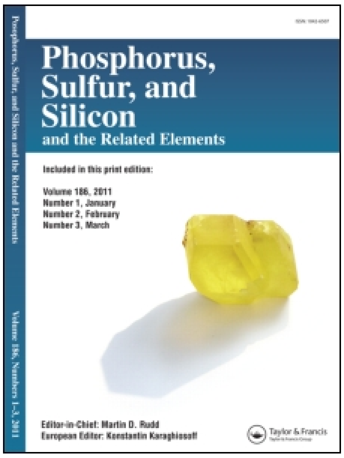

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A MASS SPECTROSCOPIC STUDY OF o-HYDROXYPHENYL DIALKYL PHOSPHINE OXIDES AND DIAKYL o-HYDROXYPHENYLPHOSPHONATES

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A MASS SPECTROSCOPIC STUDY OF *o*-HYDROXYPHENYL DIALKYL PHOSPHINE OXIDES AND DIAKYL *o*-HYDROXYPHENYLPHOSPHONATES†

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The electron impact mass spectra of a series of *o*-hydroxyphenyl dialkyl phosphine oxides (**1**) and dialkyl *o*-hydroxyphenylphosphonates (**2**) were investigated. The principal fragmentation pathways are the cleavage of P—$C_{sp}3$ bond, the McLafferty rearrangement involving P=O group and the mixed process of these two pathways for *o*-hydroxyphenyl dialkyl phosphine oxides, but for dialkyl *o*-hydroxyphenylphosphonates, the successive McLafferty rearrangements are observed to be the predominant one without the cleavage of P—$C_{sp}2$ bond which occurs as a minor process in the fragmentation of compound **1**.

Key words: mass spectra, *o*-hydroxyphenyl dialkyl phosphine oxides, dialkyl *o*-hydroxphenylphosphonates.

INTRODUCTION

There have been intensive studies on the mass spectra of phosphorus-containing compounds,[1,2] and detailed reports on the cleavage patterns of these compounds also appeared in literature. But only a few reports have appeared concerning phosphine oxides[3,4,5] and dialkyl phenylphosphonates.[6] Mass spectral study on the title compounds has not been published until now.

We have recently synthesized a series of *o*-hydroxyphenyl dialkyl phosphine oxides (**1**) and dialkyl *o*-hydroxyphenylphosphonates (**2**).[7] These compounds may exhibit bioactivity because of their close structures to salicylic acid and its derivatives. In order to confirm their structures, the electron impact mass spectra of **1** and **2** were examined. In this paper we present the results of such an investigation. The fragmentation patterns may be useful in structural identification of analogous substances. The structures of **1** and **2** are shown in the following.

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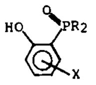
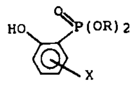


1



2

R	C_2H_5	C_2H_5	C_2H_5	C_2H_5	C_2H_5	n-C_3H_7	i-C_3H_7	n-C_4H_9	i-C_4H_9
X	H	3-CH_3	4-CH_3	5-CH_3	5-OCH_3	H	H	H	H
NO.	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**
		2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	

R	i-C_4H_9	s-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_6H_{13}	n-C_8H_{17}	n-$C_{12}H_{25}$
X	6-OCH_3	H	H	H	5-CH_3	H	H
NO.			**1j**	**1k**		**1l**	**1m**
	2h	**2i**			**2j**		

TABLE I

Abundance of fragments of *o*-hydroxyphenyl dialkyl phosphine oxides

	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**
1a	199 (30.85)	198 (50.69)			170 (52.69)		141 (100.00)	142 (36.14)
1b	213 (67.15)	212 (100.00)			184 (51.91)		155 (67.38)	156 (25.11)
1c	213 (23.06)	212 (41.49)			184 (35.86)		155 (66.94)	156 (18.84)
1d	213 (34.50)	212 (91.55)			184 (69.01)		155 (100.00)	156 (36.04)
1e	228 (46.82)	228 (100.00)			200 (40.76)		171 (10.20)	172 (5.64)
1f	227 (12.44)	226 (38.04)	198 (0.96)	170 (12.68)	184 (83.15)	156 (72.39)	141 (100.00)	142 (95.67)
1g	227 (100.00)	226 (38.94)			184 (9.61)		141 (20.28)	142 (10.93)
1h	255 (100.00)	254 (26.73)	212 (1.44)	170 (46.85)	198 (22.88)	156 (83.52)	141 (46.85)	142 (12.65)
1i	255 (94.00)	254 (25.53)	212 (1.16)	170 (26.40)	198 (68.18)	156 (75.72)	141 (91.40)	142 (100.0)
1j	283 (100.00)	282 (25.04)	226 (1.98)	170 (18.11)	212 (16.25)	156 (38.75)	141 (14.46)	142 (8.99)
1k	311 (83.42)	310 (21.62)	240 (2.52)	170 (50.99)	226 (38.00)	156 (100.00)	141 (40.19)	142 (26.23)
1l	367 (93.10)	366 (22.58)	268 (2.88)	170 (52.38)	254 (45.09)	156 (100.00)	141 (41.87)	142 (36.62)
1m	479 (38.69)	478 (19.14)	324 (5.05)	170 (28.86)	310 (60.22)	156 (67.11)	141 (19.68)	142 (26.31)

TABLE II

Abundance of fragments of *o*-hydroxyphenyl dialkyl phosphine oxides

	i	j	k	l	m	n	o	f'
1a	124	123	105	47	169	140	77	
	(4.02)	(12.31)	(5.20)	(13.58)	(7.14)	(6.02)	(34.75)	
1b	138	137	119	47	183	154	77	
	(3.80)	(6.63)	(2.67)	(5.43)	(5.31)	(13.73)	(10.71)	
1c	138	137	119	47	183	154	77	
	(2.04)	(6.60)	(14.12)	(7.26)	(9.06)	(8.22)	(24.07)	
1d	138	137	119	47	183	154	77	
	(5.40)	(6.55)	(4.49)	(7.52)	(6.97)	(5.68)	(4.36)	
1e	154	153	135	47	199		77	
	(7.37)	(0.10)	(2.73)	(7.37)	(4.58)		(12.99)	
1f	124	123	133	47	183	140	77	155
	(8.91)	(19.50)	(1.52)	(28.01)	(16.61)	(7.78)	(65.57)	(3.93)
1g	124	123	133	47	183		77	
	(1.37)	(3.92)	(1.24)	(3.53)	(1.81)		(9.54)	
1h	124	123	161	47	197	140	77	155
	(2.23)	(10.71)	(0.85)	(14.26)	(6.92)	(3.97)	(37.33)	(4.79)
1i	124	123		47	197	140	77	155
	(8.27)	(18.83)		(23.82)	(15.21)	(32.06)	(58.03)	(6.60)
1j	124	123	189	47	211	140	77	155
	(0.88)	(3.87)	(0.74)	(3.39)	(5.67)	(1.79)	(11.89)	(2.79)
1k	124	123	207	47	225	140	77	155
	(2.90)	(9.86)	(0.63)	(8.89)	(11.67)	(3.93)	(27.62)	(7.28)
1l	124	123		47	253	140	77	155
	(2.70)	(9.68)		(6.94)	(10.08)	(3.99)	(21.97)	(8.03)
1m	124	123		47	309	140	77	155
	(1.09)	(3.06)		(1.52)	(9.35)	(1.37)	(5.31)	(6.00)

TABLE III

Abundance of fragments for simple C—C single bond cleavage of *o*-hydroxyphenyl dialkyl phosphine oxides

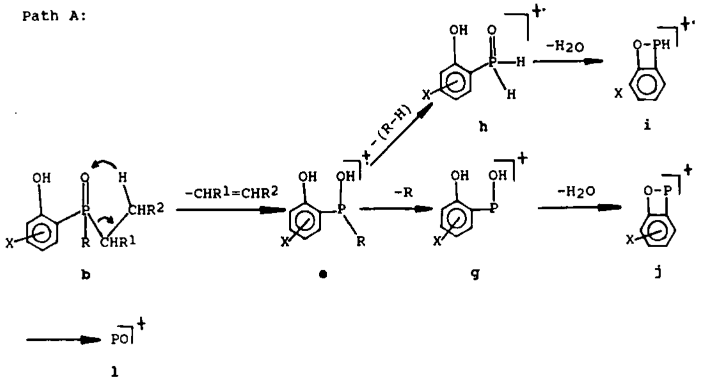
	M-15	M-29	M-43	M-57	M-71	M-85	M-99	M-113	M-127	M-141
1f	211	197								
	(73.84)	(2.65)								
1h	225									
	(45.88)									
1i	239									
	(41.10)									
1j	267	253	239							
	(1.32)	(1.28)	(16.04)							
1k	295	281	267	263						
	(5.80)	(9.22)	(2.72)	(41.38)						
1l	351	337	323	309	295	283	225	211	197	
	(2.47)	(9.10)	(12.77)	(9.49)	(2.74)	(4.54)	(9.84)	(10.33)	(8.26)	
1m	463		435	421	407	393	379	365	351	337
	(3.52)		(5.25)	(5.02)	(4.52)	(5.81)	(6.71)	(5.43)	(2.12)	(16.19)

RESULTS AND DISCUSSIONS

1. The Mass Spectra of o-Hydroxyphenyl Dialkyl Phosphine Oxides

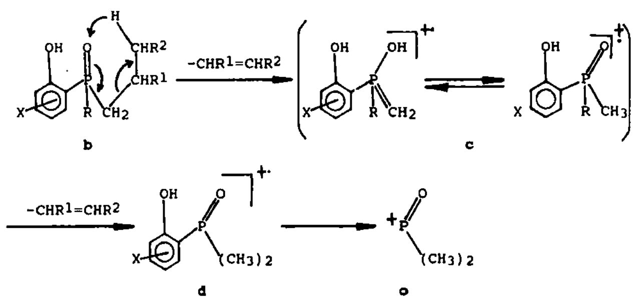
The major peaks observed in electron impact mass spectra of **1** are listed in Table I, Table II and Table III. As shown in Table I, all compounds gave relatively strong M + 1 peaks. The longer the carbon chain, the higher the intensity of M + 1 ions. This means that the parent ions of these phosphine oxides with longer chain are less stable than the corresponding protonated molecules. With the increase of carbon chain length, the thermal stability of molecular ions decrease. In some cases, M + 2 peaks were also observed. Especially, when R is n-$C_{12}H_{25}$, M + 2 ion becomes the base peak. Further fragmentation of **1** can be classified into four paths.

Path A:

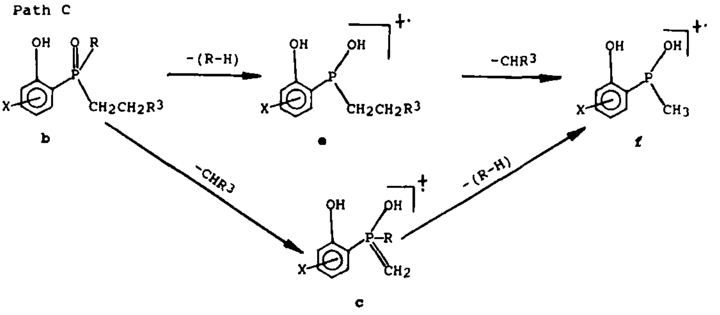


Path A is one of the major processes to all compounds **1** studied. The cleavage of P—$C_{sp}3$ bond involves the migration of hydrogen on the β carbon of the alkyl group through five membered ring transition state. This is consistent with the P—$C_{sp}3$ bond cleavage patterns in many other organophosphorus compounds.[3,8] When the alkyl groups are of sufficient length, the McLafferty rearrangement via a six-membered ring transition state apparently occurs, which leads to the cleavage of C—C bond which is β to the phosphorus atom. This process (Path B) accounts for peaks **c**, **d** and **o**.

Path B:

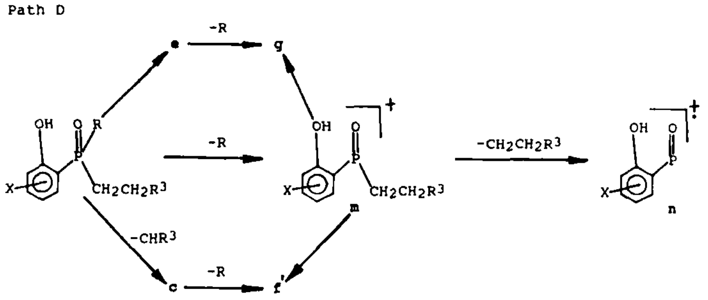


As shown in Table I, although peak **c** is weak, the intensity of peak **d** is relatively strong. This path is also one of the main cleavage ways. When the alkyl chain is not less than three carbons, path A may compete with path B, and a mixed process (Path C) appears.



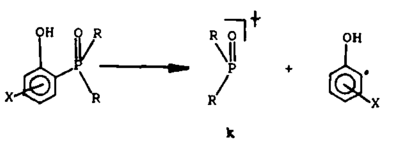
This path is supported by the appearence of peak **f**. The intensity of peak **f** indicates that this path is as important as path A.

In the process of P—$C_{sp}3$ bond fragmentation, another kind of cleavage pattern is also observed. The P—$C_{sp}3$ bond is cleaved directly and no hydrogen-transfer takes place (Path D):



Path D is a minor process, and the probability of subsequent loss of two alkyl groups is much less, but **1i** (R = i-C_4H_9) gives relatively high intensity of peaks **m** and **n** (see Table II).

Compared with P—$C_{sp}3$ bond, the P—$C_{sp}2$ bond is more difficult to be cleaved. The fragmentations related to cleavage of P—$C_{sp}2$ bond are shown in following:



But in those small fragments the cleavage of P—$C_{sp}2$ bond is easier. For example, in path B, peak **o** ($m/e = 77$) is relative strong, and much higher than that observed in compounds **2**. We rationalized that this peak mainly resulted from the contribution of **o** instead of that from phenyl ring.

Simple cleavage of C—C single bond in the alkyl group also took place. In **1**, these cleavage generated a series of ions, M-15, M-29, M-43, ... This is a much weaker process, except for n-Pr and i-Bu groups which have relatively high M-15 peak (see Table III). It indicates that the methyl group at the γ-position to the phosphorus atom is much easier to be cleaved.

TABLE IV

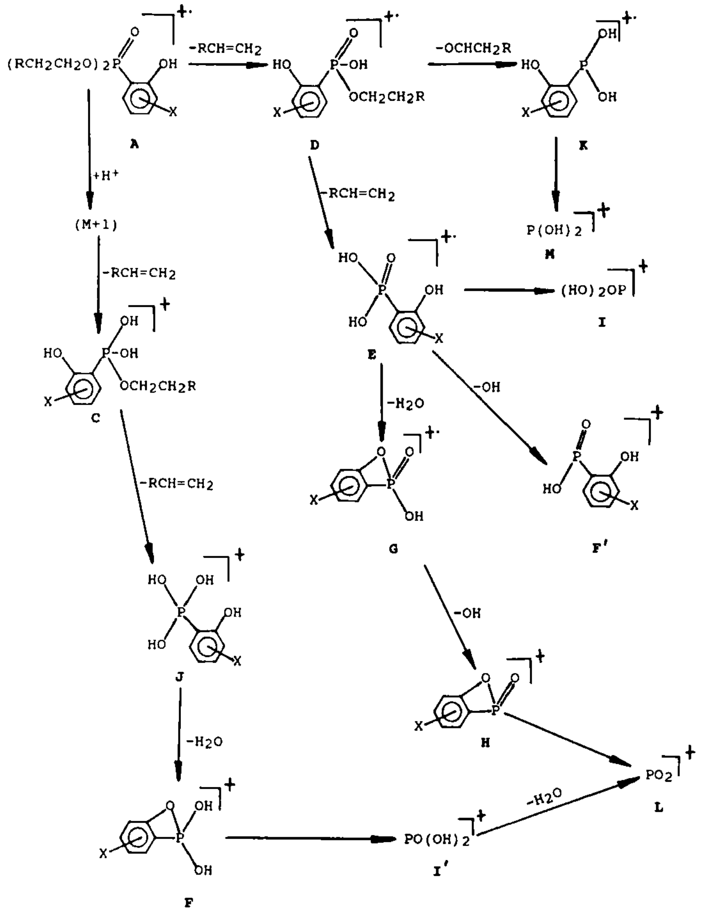
Abundance of fragments of dialkyl *o*-hydroxyphenylphosphonates

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**	**2j**
A	244 (100.0)	244 (96.71)	244 (100.0)	260 (100.0)	258 (64.95)	258 (56.43)	286 (55.12)	316 (37.97)	286 (55.32)	356 (61.20)
B	245 (54.05)	245 (54.42)	245 (34.61)	261 (45.11)	259 (100.0)	259 (100.0)	287 (100.0)	317 (22.77)	287 (100.0)	357 (100.0)
C	217 (3.23)	217 (3.90)	217 (3.18)	233 (3.00)	217 (4.13)	217 (5.72)	231 (6.68)	361 (5.61)	231 (11.78)	273 (4.07)
D	216 (21.29)	216 (25.61)	216 (23.60)	232 (21.46)	216 (5.79)	216 (3.80)	230 (8.68)	260 (11.56)	230 (8.30)	272 (6.94)
E	188 (75.48)	188 (87.59)	188 (76.42)	204 (49.12)	174 (52.97)	174 (21.98)	174 (76.70)	204 (100.0)	174 (100.0)	188 (62.25)
F(F')	171 (15.76)	171 (22.69)	171 (16.76)	187 (17.20)	157 (6.70)	157 (2.17)	157 (7.28)	187 (8.52)	157 (5.14)	171 (4.58)
G	170 (82.13)	170 (100.0)	170 (95.93)	186 (79.57)	156 (24.72)	156 (8.05)	156 (33.66)	186 (32.33)	156 (15.09)	170 (17.38)
H	153 (6.78)	153 (8.75)	153 (6.89)	169 (4.36)	139 (4.86)	139 (1.17)	139 (4.77)	169 (0.76)	139 (2.49)	153 (2.36)
I(I')	81 (3.72)	81 (5.98)	81 (4.24)	81 (4.52)	81 (3.56)	81 (1.22)	81 (4.82)	81 (4.90)	81 (2.45)	81 (2.05)
J	189 (3.71)	189 (9.28)	189 (7.88)	205 (4.35)	175 (7.31)	175 (5.79)	175 (14.57)	205 (22.26)	175 (18.19)	189 (11.29)
K	172 (4.76)	172 (11.48)	172 (5.10)	188 (6.71)	158 (1.22)	158 (0.27)	158 (0.89)	188 (1.36)	158 (0.51)	172 (0.49)
L	63 (3.00)	63 (4.51)	63 (2.50)	63 (5.56)	63 (5.01)	63 (3.06)	63 (3.84)	63 (2.26)	63 (2.93)	63 (1.07)
M	65 (7.74)	65 (11.08)	65 (7.59)	65 (7.46)	65 (7.03)	65 (3.56)	65 (9.82)	65 (10.11)	65 (6.53)	65 (1.87)

2. *The Mass Spectra of Dialkyl o-Hydroxyphenylphosphonates*

Kwon *et al.*[6] have reported the EI mass spectra results of diethyl phenylphosphonate and some five-membered ring compounds containing a phenyl group. For diethyl phenylphosphonate, no P—$C_{sp}2$ bond cleavage was observed and the fragmentation of OCH_2CH_3 group was a main pathway. But for 2-phenyl-1,3,2-dioxaphospholane 2-oxide, the major fragmentation path involves initial cleavage of P—O and C—O bond with successive phenyl-group migration which lead to the cleavage of P—$C_{sp}2$ bond. For compounds **2** we studied, although the major processes are still the fragmentation of RO groups, because of the influence of ortho-hydroxy group, the spectroscopic behavior of these compounds shows some special characteristics. The fragmentation processes are given below.

From the data listed in Table IV, we can conclude that the successive McLafferty rearrangements are predominate. The cleavage of protonated molecules via McLafferty rearrangement is a weak process. The cleavage of P—O bond is even much weaker, but this is one of the major processes in the cleavage of 2-phenyl-1,3,2-dioxaphospholane 2-oxide derivatives.[6]



The cleavage of P—$C_{sp}2$ bond is not observed. In contrast, that is observed in compound **1**, though it is a minor process. This may be because the H-migration takes place much easier in **2** than in 1; that process is avoided by the McLafferty rearrangement in compounds **2**.

EXPERIMENTAL

1 and **2** were synthesized by the method introduced by us.[7] All mass spectra were determined with a Finnigan 4021 spectrometer. Samples were introduced directly keeping the temperature at 200–350°C, electron energy 70 ev and sample pressue 0.3 Torr.

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