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PHOSPHA-s-TRIAZINES

II. MASS SPECTRA OF MONO(DIARYLPHOSPHA)-s-TRIAZINES

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SUMMARY

Electron impact fragmentation patterns were obtained for 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, 1-diphenylphospha-3,5-bis $[C_3F_7(OCF(CF_3)CF_2)_xOCF(CF_3)]$-2,4,6-triazine (x=1 and 2) and their pentafluorophenyl analogues. In each instance the ion $R_2PN_2C^+$ ($R=C_6H_5$ or C_6F_5) constituted the base peak. Based on the observed metastable peaks, fragmentation pathways leading to the formation of this and other significant ions are postulated and similarities to s-triazine and diphenyl phosphazene trimer breakdown patterns are discussed.

INTRODUCTION

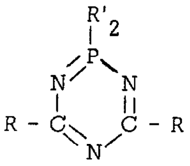
Monophospha-s-triazines represent a novel heterocyclic ring arrangement. The physical and chemical properties of these materials bear definite resemblances to the similarly substituted s-triazines and phosphazenes [1]. Also the synthesis process is directly analogous to that employed in the preparation of diphenyl phosphazene trimer [1,2]. In view of the above, it became of interest to determine to what degree, if any, the mass spectral breakdown patterns of these compounds are related to the "parent" ring systems.

RESULTS AND DISCUSSION

The five monophospha-s-triazines investigated are listed in Table 1 and their mass spectral breakdown patterns are presented in Tables 2 and 3.

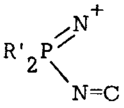
Table 1

Monophospha-s-triazines



R	R'	MW	m.p. °C
$CF_3(CF_2)_6$, (I)	C_6H_5	989	73-74.5
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$, (II)	C_6H_5	1153	-
$C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_3)$, (III)	C_6H_5	1485	-
$CF_3(CF_2)_6$, (IV)	C_6F_5	1169	74-75
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$, (V)	C_6F_5	1333	-

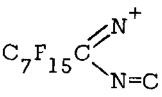
As can be seen from these compilations, in each instance the fragment



R' = C_6H_5, m/e = 225

R' = C_6F_5, m/e = 405

constitutes the most intense or base peak. It should be noted that a related ion,



m/e, 421

Table 2

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

m/e	I	II	III	m/e	I	II	III	m/e	I	II	III
31	3.3	3.6	3.7	150		3.1	4.1	491		3.0	4.2
47		4.2	4.9	154	3.3	3.0		575	8.8		
50	3.9	4.8	5.9	169	3.7	16.0	29.5	620	4.6		
51	5.4	3.0	3.1	180	8.3	4.0	3.7	802		11.1	
69	20.2	20.0	33.7	181	3.3			868		4.1	
76	3.7			183	14.1	8.3	7.0	968		4.4	12.4
77	18.2	9.4	8.1	185	6.3	4.0	4.1	970	14.3		
91	3.8			198	3.2			971	5.4		
97		3.0	4.3	204	3.0	5.3	6.4	988	58.6		
100	5.6	6.2	7.7	219			3.9	989	61.2		
107	6.4	4.0	3.1	223	5.9	4.9	4.2	990	27.2		
108	8.6	5.0	3.7	224	5.8	4.4	3.4	991	4.3		
112	3.1			225	100.0	100.0	100.0	1034		8.6	4.8
119	6.5	9.5	12.8	226	25.1	24.9	26.6	1134		8.0	
122	4.1			227	3.1	3.0		1152		22.7	
126		4.8	6.4	275		5.5	6.4	1153		47.6	
127	7.5	4.4	4.7	292		3.1		1154		16.8	
131	6.6			325		11.9	18.3	1155		3.4	
147		3.3	5.6								

a) Peaks having intensities less than 3% of the base peak are not reported.

is produced by trisperfluoro-n-heptyl-s-triazine [3], but it represents less than 1% of the base peak (m/e 866, M-C_6F_{13}).

Apparently the presence of aromatic groups on phosphorus stabilizes the molecular ion in the monophospha-s-triazines inasmuch as for compounds I, II, IV, and V molecular ions of intensities higher than 30% of the base peak were observed. No molecular ion was recorded for compound III due to instrument

Table 3

Ion Fragments and Intensities Relative to Base Peak of 1-Di(pentafluorophenyl) phospha-3,5-bis(perfluoroalkyl and perfluoroalkylether)-2,4,6-triazines[a]

m/e	IV	V
31		3.8
47		4.5
50		4.1
69	31.8	33.1
71	5.4	3.0
100	5.4	5.5
119	6.9	10.5
126		5.4
129	4.5	4.3
131	6.0	
141	3.5	
169		22.5
198	5.1	5.0
212	3.4	3.3
217	10.9	9.4
255		3.2
257	21.3	17.2
258	3.0	3.0
296	3.2	3.1
335		3.1
365	12.7	10.2
384		3.3
386		3.0
403		3.0
405	100.0	100.0
406	27.9	27.9
407	3.1	4.9
455	4.7	13.7
456		2.7
505		21.3
521		11.4
593		10.2
671		4.5
755	7.2	
800	3.7	
882		6.4
982		12.1
983		3.2
1048		12.6
1148		6.9
1150	12.5	
1151	3.6	
1169	31.8	
1170	9.9	
1314		9.8
1333		37.1

a) Peaks having intensities less than 3% of the base peak are not reported.

limitation. In the mass spectrum of diphenylphosphazene trimer the molecular ion is the most intense ion [4]; however, in trisperfluoro-n-heptyl-s-triazine the molecular ion is only of low intensity (2% of the base peak).

In the perfluoro-n-heptyl monophospha-s-triazines (compounds I and IV) cleavage occurs mainly α to the ring (m/e, 620 and 800 respectively) whereas fragmentation β to the ring takes place to a low extent which is opposite to that observed for the triazines [3]. Scissions β to the ring (m/e 802, 982; compounds II and V, respectively) are favored in the perfluoroalkylether-substituted materials due to the presence of the oxygen function [5,6]; however, here cleavage α to the ring also exists as shown by the presence of m/e 702 ion (compound II, 2% of base peak) which arises via the process 1153^+ (M) $\longrightarrow 702^+ + 451$ $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$ indicated by the metastable peak at m/e ~ 428. Loss of nitrile from the 702^+ ion results in the base ion m/e 225, i.e.,

$$702^+ \longrightarrow 225^+ + 477\ [C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN].$$

This path is proven by the presence of a metastable peak at m/e ~ 72.

In the mass spectrum of 1-diphenylphospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, two metastable peaks were found at m/e ~ 341 and 144. The m/e ~341 is due to the process

$$970^+ \longrightarrow 575^+ + 395[C_7F_{15}CN]$$

whereas the m/e ~144 is associated with fragmentation of the 225^+ ion,

$$225^+ \longrightarrow 180^+ \quad \text{(metastable peak at m/e} \sim 144)$$

and was observed in the spectra of the three phenyl-subsituted monophospha-s-triazines (compounds I-III).

Based on the breakdown pattern and metastable peaks produced by 1-bis (pentafluorophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (compound IV), it can be deduced that the m/e 405 ion is formed by cleavage α to the ring followed by nitrile elimination, which was also the case in the phenyl analogues, i.e.,

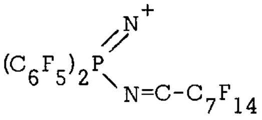
$$1169^+(M) \longrightarrow 800^+ + 369\ [C_7F_{15}],\ \text{metastable peak at m/e} \sim 547$$

$$800^+ \longrightarrow 405^+ + 395\ [C_7F_{15}CN],\ \text{metastable peak at m/e} \sim 205$$

In addition this process also occurs in one step from the molecular ion, i.e.,

$$1169^{+}(\mathrm{M}) \longrightarrow 405^{+} + 369 + 395$$

as indicated by the metastable peak at m/e ~ 140. An ion related to the m/e 405 fragment



is formed from the M-F ion (m/e 1150) via a loss of nitrile, i.e.,

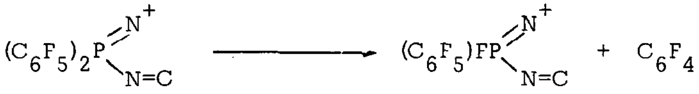
$$1150^{+} \longrightarrow 755^{+} + 395, \text{ metastable peak at m/e} \sim 495.$$

In the case of the perfluoroalkylether-substituted analogue, compound V, only the metastable peak m/e ~ 584 for the process

$$1333^{+}(\mathrm{M}) \longrightarrow 882^{+} + 451\ [C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$$

was found, although it would seem reasonable to assume that here the breakdown occurs by paths similar to those operative for the other monophospha-s-triazines especially since analogous ions are produced (see Tables 2 and 3).

Cleavage of the major fragment, m/e 405, was encountered in both of the pentafluorophenyl-substituted materials, compounds IV and V,



m/e 405 m/e 257

shown by the presence of a metastable peak at m/e ~ 163.

Based on the above discussion and the data presented it can be argued that monophospha-s-triazines exhibit similarities in their breakdown patterns to the two parent ring systems; however, for the most part the spectra are unique to this series of compounds. The question remains whether the observed ring breakdown is predominantly influenced by the presence of the aromatic groups, i.e. phenyl and pentafluorophenyl, on phosphorus or whether phosphorus itself is the determining factor. Studies of compounds containing aliphatic substituents on phosphorus should help to clarify this aspect.

EXPERIMENTAL

A DuPont 21-491B double focusing mass spectrometer was employed to obtain the mass spectra using an ionizing voltage of 70 eV and an ion accelerating voltage of 1400 V. The mass spectra were recorded with the aid of a DuPont 21-094 data acquisition/processing system and a CEC 5-124A oscillograph, the latter to detect metastable peaks and to obtain masses above m/e 1066 which is the upper limit of the data system. The solid samples and liquids exhibiting low vapor pressures were introduced via the direct introduction probe, which was not heated. The temperature of the source was 220 - 240°C.

The syntheses, characterizations, and stability determinations for compounds I-V have been reported elsewhere [1].

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REFERENCES

1 R. H. Kratzer, K. J. L. Paciorek, J. Kaufman and T. I. Ito, J. Fluorine Chem., 10, 231 (1977).

2 D. L. Herring and C. M. Douglas, Inorg. Chem., 3 (3), 428 (1964).

3 T. Aczel, Anal. Chem., 40 (12), 1917 (1968).

4 K. J. L. Paciorek, R. H. Kratzer, and J. H. Nakahara, unpublished results.

5 K. J. L. Paciorek, J. H. Nakahara, R. H. Kratzer, and R. W. Rosser, Org. Mass Spectrom., 12 (2), 71 (1977).

6 K. J. L. Paciorek, J. H. Nakahara, and R. H. Kratzer, Org. Mass Spectrom., 11, 1217 (1976).