

EFFECT OF PARA SUBSTITUENTS IN THE ACYLATION OF AROMATIC AMINES

L. Chas. Raiford and A. F. Whipple, 1916.

Raiford and McBride*found that certain acid-forming substituents in the ortho position to amino group in an aromatic amine accelerated the formation of a diacetyl derivative. The report that follows contains the results of work done to answer the following question:

(a) What effect on the acylation of the amino group will be produced by the presence of an acid-forming substituent in the para position?

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In the study of this question, the four bases mentioned in the subjoined table were acylated in accordance with the method des-

cribed by Sudborough†, and the amount of mono and diacetylated derivative determined in each case.

Base	Mol. wt. of Substituent	Monoacetyl derivative	Diacetyl derivative	Total per cent recov'd
Aniline		38.5	53.0	91.5
p-Chloraniline	(35.46)	45.1	39.2	84.3
p-Nitroaniline	(46)	85.5	13.0	98.5
p-Bromoaniline	(80)	34.6	48.4	83.0

When the amounts of diacetyl derivative obtained from the bases containing acid-forming substituents in the para position are compared with the amount obtained from aniline (which is unsubstituted) it is seen that:

(a) The presence of acid-forming substituents in the para position retards the reaction.

(b) The retardation cannot be due to steric hindrance wholly, because the increase in retardation is not in accord with the increase in the molecular weight of the substituent. Comparison of the bromine and nitro substituted compounds brings out this difference strikingly.

(c) The effect must be due chiefly to the chemical character of the substituent.