-(=NH)-N=C(NH_2)C_7F_{15} (2.60 g, 3.22 mmol) and bis(pentafluorophenyl)-trichlorophosphorane (1.54 g, 3.27 mmol) was heated under nitrogen by-pass for 76 hr at 90-108°C. The resulting product was boiled with heptane and filtered hot, giving on cooling 2.47 g (65.7% yield) of 1-bis(pentafluorophenyl)phospha-3,5-bis(perfluoroheptyl)-2,4,6-triazine, mp, 70-74; second recrystallization from heptane afforded 1.74 g (46.3% yield) of pure product, mp, 74-75°C. Anal. Calcd. for $C_{28}F_{40}N_3P$: C, 28.76; F, 64.99; N, 3.54; P, 2.65; MW, 1169.24. Found: C, 27.94; F, 65.09; N, 4.08; P, 2.70; MW, 1100.

Preparation of 1-bis(pentafluorophenyl)phospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2$-$OCF(CF_3)$]-2,4,6-triazine (V)

A mixture of the perfluoroalkylether-substituted imidoylamidine $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C$(=NH)-N=C($NH_2$)$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2.25 g, 2.32 mmol) and bis(pentafluorophenyl)trichlorophosphorane (1.21 g, 2.57 mmol) was heated under nitrogen by-pass for 24 hr at 100°C and 124 hr at 140-150°C. The resulting product was distilled in vacuo giving 1-bis-(pentafluorophenyl)phospha-3,5-bis[$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-2,4,6-triazine, 2.29 g (74.1% yield), bp, 119-120°C/0.001 mm Hg (bp = 325°C at 760 mm Hg; from DTA scan). Anal. Calcd. for $C_{30}F_{44}N_3O_4P$: C, 27.03; F, 62.70; N, 3.15; P, 2.32; MW, 1333.23. Found: C, 26.46; F, 59.05; N, 3.57; P, 2.12; MW, 1300.

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