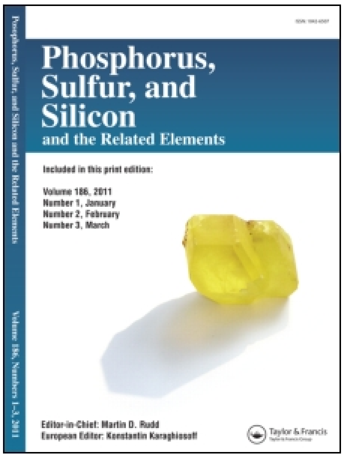


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

COMPARATIVE STUDY OF DESORPTION ANDDIRECT INLET ELECTRON IMPACT ANDCHEMICAL IONIZATION MASS SPECTROMETRYOF SOME 2-CHLOROETHYL PHOSPHONIC ACIDMONO AND DIESTERS

J. E. Causse[a]; S. Ibrahim[bc]; F. Plenat[b]; H. J. Cristau[b]
[a] Laboratoire de Biochimie A, Institut de Biologie, Montpellier, France [b] Laboratoire de chimie organique, ENSCM, Montpellier Cedex 1, France [c] Universitas Andalas, Sumbar, Indonesia

To cite this Article Causse, J. E. , Ibrahim, S. , Plenat, F. and Cristau, H. J.(1991) 'COMPARATIVE STUDY OF DESORPTION ANDDIRECT INLET ELECTRON IMPACT ANDCHEMICAL IONIZATION MASS SPECTROMETRYOF SOME 2-CHLOROETHYL PHOSPHONIC ACIDMONO AND DIESTERS', Phosphorus, Sulfur, and Silicon and the Related Elements, 60: 1, 39 — 48

To link to this Article: DOI: 10.1080/10426509108233923

URL: http://dx.doi.org/10.1080/10426509108233923

Phosphorus, Sulfur, and Silicon, 1991, Vol. 60, pp. 39–48
Reprints available directly from the publisher
Photocopying permitted by license only

COMPARATIVE STUDY OF DESORPTION AND DIRECT INLET ELECTRON IMPACT AND CHEMICAL IONIZATION MASS SPECTROMETRY OF SOME 2-CHLOROETHYL PHOSPHONIC ACID MONO AND DIESTERS

J. E. CAUSSE,† S. IBRAHIM,‡[a] F. PLÉNAT‡[b] and H. J. CRISTAU‡
†Laboratoire de Biochimie A, Institut de Biologie, Boulevard Henri IV, 34000 Montpellier France; ‡Laboratoire de chimie organique, ENSCM, 8 rue de l'Ecole Normale, 34053 Montpellier Cedex 1 France

(Received October 15, 1990; in final form November 15, 1990)

The application of desorption and direct inlet with electron impact and chemical ionization mass spectrometry of some 2-chloroethyl phosphonates related to etephon is described. Comparison of these methods showed that there are highly useful for obtaining: 1) adduct ions, especially protonated molecular ions: chemical ionization. 2) significant fragment ions: methane and electron impact ionization. Interpretation of spectra, based on the considerable analogy between the different structures of the phosphonates is described in this work. A choice between EI and CI mass spectrometry with either direct inlet or desorption technics, depending on the volatility of the compounds and the purpose of analysis, is done. The low fragmentation obtained by ammonia chemical ionization was used to analyze different mixtures of phosphonates.

Key words: Mass spectrometry; chemical ionization; electron impact; phosphonates; etephon.

INTRODUCTION

Mass spectrometry has been used as a tool for characterizing and identifying a variety of organophosphorus compounds.[1] Concerning the subclasses of phosphorus structure (mainly alkyl phosphonates), most of the investigations in the literature,[2–11] have been limited to EI ionization (EI) MS. For many compounds, the association of desorption and electron impact MS conditions makes unambiguous identification quite difficult, especially in the case of mixtures, due to excessive fragmentation. When performed,[2–11] chemical ionization (CI) mass spectrometry has been found to enhance the possibility of identification. The same inference was drawn from fast atom bombardment (FAB) mass spectrometry in the very peculiar case of aminophosphonic acids and phosphonopeptides.[12]

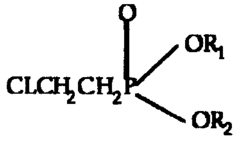
The investigations reported here concern seven selected 2-chloroethyl phosphonates **2–8** related to etephon **1** (cf. Table I) which is used to accelerate the preharvest ripening of fruit and vegetables.[13] Electron impact and chemical ionization with methane, isobutane and ammonia, were performed with desorption (DEI and DCI) and direct inlet technics to obtain mass spectra of these compounds,

---

[a] Now at Universitas Andalas, Padang, Sumbar, Indonesia.
[b] To whom correspondence should be addressed.

TABLE I

Compounds



Sample identification	R_1	R_2	MW
1 etephon	H	H	144
2	H	$C_{14}H_{29}$	340
3	H	$CH_3(OCH_2CH_2)_2$	246
4	$C_{14}H_{29}$	$C_{14}H_{29}$	536
5	$CH_3(OCH_2CH_2)_2$	$CH_3(OCH_2CH_2)_2$	348
6	$C_6H_5CH_2$	$C_6H_5CH_2$	324
7	$C_6H_5CH_2$	$C_{14}H_{29}$	430
8	$C_6H_5CH_2$	$CH_3(OCH_2CH_2)_2$	336

which have few structural differences, for comparative purposes, in an attempt to estimate the specificity of each in qualitative and quantitative analysis. EI MS of O,O-diethyl 2-chloroethylphosphonate is the only analysis previously described.[5]

RESULTS

Molecular and Adduct Ions

Molecular M^+ ions are generally not observed, except for **8** (rel. ab. 2%) and **7** (rel.ab. 18%). The adduct ions are summarized in Table III. Usually, [M + 1] ions were quite abundant (cf. Table II), and often give the base peak with chemical ionization. $[M+18]^+$ ions were significant in ammonia CI of all compounds except for **8** (etephon also giving a $[M+35]^+$ ions of rel.ab. 15%). Adduct ions $[M+91]^+$ were particularly observed with direct inlet technics by methane ionization (cf. Table III).

Fragmentations

Table IV shows the principal fragment ions observed in the mass spectra of esters **2–8**. Those ions which are not characteristic of the individual esters, (namely the following ions

$\overline{OCH_2CH_2P}(OH)_2^+$: m/z 109 $PO(OH)_2^+$: m/z 81

$HPO(OH)_2^{+\cdot}$: m/z 82 $HPO(OH)^+$: m/z 65 PO_2^+ : m/z 63)

are listed in Table V and those due to fragments R1 and R2 and their breakdown in Table VI.

TABLE II

Relative abundance (%) of $[M+1]^+$ ions of compounds **1–8** in DEI and DCI

	COMPOUNDS							
METHODS	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
*DEI**	7	<1	6	3	1	4	-	-
Methane DCI	100	26	50	100	100	16	78	93
Isobutane DCI	100	22	91	100	100	100	100	100
Ammonia DCI	1	8	100	100	100	100	100	100

* Chemical autoionization.

TABLE III

Relative abundance (%) of adduct ions of compounds **1–8** in DCL

		COMPOUNDS							
IONS		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$[M+18]^+$	Ammonia	100	100	49	18	11	60	27	6
$[M+29]^+$	Methane	4	4	2	19	4	-	10	2
	Isobutane	10	-	-	4	-	-	2	-
$[M+41]^+$	Methane	2	-	2	4	3	-	2	2
	Isobutane	2	1	2	4	2	1	3	3
$[M+91]^+$	Methane	-	-	-	-	-	4 (40*)	-	4(100)*
	Isobutane	-	-	-	-	-	-	<1	8
	Ammonia	-	-	3	-	8	-	-	-
$[M+103]^+$	Methane	-	-	-	-	7	-	-	-
	Isobutane	-	-	2	-	-	-	-	2
	Ammonia	5	5	-	-	-	2	-	-

* Direct inlet at the highest probe temperature: 706°C.

TABLE IV

Comparison of characteristic fragments of phosphonates **2–8** with DEI and DCI.[5] The following abbreviations are employed for DCI technics: M (methane) I (isobutane) A (ammonia)

Monoesters	$(R\text{-}HCl)PO(OR')OH^+$				$RP(OH)_2^{+\cdot}$				$RP(OH)_3^+$			
	$[MH\text{-}36]^+$				m/z = 128				m/z=145			
	EI	M	I	A	EI	M	I	A	EI	M	I	A
rel.ab.%												
compound **2**	1	10	2	1	1	-	7	-	96	100	100	-
compound **3**	-	12	6	19	-	-	-	-	22	3	11	-
Diesters[a]	$(R\text{-}HCl)PO(OR_1)(OR_2)^+$				$RP(OR')(OH)_2^+$				$RP(OH)_3^+$			
	$[MH\text{-}36]^+$								m/z=145			
	EI	M	I	A	EI	M	I	A	EI	M	I	A
rel.ab.%												
compound **4**	2	62	5	5	27	41	11	15	100	63	22	10
compound **5**	-	19	2	-	10	6	61	3	3	-	-	-
compound **6**	-	16	2	2	40	7	10	1	-	5	4	-
compound **7**	<1	51	2	3					42	63	4	-
$R' = CH_2Ph$					-	16	3	1				
$R' = C_{14}H_{29}$					-	2	-	-				
compound **8**	-	29	3	-					2	-	-	-
$R' = CH_2Ph$					1	-	-	-				
$R' = (CH_2CH_2O)_2CH_3$					-	2	-	-				

[a] The $RPO(OR')(OH)^{+\cdot}$ ion is found only for **7** (82%) and **8** (5%) with EI ionization.

TABLE V

Comparison of characteristic fragment ions[5] of etephon **1** with DEI and DCI*

m/z	109	82**	81	65	63
	rel.ab.%				
DEI	21	100	33	12	6
Methane DCI	27	5	2	2	1
Isobutane DCI	15	37	15	9	14
Ammonia DCI	-	-	-	-	3

* The same ions, when present in **2–8**, were mostly of low abundance, except for m/z 109 in **2** with DEI, MDCI, IDCI [15%], and m/z 65 in **3** [15%], **6** [88%], **7** [14%] and **8** [23%] with DEI.

** Cf. discussion p. 45: odd-electron ion.

TABLE VI

Relative abundance of fragments R_1 and R_2 and their breakdown, under DCI conditions, for compounds **2–8**. M = methane, I = isobutane, A = ammonia

R = $CH_3O(CH_2)_2OCH_3$

m/z / Compounds	103				59				58*			
	EI	CI			EI	CI			EI	CI		
Ionization method		M	I	A		M	I	A		M	I	A
3	-	58	100	3	84	100	-	-	100	20	-	-
4	59	85	28	10	100	22	-	-	82	12	-	-
5	21	36	6	4	100	13	-	-	52	8	-	-

R = $C_{14}H_{29}$

m/z / Compounds	57				71			
	EI	CI			EI	CI		
Ionization method		M	I	A		M	I	A
2	53	4	-	-	17	1	5	-
4	43	8	-	-	25	2	2	2
7	-	6	-	-	4	2	1	1

R = $C_6H_5CH_2$

m/z / Compounds	91				92*			
	EI	CI			EI	CI		
Ionization method		M	I	A		M	I	A
6	58	100	58	10	66	8**	11*	1**
7	100	100	11	12	-	8**	3	1**
8	89	100	10	-	13	8**	2	-

---

* Cf. discussion p. 45: odd-electron ion.

** Provided by the isotope ^{13}C.

DISCUSSION

Molecular and Adduct Ions

Molecular and adduct ions (number and abundance) are of great use in determining molecular weight and identifying organic compounds.

In the cases of etephon, EI provides the unexpected molecular ion $[M+1]^+$ and not $M^{+\cdot}$, with both desorption and direct inlet technics, even with the most diluted solution, probably by a chemical autoionization mechanism. In fact, molecular $M^{+\cdot}$ ions were found only in the cases of **7** and **8** (<2% for **8**); it is well known that EI, the most often, fails to provide ions indicative of intact molecular species: O,O-diethyl 2-chloroethyl phosphonate gave an $M^{+\cdot}$ ion with a low relative abundance.[5]

Methane DCI provided quite abundant $[M+1]^+$ ions (Table II). Other adduct ions (Table III) of too weak intensity seemed to be useless for identification, except $[M+91]^+$, quite abundant for benzyl phosphonates **6** and **8** with direct inlet technics. It may also result from a chemical autoionization.

Isobutane DCI was also effective (see compounds **3**, **6**, **7**) for $[M+1]^+$ ions.

Ammonia usually produced a low exothermic reaction and consequently low fragmentation.[16] Indeed, ammonia DCI gave for the all phosphonates studied here, both $[M+1]^+$ and $[M+18]^+$ ions (Tables II and III); this is highly favorable for identification purposes: the lower the relative abundance ratio, $R = [M+1]^+/[M+18]^+$, the better the identification analysis. From this point of view, the data in Table VII indicate 110°C as the best source temperature for obtaining easily recognizable inprints of individual compounds in a mixture (see Figure 1), which can be a great benefit.

Consequently, ammonia DCI seems to be the best method for identifying phosphonates structures.

In Figure 2, which shows the theoretical and observed isotopic ratio for $[M+1]^+$, $[M+2]^+$ and $[M+3]^+$ ions, it can be seen that DCI give the correct values in most cases.

Fragmentations and Characterization

In the case of O,O-diethyl 2-chloroethyl phosphonate,[5] the data indicate a base peak arising from the cleavage of the P—C bond during EI. Other important peaks resulted from the neutral loss of esterifying ethyl groups.[2]

For the compounds studied here, the $[MH\text{-}36]^+$ ion, corresponding to the loss of HCl, was observed in DCI in high abundance for all samples with methane (see Table IV), but not in DEI. The cleavage of the P—C bond, which gives $[M\text{-}62]^{+\cdot}$ and $[M\text{-}63]^{+\cdot}$ ions, frequently observed with DEI of O,O-dialkyl phosphonates,[8] was overshadowed by the ready occurrence of the PO-R cleavage giving the fragment ions (see Tables IV and VI). In DEI and/or methane DCI spectra (Table IV), the m/z 145 ion is especially abundant. Otherwise, fragment ions and their breakdown (Table VI), together with recombination ions, $[M+91]^+$, and $[M+103]^+$ (Table III), were present (for compounds **3**, **5**, **6** and **8**). $[M+91]^+$ and $[M+103]^+$ may be provided by a complexation respectively of compounds **6** and **8** with $\Phi CH2^+$ and **3** and **5** with the radical chain ion (m/z 103 is the base peak of isobutane DCI

TABLE VII

Source temperature (T.S. : °C) influence on relative abundance $[M+1]^+$ (A) and $[M+18]^+$ (B) ions in phosphonate diesters **4–8** studied here, pure or in mixtures M_1 (compounds **4**, **6**, **7**) and M_2 (compounds **5**, **6**, **8**) 1/1/1 w/v, with ammonia DCI

		COMPOUNDS										
T.S.		**4**		**7**		**6**			**5**		**8**	
°C		pure	M1	pure	M1	pure	M1	M2	pure	M2	pure	M2
	IONS	rel.ab.%										
110	A	100	68	100	100	100	66	49	100	54	100	100
	B	60	28	56	50	90	47	40	16	11	10	12
	R[a]	1.7	2.4	1.8	2	1.1	1.4	1.2	6.3	4.9	10	8.3
130	A	100	65	100	100	100	60	38	100	56	100	100
	B	18	11	28	21	60	24	16	11	10	6	7
	R[a]	5.6	6.1	3.6	4.8	1.7	2.5	2.4	9.1	5.6	16.7	14.2
150	A	100	69	100	100	100	61	40	100	49	100	100
	B	6	5	25	16	47	19	14	7	8	5	6
	R[a]	16.7	14	4	6.2	2.1	3.2	2.9	14.3	6	20	16.6
180	A	100	60	100	100	100	60	41	100	54	100	100
	B	2	0.9	7	7.4	21	9	13	3	6	1	5
	R[a]	50	67	14.3	13.5	4.8	6.7	3.2	33	9	100	20

[a] R = (Rel.ab. A/rel.ab. B) %.

spectra of compounds **3**, cf. Table VI). When the m/z 145 ion was abundant, DEI was able to indicate the characteristic fragment ions of etephon itself better than methane or isobutane DCI (Table V). In some cases (Tables V and VI), odd-electron ions $OE^{+\cdot}$ were identified in methane or isobutane DCI spectra of compounds **1** (m/z 82), **3**, **5** (m/z 58) and **6** (m/z 92 with isobutane). They might be produced by a charge exchange reaction.[17,18]

In view of these results, we suggest that DEI and methane DCI are the best MS technics for characterizing O,O-dialkyl 2-chloroethyl phosphonates. Methane DCI seems to provide more information on the (2-chloroethyl) nature and the structure of these compounds.

EXPERIMENTAL

The phosphonates compounds **1–8** were of 99.5% and higher purity as determined by microanalysis[14] and applied as solutions of 0.1 g/L in methanol, which is the best solvent. All the samples examined

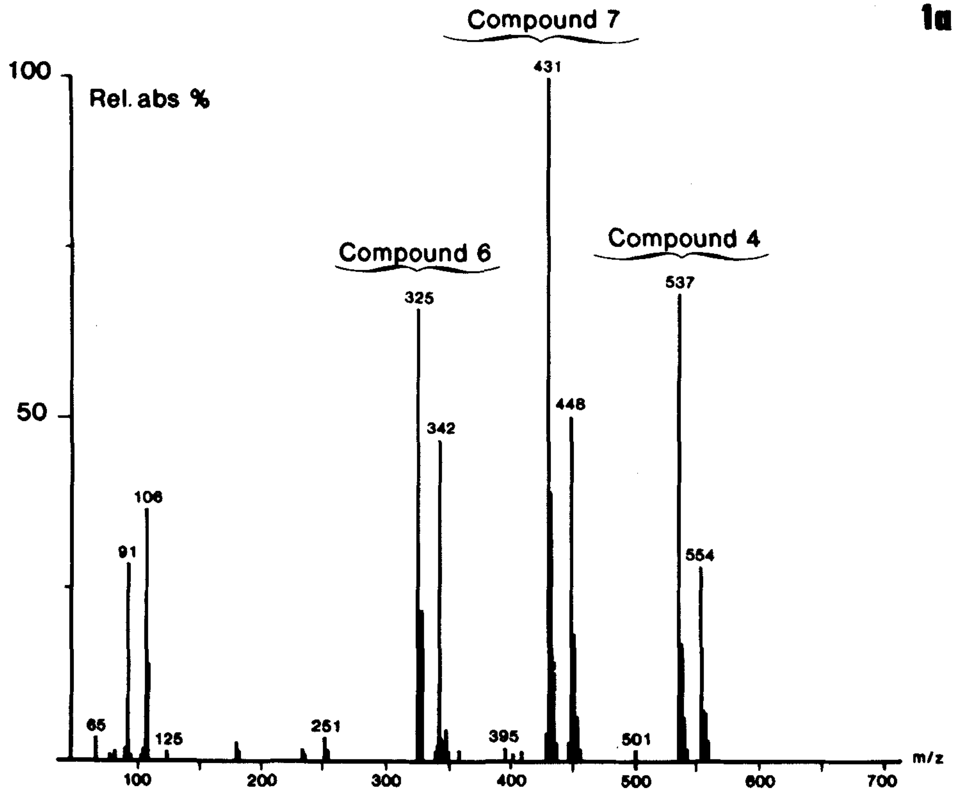
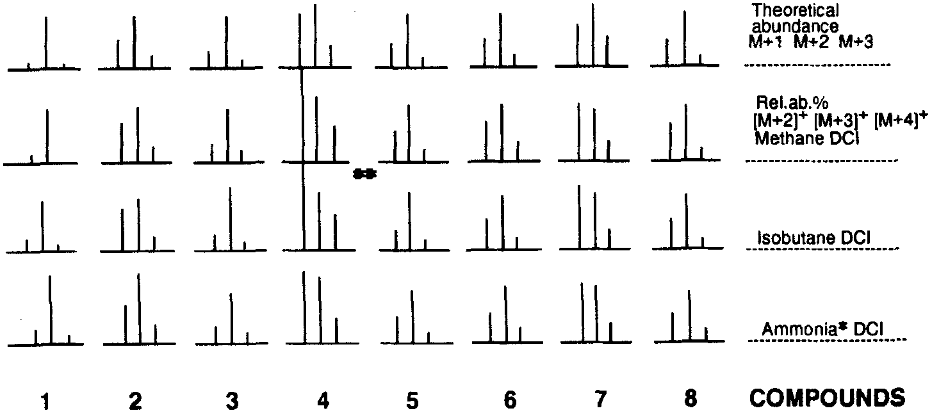


FIGURE 1 Ammonia CI mass spectra of M1 (Figure 1a) and M2 (Figure 1b) at a source temperature of 110°C. For M2, the three compounds are labeled ($[M+1]^+$ and $[M+18]^+$) with, just below, the number of the compound (Table I). In each case, the isotopic ratio due to the chlorine atom can be observed.



*For 1. $[M+18]^+[M+19]^+[M+20]^+$

** The top value for $[M+2]^+$ is 100%

FIGURE 2 Theoretical and observed isotopic abundances in the DCI mass spectra of compounds **8–8**.

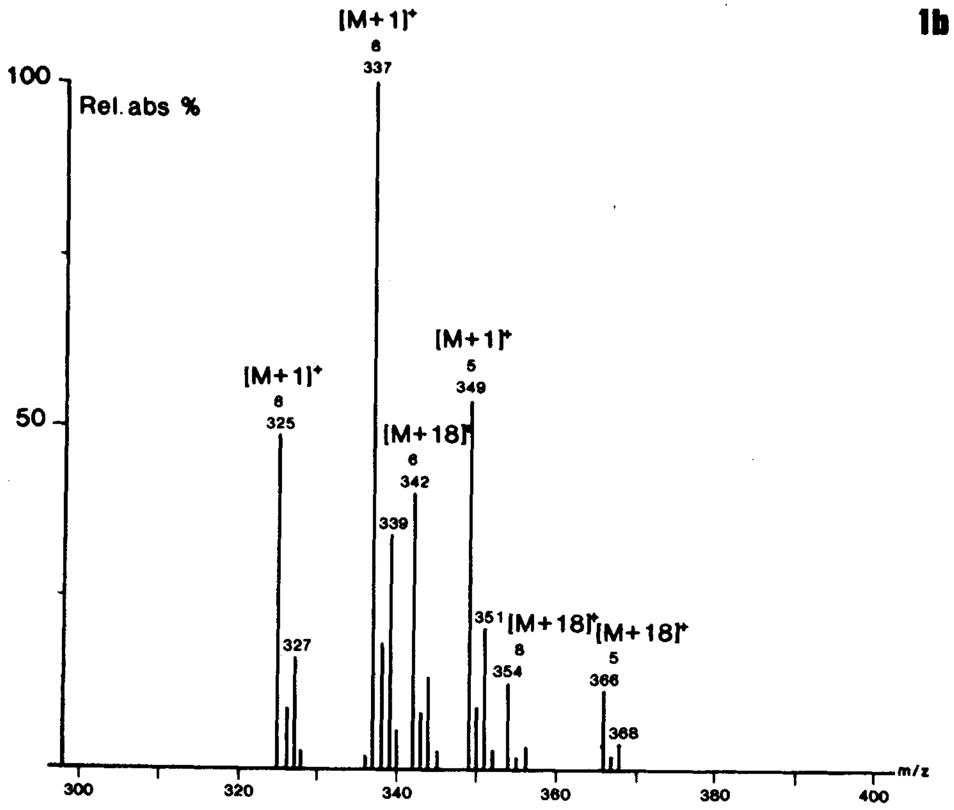


FIGURE 1 (*continued*)

were introduced directly into the source with an appropriate probe in the usual manner. The spectra were obtained using a Nermag R-10-10-H spectrometer (Rueil Malmaison, France), with a combined CI, EI source, probe with fine wire (desorption) and small cup (direct inlet). The reagents employed for the CI spectra were methane N30, isobutane N25, and ammonia N36 supplied by Air Liquide (division scientifique Alphagaz France).

The EI spectra reported here were obtained at 70 eV with a source temperature of 130°C. The source chamber was maintained at 4.4×10^{-7} Torr, as measured with an ionization gauge. The CI spectra were determined using 83 eV to ionize the reagent gases at 130°C. With ammonia, and for diesters compounds and two mixtures of them, prepared with equal parts of pure methanolic solutions of **4**, **6**, **7** and **5**, **6**, **8** noted M1 and M2 respectively, various temperatures were used: 110°C, 130°C, 150°C and 180°C. The source chamber was maintained at 1×10^{-5} Torr which controlled the source pressure at about 1 Torr for the three gases. In all cases, DCI and DEI spectra were obtained by desorption from a rhenium wire, produced by a heater current varying from 50 mA to 1 A at 0.1 A/s. Direct inlet spectra, with small cups, were also made for **1** (two solutions, at 0.1 g/L and 0.01 g/L) (EI); **3**, **5**, **6**, **8** (CI : methane); **3**, **6**, **8** (CI : isobutane), successively heating the cup at 180°C, 280°C, 380°C, and 680°C (1°C/s), and waiting 5s at each of these temperatures. The spectra were obtained at the top of the total ionic current, where a 91% reproducibility of spectra, at least, was obtained.

ACKNOWLEDGMENTS

The authors acknowledge Doctor Jean-Claude PROME for his kind interest in this work and profitable discussion.

REFERENCES

1. I. Granoth, *Topics in Phosphorus Chemistry*, **8,** 41–98 (1976).
2. S. Sass and T. L. Fischer, *Org. Mass. Spectrom.*, **14,** 257 (1979).
3. B. M. Kwon and D. K. Oh, *Phosphorus and Sulfur*, **11,** 177 (1981).
4. S. Yanai, *Phosphorus and Sulfur*, **12,** 369 (1982).
5. J. L. Occolowicz and J. M. Swan, *Aust. J. Chem.*, **19,** 1187 (1966).
6. J. L. Occolowicz and G. L. White, *Anal. Chem.*, **35,** 1179 (1963).
7. T. Nishiwaki, *Tetrahedron*, **23,** 2181 (1967).
8. W. R. Griffiths and J. C. Tebby, *Phosphorus*, **5,** 273 (1975).
9. J. R. Holtzclaw, J. R. Wyatt and J. E. Campana, *Org. Mass. Spectrom.*, **20,** 90 (1985).
10. H. J. Callot and C. Benezra, *Org. Mass. Spectrom.*, **5,** 343 (1971).
11. P. A. Cload and D. W. Hutchinson, *Org. Mass. Spectrom.*, **18,** 57 (1983).
12. F. Bawa and D. G. Cameron, *Phosphorus and Sulfur*, **30,** 743 (1987).
13. Etephon *in* "Annal of Pesticides" 8th Ed., E. K. Woodford Ed. (1987) p. 346.
14. F. Plenat, S. Ibrahim and H. J. Cristau, *Synthesis*, 912 (1988).
15. The figures give the relative intensity of each ions compared to that of the base peak 100%.
16. P. Arpino, *L'actualité chimique*, **Avril** 19–28 (1982).
17. P. Longevial, *in* "Principes de la spectrométrie de masse des substances organiques", Masson Ed. (1981) p. 147.
18. F. W. McLafferty, in "Interpretation of Mass Spectra" 3rd Ed., N. J. Turro Ed. (1980) p. 92.