responsible for the different behavior between the thiophene and benzene substrates because it would possibly cause different selectivities, but not an inverted trend of reactivity.

Through-conjugation of the methoxyl with the electron-withdrawing substituents is expected to enhance the stabilization of the initial substrates and could in principle be responsible for the low reactivity of the position 1 of TNA.[3] However, the relatively high rates of reaction of the methoxy thiophenes can hardly be rationalized by this view; in fact, an even stronger rate-depressing effect than in the benzene series is anticipated on the ground of a substantially lower steric inhibition of resonance effect.

The decrease in reactivity observed in going from 2,4-dinitro-5-methoxythiophene to the cyanonitromethoxythiophenes, and from 2,4-dinitrothiophene to 4-cyano-2-nitrothiophene, can be safely attributed to the lower electron-attracting properties of the cyano group. Surprisingly, no large rate decrease is observed in going from TNA to 2-cyano-4,6-dinitroanisole and to 2,6-dicyano-4-nitroanisole (Table II). The change in polar effect is clearly offset here by some other factor. We propose that a major factor for the observed difference in the two systems is the different geometry of the five- and six-membered rings. In benzene derivatives an ortho-substituted bulky group is expectedly more subject to steric inhibition of resonance than in thiophene compounds. In particular, in TNA the steric interaction between the methoxyl and the flanking nitro groups will prevent the attainment of full coplanarity of these groups with the ring.[18] Furthermore, rotation of one or more groups out of the ring plane may increase the F-strain on the approach of the nucleophile to the methoxyl-bearing reaction center. This effect seems to be even more important than that of steric inhibition of resonance, since the attack to the position 3 of TNA (k, at 25 °C, in CH_3OH = 950 l. mol^{-1} s^{-1})[1] is only nearly one order of magnitude slower than the formation rate of **3**. Steric hindrance is probably relieved in the adduct, owing to the change in hybridization of the carbon atom at the reaction center. A transition state not too closely resembling the product may be envisaged in order to allow for the different steric requirements of adduct 1 and the transition state leading to it. The substitution of a nitro group with a less bulky, linear cyano group brings about a decrease of steric hindrance at the reaction center, keeping the reactivity of position 1 of 2-cyano-4,6-dinitroanisole at a level comparable to that of position 1 of TNA, in spite of the smaller electron-withdrawing power of one of the substituents.

Registry No.—**4**, 42137-23-5; **5**, 49620-82-8; **6**, 58703-24-5; **7**, 42133-96-0; **8**, 49796-96-5; **9**, 58702-90-2; 3-cyanothiophene, 1641-09-4; 2-cyano-5-methoxythiophene, 58703-25-6; 2-formyl-5-methoxythiophene, 35087-46-8; nitric acid, 7697-37-2; 2-bromo-3-cyano-5-nitrothiophene, 58703-24-5.

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Elucidation of the Role of *syn*- and *anti*-Arylazo Alkyl Ethers in the Dediazoniation of Aryldiazonium Salts in Basic Alcoholic Solvents

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From kinetic studies of ionization rates of *anti*-arylazo alkyl ethers in methanol and ethanol and of dediazoniation rates in both solvents, it is concluded that when an aryldiazonium ion is dissolved in basic methanol a partitioning between *syn*- (k_{1S}) and *anti*- (k_{1A}) arylazo methyl ether occurs (k_{1S}/k_{1A} = 120 for Ar = 4-NO_2Ph) and subsequent protection of the diazonio function (i.e., conversion of *syn*- into *anti*-arylazo ether) occurs via an ionization–recombination pathway ($k_{-1S} \rightarrow k_{1A}$). Decomposition of *p*-nitrobenzenediazonium ion occurs from the *syn*-arylazo ether ($k_{1S} \rightarrow k_{1D}$) presumably by the electron transfer mechanism of Bunnett. Dediazoniation of the anti *p*-nitrophenylazo ether also occurs from the *syn*-arylazo ether which is formed via prior ionization of the anti ether ($k_{-1A} \rightarrow k_{1S} \rightarrow k_D$). Steric acceleration was observed for some reactions of the 2-chlorobenzenediazonium system (k_{-1A} and k_{-1S}).

The decomposition of aryldiazonium salts (ArN_2^+) in methanolic solution was studied by DeTar and co-workers almost 20 years ago.[1,2] It was found that in neutral or acidic methanol the major product was the corresponding anisole ($ArOCH_3$) presumably formed via a carbonium ion intermediate. In weakly basic solution (sodium acetate) the yield of anisole was much less and the major products were reduction products (ArH) and biaryls (Ar–Ar). Since the reaction in basic solution was affected by the presence of oxygen it was concluded that the dediazoniation ($ArN_2^+ \rightarrow$ ArH) reaction was free radical in nature.

Bunnett subsequently looked at reactions of aryldiazonium salts in more strongly basic solution (MeO^-/MeOH) and found that dediazoniation yields were high enough to be of

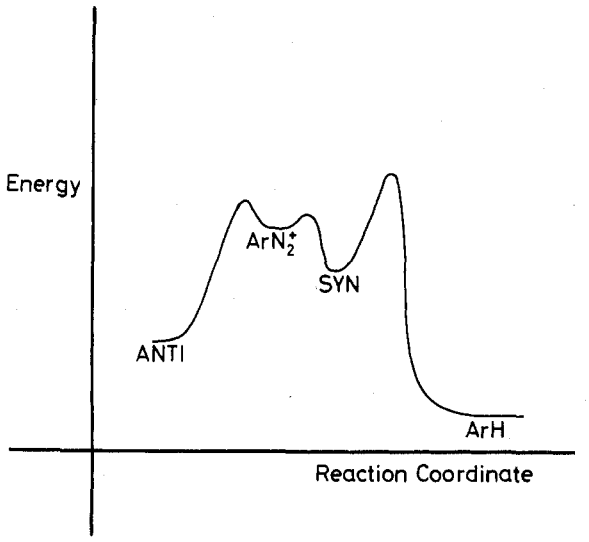
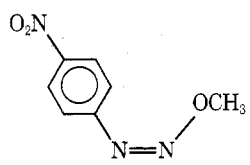


Figure 1. Free energy diagram for the reactions of the *p*-nitrobenzenediazonium salt, the *syn*- and the *anti*-arylazo methyl ethers in basic methanol.

preparative interest,[3] that the mechanism could be either free radical or carbanionic in nature,[4] and that the mechanism depended on the base concentration[4] and on the substituent on the aromatic ring.[4] It was found that 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 increased but that further increase in the electron-withdrawing power of the substituent (4-NO_2) caused a complete reversion to the radical mechanism.[4] It has since been reported that the 4-acetyl substituent also strongly favors the radical mechanism[5] indicating that the sudden change of mechanism is probably the result of strong electron-withdrawing substituents rather than a specific (e.g., radical anion)[6,7] effect of the 4-nitro substituent.

Ritchie[8] has shown that "*p*-nitrophenyl diazonium ions in buffered solutions of methoxide ion in methanol rapidly reaches an equilibrium with a stoichiometry of 1 mol of methoxide ion and 1 mol of diazonium ion". He concluded that the product of this rapid reaction was the *syn*-*p*-nitrophenylazo methyl ether (**1**), a conclusion supported by Zollinger.[9]



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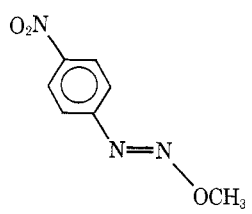
Bunnett and co-workers[10] have reported production of the *anti*-*p*-nitrophenylazo methyl ether (**2**) in alkaline methanol



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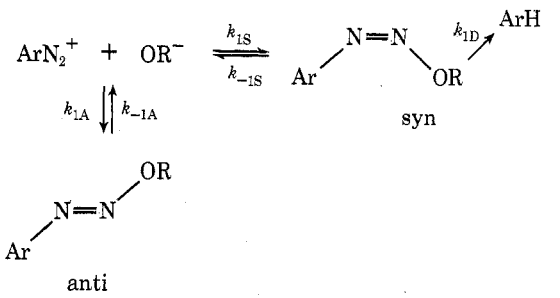
and conclude that the anti isomer is formed along with some dediazoniation ($PhNO_2$) product from the initially formed *syn*-arylazo methyl ether. However, it is still unclear whether conversion of the *syn*- into the *anti*-arylazo methyl ether involves preliminary dissociation into diazonium ions or bond (N=N) rotation and whether the dediazoniation product is produced from the *syn*-arylazo methyl ether or from free diazonium ions. The *anti*-arylazo methyl ether subsequently also produces dediazoniation product at a much slower rate of reaction,[10] but the role of free diazonium ions and the *syn*-arylazo methyl ether in this reaction is also unclear. This work was designed in an attempt to clarify these questions for the *p*-nitro compound.

Discussion

The most complete mechanistic scheme relating the role of the free diazonium ion, the *syn*-arylazo alkyl ether, and the *anti*-arylazo alkyl ether in the decomposition of diazonium salts in basic alcohol solvents is shown below.



The relative energies of these species and the transition states for their interconversion are shown in Figure 1.

Phase 1. Partitioning of Free Diazonium Ion. According to Ritchie the first interaction of a diazonium ion on dissolution in basic methanol is a very rapid complexation to form the *syn*-arylazo methyl ether ($k_{1S} = 3 \times 10^8\ M^{-1}\ s^{-1}$ for Ar = 4-NO_2Ph in MeOH at 23 °C). The equilibrium constant ($K = k_{1S}/k_{-1S}$) for this reaction is $5.6 \times 10^7\ M^{-1}$. Consequently the rate of ionization of the *syn*-arylazo methyl ether (k_{-1S}) is $5.4\ s^{-1}$. This stage of reaction ($k_{1S} - k_{-1S}$) can be called phase 1 to clarify later discussion. Obviously with such a high rate constant (k_{1S}) this phase of reaction is essentially complete as soon as the diazonium salt is dissolved. Ritchie assumed that the product of phase 1 was pure syn ether rather than a mixture of syn and anti ethers.

Phase 2. Partitioning of *syn*-Arylazo Ether. This extremely rapid phase 1 is then followed by a rapid partitioning (phase 2) which is complete in 60 s at 30 °C.[10] During this phase of reaction, part of the *syn*-arylazo methyl ether is decomposed to dediazoniation product (ArH) and the remainder is converted into *anti*-arylazo methyl ether (protected). These reactions of the *syn*-arylazo methyl ether can be designated k_D and k_P (protection), respectively, and they are defined as follows:

$$k_D \equiv \textit{syn}\text{-ArN=N—OR} \rightarrow \text{ArH}$$

$$k_P \equiv \textit{syn}\text{-ArN=N—OR} \rightarrow \textit{anti}\text{-ArN=N—OR}$$

(see eq 1)

Rate measurements within the temperature range −16.4 to 2.5 °C have been carried out[10] for the *p*-nitro compound and activation parameters have been calculated from which the rate of k_P and k_D at 23 °C can be calculated. $k_D = 2 \times 10^{-2}\ s^{-1}$ (23 °C) and $k_P = 4.5 \times 10^{-2}\ s^{-1}$ (23 °C). It should be noted that k_P is considerably less than k_{-1S}, the ionization rate of the *syn*-arylazo methyl ether ($k_{-1S}/k_P = 120$).

Phase 3. Decomposition of the *anti*-Arylazo Ether. A subsequent slow reaction (phase 3, rate k_Ψ) then occurs as the *anti*-arylazo methyl ether is dediazoniated ($t_{1/2}$ 30 °C ~ 2 h), where:

$$k_\Psi \equiv \textit{anti}\text{-ArN=N—OR} \rightarrow \text{ArH}$$

(see eq 2, 3)

Table I. Rate Constants (k_{-1A}) for the Ionization of *anti*-Arylazo Alkyl Ethers (2) in Basic Alcoholic [a] Solvents in the Presence of α-Naphthol [b] at 30 °C

		$10^4 k_{-1A}$, s^{-1}	
Registry no.	Substrate	MeOH	EtOH
16020-14-7	4-NO_2-Ph-N=N-OCH_3	2.91[d](3.0)[e]	0.45[d]
58692-48-1	4-NO_2-Ph-N=N-OC_2H_5	1.15[d]	0.19[d]
58692-49-2	4-NO_2-Ph-N=N-OC-$H(CH_3)_2$	0.24[d]	
58692-50-5	3-NO_2-Ph-N=N-OCH_3	2.95[e]	
58692-51-6	4-CN-Ph-N=N-OCH_3	6.81[e]	
58692-52-7	3-CNPh-N=N-OCH_3	8.66[e]	
58692-53-8	4-CF_3-Ph-N=N-OCH_3	16.7[e]	
58692-54-9	3-CF_3-Ph-N=N-OCH_3	17.7[e]	
58692-55-0	3-Cl-Ph-N=N-OCH_3	58.1[e]	
58692-56-1	4-Cl-Ph-N=N-OCH_3	209[e]	
58692-57-2	2-Cl-Ph-N=N-OCH_3	118[e]	

[a] Base concentration in range 0–0.10 M. Rate of reaction independent of base concentration in this range. [b] α-Naphthol concentration 0.01–0.04 M. Rate constants were independent of α-naphthol concentration within this range. [c] Substrate concentration 2–3 × 10^{-5} M. [d] Pure *anti*-arylazo alkyl ether used. [e] Arylazo alkyl ether generated in situ.

If the *anti*-arylazo methyl ether is prepared externally and is added to basic methanol only a slow reaction (phase 3) is observed because there is no free diazonium ion to undergo phases 1 or 2.

Measurement of Ionization Rate (k_{-1A}) of *anti*-Arylazo Ethers. A. Reactions in the Presence of α-Naphthol. In the presence of α-naphthol it is possible to measure the rate of ionization of the *anti*-arylazo alkyl ethers (k_{-1A}). Previous[5] attempts to measure k_{-1A} have been unsuccessful because the coupling agents chosen, i.e., β-naphthol and sodium 1-naphthol-4-sulfonate, are not sufficiently reactive to trap all the diazonium ion without complications arising from side reactions (k_P and k_D). Consequently, results obtained were low and in some cases (*p*-acetyl, *p*-benzoyl) k_{-1A} results were even lower than overall dediazoniation rates (k_Ψ). This is not possible if the k_{-1A} values are reliable since the ionization step (k_{-1A}) is part of the overall decomposition pathway.

α-Naphthol, however, is a much more effective coupling agent and it traps all the product of ionization of the *anti*-arylazo alkyl ether. Bunton[11] has measured the rates of azo coupling of several phenolic compounds with 4-pyridyl diazonium salt in water. For α-naphthol the rate of coupling (k_C = 1.9 × 10^9 M^{-1} s^{-1} at 25 °C) was 100 times faster than that for β-naphthol (k_C = 1.1 × 10^7 M^{-1} s^{-1}). It was found that all the diazonium ion produced by acidification of the *anti*-4-pyridine diazotate was trapped by the naphthol, i.e., the rate of coupling was significantly greater than the rates of possible competing processes.

In our reactions the 4-nitrobenzenediazonium salt should behave similarly to the 4-pyridinediazonium salt and hence the rate of coupling with α-naphthol will be greater than either k_D or k_P. Consequently, the rate of production of azo dye **6** should equal k_{-1A}. Both k_{1S} and k_{-1S} are rapid so that any ArN_2^+ converted to *syn*-arylazo alkyl ether is effectively trapped by the naphthol provided k_C is of similar magnitude to k_{1S} and is significantly greater than k_{1A} (see later) and provided k_D is much less than k_{-1S}.

The rate of reaction is independent of the α-naphthol concentration and this shows that the α-naphthol does not react directly with the *anti*-azo ether but with some product formed from it. We conclude that the naphthol reacts with the free diazonium ion and that the ionization (k_{-1A}) is the rate-determining step.

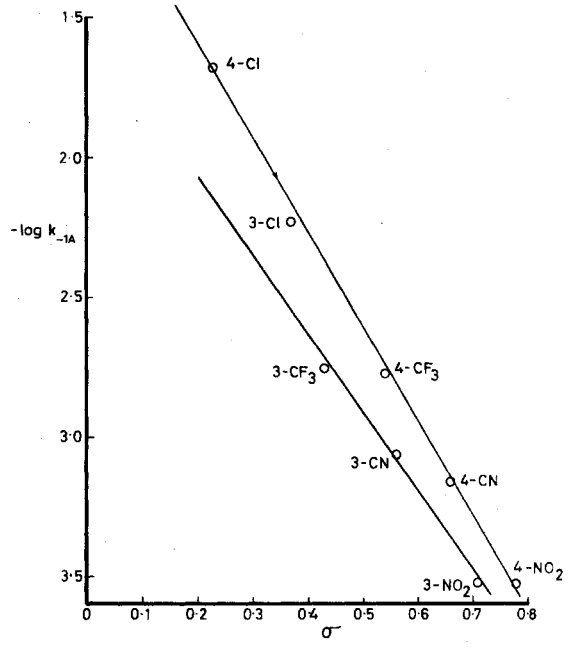


Figure 2. Hammett plot for the ionization of *anti*-arylazo methyl ethers (k_{-1A}) in methanol at 30 °C.

B. Solvent Effects on k_{-1A}. The ionization of *anti*-*p*-nitrophenylazo alkyl ethers is more rapid in methanol than in the less polar ethanol [$k_{-1A}^{MeOH}/k_{-1A}^{EtOH}$ = 6.5 (methyl ether); 6.0 (ethyl ether)] which is predicted by the Hughes–Ingold solvent theory for a reaction producing ions.[12]

C. Substituent Effects on k_{-1A} (Table I). There is a considerable substituent effect on this ionization reaction (Table I) and the reaction rate increases as the electron demand of the substituent is reduced (4-NO_2 → 4-Cl) as would be expected for a reaction in which a positively charge species is being produced. A Hammett plot of log k_{-1A} vs. σ constants for the substituents involved gave two straight lines, one for the meta (ρ = −2.8) and one for the para substituents (ρ = −3.2) (see Figure 2). This suggests that a different blend of resonance and inductive effects is required than that provided by a single substituent constant. A dual parameter treatment[13] of the data would be useful to pinpoint the appropriate blend of resonance and inductive effects but unfortunately we do not have sufficient substituents to make a meaningful attempt at this exercise.[13] We would like some results for electron-donating substituents but here the rate constants are too high to measure by our conventional techniques.

D. Steric Effects of a 2-Chloro Substituent on k_{-1A}. The rate of ionization of the 2-chloro compound is of some interest in that it is faster than that for the 3-chloro compound. Because of the strong inductive effect of a 2-chloro substituent[14] we would expect that ionization of the *anti*-2-chlorophenylazo methyl ether would be slower than that of the 3-chloro isomer where this effect is much less owing to the greater distances involved. Indeed this effect is seen in both the basicity of chloroanilines[15] (i.e., 4-chloro > 3-chloro > 2-chloro) and the solvolysis of the chlorocumyl chlorides.[14] In these examples, the through-space field effect of the 2-chloro substituent overwhelms the electron-releasing resonance effect which would otherwise allow the 2-chloro compound to behave similarly to the 4-chloro compound, i.e., the 2-chloroaniline would be more basic than the 3-chloroaniline and the 2-chlorocumyl chloride would react faster than the 3-chloro compound.

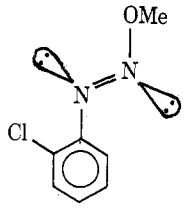
In the ionization of the *anti*-chlorophenylazo alkyl ethers, there must be some additional effect of a 2-chloro substituent to increase the rate of ionization of that compound. Molecular models show that in the planar *anti*-2-chlorophenylazo alkyl

Table II. Rate Constants at 0 °C for the Phase 2 Reactions of *p*-Nitrobenzenediazonium Tetrafluoroborate in Basic Methanol and Ethanol [a]

	$10^4 k_P$, s^{-1}	$10^4 k_D$, s^{-1}
MeOH	41.3	16.7
EtOH	2.0	22.3

[a] Substrate concentration 5×10^{-4} M; base concentration 0.1 M.

ethers there is a strong nonbonded interaction between the chlorine and the lone pair on the α nitrogen in structure **3** and between the chlorine and the lone pair on the β nitrogen in structure **4**. This steric interaction provides a driving force to



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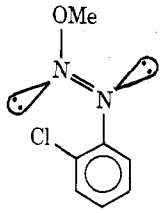

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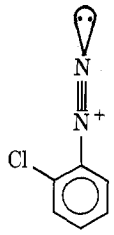
accelerate the rate of ionization of the 2-chlorophenylazo ether that is not present in the 3-chloro isomer. The product diazonium ion (**5**) is sterically less crowded because of the linear



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arrangement of bonds. Further work on this effect is being carried out at present.

E. Effect of Alkyl Group on k_{-1A} (Table I). The ionization rate (k_{-1A}) for several *p*-nitrophenylazo alkyl ethers was measured in both methanol and ethanol. The reactivity order Me > Et > *i*-Pr applies in methanol and in ethanol Me > Et. The isopropyl ether reacted too slowly to measure in ethanol. The decrease in reactivity in the above order probably reflects increasing basicity of the leaving groups[16] and hence increasing N–O bond strength.

Rate Measurements at 0 °C. Phase 2 Reactions k_P and k_D. Mechanism of Syn-Anti Interconversion. If reactions are carried out at 0 °C, it is possible[10] to measure the rate constants for the protection and decomposition steps involved in phase 2. This was done for the *p*-nitrobenzenediazonium salt in both methanol and ethanol (Table II). It was found that the ratio of protection to decomposition was much larger in methanol (k_P/k_D = 2.2) than in ethanol (k_P/k_D = 0.1). This change in ratio was found to be the result of a large reduction in the rate of protection in ethanol. The rate of decomposition was slightly greater in ethanol than methanol.

It will be noted that the solvent effect on protection rate (k_P^{MeOH}/k_P^{EtOH}) is 20 whereas the relative rates of ionization of the *anti-p*-nitrophenylazo methyl ether in methanol and the ethyl ether in ethanol is 15.3. This solvent effect on the rates of these two reactions is very illuminating concerning the mechanism of the protection step. The protection step involves conversion of the *syn*-azo ether into the *anti*-azo ether but the actual mechanism is unknown. As mentioned in the introduction, two possibilities are firstly preliminary dissociation and recomplexation to give *anti*-azo ether or secondly a (N=N) bond rotation from syn to anti compound. A third possibility[17] involves nitrogen inversion by way of an sp-hybridized transition state. The solvent effect on protection rate is strong evidence to support ionization–recomplexation (i.e., $k_{-1S} \rightarrow k_{1A}$) as the mechanism of protection with ionization as the rate-determining step. Hence there is a similarity between k_{-1A} and the protection step since both involve ionization of an arylazo ether as the rate-determining step and consequently have similar solvent effects on rate. It is difficult to explain the solvent effect on protection rate in terms of N=N bond rotation or nitrogen inversion.

Table III. Rate Constants (k_Ψ) for the Dediazoniation of Aryldiazonium Salts and *anti*-Arylazo Alkyl Ethers in Basic [a] Alcoholic Solvents at 30.0 °C

		$10^4 k_\Psi$, s^{-1}	
Registry no.	Substrate	MeOH	EtOH
	$4\text{-}NO_2\text{-}Ph\text{-}N{=}N\text{-}OCH_3$	1.19[b,c]	0.43[c]
	$4\text{-}NO_2Ph\text{-}N{=}N\text{-}OC_2H_5$	0.60[c]	0.17[c]
16278-29-8	$3\text{-}NO_2PhN_2^+$	1.28[b]	
19262-72-7	$4\text{-}CNPhN_2^+$	2.67[c]	
30928-21-3	$3\text{-}CNPhN_2^+$	2.35[c]	
46061-31-8	$4\text{-}CF_3PhN_2^+$	2.25[c]	
35665-28-2	$3\text{-}CF_3PhN_2^+$	3.83[c]	
17333-85-6	$4\text{-}ClPhN_2^+$	34.4[c]	
17333-84-5	$3\text{-}ClPhN_2^+$	12.3[c]	
17333-83-4	$2\text{-}ClPhN_2^+$	8.04[c]	

[a] [Base] 0.05–0.10 M. Rate constants were independent of base concentration within this range. [b] k_Ψ measured by NED method. [Substrate] 0.3–8 × 10^{-4} M. [c] k_Ψ measured by direct uv analysis. [Substrate] 2.8 × 10^{-5} M.

Initial Partitioning of Diazonium Ion (Syn vs. Anti). For *p*-nitrobenzenediazonium ion $k_P = 4.5 \times 10^{-2}$ s^{-1} at 23 °C while Ritchie found $k_{-1S} = 5.4$ s^{-1} and $k_{1S} = 3 \times 10^8$ M^{-1} s^{-1}. We must remember that once the *syn*-arylazo alkyl ether ionizes the diazonium ion can repartition to give a mixture of syn (k_{1S}) and anti (k_{1A}) products.

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

From this equation and using the above values of k_P, k_{-1S}, and k_{1S} we can calculate $k_{1A} = 2.5 \times 10^6$ M^{-1} s^{-1}. The ratio k_{1S}/k_{1A} = 120, i.e., the diazonium ion partitions in favor of the *syn*-azo ether (120:1 syn:anti). This is in accord with Ritchie's[8] observation of initial *syn*-arylazo ether production in phase 1.

Species Undergoing Dediazoniation. Since the decomposition rates (k_D) of the *syn*-arylazo ether do not show a solvent effect on rate, we conclude that at least for the *p*-nitro compound dediazoniation occurs from the *syn*-arylazo ether as suggested by Bunnett.[4]

Thus, decomposition of the *anti*-arylazo ether occurs via the $k_{-1A} \rightarrow k_{1S} \rightarrow k_D$ pathway with partitioning at the diazonium ion (between k_{1S} and k_{1A}) and partitioning at the *syn*-arylazo ether (between k_{1D} and k_{-1S}). Dediazoniation occurs from the *syn*-azo ether. This clarifies the role of the species in the dediazoniation reaction for the *p*-nitro compound but the mechanism of the dediazoniation step itself (k_{1D}) still remains to be settled.

Dediazoniation Rates (k_Ψ) at 30 °C (Table III). At 30 °C we see the partitioning of *syn*-arylazo ether (phase 2) as a fast initial reaction—the amount of fast initial dediazoniation vs. protection giving information about the ratio k_P/k_{1D}—and a slow measurable reaction (k_Ψ) which is decomposition of the *anti*-arylazo ether (phase 3).

Table IV. Values of Percent Protection (and k_P/k_D) for Phase 2 of the Decomposition of Diazonium Ions at 30 °C Determined by Several Methods

	Percent protection (k_P/k_D)		
Ar	% fast reaction from experimental observation at 30 °C	Rate constants at 0 °C and Arrhenius parameters	Rates k_{-1A} and k_Ψ at 30 °C
4-NO_2	58	62[a] (1.66)[a] 55[b] (1.22)[b]	59 (1.44)
3-NO_2	60		56 (1.27)
4-CN			60 (1.51)
3-CN			73 (2.77)
4-CF_3			86 (6.33)
3-CF_3			78 (3.49)
3-Cl			(78) (3.64)
4-Cl	85[c,d]		(83) (4.87)
2-Cl	88[d]		(93) (13.75)

[a] Reference 10. [b] Reference 5. [c] For 4-Br compound. [d] T. J. Broxton and J. F. Bunnett, unpublished results.

The overall dediazoniation rate (k_Ψ) is related to the ionization rate (k_{-1A}) in the following way

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

where k_P is defined in eq 1.

Now since $k_{1S} = 120k_{1A}$

$$\frac{k_{1S}}{k_{1S}+k_{1A}} \approx 1$$

Therefore eq 2 can be simplified to give eq 3.

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

Thus from measurements of k_Ψ and k_{-1A} it is possible to get a measure of the fraction of decomposition and hence the fraction and percent protection during phase 2 of the reaction of diazonium ions.

Thus we are now in a position to obtain the percent protection during phase 2 of the reaction in three independent ways (Table IV), i.e., from experimental observation of the reaction mixture, from rate measurements at 0 °C, and finally from measurements of the rates of ionization (k_{-1A}) and overall decomposition (k_Ψ). In fact the agreement between these determinations confirms our confidence that the α-naphthol is trapping all the free diazonium ion in the k_{-1A} measurements.

Ratios of k_P/k_D. For most of the diazonium salts studied k_P/k_D = 1–5 in methanol but the result for the 2-chloro compound is much greater (13.75). Obviously this could be explained by either an increase in k_P or a decrease in k_D. The observation that the phase 2 reactions at 0 °C are too fast to measure (cf. 4-NO_2 compound) suggests that the former explanation is correct. The reason for an increase in k_P (see eq 1) is that k_{-1S} would be expected to experience steric acceleration caused by strong nonbonded interactions between the 2-chloro substituent and either the lone pair or the α nitrogen or the methoxy group as did k_{-1A} for that compound.

Experimental Section

Preparation of Aryldiazonium Salts. *p*- and *m*-nitro, *p*-, *m*-, and *o*-chloro, *p*- and *m*-trifluoromethyl-, and *p*- and *m*-cyanobenzenediazonium tetrafluoroborates were synthesized by diazotization of the corresponding anilines as described by Bunnett.[3] The salts were characterized by measuring the extinction coefficient at the wavelength of maximum absorbance of a solution in 0.01 M sulfuric acid,[18] since melting points are not reliable.

Table V. Spectroscopic Data for *anti*-*p*-Nitrophenylazo Alkyl Ethers (2)

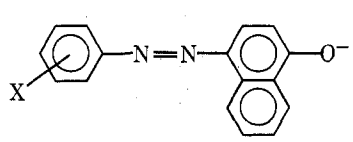
	NMR[a]			Mass spectral mol wt	
Alkyl	Ar	$-OCH_2-$	$O-C-CH_3$	Calcd	Found
Me	8.35, 7.65	4.32			
Et	8.22, 7.52	4.56	1.45	195.064	195.064
i-Pr				209.080	209.080

[a] Chemical shift (δ) in parts per million.

Alkyl *p*-Nitrophenylazo Ethers. Methyl *p*-nitrophenylazo ether, mp 81 °C (lit.[19] 82–83 °C), was prepared as described by Bunnett.[3] Ethyl *p*-nitrophenylazo ether and isopropyl *p*-nitrophenylazo ether were prepared by the alkylation of a suspension of silver *p*-nitrobenzeneisodiazotate (10 g) in ether (100 ml) with ethyl iodide and isopropyl bromide, respectively. The ethers were characterized by a combination of ^1H NMR (Varian Associates T60 NMR spectrometer) and high-resolution mass spectrometry (JEOL JMS-D-100 double focusing spectrometer) (Table V). Molecular weights were measured by peak matching using a perfluorokerosene reference sample.

Kinetic Methods. Alcoholic solvents (MeOH, EtOH) were dried by distillation from the corresponding magnesium alkoxide.[20] Three different types of kinetic measurement were used, one using an internal coupling agent (α-naphthoxide), one using an external coupling agent (*N*-1-napthththalene ethylenediamine, NED) and the other using direct uv spectroscopic analysis.

A. Kinetics in Presence of α-Naphthol. This technique was used for measuring the rates of ionization (k_{-1A}) of the *anti*-arylazo alkyl ethers, whether the reactant was added directly or prepared in situ from the diazonium and alkoxide ions before the α-naphthol was added. This latter method was particularly useful in cases where the *anti*-arylazo alkyl ethers were too unstable to be easily prepared. Tests were carried out on the *p*-nitro compound and rates of ionization (k_{-1A}) were within experimental error whether the *anti*-*p*-nitrophenylazo methyl ether or the free diazonium salt was used. This technique involved dissolution of the solid diazonium salt in 10 ml of 1 M sodium methoxide in a 100-ml volumetric flask. An aliquot of α-naphthol solution (10–40 ml, 0.1 M α-naphthol) was then added and the mixture was diluted to 100 ml with dry methanol. A sample of this solution was then placed into a cuvette in a thermostatically jacketed holder in the sample compartment of a Varian Techtron 635 uv–visible recording spectrophotometer. The rate of production of azo dye **6** was followed at the wavelength of maximum absorbance for



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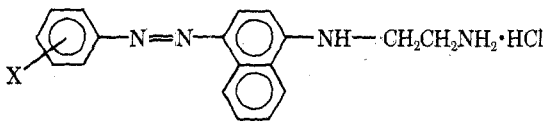
that particular diazonium salt. Plots of log Abs_t against time were linear for at least 2 half-lives. The results are in Table I.

B. Kinetics using NED. The rate of overall decomposition (dediazoniation) was followed either by sampling aliquots and coupling with NED in acidic methanol or directly on the uv machine. The NED coupling technique analyzes total diazonium function, i.e., free ions plus arylazo alkyl ethers which are converted to free ions in acidic solution. As for the α-naphthol runs, kinetic measurements could be carried out using the arylazo alkyl ethers either added directly or prepared in situ. Reactions were carried out at 30 °C to follow the slow decomposition (phase 3) (k_Ψ) or at 0 °C to follow the rapid partitioning (phase 2) (k_D and k_P). No attempt was made to follow the initial complexation (phase 1) to form the *syn*-arylazo alkyl ether and Ritchie's results[8] will be used in discussion of this stage of reaction.

Each sample (aliquot) was acidified (dilute HCl), coupled (NED), and diluted to volume and the concentration of azo dye **7** was measured.



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Rate constants at 30 °C (k_ψ) were obtained from a plot of log (Abs_t − Abs_∞) vs. time. Rate constants at 0 °C (k_P and k_D) were obtained as follows. The linear section of a plot of Abs_t vs. time was extrapolated to $t = 0$ to give an estimate of the amount of protection. Subtraction of this from A_0 gave the amount of decomposition and a value of R (where R = protection/decomposition) was obtained.

Now A_t = total *syn*- and *anti*-arylazo ether at time t and $(A_0 - A_t)$ = a measure of decomposition at time t (i.e., ArH). Therefore $R(A_0 - A_t)$ = protection at time t (i.e., *anti*-arylazo ether) and $A_t - R(A_0 - A_t)$ = *syn*-arylazo ether at time t. Now from a plot of log $[A_t - R(A_0 - A_t)]$ vs. time we get a measure of the total rate of reaction of *syn*-arylazo ether ($k_P + k_D$).

Knowing the fraction of protection and decomposition we obtain k_P and k_D from the total rate.

All solvents were chilled to 0 °C before the addition of reagents.

C. Kinetics Using Direct Uv Analysis (k_ψ). The rate of dediazoniation could also be measured by direct uv analysis of the reaction solution. The reaction was carried out in a thermostatically jacketed cuvette in the uv machine and the rate of decomposition was followed by monitoring the decrease in absorbance due to the *anti*-arylazo alkyl ether. The rate constant was obtained from a plot of log $(A_t - A_\infty)$ vs. time. Rate constants (k_ψ) measured by methods B and C are in Tables II and III.

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Registry No.—*p*-Nitrobenzenediazonium tetrafluoroborate, 456-27-9.

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Solvolysis of 3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2-yl *p*-Nitrobenzoates and Its Related System

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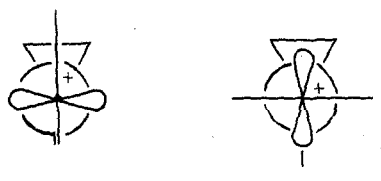
3,4-Benzotricyclo[4.3.1.0^{1,6}]dec-3-en-2- (*anti*- and *syn*-) yl *p*-nitrobenzoate (4-OPNB) and its homoallylic isomer (**5**-OBs) were prepared via 11- and 10-step synthesis, respectively, starting with 2-benzyl-2-methoxycarbonylcyclopentanone. Solvolysis of the syn **4s**-OPNB in 80% aqueous acetone proceeded at 25 °C with a rate of 1.73×10^{-4} s^{-1} which was two times faster than a rate of 0.86×10^{-4} s^{-1} for the anti **4a**-OPNB. Also, these rates were considerably fast (ca. $\times 10^2$) in comparison with ordinary cyclopropylphenylmethyl system. Brosylate **5**-OBs was solvolyzed with a rate of 0.65×10^{-4} s^{-1} at 25 °C. In the presence of base, **4a**-OPNB and **5**-OBs gave similar products, a mixture of **4a**-OH (13%), **4s**-OH (42%), and **6**-OH (45%). Treatment of **4a**-OH with acid catalyst or solvolysis of **4a**-OPNB in the absence of base afforded exclusively the tertiary alcohol, **6**-OH. The implications of these and other results are discussed together with available data.

From enormous investigations by a number of forerunners[1-3] it has been established that solvolytic displacements of almost all cyclopropylmethyl systems proceed with remarkably accelerated rates in comparison with those of other alkyl systems. This is particularly enhanced when the geometric arrangement of the reactants favors the formation of such a transition state that the plane of a cyclopropane is orthogonal to that of an electron-deficient carbon atom. The interaction between these planes has been widely studied by NMR spectroscopy at low temperatures[4] or by molecular orbital calculation.[5]

Recently the key discussion[6] in solvolysis of cyclopropylmethyl systems is to concentrate on character at the transition state. Winstein et al.[7] reported that the first-order rate constant of **1a**-OPNB in solvolysis in 80% aqueous acetone was 7.70×10^{-3} s^{-1} at 25 °C, the value being one-half the rate constant of **1s**-OPNB.

It is evident from these studies that the "bisected" conformation is more stable than the "perpendicular" one in the intermediate cyclopropylmethyl cation.[4,5,7,8]



bisected perpendicular