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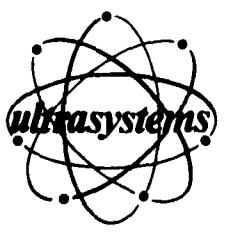
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SYNTHESES OF PHOSPATRIAZINES FOR
POTENTIAL HIGH TEMPERATURE FLUIDS
AND ELASTOMERS APPLICATIONS

Contract No. F49620-79-C-0037

Final Report, SN-8340-F

30 April 1982

Ultrasystems, Inc.
2400 Michelson Drive
Irvine, California 92715

K. L. Paciorek, T. I. Ito, J. H. Nakahara,
D. H. Harris, and R. H. Kratzer

Air Force Office of Scientific Research
Directorate of Chemical Sciences
Bolling Air Force Base
Washington, D.C. 20332

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#20. The symmetrical and unsymmetrical tetraazacyclooctatetraenes were found to be thermally less stable than the analogously substituted six-membered phospho-s-triazines. Both materials at 316°C underwent transformation to phospho-s-triazines; the symmetrical arrangement giving diphospho-s-triazine and the corresponding nitrile; the unsymmetrical isomer forming monophospho-s-triazine and diphenylphosphazene trimer. No polymeric compounds could be synthesized having the symmetrical octatetraene ring arrangement as a chain component; only bicyclics were formed. Unsymmetrical polydiphosphatetraazacyclooctatetraenes having thermal and thermal oxidative stabilities directly comparable to those of their monomeric analogues were successfully prepared.

Two polymeric systems involving phospho-s-triazine units were synthesized: poly[monophospho-s-triazines] and monocyclic mono- and diphospho-s-triazines substituted by polyperfluoroalkylether chains on the ring carbon atoms. The latter materials had molecular weights of ~ 5000 and exhibited good thermal and oxidative stability. The molecular weight of poly(monophospho-s-triazines) was ~ 7000; these materials were found to undergo some degradation at 235°C in air.

A novel bis(trichlorophosphorane) intermediate, necessary for the preparation of aryl-linked dumbbell- and poly-(monophospho-s-triazines), was synthesized by a 4-step process in an overall 58% yield. The interaction of the bis(trichlorophosphorane) with perfluoroalkyl- and perfluoroalkyletherimidoylamidines afforded the desired phenyl-bridged dumbbell monophospho-s-triazines. Electron impact fragmentation patterns of these compounds could be correlated with those of the monomeric monophospho-s-triazines. The thermal and thermal oxidative stability of the phenyl-bridged materials was lower than that of the corresponding monomeric mono- and diphospho-s-triazines.

All the six- and eight-membered heterocyclics synthesized under this program were found to possess antioxidative and anticorrosive properties when utilized as additives for poly(hexafluoropropene oxide) fluids in the presence of M-50 alloy. The polyperfluoroalkylether-substituted phospho-s-triazines were the most effective of the compositions tested. A monophospho-s-triazine was the only member of the series evaluated as an additive in Fomblin Z and E-fluids, where it exhibited better action than that shown by other types of additives.



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FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. under Contract F49620-79-C-0037, "Syntheses of Phosphotriazines for Potential High Temperature Fluids and Elastomers Applications". The investigations were carried out during the period 1 March 1979 to 28 February 1982 by T. I. Ito, J. H. Nakahara, D. H. Harris, R. H. Kratzer, and K. L. Paciorek, Project Manager. This contract was administered by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, with Dr. Anthony J. Matuszko as Technical Program Manager.

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1. ABSTRACT

The eight-membered heterocyclics, 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene and 1,3-bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene were found to be thermally less stable than the analogously substituted phospho-s-triazine. Both materials at 316°C underwent transformation to phospho-s-triazines; the symmetrical arrangement giving diphospho-s-triazine and the corresponding nitrile; the unsymmetrical isomer forming monophospho-s-triazine and diphenylphosphazene trimer. No polymeric compounds could be synthesized having the symmetrical octatetraene ring arrangement as a chain component; only bicyclics were formed. Unsymmetrical polydiphosphatetraazacyclooctatetraenes having thermal and thermal oxidative stabilities directly comparable to that of their monocyclic analogues were successfully prepared.

Two polymeric systems involving phospho-s-triazine units were synthesized: poly[1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazines] and monocyclic mono- and diphospho-s-triazines substituted by polyperfluoroalkylether chains on the ring carbon atoms. The latter materials had molecular weights of ~ 5000 and exhibited good thermal and oxidative stability. The molecular weight of poly(monophospho-s-triazines) was ~ 7000; these materials were found to undergo some degradation at 235°C in air. Comparison of the degradation data with that of the corresponding dumbbell compounds indicated the low thermal stability to be associated with the polymerization process.

A novel bis(trichlorophosphorane) intermediate, $\text{Cl}_3\text{P}(\text{C}_6\text{H}_5)\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)\text{Cl}_3$, necessary for the preparation of aryl-linked dumbbell and poly(monophospho-s-triazines), was synthesized by a 4-step process in an overall 58% yield. The interaction of the bis(trichlorophosphorane)

with perfluoroalkyl- and perfluoroalkyletherimidoylamidines afforded the desired phenyl-bridged dumbbell monophospha-s-triazines. Electron impact fragmentation patterns of these compounds could be correlated with those of the monomeric monophospha-s-triazines. The thermal and thermal oxidative stability of the phenyl-bridged materials was lower than that of the corresponding monomeric mono- and diphospha-s-triazines.

All the six- and eight-membered heterocyclics synthesized under this program were found to possess antioxidative and anticorrosive properties when utilized as additives for poly(hexafluoropropene oxide) fluids in the presence of M-50 alloy. The polyperfluoroalkylether-substituted phospho-s-triazines were the most effective of the compositions tested. 1-Diphenylphospha-3,5-bis[C₃F₇OCF(CF₃)CF₂OCF(CF₃)]-2,4,6-triazine was the only member of the series evaluated as an additive in Fomblin Z and E-fluids, where it exhibited better action than that shown by other types of additives.

2. INTRODUCTION

Under Contract No. F44620-76-C-0065, novel six- and eight-membered heterocyclics containing carbon, nitrogen, and phosphorus ring atoms were synthesized [1-5]. The phospho-s-triazines, when substituted by phenyl groups on the phosphorus and perfluoroalkylether groups on the ring carbons, were found to exhibit good thermal and oxidative stabilities [6], as well as antioxidative and corrosion-inhibiting action when utilized as additives in other fluorinated fluids in the presence of metals. No investigations regarding these characteristics were carried out on the octatetraenes analogues. Perfluoroalkyl and perfluoroalkylether-bridged dumbbell compounds were prepared [4,5]; the corresponding phenyl-bridged compounds have not been investigated to date.

In actual applications, high molecular weight materials, both as fluids and additives, offer many advantages as compared to the relatively low molecular weight compounds developed under Contract No. F44620-76-C-0065. Accordingly, the major effort under the current program was directed to extend the phosphotriazine and phosphatetraazaooctatetraene technologies to high molecular weight systems. Understanding the behavior of monomeric materials at elevated temperatures permits potential stability deductions for the corresponding polymeric compositions. Thus, degradation studies of the novel compounds obtained formed an important aspect of this investigation.

3. RESULTS AND DISCUSSION

3.1 Diphosphatetraazacyclooctatetraenes Stability Investigation

The syntheses of the two isomer eight-membered ring systems, namely the 1,5- and 1,3-diphosphatetraazacyclooctatetraenes, were accomplished under Contract No. F44620-76-C-0065. If one considers phospho-s-triazines to be equivalent to phosphazene trimers, then diphosphatetraazacyclooctatetraenes would be equivalent to the tetramers. Following this reasoning further, cyclooctatetraenes would be thus expected to exhibit better or at least comparable thermal stability to that of the phosphatriazines [7].

Based on the degradation data (Tables I and II) [8], the eight-membered ring compounds are thermally markedly less stable than the six-membered analogues. Furthermore, contrary to expectations, the symmetrical isomer, 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, I, was found to exhibit significantly lower thermal stability than the unsymmetrical cyclooctatetraene, II. Both of the isomers decomposed into phospho-s-triazines, i.e.,

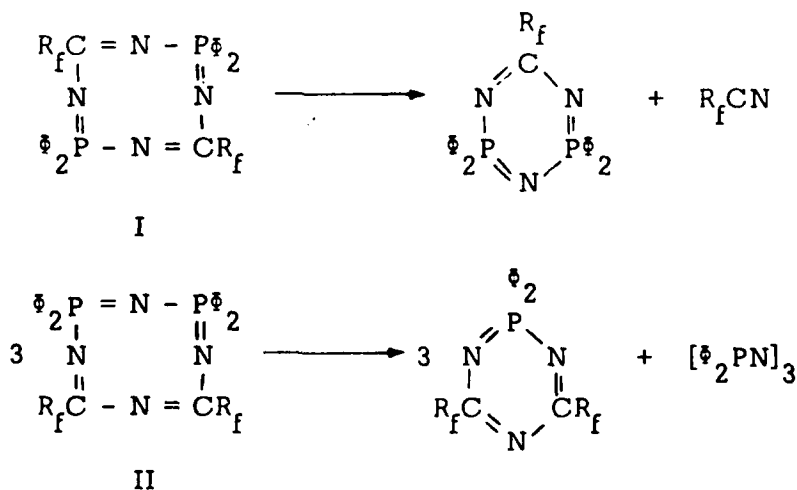


TABLE I
 DEGRADATIONS OF SYMMETRICAL AND UNSYMMETRICAL
 DIPHOSPHATETRAAZACYCLOOCTATETRAENES

Test No.	Compound ^a	Conditions ^b		Starting Materials		Oxygen Consumed	Volatile Products
		Temp °C	Atm	Used mg	Recovered % ^c	mg	% ^d
1	s-[R _f 'CN] ₂ [(Φ) ₂ PN] ₂	235	Air	458.5	79	0.1	1.8 4.2
2	s-[R _f 'CN] ₂ [(Φ) ₂ PN] ₂	316	N ₂	333.7	0.3	-	- 30.5
3	s-[R _f 'CN] ₂ [(Φ) ₂ PN] ₂	316	Air	377.6	0	1.7	26.7 48
4	u-[R _f "CN] ₂ [(Φ) ₂ PN] ₂	235	Air	357.5	87	0.1	2.1 1.0
5	u-[R _f "CN] ₂ [(Φ) ₂ PN] ₂	316	N ₂	364.1	13	-	- 5.5
6	u-[R _f "CN] ₂ [(Φ) ₂ PN] ₂	316	Air	249.1	25	2.5	8.2 4.5

a) R_f' = C₃F₇OCF(CF₃); R_f" = C₃F₇OCF(CF₃)CF₂OCF(CF₃).

b) All the tests were performed over a period of 24 hr.

c) Weight percent of starting material.

d) Percent of oxygen available.

TABLE II

 DEGRADATIONS OF SYMMETRICAL AND UNSYMMETRICAL
 DIPHOSPHATETRAAZACYCLOOCTATETRAENES:

MAJOR PRODUCTS FORMED

Test No.	Compound ^a	Cond.	$[R_f'CN]_2[\phi_2PN]_2$ % ^b	$[R_f'CN][\phi_2PN]$	$[R_f'CN][\phi_2PN]_2$	$[\phi_2PN]_3$ %	$\phi_2P(O)F$ %	$R_f'CN^c$ %	$R_f'H^c$ %	C_6H_6 %
1	s- $[R_f'CN]_2[\phi_2PN]_2$	235, Air	-	15	-	-	-	4.2	T	-
2	s- $[R_f'CN]_2[\phi_2PN]_2$	316, N ₂	-	69	-	-	T	30	0.3	0.2
3	s- $[R_f'CN]_2[\phi_2PN]_2$	316, Air	-	12	17	22	22	39	0.3	9
4	u- $[R_f''CN]_2[\phi_2PN]_2$	235, Air	13	-	?	-	-	0.1	T	-
5	u- $[R_f''CN]_2[\phi_2PN]_2$	316, N ₂	63	-	11	?	?	4.1	0.5	0.1
6	u- $[R_f''CN]_2[\phi_2PN]_2$	316, Air	59	-	12	?	?	3.7	0.3	0.1

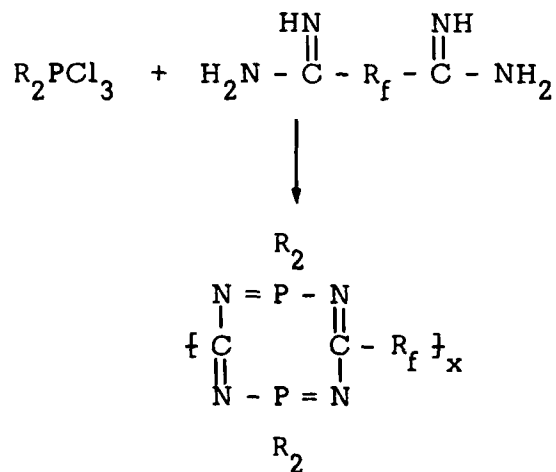
a) $R_f' = C_3F_7OCF(CF_3)$; $R_f'' = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$. b) Weight percent of starting material. c) R_f' is any perfluoroaliphatic or perfluoroalkylether group; in all the tests, the nitrile derived from the carbon atom substituent amounted to >95% of the perfluorinated nitriles identified and quantitated.

It should be noted that both of the isomers exhibited anticorrosive and antioxidative characteristics when utilized as additives in perfluoroalkyl-ether fluids.

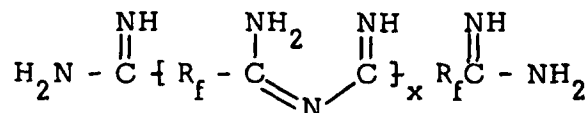
3.2 Polydiphosphatetraazacyclooctatetraenes

It was of interest to determine whether the low thermal stability found in the monomeric diphosphatetraazacyclooctatetraenes will persist in a polymer environment wherein the segment elimination is much more difficult than the liberation of monofunctional species due to the absence of volatile primary products and the possibly existing cage effects.

Based on the mechanism of formation of s-diphosphatetraazacyclooctatetraene, it was assumed that utilizing a diamidine, a polymeric system should result, i.e.,

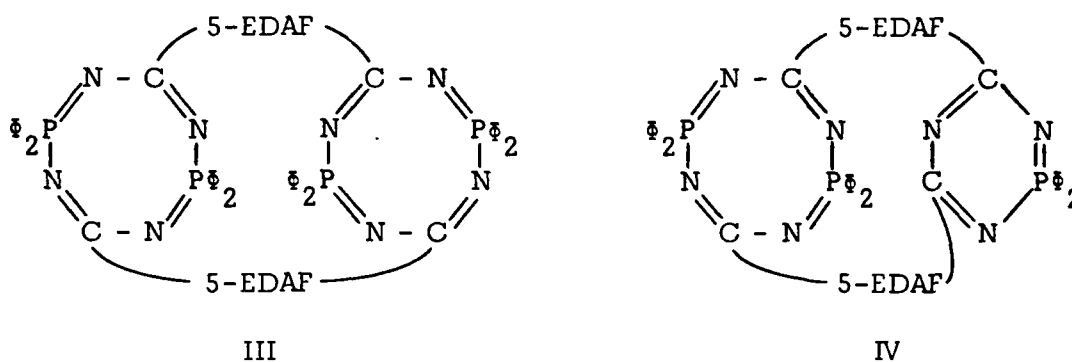


The production of polymeric species should not be prevented by the presence of the unavoidable imidoamidine linkages in the amidines, i.e.,



since in this case instead of poly(diphosphatetraazacyclooctatetraene), a poly(diphosphatetraazacyclooctatetraene-monophospha-s-triazine) would result.

Interaction of the imidoamidine/amidine mixture derived from 5-EDAF-dinitrile, $N\equiv CCF(CF_3)[OCF_2(CF_3)CF]_m O(CF_2)_5 O[CF(CF_3)CF_2O]_n - CF(CF_3)C\equiv N$ (wherein $m + n = 3$), with diphenyltrichlorophosphorane did not lead to polymerization. Based on elemental analysis, molecular weight determination, and infrared spectral analysis, a mixture of cyclic compounds, depicted by III and IV, formed the major portion of the products obtained.



It is thus obvious that this process does not lend itself to polymer synthesis. The thermal and thermal oxidative stability of the materials containing the *s*-diphosphatetraazacyclooctatetraene unit was even lower than that of the pure monomeric compounds (compare Tables I and III). After exposure to 235°C in air, based on infrared analysis, all the octatetraene rings were destroyed, not transformed into diphospho-*s*-triazines. These results show clearly that the involatile nature of the components not only does not prevent degradation but may actually alter the decomposition path leading to a more extensive breakdown.

The studies performed on the monocyclic octatetraenes showed the unsymmetrical isomers to be substantially more thermally stable than the symmetrical analogues [8]. The corresponding polymers, VI, were synthesized from polyimidoamidines, V, using the reaction sequence given below:

TABLE III
 DEGRADATION OF SYMMETRICAL AND UNSYMMETRICAL
 POLYDIPHOSPHATE TRAZACYCLOOCTALTRAINES

Compound	Conditions ^a		Starting Material mg	Residue MW	Oxygen Consumed mg	Total Formed mg	Volatile		
	Temp °C	Atm					CO mg	C ₆ H ₆ mg	Other mg
s-poly(s-EDAF-C ₂ N ₄ P ₂)} 4 2 4 }	235	Air	445.6	2030	6.1	23.9	0.1	2.7	21.2
s-poly(s-EDAF-C ₂ N ₄ P ₂)} 4 2 4 }	316	N ₂	468.8	n.d. ^d	n.a. ^e	116.4	0.1	12.4	104.0
s-poly(s-EDAF-C ₂ N ₄ P ₂)} 4 2 4 }	316	Air	459.6	n.d.	6.1	104.8	0.3	35.0	69.8
u-poly(s-EDAF-C ₂ N ₄ P ₂)} 4 2 4 }	235	Air	481.5	7150	0.0	0.5	-	Trace	0.5
u-poly(s-EDAF-C ₂ N ₄ P ₂)} 4 2 4 }	316	N ₂	467.6	2450	n.a.	15.4	0.1	0.5	14.9

a) All the tests were performed over a period of 24 hr.

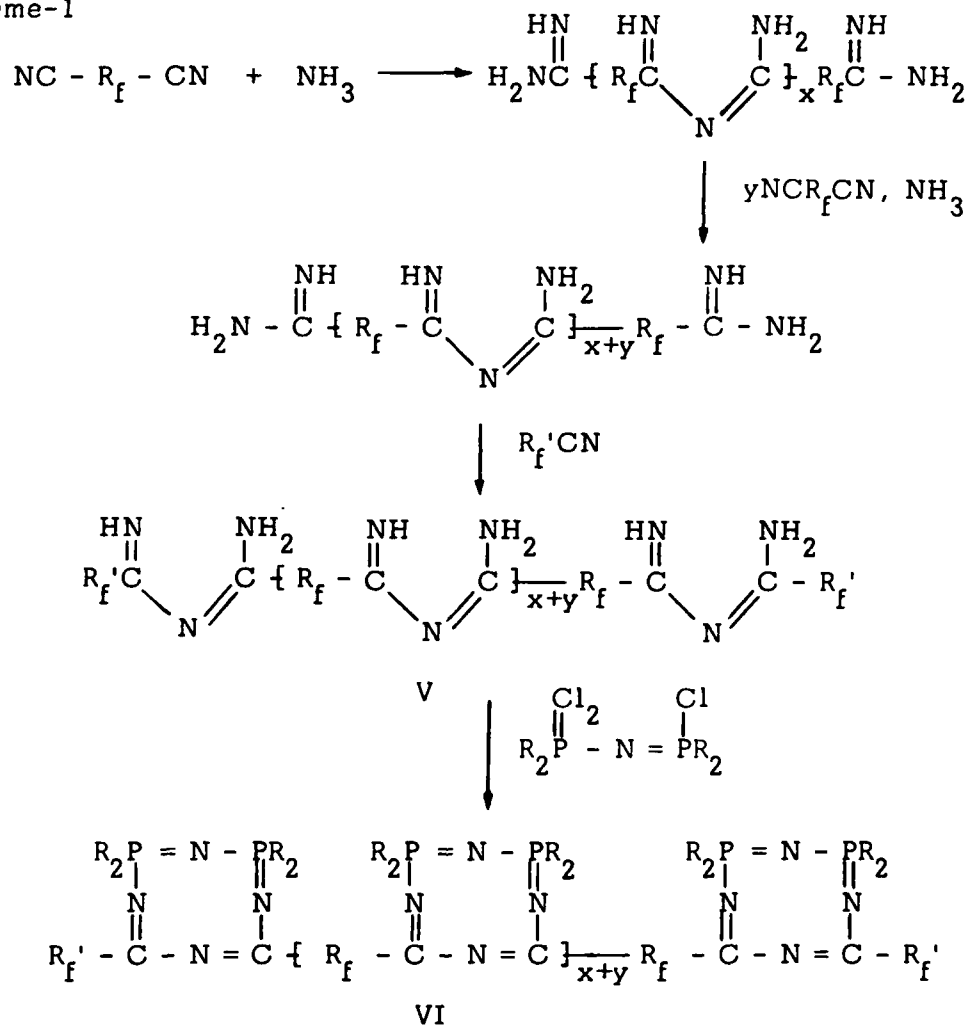
b) Percent of oxygen available.

c) Weight percent of starting material.

d) Not determined.

e) Not applicable.

Scheme-1



$\text{R}_f = \text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_m \text{O}(\text{CF}_2)_5 \text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n \text{CF}(\text{CF}_3)$, $m + n = 3$

The abbreviation used for this segment is 5-EDAF.

$\text{R}'_f = \text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)$

The poly-u-diphosphatetraazacyclooctatetraenes thus obtained exhibited thermal and thermal oxidative behavior directly comparable to that of the corresponding monocyclic compounds. At 235°C , the oxygen up take, if any, was minimal and the same applied to molecular weight lowering and volatiles production showing virtual absence of degradation

(compare Tables I and III). However, at 316°C a definite drop in molecular weight took place and, as shown by infrared spectral examination, all the octatetraene rings were transformed into monophospha-s-triazine moieties, via elimination of $(C_6H_5)_2PN$ units, in agreement with the results obtained for the monocyclic analogues.

It is obvious from the above studies of symmetrical and unsymmetrical octatetraenes that the eight-membered ring compounds are thermally unstable. Consequently, materials containing these rings cannot be considered for any elevated temperature applications. Of the two isomeric structures, the unsymmetrical arrangement exhibits definitely better thermal and thermal oxidative stability, both in monocyclic and polymeric materials, than the symmetrical system.

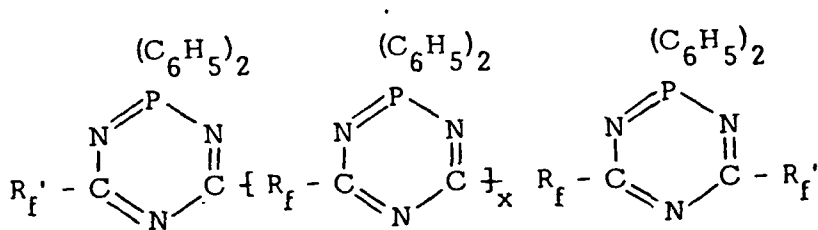
3.3 Phospha-s-Triazine Derived Polymers

One can visualize phospha-s-triazine polymers as arrangements of rings joined by chains or as single ring compounds substituted by very long side chains. The former concept is the more conventional and one which could lead to high molecular weight compositions. On the other hand, this approach requires that the ring closing process proceeds to completion and that the polymers are capped by unreactive end groups. The second system necessitates conducting all the reactions on polymeric materials. Consequently, in both instances incompleteness of any given process would be expected to result in low stability of the final product. To assess the advantages of either one of these arrangements, it appeared best to synthesize the representative materials and determine their thermal and oxidative stabilities in addition to their applicability as antioxidants and anticorrosion additives for perfluoroalkylether fluids.

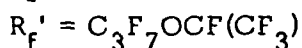
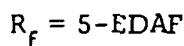
3.3.1 Poly(perfluoroalkylether)monophospha-s-triazines

In the preparation of the poly(imidoylamidine) precursor, both the addition of the bis-amidine to the dinitrile and the dinitrile to the bis-

amidine were employed. To ensure amidine termination, the product was treated with ammonia, followed by treatment with monofunctional perfluoroalkylether nitrile to provide the unreactive end groups. The overall sequence was given in Scheme-1 in Section 3.2. Here the ring closure was accomplished via reaction with diphenyltrichlorophosphorane, giving the arrangement VII.



VII



The molecular weights of the final products (7200, 6800) appear to be independent of the addition mode employed in the synthesis of the imidoamidine precursor. As evident from Table IV, both materials exhibited lower thermal and thermal oxidative stability than that found for the corresponding monomeric analogues [6]. The observed discrepancy in the thermal behavior between the two systems could be caused by the possible presence of a CF_2 group adjacent to the ring derived from the potential 5-EDAF isomer, $-CF_2(CF_2)_3O[CF(CF_3)CF_2O]_4CF(CF_3)-$. No easy tests are available [9] to determine the presence and relative quantity of this isomer in, e.g., 5-EDAF-dinitrile, and furthermore, even if this isomer was found to be present, it cannot be unequivocally assumed that the CF_2 -group adjacent to the ring is the cause of the lowered thermal stability. To prove whether indeed the lowered thermal stability is due to the 5-EDAF group, the dumbbell compound VIII, wherein the two rings are joined by the 5-EDAF link, was synthesized from imidoamidines

TABLE IV
DEGRADATION OF POLYMONOPHOSPHIA-S-TIAZINES

Test No.	Conditions ^a		Starting Material		Residue		Oxygen Consumed		Volatiles Total Formed	
	Temp °C	Atm	mg	MW	% ^b	MW	mg	% ^c	mg	% ^b
1 ^d	235	Air	527.7	7200	96.9	4800	1.42	22.5	15.2	2.9
2 ^d	316	Air	488.6	7200	92.5	1600	4.61	72.1	47.5	9.7
3 ^d	316	N ₂	491.8	7200	94.2	1900	-	-	29.8	6.1
4 ^d	235	Air	459.9	6800	98.5	4800	1.08	16.6	5.2	1.1
5 ^d	316	Air	476.1	6800	91.8	1600	5.31	84.0	45.4	9.5
6 ^d	316	N ₂	532.7	6800	93.9	2400	-	-	28.7	5.4
7 ^e	235	Air	553.5	2230	99.4	2210	0.0	0.0	2.8	0.5
8 ^e	235	Air	634.2	2220	99.3	2210	0.0	0.0	4.2	0.7
9 ^e	235	Air	559.2	2050	99.6	2040	0.0	0.0	2.1	0.4
10 ^e	235	Air	601.3	2040	99.7	2020	0.0	0.0	1.7	0.3

a) All the tests were performed over a period of 24 hr.

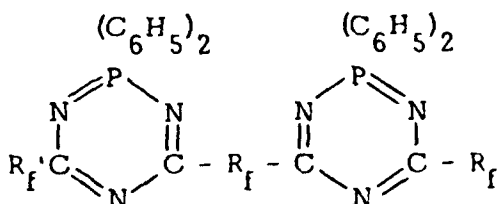
b) Weight percent of starting material.

c) Percent of oxygen available.

d) Tests 1-3 were carried out using the polymer prepared from polyimidoylamidine obtained by adding 5-EDAF-bisamide to the corresponding dinitrile; the polyimidoylamidine employed in Tests 4-6 was formed by the reverse addition.

e) Tests 7-10 were carried out on dumbbell materials. The compounds utilized in experiments 7 and 8 were obtained from an imidoylamidine prepared via reaction of 5-EDAF-bisamide with C₃F₇OCF(CF₃)CN; compounds utilized in experiments 9 and 10 were prepared via reaction of C₃F₇OCF(CF₃)C(=NH)NH₂ with 5-EDAF-dinitrile. Purification in Tests 7 and 9 was accomplished via filtration through neutral Woelm alumina; in Tests 8 and 10, acidic Woelm alumina was employed.

obtained by the two different addition procedures.



VIII

$R_f = 5\text{-EDAF}$

$R_f' = \text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)$

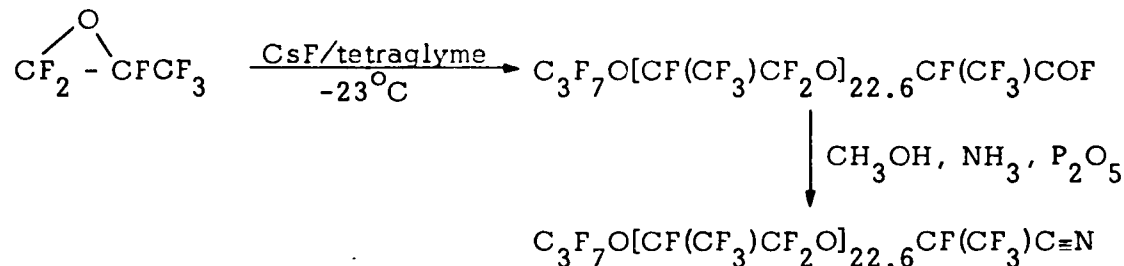
The dumbbell compounds exhibited thermal oxidative stability, at least at 235°C (see Table IV), comparable to that of the monomeric compounds [6]. Consequently, it must be deduced that the low stability of the polymonophospha-s-triazines must be due to some aspect of the polymerization process resulting in the formation of weak links.

3.3.2 Monomeric phospho-s-triazines carbon substituted by polymeric perfluoroalkylether chains

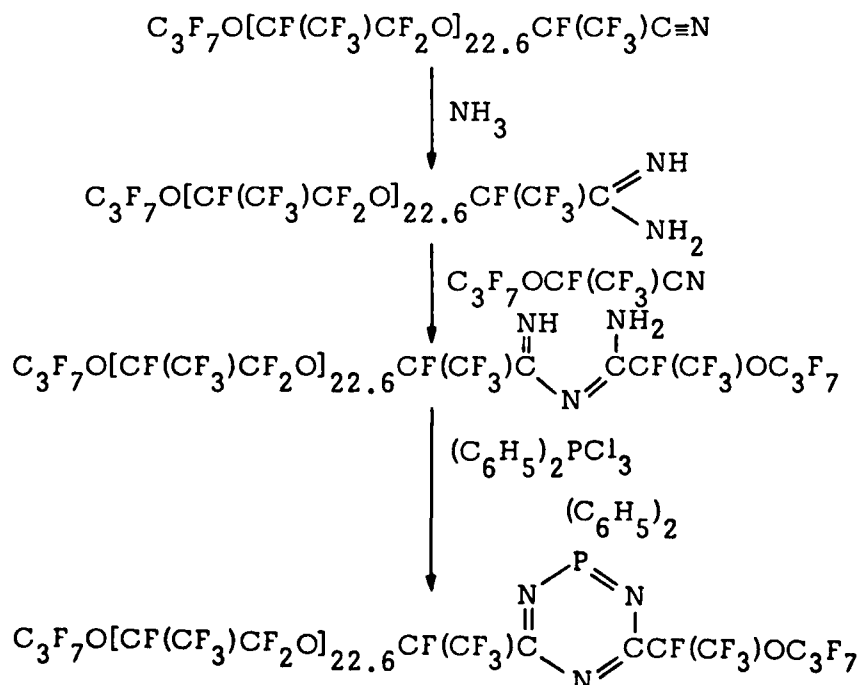
Monophospha- and diphospha-s-triazine substituted on the ring carbon atoms by poly(hexafluoropropene oxide) chains of the general formula $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_x\text{CF}(\text{CF}_3)-$ ($x = 1$ or 2) were found to exhibit good thermal and oxidative properties in addition to providing an antioxidative and anticorrosive protection when utilized as additives to Krytox fluids in the presence of M-50 alloy [1,2]. However, in view of their relatively low molecular weight, these materials were not suited as high temperature fluids. Furthermore, it was of interest to determine whether these types of phospho-s-triazines, wherein the ring itself constitutes only a very small portion of the molecule, will still possess the anticorrosive and antioxidative properties. In view of the availability of the low temperature, high yield synthesis process, originally developed for the preparation of the eight-membered ring compounds, the purification via distillation became

unnecessary and the synthesis of materials where $x \sim 23$ became feasible.

The preparation of the long chain acid fluorides directly from hexafluoropropene oxide, followed by transformation to the nitrile, was carried out utilizing the previously-described procedures [10,11]. The reaction scheme is given below:



To obtain the monophospha-s-triazine substituted by the long chain perfluoroalkylether on one carbon and by the short chain ether, $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)-$ on the other, the above nitrile was transformed into an amidine which was then treated with the short chain nitrile, $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CN}$. The ring closure was subsequently affected by reaction with diphenyltrichlorophosphorane, i.e.:



stipulation (see Table V). Both the monophospha- and diphospha-s-triazines containing only one polymeric perfluoroalkylether substituent exhibited very good thermal and oxidative stabilities as shown by the data given in Table V.

It would thus appear from these studies that the poly(hexafluoropropene oxide) units capped by phospho-s-triazine rings offer much better candidates for high temperature fluids and fluid additives (this to be discussed in Section 3.5) than poly(monophospha-s-triazines).

3.4 Phenyl-Bridged Phospha-s-Triazines

Poly(monophospha-s-triazines) prepared to date were linked by perfluoroalkyl and perfluoroalkylether groups [4,5]. To form aryl-linked systems required the use of the unknown bis(trichlorophosphoranes). In the early sixties, Evleth, et al. [12] was able to synthesize $\text{ClCH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Cl}$. The major aspect of the concept to form the aryl-linked poly(monophospha-s-triazines) was the feasibility of the synthesis of the intermediate $\text{Cl}(\text{C}_6\text{H}_5)\text{P}-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)\text{Cl}$. The visualized reaction sequence leading to bis(trichlorophosphorane) is given below:

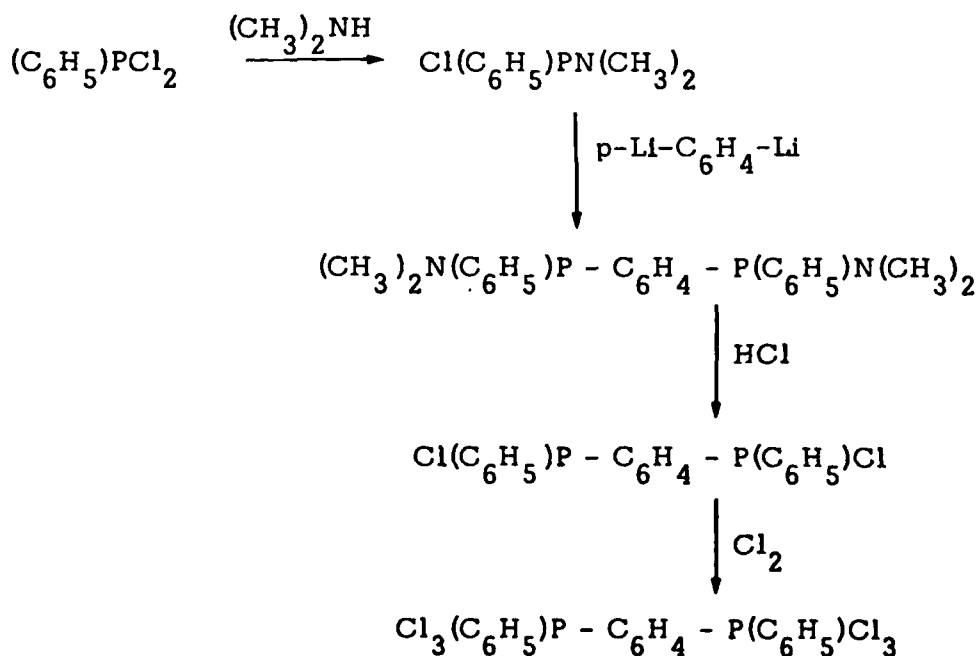


TABLE V
 DEGRADATION OF POLY(HEXAFLUOROPROPENE OXIDE) SUBSTITUTED MONO- AND DIPHOSPHA-S-TRIAZINES

Material	Conditions ^a		Starting Material mg	Residue % ^b	MW	Oxygen		Volatiles				
	Temp °C	Atm				Consumed mg	% ^c	Total Formed mg	% ^b	Type R _x CN _y	C ₆ H ₆	
[(poly HFPO)CN]₂[(Φ₂PN)₂] ^e	235	Air	563.2	99.9	4700	0.0	0.0	0.5	0.1	-	0.09	0.01
-ditto-	316	Air	394.3	98.6	4700	0.3	0.8	5.0	1.3	0.01	0.16	0.10
-ditto-	316	N₂	378.3	99.7	4700	-	-	1.2	0.3	-	0.16	0.02
[(poly HFPO)CN]₂[(Φ₂PN)₂] ^f	235	Air	637.7	99.9	4700	0.0	0.0	0.6	0.1	-	0.003	0.02
-ditto-	316	Air	292.5	98.5	4700	2.3	7.3	4.1	1.4	-	0.01	0.53
-ditto-	316	N₂	299.8	99.1	4700	-	-	2.2	0.7	-	0.07	0.19
[(poly HFPO)CN]₂[(Φ₂PN)₂] ^g	235	Air	496.9	99.96	5000	0.0	0.0	0.1	0.02	-	-	-
-ditto-	316	Air	432.3	99.5	5000	0.6	2.0	2.1	0.5	0.01	0.13	0.16
-dit o-	316	N₂	446.0	99.5	5000	-	-	0.9	0.2	-	0.06	0.09

a) All the tests were performed over a period of 24 hr.

b) Weight percent of starting material.

c) Percent of oxygen available.

d) P_xCN corresponds to perfluoroalkyl and perfluoroalkylether nitrile.

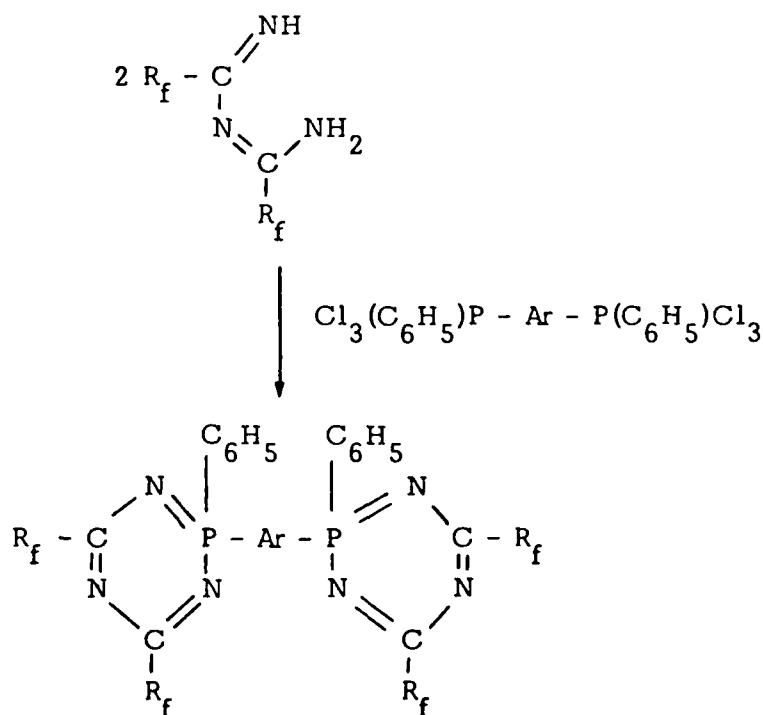
e) [(poly HFPO)CN]₂[(HFPO)₂CN]₂[(Φ₂PN)₂] represents 1-diphenylphospha-3-(C₃F₇O)(CF₃)CF₂O-CF(CF₃)-5-(C₃F₇OOCF(CF₃))-2,4,6-triazine.

f) [(poly HFPO)CN]₂[(Φ₂PN)₂] represents 1,3-bis(diphenylphospha)-5-(C₃F₇O)(CF₃)CF₂O-CF(CF₃)-2,4,6-triazine.

g) [(poly HFPO)CN]₂[(Φ₂PN)₂] represents 1-diphenylphospha-3,5-bis(C₃F₇O)(CF₃)CF₂O-CF(CF₃)-2,4,6-triazine.

Phenyldichlorophosphine is available commercially, dimethylamino-phenylchlorophosphine was prepared by Evleth, et al. [12], the next three compounds have not been described in the literature. Under the current program, dimethylaminophenylchlorophosphine was obtained in 93% yield; the subsequent intermediate was afforded in an essentially quantitative yield. The next 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 imidoamidines gave the phenyl-bridged dumbbell monophospho-s-triazines.



The properties of the perfluoroalkyl and perfluoroalkylether substituted representative members of the series are given in Table VI. In good agreement with previous findings, the material where $\text{R}_f = n\text{-C}_7\text{F}_{15}$ was a solid, whereas the compound where $\text{R}_f = \text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)$ was a liquid at room temperature. The mass spectra of the two compounds

TABLE VII
 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

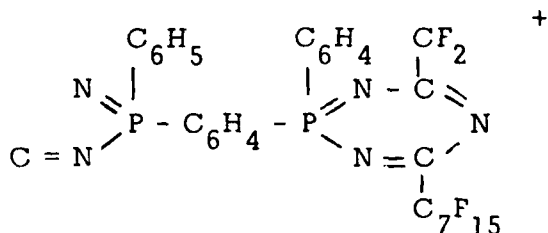
m/e	% of base peak	m/e	% of base peak	m/e	% of base peak
31	6.5	93	4.4	219	3.9
32	12.5	95	5.0	228	3.2
39	4.6	96	4.0	247	4.3
41	10.0	97	8.1	259	11.8
43	10.2	100	16.0	261	3.6
44	32.2	102	4.7	278	5.0
50	10.6	107	3.9	281	3.0
51	8.9	109	3.1	303	16.2
52	9.2	113	3.6	304	3.3
53	3.0	116	3.2	305	19.6
55	9.8	119	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.	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.

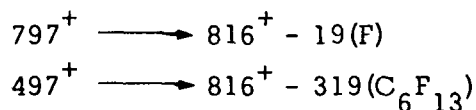
TABLE VIII
 ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE PEAK OF
 1,4-BIS[1-PHENYLPHOSPHA-3,5-BIS(PERFLUOROALKYLETER)-
 2,4,6-TRIAZINO]BENZENE^{a,b}

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

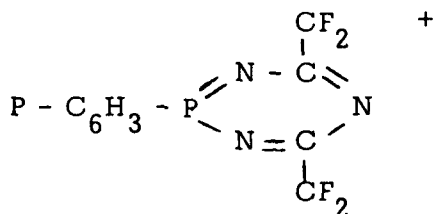
- a) The perfluoroalkylether group, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$
 b) Peaks having intensities less than 3% of the base peak
 below m/e, 900 are not reported.



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.,

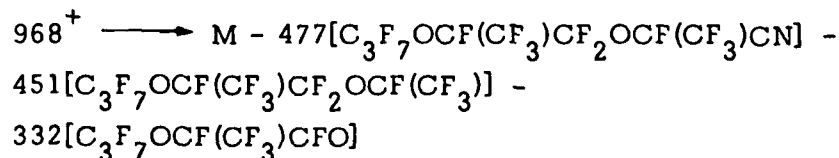


It is quite probable that the 305⁺ and 197⁺ ions are also derived from the 816⁺ ion. The possible arrangement for the 305⁺ ion is given below:

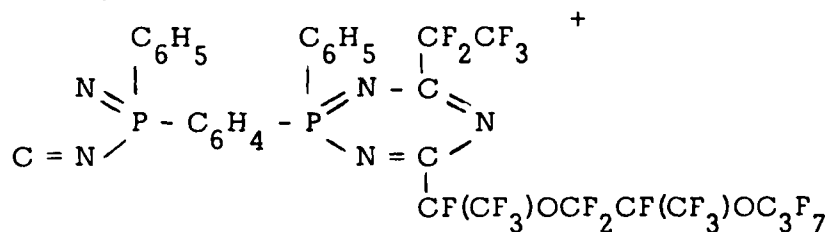


The loss of the fragment C₆H₃-P would then afford the 197⁺ ion.

The mass spectrum of the perfluoroalkylether-substituted analogue (Table VIII) 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 monophospho-s-triazines and 1,4-bis[1-phenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazino] benzene, is most likely derived by a process:



giving the arrangement:



The thermal and thermal oxidative stabilities of the phenyl-bridged materials, as evident from the data given in Table IX, are significantly lower than those of the analogously-substituted monophospha-s-triazines. 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 surprising.

The phenyl-bridged materials did exhibit antioxidant and anticorrosive properties when used as additives in perfluoroalkylether fluids (Section 3.6).

Preparation of polymers via the condensation of bis(imidoamidine) and bis(trichlorophosphorane) following the sequence given below:

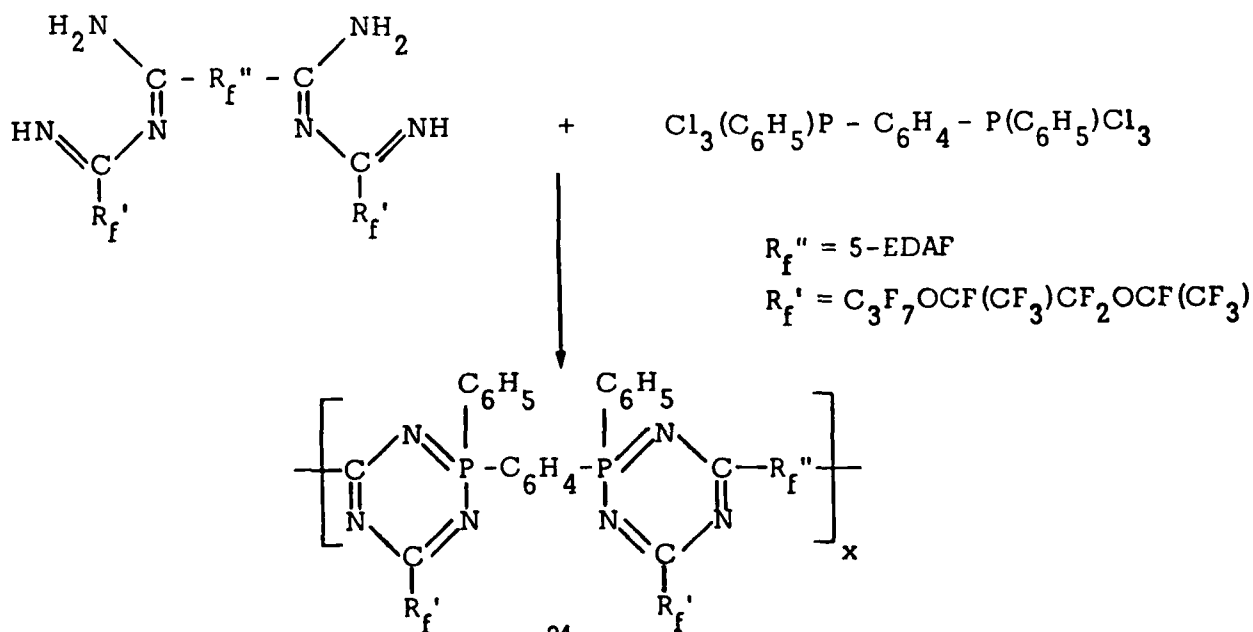


TABLE IX
 DEGRADATIONS OF PHENYL-BRIDGED DUMBELL MONOPHOSPHA-S-TRIAZINES

Test No.	Material ^a	Duration of test hr	Temp °C	Atm.	Starting Materials		Oxygen Consumed mg	Oxygen Consumed % ^c	Total Formed mg	Volatile Products			
					Used mg	Recovered % ^b				CO % ^b	R _f CN % ^b	C ₆ H ₆ % ^b	
2	Ar{(R _f CN) ₂ (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 _f CN) ₂ (PN)} ₂	24	316	N ₂	302.5	74	-	-	19.6	6.5	0.02	5.6	0.01
6	Ar{(R _f CN) ₂ (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 _f CN) ₂ (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 (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 (PN)} ₂	24	316	N ₂	400.2	14	-	-	135.	33.8	0.00	31.4	?

a) R_f = C₃F₇OCF(CF₃)CF₂OCF(CF₃) ; Ar = C₆H₄ ; R_f' = n-C₇F₁₅ ; Ø = C₆H₅.

b) Weight percent of starting material.

c) Percent of oxygen available.

afforded a material which had a molecular weight of 6850. Based on the molecular weight, x must be equal to ~ 3 . The unavoidable presence of ~ 10 mole percent of the monomeric imidoamidine, derived from the perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, is probably partly responsible for the low molecular weight attained. Although, if this end-capping reaction was the only chain termination process, molecular weight of an order of 20,000 could be expected. In view of the low molecular weight attained and in conjunction with the relatively low thermal and oxidative properties of the monomeric "model" compounds, no further effort was expended to optimize the polymerization reaction.

3.5 Anticorrosive/Antioxidative Action of Different Additives

All of the heterocyclics developed under Contract Nos. F44620-76-C-0065 and F49620-79-C-0037 exhibited anticorrosive and anti-oxidative action when used in poly(hexafluoropropene oxide) fluids, as represented by DuPont Krytox. However, to date no direct comparisons of these properties for the different six- and eight-membered heterocyclics were made. Furthermore, in view of the relatively ready availability of some of these materials, it was of interest to determine whether these compositions exhibit this type of action with pure hydrogen-terminated fluids such as Freon E-fluids, $C_3F_7O[CF(CF_3)CF_2O]_xCF(CF_3)H$, and the linear Fomblin-Z fluids. The results of all these tests, as well as the results of the P-3 ($[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2(C_6F_4)]_3P$) additive investigations, are presented in Table X. It should be noted that the tests involving Fomblin Z fluid were carried out under NASA sponsorship [14].

The comparison of the monomeric six- and eight-membered ring heterocyclics in Krytox fluids, based on the volatiles evolved, shows the unsymmetrical tetraazacyclooctatetraene (Example No. 6) to be most effective. The "polymeric" phospho-s-triazines wherein at least one of

TABLE X
COMPARISON OF ADDITIVES' ACTION ON
PERFLUOROALKYLETHER FLUIDS IN THE PRESENCE OF M-50 ALLOY
AT ELEVATED TEMPERATURES IN OXYGEN OVER A 24 HR PERIOD^a

Ex. No.	Fluid			Additive	Temp °C	Total Products Formed ^b	
	Type		g			mg	mg/g
1	Krytox	(MLO-71-6)	12.13	None	316	576.7	47.5
2	Krytox	(MLO-71-6)	13.28	1% P-3 ^c	316	3.3	0.2
3	Krytox	(MLO-71-6)	8.59	1% C ₂ PN ₃ ^d	316	6.1	0.7
4	Krytox	(MLO-71-6)	16.36	1% CP ₂ N ₃ ^e	316	12.7	0.8
5	Krytox	(MLO-71-6)	12.16	1% s-C ₂ P ₂ N ₄ ^f	316	34.9	2.9
6	Krytox	(MLO-71-6)	13.33	1% u-C ₂ P ₂ N ₄ ^g	316	1.8	0.1
7	Krytox	(MLO-71-6)	12.91	1% (poly HFPO) ₂ C ₂ PN ₃ ^h	316	1.7	0.1
8	Krytox	(MLO-71-6)	13.38	1% (poly HFPO)CP ₂ N ₃ ⁱ	316	2.4	0.2
9	Krytox	(MLO-71-6)	12.39	1% (poly HFPO) ₂ C ₂ PN ₃ ^j	316	2.0	0.2
10	Krytox	(MLO-71-6)	4.83	1% Ar(C ₂ PN ₃) ₂ ^k	316	6.3	1.3
11	Fomblin Z	(MLO-72-22)	4.24	None	316	total degradation	
12	Fomblin Z	(MLO-72-22)	4.08	1% P-3 ^c	316	1176.2	288.3
13	Fomblin Z	(MLO-72-22)	3.39	1% C ₂ PN ₃ ^d	316	535.1	157.8
14	Fomblin Z	(MLO-72-22)	3.34	None	288	1117.1	421.6
15	Fomblin Z	(MLO-72-22)	3.34	1% C ₂ PN ₃ ^d	288	1.1	0.3
16	Fomblin Z	(MLO-72-22)	3.57	1% P-3 ^c	288	3.4	0.9
17	Fomblin Z	(MLO-72-22)	4.14	1% Ar(C ₂ PN ₃) ₂ ^k	288	7.9	1.9
18	Freon E-7	(ELO-66-55)	1.16	None	288	1215.1	1047.5
19	Freon E-7	(ELO-66-55)	1.21	1% P-3 ^c	288	23.5	19.9
20	Freon E-7	(ELO-66-55)	1.10	1% C ₂ PN ₃ ^d	288	17.0	15.5

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) Products formed in mg/g of fluid used.

c) $(C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2(C_6F_4))_3P$.

d) 1-Diphenylphospha-3,5-bis[$(C_3F_7OCF(CF_3)CF_2OCF(CF_3))$]-2,4,6-triazine.

e) 1,3-Bis(diphenylphospha)-5-[$(C_3F_7OCF(CF_3)CF_2OCF(CF_3))$]-2,4,6-triazine.

f) 1,5-Bis(diphenylphospha)-3,7-bis[$(C_3F_7OCF(CF_3))$]-2,4,6,8-tetraazacyclooctatetraene.

g) 1,3-Bis(diphenylphospha)-5,7-bis[$(C_3F_7OCF(CF_3)CF_2OCF(CF_3))$]-2,4,6,8-tetraazacyclooctatetraene.

h) 1-Diphenylphospha-3-($C_3F_7O(CF(CF_3)CF_2O)CF(CF_3)$)-5-($C_3F_7OCF(CF_3)$)-2,4,6-triazine.

i) 1,3-Bis(diphenylphospha)-5-($C_3F_7O(CF(CF_3)CF_2O)CF(CF_3)$)-2,4,6-triazine.

j) 1-Diphenylphospha-3,5-bis[$(C_3F_7O(CF(CF_3)CF_2O)CF(CF_3))$]-2,4,6-triazine.

k) 1,4-Bis[1-phenylphospha-3,5-bis[$(C_3F_7OCF(CF_3)CF_2OCF(CF_3))$]-2,4,6-triazino]benzene.

the ring carbon atoms was substituted by a poly(hexafluoropropene oxide) chain, were found to be as effective as the best of the monomeric materials, including the P-3 additive, in preventing fluid degradation (Example Nos. 7-9). This is in particular surprising if one realizes that the phosphorus content of the "polymeric" monophospha-s-triazines (Example Nos. 7,9) is only ~ 0.5%.

Based on the values found, it would appear that in Fomblin Z and Freon E-fluids, the monophospha-s-triazines seem to have a more pronounced degradation-arresting action than the P-3 additive. This is especially evident with Fomblin Z fluid (compare Example Nos. 12 and 13; 15 and 16). It is noteworthy that in this instance at the lower temperature (288°C), the coupon recovered from the test where the monophospha-s-triazine was employed exhibited no visual signs of corrosion or film deposit. Some dark film deposit was observed in the experiment involving the P-3 additive. The phenyl-bridged dumbbell monophospha-s-triazine (Example Nos. 10 and 17) was not as effective an additive both in Fomblin Z and Krytox fluids as P-3 and the other heterocyclics investigated.

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6. "Phospha-s-triazines. VI. Polymeric Systems", to be submitted to the Journal of Fluorine Chemistry.
7. "Phospha-s-triazines. VII. Phenyl-Bridged Phospha-s-triazines", to be submitted to the Journal of Fluorine Chemistry.
8. Patent disclosure "Phenyl-Bridged Phospha-s-triazines", in preparation.

