Syntheses and Electron Impact Spectra of 2-Aryl Substituted Octahydro-1H-1,3,2benzodiazaphosphole 2-Oxides

The 70 eV electron impact (EI) mass spectra of the 2-aryl substituted octahydro-1H-1,3,2-benzodiazaphosphole 2-oxides (1-9) have been studied. The 40 eV EI mass spectra for compounds 1, 2, 3, 5, 7 and 9 were recorded as their molecular ion peaks were not observed in the 70 eV mass spectra. An interpretation of the mass spectra of 2-(3-methylphenyl)octahydro-1H-1,3,2-benzodiazaphosphole 2-oxide (3) is presented in Scheme 1 and Fig. 1 as a typical representative of the series.

Compound 3 shows the molecular ion $[C_{13}H_{19}N_2O_2P]^+$ at m/z 266 (4%). Scission of the P-O bond with simultaneous elimination of 3-methylphenoxy radical from [M]⁺ leads to the formation of a more stable octahydro-1H-1,3,2-benzodiazaphosphole 2-oxide ion $[C_6H_{10}N_2OP]^+$, m/z 159 (71%). Subsequent loss of a hydrogen molecule from this ion leads to the formation of hexahydro-1,3,2-benzodiazaphosphole 2-oxide ion $[C_6H_{10}N_2OP]^+$ at m/z157 (7%) which on further loss of an oxygen atom forms the hexahydro-1,3,2-benzodiazaphosphole ion $[C_6H_{10}N_2P]^+$ at m/z 141 (16%). Loss of oxygen from the diazaphosphole 2-oxide ion is supported by the presence of a metastable peak at m/z 126.5. The diazaphosphole ion might even have been derived directly from the diazaphosphole 2-oxide ion by loss of a water molecule.

The 1,2-diaminocyclohexane ion $[C_6H_{14}N_2]^+$ is formed at m/z 114 (25%) by the concerted homolytic fission of the P—N bonds with simultaneous abstraction of the two hydrogens by the nitrogen atoms from the benzene moiety¹ of the molecular ion



Cleavage of the two C—N bonds in the 1,2-diaminocyclohexane ion results in the formation of $[C_6H_{10}]^{+*}$ at m/z 82 (41%) with elimination of the hydrazine molecule. A metastable peak detected at m/z 59.2 supports this decomposition route.

The high intensity ion $[C_3H_6N]^+$, m/z 56 $(33\%)^2$ is formed by further cleavage of the

diaminocyclohexane ion at the γ -carbon with the elimination of a hydrogen molecule. The more stable 1-aminobutadiene ion, $[C_4H_7N]^+$ m/z 69 (32%) might have resulted from α -cleavage and simultaneous migration of hydrogen atoms² in the cyclohexanediamine ion with ethylamine elimination as shown in Scheme 2.



Scheme 1. Electron impact spectra of 2-(3-methyl phenoxy)octahydro-1H-1,3,2-benzodiazaphosphole 2-oxide at 70 eV.



Figure 1. Electron impact spectrum of 2-(3-methyl phenoxy)octahydro-1H-1,3,2-benzodiazaphosphole 2-oxide at 70 eV.



CH₂=CH--CH=CH \vec{N} H₂ m/z 69 (32%)



Loss of the diaminocyclohexane moiety from the molecular ion by the homolytic cleavage of the P—N bonds leads to the formation of the ion radical $[C_7H_7O_2P]^{+\cdot}$ at m/z 154 (7%). The $[C_7H_7O_2P]^{+\cdot}$ ion loses a phosphoryl radical³ and forms a 3methylphenoxide ion at m/z 107 (83%). This ion might also be derived from the $[M]^{+\cdot}$ ion through the 3-methylphenol ion $(m/z \ 108)$ which is the base peak of the spectrum and probably exists as the more stable hydroxytropylium cation.⁴

Molecular ions are observed for 3, 7 and 8 at 70 eV, but other compounds, except 1,

exhibited molecular ion peaks only at 40 eV. In all the compounds the $[M]^{+}$ ions appeared in very low abundance showing that they are rather unstable under electron impact. This behaviour is in contrast with their aromatic analogues⁵⁻⁷ where the molecular ions appear at 70 eV with relatively high abundance and in some cases form the base peak of their spectra. This seems to be due to the presence of an inherent steric strain and the impossibility of resonance in the bicyclic system of octahydro-1H-1,3,2 -benzodiazaphosphole 2-oxide.

The molecular ions of all these compounds appear to decompose essentially by four major routes forming the ions corresponding to the diazaphosphole 2oxide $[M-RC_6H_4O]^+$, diaminocyclohexane $[M-RC_6H_4O_2P]^+$, phenoxyphosphoryl moiety $[M-C_6H_{12}N_2]^{++}$ and phenol $[M-C_6H_{12}N_2OP]^{++}$ by cleavage of the P—O and P-N bonds.

The ions at m/z 114, 96, 82, 69, 56 are derived from the 1,2-diaminocyclohexane moiety⁸ of the molecular ion, and the ion at m/z 56 appears as the base peak for the

compounds 1, 5, 6 and 7. The base peaks for the compounds 2, 3, 4, 8 and 9 are due to the ions at m/z 107, 107, 108, 128 and 128, which are derived from the phenoxy moiety of the respective $[M]^{+\cdot}$ ions.

1,2-Diaminocyclohexane was procured from Pfaltz and Bauer Inc., (Stamford, Connecticut USA) and used after distillation under vacuum b.p. 100 °C/8 mm (lit.⁹ 183– 185 °C/720 mm). Triethylamine was dried over KOH and distilled before use. The aryl phosphorodichloridates were prepared by reacting the respective phenols with phosphorus oxychloride according to the conventional procedures.¹⁰

Mass spectra were recorded on a Hitachi RMU 6L instrument, with electron energies of 40 eV and 70 eV and trap current 100 μ A, at the Regional Research Laboratories, Hyderabad, India. Infrared spectra were recorded with a Beckmann IR-18A spectrophotometer in KBr (1-5, 8) and nujol mull (6, 7, 9). The elemental analysis were performed at CDRI, Lucknow, India. All melting points were determined on a Mil-Temp apparatus and were uncorrected.

Table 1. Syntheses of substituted phenoxyoctahydro-1H-1,3,2-benzodiazaphosphole 2-oxides

Com- pound	Yield" (%)	m.p. (℃)		Infrared frequencies (cm ⁻¹)				
			Molecular formula	P==0	P-NH	P-N-C aliphatic	PC aromatic	
1	35	220 dec	C ₁₂ H ₁₇ N ₂ O ₂ P. 1 ¹ / ₂ H ₂ O	1200	3220	1060	1220	960
2	45	230 dec	C ₁₃ H ₁₉ N ₂ O ₂ P. 1 ¹ / ₂ H ₂ O	1200	3220	1060	1240	950
3	49	240 dec	C ₁₃ H ₁₉ N ₂ O ₂ P. H ₂ O	1 19 0	3220	1050	1230	950
4	50	220 dec	C ₁₃ H ₁₉ N ₂ O ₂ P. H ₂ O	1200	3220	1060	1240	960
5	60	223-35	C ₁₄ H ₂₁ N ₂ O ₂ P. H ₂ O	1200	3240	1060	1160	960
6	55	249-51	C14H21N2O2P. 11H2O	1170	3220	1050	1230	950
7	54	23638	C ₁₄ H ₂₁ N ₂ O ₂ P. 1 ¹ / ₂ H ₂ O	1180	3220	1060	1150	950
8	50	250 dec	C12H16N2O2PCI. H2O	1200	3220	1060	1230	950
9	40	240 dec	C12H16N2O2PCI. H2O	1210	3220	1060	1240	950
Product	t isolate	d after on	e crystallization. Produc	ts 1 and	d 4 cryst	allized fr	om MeOH	: 2. 3. 5

crystallized from MeOH and THF mixture (2:1). All products gave satisfactory microanalyses: $C, \pm 0.68$; $H, \pm 0.60$; $N, \pm 0.58$.

Octahydro-2-phenoxy-1H-1,3,2-benzodiazaphosphole 2-oxide (1).

1,2-Diaminocyclohexane 2.3 g (0.02 mol)and triethylamine 4.04 g (0.04 mol) in 60 cm^3 of dry benzene were heated to 40– 50 °C with stirring. A solution of phenyl phosphorodichloridate 5.2 g (0.02 mol) in 30 cm^3 of dry benzene was added dropwise over a period of 30 min. Stirring was continued for 5 h at the same temperature. The progress of the reaction was monitored by thin-layer chromatography. Triethylamine hydrochloride was removed by filtration. The filtrate was evaporated in a rotavapor and the residue recrystallized from methanol.

The same procedure was adopted for the syntheses of the compounds 2-9.

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C. DEVENDRANATH REDDY and C. V. NAGESWARA RAO Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India

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Book Review

J. H. BEYNON and A. G. BRENTON

An Introduction to Mass

Spectrometry

University of Wales Press, Cardiff, 1982. pp. 57. £3.95.

This little book is precisely what its title says it is. Starting with J. J. Thompson's mass spectrograph the reader is led to discussions of the vacuum system, production, separation and detection of ions in a mass spectrometer. The last chapter describes some of the applications of mass spectrometry to organic chemistry, physical chemistry, physics and geology. Mathematics is kept to a minimum and the various aspects of mass spectrometric concepts are lucidly explained.

The potential readers of this volume, in

the opinion of the reviewer lie in the ranks of sixth formers, junior undergraduates and those members of the general public interested in learning something about what mass spectrometrists are doing.

> ALLAN MACCOLL University College, London