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PYROLYTIC AND MASS-SPECTROMETRIC FRAGMENTATION OF ALIPHATIC SIDE-CHAINS IN ALKYLRESORCINOLS

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SUMMARY

The stabilities of saturated aliphatic side-chains and the compositions of the fragmentation products in pyrolytic and mass spectrometric reactions have been studied with respect to the chain-length and the position of the chains in the resorcinol molecule. In spite of some common features between these reactions (in particular, predominant β-cleavage of the alkyl chain), the behaviour of alkylresorcinols under thermal and electron impacts varies significantly.

INTRODUCTION

It is well known that alkyl chains attached to an aromatic nucleus undergo β-cleavage as the principal mode of fragmentation. According to molecular-orbital calculations, the probability of β-cleavage in a pyrolytic reaction is equal to that in a mass spectrometric reaction[1]. However, the free-radical mechanism of the former and possibilities for rearrangement owing to a high energy level of the latter may considerably affect the analogy between these reactions. For example, the pyrolysis of butylbenzene yields, besides toluene, a considerable amount of styrene and naphthalene as a result of hydrogen abstraction, dehydrogenation and cyclodehydrogenation[2]. Nevertheless, a comparative study of pyrolytic and mass spectrometric fragmentation data may give valuable information about these processes[3,4].

EXPERIMENTAL

Alkylresorcinols were prepared in our laboratory[5,6] and their purities were tested by means of gas chromatography (GC) and IR and NMR spectroscopy. The pyrolysis was carried out in a 6-mm I.D. quartz tube, using a PYR-1A pyrolyzer attached to a Shimadzu GC-1C gas chromatograph. Helium was used as the carrier gas at a flow-rate of 40 ml/min[7]. The starting material for the pyrolysis and katharometer calibration (about 1 mg) was weighed with accuracy ± 0.03 mg. The products were analyzed by using a column of 110 × 0.4 cm containing 15% of Apiezon M on Chromosorb W. The products were identified as follows: Ph_1CH_3 — $I_c = 1290$, max. in UV region $= 270 - 274, 279$ nm; Ph_2CH_3 — $I_c = 1295$, max. $= 280 - 285$ nm; Ph_3CH_3 — $I_c = 1318$, max. $= 275, 281$ nm; resorcinol — $I_c = 1200$, max. $= 276, 282$ nm; derivative of hydroxybenzofuran — $I_c = 1200$, max. $= 244, 251, 290$

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nm; alkenylresorcinol or 5,7-dihydroxyindene — $I_c = 1517$, max. = 258 – 265 nm; compound containing >C=O group — $I_c = 1517$, max. = 303 nm. Mass spectra were measured by using an MS-2H mass spectrometer operating at 70 eV (ref. 8). The spectra were compared in terms of peak intensities greater than 5% of the base peak. The following are the *m/e* values obtained (intensity of an ion from 2-*n*-hexyl-, 2-*n*-nonyl- and 5-*n*-heptylresorcinol, respectively): 236 (—, 10, —); 208 (—, —, 13); 194 (13, —, —); 137 (—, —, 15); 124 (11, 9, 100); 123 (100, 100, 33); 77 (5, —, —); 43 (—, 6, 6); 41 (6, 6, 8).

RESULTS AND DISCUSSION

The results of our experiments on the pyrolysis of alkylresorcinols in a GC micro-reactor showed that there was almost no difference in the stabilities of methyl groups in isomeric methylresorcinols (Fig. 1). However, with an increase in the aliphatic chain-length (*n* carbon atoms), the stability of the side-chains in the *ortho* and *para* positions relative to hydroxyl groups decreases to a greater extent than that of chains in the *meta* position. The side-chains in the *meta* position therefore exhibit a greater stability than those in the *ortho* or *para* position ($n \geqslant 4$).

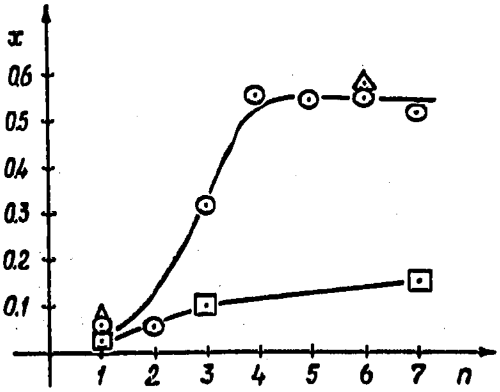


Fig. 1. Degree of conversion (x) *vs.* number of carbon atoms in the side-chain (n). △, 2-*n*-alkyl-, ⊙, 4-*n*-alkyl-, ⊡, 5-*n*-alkylresorcinol (680°).

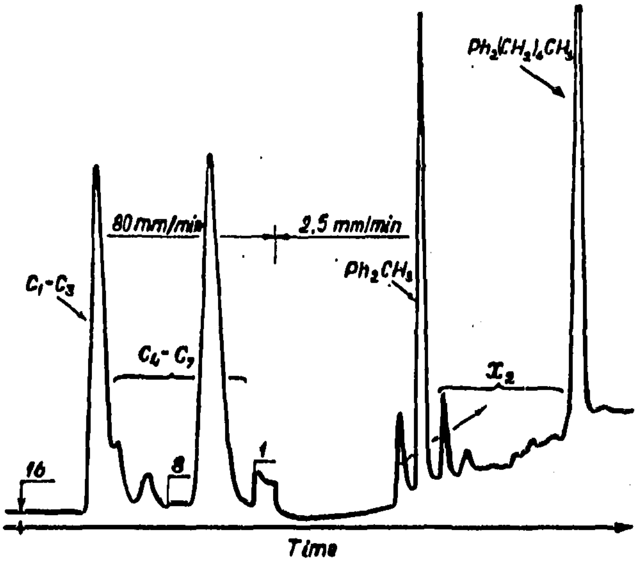
The composition of the pyrolysis products also depends on the position of the side-chains. In the following scheme, the composition of the pyrolytic products is shown, the degree of conversion (x) being 80–90%:

$$\underset{(1),\,(2)}{Ph_{1,2}(CH_2)_6CH_3} \xrightarrow{700^\circ} \underset{55-70}{Ph_{1,2}CH_3} + \underset{20-25}{X_{1,2}} + \underset{55-60}{(C_4-C_7)} + \underset{75-140}{(C_1-C_3)}$$

$$\underset{(3)}{Ph_3(CH_2)_6CH_3} \xrightarrow{800^\circ} \underset{30}{Ph_3CH_3} + \underset{35}{X_3} + \underset{30}{(C_4-C_7)} + \underset{340}{(C_1-C_3)}$$

where $Ph_{1,2}$ is the (1)2,6 or (2)2,4-dihydroxyphenyl radical, Ph_3 is the (3)3,5-dihydroxyphenyl radical, $X_{1,2}$ is resorcinol, a derivative of hydroxybenzofuran, and X_3 is alkenylresorcinol or 5,7-dihydroxyindene, a compound containing a >C=O group. Yields are given in moles per 100 moles of the converted phenol.

Side-chains in the *ortho* or *para* position relative to hydroxyl groups undergo selective cleavage by the rupture of the C–C bond in the β-position relative to the aromatic nucleus. For chains in the *meta* position, a less selective cleavage is observed, due to the additional rupture of more remote C–C bonds, and probably also to the rearrangement of a part of the nucleus with simultaneous destruction of the aromatic system (appearance of >C=O groups). The cleavage of side-chains in the *meta* position also yields more gaseous products than that of side-chains in the *ortho* or *para* positions (Figs. 2 and 3). The occurrence of dehydrogenation and cyclodehydrogenation reactions is confirmed by the appearance of compounds that contain a double-bond conjugated to the aromatic nucleus.



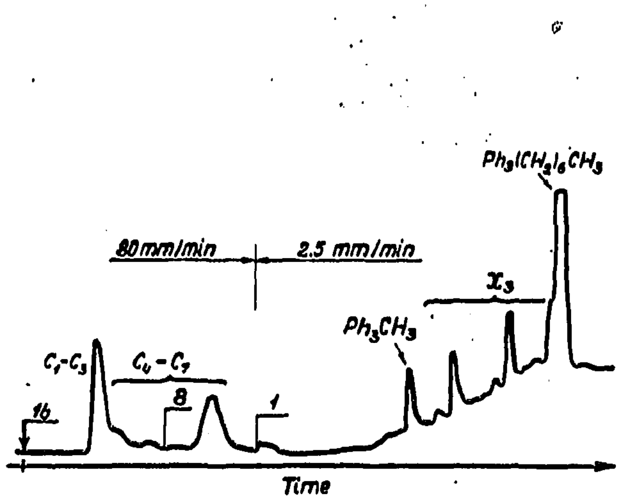


Fig. 2. Pyrogram of 4-*n*-heptylresorcinol (650°).

Fig. 3. Pyrogram of 5-*n*-heptylresorcinol (650°).

The stability of the alkylresorcinol molecule under electron impact is determined by the number of carbon atoms in the side-chain, irrespective of the position of the side-chain relative to the hydroxyl group (Fig. 4). Highly selective β-fission

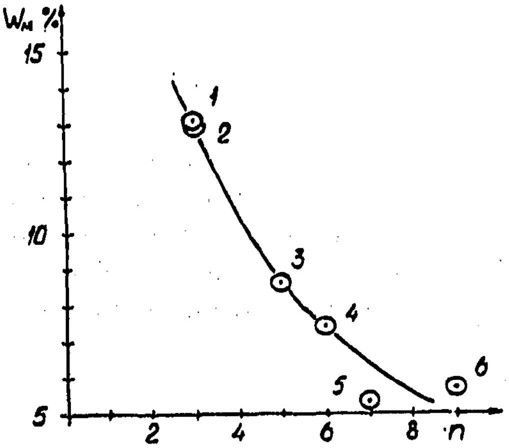


Fig. 4. Stability to electron impact (W_M) *vs.* number of carbon atoms in the side-chain (n). 1 = 2-*n*-propyl-; 2 = 5-*n*-propyl-; 3 = 4-*n*-pentyl-; 4 = 2-*n*-hexyl-; 5 = 5-*n*-heptyl-; and 6 = 4-*n*-nonylresorcinol.

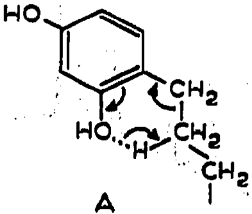
predominates, however, in the case of 5-isomers, owing to the rearrangement of hydrogen atoms.

$$[1]^+, [2]^+ \rightarrow [Ph_{1,2}CH_2]^+$$

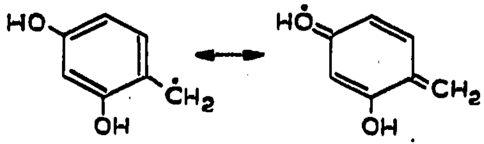
$$[3]^+ \rightarrow [Ph_3CH_3]^+$$

Furthermore, the presence of a peak at the m/e value for γ-fission and a relatively intense peak at $m/e = 41$ ($C_3H_3^+$) are characteristic of the spectra of the 5-isomer.

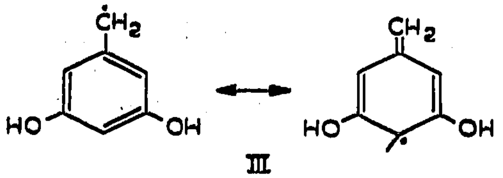
The lower thermal stability and higher selectivity of β-cleavage for 2- and 4-alkylresorcinols compared with that for a 5-isomer or for aromatic hydrocarbons can be explained by (*i*) the stabilization of the transition state of the former by the shift of an electron pair in a six-membered cycle (A); (*ii*) the greater stabilization of radicals I and II compared with that of radical III ($I\text{-}Ph_1\dot{C}H_2$). Apparently for these reasons dehydrogenation and cyclodehydrogenation reactions play the major role in the decomposition of the side-chain in position 5.



A

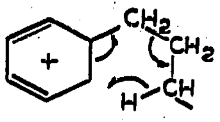


II

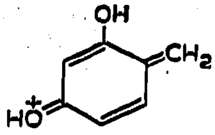


III

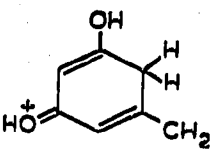
Under electron impact, the rearrangement[9] of the molecular ion-radical B confers additional stabilization on ion-radical IIIa, which is produced as a result of the β-fission of the side-chain. It is possible that for this reason the stability of the side-chain is almost independent of its position relative to the hydroxyl groups.



B



IIa



IIIa

Therefore, for 2- and 4-alkylresorcinols, hydroxyl groups in the *ortho* or *para* position relative to the side-chain influence the pyrolytic and mass spectrometric reactions in the same direction, thus giving such reactions high selectivity. However, for 5-isomers, the lower energy level of the pyrolytic reaction makes it impossible for the hydrogen atom to be transferred in a similar manner to that under electron impact. Therefore, for 5-isomers, thermal and mass spectrometric fragmentation of the side-chain lead to essentially different results.

CONCLUSIONS

In a pyrolytic reaction, the alkyl side-chains ($n \geqslant 4$) of alkylresorcinol molecules in the *ortho* and *para* positions, relative to hydroxyl groups, are less stable and undergo selective β-fission relative to the aromatic nucleus. Side-chains in the *meta* position are more stable and their β-fission is less selective.

Under electron impact, all the alkylresorcinol isomers are subjected to a highly selective β-fission. For 5-isomers, this fission is connected with the rearrangement of hydrogen atoms. The stability of alkyl side-chains is determined solely by the chain-length, regardless of the position of the side-chain on the aromatic nucleus.

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