Structure of Gas Phase $[C_5H_6]^{+\cdot}$ Ions

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Charge-stripping spectra have been used to differentiate ionized cyclopentadiene from its acyclic isomers. The minimum amounts of translational energy lost during the charge-stripping processes and the relative charge-stripping efficiencies, which are also structurally important parameters, have been measured for these ionic species. $[C_5H_6]^{+\cdot}$ ions, formed by dissociative ionization of various precursors in the ion source are found, usually, to be a mixture of cyclic and acyclic ions. In contrast, $[C_5H_6]^{+\cdot}$ ions, derived from the dissociation of metastable molecular ions from a series of organic compounds, have the cyclopentadienyl structure. This structure was confirmed by collision-induced dissociation of ions formed in the first field-free region of a triple sector mass spectrometer.

INTRODUCTION

Collisional activation achieved by sending beams of ions of high translational energy into a neutral target gas constitutes the method of choice for the study of the structures of gaseous organic ions.[1] Among the various processes which result from this interaction, the collision-induced dissociation (CID) of singly charged ions has been the most widely used.[2] The complementary nature of the information which could be obtained from charge-stripping processes was first demonstrated for isomeric $[C_6H_6]^{+\cdot}$ ions.[3] More recently, we have shown that the relative abundances of the charge-stripping peak and the peaks due to its doubly charged fragments (commonly called the charge-stripping spectrum) represent a very sensitive structural tool.[4] Such charge-stripping spectra have been applied to confirm the structure of hydrocarbon ions,[5–9] oxygenated ions[10,11] and nitrogen-containing ions.[12–15] In addition, some unusual structures such as ion–dipole complexes have been identified from charge-stripping peaks.[16]

The nature of the target gas is an important factor which affects the relative abundances of the peaks in the charge-stripping spectrum. The use of oxygen as collision gas gives a higher yield of stable doubly charged parent ions relative to the doubly charged fragments, possibly because of more favourable resonant electron capture.[17] Slit settings are another important factor which can affect the charge-stripping spectrum due to the narrow width of the parent charge-stripped peak relative to that of its doubly charged fragment peaks.[4] Unreliable results have been described for isomeric $[C_3H_5]^+$ ions[18] and it appears that the translational energy of the singly charged parent ions is an important parameter in this particular case.[19]

As well as the charge-stripping spectrum, the minimum loss of translational energy (Q_{min}) and the relative charge-stripping efficiencies are two other measurements which may be derived from charge-stripping processes.[20] Recent results show that Q_{min} values, together with charge-stripping spectra, can be used to differentiate isomeric $[C_7H_8]^{+\cdot}$ ions.[9b]

In this paper, we report on gas phase $[C_5H_6]^{+\cdot}$ ions generated by direct electron ionization of C_5H_6 isomers or dissociative ionization of other precursor molecules. CID spectra have been shown previously[4] not to distinguish these isomeric ions clearly when they are formed in the source. Charge-stripping experiments have been performed to elucidate the structures of ions produced in the source of the mass spectrometer, whilst the $[C_5H_6]^{+\cdot}$ ions formed by the unimolecular dissociation of metastable precursors have been studied by means of their CID spectra.

RESULTS AND DISCUSSION

$[C_5H_6]^{+\cdot}$ ions formed in the source

The compounds **1–13** have been selected to generate $[C_5H_6]^{+\cdot}$ ions by direct electron ionization in the case of **1**, **11** and **12**, or by dissociative ionization for the remaining samples.

The charge-stripping spectra shown in Table 1 have been obtained on a triple sector mass spectrometer of geometry *E/B/E* using helium as the collision gas in the third field-free region. The results are listed according to the relative abundance of the charge-stripped peak at *m/z* 33.

The base peak in the charge-stripping spectrum of **1** is observed at *m/z* 33, with *m/z* 32 having nearly the same abundance as *m/z* 31. A similar spectrum is obtained for *m/z* 66 ions of **2** at a 'normal' sample inlet system temperature (150 °C). Flash-vacuum thermolysis of **2** at 450 °C results in the disappearance of the molecular ion of this dimer (*m/z* 132) and, within experimental error, the charge-stripping spectrum of

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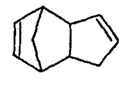
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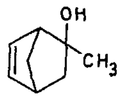
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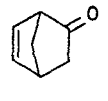
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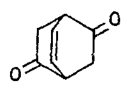
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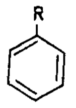
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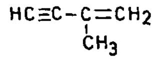
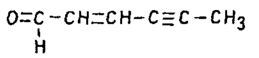
8: R=NH$_2$
9: R=OH
10: R=OC$_3$H$_7$

HC≡C−CH=CH−CH$_3$

11


$HC{\equiv}C{-}C(CH_3){=}CH_2$

12


$O{=}C(H){-}CH{=}CH{-}C{\equiv}C{-}CH_3$

13

the *m/z* 66 ions matches that of **1** above, confirming the formation of cyclopentadiene (**1**) from the dimer **2** by flash vacuum thermolysis. The thermal energy of the precursor cyclopentadiene molecules therefore appears to have no influence on the charge-stripping spectrum. The acyclic isomers **11** and **12** show very similar spectra which are readily distinguished from those obtained from **1** and **2**. They are characterized by an increase in the relative abundances of the doubly charged fragments, especially *m/z* 31.5 and *m/z* 31. The difference in relative intensities for the charge-stripped peaks at *m/z* 33 was, however, too small to allow unambiguous characterization of these two isomers **11** and **12** by means of these spectra. The *m/z* 66 ions formed from the unsaturated aldehyde **13** would be expected to have an acyclic structure, isomeric with those formed from **11** and **12**. The charge-stripping spectrum of these ions (i.e. from **13**) also shows a much weaker charge-stripped peak at *m/z* 33, relative to the cyclic structure, **1** and **2**, confirming their acyclic nature.

Table 1. Charge-stripping spectra of $[C_5H_6]^{+\cdot}$ ions[a]

Precursors		Doubly charged ions[b]				
	m/z =	33	32.5	32	31.5	31
Cyclopentadiene (1)		35	14	22	8	21
Dicyclopentadiene (2)		33	15	21	8	23
Dicyclopentadiene (2)[c]		33	14	21	9	23
2-Hydroxy-2-methyl-5-norbornene (3)		30	14	22	9	25
Thiophenol (7)		29	13	24	11	24
Norbornadiene (4)		24	12	25	12	28
2-Oxo-5-norbornene (5)		23	14	24	10	29
Bicyclooctenedione (6)		17	13	24	13	34
Aniline (8)		16	16	24	12	32
2-Hexen-4-yn-1-al (13)		10	9	27	16	39
Phenol (9)		9	10	24	18	40
3-Penten-1-yne (11)		6	9	23	16	47
3-Methyl-3-buten-1-yne (12)		4	9	22	19	46

[a] Triple sector mass spectrometer, helium collision gas, 8 keV ion kinetic energy. Compound **10** is not included due to the presence of interfering singly charged ions generated by consecutive CID processes.
[b] Abundances relative to the sum of all doubly charged ions.
[c] Flash vacuum thermolysed at 450 °C.

For the bicyclic compounds **3–5**, a progressive decrease in the relative abundance of the charge-stripped peak is observed, suggesting that the singly charged $[C_5H_6]^{+\cdot}$ precursor ions contain increasing contributions from an acyclic isomeric ion(s) present together with the ions of cyclopentadiene. As proposed previously,[4] thiophenol (**7**) gives rise to the cyclopentadienyl ion predominantly, by the loss of CS. The bicyclooctenedione **6** has the base peak at *m/z* 66 in its mass spectrum.[21] Although the reaction $[C_6H_6O]^{+\cdot} \rightarrow [C_5H_6]^{+\cdot}$ is observed to occur unimolecularly in the field-free region and the structure of the resulting ions is established as cyclopentadienyl (*vide infra*), the structure and mechanism of formation of the ions produced in the source may be different. The charge-stripping spectrum which is observed is in agreement with the production of a mixture of cyclic and acyclic $[C_5H_6]^{+\cdot}$ isomers. A similar mixture is probably formed in the case of **8** which has a very similar spectrum (Table 1). For **9**, the relative abundance of the charge-stripped peak, *m/z* 33, has decreased to a level at which the contribution of the cyclic $[C_5H_6]^{+\cdot}$ species to the precursor ion beam must be minimal.

A similar trend in the charge-stripping spectra has also been observed on a ZAB-2F instrument using nitrogen as the collision gas. The choice of target gas species of lower ionization energy than helium favours the formation of more stable charge-stripped ions which are observed at *m/z* 33 (Table 2). The spectra shown are corrected for contributions from $[^{13}CC_4H_5]^+$. Only **9**, **11** and **12** show significant differences from the uncorrected spectra.

Table 3 gives the results obtained on the ZAB-2F mass spectrometer for measurements of Q_{min} and of the relative charge-stripping efficiencies for the compounds examined. Though the experimental error in the Q_{min} results was taken to be ±0.5 eV, the cyclic precursor **2** had a value of 16.1 eV which was always reproducibly greater than that of the two acyclic pre-

Table 2. Charge-stripping spectra of $[C_5H_6]^{+\cdot}$ ions[a]

Precursors		Doubly charged ions[b]				
	m/z =	33	32.5	32	31.5	31
Dicyclopentadiene (2)		51	9	15	6	19
2-Hydroxy-2-methyl-5-norbornene (3)		47	9	16	7	21
Thiophenol (7)		48	8	16	7	21
Norbornadiene (4)		39	8	18	10	25
2-Oxo-5-norbornene (5)		41	8	18	8	25
Bicyclooctenedione (6)		39	8	17	10	26
Aniline (8)		31	10	20	10	29
Phenol (9)		20	8	23	12	37
3-Penten-1-yne (11)		18	6	22	12	42
3-Methyl-3-buten-1-yne (12)		2	8	26	16	48

[a] ZAB-2F mass spectrometer, nitrogen collision gas, 6 keV ion kinetic energy.
[b] Abundances relative to the sum of all doubly charged ions. Corrected for contributions from $[^{13}CC_4H_5]^+$.

Table 3. Minimum loss of translational energy (Q_{min}) and relative charge-stripping efficiencies of $[C_5H_6]^{+\cdot}$ ions[a]

Precursors	Q_{min}(eV)[b]	Relative efficiencies[c]
Dicyclopentadiene (**2**)	16.1	1.00
2-Hydroxy-2-methyl-5-norbornene (**3**)	15.9	0.67
Thiophenol (**7**)	15.9	0.90
Norbornadiene (**4**)	15.7	0.63
2-Oxo-5-norbornene (**5**)	16.1	0.69
Bicyclooctenedione (**6**)	16.1	0.67
Aniline (**8**)	15.5	0.46
Phenol (**9**)	15.5	0.42
3-Penten-1-yne (**11**)	15.4	0.32
3-Methyl-3-buten-1-yne (**12**)	15.4	0.02

[a] ZAB-2F mass spectrometer, nitrogen collision gas, 6 keV ion kinetic energy.

[b] ±0.5 eV—calibrated against toluene $[92]^+ \rightarrow [92]^{2+}$ (15.7 eV).

[c] ±10%—relative to dicyclopentadiene $[66]^{2+}/[66]^+$ (absolute $= 1.2 \times 10^{-4}$). Corrected for contributions from $[^{13}CC_4H_5]^+$ to the singly and doubly charged ions.

cursors, **11** and **12**, whose Q_{min} values were the same, 15.4 eV. A mixture of **2** and **11**, such that each contributed 50% to the $[C_5H_6]^{+\cdot}$ precursor ion current, had a measured Q_{min} value of 15.8 eV. This result, where the Q_{min} value for a mixture of structures lies between the Q_{min} values for each structure independently, has been seen for the $[C_7H_8]^{+\cdot}$ ions,[9b] though, in that case, the result was more readily observed since the two structures had Q_{min} values differing by 1.4 eV.

The remaining precursors gave Q_{min} values which fell within these outer limits. The experimental errors do not allow any firm conclusions as to the percentage of cyclic and acyclic ions in the stable precursor ion beam but the results are not incompatible with any of the conclusions reached earlier on the basis of the charge-stripping spectra.

The relative charge-stripping efficiencies given in Table 3 give similar information to that given by the Q_{min} values, except that a firm distinction can now be made between the two acyclic precursors **11** and **12**, **12** having a considerably lower relative efficiency. Thiophenol (**7**) gives results close to those obtained for dicyclopentadiene (**2**). The bicyclic compounds **3**–**6** give efficiencies more similar to those obtained for the cyclic compound than the acyclic compounds. Compounds **8** and **9** have relatively lower efficiencies, but still greater than that of **11**. The relative efficiency for the mixture of **2** and **11** described above, is 0.65.

$[C_5H_6]^{+\cdot}$ ions formed in the first field-free region

The dissociation of low-energy aniline and phenol molecular ions has received much attention recently. Appearance energy measurements,[22] PIPECO investigations[23] and time-resolved appearance energies[24] are interpreted on the basis of cyclopentadienyl ion formation at threshold energies (together with HNC and not HCN in the case of aniline[24,25]). We have investigated the structure of $[C_5H_6]^{+\cdot}$ ions produced in the first field-free region of a triple sector mass spectrometer (*E*/*B*/*E*) by obtaining their CID spectra, and the results are given in Table 4. The CID spectra were initially recorded with a source accelerating voltage in the range 8–9 kV. The $[C_5H_6]^{+\cdot}$ ions therefore had differing kinetic energies depending upon the mass ratio between the $[C_5H_6]^{+\cdot}$ fragment ion and the metastable parent ion. Important differences were observed for the relative abundances of *m*/*z* 65 and *m*/*z* 64 ions (Table 4). These differences, however, were due to interference from the main beam of $[C_5H_6]^{+\cdot}$ ions, this interference increasing as the kinetic energy decreased. This can be seen in the results for **7** and **8** (Table 4). The overall similarity of the spectra points to the fact that a common structure is formed in all cases. The close similarity with the CID spectrum of $[C_5H_6]^{+\cdot}$ ions from dicyclopentadiene (**2**),

Table 4. CID spectra of $[C_5H_6]^{+\cdot}$ ions from metastable precursors[a]

Metastable precursors	Reactions used	$[C_5H_6]^{+\cdot}$ kinetic energy (eV)	Collision-induced dissociation spectrum[b]														
			m/*z* = 65	64	63	62	61	52	51	50	49	40	39	38	37	27	26
2-Hydroxy-2-methyl-5-norbornene (**3**)	$[M]^{+\cdot}-C_3H_6O$	4435	610	29	76	26	6	5	21	14	5	62	100	26	12	7	5
2-Oxo-5-norbornene (**5**)	$[M]^{+\cdot}-C_2H_2O$	4890	718	44	78	28	9	6	18	13	3	59	100	24	6	6	3
Bicyclooctenedione (**6**)	$[M-C_2H_2O]^{+\cdot}-CO$	6319	418	25	73	31	13	4	18	15	3	60	100	25	10	6	4
Thiophenol (**7**)	$[M]^{+\cdot}-CS$	5400	538	39	78	30	11	4	21	16	3	64	100	25	8	7	3
		5000	548	39	73	27	10	5	19	15	4	62	100	25	10	7	4
		4800	634	45	79	29	9	5	20	16	4	67	100	24	8	7	4
Aniline (**8**)	$[M]^{+\cdot}-HNC$	5677	432	30	72	31	12	3	18	15	4	65	100	27	10	6	4
		5400	507	34	74	29	10	3	19	14	3	66	100	24	8	6	3
		5000	552	36	79	30	11	3	20	15	5	64	100	26	9	6	4
Phenol (**9**)	$[M]^{+\cdot}-CO$	6319	395	25	68	32	14	3	20	16	5	70	100	27	10	6	4
Propyl phenyl ether (**10**)	$[M-C_3H_6]^{+\cdot}-CO$	5000	489	30	64	29	10	3	19	14	4	70	100	26	9	7	4
2-Hexen-4-yn-1-al (**13**)	$[M]^{+\cdot}-CO$	5620	404	32	71	35	13	3	20	18	5	61	100	28	9	6	4
$[C_5H_6]^{+\cdot}$ from dicyclopentadiene (**2**)	Source	5800	(781)[c]	38	74	29	11	3	16	12	3	(76)[c]	100	24	9	7	4

[a] $[C_5H_6]^{+\cdot}$ daughters generated in the first field-free region of a triple sector mass spectrometer. Collision gas—helium in the third field-free region.

[b] Abundances (peak heights) relative to *m*/*z* 39 (= 100%).

[c] Peaks already present without the collision gas.

formed in the source and accelerated to an energy of 5800 eV, suggests that this common structure is the cyclopentadienyl ion which has been reported to be the most stable $[C_5H_6]^{+\cdot}$ isomer.[26] The aldehyde (**13**) metastable molecular ions generate a $[C_5H_6]^{+\cdot}$ daughter which gives the same CID spectrum as the *m/z* 66 ions from all the other metastable precursors. This implies that this aldehyde, too, generates the cyclopentadienyl ion at threshold energies, in contradistinction to its behaviour in the ion source, where it forms an acyclic *m/z* 66 daughter.

CONCLUSIONS

Charge-stripping processes produce three kinds of information of structural significance for organic ions: the relative abundances of the charge-stripped peak and its doubly charged fragment peaks (the charge-stripping spectrum), the minimum loss of translational energy (Q_{min}) and the relative charge-stripping efficiency. The present measurements have been made for $[C_5H_6]^{+\cdot}$ ions produced by electron ionization in the ion source or by dissociative ionization of a series of precursor molecules. Either helium or nitrogen target gas was used. The cyclopentadienyl ion is readily distinguished from two of its acyclic isomeric ions on the basis of their charge-stripping spectra. Relative charge-stripping efficiencies similarly distinguish the cyclic ion from the acyclic isomeric ions and, in addition, the two acyclic species have significantly different efficiencies. Q_{min} measurements are, however, less informative since the difference in the Q_{min} values for the cyclopentadienyl ion and its acyclic isomeric ions is only 0.7 eV.

The results for the $[C_5H_6]^{+\cdot}$ species produced by fragmentation of molecular ions in the ion source suggest that mixtures of cyclic and acyclic species are produced. By comparison, $[C_5H_6]^{+\cdot}$ ions from thiophenol (**7**) appear to be predominantly cyclic and $[C_5H_6]^{+\cdot}$ ions from phenol (**9**) predominantly acyclic. The aldehyde **13** generates $[C_5H_6]^{+\cdot}$ ions which are acyclic, and probably isomeric with the $[C_5H_6]^{+\cdot}$ ions generated from **11** and **12**. The remaining compounds yield mixtures of cyclic and acyclic species, as particularly evidenced by their charge-stripping spectra and relative charge-stripping efficiencies, which lie between those of the pure cyclic and acyclic $[C_5H_6]^{+\cdot}$ ions.

$[C_5H_6]^{+\cdot}$ ions formed by the unimolecular dissociation of metastable precursors in the field-free region all have the same structure, as is shown by their identical CID spectra. Since this spectrum is identical to that obtained for $[C_5H_6]^{+\cdot}$ ions formed in the source from cyclopentadiene, this structure is therefore that of the more stable cyclopentadienyl ion.

EXPERIMENTAL

Measurements were made on either a reversed geometry ZAB-2F mass spectrometer or a triple sector (*E*/*B*/*E*) mass spectrometer. The operating conditions have been published previously.[20,26] Most of the compounds are commercially available and were used without further purification: Compounds **5**, **6** and **11** were synthesized according to procedures described in the literature.[27–29] **3** was synthesized by the Grignard reaction of methyl magnesium iodide with **5**. *trans*-2-Hexen-4-yn-1-al (**13**) was prepared by condensation of propargyl alcohol and propargyl chloride,[30] followed by reduction with $LiAlH_4$ in dry ether[31] and oxidation of the so-obtained 2-hexen-4-yn-1-ol with DDQ[32] in benzene.

REFERENCES

1. R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam (1973).
2. K. Levsen and H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **15**, 509 (1976).
3. R. G. Cooks, J. H. Beynon and J. F. Litton, *Org. Mass Spectrom.* **10**, 503 (1975).
4. A. Maquestiau, Y. Van Haverbeke, R. Flammang, C. De Meyer and A. Menu, *Org. Mass Spectrom.* **12**, 706 (1977).
5. (a) W. Wagner, K. Levsen and C. Lifshitz, *Org. Mass. Spectrom.* **15**, 271 (1980); (b) J. W. Dallinga, N. M. M. Nibbering and A. J. H. Boerboom, *J. Chem. Soc., Perkin Trans. 2* 281 (1983); (c) A. A. Mommers, P. C. Burgers, J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **19**, 7 (1984).
6. (a) J. L. Holmes, J. K. Terlouw, P. C. Burgers and R. T. B. Rye, *Org. Mass Spectrom.* **15**, 149 (1980); (b) F. W. McLafferty, M. P. Barbalas and F. Turecek, *J. Am. Chem. Soc.* **105**, 1 (1983); (c) R. D. Bowen, M. P. Barbalas, F. P. Pagana, P. J. Todd and F. W. McLafferty, *Org. Mass Spectrom.* **15**, 51 (1980).
7. W. Wagner, K. Levsen, H. Schwarz and W. Zummack, *Org. Mass Spectrom.* **16**, 365 (1981).
8. (a) D. L. Miller and M. L. Gross, *Org. Mass Spectrom.* **18**, 239 (1983); (b) C. Dass and M. L. Gross, *Org. Mass Spectrom.* **18**, 542 (1983).
9. (a) P. C. Burgers, J. K. Terlouw and K. Levsen, *Org. Mass Spectrom.* **17**, 295 (1982); (b) M. Rabrenovic, A. G. Brenton and T. Ast, *Org. Mass Spectrom.* **18**, 587 (1983).
10. P. C. Burgers, J. K. Terlouw and J. L. Holmes, *Org. Mass Spectrom.* **17**, 369 (1982).
11. P. C. Burgers, J. L. Holmes, F. P. Lossing, A. A. Mommers, F. R. Pavel and J. K. Terlouw, *Can. J. Chem.* **60**, 2246 (1982).
12. A. Maquestiau, Y. Van Haverbeke, R. Flammang and P. Meyrant, *Org. Mass Spectrom.* **15**, 80 (1980).
13. A. Maquestiau, Y. Van Haverbeke, R. Flammang and A. Menu, *Bull. Soc. Chim. Belges* **88**, 53 (1979).
14. M. M. Sarneel, W. Heerma and G. Dijkstra, *Org. Mass Spectrom.* **17**, 155 (1982).
15. A. Maquestiau, Y. Van Haverbeke, R. Flammang, A. Menu and C. Wentrup, *Org. Mass Spectrom.* **13**, 518 (1978).
16. H. Schwarz, *Nachr. Chem. Tech. Lab.* **31**, 451 (1983).
17. M. P. Barbalas, F. Turecek and F. W. McLafferty, *Org. Mass Spectrom.* **17**, 595 (1982).
18. J. O. Lay and M. L. Gross, *J. Am. Chem. Soc.* **105**, 3445 (1983).
19. P. C. Burgers, J. L. Holmes, A. A. Mommers and J. E. Szulejko, *Org. Mass Spectrom.* **18**, 596 (1983).
20. M. Rabrenovic, C. J. Proctor, T. Ast, C. G. Herbert, A. G. Brenton and J. H. Beynon, *J. Phys. Chem.* **87**, 3305 (1983).
21. A. Maquestiau, Y. Van Haverbeke, R. Flammang, C. De Meyer, K. G. Das and G. S. Reddy, *Org. Mass Spectrom.* **12**, 631 (1977).
22. J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.* **15**, 383 (1980).
23. (a) T. Baer and T. E. Carney, *J. Chem. Phys.* **76**, 1304 (1982);

(b) M. L. Fraser-Monteiro, L. Fraser-Monteiro, J. de Wit and T. Baer, *J. Chem. Phys.* **88**, 3622 (1984).
24. (a) C. Lifshitz, P. Gotchignian and R. Roller, *Chem. Phys. Lett.* **95**, 106 (1983); (b) C. Lifshitz and S. Gefen, *Org. Mass Spectrom.* **19**, 197 (1984).
25. P. C. Burgers, J. L. Holmes, A. A. Mommers, J. E. Szulejko and J. K. Terlouw, *Org. Mass Spectrom.* **19**, 442 (1984).
26. A. Maquestiau, P. Meyrant and R. Flammang, *Org. Mass Spectrom.* **17**, 96 (1982).
27. P. K. Freeman, D. M. Batts and D. J. Brown, *J. Org. Chem.* **33**, 2211 (1968).
28. C. A. Grob and A. Weiss, *Helv. Chim. Acta* **43**, 1390 (1960).
29. G. Eglington and M. C. Whiting, *J. Chem. Soc.* 3650 (1950).
30. E. Flickinger, *Chem. Abstr.* **55**, 27056 (1961).
31. H. J. Walther, H. Eyer, U. P. Schlunegger, C. J. Porter, E. A. Larka and J. H. Beynon, *Org. Mass Spectrom.* **17**, 81 (1982).
32. D. Burn, V. Petrow and G. O. Weston, *Tetrahedron Lett.* 14 (1960).

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