Thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide): 2. Mass spectroscopic analysis of dimeric products from degradation of poly(2,6-dimethyl-1,4-phenylene oxide)

J. Jachowicz and M. Kryszewski

Polymer Institute, Technical University, Łódź 90-542, Poland
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The mass spectra of dimeric degradation products of poly(2,6-dimethyl-1,4-phenylene oxide) are discussed. It has been found that the main fragmentation mechanism of rearranged dimer is β-benzyl cleavage giving rise to odd-mass ions and *ortho* hydroxyl hydrogen transfer yielding even-mass ions. The mass spectra of unrearranged dimers are very similar though it could not be concluded that Fries-type rearrangement takes place on electron impact.

INTRODUCTION

In a previous paper we have stated that the thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) proceeds through Fries-type rearrangement followed by statistical scission[1]. In the first degradation step benzyl bonds are produced. Their scission leads to the formation of monomers, dimers and higher oligomers. The rearrangement is, however, not complete at degradation conditions used in this work, and apart from oligomers containing benzyl bonds, those with ether bonds could be observed as well. The mechanism of thermal breakdown of PDMPO proposed in this paper assumes that the elementary process of benzyl bond scission takes place through disproportionation with hydroxyl or benzyl hydrogen transfer. This is why it seemed to us interesting to examine the fragmentation reactions of dimeric compounds separated by gas chromatography from the after-degradation mixture. According to the proposed mechanism, two kinds of dimers are produced during the thermal degradation of PDMPO. (1) Dimers with two hydroxyl groups which are produced by statistical cleavage of completely rearranged polymer. (2) Dimers with one hydroxyl group in which an ether bond is retained and which are produced by statistical cleavage of partly rearranged polymer:
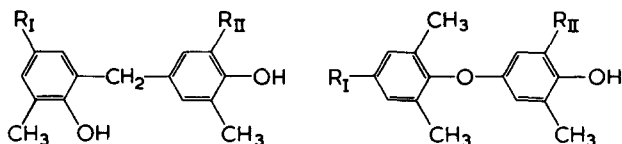
(I) $R_I = R_{II} = CH_3$; (II) $R_I = CH_3$, $R_{II} = H$; (III) $R_I = H$, $R_{II} = CH_3$; (IV) $R_I = R_{II} = H$.

In the present paper the mass spectra of all these compounds are discussed. In order to demonstrate that hydrogen transfer reactions take place during the electron-impact induced fragmentation silyl and deuterium analogues of these dimers were prepared.

The structure of unrearranged dimers was confirmed by synthesizing them according to the method described by Bruice *et al.*[2] and stating that their mass spectra compared with the mass spectra of dimers obtained from degradations are identical.

EXPERIMENTAL

The mixture of the degradation products was obtained by the method described in the previous paper[1].

The silyl analogues were obtained by reacting the mixture of the degradation products with an excess of hexamethyldisilazane at room temperature.

The deuterium analogues were prepared by reacting the mixture of the degradation products in the water-free THF solution with calcium hydride, and then adding D_2O (99.75%).

Gas chromatographic – mass spectrometry analysis

Gas chromatography–mass spectrometry (GC–MS) analysis was carried out using a 2091 LKB gas chromatograph–mass spectrometer connected with PDP 11 digital computer. For all separations a 2 m column packed with 10% OV-101 glass was used. Programmed heating conditions were used from 80° to 250°C with the heating rate 5°C/min. The spectra were obtained under the operating conditions 70 eV, ion source temperature 250°C, accelerating voltage 3.5 kV and resolving power up to 1000.

RESULTS AND DISCUSSION

Rearranged dimers

There are two strong fragmentation ions present in each mass spectrum of rearranged dimers. The ions *m/e* 135 or *m/e* 121 are produced by β-benzyl bond cleavage (*Figures 1–4* and *Table 1*). This type of cleavage has already been reported in the studies on fragmentation of various oligomeric benzyls[3].
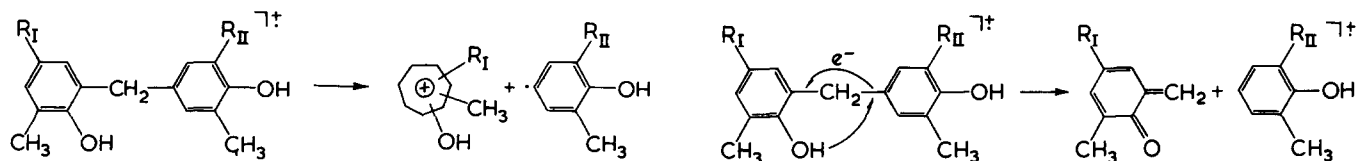
On the other hand, the formation of the ions m/e 122 or m/e 108 (*Figures 1–4* and *Table 1*) cannot be simply explained without postulating the hydrogen transfer from *ortho* hydroxyl group in one ring to *para* position with respect to the hydroxyl group in the second ring. This process is justified as the *para* position is activated by increased electron density.

This type of hydrogen transfer was not observed in the case of the compounds without a *para* hydroxyl group with respect to the benzyl bond[4]. In order to test this suggestion we obtained mass spectra of deuterated dimers which supported it by exhibiting peaks due to the ions m/e 124 or m/e 110.

It should be stressed that the presence of even-mass ions supports our predictions that the hydroxyl group is in the

Table 1 Main fragmentation ions of rearranged dimers and of their silyl analogues

| m/e	Intensity (%)	Fragment	Mechanism of fragmentation	m/e	Intensity (%)	Fragment	Mechanism of fragmentation
256	27.5		Molecular ion	242	42.9		Molecular ion
135	100		β-Cleavage of benzyl bond	121	100		β-Cleavage
122	48.8		*Ortho* hydroxyl hydrogen transfer	122	91.4		*Ortho* hydroxyl hydrogen transfer
400	39.0		Molecular ion	386	34.5		Molecular ion
207	15.4		β-Cleavage of benzyl bond	193	12.6		α or β-Cleavage
193	43.0		α-Cleavage of benzyl bond	206	6.3	not established identity	
191	100	not established identity		207	3.0		β-Cleavage
242	58.0		Molecular ion	228	45.0		Molecular ion
135	100		β-Cleavage of benzyl bond	121	100		β-Cleavage
121	65.3		β-Cleavage of benzyl bond	108	53.6		*Ortho* hydroxyl hydrogen transfer
108	32.0		*Ortho* hydroxyl hydrogen transfer	372	38.0		Molecular ion
386	38.0		Molecular ion	193	11.3		β-cleavage
207	8.4		β-Cleavage	179	4.9		α-Cleavage
193	10.2		α or β-Cleavage	177	6.7	not established identity	
191	6.3	not established identity					
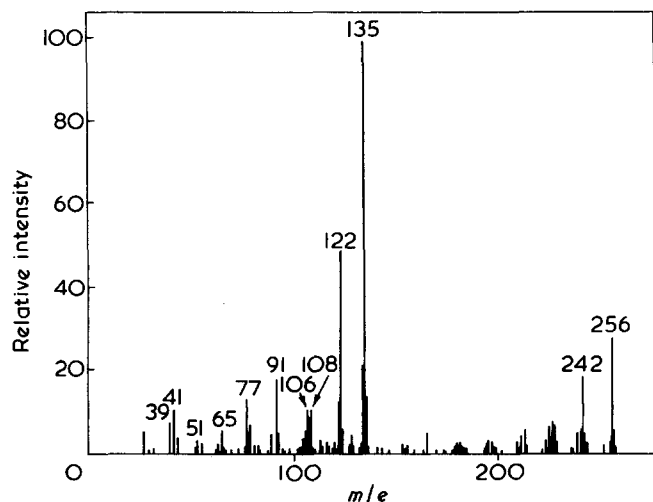
Figure 1 The mass spectrum of rearranged dimer I

Figure 2 The mass spectrum of rearranged dimer II

Figure 3 The mass spectrum of rearranged dimer III

tra (*Tables 1* and *3*). Apart from two strongest ions appearing on the mass spectra of rearranged dimers, characteristic ions of phenols and aromatic compounds are observed too. The highest intensity peaks are due to the following ions: m/e 91, 77, 65, $[P-CO]^+$, $[P-CHO]^+$. The identity of the
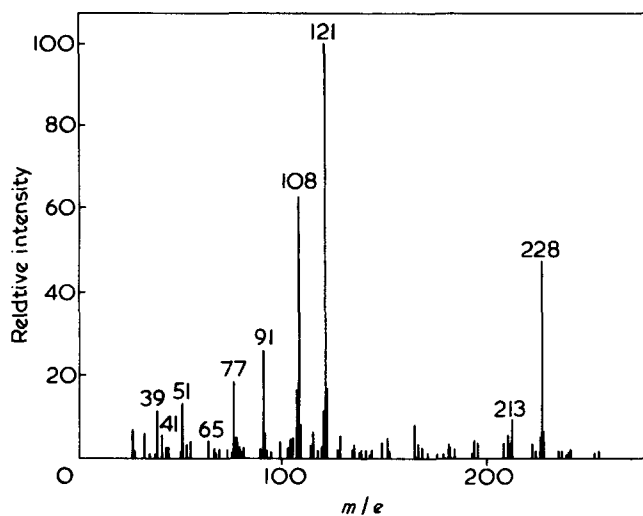
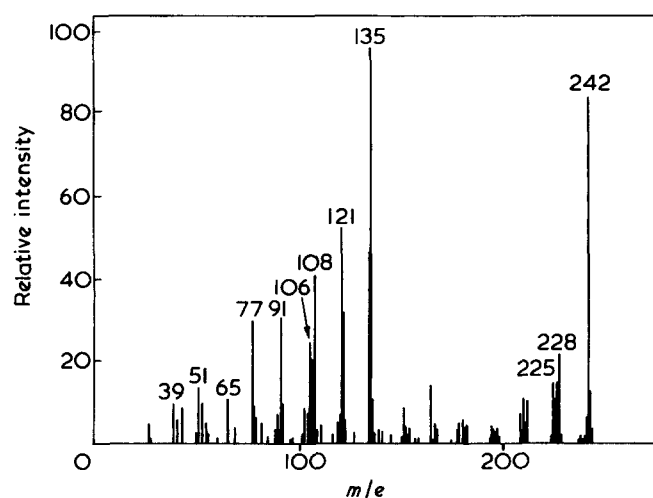*Figure 4* The mass spectrum of rearranged dimer IV

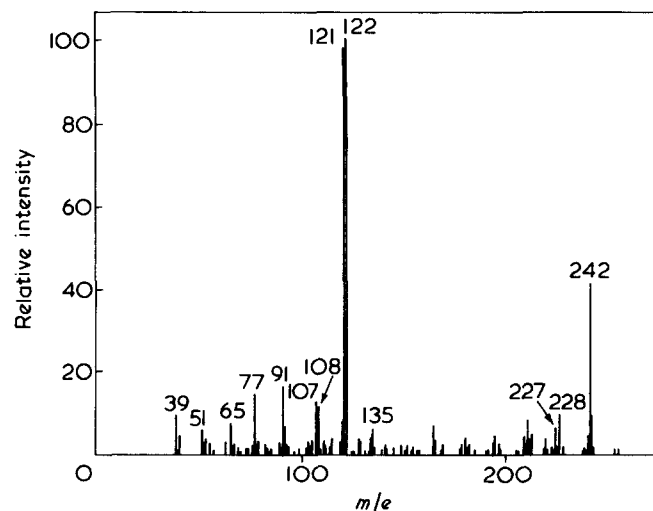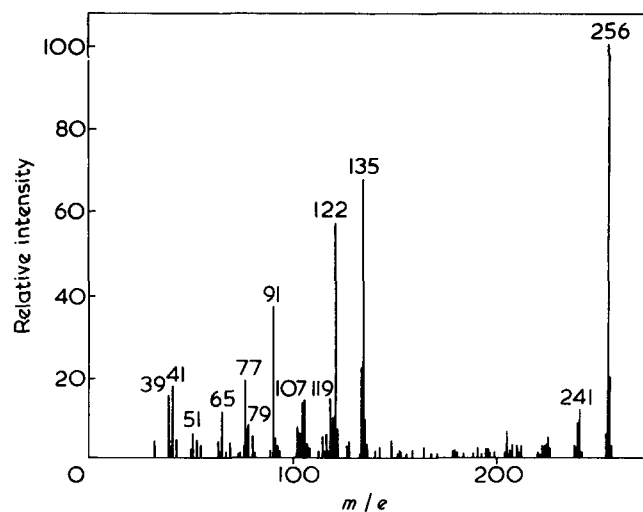*Figure 5* The mass spectrum of unrearranged dimer I
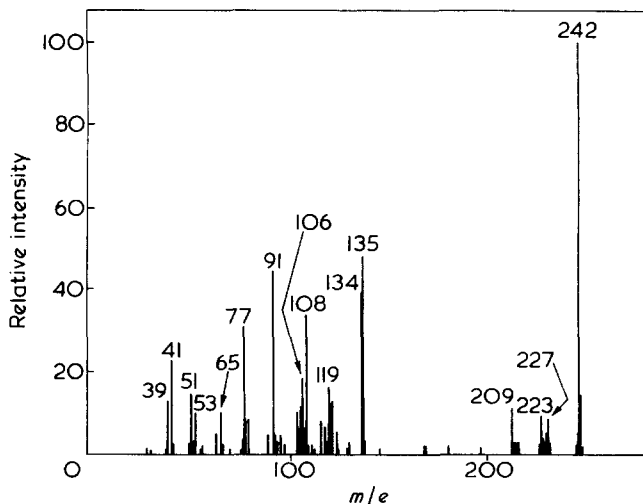
Figure 6 The mass spectrum of unrearranged dimer II

ortho position to the benzyl bond because the observed hydrogen transfer effect is possible only then.

In the case of silyl analogues the *ortho* hydrogen transfer effect disappears. Odd-mass fragmentation ions, being the result of α- and β-benzyl bond cleavage, appear in the spec-

ions P-14 was not established (*Figures 1–4*). In the spectra of silyl analogues we also observe strong peaks due to the ions $[P–CH_3]^+$ and $[Si(CH_3)_3]^+$ and ions formed by a methyl group loss from various fragments (*Tables 1* and *3*).

Unrearranged dimers

Examination of the mass spectra of unrearranged dimers shows a very similar picture compared to the mass spectra of rearranged dimers. Although we are unable to present any unequivocal evidence to that effect one cannot exclude the possibility that Fries-type rearrangement takes place on electron impact or is caused by the high temperature in the ion source (250°C). Such mechanism of rearrangement and fragmentation of aromatic ethers has already been suggested[5]. Two strong fragmentation ions appear on each spectrum; one of odd mass is due to ether link cleavage (or benzyl bond cleavage if rearrangement takes place), the second of even mass is produced by hydrogen transfer from *ortho*

methyl group (or hydroxyl group) (*Figures 5–8* and *Table 2*). In contrast to silyl analogues of rearranged dimers, even-mass ions appear in the spectra of silyated unrearranged dimers (*Tables 2* and *3*). This may be caused by hydrogen transfer from the *ortho* methyl group or, if rearrangement takes place, by hydrogen transfer from the liberated OH groups.

Table 2 Main fragmentation ions of unrearranged dimers and of their silyl analogues

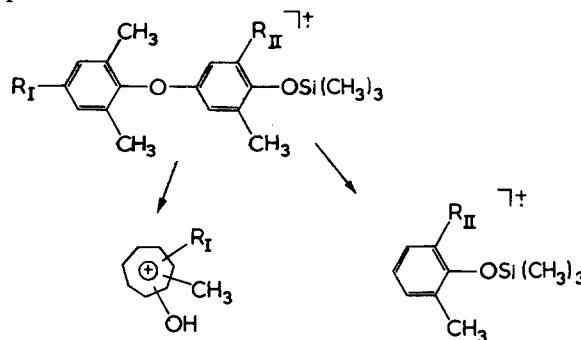| m/e	Intensity	Fragment	Mechanism of fragmentation	m/e	Intensity	Fragment	Mechanism of fragmentation
256	100		Molecular ion	314	100		Molecular ion
135	70.0		Ether or β-benzyl link cleavage	135	59.1		Ether or β-benzyl link cleavage
122	60.0		Ortho methyl or hydroxyl hydrogen transfer	180	20.1		Ortho methyl or hydroxyl hydrogen transfer
328	100		Molecular ion	165	31.0		
194	28.2		Ortho methyl or hydroxyl hydrogen transfer	242	100		Molecular ion
179	43.0			122	92.8		Ortho methyl or hydroxyl hydrogen transfer
135	36.6		Ether or β-benzyl link cleavage	121	65.7		Ether or β-benzyl link cleavage
242	100		Molecular ion	228	79.2		Molecular ion
135	46.4		Ether or β-benzyl link cleavage	121	100		Ether or β-benzyl link cleavage
134	36.4		Ortho methyl or hydrogen transfer	108	74.2		Ortho methyl or hydroxyl hydrogen transfer
108	27.1		Ortho methyl or hydroxyl hydrogen transfer				
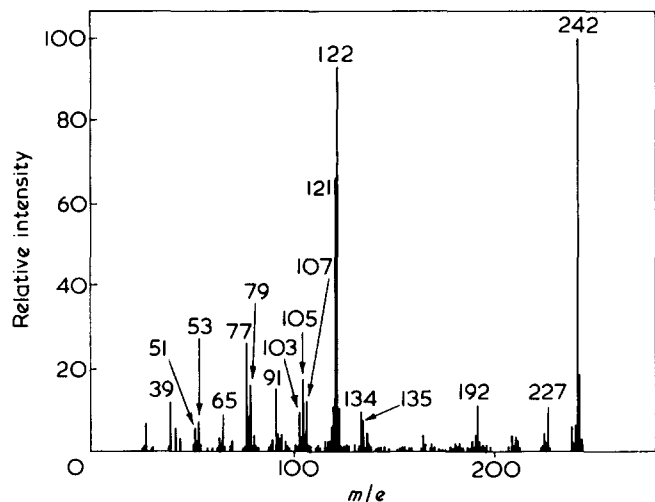
Figure 7 The mass spectrum of unrearranged dimer III
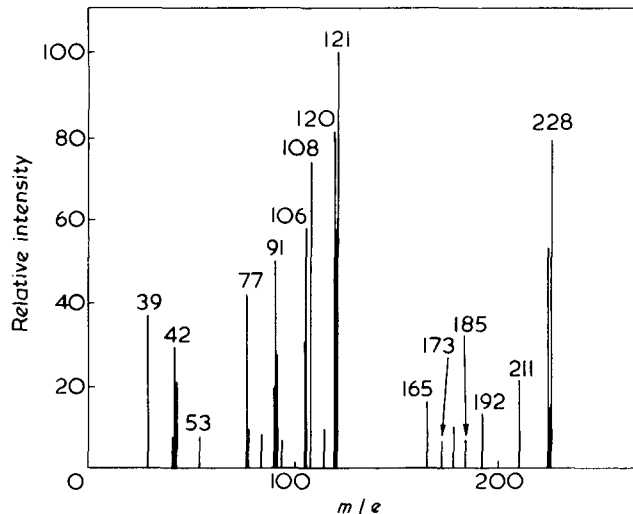
Figure 8 The mass spectrum of unarranged dimer IV

Table 3 70 eV mass spectra of silyl analogues of rearranged and unrearranged dimers

Rearran-	m/e	45	59	73	74	75	91	105	119	133	147	161	
ged	I (%)	16.2	4.6	100	7.7	6.6	1.5	2.9	1.5	1.6	2.2	2.0	
dimer I:	m/e	163	175	177	178	179	189	191	193	205	207	251	
	I (%)	5.0	2.0	3.5	2.8	2.8	2.8	9.9	2.5	3.2	16.2	2.0	
	m/e	295	297	311	312	327	369	370	371	395	396	397	
	I (%)	3.1	3.5	7.0	2.8	2.4	2.0	2.0	5.3	38.7	18.3	6.0	
	m/e	400	401	402									
	I (%)	38.2	14.0	4.8									
Rearran-	m/e	45	59	73	74	75	91	105	147	149	161	163	
ged	I (%)	16.2	4.3	100	8.1	7.4	2.8	1.7	2.4	3.8	2.1	3.5	
dimer II:	m/e	165	175	177	178	179	191	192	193	194	206	207	
	I (%)	3.5	2.1	7.4	4.2	3.1	6.3	2.1	10.2	2.0	4.2	8.4	
	m/e	208	209	223	251	281	283	297	311	312	313	355	
	I (%)	3.1	2.1	1.9	2.0	2.2	1.9	4.2	2.1	2.1	2.1	2.0	
	m/e	356	371	372	373	386	387	388					
	I (%)	1.8	35.0	11.1	4.2	38.0	13.6	4.8					
Rearran-	m/e	45	59	73	74	75	147	149	163	164	165	177	
ged	I (%)	12.7	2.2	100	8.8	7.8	5.0	2.0	4.2	1.5	1.6	4.2	
dimer	m/e	178	191	192	193	206	207	223	237	281	283	297	
III:	I (%)	2.2	4.9	3.0	12.6	6.3	3.0	1.5	1.6	1.7	4.2	2.0	
	m/e	357	371	372	373	386	387	388					
	I (%)	5.9	27.4	12.0	5.6	34.5	11.4	4.1					
Rearran-	m/e	45	59	73	74	75	91	105	119	135	147	149	161
ged	I (%)	11.6	3.8	100	7.1	7.0	2.7	1.5	1.5	1.8	6.3	4.2	1.6
dimer	m/e	163	164	165	175	177	178	179	191	192	193	194	209
IV:	I (%)	3.5	1.7	2.2	1.5	6.7	2.5	4.9	2.2	2.3	11.3	2.0	1.8
	m/e	237	277	279	283	299	341	357	358	359	371	372	373 374
	I (%)	2.0	2.2	3.5	3.4	1.9	2.0	26.1	9.9	3.5	3.2	38.0	12.0 4.6
Unre-	m/e						18	27	39	41	43	45	47
arranged	I (%)						2.0	1.9	2.8	5.6	2.9	18.0	2.0
dimer I:	m/e	51	53	59	65	73	74	75	77	78	79	91	92
	I (%)	2.2	2.3	7.0	5.3	74.0	6.7	7.2	8.9	2.8	6.0	18.3	3.9
	m/e	103	104	105	107	115	117	119	121	135	136	149	157
	I (%)	3.8	2.8	9.0	2.8	3.2	3.1	9.2	3.0	36.6	3.5	3.6	4.2
	m/e	163	164	165	177	178	179	180	181	193	194	195	196
	I (%)	9.0	2.9	3.5	3.8	10.9	43.0	6.4	3.2	3.5	28.2	5.7	2.0
	m/e	209	223	255	311	313	314	315	328	329	330		
	I (%)	2.0	2.2	2.3	2.1	13.4	6.4	2.2	100	26.8	7.1		
Unre-	m/e	29	39	41	43	45	51	52	53	59	73	74	75
arranged	I (%)	2.0	2.8	4.6	2.7	17.6	3.5	2.0	2.7	3.9	66.1	5.6	8.3
dimer II:	m/e	77	78	79	83	91	103	104	105	107	115	117	119
	I (%)	9.1	5.4	8.9	2.0	18.5	2.7	2.9	8.2	3.5	2.0	2.1	9.1
	m/e	121	135	136	149	150	163	164	165	166	177	178	179
	I (%)	2.4	59.1	5.6	6.0	3.6	5.7	5.5	31.0	5.4	2.1	9.1	9.5
	m/e	180	181	194	209	283	297	298	299	300	312	314	315
	I (%)	20.1	4.6	5.3	2.0	2.0	3.9	2.2	13.2	3.0	5.2	100	26.0
	m/e	316											
	I (%)	6.3											

The splitting of an ether bond with simultaneous hydrogen transfer can be performed in another way which also leads to the formation of even-mass ions:
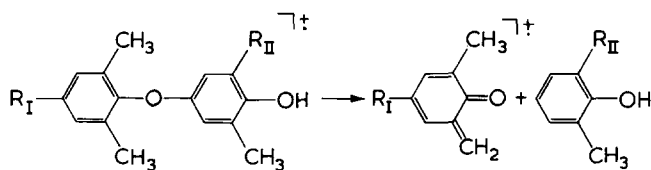
This type of splitting has been found to be characteristic of o-hydroxyl diaryl ethers[4]. In the spectra of unrearranged dimers we observe the ions m/e 134 and m/e 120 which are probably due to this process.

CONCLUSIONS

The data presented above seem to confirm the structure of the main degradation products of PDMPO. The electron-impact induced fragmentation of rearranged and unrearranged dimers can be summarized as follows.

(a) β-Benzyl cleavage gives rise to odd-mass ions either in the case of simple dimers or of their silyl analogues.

(b) The appearance of even-mass ions is due to hydroxyl hydrogen transfer group with respect to the benzyl bond.

(c) The mass spectra of unrearranged dimers are very similar to their rearranged isomers, though not identical. This does not allow us to draw the conclusion that Fries-type rearrangement takes place on electron impact. On the other hand, it can be postulated that partial rearrangement is caused by high temperature in the ion source.

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