Charge Control in the Protonation of Allylic Anions

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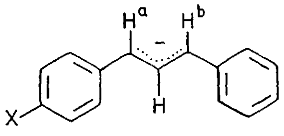
Summary The product ratio obtained when anions of type (III) are protonated has been shown to correlate with the charge distribution as measured by n.m.r. spectroscopy.

Three main theories have been advanced to explain the product ratio obtained when an allylic anion is protonated: (i) the Hughes–Ingold rule[1] (based on product stabilities),

(ii) charge control,[2] and (iii) the theory of least motion.[3] Cram has shown that the Hughes–Ingold rule is unreliable[4] but quantitative support for the other two proposals has been difficult to obtain as they presuppose knowledge of the charge distribution in the anion and of its geometry. In suitable systems, however, n.m.r. spectroscopy can be used as a 'probe' for charge distribution and this has been applied to anions of type (III), generated by treating the corresponding hydrocarbon (I) or (II) with sodamide in liquid ammonia. The n.m.r. spectrum reveals only the all-*trans*-species and, as this is virtually the same when lithamide is used instead of sodamide, it seems that solvent separated ion pairs are formed.[5] In separate experiments solutions of these anions were quenched with ammonium-chloride in liquid ammonia and the product ratio [(I)]/[(II)] determined.† If it is assumed that there is a linear relationship between charge and chemical shift[6] and that the energy barrier to protonation decreases linearly with increasing charge[7] it can readily be shown that log ([(I)]/[(II)]) = A ($\tau_a - \tau_b$), where A is a constant and τ_a and τ_b are the chemical shifts of H^a and H^b respectively. Even at this level of approximation, quite good agreement is obtained between theory and experiment (A = 1·75 p.p.m.$^{-1}$; standard deviation 0·17; correlation coefficient 0·986; 5 × 2 points, X = Cl, F, Me, Bu^t, and MeO). This correlation can be improved if, instead of assuming a linear relationship, the charge is calculated using the Buckingham equation[8] but uncertainties in the relevant parameters render the method open to criticism. No improvement in correlation is afforded by adding a factor relating to product stability.[9]

$p\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH=CHPh}$ (I)

$p\text{-X}\cdot\text{C}_6\text{H}_4\cdot\text{CH=CH}\cdot\text{CH}_2\text{Ph}$ (II)



(III)

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† Quenching experiments were performed in duplicate and were reproducible to within 3%.

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