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Registry No.—1, 274-66-8; 2, 61900-67-2; 3, 61900-68-3; 4, 61900-69-4; 5, 61900-70-7; 6, 61900-71-8; 7, 61900-72-9; 8, 61900-73-0; 9, 61900-74-1; 10, 61900-75-2; 17, 61900-76-3; 18, 61900-77-4; 19, 61900-78-5; 20, 61900-79-6; 21, 61915-57-9; 22, 61900-80-9; 23, 61900-81-0; 24, 61900-82-1; 25, 61900-83-2; 26, 61900-84-3; 27, 61900-85-4; 28, 61900-86-5; 29, 61900-87-6; 30, 61900-88-7; 31, 61900-89-8; 32, 61900-90-1; 33, 61900-57-0; 34, 61900-58-1; 35, 61900-59-2; 37, 61900-60-5; 38, 61900-61-6; 39, 61900-62-7; 40, 61900-63-8; 41, 61900-64-9; 2-methylpyrimidine, 5053-43-0; ethyl bromopyruvate, 70-23-5; 8-azaindolizine-2-carboxylic acid K, 61900-65-0; 8-azaindolizine-2-carboxylic acid HCl, 61900-66-1; bromoacetone, 598-31-2; 3-bromo-2-butanone, 814-75-5; phenacyl bromide, 70-11-1; 2,4-dimethylpyrimidine, 14331-54-5; 4-methoxy-2-methylpyrimidine, 7314-65-0; 4-hydroxy-2-methylpyrimidine, 19875-04-8; DAD, 762-42-5.

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Reactions of Aryl Diazonium Salts and Arylazo Alkyl Ethers in Basic Alcoholic Solvents.[1] Steric and Mechanistic Studies

Christopher S. Anderson and Trevor J. Broxton*

Department of Organic Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

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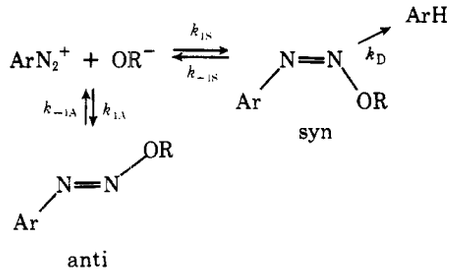
Kinetic studies of the rate of ionization of halo-substituted *anti*-arylazo alkyl ethers show that the enhanced reactivity of the 2-halo substituted compounds is a function of the size of the halogen atom concerned. It is concluded that this effect is a steric effect. Comparison of the effects of *o*- and *p*-nitro groups on the rates of ionization of *syn*- and *anti*-arylazo alkyl ethers leads to the conclusion that the transition state for ionization of the syn ether is later than the transition state for ionization of the anti ether. This interpretation is consistent with the observed solvent and substituent effects on the two processes. Solvent and substituent effects on the initial partitioning of the diazonium salt are also explained on the basis of this interpretation. For carbanionic dediazoniation of the 2-chloro and 3-chloro compounds the species undergoing dediazoniation is shown to be the *syn*-arylazo alkyl ether.

Dediazoniation of aryldiazonium salts in basic methanolic solution can occur by either a free-radical or a carbanionic mechanism.[2] The mechanism depends on the base concentration[2] and on the substituent on the aromatic ring.[2] As the electron-withdrawing power of the substituent on the aromatic ring is increased (4-CH_3O → 2,4-Cl_2) the amount of anionic reaction increases, but a further increase in the electron-withdrawing power of the substituent (4-NO_2) causes a complete reversion to the radical mechanism.[2] In the case of the 4-nitro substituted compound it has been shown[1] that the processes occurring on dissolving the diazonium salt in basic methanol are as in Scheme I.

Scheme I



These reactions occur in three distinct stages. Phase 1 involves partitioning of the diazonium ion between the *syn*- and *anti*-arylazo alkyl ethers. This occurs extremely rapidly and Ritchie[3] has estimated a rate constant for production of the syn ether at 23 °C in methanol ($k_{1S} = 3 \times 10^8\ M^{-1}\ s^{-1}$), and also an equilibrium constant ($K = k_{1S}/k_{-1S} = 5.6 \times 10^7\ M^{-1}$). A small fraction of *anti*-arylazo alkyl ether is also produced[1] and the rate constant, $k_{1A} = 2.5 \times 10^6\ M^{-1}\ s^{-1}$. Thus the ratio $k_{1S}/k_{1A} = 120$.

Phase 2 involves a slower partitioning of the syn ether between decomposition and protection. Protection involves conversion of the syn ether into the anti ether via the free diazonium ion.

$$k_p = (\text{syn} \rightarrow \text{anti})$$

$$k_p = k_{-1S}\frac{k_{1A}}{k_{1A} + k_{1S}} \quad (1)$$

In the case of the *p*-nitro compound, which decomposes via a free-radical mechanism, it is the syn ether that actually undergoes decomposition, not the free diazonium ion[1] (k_D = syn → ArH).

Phase 3 involves the slow dediazoniation of the anti ether via the free diazonium ion and the syn ether. The rate of this process (k_ψ, i.e., anti → ArH) is defined as follows.

Table I. Rate Constants (k_{-1A}) for the Ionization of *anti*-Arylazo Alkyl Ethers in Basic Alcoholic Solvents in the Presence of α-Naphthol[a]

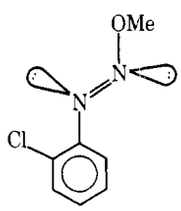
Substrate[b]	10^4k_{-1A}, s^{-1} (temp, °C) Methanol (R = CH_3)	Registry no.	Ethanol (R = C_2H_5)	Registry no.
2-FC_6H_4N=NOR	24.2 (15)	62375-77-3		
3-FC_6H_4N=NOR	16.8 (15)	62375-78-4		
4-FC_6H_4N=NOR	322. (15)	62375-79-5	10.3 (15)	62375-80-8
2-ClC_6H_4N=NOR	36.4 (15) 118 (30)[c]	58692-57-2	1.25 (15) 5.8 (30)	62375-81-9
3-ClC_6H_4N=NOR	14.4 (15)	58692-55-0	0.59 (15)	62375-82-0
4-ClC_6H_4N=NOR	75.5 (15)	58692-56-1	3.18 (15)	62375-83-1
2-BrC_6H_4N=NOR	27.1 (15)	62375-84-2		
3-BrC_6H_4N=NOR	16.5 (15)	62375-85-3		
4-BrC_6H_4N=NOR	64.2 (15)	62375-86-4		
2-IC_6H_4N=NOR	49.7 (15)	62375-87-5		
3-IC_6H_4N=NOR	27.5 (15)	62375-88-6		
4-IC_6H_4N=NOR	86.7 (15)	62375-89-7		
2-$NO_2C_6H_4N$=NOR	2.63 (30)	62375-90-0		
4-$NO_2C_6H_4N$=NOR	2.9[c] (30)	16020-14-7	0.19[c] (30)	58692-48-1

[a] Base concentration 0.1 M. α-Naphthol concentration 0.01–0.02 M. Rate constants were independent of α-naphthol concentration within this range. [b] Substrate concentration 2–3 × 10^{-5} M. [c] Reference 1.

$$k_\psi = k_{-1A}\left(\frac{k_{1S}}{k_{1A} + k_{1S}}\right)\left(\frac{k_D}{k_P + k_D}\right) \quad (2)$$

It is of interest to determine what species undergoes dediazoniation for a reaction proceeding by a carbanionic mechanism. It is also of considerable interest to measure directly k_{-1S} since this in conjunction with k_P would provide an independent method to measure the ratio k_{1S}/k_{1A} using eq 1, and allow us to determine substituent and solvent effects on this ratio.

It has also been observed[1] that the rate of ionization of the anti ether (k_{-1A}) for the 2-chloro compound was faster than expected on purely electronic grounds. This rate acceleration has been attributed to a steric effect in which a nonbonded interaction between the chlorine and the lone pair on either the α nitrogen (structure **1**) or β nitrogen (structure **2**) provides



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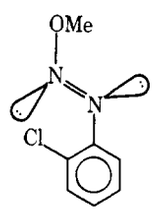

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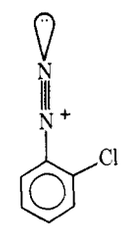
a driving force for the ionization. To confirm the steric nature of this effect, it is of interest to see if the magnitude is dependent on the size of the ortho substituent.

Discussion

Steric Effects of Ortho Substituents on k_{-1A} Values. Rate constants (k_{-1A}) for the ionization of *anti*-arylazo alkyl ethers are in Table I. For all of the halogen derivatives it can be seen that the rate of reaction for the ortho isomer is greater than that of the meta isomer. Since the electron-withdrawing inductive effect of the halogens would be much greater from the ortho position than from the more distant meta position, the rate of reaction for the ortho compounds should be less than that for the meta compounds. Indeed this effect is seen both in the hydrolysis of the corresponding halo-substituted cumyl chlorides[4] and in the basicity of the halo-substituted anilines.[5]

Thus the ortho-substituted arylazo methyl ethers must be experiencing some other effect to produce these results. This has been postulated as being a steric acceleration caused by a nonbonded interaction between the ortho halogen and the lone pair of either the α or β nitrogen.[1] This steric interaction would be less in the transition state for this reaction because of the linear arrangement of the nitrogen atoms in the product diazonium ion (**3**). If this is a steric acceleration then the



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magnitude should be dependent on the size of the halogen atom at the ortho position.

To enable us to get a quantitative measure of this steric acceleration for each halogen atom it is necessary to isolate the steric acceleration from other steric effects and from electronic effects of the substituents. To do this the ortho/para rate ratios for the ionization of the *anti*-arylazo methyl ethers are compared with the ortho/para rate ratios for the cumyl chloride solvolyses (Table II).

It can be seen that the ortho/para rate ratios for the hydrolyses of the fluoro, chloro, and bromo substituted cumyl chlorides are quite similar. This is the result of a balance[4] between the inductive effects of the ortho halogen groups (F > Cl > Br) and steric inhibition of resonance of the ortho halogen groups (Br > Cl > F).

For the ionization of the *anti*-arylazo methyl ethers, however, the ortho/para rate ratio for the fluoro compounds is much less than for the other halogens. This is because of the enhanced reactivity of the ortho chloro, bromo, and iodo compounds. Thus the steric acceleration for the ortho halogen substituted compounds is reflected in the ratio

$$\frac{\text{ortho/para rate ratio} - \text{anti ethers}}{\text{ortho/para rate ratio} - \text{cumyl chlorides}}$$

It can be seen that as the size of the halogen atom is increased (van der Waals' volumes) (F → Cl) then the steric acceleration becomes apparent. The steric acceleration is, however, lessened in the bromo and iodo compounds compared to the chloro compound possibly because of the in-

Table II. Comparison of Steric Effects in the Ionization of *anti*-Arylazo Methyl Ethers and the S_N1 Solvolyses of Cumyl Chlorides[a]

Halogen	Bond length[b] (C–halogen), Å	van der Waals[c] volume, cm^3/mol	Solvolysis of cumyl chlorides ortho/para ratio	Ionization of *anti*-arylazo methyl ethers ortho/para ratio	Ortho/para anti ethers / ortho/para cumyl chlorides
F	1.41	5.8	0.0234	0.0751	3.2
Cl	1.76	12.0	0.0258	0.482	18.7
Br	1.91	15.1	0.0292	0.422	14.5
I	2.10	19.6	0.0452	0.573	12.7

[a] Reference 4. [b] Reference 6. [c] Reference 7.

creased carbon–halogen bond length, but it is still considerably greater than for the fluoro compound.

In the cumyl chloride solvolysis, the planar intermediate would experience as much steric interaction between the side chain and an ortho substituent as the reactant. Thus there is no relief of steric strain on going from ground state to transition state for that reaction and no steric acceleration is observed.

Steric Effects of Ortho Substituents on k_P/k_D Ratios. From k_{-1A} and k_ψ values it is possible to derive k_P/k_D ratios for phase 2 reactions using eq 2. Since $k_{1S} \gg k_{1A}$ eq 2 can be simplified to give

$$k_\psi = k_{-1A}\left(\frac{k_D}{k_P + k_D}\right) \quad (3)$$

which on rearrangement gives

$$\frac{k_P}{k_D} = \left(\frac{k_{-1A}}{k_\psi} - 1\right) \quad (4)$$

From Table III we can see that k_P/k_D ratios are high for the ortho chloro, bromo, and iodo compounds when compared to the other halo derivatives. This is probably due to a steric acceleration in k_{-1S} values for the ortho compounds similar to the steric effects on the k_{-1A} values. It is obviously of interest to measure the rate of ionization of the *syn*-arylazo alkyl ethers (i.e., k_{-1S}).

Measurement of k_{-1S} Values. Since the rate of ionization of the *syn*-arylazo alkyl ethers (k_{-1S}) is very rapid, it is necessary to use a stopped-flow technique at 0 °C to follow this reaction. In addition it is only currently possible to measure k_{-1S} for compounds containing strong electron-withdrawing substituents (e.g., NO_2, CN, and CF_3) because of the manipulations that are required.

Cold solutions of the aryl diazonium salt and methoxide ion are rapidly mixed and are added to one of the syringes of the stopped-flow machine. The other syringe contains α-naphthol solution. On triggering the stopped-flow machine, the solutions are mixed in the reaction chamber and k_{-1S} is obtained from the rate of production of the azo dye **6**. It is necessary to premix the diazonium salt and methoxide ion solutions to ensure that there is no free diazonium ion present when the α-naphthol is added. As soon as the *syn*-arylazo alkyl ether is ionized, the product, i.e., the diazonium ion, is trapped by the α-naphthoxide ions in solution. The factor limiting measurement of k_{-1S} rates is that for some diazonium salts the phase 2 reactions are so rapid that by the time the solution is mixed with the naphthol solution all the syn ether has been converted either to dediazoniation product or to anti ether.

Comparison of k_{-1S} and k_{-1A} Values. From Table IV it can be seen that k_{-1S} for the *o*-nitro compound is much less than for the *p*-nitro compound. However, k_{-1A} values for the *o*- and *p*-nitro compounds (Table I) are very similar.

It is difficult to explain why k_{-1S} for the ortho compound is less than k_{-1S} for the para compound when k_{-1A} is so similar for these compounds. In fact molecular models show that steric interactions with ortho substituents are more serious in the ground states for the *syn*- than for the *anti*-arylazo alkyl ethers and we would expect k_{-1S} (ortho NO_2) > k_{-1S} (para NO_2) due to steric acceleration. This effect is being overshadowed by some more important effect.

Table III. Rate Constants (k_ψ) for the Dediazoniation of *anti*-Arylazo Alkyl Ethers in Basic[a] Alcoholic Solvents at 15 °C and k_P/k_D Ratios Derived from k_{-1A} and k_ψ

Substrate[b]	$10^4 k_\psi$, s^{-1} (k_P/k_D): Methanol (R = CH_3)	Ethanol (R = C_2H_5)
2-FC_6H_4N=NOR	2.22 (9.9)	
3-FC_6H_4N=NOR	1.91 (7.8)	
4-FC_6H_4N=NOR	14.9 (20.7)	6.84 (0.56)
2-ClC_6H_4N=NOR	1.15 (30.7)	0.83 (0.5)
	8.04[c] (13.8)	
3-ClC_6H_4N=NOR	1.60 (8.0)	0.59 (<0.1)
	12.3[c] (3.6)	
4-ClC_6H_4N=NOR	4.20 (17.0)	
	34.4[c] (4.9)	
2-BrC_6H_4N=NOR	1.35 (19.0)	
3-BrC_6H_4N=NOR	2.16 (6.6)	
4-BrC_6H_4N=NOR	4.54 (13.1)	
2-IC_6H_4N=NOR	1.25 (38.8)	
3-IC_6H_4N=NOR	3.58 (6.7)	
4-IC_6H_4N=NOR	4.31 (19.1)	
2-$NO_2C_6H_4N$=NOR	0.526[c] (4.0)	

[a] Base concentration 0.1 M. [b] Substrate concentration 2–3 × 10^{-5} M. [c] Temperature 30.0 °C.

An explanation that we favor is that for ionization of the *syn*-arylazo alkyl ether there is a later transition state with more charge development than for the ionization of the *anti*-arylazo alkyl ether. Thus for the syn ether the strong electron-withdrawing inductive effect of the *o*-nitro group caused a large reduction in the rate of ionization compared to the *p*-nitro compound. For ionization of the anti ether the early transition state with much less charge development is less sensitive to the inductive effect of the *o*-nitro group.

Some support for this explanation is available from the work of Zollinger.[8] Zollinger states that for reactions of diazonium salts with nucleophiles, if the transition state is reactant-like (early) then nucleophilic attack in the syn configuration is preferred. Similarly if the transition state is product-like (late) then nucleophilic attack in the anti configuration is preferred. By the law of microscopic reversibility therefore, ionization of the syn ether must have a late transition state and ionization of the anti ether must have an early transition state (Scheme II).

Substituent Effects on k_{-1S} and k_{-1A}. The above mechanistic conclusions depend on the relative electronic effects of *p*- and *o*-nitro groups on k_{-1A} and k_{-1S}. To exclude

Table IV. Rate Constants (k_{-1S}) for the Ionization of *syn*-Arylazo Alkyl Ethers in Basic[a] Alcoholic Solvents in the Presence of α-Naphthol[a] at 0 °C

Substrate[b]	10^4k_{-1S}, s^{-1} Methanol (R = CH_3)	Registry no.	Ethanol (R = C_2H_5)	Registry no.
2-$NO_2C_6H_4N$=NOR	910	62375-91-1	6.20	62375-92-2
4-$NO_2C_6H_4N$=NOR	9800	58909-76-5	120	62375-93-3
4-CNC_6H_4N=NOR	26 000	62375-94-4		
4-$CF_3C_6H_4N$=NOR	107 000	62375-95-5		

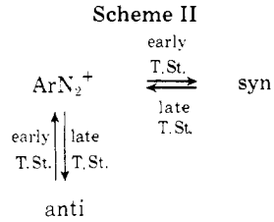
[a] Base concentration 0.1 M. α-Naphthol concentration 0.01 M. [b] Substrate concentration 8×10^{-5} M.

Table V. Rate Constants at 0 °C for the Phase 2 Reactions in Basic Methanol and Ethanol[a]

Substrate	10^4k_P, s^{-1} Methanol	Ethanol	10^4k_D, s^{-1} Methanol	Ethanol
2-$NO_2C_6H_4$-N=NOR	3.6		3.2	
4-$NO_2C_6H_4$-N=NOR	41.3	2.0	16.7	22.3

[a] Base concentration 0.1 M. Substrate concentration $2\text{–}3 \times 10^{-4}$ M.

Scheme II



alternative steric arguments the magnitude of the effects of para substituents on k_{-1A} and k_{-1S} was studied.

From Table IV and Figure 1, it can be seen that k_{-1S} is more sensitive to substituent effects than k_{-1A}.[1] This supports the interpretations based on the results for the nitro compounds.

Because of the problems associated with measurements of k_{-1S} the results for the 4-CN (±20%) and 4-CF_3 (±8%) compounds are not as dependable as those for the 4-NO_2 (±4%) compound.

Solvent Effects on k_{-1S} vs. k_{-1A}. If the transition state for ionization of the *syn*-arylazo alkyl ether is later (i.e., has a greater charge) than that for ionization of the *anti*-arylazo alkyl ether, then this should be reflected by the solvent effects on the two processes.

The effect of increasing the ion solvating power of the solvent by changing the solvent from ethanol (dielectric constant 24.2) to methanol (dielectric constant 31.5) is to increase k_{-1A} 15 times for the 4-nitro compound,[1] whereas the solvent effect on k_{-1S} is 82 (4-nitro) and 147 (2-nitro). These solvent effects are consistent with the transition states postulated above.

Solvent and Substituent Effects on Partitioning of the Diazonium Ion (k_{1S}/k_{1A}). Rate constants (k_P and k_D) for the phase 2 reactions of the *syn*-arylazo alkyl ethers are in Table V. From k_{-1S} and k_P values it is possible to calculate k_{1S}/k_{1A} ratios using eq 1.

For the *p*-nitro compound at 0 °C k_{1S}/k_{1A} = 237 in methanol and k_{1S}/k_{1A} = 54 in ethanol. For the *o*-nitro compound at 0 °C in methanol k_{1S}/k_{1A} = 252. That is, the syn ether is more favored in methanol, the more polar solvent. This is reasonable since the transition state to produce the syn isomer is early (i.e., high charge density) whereas that for the anti ether is later (i.e., lower charge density). Consequently, the more polar solvent favors the transition state with the least

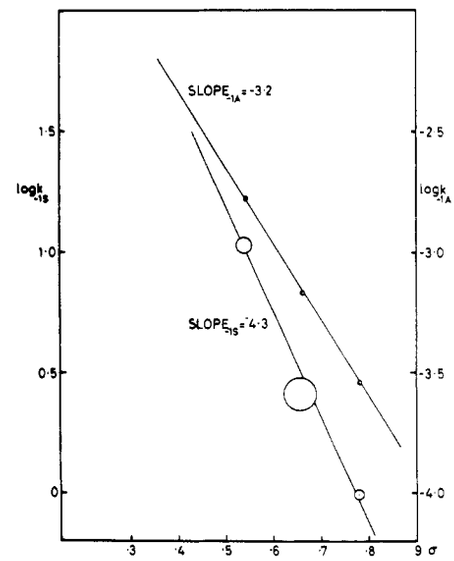


Figure 1.

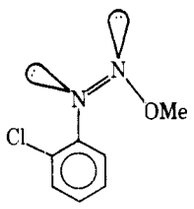
charge dispersal, which is consistent with the Hughes–Ingold solvent theory.[6]

The value of k_{1S}/k_{1A} for the 4-nitro compound (237) compares favorably with the previously obtained value (120), which was calculated using published data for k_P[9] and k_{-1S},[3] when you consider that the accuracy of Ritchie's rate (k_{1S}) and equilibrium ($K = k_{1S}/k_{-1S}$) constants is ca. 50% and that the k_P value was obtained by extrapolation to 23 °C of rate constants obtained between −16.4 and 2.5 °C.

The k_{1S}/k_{1A} ratios for the *p*-nitro compound (237) and the *o*-nitro compound (252) are very similar. It appears as if there is no substituent effect operating. However, it is quite feasible that the observed results are a composite of two opposing effects, i.e., a steric effect of the *o*-nitro group which may increase k_{1S}/k_{1A} since steric effects would be more severe in the reaction with the later transition state (production of the anti ether) and an electronic effect of the *o*-nitro group which may decrease k_{1S}/k_{1A} since the more electron-withdrawing *o*-nitro group should favor the reaction with the most charge dispersal (production of the anti ether).

Steric Effects on k_{-1A} vs. k_{-1S}. Since there is a later transition state (more bond breaking) for ionization of the syn ether than for ionization of the anti ether we would expect the steric effect of ortho halogens to be more pronounced for ionization of the syn ethers, because there is greater release of steric interactions on moving from reactant to transition state. In addition molecular models show that steric effects are more serious in the reactant ground state for the syn ethers (structures **4** and **5**) than for the anti ethers (structures **1** and **2**).

A result of the steric acceleration of k_{-1S} by ortho halogen groups is an increase in k_P which causes an increase in the



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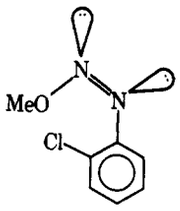

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k_P/k_D rate ratio for the ortho-substituted compounds compared to the corresponding meta- and para-substituted compounds (Table III). Variation of k_D cannot, however, be ruled out as an additional factor in the large k_P/k_D rate ratios for these compounds.

For the halo compounds the ortho/para ratio of k_P/k_D is consistently greater than the ortho/para ratio of k_{-1A}, i.e., the steric effect is more significant in k_{-1S} than k_{-1A}.

What Species Is Undergoing Dediazoniation? For the *p*-nitro compound it was concluded that the syn ether was the species actually undergoing dediazoniation.[1] This decomposition occurs by a free-radical mechanism. An example of a compound for which the mechanism of decomposition is ionic is the 2-chloro compound.[2]

For the *p*-nitro compound it was found that k_P, which involves ionization of the syn ether, was greatly reduced on solvent transfer (MeOH → EtOH), but k_D was slightly increased. The net result of this was a large reduction of the k_P/k_D ratio on transfer from methanol (k_P/k_D = 2.5) to ethanol (k_P/k_D = 0.09) at 0 °C.

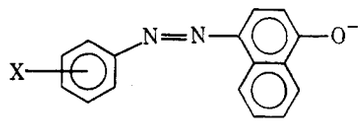
If the free diazonium ion is the species being dediazoniated then we would expect k_D also to be greatly reduced on solvent transfer and thus we would expect the ratio k_P/k_D to be relatively independent of the solvent.

From Table III it is clear that for both the 2-chloro and 3-chloro compounds the k_P/k_D ratio is greatly reduced on solvent transfer. Thus we conclude that in the carbanionic mechanism the species undergoing dediazoniation is also the *syn*-arylazo alkyl ether.

Experimental Section

Diazonium salts were prepared as described previously.[1] Alcoholic solvents (MeOH, EtOH) were dried by distillation from the corresponding magnesium alkoxide.[10]

Kinetic Methods. A. Kinetics in the Presence of α-Naphthol. The technique used to measure the rate of ionization of the anti ethers (k_{-1A}) has been described.[1] To measure the much faster rate of ionization of the syn ethers (k_{-1S}) the above method was adapted for use of the stopped-flow apparatus. Solutions of diazonium salt in acidic solution (0.004 M toluenesulfonic acid), α-naphthol, and sodium alkoxide were all cooled to 0 °C. The α-naphthol solution (0.02 M) was placed into one of the syringes of the stopped-flow apparatus which was also equilibrated to 0 °C. Then the diazonium salt solution (2×10^{-4} M, 4 mL) and sodium methoxide solution (1 M, 1 mL) were rapidly mixed and added to the other syringe of the stopped-flow apparatus. The stopped-flow apparatus was triggered, equal aliquots from each syringe were mixed, and the rate of production of the azo dye **6** was followed spectrophotometrically.



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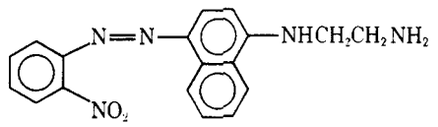
B. Kinetics in the Presence of *N*-1-Naphthylethylenediamine (NED). At 0 °C the kinetics of the phase 2 reactions (i.e., k_P and k_D) were followed as described previously[1] except that the azo dye produced from the *o*-nitro compound and NED (7) was not stable in



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acidic solution. Thus after sampling the reaction mixture and coupling in acidic NED, the mixture was made basic with a fixed amount of sodium methoxide. In basic methanol the azo dye **7** was quite stable.

C. Kinetics Using Direct UV Analysis (k_ψ). The rate of dediazoniation of the anti ether (k_ψ = anti → ArH) was measured by direct UV analysis as described previously.[1]

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