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PHOSPHA-s-TRIAZINES. IV. DEGRADATION STUDIES OF 1-DIARYLPHOSPHA-3,5-BIS(PERFLUOROALIPHATIC)-2,4,6-TRIAZINES AND 1,3-BIS(DIARYLPHOSPHA)-5-PERFLUOROALIPHATIC-2,4,6-TRIAZINES

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SUMMARY

Thermal and thermal oxidative stability evaluations were performed on mono- and diphospha-s-triazines at 235 and 316°C using sealed Pyrex ampoules. The specific compounds studied were: 1-diphenylphospha-3,5-bis-(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazines, their respective pentafluorophenyl analogues, 1,3-bis(diphenylphospha)-5-perfluoro-n-heptyl-2,4,6-triazine and 1,3-bis-(diphenylphospha)-5-perfluoroalkylether-2,4,6-triazine. All the compounds wherein phenyl groups were present on the phosphorus exhibited good thermal stability up to 316°C; the analogous pentafluorophenyl substituted materials were degraded extensively at these temperatures. The oxidative stability of both the mono- and diphospha-s-triazines was excellent at 235°C, but at 316°C some degradation was observed. This was more pronounced in compounds containing the perfluoroalkyl moiety on carbon than in the perfluoroalkylether substituted members of the series.

INTRODUCTION

One of the potential applications of phospha-s-triazines is as high temperature fluids and additives. Preliminary studies have shown monophospha-s-triazines to exhibit good thermal and oxidative stabilities [1]. However, no detailed testing was performed to determine the influence of the substituents on the carbon and phosphorus ring atoms upon these properties. Regarding diphospha-s-triazines [2] no stability evaluations were carried out. Furthermore, it was of interest to compare the two carbon and the two phosphorus ring arrangements, as present in the monophospha- and diphospha-s-triazines, with respect to the stability characteristics of these novel heterocycles as well as in relation to these characteristics of the parent triazines and phosphazenes.

RESULTS AND DISCUSSION

The results of the degradation studies are summarized in Tables 1 and 2. The perfluoroalkyl and perfluoroalkylether groups present on the carbons are both strongly electron-withdrawing, but in the perfluoroalkylether substituent the $-CF(CF_3)-$, not the $-CF_2-$ moiety, is adjacent to the ring. The steric effect of this arrangement was found to enhance the stability of perfluoro-substituted heterocycles as compared to compounds containing a $-CF_2-$ group adjacent to the ring [3,4]. Comparing Runs No. 1-4 with the 6-9 Run-series and the 13-15 Tests with Runs No. 16-18 it is apparent that this effect is also operative in the phosphatriazines which is not surprising, inasmuch as similar structural arrangements are involved.

It should be noted that in the case of 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine heat treatment at 316°C resulted in increased thermal stability as shown clearly by comparison of Tests No. 2 and 3. The specific sample employed in Tests No. 1-4, with exception of Test No. 3, contained a trace of the imidoylamidine precursor. Perfluoroalkylimidoylamidines on heating above 100°C form triazines by ammonia elimination. Brown [5] in his studies found that nitrogen bases degrade triazines and this process apparently also takes place in phosphatriazines as evidenced by the results of Test No. 3. This test was conducted using the residue of Run No. 2 from which all volatiles had been removed so that the sample was rendered ammonia free.

TABLE 1

Results of Degradation Studies Performed on Mono(diarylphospha)-s-triazines[a]

Test No.	Compound[b]	Temp. °C	Atmosphere	Starting Material Used	Starting Material Recovered	Oxygen Consumed		Volatile Products
				mg	%[c]	mg	%[d]	%[c]
1	$[n\text{-}C_7F_{15}CN]_2[Ph_2PN]$	235	Air	347.1	98	0.3	5	1.4
2	- Ditto -	316	Vacuo	397.7	89	n.a[e]	n.a	6.5
3	- Ditto -[f]	316	Vacuo	361.0	93	n.a	n.a	4.1
4	- Ditto -	316	Air	324.9	73	0.7	12	10.8
5	$[n\text{-}C_7F_{15}CN]_2[Ph_{f2}PN]$	316	Vacuo	451.4	?	n.a	n.a	37.0
6	$[R_fOR_fCN]_2[Ph_2PN]$	235	N_2	209.5	99	n.a	n.a	1.1
7	$[R_f'OR_f'CN]_2Ph_2PN]$	235	Air	498.7	>99	0.2	4	0.9
8	$[R_fOR_fCN]_2[Ph_2PN]$	325	N_2	191.8	96	n.a	n.a	3.5
9	$[R_f'OR_f'CN]_2Ph_2PN]$	316	Air	220.9	89	0.4	7	9.8
10	$[R_fOR_fCN]_2[Ph_{f2}PN]$	235	N_2	354.1	>90	n.a	n.a	2.4
11	- Ditto -	235	Air	382.9	>90	0.2	4	2.8
12	- Ditto -	316	Vacuo	318.4	10	n.a	n.a	54.6

a) The degradations were performed in sealed Pyrex ampoules of *ca* 50 ml volume, over a period of 24 hr at the specified conditions. b) Ph = C_6H_5; $Ph_f = C_6F_5$; $R_fOR_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$; $R_f'OR_f' = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$. c) Weight percent of starting material. d) Percent of oxygen available. e) n.a = not applicable. f) The residue from the preceding Test No. 2 was employed here.

TABLE 2

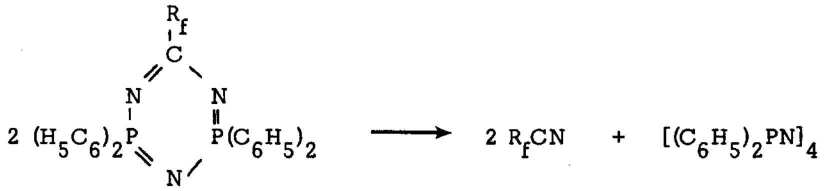
Results of Degradation Studies Performed on Bis(diarylphospha)-s-triazines[a]

Test No.	Compound[b]	Temp. °C	Atmosphere	Starting Material Used mg	 Recovered %[c]	Oxygen Consumed mg	 %[d]	Volatile Products %[c]
13	$[C_7F_{15}CN][Ph_2PN]_2$	235	Air	418.0	>99	0.1	2	0.3
14	- Ditto -	316	N_2	324.3	93	n.a[e]	n.a	4.7
15	- Ditto -	316	Air	154.1	60	0.1	2	17.7
16	$[R_fOR_fCN][Ph_2PN]_2$	235	Air	469.3	>99	0.1	2	0.1
17	- Ditto -	316	N_2	432.2	98	n.a	n.a	1.6
18	- Ditto -	316	Air	468.6	86	0.7	11	6.9

a) The degradations were performed in sealed Pyrex ampoules of ca 50 ml volume, over a period of 24 hr at the specified conditions. b) Ph = C_6H_5; $R_fOR_f = C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)$. c) Weight percent of starting material. d) Percent of oxygen available. e) n.a = not applicable.

Based on the data presented in Tables 1 and 2 the thermal stability of mono- and diphospha-s-triazines containing phenyl groups on the phosphorus atoms and perfluoroalkylether substituents on the carbons is comparable and corresponds to that of tris-perfluoroalkylether triazines [3]. The oxidative stability of these materials, however, is somewhat lower. This is not due to oxidation of the phenyl or the perfluoroalkyl or perfluoroalkylether groups as shown by the negligible oxygen consumption (see Tables 1 and 2) and the type of products formed as listed in Table 3. In view of the finding that phosphonitrilic chloride trimer can be transformed into polymeric materials only if traces of oxygen are present [6], it is plausible that also in the phospha-triazines series oxygen does catalyze ring opening. The almost exclusive production of perfluorinated nitriles, monophospha-s-triazines, and phosphazene trimer by the diphospha-s-triazines shows clearly that "dissociation", not oxidation, is the predominant degradation process here. The same applies to the monophospha-s-triazines where the nitrile, triazine and phosphazene tetramer were found. No diphospha-s-triazines were observed among the degradation products. The latter produce a characteristic peak at m/e 424 in their mass spectra [2] and since all of the involatile degradation residues were subjected to the probe-mass spectral analysis their presence would have been detected.

One would expect the decomposition of diphospha-s-triazines to lead to phosphazene tetramer via perfluoroalkyl nitrile elimination, e.g.



However, definite absence of the tetramer together with the formation of the phosphazene trimer and monophospha-s-triazines (see Tests No. 15 and 18, Table 3) tends to indicate the occurrence of a disproportionation process wherein two molecules of diphospha-s-triazine rearrange to give a molecule of phosphazene trimer and a molecule of monophospha-s-triazine, in addition to nitrile formation. It should be noted that the degradation path involving

TABLE 3

Degradation of Mono- and Diphospha-s-triazines; Products Formed[a]

Test No.	R_fCN %[d]	$(R_fCN)_3$ %	$[R_fCN]_2[Ph_2PN]$ %	$[Ph_2PN]_x$[b] %	$R_f'H$[c] %	SiF_4 %	C_6H_6 %
1	1.4	-	n.a[e]	-	T[f]	T	T
2	6.4	4.2	n.a	-	T	T	0.1
3	3.8	2.1	n.a	-	T	T	0.2
4	10.6	10.7	n.a	3.6[g]	T	T	0.1
5	27	11.3	n.a	-	?	2.5	3.0[h]
6	0.9	-	n.a	-	T	T	T
7	0.8	-	-	-	T	T	T
8	2.9	?	n.a	-	T	T	T
9	9.1	?	n.a	?	0.2	T	T
10	1.8	0.9	n.a	?	T	T	0.5[h]
11	2.3	1.5	n.a	?	T	T	0.4[h]
13	T	-	0.2	-	-	-	-
14	4.3	-	0.2	2.3[i]	T	T	0.3
15	17.3	-	5.4	14.2[i]	T	T	0.4
16	T	-	-	T	-	-	T
17	1.2	-	?	?	T	T	0.1
18	5.5	-	1.8	4.9[i]	0.9	T	0.2

a) The degradations are summarized in Tables 1 and 2; R_f corresponds to the fluorinated substituent originally present. b) x = 3 or 4. c) R_f' is any perfluoro-aliphatic group. d) Percent of starting material. e) Not applicable since monophospha-s-triazine was here the starting material. f) T <0.1%. g) This was $[Ph_2PN]_4$. h) In these instances it was not C_6H_6 but C_6F_5H. i) This was $[Ph_2PN]_3$.

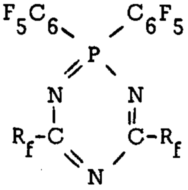
nitrile elimination is not indicated by mass spectral data thus possibly supporting the bimolecular mechanism delineated above. On the other hand monophospha-s-triazines, based again on mass spectral breakdowns patterns, would be expected to decompose by nitrile elimination [7].

As is clearly evident from the compilation given in Table 1 the pentafluorophenyl substituted monophospha-s-triazines, Runs No. 5 and 10-12,exhibited drastically lower thermal stability than the corresponding phenyl group-containing compounds. In the case of 1-bis(pentafluorophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (see Run No. 5) the perfluoro-n-octanonitrile produced amounted to 73 weight percent of the volatiles, the other major constituents being pentafluorobenzene (23.1%) and silicon tetrafluoride (6.9%). In the involatile residue tris-perfluoro-n-heptyl-s-triazine added up to 11.3 weight percent of the monophospha-s-triazine originally employed; no other involatile compounds were identified. The nitrile together with the triazine accounted for 59% of the "$C_7F_{15}CN$" constituent present in the starting material. The results obtained for the perfluoroalkylether substituted bis-pentafluorophenyl analogue, see Test No. 12 and the product listing given in Table 4, are directly comparable. Here, the perfluoroalkylether triazine and nitrile account for 56% of the "$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$" constituent of the monophosphatriazine. Based on these data it is obvious that dissociation of the phosphatriazine ring is the major degradation process. It is accompanied by some rearrangement of the pentafluorophenyl substituents as shown by the formation of the 1-(pentafluorophenyl)fluorophospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine. Both of these degradation modes are supported by the mass spectral breakdown patterns of the monophospha-s-triazines [7]. This thermal instability and the ease of dissociation must be due to the electronegative effect of the pentafluorophenyl groups and the resultant "unavailability" of the 3s electrons in the ring bonding.

The aspect of electron concentration at the phosphorus atom is further illustrated by the hydrolytic instability of the 1-bis(pentafluorophenyl)phospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine which on long (~ one year) exposure to the atmosphere was found by GC-MS to contain only 3% of the phospha-s-triazine. Based on the GC-MS data the perfluoroalkylether component was degraded mainly into the corresponding imidoylamidine, ~ 89%, and the

TABLE 4

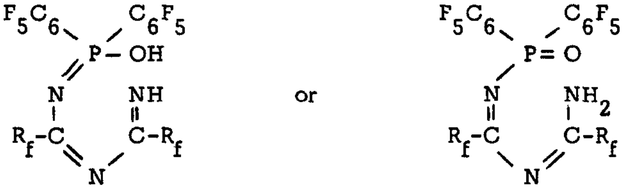
Products Identified[a]; Thermal Degradation of:



Compound	% Starting Material
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$	35.8
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_3$	4.3
$C_3F_7OCF(CF_3)CN$	1.4
$C_3F_7OCF(CF_3)H$	3.0
C_6F_5H	3.9
SiF_4	5.5
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2[P(C_6F_5)_2N]$	10.1
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2[P(C_6F_5)(F)N]$	5.6

a) This is Test No. 12, Table 1; $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

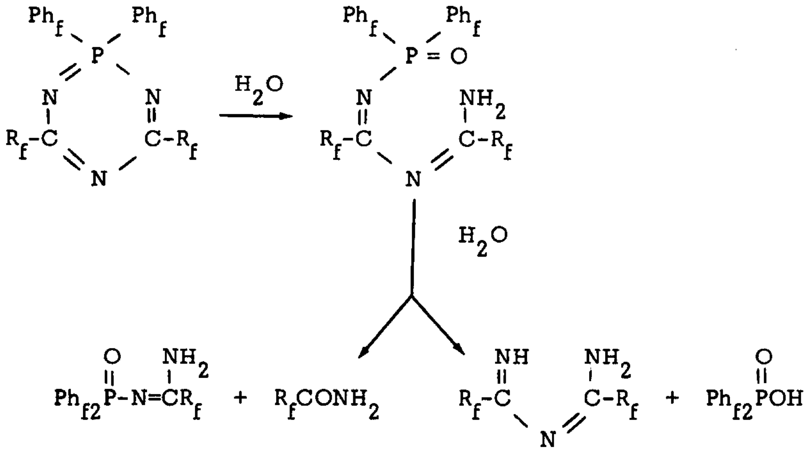
amide ~ 10%. Identification of trace quantities, ~ 0.1%, of $(C_6F_5)_2P(O)N{=}C(NH_2)CF(CF_3)OCF_2(CF_3)CFOC_3F_7$ is in agreement with the subsequent studies which revealed that the initial hydrolysis occurs via a ring opening reaction yielding the apparently relatively stable intermediate



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

This material was identified by its mass spectral breakdown pattern, specifically by the presence of the ions 1351^+ (M), 1332^+ (M-19), 900^+ (M-451) and 381^+

$[(C_6F_5)_2PO]$. In view of the isolation of the imidoylamidine, the amidine, and the intermediates discussed above it is reasonable to assume that the following reactions take place:



No attempt was made to isolate bis(pentafluorophenyl)phosphinic acid.

CONCLUSIONS

It can be concluded that in the temperature region studied there is not much difference between the analogously substituted mono- and diphospha-s-triazines. The effect of the nature of the carbon substituents is of importance insofar as steric factors are concerned. On the other hand only highly electronegative groups were investigated; their selection being governed by melting or fluid range requirements. Contrary to expectations the replacement of the phenyl group by a pentafluorophenyl moiety lowered the thermal and hydrolytic stability of the monophosphatriazine ring system. This has been attributed to changes in electron density around the phosphorus atom when the phenyl groups are substituted by electronegative pentafluorophenyl moieties.

EXPERIMENTAL

The degradation investigations were performed in sealed Pyrex ampoules of <u>ca</u> 50 ml volume, over a period of 24 hr at the specified temperatures. The media studied were vacuum, nitrogen and air; the gas pressures used were ca 350 mm Hg at room temperature. At the conclusion of an experiment the ampoules were cooled in liquid nitrogen and were opened into the vacuum system. The liquid nitrogen noncondensibles were measured and determined by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through -23, 78°C traps into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy, batch mass spectrometry and GC-MS. The residue itself was weighed and subjected to batch mass spectrometry, GC-MS, and infrared spectral analyses.

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