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PHOSPHA-s-TRIAZINES. III. SYNTHESES AND PROPERTIES OF 1,3-BIS(DIARYLPHOSPHA)-5-PERFLUOROALIPHATIC-2,4,6-TRIAZINES

R. H. KRATZER, K. J. L. PACIOREK, J. KAUFMAN, T. I. ITO
and J. H. NAKAHARA

Ultrasystems, Inc., 2400 Michelson Drive
Irvine, California 92715 (U.S.A.)

SUMMARY

Diphospha-s-triazines, namely 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazines, $[(C_6H_5)_2PN]_2[C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)CN]$, were synthesized by interaction of imido-tetraphenyl-diphosphinic acid trichloride and the respective amidines. Yields of 30-65% were realized; the perfluoroalkylether substituted compounds were liquids whereas the perfluoro-n-heptyl group-containing material was a solid. The diphospha-s-triazines exhibited characteristic infrared absorptions and mass spectral breakdown patterns. One of the 1,3-bis(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazines was found to be an effective anti-corrosion and oxidation inhibiting additive for perfluoroalkylether fluids.

INTRODUCTION

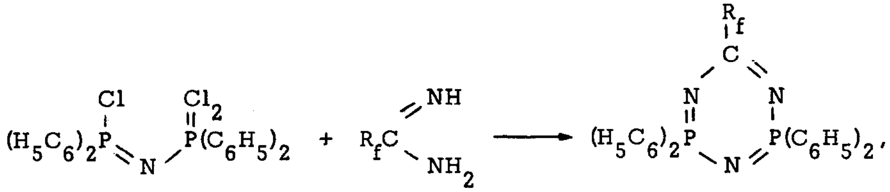
The recently reported [1] monophospha-s-triazines containing perfluorinated substituents on the ring carbon atoms exhibited physical properties surprisingly similar to those of correspondingly substituted triazines. A ring system, in which two of the carbon atoms of s-triazines are replaced by phosphorus, as e.g. represented by 1,3-bis(diphenylphospha)-5-perfluoroalkyl(or perfluoroalkylether)-2,4,6-triazines, might be expected to resemble in its general characteristics more the diphenylphosphazene trimer than the perfluorinated triazine. On the other hand, the presence of one perfluoroalkylether substituent on the remaining ring carbon atom may be sufficient to impart low melting characteristics desirable for fluid or fluid additive and to ensure miscibility with fluorinated base fluids. At the same time the increased phosphorus content in diphospha-s-triazines as compared to monophospha-s-triazines may result in an enhancement of the antioxidant and corrosion inhibitor characteristics, possibly providing simultaneously increased lubricating action.

Having available synthetic procedures for all members of the series from triazine to mono- and diphospha-s-triazine as well as trimeric phosphazene it should be possible to produce materials with closely tailored properties for specific applications. The properties amenable to modification by variation of ring atoms and ring atom substituents include liquid ranges, miscibility, lubricity, oxidation and corrosion inhibiting action, and volatility without drastically sacrificing desired thermal, oxidative, or hydrolytic stabilities.

RESULTS AND DISCUSSION

It was established by Brown, et al. [2] that interaction of an imidoylamidine with a perfluoroacyl halide results in triazine ring formation. On the basis of this cyclization reaction it could be expected that the imidoylamidine may be replaced by an imino-bis(aminophosphorane),e.g. $(C_6H_5)_2P(NH_2){=}N{-}P{-}({=}NH)(C_6H_5)_2$, yielding in a parallel fashion a diphospha-s-triazine. An attempt to prepare this mixed heterocycle via such a condensation, however, resulted in the formation of the corresponding perfluoroalkyl nitrile and oxygen analogues of the imino-bis(aminophosphorane), e.g. $(C_6H_5)_2P(NH_2){=}N{-}P(O){-}(C_6H_5)_2$ and $(C_6H_5)_2P(OH){=}N{-}P(O)(C_6H_5)_2$. Treatment of the imino-bis(aminophosphorane) with perfluoroalkylamidine or nitrile also failed to produce the desired diphospha-s-triazine.

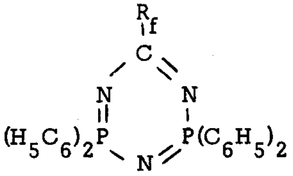
Schmidpeter and Ebeling [3] prepared pentaphenyldiphospha-s-triazine via a reaction of imido-tetraphenyl-diphosphinic acid trichloride with phenylamidine. Using this process, e.g.:



the perfluoroalkyl and perfluoroalkylether substituted bis(diphenylphospha)-s-triazines listed in Table 1 were synthesized.

TABLE 1

Diphospha-s-triazines



R_f	Yield %	MW	m.p. °C	b.p. °C
$CF_3(CF_2)_6$, I	32	793	84.5-85.5	
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$, II	56	875		158/0.001 mm Hg
$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$, III	65	1041		170/0.001 mm Hg

The synthesis of the required amidines was accomplished without difficulty and in excellent yields in the case of the perfluoroalkylamidine by adding perfluoro-n-octanonitrile to refluxing liquid ammonia. The preparation of the respective perfluoroalkylether amidines, however, was invariably accompanied by imidoylamidine formation, which occurred with both slow and fast addition of the nitriles, $C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)CN$ ($x = 1$ and 2), to refluxing liquid ammonia, including injection of the nitrile with the aid of a syringe directly into the liquid. At best 95% pure amidines could be obtained with the remainder being transformed into imidoylamidine which was found to be impossible to separate by distillation. It is of interest to note that all crude perfluoroalkylether substituted diphospha-s-triazines contained up to ~ 1% of the respective monophospha-s-triazines, which may be a consequence of the presence of imidoylamidine although the origin of the $(C_6H_5)_2P$- fragment needed for this ring closure is obscure. On the other hand in view of the results of the thermal studies (see Part IV of this series) the occurrence of disproportionation on prolonged heating at 120-156°C is a possibility.

Inspection of Table 1 shows that both perfluoroalkylether substituted diphospha-s-triazines are liquids at room temperature which may be surprising if a comparison with the melting points of pentaphenyldiphospha-s-triazine [3] or trimeric diphenylphosphazene is made. On the other hand this drastic melting point "depression" is an obvious indication of the "plasticizing" potential of perfluoroalkylether moieties. The product yields given in Table 1 show the cyclization process to be relatively free of side reactions when considering the scale on which the syntheses were performed (10-20 mmoles). The exception in this regard is the preparation of the perfluoro-n-heptyl-substituted diphospha-s-triazine where the formation of imidoylamidine and triazine by-products occurred to a measurable extent, which is reflected in the lower diphospha-s-triazine yield.

All three compounds listed in Table 1 showed strong absorption in their infrared spectra at 6.55 μ ; this band seems to be characteristic for the diphospha ring system. It is noteworthy that for monophospha-s-triazines an equivalent band is observed at 6.3 μ , whereas for perfluoroalkyl and perfluoroalkylether substituted triazines the ring absorption is present at 6.4 μ .

The diphospha-s-triazines, in a manner similar to that of monophospha-s-triazines, were 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. This is illustrated by the data given in Table 2.

TABLE 2

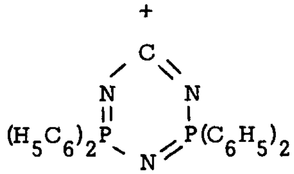
Degradation of Krytox Fluid in the Presence of M-50 Alloy Coupon at 316°C in Oxygen for 24 hr[a]

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
16.36	1%[e] Compd. II	0.0	0.0	0.0	12.7	0.78

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.

It should be noted that the volatile condensibles (12.7 mg) produced in the presence of the additive consisted mainly of the nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$ (90 mol %), some benzene (8%) and traces of the shorter chain nitriles and hydrogen terminated species, e.g. $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$.

The mass spectral breakdown patterns of the diphospha-s-triazines differ from those of the s-triazines and monophospha-s-triazines [4] and show characteristic ions apparently specific to this ring system. The results of the mass spectral analyses are presented in Table 3. As can be seen from these compilations, the fragment



m/e = 424

formed by the loss of a perfluoroalkyl or perfluoroalkylether group constitutes the

TABLE 3

Ion Fragments and Intensities Relative to Base Peak of 1,3-Bis(diphenylphospha)-5-perfluoroalkyl and Perfluoroalkylether-2,4-6-triazines[a)]

m/e	I	II	III	m/e	I	II	III
69	4.7	3.0	30.3	306	10.8	4.4	7.2
77	6.2		8.7	307	3.1		
96	3.1		5.0	325			5.7
97			7.6	335			3.2
100			10.1	421			3.8
107	3.5			422	4.6		
108	3.9		3.7	423	3.0		4.1
119			15.1	424	100.	100.	100.
122	9.4		5.2	425	27.1	27.1	27.1
127			3.2	426			9.3
131	3.5		3.7	524		8.7	10.7
147			4.8	525		3.4	3.5
150			5.1	716	3.4		
152	3.7			774	9.8		
153			3.9	792	33.1		
160	18.1	3.9	14.1	793	42.0(M^+)		
161	5.2		3.4	794	13.4		
169			26.4	856		4.9	
183	16.1	5.6	11.3	874		19.3	
185	4.4		5.0	875		34.8(M^+)	
192			3.7	876		12.4	
198	6.6		3.2	877		2.4	
199	13.6	3.1	8.4	922			3.2
200	13.6		4.6	968			4.1
204			3.1	1022			6.8
212	6.5			1040			13.1
225	5.8	10.6	32.1	1041			40.2(M^+)
226			11.2	1042			15.8
272			5.4	1043			3.0
275			3.0				

a) Peaks lower than m/e 69 and those having intensities less than 3% of the base peak are not reported.

most intense or base peak. The related ion in the 1-diphenylphospha-3,5-bis-(perfluoro-n-heptyl)-2,4,6-triazine amounted only to 4.6% of the base peak [4] whereas no corresponding ion was observed in the perfluoroalkylether substituted monophospha-s-triazines. In tris(perfluoroheptyl)-2,4,6-triazine the related ion, m/e = 816, is only 0.88% of the base peak [5]. The formation of the m/e

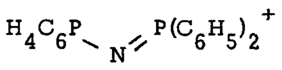
424 ion would tend to indicate that the diphospha-s-triazine ring arrangement is stable to electron impact which, based on other studies, can be extrapolated to thermal stability [4,6-10]. It should be noted that in diphenylphosphazene trimer the M-C_6H_5 ion constitutes 86% of the base peak, which in this case is the molecular ion M^+.

In agreement with past investigations [4,9] the presence of aromatic groups was found to stabilize the molecular ions, shown here by the relatively high intensities of 42.0, 34.8 and 40.2%, for the respective parent ions M^+ (compounds I, II and III). The three compounds exhibit very similar breakdown patterns which is not surprising due to the identical base ion, 424^+, remaining after the loss of the perfluorinated groups. This ion is most likely formed from the parent ion; unfortunately no metastable for this process was observed in the perfluoro-n-heptyl substituted diphospha-s-triazine (I). However, in the case of materials II and III metastables at m/e 205.5 and 172.7 proved the occurrence of these processes:

$$875^+(M) \longrightarrow 424^+ + 451\ [C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$$

$$1041^+(M) \longrightarrow 424^+ + 617\ [C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)]$$

In view of the past work [4,9,10], one would expect the fragmentation of the perfluoroalkylether substituted analogue to be governed by the oxygen functions in the side chain; the only significant ion due to such a cleavage is the 524^+ ion wherein the loss of $OCF_2CF(CF_3)OC_3F_7$ and $OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ groups took place. The remainder of the prominent ions are derived from the breakdown of the fragment free of the fluorinated side chain, i.e. the ion m/e 424. One of these is the fragment



$$H_4C_6P\diagdown_{N}\diagup\!\!\!\diagup P(C_6H_5)_2^{\,+} \qquad m/e\ 306$$

This ion in turn produces $(C_6H_5)_2\overset{-}{P}N^+$ (m/e = 199) as shown by a metastable peak at m/e 129.4:

$$306^+ \longrightarrow 199^+ + 107$$

The 199^+ ion undergoes further cleavage:

$$199^+ \longrightarrow 160^+ + 39 \qquad \text{metastable at m/e 128.5}$$

CONCLUSIONS

Based on the mass spectral data, it could be surmised that diphospha-s-triazines at least in their behavior under electron impact resemble more the phosphazene trimer than the perfluoroalkyl and perfluoroalkylether substituted s-triazines. On the other hand, the melting characteristics and the relatively high volatility, e.g. the ease of distillation, point to a strong influence of the fluorinated substituents. The observed corrosion inhibition and anti-oxidative action seems to be specific to the hybrid ring arrangement as exemplified by mono- and diphospha-s-triazines, since neither of the parents exhibit these 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. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometric 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 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine (I) (n.c.)

Under nitrogen by-pass into a hot suspension of imido-tetraphenyl-diphosphinic acid trichloride (7.62 g, 15.53 mmol), prepared by using the procedure of Fluck and Goldmann [11], in s-tetrachloroethane (110 ml) was added perfluoro-n-heptylamidine (6.01 g, 14.58 mmol) over a period of 1.5 hr. The resulting mixture was then heated at 96-100°C for 110 hr. After solvent removal, followed by treatment with hot heptane 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine (3.68 g, 32% yield) mp 82-85°C was obtained. Recrystallization from heptane raised the melting point to 84.5-85.5°C; based on gas chromatographic analysis, no monophospha-s-triazine was present. Anal. Calcd. for $C_{32}H_{20}F_{15}N_3P_2$: C, 48.49; H, 2.54; F, 35.92; N, 5.30; P, 7.81; MW, 793.45. Found: C, 47.74; H, 2.49; F, 37.27; N, 4.89; P, 7.84; MW, 830.

Preparation of 1,3-bis(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazine, $[Ph_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]$, (II) (n.c.)

A mixture of imido-tetraphenyl-diphosphinic acid trichloride (5.50 g, 11.21 mmol) and perfluoroalkylether amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-$C(=NH)NH_2$, (4.64 g, 9.40 mmol) was heated under nitrogen by-pass at 125-130°C for 158 hr. The residue was subsequently distilled in vacuo giving 1,3-bis(diphenylphospha)-5-(perfluoroalkylether)-2,4,6-triazine, 4.51 g (56% yield); bp 153-158°C/0.001 mm Hg. Anal. Calcd. for $C_{33}H_{20}$-$F_{17}N_3O_2P_2$: C, 45.28; H, 2.30; F, 36.89; N, 4.80; P, 7.08; O, 3.66; MW, 875.46. Found: C, 45.52; H, 2.45; F, 39.66; N, 4.30; P, 6.95; MW, 895.

Preparation of 1,3-bis(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazine, $[Ph_2PN]_2[C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)CN]$, (III) (n.c.)

A mixture of imido-tetraphenyl-diphosphinic acid trichloride (5.94 g, 12.10 mmol) and perfluoroalkylether amidine, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$-

C(=NH)NH_2, (7.64 g, 11.57 mmol) was heated under nitrogen by-pass at 120-156°C for 10 days. The residue was subsequently filtered as a solution in Freon-113 through a 1.8 x 20 cm column of basic alumina and then distilled in vacuo giving 1,3-bis(diphenylphospha)-5-(perfluoroalkylether)-2,4,6-triazine, 7.80 g (65% yield); bp 167-170°C/0.001 mm Hg. Anal. Calcd. for $C_{36}H_{20}F_{23}N_3O_3P_2$: C, 41.52; H, 1.94; F, 41.96; N, 4.03; P, 5.95; O, 4.61; MW, 1041.48. Found: C, 41.30; H, 2.21; F, 43.88; N, 3.71; P, 5.25; MW, 1130.

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