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PHOSPHA-S-TRIAZINES. X. THIOPHENYL-SUBSTITUTED PHOSPHA-S-TRIAZINES

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SUMMARY

A series of thiophenyl-substituted mono- and diphospha-s-triazines was prepared. These materials exhibited physical characteristics similar to those of the corresponding phenyl analogues, but the mass spectral breakdown patterns were dominated by the loss of the thiophenyl group and differed significantly from that of the other phospha-s-triazines investigated to date. The thiophenyl-phospha-s-triazines exhibited anticorrosive and antioxidative action when used as additives in perfluoroalkylether fluids. At elevated temperatures, 316°C, these materials were less effective than the phenyl analogues. The monophospha-members of the series were thermally and oxidatively less stable than the corresponding diphospha-s-triazines: 67 versus 96% starting material recovery after exposure to air at 235°C for 24 hr. Both the mono- and diphospha-s-triazines were completely degraded in 24 hr at 316°C in nitrogen.

INTRODUCTION

Past investigations [1-4] have shown phospha-s-triazines, as well as the diphosphatetraazacyclooctatetraenes [5] to exhibit anticorrosion and antioxidative action when used in perfluoroalkylether fluids in the presence of metals or metal

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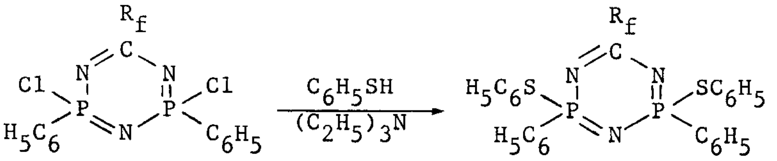
alloys. Generally, compounds containing phosphorus and sulfur are known to enhance a fluids' lubricity. The availability of the chloro-substituted phospha-s-triazines [6,7] permitted the introduction of groups other than phenyl onto the ring phosphorus atoms and thus opened new avenues to structure-property tailoring. This particular phase of the research was directed at synthesis and evaluation of thiophenyl-substituted phospha-s-triazines with the ultimate aim to develop materials which would act as oxidation and corrosion inhibitors in addition to serving as lubricity additives.

RESULTS AND DISCUSSION

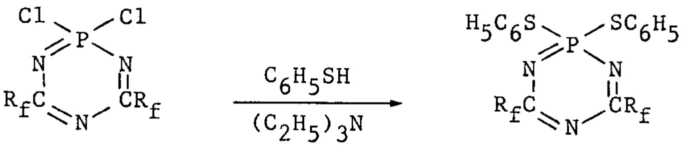
Synthesis and characterization

Interaction of the chloromonophospha- and diphospha-s-triazines with thiophenol following the procedure of Allcock and Kugel [8] gave the desired products in good yields as evident from the data summarized in Table 1, *i.e.*,



I, $R_f = n\text{-}C_7F_{15}$

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



III, $R_f = n\text{-}C_7F_{15}$

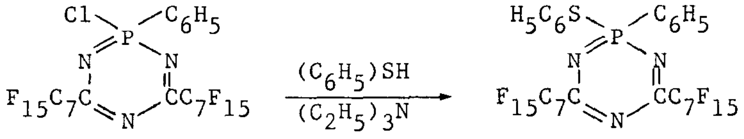
IV, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

TABLE 1

Thiophenyl-substituted diphospha- and monophospha-s-triazines

Compound[a]	Yield	MP °C	BP °C	IR Bands (cm^{-1})[b]		MW[c]	Elemental Analyses, %					
							C	H	F	N	S	P
$[n\text{-}C_7F_{15}CN][C_6H_5(SC_6H_5)PN]_2$ I	71	89-91	-	1495(vs),1502(sh)	Calcd	857.58	44.82	2.35	33.23	4.90	7.48	7.22
					Found	880.	44.70	2.37	33.98	4.96	7.68	7.21
$[R_fCN][C_6H_5(SC_6H_5)PN]_2$ II	92	-	189/0.001 mm Hg	1495(vs),1502(sh)	Calcd	939.59	42.18	2.15	34.37	4.47	6.83	6.60
					Found	950.	42.35	2.33	34.65	4.47	n.d.[d]	6.17
$[n\text{-}C_7F_{15}CN]_2[(SC_6H_5)_2PN]$ III	71	65.5-67	-	1547(vs),1555(sh)	Calcd	1053.46	31.92	0.96	54.10	3.99	6.09	2.94
					Found	1080.	32.19	1.12	52.26	3.68	n.d.	3.01
$[R_fCN]_2[(SC_6H_5)_2PN]$ IV	62	-	n.d.	1547(vs),1555(sh)	Calcd	1217.48	29.60	0.83	53.06	3.45	5.27	2.54
					Found	1230.	29.29	1.16	50.90	3.61	5.29	2.38
$[n\text{-}C_7F_{15}CN]_2[C_6H_5(SC_6H_5)PN$ V	83	81-82	-	1560(vs)	Calcd	1021.40	32.93	0.99	55.80	4.11	3.14	3.03
					Found	1000.	33.26	1.19	54.93	4.32	2.94	3.04

[a] $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$-.
[b] The absorption bands given are characteristic of phosphatriazine ring.
[c] Molecular weights determined in C_6F_6 by vapor pressure osmometry.
[d] Not determined.



V

As has been observed for other phospha-s-triazines synthesized to date, the perfluoroalkylether-substituted materials were usually liquids, whereas the perfluoro-n-heptyl group-containing analogues were solids [1,2]. The formation of the thiophenyl derivatives was invariably associated with production of diphenyl disulfide, which had to be removed by sublimation and/or extraction. It should be noted that, aside from the formation of diphenyl disulfide, the reaction proceeded very cleanly. The purity of all the materials was verified by gas chromatography. 1,3-Bis[phenyl(thiophenyl)phospha]-5-perfluoroalkylether-2,4,6-triazine (II) was found to have two peaks in 3:1 ratio (retention times 38.5, 39.5 min) of the same mass spectral patterns pointing to the presence of isomers. The relative ratio of the isomers was not changed by distillation, i.e., residence at elevated temperature. The corresponding perfluoro-n-heptyl substituted analogue (I) consisted of one isomer only. However, exposure to 235°C resulted in the transformation of ∿75% of the material into another isomer as determined by gas chromatography (retention times 43.4 and 44.8 min). Crystallization from hexane gave the 'new' isomer, mp 104-109°C, admixed with ∿10% of the initial material. The mass spectral breakdown pattern and the molecular weight (Calcd. 857.58; Found 900) prove beyond doubt that isomerization did take place. The melting point of what appears to be the thermodynamically more stable isomer is higher than that of the initially formed material which had a melting point of 89-91°C. The existence of cis-trans isomerism in diphospha-s-triazines having two different substituents on the phosphorus atoms is to be expected in analogy with phosphazene chemistry [9]. Two isomers were also found in the case of 1,3-bis[phenyl (perfluoro-n-octanoylamidino)phospha]-5-perfluoro-n-heptyl-2,4,6-

triazine [6]. What is surprising is the absence of the isomerism in the chloro-precursors of the phenylthio-compounds. On the other hand, it can be argued that the method of synthesis leads to one isomer only.

Mass spectra

The mass spectral fragmentation patterns of the thiophenyl-substituted materials (Table 2) differ greatly from those of their phenyl, chloro, or even azido and amidino analogues [2,6, 7,10]. In the diphospha-s-triazines, the 100% peak, with the exception of the diazido derivative, was formed by the loss of the perfluoroalkyl or perfluoroalkylether moiety. In the phenylthio-group containing materials, the corresponding ion, m/e 488, amounts to 2%, whereas the loss of the phenylthio-substituent is the predominant process. The presence of metastables at m/e 652.9 and 733.7 for compounds I and II, respectively, shows clearly that the m/e 748 and 830 ions are formed from the molecular ion, i.e.,

$857^+(M) \longrightarrow 748^+ + 109[SC_6H_5]$ m* 652.9

$939^+(M) \longrightarrow 830^+ + 109[SC_6H_5]$ m* 733.7

No metastables were observed for the subsequent breakdown of the 748^+ and 830^+ ions. Yet, the most prominent peaks in the spectra involve the loss of the thiophenyl group. This is illustrated for 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine (I) by the 429^+, 353^+, and 270^+ ions:

$429^+ \longrightarrow M - 109[C_6H_5S] - 319[C_6F_{13}]$

$353^+ \longrightarrow M - 109[C_6H_5S] - R_fCN$

$270^+ \longrightarrow M - (2)109[C_6H_5S] - 369[C_7F_{15}]$

In this particular compound, the loss of the $(C_6H_5)_2PN$ unit, m/e 199, seems to occur to a significant degree as apparent from the 658^+ and 230^+ ions, i.e.,

$658^+ \longrightarrow M - 199[(C_6H_5)_2PN]$

$230^+ \longrightarrow 429^+ - 199[(C_6H_5)_2PN]$

TABLE 2

Ion fragments and intensities relative to base peak of 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine (I), 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoroalkylether-2,4,6-triazine (II), 1-di(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (III), 1-di(thiophenyl)phospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (IV), and 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (V)[a]

m/e	I	II	III	IV	V	m/e	I	II	III	IV	V	m/e	I	II	III	IV	V
39	6.3		8.1	11.8		172			7.6	11.4		833		7.0			
50	8.5			10.4		183	9.9	6.2				857	8.4(M$^+$)				
51	12.6		6.2	10.3		184	6.0					866				15.4	
63			8.3	12.2		185	7.4			8.5	7.5	867				7.4	
65	8.2	6.4	19.7	23.4		186			7.7	17.5		912			46.2		<u>100.0</u>
66	7.0	6.3		8.8		217		8.7				913			19.3		37.4
69	17.8	18.0	21.1	44.4	11.5	218			28.0	43.0		914					7.4
71			37.7	23.9		219			7.4	13.0		920		6.8			
72			6.1			220				9.4		932				10.3	
76				7.4		225	13.8	7.0				939		15.4(M$^+$)			
77	23.7	10.0	9.0	13.8	31.9	230	18.0					940		8.0			
78	6.8					248	6.5					942				19.3	
84	7.6					257					7.3	943				6.9	
86	8.2					270	11.6					944			45.6		
96	6.3					272				17.7		945			16.2		
97				7.1		275		12.0				946			7.7		
100				8.7		289				7.7		963			6.2		
107	7.9			6.0		299				6.2		976			6.3		
108	9.8		7.3	13.2	12.5	353	13.6					999				9.0	

TABLE 2 Continued

109	10.9	14.0	100.0	100.0	14.5	389				11.5		1002					31.6
110	17.3	16.6	24.6	27.4		465				15.8		1003					12.2
111			12.2	15.8		498		33.4				1020					12.4
119		9.8		13.2		499		9.8				1021					86.4(M^+)
121				6.3		554				8.6		1022					36.6
122	18.8	8.2			6.2	555				6.0		1023					12.8
126				7.1		588		6.4				1032				9.4	
127	10.5	6.1			12.8	607					6.2	1034			24.7		
128	6.5			9.0		652					9.3	1035			11.9		
139				7.1		658	16.1					1053			76.6(M^+)		
140				8.2	25.4	674	13.6					1054			33.2		
141				6.8		748	100.0					1055			19.1		
154			12.6	12.9		749	45.0					1056			6.4		
159				11.1		750	18.7					1076				34.0[b]	
164				6.3		776				6.5		1098				8.0	
167					11.5	830		100.0				1108				14.0	
169		9.2		25.7		831		48.7				1198				9.2	
171				11.9		832		21.2				1217				42.0(M^+)	

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[a] Peaks having intensities lower than 6% of the base peak are not reported; peaks m/e less than 39 are omitted.

[b] Relative intensities for ions above m/e 1066 were determined by comparative measurement of oscillograph peaks.

The attendant rearrangement, also observed in the case of the diazido derivative [6], is further supported by the presence of $(C_6H_5)_2P$ fragment, 185^+ ion, in the mass spectrum.

The fragmentation of the perfluoroalkylether chain is responsible for a number of prominent peaks in the spectrum of 1,3-bis(phenylthiophenylphospha)-5-perfluoroalkylether-2,4,6-triazine (II), i.e.,

$$588^+ \longrightarrow M - 351[OCF_2CF(CF_3)OC_3F_7]$$

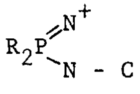
$$498^+ \longrightarrow M - 109[C_6H_5S] - 332[FOCCF(CF_3)OC_3F_7]$$

As in the case of the perfluoro-n-heptyl substituted material, the majority of ions involve the loss of the thiophenyl group. This applies to the 498^+, 353^+, and 275^+ ions. The last two ions involve the breakdown of the ring, i.e.,

$$275^+ \longrightarrow M - 109[C_6H_5S] - H - 77[C_6H_5] - R_fCN$$

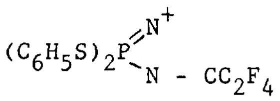
It should be noted that the 353^+ ion formed by the loss of the thiophenyl group and the nitrile moiety is of high intensity in compound I, whereas the 275^+ ion is of high intensity in compound II. This shows the influence of the perfluorinated chain upon the fragmentation path. In this connection, it is of interest that no loss of $(C_6H_5)_2PN$ fragment is evident in compound II indicating that here the loss of phenyl group occurs in preference to the rearrangement.

In the breakdown patterns of the di(thiophenyl)monophospha-s-triazines, the fragment 'A', m/e 289,



A

characteristic of other monophospha-s-triazines synthesized to date [7,10] was present only in a low proportion. A related ion,



$$(C_6H_5S)_2P\overset{\diagup N^+}{\underset{\diagdown N - CC_2F_4}{}}$$ m/e, 389

was produced by 1-di(thiophenyl)phospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (IV). However, the major processes involved the loss of thiophenyl and phenyl disulfide moieties as evidenced by the presence of metastables at m/e 846.3, 789.9, 1008.8, and 951.3 in the mass spectra of compounds III and IV, respectively, <u>i.e.</u>,

$$1053^+(M) \longrightarrow 944^+ + 109[SC_6H_5] \qquad m^* \ 846.3$$

$$1053^+(M) \longrightarrow 912^+ + 141[SSC_6H_5] \qquad m^* \ 789.9$$

$$1217^+(M) \longrightarrow 1108^+ + 109[SC_6H_5] \qquad m^* \ 1008.8$$

$$1217^+(M) \longrightarrow 1076^+ + 141[SSC_6H_5] \qquad m^* \ 951.3$$

Apparently, the loss of diphenyl disulfide also takes place, as shown by the high intensity peak at m/e 218. The remaining fragment, m/e 835, is of very low intensity, 1% in the case of compound III, although it is relatively intense, 9% (999^+), in compound IV. In both compounds, the thiophenyl moiety, m/e 109, constitutes the 100% peak. As would be expected in the case of 1-di(thiophenyl)phospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine, fragmentation of the perfluoroalkylether side chain is responsible for a number of the high mass peaks, <u>e.g.</u>, m/e 1198, 1051, 932, 866, and 766.

The breakdown pattern of 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (V) followed closely those of the other thiophenyl-substituted phospha-s-triazines. Thus, the ion (m/e 912) corresponding to the loss of the thiophenyl group was the most intense peak and as evident from the metastable at m/e 814.6 is derived from the molecular ion, <u>i.e.</u>,

$$1021^+ \longrightarrow 912^+ + 109[SC_6H_5]$$

Fragmentation leading to arrangement A was found to occur here only to a limited degree, m/e 257 (7.3%).

Based on the mass spectra of the thiophenyl group-containing phospha-s-triazines, these compounds would be expected to liberate diphenyl disulfide on thermal degradation.

Thermal and thermal oxidative stability

To obtain a meaningful comparison of the thermal and thermal oxidative stabilities of the mono- versus diphospha-s-triazines, substituted by thiophenyl groups, the investigations were performed on 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine and 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine. It is evident from the data listed in Table 3 that the diphospha-s-triazine is definitely more thermally and oxidatively stable, at least at 235°C in air, than the monophospha-s-triazine. Essentially no difference in stability was observed between the corresponding phenyl-substituted mono- and diphospha-s-triazines [11]. The production of diphenyl disulfide is in agreement with the predictions based on mass spectral breakdown patterns, discussed above.

The destabilizing effect of the thiophenyl as compared to the phenyl group is obvious from the complete decomposition of the thiophenylphospha-s-triazines at 316°C. Under parallel conditions, >90% of the diphenylphospha analogue was recovered unchanged [11]. The four products identified and quantified were perfluoro-n-octanonitrile, perfluoro-n-heptyl-s-triazine, diphenyl disulfide, and diphenyl sulfide. The thermal trimerization of perfluoroalkyl nitriles is well established [12]. Exposure of diphenyl disulfide in nitrogen to 316°C for 24 hr resulted in 30% recovery of the starting material and 70% transformation into diphenyl sulfide. It can be thus deduced that the triazine and diphenyl sulfide are derived from the primary products, namely perfluoro-n-octanonitrile and diphenyl disulfide. On the other hand, it is plausible that at these elevated temperatures diphenyl sulfide is produced directly from thiophenyl radicals. One would expect the latter to be the initial products of degradation based on the mass spectral

TABLE 3

Degradation studies[a]

Test No.	Compound	Temp °C	Atmos-phere	Starting Material Used mg	Starting Material Recovered %	Oxygen consumed mg	Oxygen consumed %[c]	Products (%)[b] $C_7F_{15}CN$	Products (%)[b] $[C_7F_{15}CN]_3$	Products (%)[b] ΦSSΦ	Products (%)[b] ΦSΦ
10	$[n\text{-}C_7F_{15}CN][\Phi(\Phi S)PN]_2$	235	Air	926.0	96	2.59	39.5	1.1	0	3.0	-
11	$[n\text{-}C_7F_{15}CN]_2[\Phi(\Phi S)PN]$	235	Air	560.4	67	3.36	41.2	9.0	2.3	6.3	0.8
13	$[n\text{-}C_7F_{15}CN][\Phi(\Phi S)PN]_2$	316	N_2	992.0	0	n.a.[d]	n.a.	24.9	0.2	2.2	16.0
12	$[n\text{-}C_7F_{15}CN]_2[\Phi(\Phi S)PN]$	316	N_2	950.7	0	n.a.	n.a.	40.4	2.6	0.7	6.1

[a] The degradations were performed in sealed pyrex ampoules of ca 50 ml volume over a period of 24 hr.

[b] *Weight percent of starting material.*

[c] Percent of oxygen available.

[d] Not applicable.

evidence. Calculations reveal that during the 24 hr exposure at 316°C, 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine liberated 82% of the potentially available thiophenyl moieties and 54% of the nitrile, whereas in the case of 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, the corresponding values were 77 and 56%, respectively. The fate of the rest of the sulfur and the remainder of the perfluoroalkyl groups is unknown. These, together with phosphorus, comprised the insoluble charred residue.

Antioxidative and anticorrosive action

The thiophenyl-substituted mono- and diphospha-s-triazines were evaluated as potential anticorrosion and antioxidation additives for perfluoroalkylether fluids, namely poly(hexafluoropropene oxide) (Krytox 143AC, product of DuPont) and the unbranched fluid, $CF_3O(CF_2O)_x(CF_2CF_2O)_yCF_3$ (Fomblin Z, product of Montedison). In as much as Ti(4Al,4Mn) alloy was found to be significantly more effective in catalyzing the degradation of perfluoroalkylether fluids [4,13,14] than M-50 which was previously used for these tests, it has been employed exclusively in the current investigations.

The results of these tests are summarized in Table 4; for comparison purposes, corresponding tests involving 1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine were also included. Based on the degradation products formed in the first 24 hr, Tests 1A and 2A, the sulfur-compounds would appear to be effective in arresting degradation. Yet, the exposure was accompanied by the formation of a brown, very fine precipitate. This could be removed by filtration and the clear solution, on re-exposure to oxygen and alloy at 316°C, did not form additional precipitate, whereas the quantity of products liberated was still significantly lower than in the absence of the additive. In Tests 5A, 6A, and 7A, the fluid was exposed to oxygen and metal coupon at elevated temperature for a short period of time, cooled, and filtered in an inert

TABLE 4

Effect of phenyl(thiophenyl)phospha-s-triazines on thermal oxidative degradation of perfluoroalkylether fluids in the presence of Ti(4Al,4Mn) alloy[a]

Test[b] No.	Fluid		Additive		Temp °C	Exposure time hr	O_2 Consumed			Total Products Formed	
	Type	g	%[c]	Type			Total mg	%[d]	mg/g[e]	mg	mg/g[f]
62	Krytox 143AC	4.79	-	none	316	24	74.9	68.1	15.7	758.7	158.4
1A	Krytox 143AC	4.78	1.0	$[(\Phi S)_2PN][R_fCN]_2$[g]	316	24	7.9	7.0	1.7	7.7	1.6
1B	Krytox 143AC	3.70	1.0	$[(\Phi S)_2PN][R_fCN]_2$	316	24	12.8	11.4	3.5	126.0	34.0
2A	Krytox 143AC	4.89	1.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	24	2.1	1.9	0.4	8.5	1.7
2B	Krytox 143AC	4.52	0.5	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	24	2.0	1.8	0.4	22.4	5.0
3A	Krytox 143AC	5.38	1.0	$[\Phi_2PN][R_fCN]_2$	316	24	0.4	0.3	0.1	4.1	0.8
3B	Krytox 143AC	5.38	1.0	$[\Phi_2PN][R_fCN]_2$	316	24	0.0	0.0	0.0	3.9	0.7
5A	Krytox 143AC	3.46	1.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	1	n.d.[h]	n.d.	n.d.	n.d.	n.d.
5B	Krytox 143AC	2.64	1.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	24	6.5	5.8	2.5	71.7	27.2
6A	Krytox 143AC	3.36	1.0	$[(\Phi S)\Phi PN]_2[C_7F_{15}CN]$	316	2.2	n.d.	n.d.	n.d.	n.d.	n.d.
6B	Krytox 143AC	3.44	0.6	$[(\Phi S)\Phi PN]_2[C_7F_{15}CN]$	316	24	18.3	16.2	5.3	141.3	41.1
7A	Krytox 143AC	3.96	1.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	4	n.d.	n.d.	n.d.	n.d.	n.d.
7B	Krytox 143AC	4.03	0.7	$[(\Phi S)\Phi PN]_2[R_fCN]$	316	24	4.2	6.0	1.0	68.5	17.1
41	Fomblin Z	3.84	-	none	288	8	51.1	17.2	13.3	2235	582
61	Fomblin Z	2.82	1.0	$[\Phi_2PN][R_fCN]_2$	288	24	0.9	0.8	0.4	2.4	0.9
8A	Fomblin Z	6.10	2.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	288	8	2.7	2.6	0.4	8.4	1.2
8B	Fomblin Z	5.13	2.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	288	8	0.8	0.8	0.2	6.8	1.3
8C	Fomblin Z	3.13	2.0	$[(\Phi S)\Phi PN]_2[R_fCN]$	288	8	n.d.	n.d.	n.d.	6.7	2.1

[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] In the A series of tests, untreated fluid admixed with the additive was utilized; in the B and C tests, the filtered residue from the preceding test was utilized. In test 3 no filtration was employed. In tests 2B, 6B, and 7B some fluid was replenished thus lowering the actual additive concentration.

[c] The percent is weight percent of additive per weight of fluid used.

[d] Percent of oxygen available.

[e] Oxygen consumed in mg/g fluid employed.

[f] Products formed in mg/g fluid employed.

[g] The R_f corresponds to $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

[h] Not determined.

atmosphere. The filtrate was then re-exposed to the elevated temperature, oxygen, and a new coupon for 24 hr. It was hoped that the pretreatment will prevent the precipitate formation on further heating. Unfortunately, this was not the case. Based on the degradation data, discussed previously, one would not expect 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoroalkylether-2,4,6-triazine to exhibit any effectiveness as a corrosion and oxidation inhibitor at 316°C, due to its thermal instability at these temperatures. The results obtained indicate that the phospha-s-triazine degradation products, most likely the phosphorus-containing portion, are the active ingredients and that these can continue to function at elevated temperatures.

At the lower temperature, 288°C, in Fomblin Z, the thiophenyldiphospha-s-triazine was found to arrest drastically the fluid's degradation as compared to the parallel experiment conducted in its absence (see Tests No. 8A, B, C, and 41). The action lasted for at least 24 hr. It should be noted that no precipitate was observed in the fluid after Test No. 8C; furthermore, the products formed consisted essentially of the perfluoroalkylether nitrile. Based on these results, the thiophenyldiphospha-s-triazines can be considered as useful additives for Fomblin Z fluids, inasmuch as at 316°C the effectiveness of the diphenyl analogues is also, at best, marginal [4].

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 DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. The thiophenyl-substituted phospha-s-triazines were analyzed by GC using a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The apparatus used for the determination of the anticorrosion and antioxidation action of the materials developed was a modified, scaled-down version of the AFML Micro-O-C-Test arrangement [13].

Degradation studies

The degradation investigations were performed in sealed Pyrex 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 *via* a long stemmed funnel. 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 -78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and gas chromatography, and, if applicable, also combined gas chromatography/mass spectrometry (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 and subjected to infrared spectral analyses, gas chromatography, and GC-MS.

Syntheses of thiophenylphospha-s-triazines

The procedure utilized was essentially identical for all the compounds. For illustration, the preparation of 1,3-bis-[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine (I) is given in detail.

In an inert atmosphere enclosure, to a stirred solution of 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine (2.00 g, 2.82 mmol) in tetrahydrofuran (10 ml) at room temperature, was added a solution of thiophenol (0.62 g, 5.64 mmol) and triethylamine (0.57 g, 5.64 mmol) in tetrahydrofuran (15 ml) over a period of 30 min. An immediate reaction was observed with formation of a white precipitate. After stirring at room temperature for 20 hr, the reaction mixture was filtered giving triethylamine hydrochloride (0.68 g, 88% yield) and a pale yellow filtrate. Removal of solvents in vacuo from the filtrate gave a pale yellow liquid which was redissolved in Freon-113 and passed through a 1.0 x 4.0 cm column of neutral Woelm alumina. The solid, which formed on standing after solvent removal, was recrystallized from hot hexane to give 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine (1.72 g, 71% yield), mp 89-91°C. Anal. calcd. for $C_{32}H_{20}F_{15}N_3S_2P_2$: C, 44.82; H, 2.35; F, 33.23; N, 4.90; S, 7.48; P, 7.22; MW, 857.58. Found: C, 44.70; H, 2.37; F, 33.98; N, 4.96; S, 7.68; P, 7.21; MW, 881.

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