

**5. *The Benzylation of Amines. Part IV. The Rate of Reaction of Benzyl Bromide with Nitrobenzylaniline and some Derivatives.***

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THE rates of reaction of *m*-nitrobenzyl chloride with primary and with tertiary aromatic amines have been found to be faster than the rates for the *p*-compound (J., 1924, **125**, 1975; 1925, **127**, 2177; *J. Physical Chem.*, 1926, **30**, 673; 1927, **31**, 535; Baker, J., 1933, 1128, has confirmed these results for aniline); moreover, the energies of activation for the *m*- are smaller than those for the *p*-compound. In the nitrobenzyl chlorides the halogen atom is separated from the nucleus by the methylene group, but when this atom is directly attached to the nucleus the order of reactivity of the *m*- and *p*-compounds is inverted (see Nagornoff, A., 1899, **76**, i, 425). Experiments have therefore been carried out to determine whether a similar relationship holds for the nitroanilines and the nitrobenzylanilines.

It has already been shown (J., 1925, **127**, 2179; where the value of  $k_{45^\circ}$  for *p*-nitroaniline should read  $< 0.0002$  instead of  $> 0.0002$ ) that benzyl chloride reacts more rapidly with *m*- than with *p*-nitroaniline in methyl-alcoholic solution, and benzyl bromide has now been found to behave similarly in acetone solution (see table, p. 17). If it be assumed that,

independently of theories of its mode of action and of the nature of X, the nitro-group will act consistently in compounds of the types (I) and (II), then, if the order is inverted in this



case also, benzyl bromide should react more rapidly with *p*- (III, R = H) than with *m*-nitrobenzylaniline (IV, R = H).

The matter can, however, be approached in another way. If the lower reactivity of *p*- than of *m*-nitrobenzyl chloride be ascribed to the greater electron-attractive effect of the nitro-group in the para-position, then (IV, R = H) should be more reactive than (III, R = H), since addition to the basic nitrogen atom would be expected to be helped by greater electron availability. Actually (see table, below) this was found to be the case. (One would expect the former to be a stronger base than the latter, but no data are available.) On the other hand, *p*-chloro-*p'*-nitrobenzylaniline (III, R = *p*-Cl) reacted more rapidly than its *m'*-isomeride (IV, R = *p*-Cl) with benzyl bromide. The effect of the nitrobenzyl group thus depends upon the nature of the base to which it is attached.

The results obtained with *p'*-nitrobenzyl-*p*-toluidine (III, R = *p*-Me) varied too greatly—possibly owing to separation of the solid hydrobromide during the reaction—for a comparison to be made with its *m'*-isomeride, but one unexpected result was definite, *viz.*, that the derivatives of *p*-toluidine reacted much more slowly than the corresponding derivatives of aniline. This seems the only known case in which the introduction of the methyl group in the para-position lowers the reactivity of an aromatic base towards a halogen compound; in all other cases the opposite result has been observed (see, *e.g.*, Menschutkin, *Z. physikal. Chem.*, 1900, **34**, 157; Thomas, *J.*, 1913, **103**, 594; Peacock, *loc. cit.*; van Opstall, *Rec. trav. chim.*, 1933, **52**, 901).

The first and most obvious explanation of this behaviour is that amine reactivity in this case is determined by the ease of removal of the hydrogen atom rather than by electron availability at the nitrogen atom. This possibility was considered earlier (*J. Physical Chem.*, 1927, **31**, 535) and is the reason why tertiary as well as primary and secondary bases have been examined; but if this explanation were true, then the *m*-methyl group should lower the reactivity to a smaller extent than the *p*-, and the introduction of the chlorine atom should raise the reactivity of the compound above that of the unsubstituted compound. It was, however, found that *m'*-nitrobenzyl-*m*-toluidine (IV, R = *m*-Me) reacted more slowly than the *p*-toluidine derivative (IV, R = *p*-Me), and that the nitrobenzylchloroanilines reacted more slowly than the nitrobenzylanilines. Thus the nitrobenzyltoluidines resembled the toluidines. The chlorine atom behaved similarly to the methyl group in that the *p*-compound reacted faster than the *m*-. From these effects, the factor influencing reactivity seems to be electron availability at the nitrogen atom, and not the ease of elimination of a proton.

The results obtained are tabulated below; the solvent used was acetone.

*Reaction of benzyl bromide with nitroanilines.*

Base.	$10^3k_{35^\circ}$ .	$10^3k_{45^\circ}$ .	<i>E</i> , cal.
Meta .....	3.7	7.45	13,570
Para .....	0.36	0.73	13,600

*Reaction of benzyl bromide with nitrobenzylaniline derivatives.*

<i>m</i> -Nitrobenzyl derivative of	Temp.	$10^3k$ .	<i>p</i> -Nitrobenzyl derivative of	Temp.	$10^3k$ .
Aniline .....	35°	9.9	Aniline .....	35°	7.0
" .....	45	17.2	" .....	45	14.0
<i>p</i> -Toluidine .....	"	1.7	<i>p</i> -Toluidine .....	"	1--2
<i>m</i> -Toluidine .....	"	1.17			
<i>p</i> -Chloroaniline .....	"	0.18	<i>p</i> -Chloroaniline .....	"	0.28
<i>m</i> -Chloroaniline .....	"	0.14			

As regards the effect of the chlorine atom, the results are similar to those obtained in other experiments (unpublished) on *m*- and *p*-chloro- and -bromo-aniline; the halogenated anilines react more slowly than does aniline, and the *p*-substituted more rapidly than the *m*-substituted bases. These results are easily explicable on the assumption that the reactivity varies with the degree of electron availability or mobility at the nitrogen atom. The more readily these electrons are displaced to the positions corresponding to the activated state, the more readily the base reacts. The *p*- is more effective than the *m*-halogen atom in producing electron availability at the amino-group, and so the experimental results agree with those expected. *m*- and *p*-Chloro-*m'*-nitrobenzylanilines (IV, R = *m*- or *p*-Cl) behave similarly, and it may be concluded that here also reactivity increases with increased electron mobility at the nitrogen atom.

In these experiments the methylene group seems able to transmit an alternating effect to the nitrogen atom. Oxford and Robinson (J., 1926, 383) found that no alternating effect was transmitted to the benzene nucleus in the nitration of the *m*- and *p*-nitrobenzyl-oxyanisoles. If, therefore, an alternating effect reached the oxygen atom, it was not further transmitted to the benzene nucleus.

#### EXPERIMENTAL.

The velocity determinations were carried out as described in earlier papers. The bases used were all prepared as in the following typical case.

3-Chloro-4'-nitrobenzylaniline.—*p*-Nitrobenzyl chloride (17.2 g.) was mixed with *m*-chloro-aniline (25 g.), sodium carbonate (5.3 g.), and water (50 c.c.), and stirred for 8—10 hours in a boiling water-bath. The product was steam-distilled to remove primary base, washed with dilute hydrochloric acid and then with aqueous sodium hydroxide, and crystallised from ethyl alcohol-ethyl acetate; m. p. 66°. The substance was dimorphous, separating in orange and in pale yellow crystals (Found : N, 11.1.  $C_{13}H_{11}O_2N_2Cl$  requires N, 10.6%).

4-Chloro-3'-nitrobenzylaniline, m. p. 81° (from butyl alcohol). 4-Chloro-4'-nitrobenzylaniline, m. p. 99.5° (from ethyl alcohol) (Found : Cl, 13.1.  $C_{13}H_{11}O_2N_2Cl$  requires Cl, 13.5%). 3-Chloro-3'-nitrobenzylaniline, m. p. 88°, and 3'-nitrobenzyl-*p*-toluidine, m. p. 89° (both from ethyl alcohol and ethyl acetate). 4'-Nitrobenzylaniline, m. p. 70.5° (Strakosch, *Ber.*, 1873, 6, 1062, gives m. p. 68°, Paal and Sprenzer, m. p. 72°). *m*-Nitrobenzylaniline, m. p. 84—85° (Purgotti and Monti, *Gazzetta*, 1900, 30, ii, 256, give m. p. 84.5°). 4'-Nitrobenzyl-*p*-toluidine, m. p. 68—69° (Lellmann and Meyer, *Ber.*, 1892, 25, 3582), and 3'-nitrobenzyl-*m*-toluidine, m. p. 79.5° (Purgotti and Monti, *loc. cit.*, give 67°).

The velocity determinations were carried out in acetone, many of the bases used being sparingly soluble in methyl and ethyl alcohol. Other bases are being examined.

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