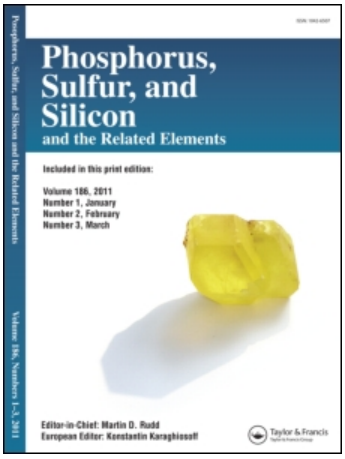


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MASS SPECTROMETRIC FRAGMENTATION OF UNSYMMETRICALLY SUBSTITUTED METHYLPHOSPHONATE DIESTERS

Shefali Saxena[a]; M. Palit Purnanand[a]; S. K. Raza[a]
[a] Defence Research & Development Establishment, Gwalior, India

To cite this Article Saxena, Shefali , Purnanand, M. Palit and Raza, S. K.(2001) 'MASS SPECTROMETRIC FRAGMENTATION OF UNSYMMETRICALLY SUBSTITUTED METHYLPHOSPHONATE DIESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 174: 1, 247 — 253
To link to this Article: DOI: 10.1080/10426500108040249
URL: http://dx.doi.org/10.1080/10426500108040249

Phosphorus, Sulfur and Silicon, 2001, Vol. 174, pp. 247-253
Reprints available directly from the publisher
Photocopying permitted by license only

MASS SPECTROMETRIC FRAGMENTATION OF UNSYMMETRICALLY SUBSTITUTED METHYLPHOSPHONATE DIESTERS

SHEFALI SAXENA, M. PALIT PURNANAND and S.K. RAZA*

Defence Research & Development Establishment, Gwalior-474 002, India

(Received September 09, 2000; In final form February 09, 2001)

A series of structurally related unsymmetrically substituted methylphosphonate diesters have been synthesised and subjected to electron impact (EI) mass spectral studies. These studies though aimed at total identification of the compounds, resulted in certain interesting observations and hence are being reported. In order to confirm the observations under electron impact and to support the mechanism of fragmentation we have also performed MS/MS experiments in both daughter ion and parent ion modes.

INTRODUCTION

Unsymmetrically substituted methylphosphonate diesters constitute an important class of compounds finding applications in nucleoside chemistry[1] and in eliciting catalytic antibodies[2]. The synthesis of unsymmetrically substituted alkylphosphonate diesters has been an exciting area for synthetic chemists and a variety of methods have been reported[3–9]. We synthesised a series of unsymmetrically substituted methylphosphonate diesters[10] and subjected them to mass spectrometric fragmentation in order to see how the two stereomers differ in the fragmentation pattern under electron impact. The mechanism of formation of various ions under electron impact has been substantiated and supported by performing tandem mass spectrometry experiments.

* Corresponding Author.

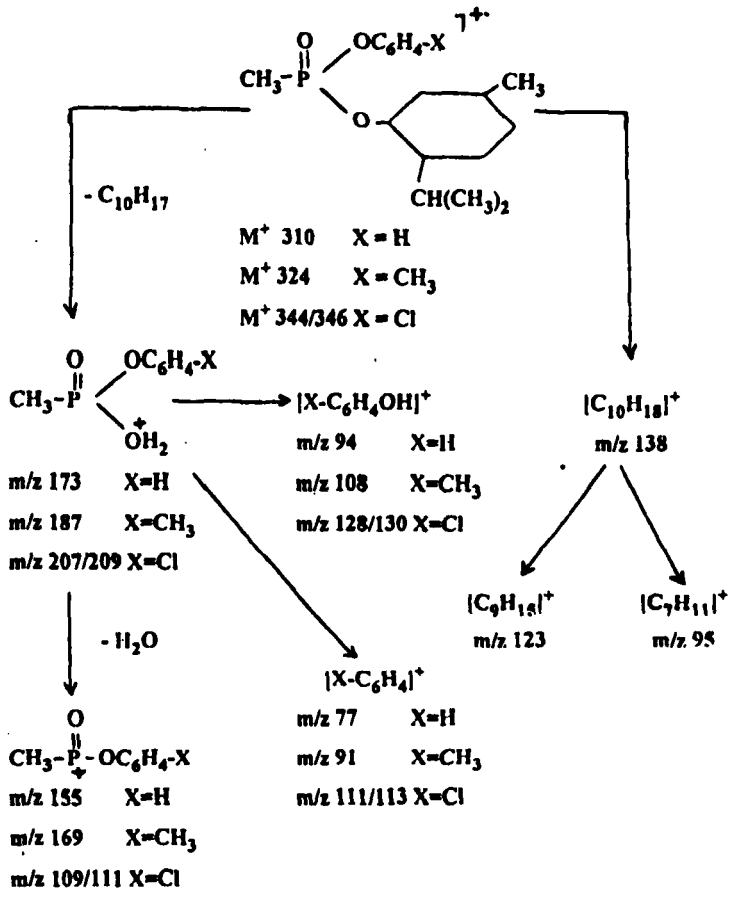
RESULTS AND DISCUSSION

The mass spectra of all the methylphosphonic diesters (**I – VIII**) (Figure 1) showed small molecular ion peaks[11]. The mass spectra of all the diesters were conspicuous by the loss of $C_{10}H_{17}$ from the O-cycloalkyl group to give the base peak. Besides this other prominent peaks were also observed corresponding to different substituents (Table I). The O-phenyl group remained intact with all phosphorus containing fragment ions showing thereby that the ions are stabilised due to the presence of phenyl ring. The results of daughter ion experiments are shown in Table II.

TABLE I EI Mass Spectral Data for Methylphosphonate Diesters

Compd. No.	*Molecular Weight*	*m/z (Relative intensity)*
I	310	310(M^+, 2.1); 173(100); 155(2.5); 138(10.2); 123(3.2); 95(12.3); 94(8.2); 77(8.4).
II	310	310(M^+, 2.3); 173(100); 155(1.2); 138(9.5); 123(5.6); 95(14.2); 94(15.3); 77(10.1).
III	324	324(M^+, 1.4); 187(100); 169(10.3); 138(5.3); 123(6.1); 108(60.3); 95(15.3); 91(20.5).
IV	324	324(M^+, 3.1); 187(100); 169(4.1); 138(4.6); 123(2.1); 108(40.0); 95(12.4); 91(15.2).
V	344/346	344/346(M^+, 2.1/0.8); 207/209(100/33); 189/191 (10.5/3.2); 138(26.5); 128/130(60.6/19.8); 123(12.1); 95(40.2).
VI	344/346	344/346(M^+, 3.1/1.1); 207/209(100/32); 189/191 (20.3/7.9); 138(30.3); 128/130(70.3/23.6); 123(15.1); 95(43.2).
VII	344/346	344/346(M^+, 5.1/1.8); 309(4.2); 207/209(100/33.5); 189/191(11.2/4.1); 171(60.1); 138(15.2); 128/130(10.3/3.5); 123(8.1); 95(10.1).
VIII	344/346	344/346(M^+, 5.6/1.8); 309(4.1); 207/209(100/33.2); 171(63.5); 189/191(10.5/3.2); 138(18.1); 128/130(12.1/3.8); 123(5.3); 95(12.1).

The mass spectra of the diesters **I** and **II** showed molecular ions at m/z 310. The base peak in both the spectra were observed at m/z 173 due to the loss of $C_{10}H_{17}$ from the O-cycloalkyl group. The other fragment ions observed in these spectra were at m/z 155, 138, 123, 95, 94 and 77. The genesis of the formation of these ions is shown in Scheme 1. The proposed mechanism of fragmentation was confirmed by performing daughter ion



SCHEME 1 Proposed Fragmentation Mechanism for Compounds I – VIII

scans in MS/MS mode. The daughter ion scans showed that while the ions at m/z 173 and 138 are the daughters of the molecular ion, the ions at m/z 155, 94 and 77 arise from the ion m/z 173 and the ions at m/z 123 and 95 arise from the ion at m/z 138. Mechanistically, the ion at m/z 155 may either be $[CH_3P(O)OC_6H_5]^+$ or $[C_{10}H_{19}O]^+$. The fact that this ion arises from the ion m/z 173 and not from the molecular ion as demonstrated by MS/MS experiment in daughter ion mode clearly confirmed that this ion at m/z 155 is $[CH_3P(O)OC_6H_5]^+$ and not the other one.

TABLE II Daughter Ions formed from Different Parent Ions in Compounds I – VIII

Compound No.	*Parent Ions m/z*	*Daughter Ions Formed m/z*
I & II	310	173, 138
	173	155, 94, 77
	138	123, 95
III & IV	324	187, 138
	187	169, 108, 91
	138	123, 95
V & VI	344/346	207/209, 138
	207/209	189/191, 128/130, 111/113
	138	123, 95
VII & VIII	344/346	309, 207/209, 138
	207/209	189/191, 171, 128/130, 111/113
	138	123, 95

The mass spectra of the diesters **III** and **IV** showed molecular ion peaks at m/z 324. The base peak in both the spectra was observed at m/z 187 due to the loss of $C_{10}H_{17}$ from the O-cycloalkyl group. This observation is contrary to the generally observed base peak at m/z 186 in O-alkyl O-benzyl methylphosphonates due to the ion $[CH_3P(O)(OC_6H_4CH_3)(OH)]^+$. The other fragment ions were observed at m/z 169, 138, 123, 108 and 95. The genesis of the formation of these ions was confirmed by performing daughter ion experiments in MS/MS mode. No significant differences were observed in the mass spectra of the two isomers and most of the ions formed in **III** and **IV** were corresponding to those observed in **I** and **II**. An additional ion was formed, as expected, at m/z 91 due to Tropylium cation.

The mass spectra of the diesters **V – VIII** showed molecular ion peaks at m/z 344/346. The base peak in all these spectra arises due to the loss of $C_{10}H_{17}$ from the O-cycloalkyl group to give ions at m/z 207/209. The other ions observed were at m/z 189/191, 138, 128/130, 123 and 95. The mechanism for the formation of these ions is shown in Scheme I. The fragmentation pathways suggested in Scheme I were confirmed by performing MS/MS experiments in daughter ion and parent ion modes. The mass spectra of compounds VII and VIII were, however, conspicuous by the

presence of two extra peaks at m/z 309 and 171 which were not observed in their isomeric compounds V and VI. The ion at m/z 309 arises due to the loss of Chlorine radical from the molecular ion while the ion at m/z 171 arises due to loss of HCl from the ion m/z 207. The ions due to the loss of Chlorine radical and HCl have been observed only in *ortho*-substituted chloro derivative and not in *para*-substituted one, most probably because of steric effects.

To conclude, there were no significant differences observed in electron impact fragmentation pathways of the sterioisomeric methylphosphonate diesters. Some differences were, however, observed in the fragmentation pattern due to the presence of different positional isomers as O-aryl substituents. The proposed fragmentation mechanism has been supported by performing MS/MS experiments. The study gives an insight into the mass spectrometric behaviour of newly synthesised unsymmetrically substituted methylphosphonate diesters.

EXPERIMENTAL

Synthesis

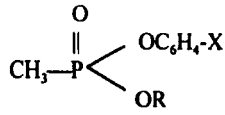
The diesters were synthesised by following a method developed in our laboratory and being reported elsewhere[10]. The compounds synthesised and subjected to mass spectral studies are shown in Figure 1.

Mass Spectral Analysis

The mass spectra were recorded on a TSQ 7000 Mass Spectrometer (Finnigan Mat, USA) at 70 eV using a direct insertion probe at a source temperature of 150°C. Tandem mass spectrometry data were obtained at a collision energy of 20 eV (laboratory frame of reference) and the collision gas was Argon introduced at such a pressure as to attenuate the parent ion beam intensity by 50%.

Acknowledgements

The authors thank Dr. R. V. Swamy, Director, for providing necessary facilities and to Dr. D. K. Jaiswal, Head Synthetic Chemistry Division for useful discussion.



Compd. No.	X	R	Mol. Wt.
I	H		310
II	H		310
III	CH_3		324
IV	CH_3		324
V	p-Cl		344/346
VI	p-Cl		344/346
VII	o-Cl		344/346
VIII	o-Cl		344/346

FIGURE 1 Structure of Methylphosphonate Diesters Subjected to Mass Spectral Studies

References

1. P. S. Miller, Biochemistry, **9**, 358 (1991).
2. C. N. Durfor, R. J. Bolin, R. J. Sugasawara, J. W. Jacobs and P. G. Schultz, J. Am. Chem. Soc., **110**, 8713 (1988).

3. T. Wada and M. Sekine, Tetrahedron Lett., **35**, 757 (1994).
4. K. Zhao and D.W. Landry, Tetrahedron, **49**, 363 (1993).
5. P. Rosmanitz, S. Fisenhardt, J. W. Bats and J. W. Engels, Tetrahedron, **50**, 5719 (1994).
6. J. C. H. M. Wijkmans, W. Ottenheim, E. Kuyl-Yeheskiely, G. A. van der Marel, W. Bloemhoff, J. H. van Boom, Synthesis, 97 (1995).
7. D. S. Tawfik, Z. Eshhar, A. Bentolila and B. S. Green, Synthesis, 968 (1993).
8. P. W. Morgan and B. C. Herr, J. Am. Chem. Soc., **74**, 4526 (1952).
9. R. M. Monarty, A. Tao, C. Condiu and R. Gilardi, Tetrahedron Lett., **38**, 2597 (1997).
10. S. Saxena, B. Lal, M. Sharma and Purnanand, Phosphorus, Sulfur and Silicone (accepted).
11. I. Granoth, in "Topics in Phosphorus Chemistry", E. J. Griffith and M. Grayson, Ed., John Wiley & Sons, Inc., New York, Vol. 8, Chapter 2 (1976).