

The Mesomerism of Propenylbenzene and of Allylbenzene Derivatives.

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Introduction.

In continuation of a previous investigation (1) it deemed of interest to study differences between the intensity of the inductive and of the mesomeric resp. electromeric effect by measuring the ultraviolet absorption curves of several derivatives of benzene with a propenyl resp. allyl sidechain. Absorption data of the following compounds are reported here and will be discussed in detail: allylbenzene, propenylbenzene, phenol, anisol, guaiacol, veratrole, anol, anethol, eugenol, isoeugenol, chavibetol, isochavibetol, safrol, isosafrol, homogenol, isohomogenol, myristicin, isomyristicin.

Discussion.

The extinction curve of allylbenzene (curve 2) is similar to that of benzene (curve 1) but influenced by the inductive effect of the allyl group. The π -electrons of the olefinic linkage are isolated from those of the benzene nucleus by a methylene group, consequently they can not participate in the mesomerism of benzene (cf. Ia). They increase only the extinction values of benzene in the ascending branch blurring thereby near to $220\text{ m}\mu$ the curve. The curve of benzene is highly influenced by the mesomerism of the adjacent double bond of the propenyl chain e. g. in the case of propenylbenzene (curve 3). Resonating forms (IIa—IIb) result in decreasing the energy for excitation, therefore the extinction curve is shifted in comparison to that of allylbenzene (curve 2) towards the visible. On the other hand, participation of polar mesomeric forms (IIa—IIb) even in the ground state causes an increase of excitation. Excitation is therefore connected with a shift of charge.

The curve of phenol (curve 4) shows a benzene spectrum (2) altered mesomerically by the hydroxyl group (IIIa—IIIb). These mesomeric forms are less probable, owing to the electronic affinity of the oxygen atom.

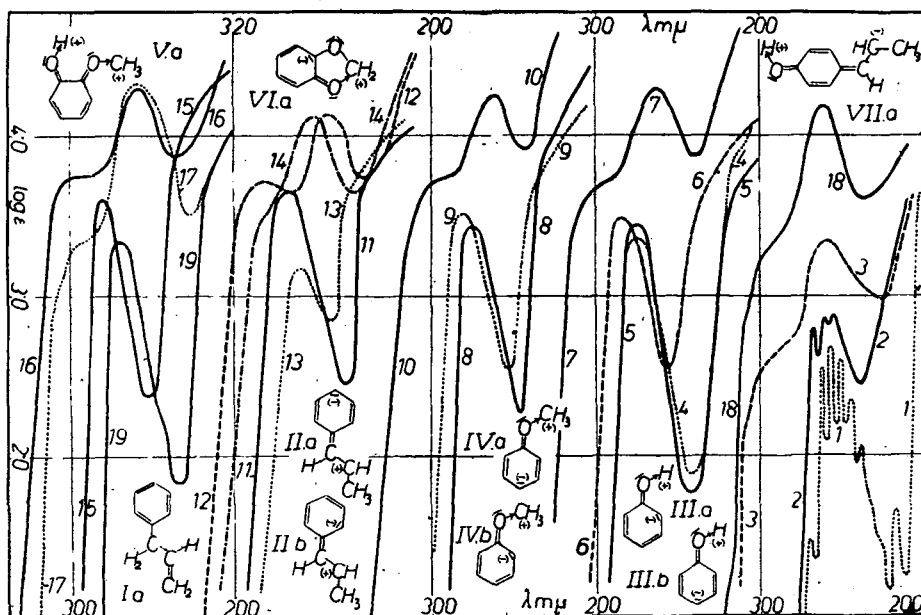
The close resemblance of the curves of phenol (curve 4) and of anisol (curve 19) proves, that etherification of a phenolic hydroxyl group does not affect the probability of mesomerism (IVa—IVb). Similarly, the curve of guaiacol (curve 5) agrees with that of phenol (curve 4), they occur consequently in related mesomeric forms. A mesomeric tendency of both groups, as by Va, seems to be improbable. This consideration is further supported by the resemblance of the curve for guaiacol (curve 5), to that for veratrol (curve 8), indicating that etherification of the second hydroxyl group is without influence upon the mesomeric system of the compound.

The curve of 1,2-methylenedioxybenzene reveals a resemblance (cf. VIa) to that of guaiacol (cf. Va) and veratrol, resp. Differences

can be explained by the strain caused by the five membered heteroring. The mesomerism of this compound was altered by entrance of a methoxy group in *o*-position, as given by 1,2-methylenedioxy-3-methoxybenzene.

These experimental facts lead to the conclusion that the extinction curves of the treated phenol derivatives are inductively or electromerically influenced benzene spectra. Only slight influence is exerted by the substituents, indicated by the percentual increase of the region limited by the extinction curves, in comparison to that of phenol.

Summarised, we can say that the curves of allyl benzene derivatives correspond closely to those of the appropriate phenols resp. phenol ethers: allylbenzene (curve 2) to benzene (curve 1), eugenol (curve 6) and chavibetol (curve 15) to guaiacol (curve 5), homogenol



(curve 9) to veratrol (curve 8), safrol (curve 11) to 1,2-methylenedioxybenzene, myristicin (curve 13) to 1,2-methylenedioxy-3-methoxybenzene. Slight differences are only due to the inductive effect of the allyl chain, estimated by the percentual increase of extinction. The own extinction of the allyl chain could only be observed in the ascending part of the curves.

The absorption spectra of all propenyl derivatives: *p*-anol (curve 17), anethole (curve 18), isoeugenol (curve 7), isohomogenol (curve 10), isosafrol (curve 12), isomyristicin (curve 14), isochavibetol (curve 16) reveal a close resemblance to that of propenylbenzene (curve 3). This fact indicates that π -electrons of the propenyl chain play an important part in the mesomerism of propenylbenzene derivatives (cf. VIIa). Differences between the extinction curves of the single propenylbenzene derivatives can be explained as well by their own mesomerism as by the inductive effect of the

substituents. This effect could be estimated quantitatively on comparing the percentual increase of extinction values with those of propenyl benzene.

Summary.

The ultraviolet absorption curves of a number of allyl and propenyl phenols and their ethers were investigated. The mesomeric effect of the substituents was in all cases apparently larger than their inductive effect.

A uniform explanation of these effects could be given by the critical examination of all possible mesomeric forms in the ground state and in the excited state. The allyl resp. propenyl groups have only a small inductive resp. a strong mesomeric effect upon the extinction curve of benzene. The difference due to this effect is to be found in case of all the investigated derivatives of allyl benzene resp. propenyl benzene.

Experimental.

The measurements of absorption spectra were carried out by Molnár (4). The method and apparatus used was the same as reported previously (5). Purification and control of the compounds was carried out according to the procedures recorded in a recent communication (1).

References.

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