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THE PROTONATION OF CONJUGATED ENOLIC DERIVATIVES : PART III

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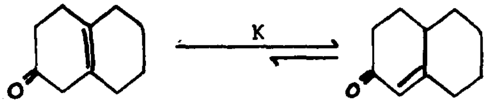
In previous communications[1] we have described the pattern of kinetically controlled protonation in a series of alkyl-substituted, conjugated dienolic ethers. In the cisoid series, a rough linear relationship between $\log k\alpha/k\gamma$ and $(q_\alpha - q_\gamma)$, the calculated charge density difference between the α- and γ-carbon atoms was established.

i.e. $\Delta \log k = A.\Delta q + B$ ....(1)

This relationship, which implies a low degree of bonding in the transition state for these protonations, the relative activation energies being largely determined by the Coulombic interaction between the protonating agent and the site of reaction, has been shown to have some predictive value.

However, a model for the transition state which ignores any bonding is clearly unsatisfactory. In an attempt to gauge the importance of product stability in these hydrolyses, we have measured the equilibrium constants for a series of cyclohexenones;[2] e.g. for the products of hydrolysis of the dienol ether (I)



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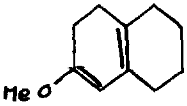
The results of hydrolysis of the cisoid dienol ether may be very well accommodated by a linear free energy relationship of the type

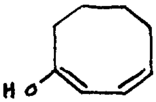
$$\Delta \log k = A.\Delta q + B \log K + C \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where A, B and C are constants. Contributions to the activation energy, both from Coulombic interaction of the type described, and from the delocalisation energy of the product are included in this expression.[3]

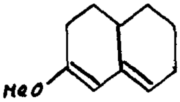
In addition, the reactivity of the transoid series of dienol ethers, together with much scattered data on the mode of protonation of conjugated dienolate ions[4,5] and dienamines[6] can be qualitatively rationalised on this basis.



(I)



(II)



(III)

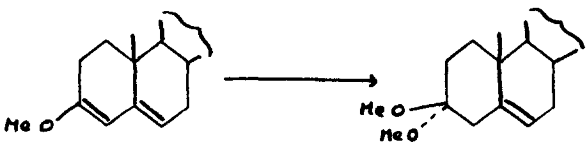
(IV)

From this standpoint, the expected result of kinetically controlled protonation of a conjugated enolic derivative would be a mixture of conjugated and unconjugated ketones, the latter being present in excess of the proportion expected for equilibrium controlled protonation by a factor proportional to the ratio A/B. This factor has already been shown to be very substantial in the case of the cisoid dienol ethers.[1] The recent observation[7] that kinetically controlled protonation of the dienol (II) leads almost exclusively to the unconjugated ketone, while the expected products of equilibrium controlled protonation would contain only 60% of that ketone, is readily understood in these terms. [Between 0.1 and 0.5% of the conjugated product is predicted by application of equation (1). This prediction is being investigated].

It was anticipated that the electronically excited state of a conjugated enolic derivative would be more polarisable than the ground state, and that protonation, if it could be achieved, would be more dependent upon charge density distribution than in the ground state reaction. To test this expectation, the dienol ether (I) was subjected to irradiation from a medium pressure U.V. source*, in an aqueous medium containing concentrations of acetic acid too low to bring about rapid hydrolysis in the dark. Under these conditions, hydrolysis occurred at a rate which was independent of the concentration of acid, over a range giving a ten-fold rate increase for the corresponding dark reaction.

The implication appears to be that the excited state is sufficiently basic to be readily protonated by water. Further, analysis of the products of this light-induced hydrolysis indicated that protonation had occurred to the extent of >98% on the α-carbon atom, as compared with 45% in the corresponding dark reaction. Similar light-induced hydrolysis of the transoid dienol ether (III) yielded about 30% of the product of α-protonation, while the dark reaction led to an undetectably small amount of this product[cf.1]. Finally, 1-methoxybutadiene (IV) under the same conditions, reacted exclusively at the γ-carbon atom, as it did in the dark reaction. All these results are qualitatively in accord with the charge density changes on excitation, calculated using the simple HMO approximation.

Our results can be directly compared with those of Havinga[8] for the light-induced protonation of anisole, in which case a close dependence upon charge density distribution in the excited state was observed. It also seems likely that similar light-induced protonations of conjugated enolic derivatives have been observed previously. Thus the reaction[9]



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* Hanovia, 1 litre reactor, with reaction vessel modified to take a maximum of 250 ml.

seems directly related to our results, methanol in this case functioning as the protonating agent. It seems possible that certain deconjugation reactions of conjugated ketones[10] may also be related. The light-induced hydration of simple olefines has recently been described[11].

We are continuing to explore the light-induced hydrolyses of conjugated enolic derivatives, and the closely related protonation of the anion radicals derived on electron transfer to systems such as (I).[12]

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