

NOTE

Electron Impact and High Resolution Mass Spectral Studies of 3-Substituted 7,8-Dimethyl-2,4,3-Benzodioxaphosphepin 3-Oxides

C. NAGA RAJU* and M.V.S. PRASAD†

Department of Chemical Engineering

S.V. University, College of Engineering, Tirupati-517 502, India

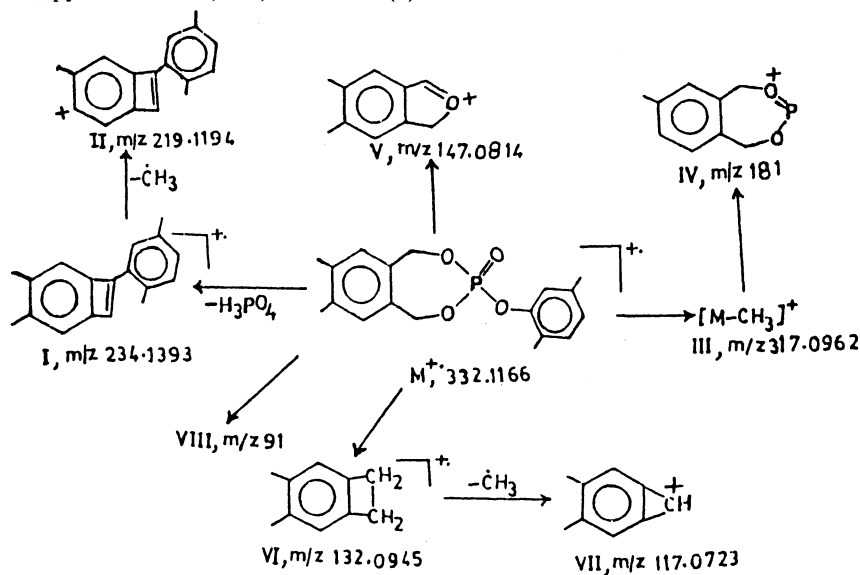
The electron impact mass spectra of 3-aryloxy/amino-1,5-dihydro-7,8-dimethyl-2,4,3-benzodioxaphosphepin 3-oxides were studied to understand their fragmentation pattern and to establish their structures. 4,5-Dimethyl-benzocyclobutane radical cation at m/z 132 is a predominant daughter ion in the title compounds. The fragmentation processes are supported by high resolution mass spectral data.

The mass spectral study of the title compounds has been undertaken because these compounds belong to new class of phosphorus heterocycles^{1,2} and their expected pesticidal activity³, stabilizers⁴ in polymers and lubricant additives⁵. The fragmentation processes occurring in these compounds (I-II) are depicted in Scheme-1 by using compound 4 as a typical example. Important fragment ions observed in the electron impact mass spectra of I-II are presented in Table-1. Fragmentations are supported by first field free region metastable transitions which were observed on the monitor while recording the spectrum and accurate mass measurements of some important ions of compound 4 (Table-2).

In the high resolution mass spectrum of 4, molecular ion appears at m/z 332.1166 (23) indicating its instability and confirming its molecular composition. Cleavage of endocyclic C—O bonds in M^+ , consequent elimination of H_3PO_4 and migration of phenyl moiety to the methylene carbon resulted in the formation of an interesting ion (I) at m/z 234.1393 with low abundance. Loss of methyl radical from I formed the ion (II) at m/z 219.1194 with low intensity. Cleavage of endocyclic P—O bond and subsequent elimination of $C_8H_9O_2POH$ as a radical resulted in the formation of a benzofuran derivative⁶ as a cation (V) at m/z 147.0814 (II). In another mode of fragmentation, the scission of both CH_2 —O bonds in M^+ leads to the formation of the most abundant ion (VI) at m/z 132.0945 as a base peak⁶ in the spectrum. Loss of methyl radical from VI resulted in the appearance of cation (VII) at m/z 117.0723 with moderate abundance⁶. In another mode of degradation, the M^+ ejects a methyl radical to give rise to a cation, $M-CH_3$ (III) at m/z 317.0962 with low intensity. Cleavage of exocyclic P—O bond and simultaneous expulsion of phenoxy moiety and an oxygen atom⁷ from

†Multi-Chem Research Centre, Baroda, India.

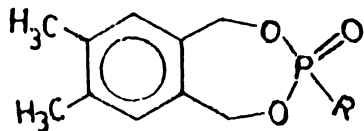
III resulted in the occurrence of a cation (IV) at m/z 181 with moderate abundance. Tropylium cation (VIII) at m/z 91 (9) is also formed from the M^+ .



All the compounds except 7, 9–11 exhibited M^+ ions. There are a few differences in the fragmentation pathways of 7–11 when compared to 1–6. This may be various substituents that are attached to phosphorus. The presence of M^+ , $[M-CH_3]^+$, $[(M-CH_3)-R, O]^+$, $[M-H_3PO_4]^+$, $[(M-R)-PO_2H]^+$, $[(M-H_3PO_4)-CH_3]^+$, $[C_{10}H_{12}]^+$ and $[C_9H_9]^+$ is the characteristic fragmentation process in most of the mass spectra of these phosphorus heterocyclic molecules.

The title compounds are new and they were not reported earlier in the literature. They were synthesised² in our laboratory and characterized by their IR, 1H , ^{13}C and ^{31}P NMR spectra. The low resolution EI mass spectra were recorded on JMS-D 300 spectrometer at 70 eV using direct probe system. The accurate mass measurements of a few selected ions from compound 4 were performed by

	R		R
1	2- CH_3 - C_6H_4O	7	Cl
2	3- CH_3 - C_7H_4O	8	N-piperazino
3	4- CH_3 - C_6H_4O	9	$\begin{array}{c} C_6H_{11} \\ \diagdown \\ N \\ \diagup \\ C_6H_{11} \end{array}$
4	2,5-(CH_3) ₂ - C_6H_3O	10	8-O-quinolino
5	4-Cl- C_6H_4O	11	S- C_6H_5
6	2,4-(Cl) ₂ - C_6H_3O		



peak matching at a resolution of 10,000 (10% valley) on a VG-7070 E-HF double focussing forward geometry mass spectrometer equipped with a PDP based data system. The samples were introduced by solid probe and heated to their melting point temperatures to vapourize into the ion source.

TABLE-1
EI MASS SPECTRAL DATA OF 1-11

Compounds	M ⁺	m/z (%)
1	318(21.4)	309(9.1), 220(7.1), 205(6.9), 181(14.2), 147(12), 132(100), 117(11.4), 91(12.8), 77(7.2).
2	318(12.1)	303(21.5), 288(35.7), 220(12.3), 181(100), 147(14), 132(42.8), 117(13.5), 91(64.3), 77(8).
3	318(13.3)	303(21.3), 288(26.6), 220(9.6), 205(9.3), 181(90.7), 147(21), 132(100), 117(16.4), 91(53.3), 77(25.3).
4	332(60.5)	317(30.3), 234(33.3), 219(6), 181(50.0), 147(16), 132(100), 117(18.6), 91(15), 77(7).
5	338(40)	340(13.5, M + 2), 303(7), 295(11), 293(14), 249(12), 247(15.8), 240(10.4), 230(18), 221(7.5), 195(10), 181(55), 167(32), 147(30), 132(17), 131(28), 130(100), 117(12), 113(24.7), 105(13), 95(18), 91(29), 77(13).
6	372(26.6)	376(6, M + 4), 374(17, M + 2), 230(8.3), 257(8.2), 181(100), 147(25), 132(43.3), 130(16), 117(10.8), 91(25), 77(15).
7	—	202(95), 169(63.1), 132(100), 91(52.6)
8	296(14.2)	227(50), 181(23.4), 132(92.8), 86(100), 58(26.6), 44(20).
9	—	181(16.6), 132(100), 100(16.6), 56(83).
10	—	246(26.6), 147(66.6), 130(100), 117(41.6), 91(33.3).
11	—	275(100), 274(45.5), 181(21), 163(52.7), 132(46.4), 121(96), 117(63.6), 115(25.4), 91(29.1).

TABLE-2
HIGH RESOLUTION MASS SPECTRAL DATA FOR IMPORTANT IONS OF 4

m/z (%)	Measured mass	Difference (mmu)	Elemental composition
332(23)	332.1166	1.1	C ₁₈ H ₂₁ O ₄ P
317(12)	317.0962	-2.0	C ₁₇ H ₁₈ O ₄ P
234(12)	234.1393	1.5	C ₁₈ H ₁₈
219(13)	219.1194	-2.1	C ₁₇ H ₁₅
147(11)	147.0814	-0.4	C ₁₀ H ₁₁ O
132(100)	132.0945	-0.6	C ₁₀ H ₁₂
131(10)	131.0853	0.8	C ₁₀ H ₁₁
117(19)	117.0723	-1.9	C ₉ H ₉
91(16)	91.0560	-1.2	C ₇ H ₇
77(9)	77.0413	-2.2	C ₆ H ₅

ACKNOWLEDGEMENT

The authors express their thanks to Dr. G.S. Reddy, Department of Environmental Health, The University of Michigan, USA for recording high resolution mass spectram.

REFERENCES

1. T. Sato and K. Goto, *J. Chem. Soc. Chem. Commun.*, 494 (1973).
2. M.V.S.R. Prasad, Ph.D. Thesis, S.V. University (1990).
3. S.V. Hummel and R.A. Yost, *Org. Mass Spectrom.*, **21**, 785 (1986).
4. P.A. Odorisio, S.D. Pastor and J.D. Spivack, *Phosphorus and Sulfur*, **19**, 1 (1984).
5. J.D. Spivack, *Brit. Pat.* 2, 087, 399 (1982); *Chem. Abstr.*, **97**, 198374 (1982).
6. C.D. Reddy, M.S. Reddy, C.V. Nageswara Rao, C. Naga Raju, Chabbil Das and G.S. Reddy, *Indian J. Heterocycl. Chem.*, **5**, 49 (1995).
7. C. Naga Raju and G.S. Reddy, *Indian J. Heterocycl. Chem.*, **6**, 119 (1996)

(Received: 21 September 1998; Accepted: 2 January 1999)

AJC-1672