

Chemical Communications

Number 5
1982

Transmission of Polar Effects: Quantitative Reversal of Substituent Dipolar Effect

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A study of the pK_a values of 1-(8-substituted naphthyl) propiolic acids has been made and a reversal of the normal substituent effect of the halogeno-substituents has been observed; this result is an almost quantitative reversal of the effects observed in a suitable model, the 3-substituted propiolic acids, thus confirming transmission by an electrostatic field effect.

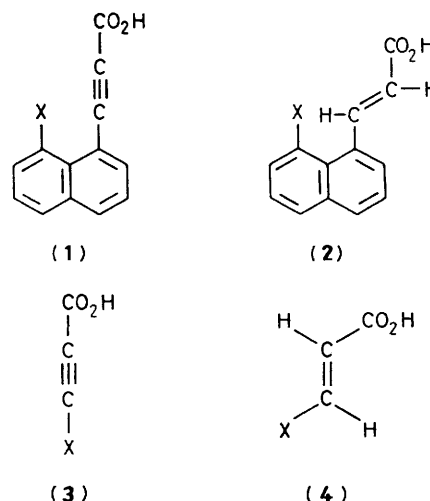
Of the evidence in favour of an electrostatic field effect, rather than an inductive, model for the transmission of substituent polar effects the most compelling appears to be the observation of reversed dipolar substituent effects in several systems.¹ However, in the models so far studied steric inhibition to solvation or intramolecular hydrogen bonding, while unlikely, could be invoked to escape the inverse field effect. We have therefore studied the reactivity of 1-(8-substituted naphthyl)propiolic acids (1) a model first postulated by Roberts and Carboni,² as well as the *trans*-3-(8-substituted 1-naphthyl)acrylic acid system (2).

The model (1) appears to include a minimisation or absence of steric 'bulk' or proximity interactions between the 8-substituent and the reaction site, together with an almost complete reversal of the substituent. The systems can be compared with the 3-substituted propiolic (3) and *trans*-3-substituted acrylic (4) acid systems where 'normal' substituent alignment occurs.

Table 1 shows the pK_a values of the 1-(8-substituted naphthyl)propiolic acids in 2-methoxyethanol-water (4:1). The halogeno-substituents exert a strong acid-weakening effect unlike their normal and expected acid-strengthening effect. The ΔpK_a value of *ca.* -0.4 unit found in aqueous 2-methoxyethanol for system (1) compares with that of *ca.* +0.5 unit in water found for the 3-halogeno-substituent in the propiolic acid system (3).³ A comparison of the two acrylic systems gives *ca.* -0.3 unit in aqueous 2-methoxyethanol for system (2) and *ca.* +0.5 unit in water for system (4).⁴ The results are confirmed by studies of reactivity of the acids with diazodiphenylmethane and the absence of significant steric 'bulk' effects observed in studies of the alkaline hydrolysis of the corresponding methyl esters.

Table 1. pK_a values of 1-(8-substituted naphthyl) propiolic acids in 2-methoxyethanol-water (4:1) at 25 °C.

Substituent	pK_a
H	4.42
Br	4.70
Cl	4.90



The almost quantitative reversal found can only be accounted for by an electrostatic field effect. A direct interaction between the 8-substituent and the unsaturated links in (1) and (2) could be postulated. However, such a possibility does not exist in other models¹ showing reversed dipolar substituent effects.

Received, 11th August 1981; Com. 985

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