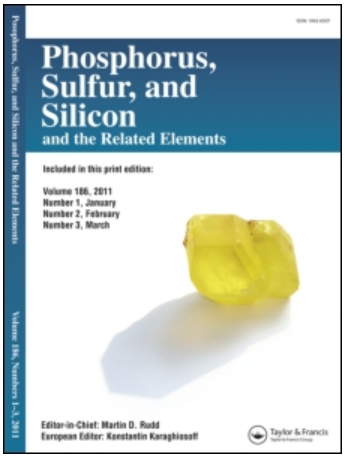

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXX. MASS SPECTROSCOPIC INVESTIGATION OF 2-ALKYL-2-OXO-1,3,2-DIOXA-PHOSPHORINANE AND-PHOSPHEPANE

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XXX. MASS SPECTROSCOPIC INVESTIGATION OF 2-ALKYL-2-OXO-1,3,2-DIOXA-PHOSPHORINANE AND -PHOSPHEPANE

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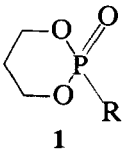
The mass spectra of 2-alkyl-2-oxo-1,3,2-dioxa-phosphorinane and -phosphepane showed that the ring opening was in competition with the cleavage of the P—C bond. According to the fragmentation pathway, which was dependent on the structure of exocyclic substituents on phosphorus, the 2-alkyl-2-oxo-1,3,2-di-oxa-phosphorinanes can be classified in two categories. The main process in category A was the ring opening and/or C—C bond cleavage. While in category B the cleavage of P—C bond was predominant. However, for 2-alkyl-2-oxo-1,3,2-dioxa-phosphepane, no matter how the structure of 2-alkyl group was, the ring opening was a dominant process.

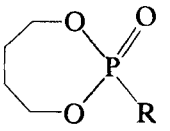
INTRODUCTION

The mass spectra of some 5,5-dimethyl-2-substituted-1,3,2-dioxaphosphorinanes[1] indicated that the ring opening was a main process in most of the compounds studied. The mass spectroscopic behaviours of these compounds showed significant dependence on the structure of the substituents. However, Oh[2,3] gave some different results. Like several acyclic organophosphorus compounds,[4–6] the mass spectra of substituted-1,3,2-dioxa-phospholanes and -phosphorinanes were characterized by the cleavage of a P—C bond. In the studies mentioned above, the nature of the substituents varied largely. There were so many factors which strongly influence the fragmentation process, therefore, the substituent effect was not very clear. Oh's results also indicated that the spectroscopic behaviours of phosphates bearing a five membered ring were similar to that of six membered cyclic phosphorus compounds.[2] There was no information available concerning the mass spectroscopic study of seven membered cyclic phosphonates. In order to evaluate the influence of the structure of exocyclic substituents and the ring size on the fragmentation process of cyclic phosphonates, we studied the mass spectra of the following 2-alkyl-2-oxo-1,3,2-dioxa-phosphrinanes and -phosphepanes:

Compounds **1** and **2** can be regarded as six or seven membered cyclic esters of alkylphosphonic acids, respectively. For convenience the abbreviated nomenclature O,O-1,3-trimethylene or O,O-1,4-tetramethylene-alkyl phosphonates were adopted for these compounds without ring substituents in this paper.



1



2

R	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9	s-C_4H_9
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
	2a	—	—	**2b**	**2c**	**2d**	**2e**

R	t-C_4H_9	s-C_5H_{11}	cyc-C_6H_{11}	CH_2=CH—CH_2
	1h	**li**	**1j**	**1k**
	2f	**2g**	—	—

RESULTS AND DISCUSSIONS

As shown by the mass spectra of compounds **1** and **2**, a M + 1 peak was observed in all cases. This means that the molecular ions of these cyclic phosphonates are very unstable and have a high tendency to decompose, while the corresponding protonated molecules, on the other hand, are very stable entities. The characteristic fragmention process of these compounds are dramatically governed either by the nature of the exocyclic substituents on phosphorus or by the ring size of the ester moiety (Tables I and II).

According to the fragmentatiom pathway the 1,3-trimethylene-aklylphosphonates studied could be classified into categories A and B:

Category A:

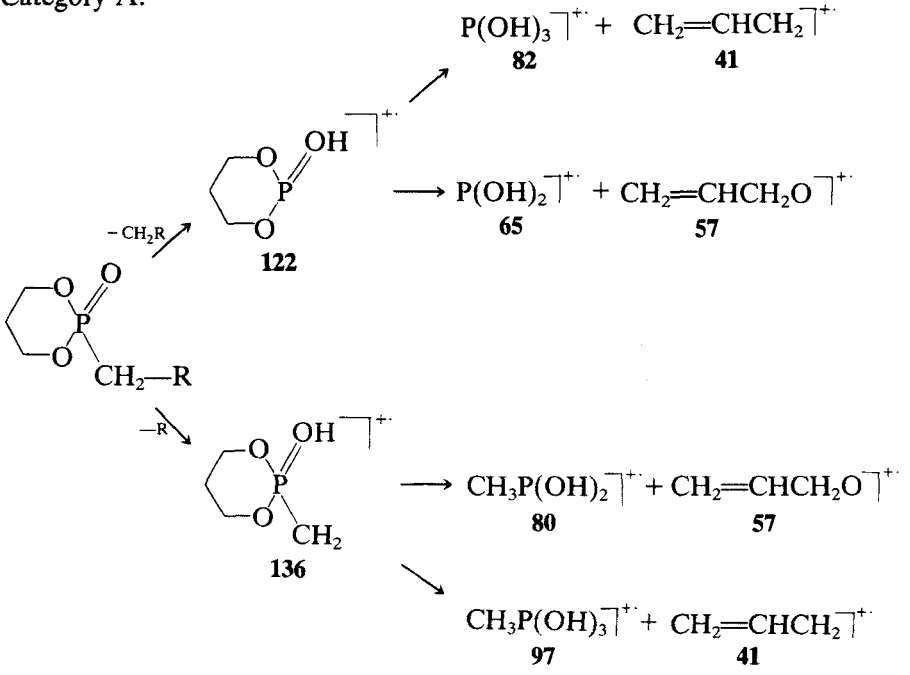


TABLE I

Abundance of fragments of O,O-1,3-trimethylene-alkylphosphonates

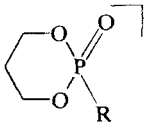
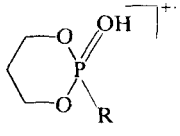
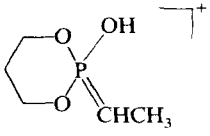
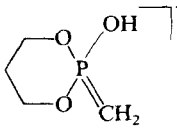
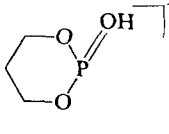
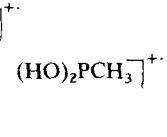
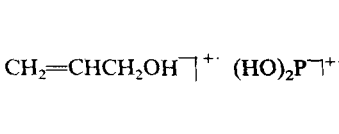
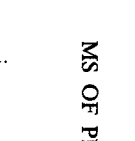
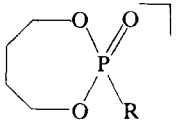
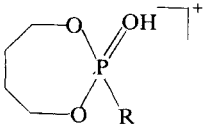
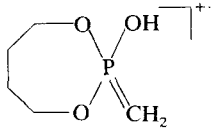
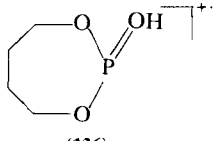
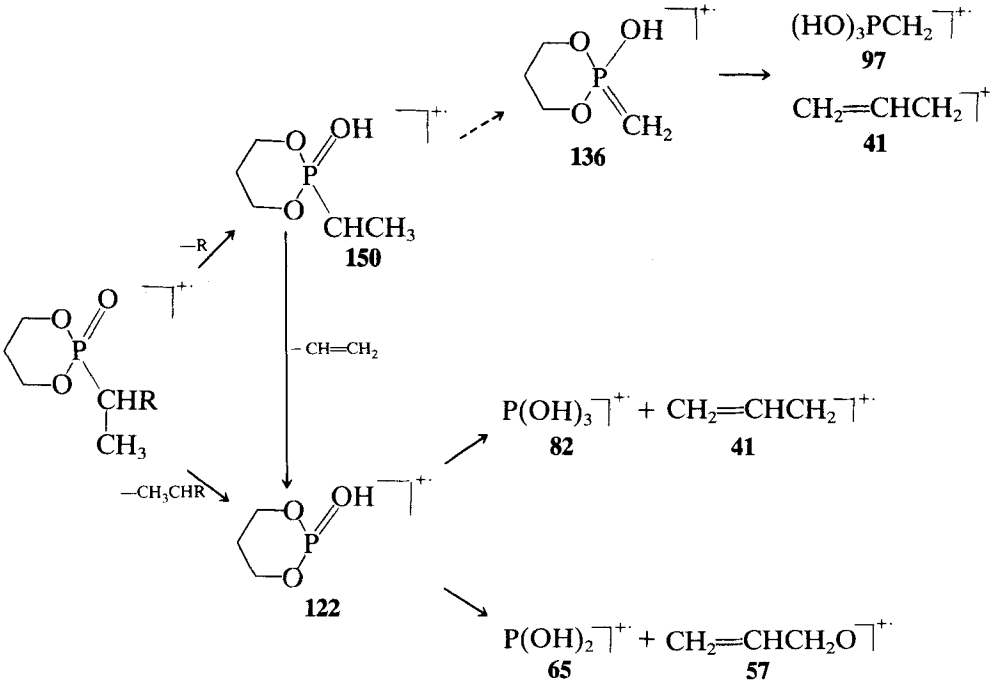
 (M)	 (M + 1)	 (150)	 (136)	 (122)	 (80)	 (58)	 (65)
CH_3 (136)	72.94	—	—	7.62	100	25.07	18
C_2H_5 (150)	28.94	—	2.47	33.46	1.08	100	24
n-C_3H_7 (164)	88.12	18.15	60.89	40.26	33.04	32.88	18
i-C_3H_7 (164)	38.07	13.60	12.35	100	1.94	66.33	25
n-C_4H_9 (178)	100	19.06	60.06	34.63	28.33	26.39	9
i-C_4H_9 (178)	15.41	1.60	100	39.04	38.83	28.52	11
s-C_4H_9 (178)	100	79.63	0.0	70.61	0.0	46.57	9
t-C_4H_9 (178)	100	1.15	9.89	74.37	0.79	41.16	9
s-C_5H_{11} (192)	98.44	100	2.03	67.08	0.75	52.57	15
cyc-C_6H_{11} (204)	18.41	0.0	12.81	26.82	69.50	18.51	10
CH_2=$CHCH_2$ (164)	27.12	39.64	13.31	100	8.65	14.41	5

TABLE II

Abundance of fragments of 0,0-1,4-tetramethylene-alkylphosphonates

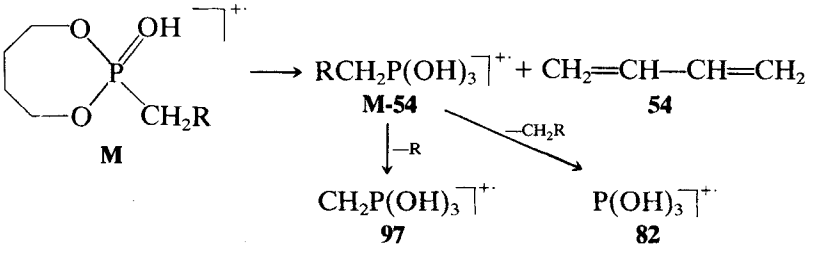
 (M)	 (M+1)	$(HO)_3P—R^{+\cdot}$ (M − 54)	$CH_2=CHCH=CH_2^{+\cdot}$ (54)	 (150)	 (136)	$(HO)_3PCH_3^{+\cdot}$ (97)	$[(HO)_3P]^{+\cdot}$ (82)
CH_3 (150)	100	28.69	54.04	—	0.0	—	0.0
i-C_3H_7 (178)	63.52	44.32	100	1.53	9.59	1.21	4.5
n-C_4H_9 (192)	83.51	17.09	100	13.02	6.88	19.85	2.8
i-C_4H_9 (192)	47.63	9.08	100	13.20	9.14	20.47	2.9
s-C_4H_9 (192)	100	13.35	36.38	0.57	12.34	0.39	6.2
t-C_4H_9 (192)	42.35	15.05	100	2.49	26.82	1.15	5.6
s-C_5H_{11} (206)	63.39	13.05	100	3.14	18.37	1.56	6.3

Category B:



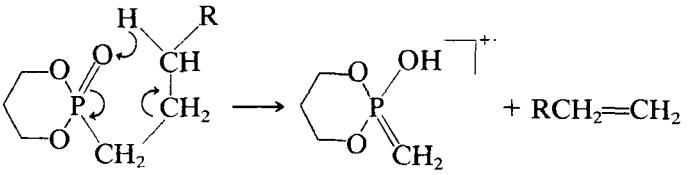
The category A compounds are classified as cyclic esters of alkyl phosphonic acids with an exocyclic primary carbon atom directly connected to phosphorus (**1a**, **1c**, **1e**, **1f**) except the ethyl group, while category B are compounds with an exocyclic secondary alkyl group directly bonded to the phosphorus atom (**1d**, **1g**, **1h**, **1i**) and as an exception also O,O-1,3-trimethylene-ethylphosphonate. The fragmentation of O,O-1,3-trimethylene-allyl-(**1k**) and cyclohexyl(**1j**) phosphonates proceeded in a more complicated way with characteristic fragmentation behaviours of both categories.

The basic fragmentation of O,O-1,4-tetramethylene alkylphosphonates is proved to be the cleavage of the cyclic ester group which is independent of the structure of exocyclic alkyl group. Then the decay of the alkyl group is similar to that of the alkyl group in O,O-1,3-trimethylene alkylphosphonates.

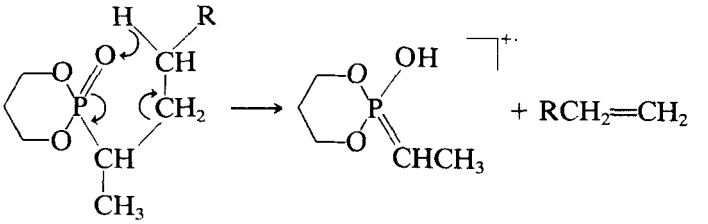


In contrast with the observation of Francis,[1] the ester linkage of O,O-1,3-trimethylene alkylphosphonates without ring substituents is comparatively stable

in mass spectrometric fragmentation except **1a** (see Table I). In the meantime, as demonstrated by the mass spectra of **1a** which showed m/z 97 (41.9%) and m/z 80 (base peak) indicating $(HO)_3PCH_2^{+\cdot}$ and $(HO)_2PCH_3^{+\cdot}$ as principal fragments. Therefore, the P—C bond is usually resistant to cleavage upon bombardment of the sample with electrons in category A, and this is in contradiction with Kwon's report.[3] In this case C—C bond is broken more easily than the others. However, in cateogry B the cleavage of the P—C bond is a main process, i.e. the P—C bond is more susceptible during the fragmentation process than others. The cleavage of C—C bond was found as a result of the McLaffty rearrangement. It was evidenced by the appearance of m/z 136 and m/z 150 fragments of both category A and B of compounds **1**, though it was a much weaker process in category B

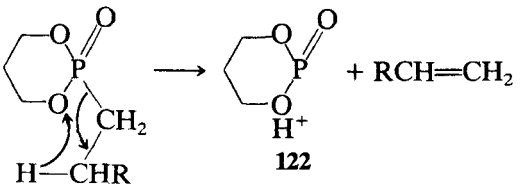


M **136**



M **150**

The formation of fragment m/z 122 in all series of compounds **1** except **1a** may be rationalized by the following process.



122

It means that such a kind of cleavage should appear for compounds **1** with more than two carbon atoms in exo-cyclic substituent on phosphorus. This cleavage process enters, however, into competition with the migration of H onto the —C atom. This is the reason why the abundance of m/z 122 is usually higher in category B than in category A of compounds **1**. All of the mass spectra of compounds **1** showed a m/z 57 peak with high abundance which was derived from fragment $CH_2CHCH_2O^{+\cdot}$ resulting from the cleavage of the cyclic ester group.

As indicated by mass spectra of compounds **2** besides M + 1, m/z 54 usually appeared as base peak. Since among other fragments with comparatively small

abundance, a peak with m/z M-54 occurred frequently, the following process may be postulated.

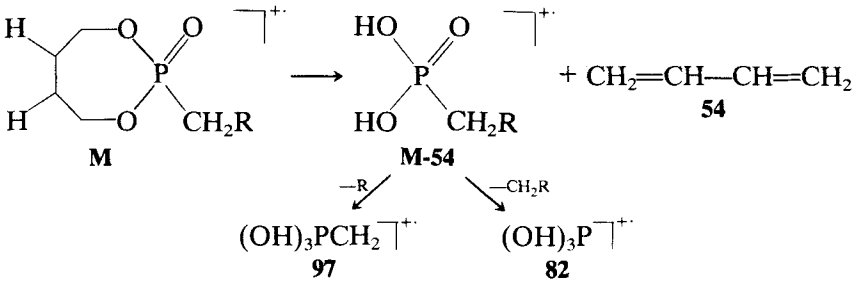
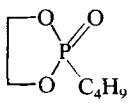


TABLE III

Influence of ring size on the abundance of fragments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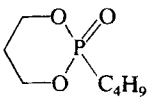
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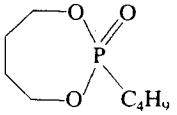
5

Compound	M + 1	M − 14	M-28	M-42	M—R	Σ/(M + 1)*
3	100	12.24	19.13	58.19	32.08	1.21
4	100	11.39	19.06	60.06	34.63	1.26
5	83.5	4.70	12.02	13.02	6.88	0.44

* Σ is the summation of the abundance of all fragments beside M + 1.

As demonstrated by the comparative study of the characteristic behaviours of O,O-1,2-dimethylene-, O,O-1,3-trimethylene-, and O,O-1,4-tetramethylene butylphosphonates, the stability of the ester ring upon bombardment with electrons is dependent chiefly on the ring size. As shown in Table III, for the five membered ester ring, the summation of fragments with ring skeleton was 1.21 times as great as M + 1, while 1.26 and 0.44 times as great as M + 1 for six- and seven membered ester ring compounds, respectively. The order of ring stability can thus be roughly evaluated as six-membered ring > five membered ring ≫ seven membered ring. The ring opening of these compounds proceeds together with the migration of proton in different manner based on the chemical structure of the ester ring.

EXPERIMENTAL

2-Alkyl-2-oxo-1,3,2-dioxa-phosphorinanes and -phosphepanes were synthesized by the methods introduced by us.[7] The mass spectra were taken on a Finnigan 4021 spectrometer, using 70 ev electrons with pressure at 0.3 Torr, and the sample was introduced directly at 200–350°C. Temperature and pressure were uncorrected.

REFERENCES

1. G. W. Francis, K. Tjessem, A. Dale and T. Gramstad, *Acta Chemica Scandinavia B* **30,** 31, 1976.
2. B. M. Kwon and D. Y. Oh, *Phosphorus and Sulfur* **11,** 177, 1981.
3. B. M. Kwon, D. Y. Oh and J. W. Park, *Phosphorus and Sulfur* **16,** 271 1983.
4. W. R. Griffiths and J. C. Tebby, *Phosphorus and Sulfur* **4,** 341, 1976.
5. H. J. Meyer, F. C. V. Larsson, S. O. Lawesson and J. H. Bowie, *Bull. Soc. Chim. Belg.* **87,** 517, 1978.
6. P. Haake and P. S. Ossip, *Tetrahedron* **24,** 565, 1968.
7. C. Yuan, S. Li and Z. Cheng, *Synthesis,* (3), 1988.