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Note

Separation and identification of phenol–formaldehyde condensates by gas chromatography–mass spectrometry

III. Hemiformal isomers in resol

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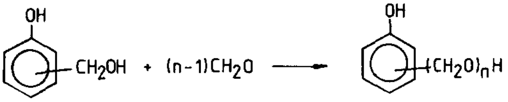
Many aspects of the main reaction routes of the base-catalysed condensation of phenol with formaldehyde have been described[1–3]. It is known that at the initial stage of the condensation the methylol-substituted phenols (the primary reaction products) can react with formaldehyde to form hemiformal compounds[2]:



Hemiformal structural units have been determined in resol following acetylation and ^{1}H NMR spectroscopy[4,5]. Recently ^{13}C NMR spectroscopy has been used to calculate the formation rate constants of different hemiformal isomers[6]. These results have been applied to the characterization of the resol in question via the concept of average chemical structure.

In the analysis of molecular species of resol, gas–liquid chromatography (GLC) has been used to separate acetylated hydroxybenzylhemiformals[7]. Trimethylsilyl derivatives of the latter compounds are particularly suitable for this purpose, and they have been identified by gas chromatography–mass spectrometry (GC–MS)[8,9]. Several hemiformal- and dihemiformal-type compounds of mononuclear methylolated phenols have been determined in resol by capillary GC–MS[2]; their mass spectral characteristics, however, have been described only very briefly and, in the absence of authentic reference compounds, the identification of the positional isomers has not been reported.

In the present paper the mass spectral fragmentation of selected hemiformal compounds present in resol is elucidated and the GLC separation and MS identification of their position isomers are described.

EXPERIMENTAL

Materials

Resol was prepared as described previously[3], but using phenol–formaldehyde in a 1:4 molar ratio and a reaction time of 1 h. Trimethylsilylation was carried out with N,O-bis(trimethylsilyl)trifluoracetamide in pyridine.

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Instrumentation

Packed-column separation was performed on a JEOL JGC-20K chromatograph coupled to a JEOL JMS-01SG-2 mass spectrometer. Electron ionization at 75 and 15 eV and a source temperature of 250°C were used. Accurate mass measurements were carried out at resolution of ≥10 000 (10% valley definition) using perfluorokerosene as mass standard[3].

A glass column (3 m × 2 mm I.D.) packed with 3% OV-1 on 100–120 mesh Chromosorb W HP was applied. Injection port and jet separator temperatures were maintained at 280°C, and the oven was programmed from 120 to 300°C at 8°C/min.

Capillary GC–MS was carried out with a Hewlett-Packard HP 5992B quadrupole instrument. Electron impact (EI) mass spectra were measured at 70 eV and 200°C source temperature. A borosilicate glass capillary (30 m × 0.45 mm I.D.) coated with OV-1 stationary phase of 0.5 μm film thickness was used. The carrier gas was helium, at a flow-rate of 2 ml/min. The injection port temperature was held at 250°C, and splitless injection was applied. The column oven was programmed from 120 to 250°C at 3°C/min.

RESULTS AND DISCUSSION

Fig. 1 shows the total ion chromatogram of resol obtained with 1:4 phenol–formaldehyde and packed-column separation following trimethylsilylation. Most of the compounds have been described previously[3]; the only exception is the presence of monohemiformals of methylolated mononuclear phenols. Their molecular ions, in the form of trimethylsilyl derivatives, are at the following mass-to-charge (m/z) values: hydroxybenzylhemiformal (I), m/z = 298; methylolhydroxybenzylhemiformal (II), m/z = 400; dimethylolhydroxybenzylhemiformal (III) m/z = 502.

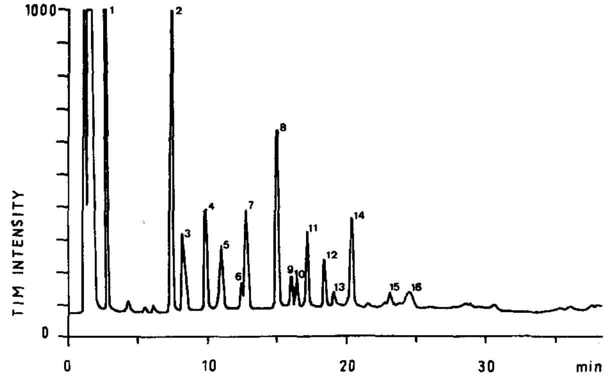


Fig. 1. Total ion current chromatogram of hemiformal-containing resol: the sample was trimethylsilylated. GC conditions: 3% OV-1 on 100–120 mesh Chromosorb W HP; glass column (3 m × 2 mm I.D.); injection port, 280°C; oven temperature programmed from 120 to 300°C at 8°C/min. Peaks (trimethylsilyl derivatives): 1 = phenol; 2 = 2-methylolphenol; 3 = 4-methylolphenol, 4 = 2-hydroxybenzylhemiformal (Ia); 5 = 4-hydroxybenzylhemiformal (Ib); 6 = 2,6-dimethylolphenol; 7 = 2,4-dimethylolphenol; 8 = methylolhydroxybenzylhemiformal (II); 9 = 2,4'-dihydroxydiphenylmethane; 10 = 2,4,6-trimethylolphenol; 11 = 4,4'-dihydroxydiphenylmethane; 12 = dimethylolhydroxybenzylhemiformal (III); 13 = 3-methylol-2,4'-dihydroxydiphenylmethane; 14 = 3'-methylol-2,4'-dihydroxydiphenylmethane and 3-methylol-4,4'-dihydroxydiphenylmethane, 15 = dimethyloldihydroxydiphenylmethane isomers; 16 = trimethyloldihydroxydiphenylmethane isomers.

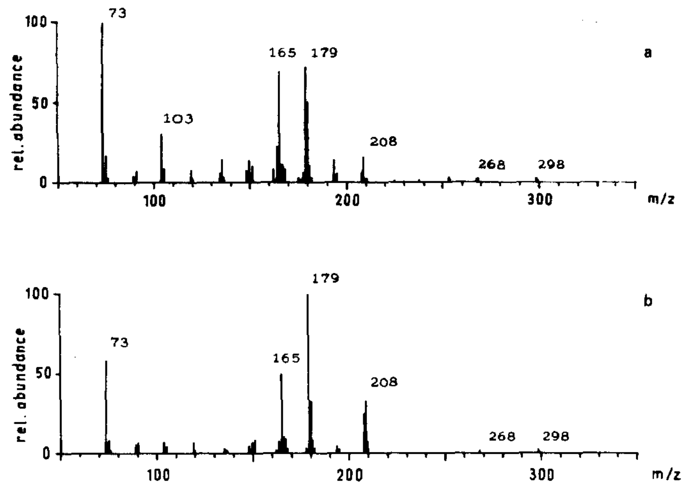


Fig. 2. Mass spectra (70 eV) of hydroxybenzylhemiformal isomers: (a) 2-hydroxybenzylhemiformal; (b) 4-hydroxybenzylhemiformal. (Source temperature, 200°C; quadrupole instrument.)

Considering *ortho* and *para* substituents relative to the hydroxyl groups, the number of possible isomers is two for I, three for II and two for III. Most of the hemiformal components can be separated by means of the applied capillary column: in case of III there was no evidence of positional isomerism.

Fig. 2 shows mass spectra (70 eV) of isomers of I. In contrast to the other compounds found in resol there is no striking difference in the molecular ion intensities, and thus no indication of the positions of the substituents. Moreover, the abundances of the fragment ions do not make direct identification possible without discussing their origin in detail. As a starting point, accurate mass measurement of principal ions in the mass spectra was performed: the inferred elemental compositions are listed in Table I.

Now some important features are apparent. First, the wide variety of odd-electron fragment ions ($\text{OE}^{+\cdot}$) such as m/z = 268 resulting from the loss of CH_2O

TABLE I

ELEMENTAL COMPOSITIONS OF CHARACTERISTIC FRAGMENTS IN THE MASS SPECTRA OF HYDROXYBENZYLHEMIFORMALS

m/z	*Elemental composition*	*Parity**
73	C_3H_9Si	EE^+
103	$C_4H_{11}OSi$	EE^+
165	$C_9H_{13}OSi$	EE^+
179	$C_{10}H_{15}OSi$	EE^+
180**	$C_{10}H_{16}OSi$	$\text{OE}^{+\cdot}$
208	$C_{11}H_{16}O_2Si$	$\text{OE}^{+\cdot}$
268	$C_{13}H_{24}O_2Si_2$	$\text{OE}^{+\cdot}$
298	$C_{14}H_{26}O_3Si_2$	$\text{OE}^{+\cdot}$ ($\text{M}^{+\cdot}$)

* EE^+ = even-electron ion; $\text{OE}^{+\cdot}$ = odd-electron ion; $\text{M}^{+\cdot}$ = molecular ion.
** Multiplet; isotopic peaks are not listed.

(formaldehyde) from the molecular ion and the loss of trimethylsilanol (m/z = 208), etc. Because these are formed in significant abundance only through special types of decomposition, such as rearrangements[10], which can take place across entropically unfavourable "tight activated complexes" (transition states) according to the Quasi-Equilibrium Theory (QET) of mass spectra, their formation is often especially characteristic of a particular molecular structure because of certain steric requirements that must be fulfilled to make the fragmentation in question possible. An important consequence of the QET is that the relative abundances of odd-electron fragment ions formed in such rearrangement processes can be increased by lowering the energy of bombarding electrons. Therefore, mass spectra were recorded at 15 eV for the positional isomers discussed above, and they are shown in Fig. 3.

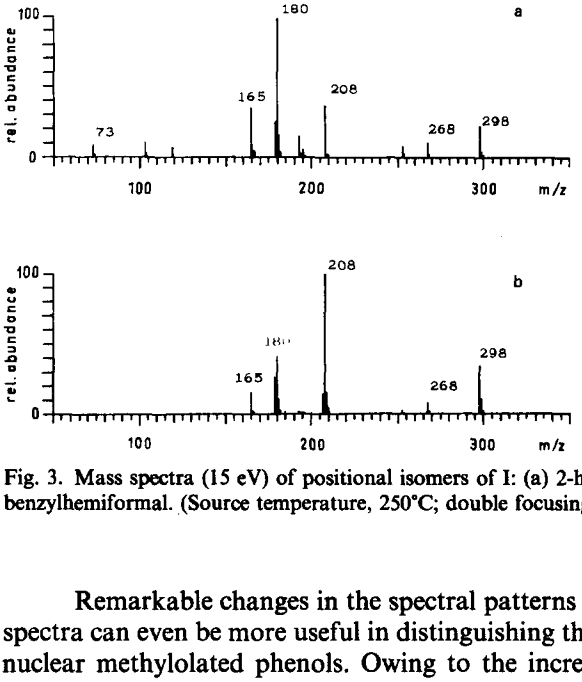
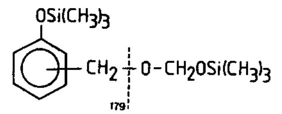


Fig. 3. Mass spectra (15 eV) of positional isomers of I: (a) 2-hydroxybenzylhemiformal; (b) 4-hydroxybenzylhemiformal. (Source temperature, 250°C; double focusing instrument.)

Remarkable changes in the spectral patterns suggest that low-voltage EI mass spectra can even be more useful in distinguishing the isomeric hemiformals of mononuclear methylolated phenols. Owing to the increased molecular ion abundances, these patterns seem to be applicable for judging the relative position of the substituents attached to the aromatic ring. According to the abundance of molecular ion, Ia is assumed to be the *ortho* isomer and Ib to be the *para* isomer. This assumption, however, might be misleading because of the decreased electron energy used for the ionization. Therefore, the principal fragment ions are taken into account in order to elucidate their relationship with the isomerism of the above-mentioned compounds.

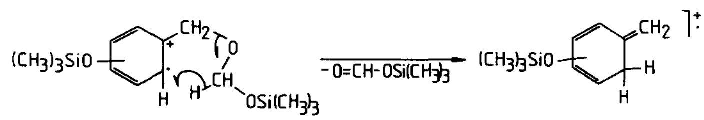
Comparing the mass spectra obtained under different conditions three ions were chosen for thorough examination; m/z = 179 is a principal ion (the base peak for Ib and the second most abundant for Ia) in 70 eV mass spectra, and probably does not involve any important rearrangement prior to fragmentation, whereas m/z = 180 and m/z = 208 are the base peaks of Ia and Ib, respectively, in the low-voltage mass spectra. The latter two ions are products of rearrangements.

Supposing that m/z = 179 is interpreted as

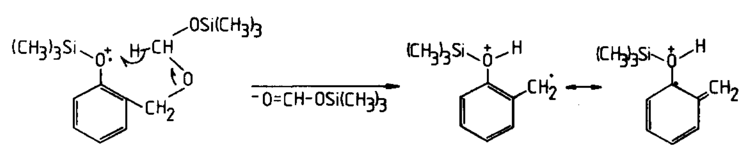


there should be only a slight effect of the relative position of the substituents on the ion abundances. This assumption can be accepted since the percentage total ion intensity of the above-mentioned fragment is approximately equal for the two isomers in the 15 eV mass spectrum (8.2 and 8.7% Σ_i respectively). Therefore, the rate of rearrangement reactions can be correlated with the reaction described previously.

One possible explanation of the origin of m/z = 180 is a radical-site rearrangement followed by the loss of an appropriate molecule (it can best be represented as a neutral trimethylsilyl formate), which can be depicted as follows:

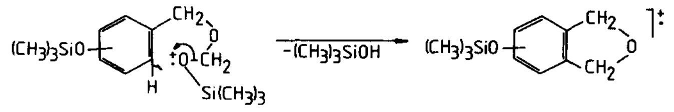


Obviously, it can take place regardless of the position of the other substituent since the rearrangement of the hydrogen atom is initiated by the aromatic ring. However, the abundance of the ion in question might have been expected to be larger in the case of Ib because there are two possible receptive sites for hydrogen atom rearrangement, in contrast with Ia where only one such position is available: surprisingly, the opposite occurs. It should not be forgotten, however, that in the *ortho* isomer the oxygen of the trimethylsiloxy group directly attached to the aromatic nucleus can act as a receptive site for the rearranging hydrogen atom; moreover, the receptive ability of the latter can be even more pronounced[10]. Thus, the fragmentation pathway is as follows:



This reaction makes the main contribution to the intensity of m/z = 180 in case of Ia.

In turn, the elimination of trimethylsilanol from the molecular ion results in the most abundant ion in the 15 eV mass spectrum of Ib (m/z = 208), but it is present in the mass spectrum of Ia as well. This ion is attributed to the fragmentation shown below:



The main driving force of the reaction is the formation of a highly stable cyclic radical cation. Considering the number of hydrogens available for this rearrangement, the ratio of the intensity of m/z = 208 is close to the expected value, *i.e. ca.* 2.5 times more abundant in Ib than in Ia since in the former case hydrogen can come from two sites on the aromatic ring.

Thus the mass spectral fragmentation patterns discussed above permit the unambiguous assignment of Ia to bis(trimethylsilyl)-2-hydroxybenzylhemiformal and Ib to bis(trimethylsilyl)-4-hydroxybenzylhemiformal.

EI mass spectra at 15 eV were not recorded for all the remaining hemiformal isomers present in resol, but on the basis of the detailed discussion above and assuming an order of retention similar to that for I the following assignments may be made: IIa, tris(trimethylsilyl)-3-methylol-2-hydroxybenzylhemiformal; IIb, tris(trimethylsilyl)-5-methylol-2-hydroxybenzylhemiformal; IIc, tris(trimethylsilyl)-3-methylol-4-hydroxybenzylhemiformal.

CONCLUSION

Mass spectra recorded at lower electron energy (15–20 eV) are highly recommended as a tool for producing readily distinguishable spectra of positional isomers of trimethylsilylated hemiformals of methylolated phenols found in resol. In the present case odd-electron fragment ions are predominant and their relative abundances reflect the structures in question more characteristically owing to certain steric requirements of the rearrangement reactions leading to such ions. It must be remembered, however, that lowering the electron energy results in a decrease in the absolute abundances. On the other hand, the ease of interpretation is a real improvement which could, at least partly, compensate for the decrease in sensitivity as far as the identification of the hemiformal isomers is concerned.

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