The remaining diamines, XI and XVI, were prepared by R. L. Bent, of these laboratories. Diamine XI was prepared as follows.

3-Isopropylaniline (H) was prepared from chlorobenzene and isopropyl alcohol, as described in the literature.[21] In our hands, however, the reduction of the intermediate, 2-chloro-5-isopropylnitrobenzene, gave 2-chloro-5-isopropylaniline rather than 3-isopropylaniline as reported. The chlorine had to be eliminated in a separate step by means of KOH, methanol, and Raney nickel catalyst, under reductive conditions.[22] The product had bp 93–95° (5 mm), n^{24}D 1.546.

N,N-Diethyl-3-isopropylaniline (I). A mixture of 30 g (0.222 mol) of H, 72 g (0.46 mol) of ethyl iodide, 84 g (0.46 mol) of sodium bicarbonate, 280 ml of ethanol, and 110 ml of water was refluxed for 18 hr. After removal of the ethanol, the product was extracted with ether and the latter dried and concentrated. The residual oil was treated with acetic anhydride to remove any primary or secondary amines, and distilled. The yield of I, bp 115–120° (7 mm), n^{25}D 1.5221, was 25.6 g (60%).

4-(2,5-Dichlorophenylazo)-N,N-diethyl-3-isopropylaniline (J). A total of 21.6 g (0.133 mol) of 2,5-dichloroaniline was dissolved in a mixture of 150 ml of concentrated hydrochloric acid and 500 ml of water on a steam bath. After cooling to 5°, the hydrochloride salt of the aniline precipitated out and slightly over the theoretical quantity of sodium nitrite was added, with stirring. When diazotization was complete, and after the excess nitrous acid was destroyed by sulfamic acid, the solution was filtered and at once added to a cold solution of 25.4 g (0.133 mol) of I in dilute hydrochloric acid. The coupling reaction was initiated by the addition of 180 g of sodium acetate. The azo dye precipitated as a gum but gradually became crystalline. The yield of J, mp 89–91° after two recrystallizations from ethanol, was 20 g (41.5%).

Anal. Calcd for $C_{19}H_{23}Cl_2N_3$: C, 62.6; H, 6.31. Found: C, 62.7; H, 6.2.

4-Amino-N,N-diethyl-3-isopropylaniline Hydrochloride (XI). The reduction of 3.64 g (0.01 mol) of J was carried out in absolute ethanol at 40 psi, with Raney nickel as catalyst. The catalyst was filtered off and washed on a funnel with alcohol, and 1 equiv of concentrated hydrochloric acid was added. The filtrate was then concentrated to a small volume and excess ether was added to precipitate the developer salt; the latter was dissolved in a small volume of absolute ethanol and again precipitated out with excess ether (the re-formed dichloroaniline remains in solution). The yield of XI, mp 215–217° after recrystallization from isopropyl alcohol, was 1.45 g (60%).

Anal. Calcd for $C_{13}H_{23}ClN_2$: C, 64.3; H, 9.48. Found: C, 64.4; H, 9.3.

Diamine XVI. N,N-Diethyl-3,5-dimethoxyaniline (K) was prepared by the dialkylation of 50 g (0.327 mol) of 3,5-dimethoxyaniline (mp 46.5–48°, from Aldrich Chemical Co.) with ethyl iodide, as already described for 3-isopropylaniline. The yield of K, bp 114–118° (1 mm) and mp 45.5–47 from petroleum ether, was 25 g (36.5%).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.8; H, 9.1. Found: C, 69.1; H, 9.3.

4-(2,5-Dichlorophenylazo)-N,N-diethyl-3,5-dimethoxyaniline (L) was prepared by the coupling of diazotized 2,5-dichloroaniline with 2.09 g (0.01 mol) of K, as already described for 3-isopropylaniline. The yield of L, mp 139–140.5° after two recrystallizations from ethanol, was 2.55 g (33%).

Anal. Calcd for $C_{18}H_{21}Cl_2N_3O_2$: C, 56.5; H, 5.49. Found: C, 56.4; H, 5.2.

4-Amino-N,N-diethyl-3,5-dimethoxyaniline Hydrochloride (XVI). The reduction of 3.82 g (0.01 mol) of L in absolute ethanol, with Raney nickel as catalyst, and the conversion of the developer base to hydrochloride salt, was carried out as described for the 3-isopropyl developer. The yield of XVI, mp 212–214° from isopropyl alcohol, was 1.25 g (48%).

Anal. Calcd for $C_{12}H_{21}ClN_2O_2$: C, 55.2; H, 8.06. Found: C, 55.6; H, 8.3.

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(21) H. Gilman, *et al.*, *J. Org. Chem.*, **19**, 1067 (1954).

(22) H. Kammerer, *et al.*, *Chem. Ber.*, **91**, 1376 (1958).

On the Mechanisms of Dediazoniation and Other Aromatic Denitrogenation Reactions Induced by Sodium Methoxide in Methanol

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Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island. Received March 15, 1968

Abstract: Reactions of compounds of types **1–4** with $NaOCH_3$ in CH_3OH afford substantial yields of products in which the nitrogenous substituent has been replaced by hydrogen. When these reactions are carried out in CH_3OD solution, the hydrogen which replaces the nitrogenous group is sometimes protium and sometimes deuterium. In this research, the percentage of monodeuteration of the denitrogenation product is determined as a function of the nitrogenous leaving group, of substituents in the parent aromatic ring, and of the $NaOCH_3$ concentration. The percentage of monodeuteration of the product is found to be greater from 1-aryl-2-benzenesulfonhydrazides (**1**) than from diazonium salts (**2**), greater at higher $NaOCH_3$ concentrations and greater from chlorine-substituted than from unsubstituted compounds. However, *p*-nitrobenzenediazonium ion gives virtually deuterium-free nitrobenzene under all conditions. Deuterated products are taken to be formed *via* aryl anion intermediates and deuterium-free products *via* aryl radicals. Radical and carbanionic mechanisms are suggested, and the factors governing competition between the mechanisms are discussed.

The mechanism of dediazoniation[2] of *o*-halobenzenediazonium ions by sodium methoxide in methanol is sharply dependent on the base concentration.[3,4] This is shown particularly by the products formed in CH_3OD solution. When only 1 equiv of $NaOCH_3$ is provided per mole of *o*-chlorobenzenediazonium ions, the chlorobenzene formed is nearly deuterium free. But when 2 *M* $NaOCH_3$ is used, it is mainly *o*-deuteriochlorobenzene.[3]

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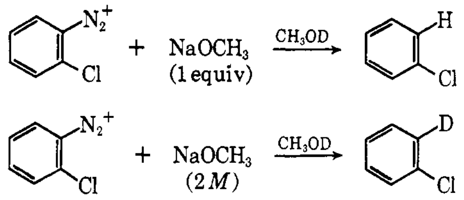
(1) University of California, Santa Cruz, Calif.

(2) "Dediazoniation" means replacement of the diazonia group ($-N_2^+$) by hydrogen.

(3) J. F. Bunnett, D. A. R. Happer, and H. Takayama, *Chem. Commun.*, 367 (1966).

(4) J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **32**, 2701 (1967).



Both the *o*-chlorophenyl radical and the *o*-chlorophenyl anion are conceivable precursors of the chlorobenzene. The former abstracts a hydrogen atom from the methyl group of CH_3OD,[5] forming ordinary chlorobenzene (eq 1). The anion acts as a base toward CH_3OD, taking deuterium from its -OD group.

$$\mathrm{Ar\cdot} + \mathrm{CH_3OD} \longrightarrow \mathrm{ArH} + \mathrm{CH_2OD} \qquad (1)$$

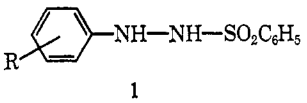
$$\mathrm{Ar:^-} + \mathrm{CH_3OD} \longrightarrow \mathrm{ArD} + \mathrm{CH_3O^-} \qquad (2)$$

These results testify that a radical mechanism predominates at low $NaOCH_3$ concentrations, and that it is almost wholly supplanted by an ionic mechanism in 2 *M* $NaOCH_3$.

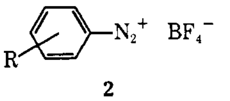
Because of our interest in several reactions in which a group with nitrogen as its first atom is replaced by hydrogen on reaction with methanolic sodium methoxide,[3,4,6–8] we undertook to apply this criterion of mechanism to a number of denitrogenation reactions. In the present study, attention is focused mainly on the following variables: (1) the group replaced ($-N_2^+$, $-NHNHSO_2C_6H_5$, $-N{=}NSO_2C_6H_5$, or $-N{=}NOCH_3$); (2) substituents in the parent aromatic ring (H, *p*-Cl, *m*-Cl, *o*-Cl, 2,4-Cl_2, or *p*-NO_2); and (3) $NaOCH_3$ concentration. Since our work was completed, Hoffmann and Guhn[9] have reported the per cent incorporation of deuterium upon denitrogenation of some halogenated 1-phenyl-2-acyldiimides in C_2H_5OD, in a study somewhat similar to ours but of lesser scope.

Results

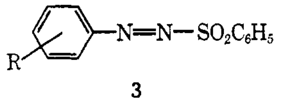
Denitrogenation of substances of structural types **1–4** was studied. In most experiments, 0.001 mol of the substrate was allowed to react with 10 ml of a CH_3OH or CH_3OD solution either 0.1 *M* or 2 *M* in $NaOCH_3$. In the former case, exactly 1 mol of $NaOCH_3$ was present per mol of substrate, while in the latter the base was in great excess.



1



2



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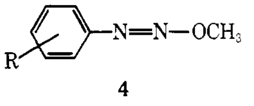

4

a, R = H
b, R = *p*-Cl
c, R = *m*-Cl
d, R = *o*-Cl
e, R = 2,4-Cl_2
f, R = *p*-NO_2

Yields of denitrogenation products obtained from several of the substrates in ordinary methanol are listed in Table I. These represent determinations by glpc, and are based on comparisons with internal standards. Yields obtained on dediazoniation of the diazonium salts are reported elsewhere.[8] In Table I, better yields were generally obtained from the hydrazides (type **1**) than from the diazonium salts[8] or the arylazo sulfones (type **3**), better yields in 2 *M* $NaOCH_3$ than when the base was supplied only in equivalent amount, and better yields when a chlorine substituent was present than when absent. In contrast, 1-(*p*-nitrophenyl)-2-benzenesulfonhydrazide (**1f**) when treated with 2 *M* $NaOCH_3$ in CH_3OD gave only a trace of nitrobenzene.

Table I. Yields of Denitrogenation Products Obtained with $NaOCH_3$ in CH_3OH

Reactant	[$NaOCH_3$], *M*	Conditions	Product	Yield, %
1a	0.1[a]	Usual[b]	C_6H_6	45
	2	Usual[b]	C_6H_6	58
	2	Usual[b,c]	C_6H_6	60
1b	2	Usual[b,c]	C_6H_5Cl	90
1d	0.1[a]	Usual[b,d]	C_6H_5Cl	68
	0.1	Usual[b,e]	C_6H_5Cl	77
	2	Usual[b,d]	C_6H_5Cl	94
	2	Usual[b,e]	C_6H_5Cl	91
1f	2	Reflux, 1 hr	$C_6H_5NO_2$[f]	Trace
3a	0.1[a]	Usual[b]	C_6H_6	41
	2	Usual[b]	C_6H_6	53
3b	0.1[a]	Usual[b]	C_6H_5Cl	69
3d	0.1[a]	Usual[b]	C_6H_5Cl	72
	2	Usual[b]	C_6H_5Cl	74

[a] 0.1 *M* $NaOCH_3$ provides 1 mol of $NaOCH_3$ per mol of reactant. [b] See Experimental Section. [c] Atmosphere was air instead of N_2. [d] Heated 45 min at *ca.* 55°, then 15 min at reflux. [e] Heated 165 min at *ca.* 55°, then 15 min at reflux. [f] Identified only by glpc retention time.

Experiments in CH_3OD solution, in which the degree of deuteration of the denitrogenation product was determined, are summarized in Table II. The deuterium content of the isolated product was in all cases assessed by mass spectrometry. Never did a product contain more than one deuterium atom per molecule. In several cases, the infrared spectra of the denitrogenation products were also determined; they served not only to confirm the mass spectrometric deuterium analyses but also to affirm that deuterium had taken the very ring position vacated by the nitrogenous leaving group. The infrared measurements involved comparison of product spectra with those of authentic samples of ordinary chlorobenzene and of the three monodeuteriochlorobenzenes; the latter were synthesized by treatment of appropriate Grignard reagents with D_2O.

Affirmation that deuterium took the site vacated by the nitrogenous group was necessary to test the possibility[10] that deuteration with 2 *M* $NaOCH_3$ in CH_3OD occurred *ortho* to chlorine, *via* conventional base-catalyzed hydrogen isotope exchange,[11] and that the actual dediazoniation involved acquisition of ordinary

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(5) R. O. C. Norman and B. C. Gilbert, *Advan. Phys. Org. Chem.*, **5**, 74 (1967).

(6) J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **31**, 2369 (1966).

(7) J. F. Bunnett, D. A. R. Happer, M. Patsch, C. Pyun, and H. Takayama, *J. Amer. Chem. Soc.*, **88**, 5250 (1966).

(8) J. F. Bunnett and H. Takayama, *J. Org. Chem.*, **33**, 1924 (1968).

(9) R. W. Hoffmann and G. Guhn, *Chem. Ber.*, **100**, 1474 (1967).

(10) Called to our attention by Professor Harold R. Ward.

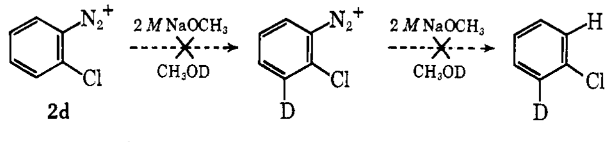
(11) G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, **77**, 4540 (1955); J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962).

Table II. Degrees of Monodeuteration of Denitrogenation Products Obtained with $NaOCH_3$ in CH_3OD

Reactant	$[NaOCH_3]$, *M*	Atmosphere	Conditions	Monodeuteration of product, %
1a	0.1[a]	N_2	Usual[b]	54
	2	N_2	Usual[b]	94
	2	Air	3 days, *ca.* 25°	17[c,d]
	2	N_2	1 hr, reflux	83[d–f]
1b	0.1[a]	N_2	Usual[b]	46[e,g,h]
	0.1[a]	Absolute N_2	24 hr, *ca.* 25°	45
	0.1[a]	Absolute N_2	1 hr, 59.4°	38[e]
	0.1[a]	Air bubbled	1 hr, 60°	76
	0.1[a]	Absolute N_2	1 hr, 59.4°, $C_6H_5NO_2$[i]	96
	0.2[j]	Absolute N_2	1 hr, 59.4°	86
	2	N_2	Usual[b]	94[g,h]
	2	Absolute N_2	48 hr, *ca.* 25°	67
	2	Absolute N_2	1 hr, 59.4°	97
1d	0.1[a]	N_2	Usual[b]	95[h,k]
	2	N_2	Usual[b]	98[h,k]
2a	0.1[a]	Air	Usual[b]	12[h]
	2	Air	Usual[b]	7[h]
2b	0.1[a]	Air	Usual[b]	3[h]
	0.1[a]	Absolute N_2	1 hr, *ca.* 25°	7
	2	Air	Usual[b]	37[e,g,h]
	2	Absolute N_2	1 hr, *ca.* 25°	40[e]
	2	O_2 bubbled	1 hr, *ca.* 25°	16
2b	2	Absolute N_2	1 hr, *ca.* 25°, $C_6H_5NO_2$[i]	16
2c	0.1[a]	Air	Usual[b]	7[h]
	2	Air	Usual[b]	78[h,l]
2d	0.1[a]	Air	Usual[b]	3[h,m]
	2	Air	Usual[b]	91[h,k,m]
2e	0.1[a]	Absolute N_2	1 hr, 29.6°	3
	0.1[n]	N_2	−30° to reflux[o]	65
	0.5	Absolute N_2	1 hr, 29.6°	73
	2	N_2	−30° to reflux[o]	94
	2	Absolute N_2	1 hr, 29.6°	83
2f	0.1[a]	Air	Usual[b]	2[h]
	2	Air	Usual[b]	4[h]
3a	0.1[a]	N_2	Usual[b]	21
	2	N_2	Usual[b]	63
3b	0.1[a]	N_2	Usual[b]	6[h]
	2	N_2	Usual[b]	69[g,h]
3d	0.1[a]	N_2	Usual[b]	8[h,m]
	2	N_2	Usual[b]	91[h,k,m]
4	Nil	Air	Usual[b]	1[h]
	2	Air	Usual[b]	3[h]

[a] One mole of $NaOCH_3$ per mole of reactant. [b] See Experimental Section. [c] 27% yield of benzene (by glpc). [d] Unpublished experiment of Mr. Carl C. Wamser. [e] Average of two concordant runs. [f] 63% yield of benzene (by glpc). [g] Product identity as chlorobenzene-4-*d* confirmed by infrared spectrum. [h] Deuterium analysis confirmed (approximately) by infrared spectrum. [i] $C_6H_5NO_2$, 0.2 *M*. [j] Two moles of $NaOCH_3$ per mole of **1b**. [k] Product identity as chlorobenzene-2-*d* confirmed by infrared spectrum. [l] Product identity as chlorobenzene-3-*d* confirmed by infrared spectrum. [m] Reported in preliminary communication, ref 3. [n] 1.3 moles of $NaOCH_3$ per mole of **2e**. [o] **2e** was dissolved in $NaOCH_3$ solution at −30°; the solution was allowed to warm to room temperature, and then heated 30 min at reflux.

hydrogen from the methyl group of CH_3OD. Such a mechanism would account for the obtaining of chlorobenzene-2-*d* from *o*-chlorobenzenediazonium ion (**2d**),[3] but it would predict a mixture of chlorobenzene-2- and -4-*d* from its *meta* isomer **2c** and chlorobenzene-3-*d* from *para* isomer **2b**. Inasmuch as no sign of the latter products was obtained from **2c** or **2b**, this alternative is dismissed insofar as their reactions are concerned and rendered very improbable for reactions of **2d**.



Discussion

Table II presents a complex array of results which tend to raise more problems than they answer. The framework of interpretation which is now offered contains some features which are considerably supported by various kinds of evidence, but other features are speculative.

Cleavages of 1-Aryl-2-benzenesulfonhydrazides of Type 1. Cleavage is believed to be initiated by base-induced elimination of the elements of benzenesulfinic acid,[6] forming an aryldiimide (**5**), which would undoubtedly be deuterated on nitrogen in CH_3OD solution (Scheme I). As suggested by other workers, the aryldiimide may decompose either by a radical route (*e.g.*, **5** → **7** → **9**)[9,12,13] or, in the presence of base, by a carbanion route (**5** → **6** → **8**).[6,9,13] As indicated in Scheme I and discussed above (*cf.* eq 1 and 2), the ultimate product by the radical route would be deuterium free (**11**) while that from the carbanion route would be deuterated (**10**). Testimony that free phenyl radicals are formed from **1a** is the fact that

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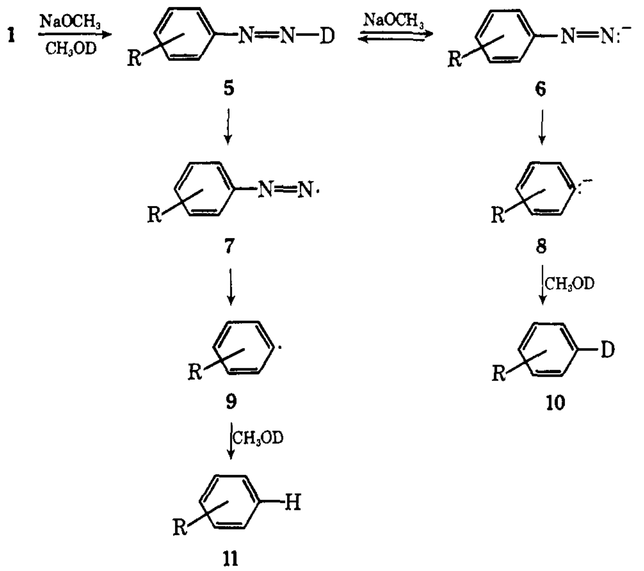
(12) S. G. Cohen and J. Nicholson, *J. Amer. Chem. Soc.*, **86**, 3892 (1964); **88**, 2247 (1966); *J. Org. Chem.*, **30**, 1162 (1965).

(13) (a) E. M. Kosower and P. C. Huang, *J. Amer. Chem. Soc.*, **87**, 4645 (1965); (b) *ibid.*, **89**, 3910 (1967).

Scheme I



decomposition of **1a** in a solution of NaOCH$_3$ and *m*-chloroiodobenzene in 67% CH$_3$OH–33% benzene forms both biphenyl and iodobenzene in appreciable amounts.[14]

Further but less probable pathways from **5** are intramolecular collapse[12] to **10** plus N$_2$, bimolecular reaction of **5** with itself to form **10** and other products,[13b] and capture of a deuterium atom from **5** by **9**, affording **10**. If **5** is deuterated on nitrogen, all three alternatives would lead to a deuterated reduction product (**10**). Intramolecular collapse as a major route to **10** is unlikely because it would not predict the degree of deuteration to increase with increase in NaOCH$_3$ concentration, as is the case (*cf.* data for **1a** and **1b** in Table II).

In acetonitrile solution, decomposition of phenyldiimide is kinetically second order, and a bimolecular mechanism involving radical partners within a solvent cage has been suggested.[13b] Whether such a mechanism would survive the change from acetonitrile to methanol solvent is uncertain; at any rate, it also does not account for the tendency of higher base concentration to increase the degree of deuteration of the product.

The radical chain cycle, **9** + **5** → **10** + **7**, plus **7** → **9** + N$_2$, appears to be energetically feasible. However, the instantaneous concentration of **5** is probably very low whereas CH$_3$OD is abundant. Therefore aryl radicals formed are much more likely to abstract hydrogen from CH$_3$OD than deuterium from **5**.

Thus there are objections to each of the three alternatives to Scheme I. However, as mentioned below, they may play some part under certain conditions.

On the basis that Scheme I is generally satisfactory as a basis for interpretation, let us examine the specific data for **1a**, **1b**, and **1c** in Table II. Two trends are evident: formation of a deuterated product is favored by higher NaOCH$_3$ concentration and by an *o*-chlorine substituent. The former is attributed to a shift of the **5** ⇄ **6** equilibrium to the right at higher base concentrations, favoring the carbanion route. The latter is ascribed to greater facility of the **6** → **8** transformation when a more stable carbanion may be formed. *o*-Halogens are known to have a particularly strong stabilizing effect on aryl anions.[11,15]

The substantial degrees of deuteration of the products from **1a** and **1b**, even when only 1 equiv of NaOCH$_3$ was provided, is perhaps due in part to one of the alternatives to Scheme I mentioned above.

The effect of nitrobenzene (0.2 *M*) on the cleavage of **1b** by 1 equiv of NaOCH$_3$ is remarkable. It increases the degree of deuteration of the chlorobenzene product from about 40 to 96%. Tentatively, we attribute this to inhibition of the radical route in Scheme I, allowing either the carbanion route, unimolecular collapse, or the bimolecular mechanism of Huang and Kosower[13b] to predominate.

Kosower and Huang have reported that oxygen reacts rapidly with phenyldiimide.[13] We obtained (with **1b**) substantially the same results under an atmosphere of ordinary commercial nitrogen (which contains traces of oxygen) and under nitrogen which had been scrupulously deoxygenated. However, a reaction of **1b** at 60°, continuously bubbled with air, gave chlorobenzene richer in deuterium than that obtained under nitrogen. On the other hand, a reaction of **1a** at room temperature under air gave benzene of unusually low deuterium content. These effects are not fully understood; it is possible that oxygen in abundance tended to block the radical route in Scheme I but that in small amounts (under quiet air) it tended to initiate formation of radicals.

Dediazoniation of Diazonium Salts. The Radical Mechanism. That dediazoniation in alkaline methanol may occur by a radical mechanism is well substantiated.[8,16] We favor a mechanism involving the chain-propagating cycle of steps 3–5. This is similar to a mechanism proposed by DeTar and Turetzky,[16] but differs in the important respect that the electron

$$\text{Ar}\cdot + \text{CH}_3\text{OH} \longrightarrow \text{ArH} + \cdot\text{CH}_2\text{OH} \qquad (3)$$

$$\cdot\text{CH}_2\text{OH} + \text{CH}_3\text{O}^- \rightleftharpoons \cdot\text{CH}_2\text{O}^- + \text{CH}_3\text{OH} \qquad (4)$$

$$\cdot\text{CH}_2\text{O}^- + \text{ArN}_2^+ \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{CH}_2\text{O} \qquad (5)$$

donor in step 5 is the ·CH$_2$O$^-$ radical anion[14] rather than the ·CH$_2$OH radical.

Ionic Mechanism. As discussed above, formation of deuterated dediazoniation products in CH$_3$OD has been taken as evidence for a mechanism involving aryl anion intermediates (see reaction 2). In further support of this interpretation are the facts that in 2 *M* methanolic sodium methoxide the proportions of bromide ion and bromobenzene from *o*-bromobenzenediazonium ion are as expected from *o*-bromophenyl anion,[4] and that the yield of chlorobenzene from **2c** under conditions that give a high degree of deuteration is not adversely affected by the presence of abundant oxygen.[8]

How aryl anions are formed from diazonium ions is not known. Two possibilities are reactions 7 and 8,

$$\text{ArN}_2^+ + \text{CH}_3\text{O}^- \rightleftharpoons \text{Ar—N=N—OCH}_3 \qquad (6)$$

$$\text{ArN}_2^+ + \text{CH}_3\text{O}^- \longrightarrow \text{Ar—N=N—H} + \text{CH}_2\text{O} \qquad (7)$$

$$\text{Ar—N=N—OCH}_3 + \text{CH}_3\text{O}^- \longrightarrow \text{Ar—N=N:}^- + \text{CH}_2\text{O} + \text{CH}_3\text{OH} \qquad (8)$$

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(14) J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **89**, 6712 (1967).

(15) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961).

(16) D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, 77, 1745 (1955); 78, 3925, 3928 (1956).

which are respectively competitive with and subsequent to reaction 6.[3, 17] In reaction 7 the terminal nitrogen of the diazonium ion, an electrophilic site, is visualized to attack a hydrogen of methoxide ion, and to capture it as a hydride ion.[18] Reaction 8 is thought of as an E2 elimination, initiated by attack of methoxide ion on a methyl hydrogen atom. In either case, an aryldiimide or the anion thereof is formed, and can further decompose as sketched in Scheme I.

Although **4f** can be synthesized by methylation of silver *p*-nitrobenzeneisodiazotate, and is stable, and a few other diazo ethers (**4**) are known as unstable oils,[19] quantitative information on the state of equilibria of type 6 is not available. Also, it is possible that the diazo ethers obtained by methylation of isodiazotate salts have *anti* geometry, while those formed by coordination of diazonium and methoxide ions may be *syn*.

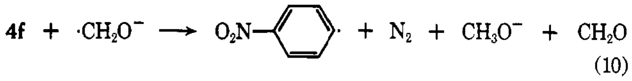
We have preliminary kinetic evidence that decomposition of **2e**, which gives mainly deuterated *m*-dichlorobenzene even when $NaOCH_3$ is in but slight excess, does not occur by reaction 8. The rate of decomposition of **2e** is nearly independent of $NaOCH_3$ concentration between 0.002 and 0.9 *M*. This result is incompatible with a mechanism of steps 6 and 8, which would call for second- and/or first-order dependence on $NaOCH_3$ concentration, depending on the state of equilibrium 6. On the other hand it is consistent with reaction *via* step 7, providing that equilibrium 6 lies mainly to the right even at 0.002 *M* $NaOCH_3$.

Competition between Ionic and Radical Routes. If the ionic pathway does indeed involve the hydride ion transfer step 7, the influence of chlorine substituents to guide dediazoniation in 2 *M* $NaOCH_3$–CH_3OD toward the carbanionic route may be attributed to two interrelated effects. First, chlorine substituents increase the electrophilicity of diazonium ions,[20] and they should therefore accelerate step 7. Second, chlorine substituents should shift equilibrium 6 toward the right, as they do the somewhat analogous equilibrium 9 in aqueous systems.[21]

$$ArN_2^+ + 2OH^- \rightleftharpoons Ar{-}N{=}N{-}O^- + H_2O \qquad (9)$$

These two effects would be expected largely to offset each other, so as to give an over-all rate of reaction by the carbanionic route that would be little affected by substituents. If so, the strong effect of substituents to govern partitioning between radical and carbanionic routes, which is evident in Table II, must be attributed to suppression of the radical mechanism when chlorine substituents are present and the $NaOCH_3$ concentration is high. We suggest that the diazo ethers are not efficient electron acceptors in a step analogous to 5, and that consequently the radical mechanism is retarded by factors that shift equilibrium 6 to the right.

What then of the behavior of *p*-nitrobenzenediazonium ion, which affords virtually deuterium-free nitrobenzene even in 2 *M* $NaOCH_3$–CH_3OD? The radical route clearly predominates throughout. In this case the nitro group makes the diazo ether (probably *syn*-**4f**) itself a good electron acceptor, according to reaction 10. Therefore shifting equilibrium 6 strongly to the right does not suppress the radical route, as it does with the other diazonium salts.



(10)

In 2 *M* $NaOCH_3$, *p*-chlorobenzenediazonium salt **2b** balances almost evenly between radical and carbanionic routes. The balance is remarkably insensitive to the composition of the atmosphere, being nearly the same under air as under oxygen-free nitrogen. However, 0.2 *M* nitrobenzene decreases the deuterium content of the chlorobenzene product, from about 40 to 16%, and thus favors the radical route. Inasmuch as nitrobenzene is a good electron acceptor which even in small amounts interferes with the electron transfer–radical deiodination of *m*-chloroiodobenzene in methanol,[14] it might be thought similarly to interfere with electron transfer–radical dediazoniation. However, the diazonium ion is an even better electron acceptor.[22] Nitrobenzene in this case may act as a go-between in electron transfer. It may take an electron from the highly reactive $\cdot CH_2O^-$, being converted thereby into the less reactive nitrobenzene radical anion, which "preserves" the odd electron until it meets a diazonium ion to which an electron is relinquished.

The contrast between the effects of nitrobenzene on cleavage of **1b** in 0.1 *M* $NaOCH_3$–CH_3OD and on dediazoniation of **2b** in 2 *M* $NaOCH_3$–CH_3OD is noteworthy. Respectively, it strongly increases and strongly decreases the degree of deuteration of the chlorobenzene formed. This points to a deep-seated difference in the reaction mechanisms involved. The mechanisms suggested in the above discussion for these two systems are indeed very different.

Cleavages of Arylazo Phenyl Sulfones 3a, 3b, and 3d. The results obtained (Table II) are intermediate between those for sulfonhydrazides **1a**, **1b**, and **1d** and diazonium salts **2a**, **2b**, and **2d**. A low degree of deuteration was obtained in 0.1 *M* $NaOCH_3$–CH_3OD,[23] as in reactions of the diazonium salts, but **3a** and **3b** gave products in 2 *M* $NaOCH_3$–CH_3OD containing distinctly more deuterium than diazonium salts **2a** and **2b** did in that medium.

Inasmuch as arylazo phenyl sulfones dissociate readily in methanol to diazonium and benzenesulfinate ions (eq 11),[24] behavior resembling that of diazonium fluoroborates is not surprising.[4, 25, 26] But the results

$$Ar{-}N{=}N{-}SO_2C_6H_5 \rightleftharpoons ArN_2^+ + C_6H_5SO_2^- \qquad (11)$$

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[17] Reaction 7 was suggested by Dr. Christoph Rüchardt in a personal communication.

[18] H. Meerwein, H. Allendörfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *Angew. Chem.*, **70**, 211 (1958).

[19] E. Bamberger, *Ber.*, **28**, 225 (1895).

[20] H. Zollinger, "Chemie der Azofarbstoffe," Birkhäuser Verlag, Basel, Switzerland, 1958, p 156.

[21] E. S. Lewis and H. Suhr, *Chem. Ber.*, **91**, 2350 (1958).

[22] Relevant polarographic half-wave reduction potentials are CH_2O, −1.71 V; nitrobenzene, −0.83 V; benzenediazonium ion (first wave), −0.15 V; *cf.* L. Meites, "Polarographic Techniques," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1965, Appendix C, and E. R. Atkinson, H. H. Warren, P. I. Abell, and R. E. Wing, *J. Amer. Chem. Soc.*, **72**, 915 (1950).

[23] That the benzene from **3a** in 0.1 *M* $NaOCH_3$–CH_3OD contains appreciably more deuterium than the chlorobenzenes from **3b** and **3d** is surprising, and we have no interpretation for it.

[24] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

[25] Thermal decomposition of **3a** in aromatic hydrocarbon solvents occurs by a radical mechanism, of which homolysis to phenylazo and phenylsulfonyl radicals is probably the initial step.[26] However, we do not believe that much if any of the reaction with $NaOCH_3$ in CH_3OH

in 2 *M* $NaOCH_3$–CH_3OD drift toward those characteristic of the sulfonhydrazides. Is it possible that the arylazo phenyl sulfones (**3**) are partially reduced to 1-aryl-2-benzenesulfonhydrazides (**1**) under those conditions?

Cleavage of Methyl *p*-Nitrophenylazo Ether (4f). Table II records that, either in neutral CH_3OD or in 2 *M* $NaOCH_3$–CH_3OD, **4f** gives nitrobenzene substantially free of deuterium. A radical mechanism is indicated,[27] and a cycle of reactions 3, 4, and 10 is probable. It is possible that **4f** prepared by methylation of silver *p*-nitrobenzeneisodiazotate[28] and that resulting from coordination of *p*-nitrobenzenediazonium with methoxide ion are stereoisomers. Even so, both stereoisomers may react as in eq 10.

Concluding Remarks. The framework of interpretation offered above comprises at least two radical mechanisms (one for aryldiimides, one for diazonium salts) and two ionic mechanisms (one for reduction of diazonium ions to aryldiimides, the other for denitrogenation of diimides) as well as discussion of the factors which govern partitioning between the radical and ionic mechanisms. The framework as a whole is rather intricate, but this is not inappropriate when the pattern of experimental results (Table II) is intricate. The evidence for some elements of the framework is not compelling; they may require revision or rejection as further data become available, but in the meanwhile they hopefully will serve as useful hypotheses to stimulate further research.

Experimental Section

Materials. Diazonium fluoroborates **2a–2f** inclusive and diazo ether **4f** were synthesized as we have described elsewhere.[8] The mp of **2e** was 154.5–156° dec,[29] and its infrared absorption at 2290 cm^{-1} is noteworthy. Arylazo phenyl sulfones **3a** (mp 75–76° dec),[30] **3b** (mp 103–104.5° dec),[31] and **3d** (mp 97–98.5° dec)[32] were prepared after Bunnett and Happer.[4] 1-Aryl-2-benzenesulfonhydrazides **1a** (mp 146–147°),[33] **1b**, and **1d** were made by zinc and acetic acid reduction of the corresponding arylazo phenyl sulfones.[6] **1b** was obtained as colorless needles, mp 136–137° dec from aqueous ethanol. *Anal.* Calcd for $C_{12}H_{11}ClN_2O_2S$: C, 50.92; H, 3.92. Found:[34] C, 50.64; H, 4.08. **1d** was obtained as pale yellow needles, mp 114.5–115.5° dec from aqueous ethanol. *Anal.* Calcd for $C_{12}H_{11}ClN_2O_2S$: C, 50.92; H, 3.92. Found:[35] C, 51.08; H, 4.04. **1f** was prepared by reaction of *p*-nitrophenylhydrazine with benzenesulfonyl chloride in dry pyridine; it was obtained as pale yellow needles, mp 163–164° dec. *Anal.* Calcd for $C_{12}H_{11}N_3O_4S$: C, 49.18; H, 3.79. Found:[34] C, 48.61; H, 3.87. Methanol-O-*d* was prepared after Streitwieser, Verbit, and Stang;[36] the infrared spectrum of each preparation showed negligible O–H absorption. Chlorobenzene-3-*d* (from *m*-chlorophenylmagnesium bromide and deuterium oxide) was determined by mass spectrometry to contain 0.98 deuterium atom per molecule. Chlorobenzene-4-*d*, prepared and analyzed analogously, contained 0.96 deuterium atom per molecule. Chlorobenzene-2-*d* was available in the laboratory from the efforts of Zoltewicz and Bunnett;[37] our mass spectrometric data indicated it to contain 0.89 deuterium atom per molecule, whereas they reported only 0.80 deuterium atom per molecule.

Procedure for Yield Determinations (Table I). The procedure was that which we have described elsewhere[8] for yield determination in dediazoniation reactions. The "usual" conditions are described below.

Procedure for Reactions in CH_3OD Solution (Table II). The "usual" procedure with diazonium fluoroborates involved combining the solid reactant (0.001 mol) with 10 ml of either 0.1 or 2.0 *M* $NaOCH_3$ in CH_3OD (or rarely in other amounts, as noted in Table II) at room temperature, allowing the spontaneous gas evolution to subside, heating the mixture to reflux and continuing reflux for 5 min, cooling, combining the mixture with 20 ml of chilled water, extracting with 30 ml of pentane, washing the pentane extract with 10 ml of water, drying it over anhydrous $MgSO_4$, concentrating it to a volume of 1–2 ml by distillation through a Vigreux column, injecting the concentrate into a small-scale preparative gas–liquid partition chromatographic apparatus (SE-30 silicone rubber column), collecting the desired denitrogenation product in a chilled V-shaped tube, and analyzing it by mass spectrometry and frequently also by infrared spectroscopy. The mass spectrometer was a Hitachi Model RMU-6.[38] The mass spectrometer was operated at ionizing voltages such that fragmentation of the various benzene derivatives was negligible. In reckoning the mass spectrometric results, due account was taken of the normal abundance of deuterium, carbon-13, and nitrogen-15.

"Air" in Table II signifies the usual laboratory atmosphere; "N_2" signifies bubbling the reaction mixture continuously with nitrogen gas directly from a commercial cylinder; "absolute N_2" signifies commercial nitrogen gas further purified by passing it twice through Fieser's solution,[39] once through a lead acetate solution, and twice through concentrated sulfuric acid.

The "usual" procedure with the arylazo phenyl sulfones and 1-aryl-2-benzenesulfonhydrazides was in most respects the same as described above; the differences were that gas evolution was not evident on mixing at room temperature and that the reaction mixtures were heated 45 min at *ca.* 50–55° and then 15 min at reflux. With **4f**, no gas evolution was observed on mixing, but the period of heating was short as with the diazonium salts.

The procedure for reactions under "absolute N_2" was somewhat different. In a special apparatus, the solid reactant and the $NaOCH_3$–CH_3OD were separately deoxygenated by cooling to *ca.* −70°, evacuating to *ca.* 0.1 torr, then with or without admission of "absolute N_2" (the results were substantially the same either way) warming the apparatus to room temperature, and repeating the cycle four additional times. After the last evacuation, "absolute N_2" was admitted, the apparatus was brought to the temperature indicated in Table II, it was manipulated so as to mix the reactant and $NaOCH_3$–CH_3OD solution, and after the time specified in Table II the product was isolated and analyzed as described above.

In virtually all reactions under air or commercial nitrogen, strong colors (*e.g.*, deep red, purple) developed, though the color was often lighter (*e.g.*, pink) at the end of the reaction. There was less tendency for strong colors to develop in reactions under "absolute N_2"; some reaction mixtures were only yellow, but others were purple or dark brown.

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involves such a step. Our results show that the reactions of **3a** with $NaOCH_3$–CH_3OH have less, not more, radical character than those of **2a**.

(26) A. J. Rosenthal and C. G. Overberger, *J. Amer. Chem. Soc.*, **82**, 108, 117 (1960).

(27) A radical mechanism was also advocated for decomposition of **2f** and **4f** in methanol by W. D. Gurowitz, Ph.D. thesis, Purdue University, 1958.

(28) H. von Pechmann and L. Frobenius, *Ber.*, **27**, 672 (1894).

(29) *Cf.* A. Pavlath and G. Olah, *Acta Chim. Acad. Sci. Hung.*, **10**, 227 (1956); *Chem. Abstr.*, **51**, 8666 (1957).

(30) *Cf.* W. Königs, *Ber.*, **10**, 1531 (1877).

(31) *Cf.* P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088 (1921).

(32) *Cf.* H. C. Freeman, R. J. W. LeFevre, J. Northcott, and I. Youhotsky, *ibid.*, 3381 (1952).

(33) *Cf.* R. Escales, *Ber.*, **18**, 893 (1885).

(34) Analysis by Triangle Chemical Laboratories, Chapel Hill, N. C.

(35) Analysis by Micro-Tech Laboratories, Inc., Skokie, Ill.

(36) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

(37) J. A. Zoltewicz and J. F. Bunnett, *J. Amer. Chem. Soc.*, **87**, 2640 (1965).

(38) Obtained by virtue of National Science Foundation Grant GP-5334.

(39) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed, D. C. Heath and Co., Boston, Mass., 1941, p 395.