Non-additivity in the Bromination of Multiply Substituted 1,1-Diarylethylenes

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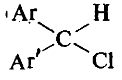
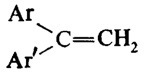
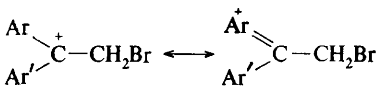
THE lack of additivity of substituent effects in the solvolysis of multiply substituted diphenylmethyl chlorides (I) has recently been demonstrated.[1,2] Two substituents, one each in Ar and Ar′, did not have the same effect as each substituent acting independently and additively. We report a study of the bromination of 1,1-diarylethylenes (II) which clearly demonstrates similar phenomena in an electrophilic addition. The rate constants cover a wide range of reactivity ($k = 1$—10^8 l. mole^{-1} sec.$^{-1}$) under a single set of conditions (25°, MeOH–0·2M-NaBr); the electrometric methods used to study these reactions have previously been described.[3]


(I)


(II)


(IIIa) (IIIb)

In order to recognise non-additive behaviour, an unequivocal ρ value of $-3·57$ ($\log k_0 = 3·314$) for the mono-substituted compounds (II; Ar = XC_6H_4, Ar′ = Ph) was established by use of the six *meta*-substituted compounds (II; X = Br, Cl, F, Me, H, and NO_2). The σ^+ constants proposed by Brown and Okamoto[4] for electrophilic side-chain reactions slightly over-correct for the resonance interaction of the *para*-substituents (X = MeO, Me, Cl, F, and Br) in terms of this ρ (since the reaction studied is not that used to define σ^+), but the data for all the mono-substituted compounds were excellently correlated by the Yukawa–Tsuno equation:[5]

$$\log k/k_0 = -3·57\ (\sigma^0 + 0·836\ \Delta\sigma^+) \qquad (1)$$

with correlation coefficient = 0·995 (s = 0·004); 0·836 is the resonance transmission coefficient r, and $\Delta\sigma^+ = \sigma^+ - \sigma^0$.

If the effects of substituents in multiply substituted compounds do exhibit additivity, then the experimental rate constants, k_{ex}, for these compounds should be equal to k_{calc}, from equation (1), when σ^0 and σ^+ are replaced by $\Sigma\sigma^0$ and $\Sigma\sigma^+$. This clearly is not the case. Thus, for example, for those compounds which have at least one p-methoxy-group (II; Ar = p-MeO·C_6H_4, Ar′ = X–C_6H_4), the deviations from additivity (as measured by $\Delta\log k = \log k_{\text{ex}} - \log k_{\text{calc}}$) are

(X, Δ log *k*) : *p*-NO_2, 1·042; *m*-NO_2, 0·870; *p*-Br, 0·043; H, (—); *p*-Me, −0·418; *p*-MeO, −1·525. It is obvious that rate constants for multiply substituted compounds cannot be estimated from equation (1) without considerable error.

We have attempted to locate the source of the non-additivity in one of the variables σ^0, r, and ρ involved in equation (1). There is considerable evidence, both theoretical[6] and experimental,[7] that simple inductive effects (as measured by σ^0) are additive. Equation (1) would be expected to fail if the two rings Ar and Ar′ were inclined at different angles to the developing carbonium ion (III).[8] Deviation from planarity is inevitable, because of steric interactions between the *ortho*-hydrogens.[9] However, the application of different r-values to the two substituents [even in the extreme case when one ring is coplanar ($r \sim 1$) and the other orthogonal to the double bond ($r \sim 0$)] was not sufficient alone to bring all of the points on to the line correlating the mono-substituted ethylenes.

On the other hand, the assumption that ρ varies throughout the series but is constant for a given group of compounds [$XC_6H_4(Ar')C{=}CH_2$] in which Ar is held constant, gave the following ρ (X): −2·25 (*p*-MeO), −2·85 (*p*-Me), −3·57 (H), −3·59 (*p*-Br), −3·62 (*m*-Me), −4·65 (*p*-NO_2); the correlation coefficients in each case are better than 0·990. These multiple ρ-values are linearly related to the electron disturbance of the constant substituent X, as measured by its σ^+ value (Figure). Much of the positive charge involved in the transition state is resonantly delocalized on to Ar when it contains an electron-donating substituent (IIIb); the second substituent in Ar′ then interacts with a diminished charge, resulting in the lower ρ-constant. When $\sigma^+ \sim -1{\cdot}5$ (Figure) then $\rho \sim 0$, implying that if Ar contained a substituent with a σ^+ value more negative than this, the rate of bromination of the ethylene (II) would be independent of the substituent in Ar, *i.e.* the system would be "saturated."

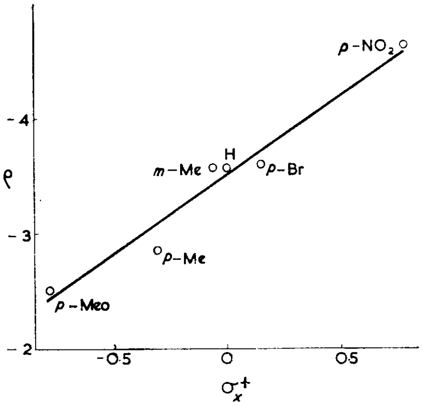


FIGURE. *Plot of* ρ (*each value obtained with substituent* X *constant,* Ar *variable*) *for the bromination of the ethylenes* $XC_6H_4(Ar')C{=}CH_2$, *against* σ^+ *of the substituent* X.

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