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THE PROTONATION OF CONJUGATED ENOLIC DERIVATIVES. PART II.

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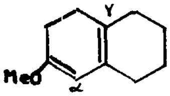
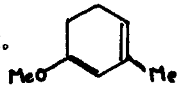
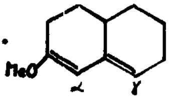
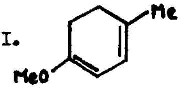
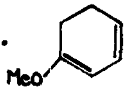
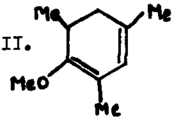
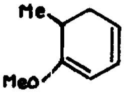
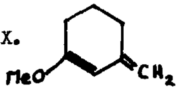
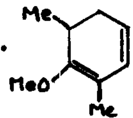
In an earlier communication(1) it was demonstrated that under kinetically controlled conditions, protonation of the homoannular, conjugated dienol ether (I) at the α- and γ-carbon atoms were competitive processes. In the same paper it was shown that protonation of the isomeric ether (II) proceeded solely at the γ-carbon atom. This investigation has now been extended to include the dienol ethers (III) to (IX). The results are summarised in Table 1.

The most striking feature of these results is the apparently great sensitivity of the preferred site of protonation to alkyl substitution in the case of the homoannular dienol ethers studied. On the other hand, neither of the transoid dienol ethers studied (II and IX) showed any sign of α-protonation under the reaction conditions chosen. The study of a wider range of substitution types seems desirable here, and this work is in hand. However, the apparently greater preference for γ-protonation in this series would seem to suggest a considerable degree of bonding in the transition state for protonation, the conjugation of the product being important in governing the energy of that transition state. Conversely, a lesser degree of bonding in the transition state for protonation of the homoannular dienol ethers is suggested. On this basis, the relative reactivities of the α- and γ-carbon atoms might be expected to show dependence upon the relative charge densities at those positions.

Table 1.

Compound	Percentage α-protonation	Compound	Percentage α-protonation
I. 	45	VI. 	10
II. 	0	VII. 	100
III. 	65	VIII. 	88
IV. 	65	IX. 	0
V. 	5		

A study of the equilibria 1). and 2). suggested that in each case the transoid isomer is the more stable by about 1 k.cal./mole.

I $\rightleftharpoons$ II .... 1).

VI $\rightleftharpoons$ IX .... 2).

This finding is in general agreement with the results obtained by Bates$^{(2)}$ in the unsubstituted hexalin field.

Application of Hammond's postulate(3) to the γ-protonation of these pairs of dienol ethers would support the idea of less bonding in the transition state for the more exothermic (or less endothermic) hydrolysis of the cisoid isomer in each case. This argument, as applied to the isomers (I) and (II), is summarised in Fig. 1.

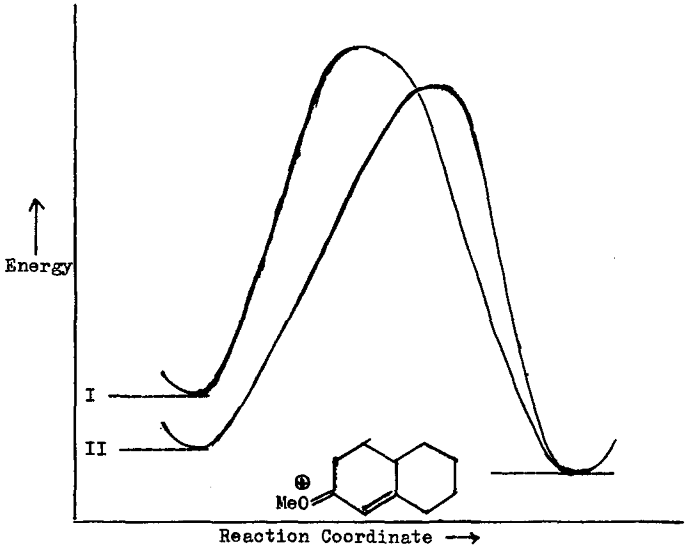


Fig. 1.

HMO calculations* have been made for the system (X) and for all the possible methylated and polymethylated isomers. A simple inductive model, a heteroatom model and a hyperconjugative model for the methyl group(cf.4) have all been used, and while the computed values of the charge densities

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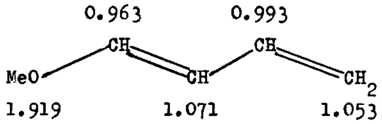
* We are grateful to Dr. M.Poole of the University of Newcastle-upon-Tyne Computing Laboratory, for a copy of his HMO Autocode Programme. The calculations were performed on the Birmingham University KDF 9 computer.

(q) vary with the model chosen, the relative values have been found to remain almost constant. The computed values of q for the basic system (X), using the parameters $\alpha_0 = \alpha + 2\beta$, $\alpha_{C-O} = \alpha + 0.1\beta$, $\alpha_{C-Me} = \alpha - 0.5\beta$ and $\beta_{C-O} = 0.8\beta$, are shown below.



X.

The dependence of the preferred site of protonation upon the relative charge densities in the case of the homoannular dienol ethers is shown by the plot of the logarithm of the relative rate constants (k_α/k_γ) against the charge density difference ($q_\alpha - q_\gamma$) illustrated in Fig. 2.

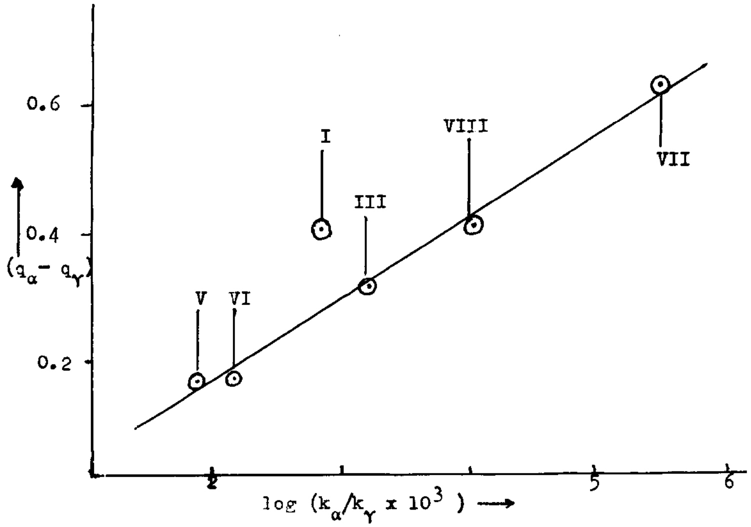


Fig. 2.

This plot shows a very satisfactory straight line relationship, only the dihydromethoxytetralin (I), in which the alkyl substituents are not methyl groups, falling badly off this line.

Entropy of activation and deuterium isotope effect data support the idea implicit in Fig. 1. These data will be discussed in detail in a full communication.

Work currently in hand is designed to explore the relationship between charge density and reactivity in a range of conjugated enolic derivatives including the enolate ions, enamines and enol ether radical anions.

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