Department of Chemistry, Ohio University

# The Mass Spectra of Phosphorus Esters. I. Bicyclic Phosphites

*David G. Hendricker*

The mass spectra of bicyclic phosphites of the type $P(OCH_2)_3CR$, where $R = CH_3$, $C_2H_5$, and $C_3H_7$ and $NO_2$, are reported, and their fragmentation patterns analyzed. Unlike trialkyl phosphites, these cyclic phosphites do not yield a large number of phosphorus-containing fragment ions resulting from hydrogen rearrangement.

The mass spectra of trialkyl phosphite esters have been previously investigated (1,2) and were found to exhibit many phosphorus-containing fragment ions resulting from hydrogen rearrangement. Trimethyl phosphite was observed to yield $P(OR)(OH)^+$, while other alkyl phosphites formed the additional species $P(OH)_3H^+$, $P(OR)(OH)_2H^+$, $P(OH)_3^+$, and $P(OH)_2^+$ in great abundance. Recently there has been considerable interest in the chemistry of the bicyclic phosphite system shown in Fig. 1 (3,4,5). It was of interest to investigate the mass spectra of such phosphites to ascertain if the cyclic system causes any marked variation in fragmentation patterns from that observed for trialkyl phosphites.

Electron impact studies of the bicyclic phosphites, 4-methyl-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, 4-ethyl-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CC_2H_5$, 4-n-propyl-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CC_3H_7$, and 4-nitro-1-phosphabicyclo[2.2.2]-octane, $P(OCH_2)_3CNO_2$ yield the fragment ions listed in Table I. Table II lists the observed metastables and the transitions which they represent. Figure 1 gives a generalized scheme for the fragmentation of the phosphite studied.

It is of interest that only one phosphorus-containing fragment ion due to hydrogen transfer is observed for each compound. The phosphites in which $R = CH_3$, $C_2H_5$ and $C_3H_7$ (Fig. 1), all exhibit the ion $PC_2H_6O_3^+$, m/e 109. The lack of such a fragment ion when $R = NO_2$ suggests that the process of hydrogen transfer to yield this ion is dependent on the presence of an alkyl "tail" group. When $R = C_2H_5$ or $C_3H_7$, a fragment with m/e 83 is observed. It would seem more probable that this represents a $C_5H_7O^+$ ion from degradation of m/e 131, $PC_5H_8O_2^+$, and not $P(OH)_3H^+$ since no m/e 83 ion is observed for $P(OCH_2)_3CCH_3$ or $P(OCH_2)_3CNO_2$. A m/e 83 peak when $R = C_3H_7$ would also be expected to arise from a $C_nH_{2n-1}^+$ fragment ion as observed in the spectra when $R = CH_3$ and $C_2H_5$. That two species appear at m/e 83 was confirmed by expanding the observed peak. A doublet

having a separation consistent with the mass difference between $C_6H_{11}^+$ and $C_5H_7O^+$ of 0.0364 a.m.u. was found. The P + 1 contribution from m/e 82 differs from $C_6H_{11}^+$ by 0.0045 a.m.u. and could not be resolved. The ion m/e 65, $H_2PO_2^+$, is found in appreciable quantities only for $P(OCH_2)_3CNO_2$. The formation of $H_2PO_2^+$ is due to a two-step degradation of the monocyclic species m/e 103 + X (Fig. 1), as indicated by metastables (Table II). The failure of these bicyclic phosphite systems to degrade to a large number of phosphorus-containing fragment ions resulting from hydrogen rearrangement must be due to the cyclic character of the larger fragment ions.

Fragment ions having m/e 81,67,53,39 and 83,69,55,41 can be assigned as $C_nH_{2n-3}^+$ and $C_nH_{2n-1}^+$ species (6) resulting from degradation of ions m/e 103 + R and m/e 103 + X in Fig. 1. The fragment ion m/e 47, observed as a major component in the mass spectra of alkyl phosphites, (1,2) phosphates, (7,8) and phosphonates (9,10) and assigned to $PO^+$ is also prominent in all spectra of bicyclic phosphite esters. The $(P+1)^+/P^+$ ratio of 1.5% for m/e 77 suggests that this ion is $PO_2CH_2^+$.
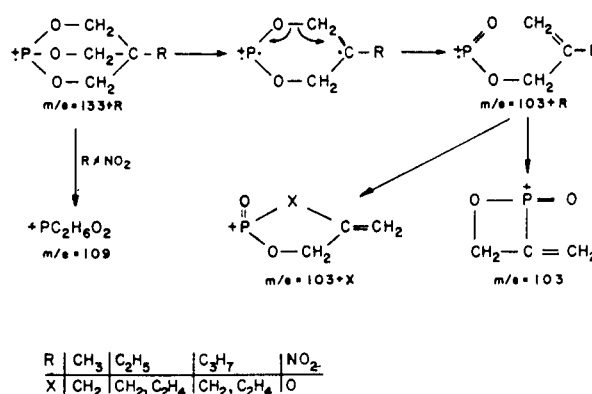


| R | $CH_3$ | $C_2H_5$ | $C_3H_7$ | $NO_2$ |
|---|---|---|---|---|
| X | $CH_2$ | $CH_2, C_2H_4$ | $CH_2, C_2H_4$ | O |

Figure 1. A generalized scheme for the fragmentation of the bicyclic phosphites studied.

## TABLE I

Partial Mass Spectra of Bicyclic Phosphites

| m/e | $P(OCH_2)_3CCH_3$ | $P(OCH_2)_3CC_2H_5$ | % $\Sigma_{39}$ $P(OCH_2)_3CC_3H_7$ | $P(OCH_2)_3CNO_2$ |
|---|---|---|---|---|
| 179 | | | | 1.3 |
| 176 | | | 2.9 | |
| 162 | | 4.2 | | |
| 149 | | | | 2.6 |
| 148 | 5.6 | | | |
| 146 | | | 6.5 | |
| 132 | | 11.4 | | |
| 131 | | 2.2 | 6.9 | |
| 119 | | | | 5.6 |
| 118 | 15.7 | | | |
| 117 | 1.4 | 2.2 | 5.6 | |
| 109 | 4.0 | 4.6 | 2.1 | |
| 103 | 1.1 | 2.0 | 1.0 | 3.7 |
| 100 | 2.0 | | | |
| 91 | | | | 1.1 |
| 83 | | 1.5 | 1.7 | |
| 82 | | | 7.6 | |
| 81 | | | 1.7 | |
| 77 | 1.1 | 1.1 | | 2.4 |
| 71 | 6.7 | | | |
| 69 | 1.1 | 9.9 | 0.8 | 1.1 |
| 68 | | 21.9 | 0.8 | |
| 67 | | 8.5 | 10.2 | |
| 65 | | | | 2.2 |
| 55 | 22.4 | 3.1 | 10.1 | 6.9 |
| 54 | 10.3 | | 3.0 | |
| 53 | 2.9 | 3.5 | 3.5 | 5.2 |
| 47 | 7.2 | 6.1 | 4.4 | 14.5 |
| 43 | 1.8 | 1.1 | 2.4 | 1.3 |
| 42 | | 1.5 | 1.1 | 1.3 |
| 41 | 3.8 | 4.6 | 8.6 | 11.7 |
| 40 | | 1.8 | 1.3 | 4.6 |
| 39 | 2.0 | 5.3 | 5.2 | 21.7 |

Ions unique to $P(OCH_2)_3CCH_3$ are those at m/e 71 and m/e 100 which are formulated as $C_4H_7O^+$ and $PC_4H_5O^+$, both of which result from fragmentation of m/e 103 + R (Fig. 1). A metastable at m/e 84.8 substantiates the m/e 118-100 pathway.

Nitro compounds in general are found to exhibit a m/e 30 peak (NO⁺) of large intensity (11,12). For $P(OCH_2)_3CNO_2$ the m/e 30 peak is observed to be about half as intense as the m/e 39 peak (% $\Sigma_{39}$ = 21.7). The m/e 91 ion, $PC_2H_4O_2^+$, unique to $P(OCH_2)_3CNO_2$, is indicated as resulting from fractionation of m/e 103 + X (Fig. 1) by a metastable peak at m/e 69.6. The degradation of $PC_2H_4O_2^+$ to give $H_2PO_2^+$ is substantiated by the metastable observed at m/e 46.4. Although they possess

TABLE II

Observed Metastable Transitions for Bicyclic Phosphites

| Molecule | Metastable Mass Exp. | Calcd. | Probable Processes |
|---|---|---|---|
| $P(OCH_2)_3CCH_3$ | 94.1 | 94.08 | $PC_4H_9O_3^+$ (148) → $PC_4H_7O_2^+$ (118) + $CH_2O$ (30) |
| | 84.8 | 84.75 | $PC_4H_7O_2^+$ (118) → $PC_4H_5O^+$ (100) + $H_2O$ (18) |
| | 80.3 | 80.28 | $PC_5H_9O_3^+$ (148) → $PC_2H_6O_3^+$ (109) + $C_3H_3$ (39) |
| | 51.1 | 51.07 | $C_4H_7^+$ (55) → $C_4H_5^+$ (53) + 2H (2) |
| | 42.7 | 42.72 | $PC_4H_7O_2^+$ (118) → $C_4H_7O^+$ (71) + PO (47) |
| | 37.8 | 37.10 | $C_3H_5^+$ (41) → $C_3H_3^+$ (39) + 2H (2) |
| | 28.2 | 28.17 | $C_4H_6^+$ (54) → $C_3H_3^+$ (39) + $CH_3$ (15) |
| | 24.7 | 24.71 | $PC_4H_7O_2^+$ (118) → $C_4H_6^+$ (54) + $HPO_2$ (64) |
| $P(OCH_2)_3CC_2H_5$ | 130.0 | 130.01 | $PC_5H_9O_2^+$ (132) → $PC_5H_8O_2^+$ (131) + H (1) |
| | 107.5 | 107.56 | $PC_6H_{11}O_3^+$ (162) → $PC_5H_9O_2^+$ (132) + $CH_2O$ (30) |
| | 73.3 | 73.34 | $PC_6H_{11}O_3^+$ (162) → $PC_2H_6O_3^+$ (109) + $C_4H_5$ (53) |
| | 66.0 | 66.01 | $C_5H_8^+$ (68) → $C_5H_7^+$ (67) + H (1) |
| | 37.1 | 37.10 | $C_3H_5^+$ (41) → $C_3H_3^+$ (39) + 2H (2) |
| | 29.4 | 29.37 | $PC_3H_4O_2^+$ (103) → $C_3H_3O^+$ (55) + HPO (48) |
| $P(OCH_2)_3CC_3H_7$ | 121.1 | 121.11 | $PC_7H_{13}O_3^+$ (176) → $PC_6H_{11}O_2^+$ (146) + $CH_2O$ (30) |
| | 117.5 | 117.54 | $PC_6H_{11}O_2^+$ (146) → $PC_5H_8O_2^+$ (131) + $CH_3$ (15) |
| | 93.8 | 93.76 | $PC_6H_{11}O_2^+$ (146) → $PC_4H_6O_2^+$ (117) + $C_2H_5$ (29) |
| | 67.5 | 67.51 | $PC_7H_{13}O_3^+$ (176) → $PC_2H_6O_3^+$ (109) + $C_5H_7$ (67) |
| | 54.8 | 54.74 | $C_6H_{10}^+$ (82) → $C_5H_7^+$(67) + $CH_3$ (15) |
| | 46.1 | 46.05 | $PC_6H_{11}O_2^+$ (146) → $C_6H_{10}^+$ (82) + $HPO_2$ (64) |
| | 37.1 | 37.10 | $C_3H_5^+$ (41) → $C_3H_3^+$ (39) + 2H (2) |
| | 36.5 | 36.45 | $C_6H_{11}^+$ (83) → $C_4H_7^+$ (55) + $C_2H_4$ (28) |
| | 28.1 | 28.17 | $C_4H_6^+$ (54) → $C_3H_3^+$ (39) + $CH_3$ (15) |
| $P(OCH_2)_3CNO_2$ | 124.0 | 124.03 | $PC_4H_6O_5N^+$ (179) → $PC_4H_6O_4^+$ (149) + NO (30)<br>and → $PC_3H_4O_4N^+$ (149) + $CH_2O$ (30) |
| | 82.9 | 82.89 | $PC_4H_6O_3^+$ (133) → $PC_3H_6O_2^+$ (105) + CO (28) |
| | 79.8 | 79.77 | $PC_4H_6O_3^+$ (133) → $PC_3H_4O_2^+$ (103) + $CH_2O$ (30) |
| | 69.6 | 69.59 | $PC_3H_4O_3^+$ (119) → $PC_2H_4O_2^+$ (91) + CO (28) |
| | 46.4 | 46.43 | $PC_2H_4O_2^+$ (91) → $PO_2H_2^+$ (65) + $C_2H_2$ (26) |
| | 37.1 | 37.10 | $C_3H_5^+$ (41) → $C_3H_3^+$(39) + 2H (2) |
| | 29.4 | 29.37 | $PC_3H_4O_2^+$ (103) → $C_3H_3O^+$ (55) + HPO (48) |

% $\Sigma_{39}$ of only 0.6, the ions $PC_4H_6O_3^+$,m/e 133, and $PC_3H_6O_2^+$, m/e 105, are of interest because of observed metastables involving them. The m/e 133 ion which may be formed either by loss of $NO_2$ from the parent ion or by loss of O from m/e 103 + R ion (Fig. 1) undergoes fragmentation by two pathways as indicated by metastables (Table II) to yield m/e 103 (Fig. 1) or to give m/e 105 fragment ion, $PC_3H_6O_2^+$.

The spectrum of $P(OCH_2)_3CNO_2$ presents an interesting question: Is the fragmentation of the parent ion to yield m/e 149 the result of the loss of a $CH_2O$ group, typical of the bicyclic phosphites, or is it the result of the loss of NO, typical of nitro compounds (11,12)? The two fragment ions formed by these two pathways, $PC_4H_4O_4^+$ and $PC_3H_6NO_4^+$, differ by 0.0126 a.m.u. The observed m/e 149 peak was expanded and found to be a doublet

with a separation consistent with this mass difference. This substantiates the proposal that there are two pathways involved in the degradation of the parent ion to give the m/e 149 ion and further suggests that there are also two pathways, the inverse of the first two, leading the formation of the ion m/e 103 + X (Fig. 1).

## EXPERIMENTAL

The instrument used to determine the mass spectra was a Hitachi Perkin-Elmer Model RMU-6E mass Spectrometer. Samples were injected as solids directly into the liquid sample chamber and volatilized at 150°. Ionization energy for all measurements was 70 ev. All compounds were re-sublimed immediately before use to insure their purity. The lack of any $P(OCH_3)(OH)^+$ peak in the observed spectra confirmed the absence of any trimethyl phosphite. Also indicative of the purity of the phosphites is the absence of unique peaks found in the mass spectra of the analogous phosphates presently under study.

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

This bicyclic phosphite was prepared using the method of Huttemann, et. al., (3).

4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

This compound was prepared using the method of Wadsworth and Emmons (13).

4-Propyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

This compound was prepared using the same procedure as for the 4-methyl analog except that 2-hydroxymethyl-2-propyl-1,2-propanediol was substituted for the tri-alcohol. This method gave 91% yield of $P(OCH_2)_3CC_3H_7$, m.p. 78-79°.

Anal. Calcd. for $C_7H_{13}O_3P$: C, 47.74; H, 7.44; mol. wt., 176. Found: C, 47.88; H, 7.46; mol. wt. 176 (mass spectrometric).

4-Nitro-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

To 27.6 g. (0.2 mole) of phosphorus trichloride cooled to 10° was added 32.2 g. (0.2 mole) of 2-hydroxymethyl-2-nitro-1,3-propanediol. Maintained under a helium flush, the mixture was stirred and slowly warmed to 80°. After six hours, hydrogen

chloride and unreacted phosphorus trichloride were removed under vacuum. The solid residue was ground to a powder and sublimed at 0.2 mm pressure and 50°, producing 0.5 g. (1.8% yield) of crystalline $P(OCH_2)_3CNO_2$, m.p. 81-82°.

Anal. Calcd. for $C_4H_6NO_5P$: C, 26.81; H, 3.36; N, 7.83; mol. wt. 179. Found: C, 26.78; H, 3.42; N, 7.92; mol. wt. 179 (mass spectrometric).

Acknowledgements.

## REFERENCES

(1) J. L. Occolowitz and G. L. White, Anal. Chem., 35, 1179 (1963).

(2) Y. Wada, Doctoral Dissertation, Kansas State University, Manhattan, Kansas, Aug. 1964.

(3) T. J. Huttemann, Jr., B. M. Foxman, C. R. Sperati, and J. G. Verkade Inorg. Chem., 4, 950 (1965).

(4) J. G. Verkade, R. E. McCarley, D. G. Hendricker and R. W. King, ibid., 4, 228 (1965).

(5) C. W. Heitsch and J. G. Verkade, ibid., 1, 392 (1962).

(6) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc. New York, N. Y., 1966, p. 215.

(7) D. A. Bafus, E. J. Gallegos, and R. W. Kiser, J. Phys. Chem., 70, 2614 (1966).

(8) F. W. McLafferty, Anal. Chem., 28, 306 (1956).

(9) J. Occolowitz and M. Swan, Australian J. Chem., 19, 1187 (1966).

(10) H. R. Harless, Anal. Chem., 33, 1387 (1961).

(11) J. H. Beynon, "Mass Spectrometry," Elsevier, Amsterdam, 1960, p. 268.

(12) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1963 p. 16.

(13) W. S. Wadsworth and W. D. Emmons, J. Am. Chem. Soc., 84, 610 (1962).