277. *The Influence of Nuclear Substituents upon Side-chain Reactions. Part III. The Base-catalysed Prototropy of Substituted Acetophenones.*

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IN the commonly accepted mechanism for the base-catalysed prototropy of carbonyl compounds (Lapworth and Hann, J., 1902, **81**, 1512), the initial step is the removal of the α-proton. It has been suggested, however (Watson, Nathan, and Laurie, *J. Chem. Physics*, 1935, **3**, 170), that the carbonyl carbon atom forms a link with the basic catalyst (compare cyanohydrin formation; Lapworth, J., 1903, **83**, 995; 1904, **85**, 1206), with simultaneous polarisation of the double bond, these processes being followed by the transformations referred to in the preceding paper as (*a*) and (*b*). On this view, the relatively high energy of activation found by Smith (J., 1934, 1744) for basic catalysis would be due to the necessarily *complete* polarisation of the double bond at the instant of reaction with the catalyst. According to either mechanism, base-catalysed prototropy will be facilitated by recession of electrons from the seat of reaction, and is therefore a reaction of " Type B " (Ingold and Rothstein, J., 1927, 1217).

We have measured the velocities of prototropic change at 35° of a number of substituted acetophenones, employing 0·1M-solutions in 75% acetic acid in presence of a constant quantity of sodium acetate, and the general order of velocities ($NO_2 > Hal > H$, *i.e.*, the reverse of that for acid-catalysed prototropy) is in accordance with expectations. The results are recorded below, the figures referring to fall of $N/50$-thiosulphate titre per minute for 20 c.c. of solution.

Substituent.	Velocity.	Substituent.	Velocity.
H	0·0192	*m*-Hal	F, 0·0261; Cl, 0·0198; Br, 0·0198; I, 0·0240
m-NO$_2$	0·0323	*p*-Hal	F, 0·0242; Cl, 0·0206; I, 0·0249
p-NO$_2$	0·0535		

It has been pointed out (preceding paper) that, on the basis of Watson, Nathan, and Laurie's mechanism for acid-catalysed prototropy, the influence of the substituent upon the second stage of the process will be opposed to its effect upon the initial reaction of the ketone with the catalyst; in the base-catalysed change, however, both stages will be influenced in the same sense, a substituent which favours the reaction of ketone with catalyst also facilitating the removal of the α-proton.

The figures in the above table provide a further example of the greater effect of *p*- than of *m*-nitroxyl (compare Dippy, Watson, and Williams, this vol., p. 348). The reverse applies to the *velocity* of acid-catalysed prototropy (preceding paper); since the values of the energy of activation are indistinguishable, however, this may be ascribed to the favourable effect of resonance upon the production of enol in the second stage of the process.

The order of the halogens among themselves is quite irregular, and it is impossible to determine how far this is due to the occurrence of the reaction in stages, both of which are influenced. Attention may perhaps be drawn to the fact that the irregularity is observed for *m*-halogen and not for *p*-halogen only; marked anomalies for halogen in the *m*-position are rare (see following paper), the most definite example being the inversion of the order of strengths in the *m*-halogenophenylboric acids (Bettmann, Branch, and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 1865). In our work on acid-catalysed prototropy (preceding paper) the differences in the energies of activation are scarcely outside the limits of experimental error.

We wish also to record that *p*-methoxyacetophenone undergoes acid-catalysed prototropy at 25° (conditions as in preceding paper) more than twice as rapidly as acetophenone, the speeds being 0·497 and 0·244 respectively. This relatively powerful acceleration by *p*-methoxyl is in accord with anticipation; the compound normally has a configuration intermediate between the unperturbed forms (compare Bennett and Glasstone, *Proc. Roy. Soc.*, 1934, **145**, *A*, 71), but will enter into reaction in the most favourable condition (electromeric effect, operative on demand).

The preparation of the nitro- and halogeno-acetophenones has been described in the preceding paper, and the velocities were determined in the usual manner, 2 g. of crystalline sodium acetate being added to each 100 c.c. of reaction mixture. *p*-Methoxyacetophenone was prepared by the Friedel–Crafts method, m. p. 38° (compare Auwers, *Annalen*, 1915, **408**, 246). The velocities of bromination of the nitro- and halogeno-compounds increased, the former very considerably, towards the end of the reaction, owing to dibromination, and the figures recorded are therefore those for the early portion of the measurements.

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