

**141.** *The Reaction of Diazonium Salts with Amines.*

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The relative reactivity of a number of monosubstituted anilines was measured, two aromatic amines being allowed to compete for a limited amount of diazonium salt and the relative amounts of diazoamino-compound formed being measured. The results are discussed in the light of electronic theory.

MOST work on the effect of substituents on the reactivity of the benzene ring has been concerned with direct substitution on one of the carbon atoms of the ring, usually by bromine or the nitro-group. The present investigation is designed to show that, under certain conditions, a suitable reagent can be caused to attack a side chain attached to the aromatic system without quantitatively altering the results to be expected for direct substitution from a consideration of various polarization and polarizability effects.

The reaction chosen was that between aromatic amines and diazonium salts, leading mainly to diazoamino-compounds. The method was to allow a mixture of one equiv. of each of two aromatic amines to react with one equiv. of diazonium salt and to determine the proportions of the two possible diazoamino-compounds formed. As one of the amines chosen contained a halogen substituent, the molar ratio ( $R$ ) of the two diazoamino-compounds could be readily determined by analysis.

The ratio of the velocity constants of the two reactions can then be calculated as follows: Let one mole of each of two amines react with one mole of diazonium salt. Then at time  $t$ ,  $y$  moles of one and  $z$  moles of the other amine will have reacted. Hence  $dy/dt = k_1(1-y)(1-x)$  and  $dz/dt = k_2(1-z)(1-x)$ , where  $x$  is the amount of diazonium salt which has reacted. Hence,  $k_2/dy/(1-y) = k_1/dz/(1-z)$  or  $k_1/k_2 = \log_e(1-y)/\log_e(1-z)$ . When reaction is complete all the diazonium salt will have reacted, hence  $y + z = 1$ , and as  $R = y/z = y/(1-y)$ , substitution leads to  $k_1/k_2 = [\log_{10} 1/(R+1)]/[\log_{10} R/(R+1)]$ .

The values thus obtained could not be correlated with known physical constants (such as dipole moments or  $pK$  values), but a reasonable correlation was established with Sutton's  $\mu_{al.} - \mu_{ar.}$  values (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668), which give a measure of the ability of the substituents to attract or repel electrons and are consequently related to the directing power of such groups. With one exception the reaction velocity was high for positive and low for negative value of this constant (see Table 1). Hence, the coupling reaction behaves as if it were essentially a nuclear electrophilic reaction, and such a reaction could not involve

the aminium ion where the nuclear electron density has been decreased to an extremely low level by the positive charge on the nitrogen atom. Wistar and Bartlett (*J. Amer. Chem. Soc.*, 1941, **63**, 413) reached a similar conclusion from other evidence.

## EXPERIMENTAL

The competitive coupling experiments were carried out as follows: 0.01 mole of each of the two amines in methanol (40 ml.) was cooled to 2°, and 0.01 mole of solid phenyldiazonium sulphate (or nitrate), in 20 ml. of ice-cold water, was added. The mixture was stirred for 30 minutes at constant temperature. The yellow precipitate was filtered off, washed with *ca.* 700 ml. of cold water, and dried at room temperature *in vacuo* (P<sub>2</sub>O<sub>5</sub>). With *o*-chloroaniline naphthalene-β-diazonium sulphate was used instead of the benzenediazonium sulphate, as the latter gave a liquid diazoamino-compound. In some experiments 0.02 mole of sodium hydrogen carbonate was added to the reaction mixture, but made no significant difference. The solubility of the products in the mixture was not such as to affect the results except for 2-bromodiazoaminobenzene, which was particularly soluble. Products from experiments involving *m*-iodoaniline tended to resinify when washed. This was avoided by washing the product with 15 ml. of ice-cold ligroin and then with water containing 0.5% of ammonia.

The values given are averages of 5–10 determinations, but reproducibility was sometimes no better than about ±20% in spite of rigid adherence to the standard conditions. The discrepancies are principally due to the instability of the diazonium salt and occasional resinification. As can be seen, however, the differences between the compounds listed are so large that the order of reactivities is undoubtedly significant.

The pure diazoaminobenzenes were prepared as follows: 0.1 mole of the substituted aromatic amine was dissolved in 20 ml. of methanol (or sufficient to hold all the amine in solution after addition of the aqueous diazonium salt solution); 0.1 mole of aniline was diazotized in the usual manner, neutralized with excess of sodium hydrogen carbonate, and slowly added to the stirred amine solution at 4–6°. After 3 hours the precipitate was collected and recrystallized. When *m*-anisidine was thus coupled with diazotized aniline only the aminoazo-compound was formed. The liquid 2-chlorodiazoaminobenzene was characterized by condensation with phenyl isocyanate (see p. 702).

The required fluoroanilines were prepared by the following method: The nitroaniline (0.1 mole) was diazotized and the filtered solution added to morpholine (0.1 mole) in water (200 ml.) containing sodium carbonate (30 g.). A yellow precipitate was rapidly formed, which was filtered off and recrystallized from ethanol (yields quantitative). The phenylazomorpholine was refluxed in a lead vessel for two hours with excess of 48% hydrofluoric acid, neutralized, and extracted with ether. The extract was washed with dilute acid, dried, and distilled *in vacuo*. The fluoronitrobenzenes (yields 30–45%) were reduced to the corresponding anilines.

These *diazoaminobenzenes* which are tabulated were recrystallized from ligroin except where otherwise stated.

Diazoamino- benzene	Form	M. p.	Formula	Found, %			Required, %		
				C	H	N	C	H	N
3-Fluoro-	Yellow needles	90°	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> F	67.0	4.3	20.1	67.0	4.6	19.5
4-Fluoro-	Yellow prisms	83		66.9	5.0	19.4			
3-Cyano-	Yellow needles *	137	C <sub>13</sub> H <sub>10</sub> N <sub>4</sub>	69.7	4.5	25.2	70.3	4.5	25.2
4-Cyano-	"	150		69.9	4.5	25.1			
2-Methoxy-	Small, yellow-brown prisms †	41	C <sub>13</sub> H <sub>13</sub> ON <sub>3</sub>	68.2	5.6	18.2	68.7	5.7	18.5 ‡
4-Methoxy-	Yellow needles	87.5		68.3	5.8	18.3			
2-Bromo-	Yellow-brown needles	67.5	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> Br	51.7	3.4	15.6	52.2	3.6	15.2 §
2-Iodo-	Yellow-brown prisms	108	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> I	44.3	3.1	13.0	44.6	3.1	13.0 ¶
3-Iodo-	Yellow plates	93		44.3	3.2	13.0			
3-Chloro-	Bunched, yellow needles	87	C <sub>12</sub> H <sub>10</sub> N <sub>3</sub> Cl	62.2	4.3	18.1	62.2	4.4	18.1 **
3-Acetyl	Yellow, hexagonal plates	105	C <sub>14</sub> H <sub>13</sub> ON <sub>3</sub>	69.9	5.5	17.4	70.3	5.4	17.6
4-Acetyl	Yellow needles	95	"	70.7	5.4	17.0	"	"	"

\* From ethyl acetate-ligroin.

† Found: OMe, 13.4. Required: OMe, 13.7%.

‡ Found: Br, 29.3. Required: Br, 29.0%.

\*\* Found: I, 39.5%.

§ Found: OMe, 13.2%.

¶ Found: I, 39.4. Required: I, 39.3%.

\*\* Found: Cl, 15.5. Required: Cl, 15.3%.

4-Amino-2-methoxyazobenzene crystallized in orange plates, m. p. 157° (Found: C, 68.2; H, 5.8; N, 18.3.  $C_{13}H_{13}ON_3$  requires C, 68.7; H, 5.7; N, 18.5%). 3-o-Chlorophenyl-1-phenyl triazen-3-carboxyanilide formed white needles (from ether-ligroin), m. p. 111° (decomp.) (Found: C, 65.1; H, 4.3; N, 16.0.  $C_{19}H_{15}ON_4Cl$  requires C, 65.1; H, 4.3; N, 16.0%), and p-nitrophenylazomorpholine yellow, bunched needles from ethanol, m. p. 81–82° (Found: C, 51.5; H, 5.2; N, 23.1.  $C_{10}H_{12}O_3N_4$  requires C, 50.9; H, 5.1; N, 23.7%).

## RESULTS AND DISCUSSION

As noted on p. 701, owing to the instability of the reagents, the following conclusions are necessarily tentative.

The interpretation of the results obtained with halogen-substituted anilines is peculiarly difficult owing to the complex interplay of the *I* and *T* effects (see Table 2).

Table 1 summarizes the results obtained from amines not containing halogen atoms. To facilitate analysis of the products, non-reactive and reactive amines were allowed to compete with *m*- and *p*-bromoaniline, respectively, since these two compounds had been shown to give the most reproducible values. It can be seen that in this series there is a good correlation between the  $\mu_{al.} - \mu_{ar.}$  values and the reactivity of the amine. In some

TABLE 1.

Substituent	$\mu_{al.} - \mu_{ar.}$	Reactivity		Electronic displacements	Remarks
		<i>p</i>	<i>m</i>		
CH <sub>3</sub>	+0.45	28.4 ± 3.5	—	+ <i>I</i>	Hyperconjugation is probably responsible for the high values obtained for this compound: <i>m</i> -toluidine gives much aminoazo-compound
OCH <sub>3</sub>	ca. +0.05	2.8 ± 0.18	—	− <i>I</i> , + <i>T</i>	<i>T</i> > <i>I</i> , $\mu_{al.} - \mu_{ar.}$ by extrapolation from Sugden's values; <i>m</i> -anisidine gives aminoazo-compound
H	±0.00	1.0	1.0	—	Reference standard
CO·CH <sub>3</sub>	−0.18	0.04 ± 0.006	0.033 ± 0.002	− <i>I</i> , − <i>T</i>	
CN	−0.43	0.0013 ± 0.0002	0.0026 ± 0.0005	− <i>I</i> , − <i>T</i>	
NO <sub>2</sub>	−0.88	0.00	0.00	− <i>I</i> , − <i>T</i>	Does not react
C <sub>6</sub> H <sub>5</sub>	—	>100	—	± <i>T</i>	Highly polarisable

cases, notably with *m*-anisidine and *m*-toluidine (Mehner, *J. pr. Chem.*, 1902, **65**, 401), the formation of large amounts of aminoazo-compound made the results valueless for purposes of comparison.

A similar relation can be observed in the reactivities of the monohalogenoanilines, the results for which are summarised in Table 2. The electronic displacements are in all

TABLE 2.

Substituent	Reactivity:			$\mu_{al.} - \mu_{ar.}$
	<i>o</i>	<i>m</i>	<i>p</i>	
H	1.00	1.00	1.00	—
F	—	0.054 ± 0.003	0.018 ± 0.002	—
Cl	0.13 * ± 0.015	0.37 ± 0.07	0.68 ± 0.08	0.59
Br	0.18 † ± 0.04	0.027 ± 0.0005	3.37 ± 0.04	0.69
I	0.45 ± 0.1	1.1 ± 0.2	17.7 ± 2.5	0.86

\* Naphthalene- $\beta$ -diazonium sulphate used.

† Corrected for solubility.

cases +*T*, −*I*, where *I* > *T*. The values are seen to tend in the same direction as the  $\mu_{al.} - \mu_{ar.}$  values. The aberrant value found for *m*-bromoaniline cannot be explained, for it is highly reproducible (±2% in eight determinations) and cannot be due to experimental error.

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