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DIPHOSPHATETRAAZACYCLOOCTATETRAENES. I. SYNTHESES AND PROPERTIES

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SUMMARY

A series of novel eight-membered heterocycles containing 1,3 and 1,5 phosphorus arrangements were synthesized. The 1,5-diphosphatetraazacyclooctatetraenes were obtained from the interaction of perfluoroalkyletheramidines and trichlorophosphoranes; the 1,3-isomers were prepared from perfluoroalkyletherimidoylamidines and imido-tetraphenyl-diphosphinic acid trichloride. The two series of cyclooctatetraenes exhibited infrared spectral absorptions characteristic for the given positional arrangement. However, electron impact fragmentation patterns of the two ring systems were closely comparable.

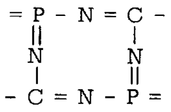
INTRODUCTION

The six-membered heterocycles as represented by mono- and diphospha-s-triazines [1-3] exhibit good thermal and thermo-oxidative characteristics and possess low pour points when substituted on the carbon atoms by perfluoroalkylether groups. In analogy with the phosphazenes [4-6], it appeared plausible that a hetero-system composed of two PN and two CN units in the ring structure will retain these desirable properties in addition to being less volatile due to the increased molecular weight.

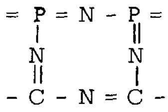
An eight-membered ring system composed of three different elements presents a number of potential isomeric structural arrangements. The current study was undertaken to develop synthetic procedures for preparing these isomers and to evaluate the effect of the position and the sequence of the ring atoms upon the cyclooctatetraene properties.

RESULTS AND DISCUSSION

Ignoring structures containing adjacent nitrogen atoms, one can visualize two arrangements for the tetraazacyclooctatetraenes, i.e.:

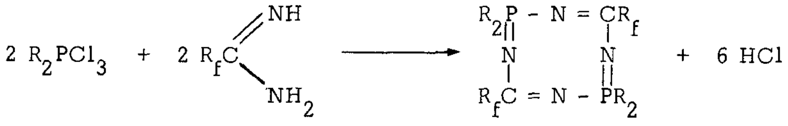


I

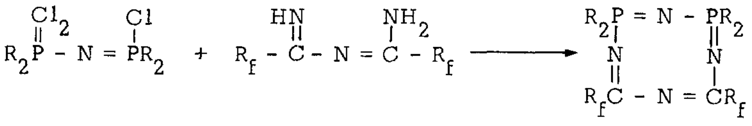


II

The process depicted below would be expected to give predominantly the 'symmetrical' isomer I:



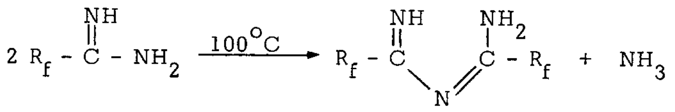
whereas utilizing imido-tetraphenyl-diphosphinic acid trichloride and a perfluoroalkylether imidoylamidine should assure production of the 'unsymmetrical' arrangement II:



Interaction of diphenyltrichlorophosphorane with the amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, in the absence of solvent at 108-132°C, in s-tetrachloroethane at 103°C, or in Freon-113-benzene-triethylamine at 50°C failed to afford the desired octatetraene of structure I as the sole product.

The last reaction condition gave the best yield of 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene. In each instance, significant amounts of the corresponding mono- and diphospha-s-triazines were formed simultaneously except when employing the short-chain amidine, $C_3F_7OCF(CF_3)C(=NH)NH_2$, in the presence of triethylamine. In this case, the yield of cyclooctatetraene was also low, but it was obtained free from phospha-s-triazines. The reason for the low yields of these symmetrical compounds of structure I is the possibly stepwise condensation of four multifunctional monomeric units to form the eight-membered ring. This type of process would be expected to permit side reactions to occur to a considerable degree. In addition, a low thermal stability of the desired end product or an instability of reactants or intermediates would naturally affect the yield.

It has been reported previously [2] that at elevated temperature, perfluoroalkyl substituted amidines are transformed predominantly into imidoylamidines:



Although this process does not proceed readily below 200°C, if the R_f moiety is a perfluoroalkylether group, it would represent a plausible pathway to the formation of monophospha-s-triazines [1]. On the other hand, during the synthesis of perfluoroalkylether amidines, the corresponding imidoylamidines are invariably formed as by-products (5-15%) [2], thus according to the imidoylamidine content (10%) of the particular amidine sample employed, the production of monophospha-s-triazine must be expected. However, the interactions of amidine with trichlorophosphorane at the elevated temperatures in the absence of triethylamine yielded up to 48% of monophospha-s-triazine showing clearly that condensation of perfluoroalkylether amidine to imidoylamidine must have occurred to a significant degree. Since this condensation is associated with ammonia liberation, it may be visualized that under the conditions employed, reaction of the evolved ammonia with trichlorophosphorane took place, forming imido-diphosphinic acid trichloride which upon reaction with amidine would produce diphospha-s-triazines [2] thus explaining the presence of these compounds among the reaction products. Yet, as already mentioned and as reported elsewhere [7], the possibility of the diphospha-s-triazine originating from the thermal decomposition of the desired symmetrical diphosphatetraazacyclooctatetraene cannot be ignored.

The reaction of imido-tetraphenyl-diphosphinic acid trichloride with perfluoroalkylether imidoylamidine ($R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$) in the absence of solvent resulted in a 92% yield of diphospha-s-triazine admixed with 4% of the monophospha-s-triazine and the cyclooctatetraene II. In the presence of s-tetrachloroethane, no cyclooctatetraene was produced. The only materials found were monophospha-s-triazine (~ 5%) and diphospha-s-triazine (~ 95%). It can be thus deduced that the major process is the dissociation of imidoylamidine into the nitrile (which was isolated) and amidine, followed by reaction of the amidine with imido-tetraphenyl-diphosphinic acid trichloride. Apparently, at the elevated temperatures in the presence of hydrogen chloride there is an equilibrium established between the nitrile, amidine, and imidoylamidine and depending on the reaction rate of any one of these compounds, the observed shift in equilibrium occurs. 1,3-Bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraenes were obtained in essentially quantitative yields by interacting imido-tetraphenyl-diphosphinic acid trichloride with imidoylamidines at 50°C in acetonitrile-Freon-113 mixed solvent in the presence of triethylamine acid acceptor.

The four cyclooctatetraenes synthesized representing the two structural arrangements are listed in Table 1.

TABLE 1

Diphosphatetraazacyclooctatetraenes $[(C_6H_5)_2PN]_2[R_fCN]_2$

R_f	Type	Yield	MW	abs. μ	mp °C	bp °C at 0.001 mm Hg
$C_3F_7OCF(CF_3)$	I	32	1020	6.05	77.5-79.5	138-139
$C_3F_7OCF(CF_3)$	II	80	1020	6.35,6.45	126-127.5	-
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	I	27	1352	6.05	-	150-153
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	II	98	1352	6.35,6.45	-	146-148

Both series of compounds exhibited characteristic absorptions in the 6-6.5μ region. Only one band was observed for the 'symmetrical' compounds in agreement with the behavior of the triazines and phospha-s-triazines. However, two distinct bands were observed for the 'unsymmetrical' analogues.

The mass spectra of the isomeric cyclooctatetraenes, as evident from the data given in Table 2, are very similar, indicating that under electron impact the two structural arrangements behave in the same fashion. This stipulation is further confirmed by the metastables at m/e ~ 530 and 245 in both series I and II (illustrated for the $C_3F_7OCF(CF_3)$ substituted materials, series A compounds) associated with the fragmentation of the molecular ion into the base ion:

$$1020 \longrightarrow 735^+ + 285\ [C_3F_7OCF(CF_3)],\ \text{metastable peak at m/e} \sim 530$$

followed by further breakdown of the 735^+ ion:

$$735^+ \longrightarrow 424^+ + 311\ [C_3F_7OCF(CF_3)CN],\ \text{metastable peak at m/e} \sim 245$$

via loss of a nitrile molecule. The respective metastables at m/e ~ 600 and 200 show the presence of parallel processes in the $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ substituted (series B compounds) cyclooctatetraenes.

The predominant cleavage α to the ring in the diphosphatetraazacyclooctatetraenes (m/e 735 and 901) is directly comparable to that observed for diphospha-s-triazines [2], whereas in the perfluoroalkylether-substituted monophospha-s-triazines [8] this was not a major breakdown path. Diphosphatetraazacyclooctatetraenes in analogy with phospha-s-triazines formed molecular ions under electron impact. The surprising aspect was that in addition to singly ionized molecular ions, doubly ionized molecular ions M^{++} (m/e, 510 IA, 676 IB) were observed for the "symmetrical", Type I structural arrangement. The correctness of this assignment was proven by the isotopic peaks at m/e, 510.5 and 676.5 and their ratio to the doubly ionized molecular ions as compared to the ratio of the singly charged molecular ions and the corresponding isotopic peaks.

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.

TABLE 2

Ion Fragments and Intensities Relative to Base Peak of 1,5-Bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraenes (IA, IB) and 1,3-Bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraenes (IIA, IIB)[a,b]

m/e	IA	IB	IIA	IIB	m/e	IA	IB	IIA	IIB
69	22.9	19.8	24.0	47.5	226	3.3	10.5		
73		3.4			243		18.8		
77	11.3	8.0	6.3	5.6	244		3.5		
78	3.7		4.4	4.3	272			3.3	
96				3.5	275	4.1	3.0		
97		3.4		6.6	306	6.8		12.1	8.1
100	3.2	3.7	3.7	8.4	307			3.2	
107	3.0				424	40.0	20.7	75.0	47.6
108	4.6		3.0		425	15.1	7.3	31.1	16.6
119	10.9	12.9	9.0	27.9	426			4.1	3.2
122	3.6		6.1	3.4	510	11.8			
147		3.5		3.9	551		4.2	3.7	3.3
150				3.0	676		7.1		
152				3.2	693		10.0		
153			3.7		694		16.3		
160			4.4	4.2	695		3.5		
165	3.4	3.1			735	100.		100.	
169		15.9		31.3	736	45.8		53.1	
183	13.6	6.1	15.0	8.0	737	11.4		12.9	
184			3.7		835	6.8		7.8	
185	8.3	4.6	5.6	3.7	836			3.9	
191			3.3		879				4.3
192			10.3	12.3	901		100.		100.
198			3.0		902		43.9		52.8
199		3.4	11.3	9.3	903		14.5		11.7
200			5.6		1001	6.1	8.7	6.2	11.8
201		19.2			1002		4.0		5.9
202		4.8	3.1	4.3	1019			3.4	
211				8.4	1020	5.0		21.9	
212			14.7	6.2	1021			8.0	
225	39.9	30.5	3.8	7.3	1352		2.4		5.6

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

b) In compounds denoted by A, the perfluoroalkylether group is $C_3F_7OCF(CF_3)$; in B it is $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$.

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. Molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The mass spectrometric analyses were carried out employing a duPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a duPont 21-094 data acquisition and processing system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York (U.S.A.)

Interaction of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$ and Diphenyltrichlorophosphorane

[redacted]

$CF_2OCF(CF_3)C(=NH)NH_2$, (5.01 g, 10.14 mmol, 94% pure) and diphenyltrichlorophosphorane (3.05 g, 10.44 mmol) was heated under nitrogen by-pass for 24 hr at 108-114°C, then at 123-132°C for an additional 144 hr. The product (6.77 g, 98.7% yield), as determined by gas chromatography, was composed of: monophospha-s-triazine $[(C_6H_5)_2PN][C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (35%), tetraazacyclooctatetraene $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]_2$, (47%), and diphospha-s-triazine $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]$, (18%). Distillation failed to separate the triazines from the cyclooctatetraene.

(b) In s-tetrachloroëthane

A mixture of the perfluoroalkylether-substituted amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, (2.89 g, 5.85 mmol, 90% pure) and diphenyltrichlorophosphorane (1.99 g, 6.83 mmol) was heated with stirring in s-tetrachloroethane (10 ml) under nitrogen by-pass for 163 hr at 103-105°C. After cooling and solvent removal in vacuo, followed by dissolution in Freon-113, filtration, and solvent evaporation, 4.09 g of product was obtained. A portion (1.3 g) of this material in Freon-113 (80 ml) was passed through a 1.5 x 3.5 cm column of Woelm neutral alumina. The product (1.13 g) was found by gas chromatography to consist of: monophospha-s-triazine, (48%), cyclooctatetraene, (45%), and diphospha-s-triazine, (6%).

(c) In benzene-Freon-113 using triethylamine as an acid acceptor

Under nitrogen by-pass, a solution of amidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)NH_2$, (3.14 g, 6.69 mmol, 88% pure) and triethylamine (5.4 ml, 38.72 mmol) in Freon-113 (25 ml) was added dropwise over 28 min to a solution of diphenyltrichlorophosphorane (3.86 g, 13.24 mmol) in benzene (25 ml) at 50°C. The resulting mixture was stirred and heated at 50°C for 114 hr. After cooling, Freon-113 (75 ml) was added and the insoluble products removed by filtration. The concentrated filtrate was then refiltered through a 1.5 x 5 cm column of Woelm neutral alumina giving a viscous liquid (3.22 g, 75% yield) which consisted of monophospha-s-triazine, (27%), cyclooctatetraene, (57%), and diphospha-s-triazine, (9.5%). Distillation failed to afford the desired separation. The best fraction (0.98 g) bp 150-153°C/0.001 mm Hg, based on gas chromatography, consisted of cyclooctatetraene, (68%), monophospha-s-triazine, (19%), diphospha-s-triazine, (13%), plus unidentified products, (~ 2%). Anal. Calcd. for $C_{42}H_{20}F_{34}N_4O_4P_2$: C, 37.30; H, 1.49; F, 47.76; N, 4.14; P, 4.58; O, 4.73; MW, 1352.55. Found: C, 38.04; H, 1.55; F, 47.77; N, 4.04; P, 4.52; MW, 1200. For spectral characterizations, a sample purified by gas chromatography was utilized.

Preparation of 1,5-bis(diphenylphospha)-3,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CN]_2$ (n.c.)

Under nitrogen by-pass, a solution of amidine, $C_3F_7OCF(CF_3)C(=NH)NH_2$, (2.89 g, 8.81 mmol, 97% pure) and triethylamine (3.9 ml, 27.96 mmol) in Freon-113 (20 ml) was added over a period of 1.7 hr to a solution of diphenyltrichlorophosphorane (5.48 g, 18.8 mmol) in benzene (50 ml) at 50°C. The mixture was then stirred and heated at 50°C for 87 hr. After removal of solvents under reduced pressure, the residue was treated with Freon-113 (5 x 15 ml) and filtered through a 1.5 x 5 cm column of Woelm neutral alumina. The product (2.17 g, 47% yield) was distilled in vacuo giving the desired cyclooctatetraene (1.46 g, 31.5%); bp 138-139°C/0.001 mm Hg; mp 77.5-79°C. Anal. Calcd. for $C_{36}H_{20}F_{22}N_4O_2P_2$: C, 42.37; H, 1.98; F, 40.96; N, 5.49; P, 6.07; O, 3.14; MW, 1020.49. Found: C, 42.56; H, 2.03; F, 41.14; N, 5.33; P, 5.42; MW, 1100.

Interaction of Imido-tetraphenyl-diphosphinic Acid Trichloride and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

(a) In the absence of solvent

A mixture of perfluoroalkylether-substituted imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (3.36 g, 3.46 mmol) and imido-tetraphenyl-diphosphinic acid trichloride (1.80 g, 3.67 mmol) was heated under nitrogen by-pass for 232 hr at 102-112°C and for an additional 21 hr at 137-138°C. The material was subsequently distilled in vacuo giving 2.30 g of fluid, bp 136-142°C/0.001 mm Hg; in addition, in a liquid nitrogen cooled trap 1.08 g (32.8%) of the corresponding perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, was collected. The distillate was shown by gas chromatography to consist of monophospha-s-triazine, (4%), cyclooctatetraene, (4%), and diphospha-s-triazine, (92%).

(b) In s-tetrachloroethane

A mixture of the perfluoroalkylether-substituted imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(NH_2)=N-C(=NH)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (3.85 g, 3.96 mmol) and imido-tetraphenyl-diphosphinic acid trichloride (2.25 g, 4.58 mmol) was heated with stirring in s-tetrachloroethane (20 ml) under nitrogen by-pass for 144 hr at 105-111°C. The residue obtained after removal of s-tetrachloroethane exhibited an infrared spectrum identical with that of diphospha-s-triazine, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN]$; the GC analysis showed only the presence of monophospha-s-triazine, (5%) and diphospha-s-triazine, (95%).

(c) In acetonitrile-Freon-113 using triethylamine as an acid acceptor

Under nitrogen by-pass to a solution of imido-tetraphenyl-diphosphinic acid trichloride (1.17 g, 2.38 mmol) in acetonitrile (10 ml) at 50°C was added dropwise over 1.75 hr a solution of the imidoylamidine, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(=NH)-N=C(NH_2)CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, (2.05 g, 2.11 mmol) and triethylamine (0.98 ml, 7.03 mmol) in Freon-113 (18 ml). The resulting mixture was heated at ~ 50°C for 142 hr. After solvent removal, the residue was tritiated with Freon-113 (4 x 10 ml) and then filtered through a 1.5 x 5 cm column of Woelm neutral alumina. The product thus obtained (2.80 g, 98% yield) was distilled in vacuo, bp 146-148°C/0.001 mm Hg. Anal. Calcd. for $C_{42}H_{20}F_{34}N_4O_4P_2$: C, 37.30; H, 1.49; F, 47.76; N, 4.14; P, 4.58; O, 4.73; MW, 1352.55. Found: C, 37.29; H, 1.55; F, 48.82; N, 4.23; P, 4.94; MW, 1400.

Preparation of 1,3-bis(diphenylphospha)-5,7-bis(perfluoroalkylether)-2,4,6,8-tetraazacyclooctatetraene, $[(C_6H_5)_2PN]_2[C_3F_7OCF(CF_3)CN]_2$ (n.c.)

Under nitrogen by-pass to a solution of imido-tetraphenyl-diphosphinic acid trichloride (1.79 g, 3.65 mmol) in acetonitrile (22 ml) at 50°C was added a solution of imidoylamidine, $C_3F_7OCF(CF_3)C(=NH)N=C(NH_2)CF(CF_3)OC_3F_7$, (2.0 g, 3.13 mmol) and triethylamine (1.38 ml, 9.89 mmol) in Freon-113 (7 ml). The mixture was then stirred at 50°C for 111 hr. Following solvent removal, the Freon-113 soluble material (3.19 g, 80% yield) was crystallized from Freon-113/acetone/pentane; mp 126-127.5°C. Anal. Calcd. for $C_{36}H_{20}F_{22}$-$N_4O_2P_2$: C, 42.37; H, 1.98; F, 40.96; N, 5.49; P, 6.07; O, 3.14; MW, 1020.49. Found: C, 42.64; H, 2.09; F, 41.33; N, 5.45; P, 6.07; MW, 1050.

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