Rearrangement reaction of the hydroxyl group of ω-hydroxyalkyltriphenyl phosphonium bromides

HE, Mei-Yu*(何美玉) YUAN, Gu(袁谷) HE, Xiao-Ran(贺晓然)
Department of Chemistry, Peking University, Beijing 100871, China

No molecular ion peak from the Electron Impact Ionization of eight ω-hydroxyalkyltriphenyl phosphonium bromides ($Ph_3P^+(CH_2)_nOHBr^-$, $n = 2$—6, 8—10) can be found, except a part of some relative powerful fragment ions can be observed only. Each compound forms a very characteristic ion $(O=PPh_3-1)^+$ at m/z 277 through hydroxyl rearrangement reaction. The intensity of this ion is closely related with the size of the carbon chain of hydroxyalkyl and with temperature of ion source and temperature of sample probe. The above rearrangement reaction and the reaction to form ion at m/z 262 take place simultaneously, thus leading to strong competition. At $n = 2$, ion at m/z 277 is the most powerful and becomes continuously the base peak. At $n = 3$ and $n = 4$, the intensity of ion at m/z 262 reaches the maximum, and is always the base peak, and the relative abundance of m/z 277 is only around 2%. At $n = 5$, 6, 8, 9, 10, m/z 277 becomes base peak when the temperature of probe is below 300℃. But, when the temperature increases from 300℃ to 350℃, m/z 262 suddenly becomes the base peak, which is not in direct proportional relation with the size of carbon chain. It is proved by MIKES and accurate mass that ion at m/z 277 produces a fragment ion $(O=PPh_2-2)^+$ at m/z 199 with the loss of the neutral benzene molecule.

Keywords Rearrangement reaction, hydroxyl, characteristic ion, intensity, base peak, competition, probe temperature

Introduction

It is reported that organophosphonium compounds have been broadly applied in synthetic and general industrial processes, and that alkyltriphenylphosphonium salts in particular are often used as effective reagents for carbon-carbon bond formation through the Wittig reaction.[1,2] We have recently synthesized ten conjugated tetradecadienyl alcohols and their acetates with different double bond positions. In order to analyze the similarity of their mass spectra and hence distinguish the double bond positional isomers, fuzzy logic methods have been applied.[3,4] Eignt ω-hydroxyalkyltriphenylphosphonium bromides $Ph_3P^+(CH_2)_nOHBr^-$ ($n = 2$—6, 8—10) have been prepared. These are the intermediates that can react with aldehydes to generate the model products in which the double-bond locations are fixed.

The Fast-Atom Bombardment (FAB) mass spectrometry of eight ω-hydroxyalkyltriphenylphosphonium bromides has been published.[5] Each compound has a very intense intact cation (C^+) ion and all C^+ ions are base peaks. All compounds show $[2M+Br]^+$ ions and some fragment ions.[5]

In the present paper, we report a new hydroxyl rearrangement of the eight compounds under EI conditions, which leads to formation of an ion $(O=PPh_3-1)^+$ at m/z 277 with special characteristics.

Experimental

The phosphonium salts, $Ph_3P^+(CH_2)_nOHBr^-$ ($n = 2$—6, 8—10) were synthesized by the reaction of ω-bromoalkanols with triphenylphosphine in our laboratory.[6] Each of the eight compounds was obtained as a white powder and characterized by elemental analysis, mass spectrometry, IR and ^1H NMR.

The Electron Impact (EI) mass spectra of eight ω-hydroxyalkyltriphenyl phosphonium bromides were obtained by using a double-focusing mass spectrometer (ZAB-HS, Micromass, Manchester, U. K.) coupled

Received March 7, 2000; accepted June 21, 2000.
Project (No. 29775004) supported by the National Natural Science Foundation of China.

with a MASPEC II data system. The resolving power was typically 1000 and the magnet was scanned at 3 s per decade. EI operation conditions were: source temperature 300℃, ionization energy 70 eV and the probe temperature was increased at 1℃/sec from room temperature (30℃) to 300℃, then to 350℃. The accurate masses of some ions were obtained by using a software peak-match method on the same instrument coupled with the MASPECII data system at a resolving power of 5000 (10% valley). The MIKE spectra were recorded with the help of the MASPECII data system.

Results and discussion

Under EI conditions, no molecular ion peak can be observed for all compounds ($Ph_3P^+(CH_2)_nOHBr^-$, n = 2—6, 8—10), nor is intact cation information available. No matter what size the carbon chain may be, only the main ions at m/z 277, 262, 201, 199, 185, 183, 152, 108, 107, 77 and 51 *etc*. could be observed (see Table 1 and Table 2). Among these m/z 262[Ph_3P^+], m/z 185[$C_{12}H_{10}P$]$^+$, m/z 183 [$C_{12}H_8P$]$^+$, m/z 152[$C_{12}H_8$]$^+$, m/z 108 [C_6H_5P]$^+$ and m/z 107 [C_6H_4P]$^+$ are all fragment ions derived from Ph_3P^+, and their mechanisms of formation are described in the literature.[6-11] We focused our attention on the ion at m/z 277. According to the report[8] by Miller and Ni, the ion at m/z 277 was $(O=PPh_3-1)^+$, formed through an oxygen rearrangement of the compound $Ph_3P + CH_2CH_2OHBr^-$ (or Cl^-), by losing CH_3CH_3. Its structure is proposed in Scheme 1, but, n = 2 only. In our work, eight ω-hydroxyalkyltriphenyl phosphonium bromides were investigated. The m/z 277 ion was observed for all compounds. A software peak-mach method was

Table 1 EI mass spectra of the triphenylphosphonium salts ($Ph_3P^+(CH_2)_nOH\cdot Br^-$ (The probe temperature 300℃→350℃)

Compound	n	a	b	c	d	e	f	g	h	i	j
1	2	277 (100)	262 (9)	201 (18)	199 (17)	183 (20)	152 (9)	108 (4)	107 (3)	77 (18)	51 (11)
2	3	277 (2)	262 (100)	201 (1)	199 (0.5)	183 (87)	152 (8)	108 (38)	107 (14)	77 (5)	51 (6)
3	4	277 (2)	262 (100)	201 (1)	199 (0.5)	183 (88)	152 (16)	108 (74)	107 (20)	77 (4)	51 (9)
4	5	277 (2)	262 (100)	201 (0)	199 (0)	183 (79)	152 (10)	108 (40)	107 (15)	77 (4)	51 (7)
5	6	277 (26)	262 (100)	201 (5)	199 (6)	183 (72)	152 (10)	108 (34)	107 (15)	77 (10)	51 (13)
6	8	277 (34)	262 (100)	201 (10)	199 (8)	183 (78)	152 (15)	108 (46)	107 (13)	77 (13)	51 (13)
7	9	277 (6)	262 (100)	201 (1)	199 (2)	183 (71)	152 (8)	108 (30)	107 (13)	77 (5)	51 (13)
8	10	277 (5)	262 (100)	201 (2)	199 (1)	183 (80)	152 (10)	108 (43)	107 (16)	77 (5)	51 (13)

Table 2 EI mass spectra of the triphenylphosphonium salts ($Ph_3P^+(CH_2)_nOH\cdot Br^-$ (The probe temperature 30℃→350℃)

Compound	n	a	b	c	d	e	f	g	h	i	j
4	5	277 (100)	262 (15)	201 (24)	199 (23)	183 (54)	152 (16)	108 (19)	107 (10)	77 (29)	51 (26)
5	6	277 (100)	262 (37)	201 (23)	199 (24)	183 (53)	152 (15)	108 (18)	107 (9)	77 (28)	51 (25)
6	8	277 (100)	262 (8.3)	201 (25)	199 (23)	183 (22)	152 (13)	108 (5)	107 (4)	77 (25)	51 (23)
7	9	277 (100)	262 (14)	201 (23)	199 (22)	183 (28)	152 (12)	108 (10)	107 (7)	77 (25)	51 (23)
8	10	277 (100)	262 (12)	201 (52)	199 (55)	183 (44)	152 (20)	108 (8)	107 (9)	77 (38)	51 (22)

Table 3 High resolution accurate mass data of *m/z* 277 and *m/z* 199 of eight compounds

Compound	*n*	Measured value	Calculated value	Difference (mmu)	Elemental composition
1	2	277.0782	277.0782	0.0	$C_{18}H_{14}OP$
2	3	277.0780	277.0782	−0.2	$C_{18}H_{14}OP$
3	4	277.0779	277.0782	−0.3	$C_{18}H_{14}OP$
4	5	277.0773	277.0782	−0.9	$C_{18}H_{14}OP$
5	6	77.0783	277.0782	+0.1	$C_{18}H_{14}OP$
6	8	277.0781	277.0782	−0.1	$C_{18}H_{14}OP$
7	9	277.0790	277.0782	+0.8	$C_{18}H_{14}OP$
8	10	277.0792	277.0782	+1.0	$C_{18}H_{14}OP$
1	2	199.0310	199.0313	−0.3	$C_{12}H_8OP$
4	5	199.0312	199.0313	−0.1	$C_{12}H_8OP$
6	8	199.0311	199.0313	−0.2	$C_{12}H_8OP$
8	10	199.0320	199.0313	+0.7	$C_{12}H_8OP$

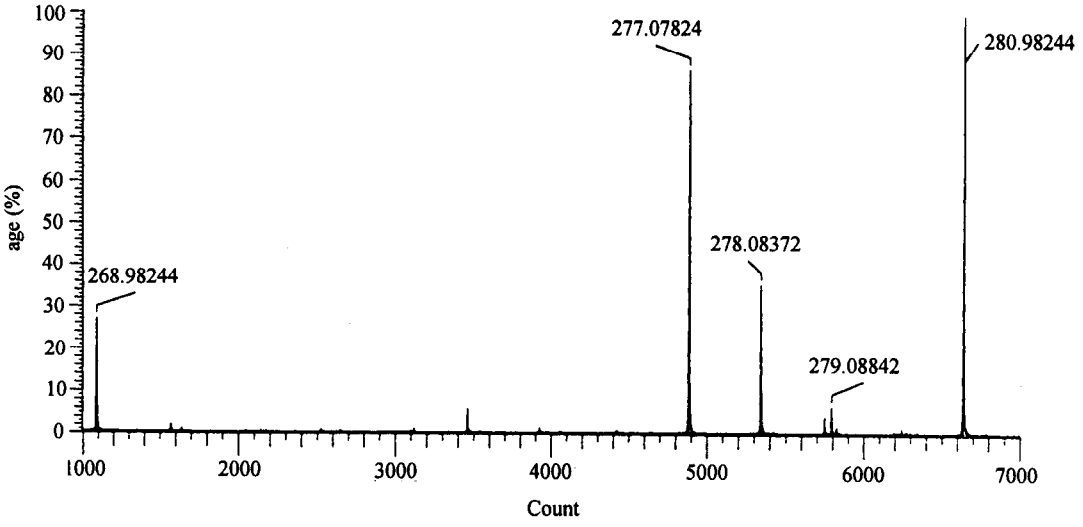


Fig. 1 High resolution accurate mass data of *m/z* 277 for compound **1**.

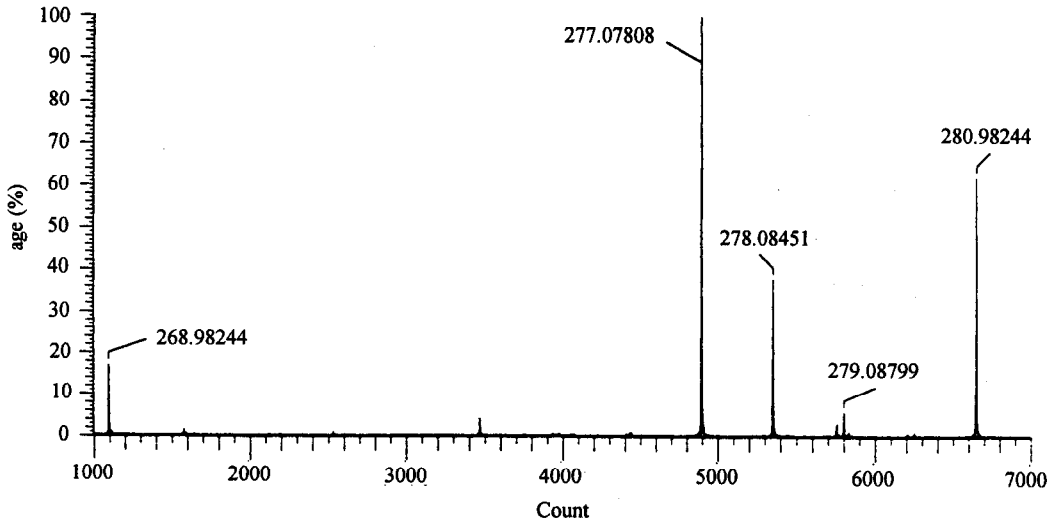
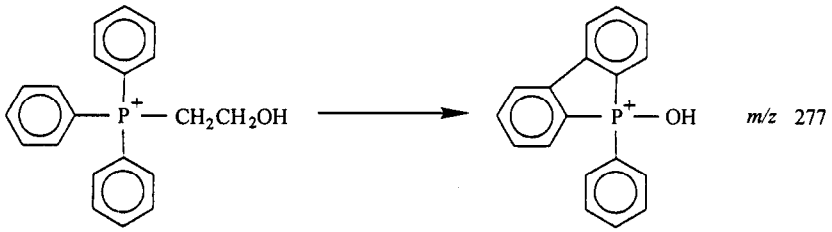


Fig. 2 High resolution accurate mass data of *m/z* 277 for compound **6**.

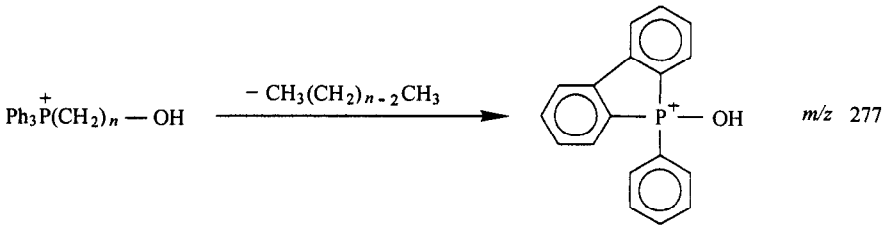
used to measure the accurate mass of *m/z* 277. The high resolution accurate mass data of *m/z* 277 for eight compounds are listed in Table 3, showing difference range from 0.0—1.0 mmu between measured and calculated values. The high resolution accurate mass spectrum of *m/z* 277 of compounds **1** and **6** are shown in Fig. 1 and Fig. 2, respectively.

The elemental composition $C_{18}H_{14}OP$ deducted from this accurate mass is in full conformity with that of the proposed structure, in Scheme 2, thus supporting the process of formation of the ion $(O=PPh_3-1)^+$ as proposed in Scheme 2.

Scheme 1



Scheme 2



A fascinating phenomenon was discovered when the relative abundance of *m/z* 277 increases or decreases, that of *m/z* 199 does also (see Tables 1 and 2, Figs. 3 and 4). Therefore, there is a close relation between them. In order to determine the structure of *m/z* 199 ion, the high resolution accurate masses of *m/z* 199 ion for compounds **1**, **4**, **6**, **8** were measured. These data are summarized in Table 3, corresponding elemental composition of $C_{12}H_8OP$, the proposed structure of which is show in scheme 3. The Mass-analyzed Ion Kinetic Energy Spectrometry (MIKES) method was used to study the relation between *m/z* 277 ion and *m/z* 199 ion. When the ion at *m/z* 277 was chosen as precursor ion, only a daughter ion at *m/z* 199 could be observed (see Fig. 5). The MIKES data are listed in Table 4. The proposed mechanism for formation of ion at *m/z* 199 is presented in Scheme 3.

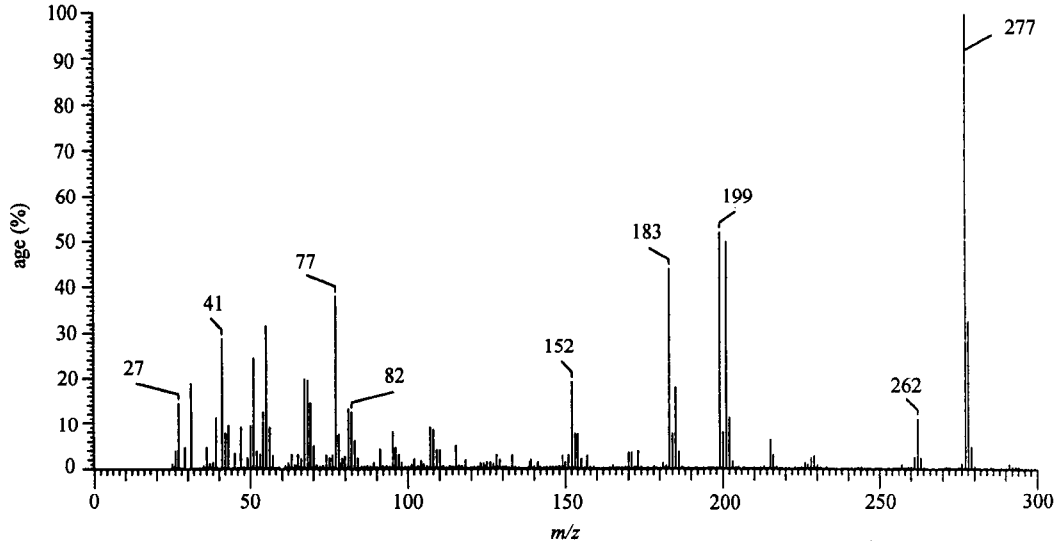


Fig. 3 EI Mass spectra of $Ph_3P^+(CH_2)_{10}OHBr^-$ (30—300℃).

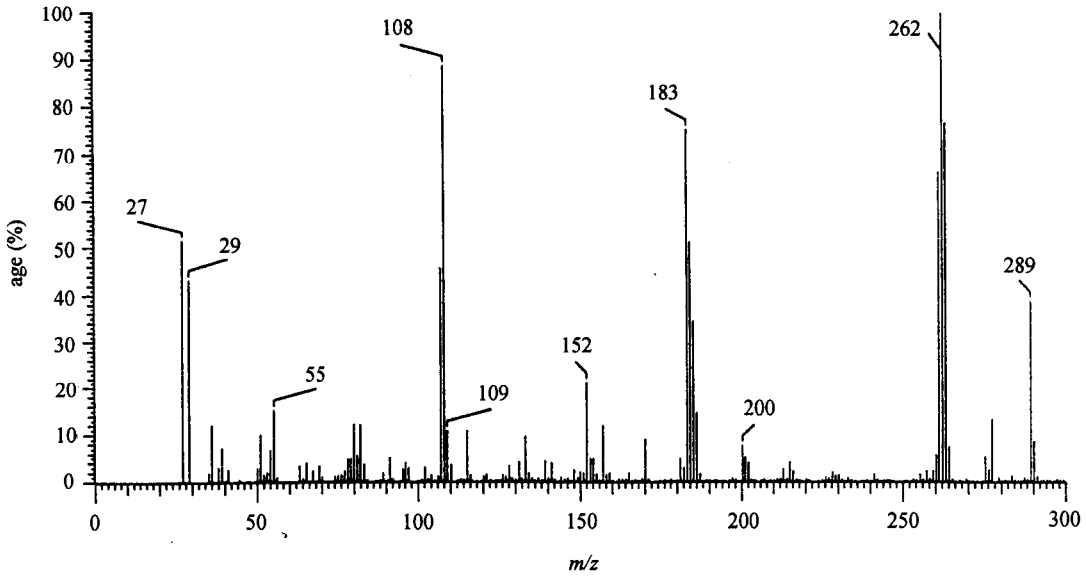


Fig. 4 EI Mass spectra of $Ph_3P^+(CH_2)_{10}OHBr^-$ (300—350℃).

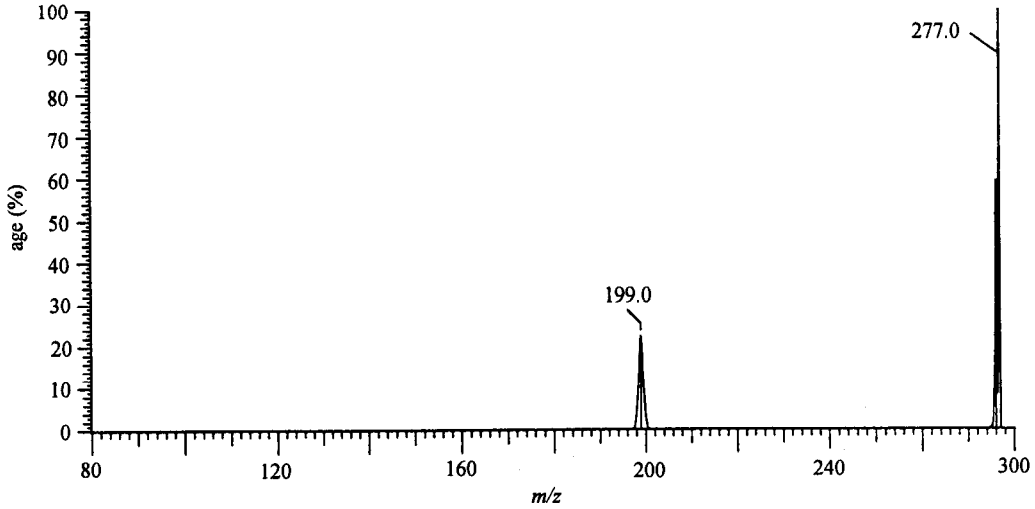
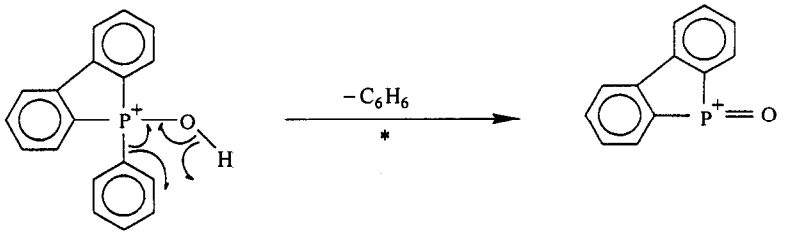


Fig. 5 MIKE spectra of m/z 277 for compound **6**.

Scheme 3



m/z 277 m/z 199

The process to form the daughter ion at m/z 199 once again supports the structure of the ion at m/z 277 as reasonable. Based on the elemental composition, structure and MIKES analyzed, it was confirmed that the mechanism for formation of m/z 277 was rearrangement reaction of the hydroxyl group.

Table 4 MIKE spectra of m/z 277 ion derived from compounds **1**, **4**, **6** and **8**, respectively

Compound	Precursor ions	Daughter ions
1	277	199
4	277	199
6	277	199
8	277	199

In the process of determining EI mass spectra of the eight compounds, it is found that the base peak of compound **1** ($n = 2$) is always located at m/z 277 when the source temperature is 300℃ and the probe temperature increases from 30℃ to 350℃. The base peaks of compounds **2** and **3** ($n = 3,4$) are always m/z 262, under the same conditions. As for compounds **4**—**8** ($n = 5, 6, 8, 9, 10$), the base peak is m/z 277 when the probe temperature rises from 30℃ to 300℃, but the base peak will be at m/z 262 when the probe temperature rises to higher than 300℃. It is obvious that formation of the ion at m/z 277 is closely related to the size of the carbon chain, and to source temperature and probe temperature as well. The reactions to form the ions at m/z 277 and m/z 262 take place simultaneously, thus leading to strong competition.

These results demonstrate that the formation of the ion at m/z 277 from compounds **4**—**8** through hydroxyl rearrangement depends on temperature and is not related to the size of carbon chain.

References

1. Henrick, C.A., *Tetrahedron*, **33**, 1854(1977).
2. Schlosser, M.; Yuing, H.B.; Schaub, B., *Tetrahedron Lett.*, **26**, 311(1985).
3. Horiike, M.; Yuan, G.; Hirano, C., *Org. Mass Spectrom.*, **27**, 944(1992).
4. Yuan, G.; He, M.Y.; He, X.R.; Horiike, M.; Hirano, C., *Rapid. Commun. Mass Spectrom.*, **7**, 591 (1993).
5. Wang, Q.B.; He, M.Y.; He, X.R.; Yuan, G., *Rapid. Commun. Mass Spectrom.*, **11**, 1728(1997).
6. Schlosser, M.; Yuing, H.B.; Schaub, B., *Tetrahedron Lett.*, **26**, 311(1985).
7. Kroha, K.J.; Busch, K.L., *Org. Mass Spectrom.*, **21**, 509(1986).
8. Miller, J.M.; Ni, J., *J. Mass Spectrom.*, **31**, 16 (1996).
9. McCrery, D.A.; Peake, D.A.; Gross, M.L., *Anal. Chem.*, **57**, 1181(1985).
10. Kroha, K.J.; Busch, K.L., *Org. Mass Spectrom.*, **21**, 507(1986).
11. Ciaereboudt, J.; Baeten, W.; Geise, H.; Ciaeys, M., *Org. Mass Spectrom.*, **28**, 71(1993).

(E200003051 JIANG, X.H.; DONG, L.J.)