10. Mechanisms of Diazo Coupling Reactions. Part XXXII. The Diazoamino Rearrangement in 20% Acetonitrile/Aqueous Buffers[1])

by **Richard P. Kelly, John R. Penton** and **Heinrich Zollinger**

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule (ETH), CH-8092 Zürich

(6.XI.81)

Summary

The rearrangements of 4′-methoxy-*N*-methyl- and *N*-methyl-4′-nitro-diazoaminobenzene have been studied in 20% acetonitrile/aqueous buffers. The reactions are specifically acid catalyzed and involve pre-equilibrium formation of amine and diazonium salt followed by rate-limiting attack of the diazonium ion at a C-atom (C-coupling) to give the corresponding aminoazo compounds. There is no evidence to suggest that, under the present conditions, mechanisms other than the established *Friswell-Green* mechanism occur. The traditional two-stage synthesis of aminoazo compounds *via* isolated diazoamino compounds can therefore be replaced by a one stage process for amines which undergo initial attack at a N-atom by diazonium ion (N-coupling).

Introduction. – Previous papers in this series have dealt with the N-coupling of aromatic amines in acetonitrile [1] [2]. For certain amines, *e.g.* *m*-toluidine and *N*,*N*-dimethylaniline which react with diazonium ions to form principally ($\geq 90\%$) aminoazo compound, initial attack of the diazonium ion is at amine N-atom and hence aminoazo formation occurs *via* some form of rearrangement and does not take place by direct attack at the C-atom. The nature of this rearrangement is not completely clear, although it is thought that two mechanisms can prevail [2]. However, the rearrangement clearly does not involve the end product of N-coupling, the diazoaminobenzene, since, under these conditions, the acid catalyzed decomposition of these compounds is slow relative to aminoazo formation from the diazonium salt and amine, and the reaction involves rate-determining protonation of the diazoaminobenzene [1] [2]. This is, to our knowledge, the first time that such a mechanism has been postulated for the rearrangement of diazoamino compounds. The mechanism of the rearrangement clearly depends on the nature of the substrate and the conditions.

[1]) Part XXXI: [1].

0018-019X/82/1/0122-11$01.00/0

The early work on diazoamino rearrangements has been well summarized [3] [4]. Briefly, all the previous evidence supported an intermolecular process, namely fast protonation of the diazoaminobenzene, fission to amine and diazonium salt followed by recombination to give the aminoazo compound – the so-called *Friswell-Green* mechanism. Under certain conditions, principally when the corresponding amine is used as solvent, another mechanism can occur. Thus *Goldschmidt* found that decomposition of the protonated diazoamino compound to amine and diazonium ion can be catalyzed by the anion of the acid when the latter is weak, *e.g.* nitrobenzoic acids [5]. With mineral acids, the anion is a weak nucleophile and no evidence was found for such a pathway, but it was postulated that here the amine itself can catalyze fission of the protonated diazoamino compound [3]. Neither of these processes has been observed in aqueous or partially aqueous solution and, in view of our previous work, we thought it of interest to investigate if either or both of these processes occur. In addition, the possibility of an intramolecular rearrangement of the protonated diazoamino compound has, to date, not been explored.

The nature of the mechanism has implications for the synthesis of aminoazo compounds. Thus, if under aqueous or partly aqueous conditions only the *Friswell-Green* mechanism holds, it should be possible [3] to prepare aminoazo compounds in a one step synthesis even from amines which undergo predominantly N-coupling. Authors of preparative organic chemistry text books quote only a two-stage synthesis of aminoazo compounds, see *e.g.* [6] in spite of the fact that all mechanistic work indicates that a one-stage process is possible. One-stage syntheses are described in patents, *e.g.* [7], but we are aware that there are industrial productions of aminoazo compounds which still follow the classical two-stage method. We report therefore also on our investigation of yields of aminoazo compounds obtained in one-stage syntheses.

Results. – 4′-Methoxy-*N*-methyl- and *N*-methyl-4′-nitrodiazoaminobenzene were chosen for this study. The use of N-monomethylated compounds avoids possible complications arising from tautomerism. In aqueous solution the solubility of the substrates is very low, so 20% v/v acetonitrile/aqueous buffer was used as solvent. Reactions were studied spectrophotometrically by following the increase in con-

Table I. *Decomposition of 4-methoxy-*N*-methyldiazoaminobenzene in acetate/acetic acid buffers at ionic strength 0.1 and 8.0°*[a])

pH	$k_{obs}(s^{-1})$	[NaOAc] (mol l^{-1})	[HOAc] (mol l^{-1})
4.54	3.01×10^{-2}	0.10	0.20
4.61	2.30×10^{-2}	0.10	0.17
4.90	1.30×10^{-2}	0.10	0.10
4.85	1.54×10^{-2}	0.10	0.10
4.90	1.40×10^{-2}	0.10	0.10
4.91	1.50×10^{-2}	0.10	0.10
5.17	7.50×10^{-3}	0.10	0.05
5.16	8.60×10^{-3}	0.04	0.02
5.16	8.80×10^{-3}	0.02	0.01
5.59	2.80×10^{-3}	0.10	0.02
5.86	1.39×10^{-3}	0.10	0.01

[a]) In all experiments reported in this publication, the buffer contained 20% v/v acetonitrile. All pH values are thus relative.

centration of aminoazo compounds when excess amine was present. In the absence of added amine the decrease in concentration of the diazoaminobenzene or the appearance of the diazonium ion was followed. Preliminary experiments with 4'-methoxy-N-methyldiazoaminobenzene demonstrated that the rate of formation of azo dye showed an induction period due to the establishment of a pre-equilibrium, which was rapid compared with the rate of dye formation. In the absence of added amine, aminoazo formation is slow, and the acid-catalyzed fission step to form diazonium ion and amine could be studied without interference from other steps. The data for measurements carried out at 8.0° in 20% *v/v* acetonitrile/acetate/acetic acid buffer are shown in *Table 1.*

Measurements at constant pH with varying buffer concentrations (at constant ionic strength) showed that, within experimental error, the reaction does not show buffer catalysis. As a further check a series of runs with varying buffer ratios were carried out. A plot of log k_{obs} against pH was linear with a slope of -1 *(Fig. 1).* Both sets of data show clearly that the reaction is specific and not general acid catalyzed. Fission of the diazoaminobenzene takes place *via* a pre-equilibrium protonation followed by a rate-limiting decomposition of the protonated compound.

Experiments were then carried out in the presence of added *N*-methylaniline. Kinetic runs were conducted at pH 5.0 and 5.7 at ionic strength 0.1 *(Table 2).* At low (0.0062 M) concentrations of amine the rate is virtually independent of acid concentration, whereas with increasing amine concentration a dependence becomes

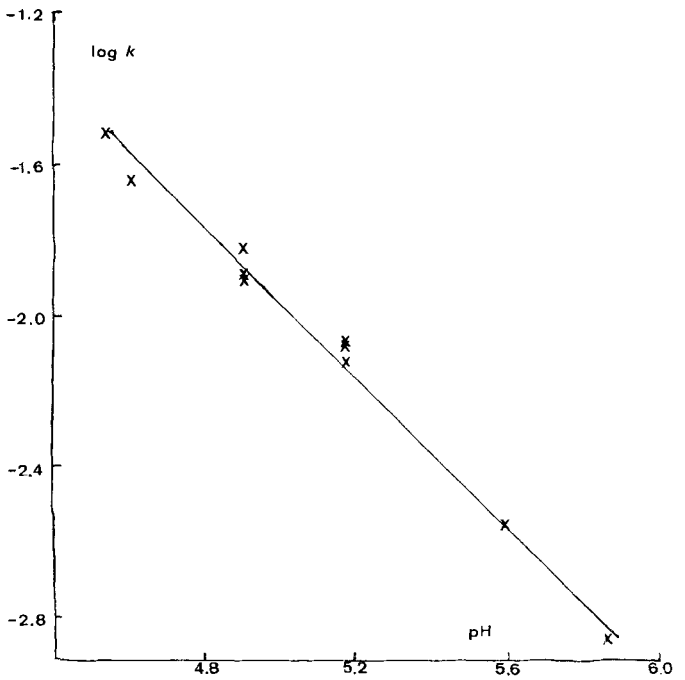


Figure 1. *Plot of log*k *against pH for data in* Table 1

apparent. Further, particularly at pH 5.7, the rate appears to be independent of amine concentration at high concentration of amine.

The effect of added nucleophiles on the rate of reaction was checked. Using 0.05 M NaOAc + 0.01 M HOAc and 0.0308 M amine concentration at 31.2°, the addition of 0.05 M Br^-, I^-, $PhCO_2^-$ had no effect; 0.05 M NaSCN produced a small increase in rate, but well within experimental error. This was checked at higher (0.8 M) concentrations of additive, but even here only a 6.6% increase in rate was found, again within the experimental error when compared with runs carried out in the presence of 0.8 M $NaClO_4$ as standard.

The reaction shows a small kinetic isotope effect *(Table 3)*. Thus with *N*-methyl-[2,4,6-$^2H_3$]aniline in two buffer solutions, k_H/k_D is 1.28 in the more concentrated buffer and 1.48 in the more dilute. No general base catalysis for runs carried out in the presence of undeuterated amine is observed.

Similar experiments were carried out with *N*-methyl-4′-nitrodiazoaminobenzene. The data for a series of runs at pH 1.22 and 1.74 are shown in *Table 4*.

As before, the pH dependence of the rate increases with increasing amine concentration, and at high amine concentration this is approximately first-order. Again, the rate becomes independent of amine concentration at high amine concentrations. This was investigated in more detail. A series of runs at higher ionic strength (1.0) and in $HClO_4/NaClO_4$-solution produced a rather odd plot of k_{obs} versus total amine concentration *(Fig. 2)*.

The plot shows a pronounced maximum at an amine concentration of *ca.* 0.1 M. To check if the decrease observed after this maximum is due to a differential salt

Table 2. *Rate of formation of 4′-methoxy-1-*N*-methylaminoazobenzene from 4′-methoxy-*N*-methyldiazoaminobenzene in the presence of* N*-methylaniline in acetate/acetic acid buffers at ionic strength 0.1 and 31.2°*

[*N*-Methylaniline] (mol l^{-1})	$10^5 k_{obs}$ (s^{-1})	pH	[*N*-Methylaniline] (mol l^{-1})	$10^5 k_{obs}$ (s^{-1})	pH
0.0062	16.3	4.99	0.0015	5.4	5.69
0.0154	37.3	5.01	0.0031	9.4	5.69
0.0318	61.9	5.05	0.0062	15.1	5.69
0.0616	89.4	5.10	0.0154	23.7	5.72
			0.0308	28.9	5.74
			0.0616	29.4	5.80

Table 3. *Kinetic isotope effect in the formation of 4′-methoxy-1-*N*-methylaminoazobenzene from 4′-methoxy-*N*-methyldiazoaminobenzene in the presence of* N*-methylaniline or* N*-methyl[2,4,6-$^2H_3$]-aniline at ionic strength 0.1 and 31.2°*

pH	([NaOAc]+[HOAc]) (mol l^{-1})	$10^4 k_H$[a]) (s^{-1})	$10^4 k_D$[a]) (s^{-1})	k_H/k_D
5.02	0.10 + 0.10	3.54 ± 0.15	2.77 ± 0.12	1.28 ± 0.06
5.09	0.04 + 0.04	3.59 ± 0.15	2.42 ± 0.12	1.48 ± 0.06

[a]) Mean of 3 determinations.

Table 4. *Rate of formation of 1-*N*-methylamino-4'-nitroazobenzene from* N*-methyl-4'-nitrodiazoaminobenzene in the presence of* N*-methylaniline at ionic strength 0.1 and 31.2° in* p*-toluenesulfonic acid/sodium* p*-toluenesulfonate buffers*

pH	[*N*-methylaniline] (mol l^{-1})	$10^3 k_{obs}$ (s^{-1})	pH	[*N*-Methylaniline] (mol l^{-1})	$10^3 k_{obs}$ (s^{-1})
1.22	0.100	5.17	1.73	0.100	1.73
1.22	0.050	4.14	1.73	0.050	1.85
1.23	0.020	2.36	1.74	0.025	1.90
1.22	0.010	1.36	1.74	0.005	1.31
1.21	0.005	0.72			

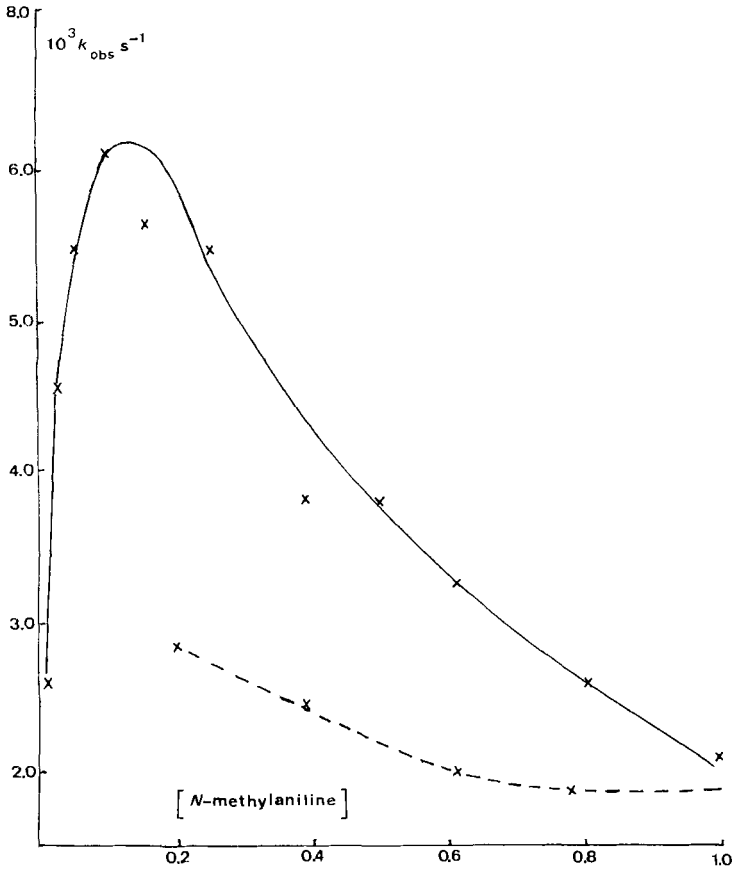


Figure 2. *Dependence of the rate of formation of 1-*N*-methylamino-4'-nitroazobenzene on* N*-methylaniline concentration at pH 1.3, ionic strength 1.0, and 31.2°* (solid line). Corrected for salt effect (dashed line, see text).

effect, *i.e.* replacement of sodium perchlorate by *N*-methylanilinium perchlorate, the effect of the two salts on the rate of reaction was studied *(Table 5)*. Clearly, varying the concentration of *N*-methylanilinium perchlorate has little effect on the rate, whereas 0.8 M sodium perchlorate results in a rate increase of approximately a factor of two.

Finally, we report our results concerning small scale preparations of 1-*N*-methylamino-4′-nitroazobenzene by rearrangement of *N*-methyl-4′-nitrodiazoaminobenzene, and by reaction of *p*-nitrobenzenediazonium tetrafluoroborate with *N*-methylaniline (see *Table 6* and *Exper. Part*).

Runs 1 and 2 serve as a check on reproducibility; the agreement is good. The effect of temperature on the yield is shown by runs 1 and 5. Reduction of the temperature (run 5) raises the yield as does reduction of the acidity (run 3) or increasing the amine concentration (run 4).

Table 5. *Effect of sodium perchlorate and* N-*methylanilinium perchlorate (NMAP) on the rate of formation of 1-*N-*methylamino-4′-nitro-azobenzene from* N-*methyl-4′-nitrodiazoaminobenzene in perchloric acid/sodium perchlorate solution at 31.2°*

$[NaClO_4]$[a]) (mol l^{-1})	I	$10^3\ k_{obs}$ (s^{-1})	[NMAP][b]) (mol l^{-1})	I	$10^3\ k_{obs}$ (s^{-1})
–	0.2	2.17	0.2	0.2	1.84
0.2	0.4	2.94	0.4	0.4	1.96
0.4	0.6	3.59	0.6	0.6	2.36
0.6	0.8	3.37	0.8	0.8	2.27
0.8	1.0	4.42	1.0	1.0	2.48

[a]) [NMAP] was constant at 0.2 M; pH = 1.31.
[b]) No $NaClO_4$ was present; pH = 1.31.

Table 6. *Small scale preparations of 1-*N-*methylamino-4′-nitroazobenzene*

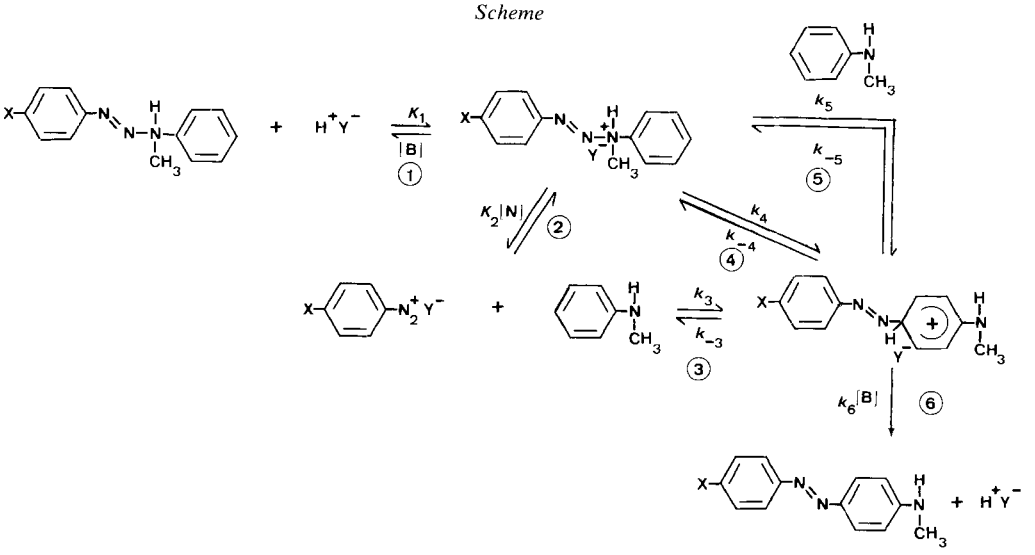
Run	Time	Method[a])	Temperature	Ratio of diazoaminobenzene or diazonium salt to amine	HCl M	% Yield
1	1 h	A	Reflux	1:0.48	1	73
2	1 h	A	Reflux	1:0.48	1	72
3	1 h	A	Reflux	1:0.48	0.33	79
4	1 h	A	Reflux	1:0.48	1	86
5	5 h	A	RT.	1:0.48	1	100
6	1 h	B	Reflux	1:1.48	1	79
7	2 min	B	Reflux/ quenched	1:1.48	1	mainly diazoaminobenzene
8	12 h	B	RT.	1:1.48	1	96
9	2.5 h	B	RT.	1:1.48	1	90
10	3 h	B[b])	Reflux	1:1.48	1	66

[a]) A: rearrangement of *N*-methyl-4′-nitrodiazoaminobenzene; B: addition of *p*-nitrobenzenediazonium tetrafluoroborate to *N*-methylaniline.
[b]) Addition carried out over a period of 2 h.

Addition of the diazonium salt over a period of 2 min to a solution of the amine in hydrochloric acid at reflux gives a yield of 79% (run 6), 6% higher than that achieved from the rearrangement. Comparison with run 7 shows that rapid formation of diazoaminobenzene occurs followed by slow rearrangement. The yield is increased by a longer reaction time (runs 8 and 9), but again a low yield is obtained when addition of the diazonium salt is carried out over a period of 2 h (run 10).

Discussion. – It is convenient to consider first the mechanisms most likely to occur in the diazoamino rearrangement. These are shown in the *Scheme*.

Scheme



We have shown that the initial reaction diazoaminobenzene + $H^+ \rightleftharpoons$ diazonium ion + amine is quickly established and can be treated as pre-equilibrium. For simplifying, we shall ignore the possibility that aminoazo formation may exhibit rate-limiting proton loss from the σ_c-complex (step 6); this does not affect our conclusions. Pathway ①-②-③-⑥ is the classical *Friswell-Green* mechanism. In certain instances this pathway may also involve nucleophilic catalysis of the fission of the protonated diazoaminobenzene (step 2). Pathway ①-④-⑥ consists of an intramolecular rearrangement of this species to the σ_c-complex. This has never been found in the diazoamino rearrangement, but almost certainly exists in the *Fischer-Hepp* rearrangement of *N*-nitrosamines [8]. Finally, pathway ①-⑤-⑥ involves attack of amine on the protonated diazoaminobenzene. Again, no evidence has been presented to confirm this mechanism. The observed rate constants (ignoring step 6) for these three pathways are shown below where HA is amine. The equations are derived assuming steady-state concentrations of protonated diazoamino compound and diazonium ion.

	Pathway ①-②-③-⑥	Pathway ①-④-⑥	Pathway ①-⑤-⑥
$k_{obs}=$	$\frac{K_1K_2k_3[N][HA][H^+]}{[HA][B]+K_1[HA][H^+]+K_1K_2[N][H^+]}$	$\frac{K_1k_4[HA][H^+]}{[HA][B]+K_1[HA][H^+]+K_1K_2[N][H^+]}$	$\frac{K_1k_5[HA]^2[H^+]}{[HA][B]+K_1[HA][H^+]+K_1K_2[N][H^+]}$
$K_1K_2[N][H^+] \gg [HA]$	$k_3[HA]$	$\frac{k_4[HA]}{K_2[N]}$	$\frac{k_5[HA]^2}{K_2[N]}$
$K_1K_2[H^+] \ll [HA]$	$K_1K_2k_3[N][H^+]$	$K_1k_4[H^+]$	$K_1k_5[HA][H^+]$

The initial equations can be simplified. They take into account that step-①, proton loss from the σ_N-complex to form diazoaminobenzene, may be base catalyzed. However, under our conditions, the reverse reaction (step ①) is specific and not general acid catalyzed. Hence, step-① is not subject to catalysis by added base. Further, assuming equilibrium 1 lies well to the left then $1 \gg K_1[H^+]$. The denominator in all three cases reduces to $[HA]+K_1K_2[N][H^+]$. We then obtain the two extreme situations for $K_1K_2[H^+][N] \gg$ or $\ll [HA]$ to give the six expressions for k_{obs} shown above.

It is immediately obvious that pathway ①-⑤-⑥, attack of amine on the protonated diazoaminobenzene, cannot take place under our conditions. This pathway demands an order with respect to amine concentration of two at high amine concentration whereas for both compounds investigated this is zero, or indeed negative *(Tables 2* and *4)*. The kinetic expressions do not, unfortunately, allow a distinction between the two other pathways. The only possible distinction would involve the different effects of a nucleophile on the reaction rates, but there is no evidence to suggest that the reaction rate is affected at all by added nucleophiles[2]). Thus both mechanisms require that at low amine concentration the rate be independent of acid and first-order in amine concentration, and at high amine concentration independent of amine concentration and first-order in acid. This is (approximately) the case *(Tables 2* and *4* and *Fig. 2)*.

The differences in the form of the expressions for the rate constant for pathways ①-②-③-⑥ and ①-④-⑥ suggest a possible method to distinguish between them. At low amine concentration for pathway ①-②-③-⑥ $k_{obs}=k_3[HA]$ and for pathway ①-④-⑥ $k_{obs}=k_4[HA]/K_2$ (assuming no effect of nucleophile). We can estimate k_4/k_2 from a knowledge of the ratio of aminoazo compound to diazonium ion formed when the diazoaminobenzene is cleaved in the absence of added amine. We can measure k_{-2} (N-coupling) independently and hence obtain k_4/K_2 and what the first-order rate constant for aminoazo formation should be if pathway ①-④-⑥ exists. Under the conditions in *Table 2* at pH 5.0 k_{-2} is 1.78 l mol^{-1}s^{-1} and from spectrophotometric determination of the products of decomposition of 4′-methoxy-*N*-methyldiazoaminobenzene in the absence of amine $k_4/k_2 < 0.01$, *i.e.* there is no detectable aminoazo compound formed. This is then an upper limit to k_{obs}, namely 1.78×10^{-2} l mol^{-1}s^{-1}. From *Table 2* at pH 5.0 the second-order rate constant for

[2]) In view of the observation that the standard used in these experiments, $NaClO_4$, itself causes a rate enhancement, the possibility that added nucleophile increases the rate cannot be completely excluded.

aminoazo formation is *ca.* 4.2×10^{-2} l mol^{-1} s^{-1}, so it is extremely unlikely that the intramolecular pathway plays a major role (and probably does not occur at all).

Thus, there is no evidence to suggest that under aqueous conditions attack of a nucleophile or an amine molecule on the protonated diazoaminobenzene occurs, and an intramolecular reaction of this species appears highly improbable. The classical *Friswell-Green* mechanism holds. One observation remains to be explained, however. The rate should be independent of amine concentration at high amine concentration, and as *Figure 2* shows, a distinct maximum is observed. This, in our opinion, is due to a differential salt effect. *Table 5* shows that while *N*-methylanilinium perchlorate has only a small effect on rate, sodium perchlorate increases the rate quite strongly. Hence, at constant ionic strength of 1.0, with increasing concentration of amine (which is practically 100% protonated under these conditions[3])) a species which strongly catalyzes the rate is replaced by one which has little effect; rates at high $NaClO_4$-concentration (low amine concentration) are more affected by this catalysis than those at low $NaClO_4$-concentration (high amine concentration).

The dashed line in *Figure 2* shows rate constants corrected for this effect of $NaClO_4$ using the data in *Table 5*. Although a levelling-off of the rate is still not achieved it is seen that the correction is in the right direction. Qualitatively at least the explanation appears reasonable and this observed decrease in rate at high amine concentrations is simply an artifact of the experimental conditions and is not evidence against the *Friswell-Green* mechanism.

Our preparative experiments *(Table 6)* also support this mechanism. The existence of a pre-equilibrium between the diazoaminobenzene + acid and diazonium salt + amine requires that aminoazo product be formed in the same yield whatever the reactants. In fact, in the rearrangement, the yield is slightly lower (73%) than reaction with diazonium salt and amine (79%). This may be due to experimental error, but could also be caused by the fact that, in the latter reaction, on addition of the diazonium salt, the system is not in equilibrium. Until equilibrium is reached the diazonium ion will react to form diazoamino and aminoazo compounds in the ratio k_3/k_{-2}; some aminoazo compound is therefore formed rapidly at this time and this leads to an enhanced yield as the diazonium ion has less chance to undergo decomposition. That these are important is shown by the effect of temperature (run 5), and amine concentration (run 4) and acidity (run 3) where, in the last two, the pre-equilibrium is shifted to the side of the diazoaminobenzene + acid by increasing the amine concentration or decreasing the acid concentration. In run 10, residual loss of diazonium salt during addition probably accounts for the lower yield.

Thus, although there is no doubt that, depending on the conditions, the mechanism of the diazoamino rearrangement can change [2], in 20% v/v acetonitrile/aqueous buffers the original suggestion of *Friswell-Green* appears correct. It is therefore no advantage to synthesize aromatic aminoazo compounds by a two-stage process. The one-stage method is simpler and gives at least as high yields.

---

[3]) We have determined the pK_a of *N*-methylanilinium ion under the conditions shown in *Figure 2* as 4.25.

Experimental Part

General. Acetonitrile was purified as previously described [1]. De-ionized water was distilled from $KMnO_4$. Acetic acid, sodium acetate and sodium perchlorate were analytical reagents. *p*-Toluenesulfonic acid was crystallized from water/HCl twice and dried (NaOH). Perchloric acid was analytical grade, *ca.* 60%. All pH values were measured using a *Metrohm* digital pH-meter with a *Radiometer* combined glass electrode and reference electrode assembly calibrated in *Metrohm* $pH = 4.00 \pm 0.02$ standard buffer.

Materials. – *4-Methoxy-*N*-methyldiazoaminobenzene* was prepared as previously described [2] and recrystallized several times from ethanol, m.p. 59.8°. N-*Methyl-4-nitrodiazoaminobenzene* was prepared as follows: NaH_2PO_4 (2.5 g) and Na_2HPO_4 (7.5 g) were added to 200 ml of 50% v/v water/acetonitrile with stirring. *N*-Methylaniline (5 g) was added to the mixture followed by *p*-nitrobenzenediazonium tetrafluoroborate (4 g) dissolved in the minimum amount of acetonitrile. The mixture was left for 2 h, acetonitrile was removed under vacuum and the product filtered off and washed with water. It was recrystallized from ethanol; yield (crude) 5.46 g; m.p. 133.1°. N-*Methyl[2,4,6-$^2H_3$]-aniline* was prepared by dissolving *N*-methylanilinium hydrochloride (1.34 g) in D_2O (2 ml). The solution was refluxed for 24 h and the solvent removed on a rotatory evaporator. This was repeated a further 4 times. The free amine was obtained by neutralization with NaOH-solution. It was extracted with ether, the ether layer was dried and the solvent removed. The amine was vacuum distilled. ^{1}H-NMR. showed virtually 100% deuteriation.

Solvent mixture: all kinetic measurements were carried out in 250 ml (dry) acetonitrile/(distilled) water 1:4. Acetic acid/acetate buffers were prepared by weighing the calculated quantities of acetic acid and sodium acetate into a volumetric flask and making the solution up to the correct volume with the standard solvent mixture. *p*-Toluenesulfonic acid/sodium *p*-toluenesulfonate buffers were prepared by dissolving the acid in a small quantity of solvent mixture and adding sufficient 1.00M aqueous NaOH to give a final solution of 0.1M sodium *p*-toluenesulfonate. Acetonitrile was then added to give a 20% v/v solution and the whole made-up to the mark with standard solvent mixture. For buffers containing N-methylaniline, *p*-toluenesulfonic acid was weighed out as before and *N*-methylaniline added to give 0.1M tosylate ion in the final solution. Perchloric acid solutions were prepared by pipetting 2 ml 1M $HClO_4$ into 100 ml volumetric flask containing a weighed amount of $NaClO_4$ to give a final concentration of 0.08M or 0.98M $NaClO_4$ required for ionic strength 0.1 or 1.0, respectively. Acetonitrile (0.5 ml) was pipetted in and the solution made-up to 100 ml with the standard solvent mixture.

Kinetic measurement procedure. – Measurements were carried out using a thermostated *Unicam* SP800 spectrophotometer. Buffer solution (3 ml) was pipetted into a 1 cm spectrophotometer cell and the required amount of amine (if any) added with a microsyringe. A small amount (*ca.* 10 µl) of a concentrated solution of the diazoaminobenzene in dry acetonitrile was then added to give a final concentration of *ca.* 5×10^{-5}M and the reaction followed at the appropriate wavelength (4′-methoxy-*N*-methyldiazoaminobenzene: appearance of aminoazo $\lambda = 425$ nm, loss of diazoamino $\lambda = 360$ nm, appearance of diazonium salt $\lambda = 300$ nm; *N*-methyl-4′-nitro-diazoaminobenzene: appearance of aminoazo compound $\lambda = 490$ nm).

Small scale preparations of 1-*N*-methylamino-4′-nitroazobenzene. – *Rearrangement* (method A). *N*-Methyl-4′-nitro-diazoaminobenzene (100 mg, 0.39 mmol) was weighed accurately into a 100 ml round bottomed flask and was dissolved in 30 ml of H_2O/acetonitrile 1:1 v/v, *N*-methylaniline (20 µl, 0.19 mmol) was added, and finally 3 ml of concentrated HCl-solution (to give a 1M concentration). The quantity of hydrochloric acid was varied in some experiments to give 3M or 0.33M. The mixture was refluxed for 1 h. The solution was allowed to cool, and then made up to 100 ml with acetonitrile. The precipitated aminoazo compound was redissolved using ultrasonic agitation, 1 ml was pipetted into a 50 ml volumetric flask, 4 ml of aqueous 0.1M NaOH added, and the solution was made up to 50 ml with acetonitrile. The concentration of aminoazo compound in this solution was measured spectrophotometrically. The extinction coefficient and λ_{max} were also measured in this solvent mixture. The yield was calculated on the basis of the exact amount of diazoaminobenzene used. The rearrangement at RT. was carried out in exactly the same way except that the solution was stirred for 5 h instead of refluxing. The reaction with the higher amine concentration used 80 µl, 0.74 mmol of amine rather than 20 µl.

Diazonium salt plus amine (method B). *p*-Nitrobenzenediazonium tetrafluoroborate (92.5 mg, 0.39 mmol) was dissolved in 15 ml of acetonitrile. *N*-Methylaniline (62 µl, 0.58 mmol) was dissolved in water (15 ml) and conc. HCl-solution (3 ml) was added. For the runs at reflux temperature the solution was heated to the correct temperature and the diazonium salt was added over 1–2 min with stirring. For the runs at RT. the diazonium salt was added over 1–2 min with stirring. The solution was refluxed for 1 h (or stirred for the time shown in the table for the RT. runs). After the reaction was over the mixture was worked up as before.

The reaction which was quenched was poured into a mixture of sufficient 0.4M NaOH to neutralize the acid and 50 ml of acetonitrile. The reaction mixture was then made up to 100 ml with acetonitrile and treated in the usual way.

Slow addition of *p*-nitrobenzenediazonium tetrafluoroborate to *N*-methylaniline solution: the procedure was identical to that above except that the diazonium salt was added in 5 ml of acetonitrile with the initial solvent, *i.e.* 25 ml acetonitrile/water 2:3. The diazonium salt was added dropwise over 2 h, by using a dropper for addition rather than a dropping funnel. The yield was increased considerably by reducing losses of the diazonium salt. The reaction was refluxed for a further 1 h and worked up as usual.

REFERENCES

[1] *J. R. Penton & H. Zollinger*, Helv. Chim. Acta *64*, 1728 (1981).
[2] *J. R. Penton & H. Zollinger*, Helv. Chim. Acta *64*, 1717 (1981).
[3] *H. Zollinger*, «Azo and Diazo Chemistry», Interscience, New York and London 1961, Chapter 8.3, p. 185.
[4] *H. J. Shine*, 'Aromatic Rearrangements', Elsevier, New York 1967, Chapter 3; idem, *M. T. P. Reviews*, Series One *3*, 89 (1973).
[5] *H. Goldschmidt, S. Johnson & E. Overwien*, Z. Phys. Chem. *110*, 251 (1924).
[6] *A. I. Vogel*, 'Practical Organic Chemistry', 3rd edition, Longmans, London 1956, p. 626.
[7] *American Cyanamid*, U.S. Patent 566594, 1975; *Rhone-Poulenc Industries*, French Patent 004638, 1977.
[8] *D. L. H. Williams*, J. Chem. Soc., Perkin II, *1977*, 44 and ref. therein.