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Reactions of Aryl Diazonium Salts and Arylazo Alkyl Ethers. 7.[†] Kinetic Studies of the Decomposition of *Z* Ethers Derived from Some Substituted 2-Nitrobenzene Diazonium Salts

Trevor J. Broxton* and Michael J. McLeish

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

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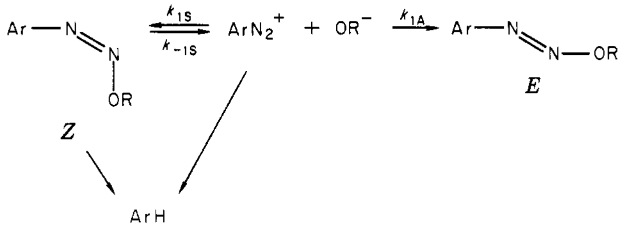
Rate constants for the decomposition of (*Z*)-syn ethers derived from some 4- or 5-substituted 2-nitrobenzenediazonium salts have been measured in both basic methanol and basic ethanol. For some compounds the rate of decomposition is independent of the base concentration while for others the rate is first order in base concentration. Solvent and substituent effects point to the base-independent mechanism occurring on the free diazonium salt formed by ionization of the *Z* ether while the base-dependent mechanism occurs on the *Z* ether itself. Mechanisms are proposed for each of these reactions.

When an aryl diazonium salt is dissolved in a basic alcoholic solution, the diazonium salt is partitioned between the (*Z*)-arylazo alkyl ether (k_{1S}) and the (*E*)-arylazo alkyl ether (k_{1A}). Formation of the *Z* ether predominates (i.e., $k_{1S} \gg k_{1A}$).[1,2] At low temperatures (10 °C) the *E* ether is stable, but the *Z* ether undergoes the following reactions (Scheme I): (i) ionization to free diazonium ion (k_{-1S}); (ii) conversion to the more thermodynamically stable (*E*)-arylazo alkyl ether (k_P); (iii) decomposition (k_D).

Scheme I



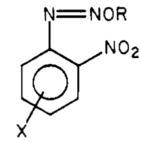
The rates of ionization (k_{-1S}), *Z*-*E* interconversion (k_P), and decomposition (k_D) have been reported[3] for the *Z* ethers derived from a number of substituted 2-nitrobenzenediazonium salts (**1a**-**f**,**h**). On the basis of a large solvent effect on rate, on transfer from methanol to ethanol,[1] and the similarity in Hammett ρ values for both ionization (-5.4) and *Z*-*E* interconversion (-5.8),[3] an ionization recombination mechanism for *Z*-*E* interconversion was proposed.[3] This was preferred to alternative bond-rotation or nitrogen-inversion pathways.[3] Thus, the rate of *Z*-*E* interconversion (k_P) could be defined by eq 1.

$$k_P = k_{-1S}k_{1A}/(k_{1A} + k_{1S}) \qquad (1)$$

This provided a method to determine the partitioning factor (k_{1S}/k_{1A}) of the free diazonium ion if k_P and k_{-1S} are known.

It is of interest to determine whether the decomposition reaction occurs directly on the *Z* ether itself or on the product of its ionization, the free diazonium salt. One way to cast some light on this problem is to compare the ionization and decomposition rates. Thus, if $k_D > k_{-1S}$ (e.g., the 4-trifluoromethyl-substituted compound **1h**) then decomposition must be on the *Z* ether. However, if $k_{-1S} > k_D$, then decomposition may be either on the free diazonium ion or on the *Z* ether. The dependence of k_D on the substituent was found to be rather unusual.[3]

Table I. Observed Rate Constants for the Decomposition of *Z* Ethers Derived from Substituted Benzenediazonium Salts in Basic Alcoholic Solvents at 10 °C



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(a) Ethanol

	10^6k_{obsd}, s^{-1}, for [NaOEt], M, of				
compd[a]	0.01	0.02	0.05	0.10	0.20
1a (4-OMe)			3670	3550	3090
1b (4-OPh)			995	997	973
1c (4-Me)			155	151	153
1d (H)			56.6	53.8	54.8
1e (4-Cl)			37.7	45.5	53.4
1f (5-Cl)			8.3	10.9	12.5
1h (4-CF_3)			18	24	28
1j (4-COPh)			39	67	121
1k (4-CN)			45	70	118
1l (4-SO_2Me)			231	452	
1m (4-NO_2)	654	1420			

(b) Methanol

	10^6k_{obsd}, s^{-1}, for [NaOMe], M of		
compd[a]	0.05	0.10	0.20
1d (H)	575	717	
1e (4-Cl)	607	593	
1f (5-Cl)	62	53	
1g (5-CF_3)	116	127	144
1h (4-CF_3)	29	32	34
1j (4-COPh)	99	104	123
1l (4-SO_2Me)		115	213
1m (4-NO_2)	491	1004	

[a] Variable substituent (X) in parentheses.

A minimum rate of decomposition was observed for the 5-chloro-substituted compound (**1f**). This suggested the existence of a V-shaped Hammett plot. Compounds with substituents that were less electron withdrawing than a *m*-chloro substituent (**1a**-**e**) form the left-hand or descending arm of the Hammett plot whereas the 4-trifluoromethyl-substituted compound (**1h**) suggested the existence of a right-hand ascending arm. Preliminary results suggested that the 4-nitro substituted compound (**1m**) decomposed very rapidly, further indicating an ascending arm to the Hammett plot. To obtain more information about the mechanism occurring in this region of the Hammett plot, we decided to investigate other compounds containing strong electron-withdrawing substituents.

[†] Part 6: *Aust. J. Chem.* **1982**, *35*, 319.

Results and Discussion

Observed rate constants for the decomposition of *Z* ethers derived from substituted 2-nitrobenzenediazonium salts (1) are given in Table I. Initial results, obtained in EtOH at 0.1 M EtO^-, confirmed the presence of a V-shaped Hammett plot, with the 4-CF_3 (**1h**), 4-COPh (**1j**), 4-CN (**1k**), and 4-SO_2Me (**1l**) substituents forming the ascending arm of the plot. The rate for the 4-NO_2-substituted compound (**1m**) was too fast to measure by our methods at 0.1 M EtO^-. The effect on the rate of reaction of changing the base concentration was studied in an effort to determine whether the ionization of the *Z* ether was involved in its decomposition. To our surprise it was found that for compounds containing the most electron-withdrawing substituents (**1j–l**) the rate of decomposition increased as the [base] was increased. This enabled us to determine the rate of reaction of the 4-nitro-substituted compound (**1m**) by working at a low [EtO^-].

For compounds with either electron-donating or no substituents (**1a-d**) it was found that the rate of decomposition was independent of [EtO^-]. For the 4-SO_2Me and 4-NO_2 compounds (**1l,m**) the rate of decomposition was first order in [EtO^-]. For intermediate compounds (**1h-k**) the effect of increasing the [EtO^-] was less marked.

This suggested two different mechanisms for the decomposition of these *Z* ethers which contain nitro groups, one that is independent of [base] and another that is first order in [base]. Product studies for the unsubstituted compound (**1d**,[4] independent of [base]) have shown that when the reaction is carried out in EtOD, the product contains only 2.9% deuterium. For the 4-NO_2 compound (**1m**, first order in [base]) reaction in EtOD also led to a product that was initially free of deuterium. However, the product (*m*-dinitrobenzene) undergoes a H/D exchange in basic solution so that the percent deuteration of the product increased with time. NMR studies have shown that it is the hydrogen on C-3 that is exchanged, not the hydrogen at C-1.

For the 4-SO_2Me compound (**1l**) reaction in basic EtOD also led to a product that was free of deuterium at the C-1 position. Mass spectrometric studies, however, showed that four protons were exchanged in basic EtOD. NMR studies showed that the three hydrogens on the SO_2Me group together with the proton on C-3 were exchanged.

Thus both the base-dependent and the base-independent mechanisms involve aryl radical intermediates.[5]

For intermediate compounds (**1h–k**) where the base dependence suggested the occurrence of both mechanisms, the observed rate was plotted against the base concentration. A good straight line was obtained in each case, and the rate constants for each mechanism were calculated by using eq 2. The second-order rate constant for the

$$k_{obsd} = k_1 + k_2[OEt^-] \qquad (2)$$

base-dependent mechanism (k_2) was obtained from the slope, and the first-order rate constant for the base-independent mechanism (k_1) was obtained from the intercept. The calculated first- and second-order rate constants are given in Table II.

The second-order rate constants (k_2) for the base-dependent mechanism correlate very well with σ^- giving ρ = 5.8 (r = 0.999) (Figure 1). This large positive Hammett ρ value indicates the development of a negative charge in the transition state.

Table II. Calculated Rate Constants for the Decomposition of *Z* Ethers Derived from Substituent Benzenediazonium Salts 1a–m in Basic Alcoholic Solvents at 10 °C

	ethanol		methanol	
compd[a]	10^6k_2,[b] L mol^{-1} s^{-1}	10^6k_1,[c] s^{-1}	10^6k_2,[b] L mol^{-1} s^{-1}	10^6k_1,[c] s^{-1}
1a (4-OMe)		3440[d]		
1b (4-OPh)		988[d]		
1c (4-Me)		153[d]		
1d (H)		55[d]		
1e (4-Cl)		46[e]		600[d]
1f (5-Cl)		11[e]		57[d]
1g (5-CF_3)				129[e]
1h (4-CF_3)	62	16[f]	37[f]	27[f]
1j (4-COPh)	546	12[f]	170[f]	89[f]
1k (4-CN)	471	23[f]		
1l (4-SO_2Me)	4550[g]		1109[g]	
1m (4-NO_2)	67300[g]		9930[g]	

[a] Variable substituent (X) in parentheses. [b] Second-order rate constant for the base-dependent mechanism. [c] First-order rate constant for the base-independent mechanism. [d] Observed rate independent of base concentration. [e] Average of observed rates, i.e., calculated by assuming no base dependence. [f] Calculated from a plot of k_{obsd} against [base]. Slope = k_2; intercept = k_1. [g] k_2 calculated from the slope of a plot of k_{obsd} against [base]. Intercept = zero. No base-independent reaction for this compound

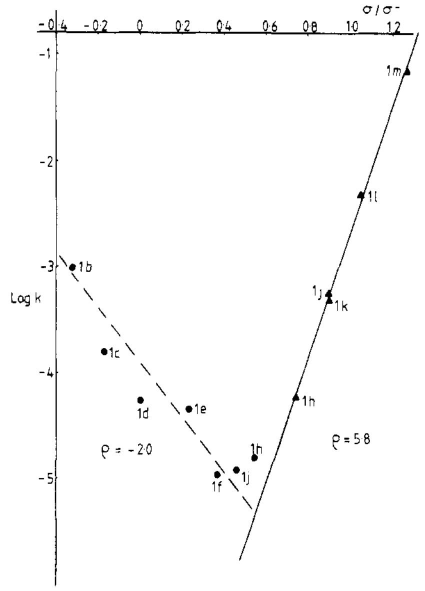

Figure 1. Hammett plot for the base-independent (vs. σ, ●) and base-dependent (vs. σ^-, ▲) mechanisms of decomposition of *Z* ethers derived from substituted 2-nitrobenzenediazonium salts in ethanol.

The first-order rate constants (k_1) for the base-independent mechanism do not correlate well with either σ or σ^+, although there is a definite decrease in reactivity as the electron-withdrawing power of the substituent is increased (ρ = −2.0, r = 0.938; Figure 1). For two compounds (**1e,f**) the rate of decomposition appears to be slightly dependent on [base]. The rate constant at 0.2 M EtO^- is 50% higher for compound **1f** (41% for **1e**) than at 0.05 M EtO^-. Although these rate constants were not obtained at constant ionic strength, it is unlikely that this rate increase is due to an ionic strength effect. For compounds **1b–d** the rate is independent of [base] within the range 0.05–0.20 M. It is also unlikely that this is due to the

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(1) Broxton, T. J.; Roper, D. L. *J. Org. Chem.* **1976**, *41*, 2157.
(2) Anderson, C. S.; Broxton, T. J. *J. Org. Chem.* 1977, *42*, 2454.
(3) Broxton, T. J. *Aust. J. Chem.* **1979**, *32*, 1031.
(4) Broxton, T. J.; Bunnett, J. F. *Nouv. J. Chim.* 1979, *3*, 133.
(5) Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.* *1968*, *90*, 5173.

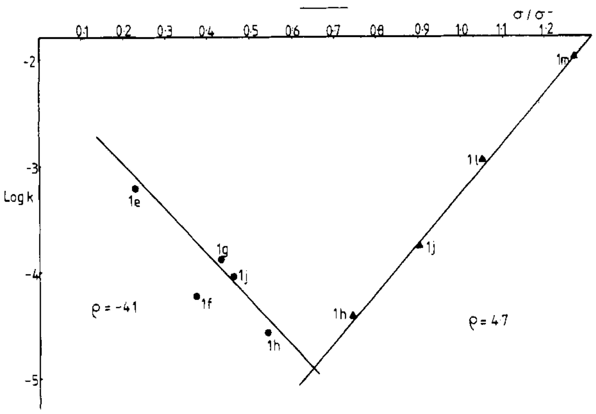

Figure 2. Hammett plot for the base-independent (vs. σ, ●) and base-dependent (vs. σ^-, ▲) mechanisms of decomposition of *Z* ethers derived from substituted 2-nitrobenzenediazonium salts in methanol.

incursion of the base-dependent mechanism for these compounds because extrapolation of the Hammett plot for that mechanism to $\sigma = 0.37$ (m-Cl, compound **1f**) or 0.23 (p-Cl, compound **1e**) leads to an extremely small second-order rate constant (4.0×10^{-7} L mol^{-1} s^{-1} for compound **1f**). This would lead to an insignificant amount of reaction by the base-dependent mechanism at the base concentrations studied. By use of eq 2 and the calculated rate constant for compound **1f**, less than 4% of the observed rate at 0.1 M EtO$^-$ could be attributed to the base-dependent mechanism. Even less than 4% of the observed rate of 0.1 M EtO$^-$ could be attributed to the base-dependent mechanism for compound **1e**. Thus the base-dependent mechanism cannot be responsible for the variation of the observed rate for compounds **1e** and **1f**. For these two compounds we have taken an average of the observed rate constants as k_1 (see Table II).

Solvent Effects. Rate constants for a number of compounds (**1d–j,l,m**) were also measured for a range of methoxide concentrations in dry methanol. Observed rate constants are given in Table I, and calculated rate constants are given in Table II. It can be seen from the first-order rate constants that the base-independent mechanism is faster in methanol than in ethanol, but from the second-order rate constants the base-dependent mechanism is slower in methanol than in ethanol. As for reaction in ethanol, the second-order rate constants for reaction in methanol correlate well with σ^- ($\rho = 4.7$, $r = 0.999$), and the first-order rate constants correlate less well with σ ($\rho = -4.1$, $r = 0.982$; Figure 2).

For compounds where reaction occurs by both mechanisms there is a greater participation by the base-dependent mechanism in ethanol than in methanol. If we substitute the calculated rate constants (k_1 and k_2) and 0.1 M base concentration into eq 2, we find that for the 4-CF$_3$ compound only 12% reaction occurs by the base-dependent mechanism in methanol compared to 28% in ethanol. For the 4-COPh compound, 16% reaction occurs by the base-dependent mechanism (at 0.1 M base) in methanol but 82% in ethanol.

Base-Dependent Mechanism. In summary, the base-dependent mechanism becomes important for compounds bearing the most electron-withdrawing substituents. The rate of reaction for different substituents correlates well with σ^- ($\rho = 5.8$ in ethanol). The rate of reaction is faster in ethanol than in methanol. Furthermore, the observed decomposition rates are considerably faster than the ionization rates (Table III) which can be obtained from extrapolation of the Hammett plot for the ionization rates of *Z* ethers derived from compounds **1a–f**.[6] The incursion of the base-dependent mechanism appears to coincide with the point where k_{-1S} becomes less than the observed k_D.

Table III. Comparison of Rate Constants for the Ionization of *Z* Ethers (k_{-1S}) Derived from Substituted 2-Nitrobenzenediazonium Salts in Ethanol at 10 °C and Their Decomposition Rates at 0.1 M EtO$^-$

compd[a]	$10^6 k_{-1S}$[b]	$10^6 k_D$[d]
1a (4-OMe)	624000	3550
1b (4-OPh)	110000	997
1c (4-Me)	55300	151
1d (H)	4700	538
1e (4-Cl)	506	45.5
1f (5-Cl)	76	10.9
1n (4-F)	1870	
1h (4-CF$_3$)	10[c]	24
1j (4-COPh)	32[c]	67
1k (4-CN)	2.5[c]	70
1l (4-SO$_2$Me)	1.2[c]	452
1m (4-NO$_2$)	0.6[c]	6540[e]

[a] Variable substituent, X, in parentheses. [b] Reference 6. Using a constant concentration of α-naphtholate and a varying concentration of ethoxide. [c] Calculated from the Hammett plot of compounds 1b–f,n ($\rho = -4.7$, $r = 0.992$). [d] Observed decomposition rate at 0.1 M EtO$^-$. [e] Calculated from rate at 0.01 M EtO$^-$ by assuming first-order dependence on [EtO$^-$].

Scheme II. Suggested Mechanism for Base-Dependent Reaction in CH$_3$OH

$$\mathrm{ArN{=}NOCH_3 + OCH_3^- \xrightarrow{RDS} ArN{=}NOCH_3^{-\cdot} + \cdot OCH_3} \quad (3)$$

$$\mathrm{ArN{=}N{-}OCH_3^{-\cdot} \longrightarrow Ar\cdot + N_2 + OCH_3^-} \quad (4)$$

$$\mathrm{Ar\cdot + CH_3OH \longrightarrow ArH + \cdot CH_2OH} \quad (5)$$

$$\mathrm{2\dot{C}H_2OH \longrightarrow HOCH_2CH_2OH} \quad (6)$$

This evidence points to decomposition occurring on the *Z* ether and to a rate-determining transition state that carries more negative charge than the *Z* ether itself. Thus, ionization is not involved in this decomposition mechanism, and this explains why the rate of decomposition is greater in ethanol than in the more polar methanol.

A mechanism (Scheme II) that is consistent with this evidence involves electron transfer from an alkoxide ion to the (*Z*)-arylazo alkyl ether, forming the radical anion of the *Z* ether (step 3). Electron transfer to aromatic nitro compounds is well-known[7] and has been reported from alkoxide ions[8] in alcoholic solution. The radical anion of the *Z* ether produced in step 3 can then decompose to aryl radical, nitrogen, and alkoxide ion (step 4).

The aryl radical may then abstract a hydrogen atom from the solvent (step 5). The fate of the $\cdot$OCH$_3$ and $\cdot$CH$_2$OH radicals is unknown, but possibly either dimerization (step 6) or colligation to form CH$_3$OCH$_2$OH may occur. The absence of a chain reaction is indicated by the fact that neither oxygen nor p-dinitrobenzene affect the rate of reaction. For compound **1l** in the presence of 0.1 M EtO$^-$ in ethanol, the observed rate of reaction for a reaction mixture that was bubbled with oxygen was 4.54×10^{-4} s^{-1}, while that for a mixture containing 7.7×10^{-4} M p-dinitrobenzene was 4.70×10^{-4} s^{-1}. The rate of reaction for compound **1l** (0.1 M EtO$^-$) in the absence of any additives was 4.52×10^{-4} s^{-1}.

Comparison of *Z* and *E* Ethers. It seemed reasonable that if a *Z* ether was able to accept an electron from an alkoxide ion, then a similarly substituted *E* ether should

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[6] Broxton, T. J.; McLeish, M. J. *Aust. J. Chem.* **1982**, *35*, 319.

[7] Russell, G. A.; Gaels, E. J. *Tetrahedron Lett.* **1963**, 1333.

[8] Russell, G. A.; Janzen, E. G. *J. Am. Chem. Soc.* **1962**, *84*, 4153.

Table IV. Rate Constants for the Decomposition of *E* Ethers Derived from Substituted Diazonium Salts 1h and 1j in Methanol at 10 °C

compd[a]	$10^6 k_{obsd}$, s^{-1}, for [NaOMe], M, of 0.04	0.05	0.10	0.15	0.20	$10^6 k_2$, L mol^{-1} s^{-1}
1h (4-CF_3)		1.10	1.96	2.72	3.45	16[c]
1h (4-CF_3)[b]	1.08		2.44		4.19	20[c]
1j (4-COPh)		5.01	8.91		17.9	88

[a] Variable substituent in parentheses. [b] Using the synthetic sample of this (*E*)-arylazo methyl ether. [c] A plot of k_{obsd} vs. [NaOMe] was linear, but there was a small positive intercept (3×10^{-7}). Thus at 0.1 M MeO^-, 87% reaction occurs by the base-dependent mechanism.

also be able to accept an electron. To search for an example of this phenomenon, we first had to detect *Z–E* interconversion for an appropriate compound. This was attempted in methanol as *Z–E* interconversion occurs to a greater extent in methanol than in ethanol. Compounds **1h** and **1j** were investigated since both of these compounds showed reaction by both the base-dependent and base-independent mechanisms. Reaction by the base-independent mechanism indicated that some ionization occurs (see below) and this is necessary for *Z–E* interconversion. Futhermore, reaction by the base-dependent mechanism indicated that electron transfer to the *Z* ether is a viable process for these compounds. Thus, for these compounds both the formation of *E* ether and electron transfer to it seemed to be possible.

To facilitate observation of this reaction, we used a larger than normal (×5) concentration of diazonium salt. This was necessary to allow a reasonable amount of *E* ether to form. Reaction mixtures (aryl diazonium salts and sodium methoxide) were prepared and were allowed to react for 18 h to consume all of the *Z* ether. After 18 h a small residual amount of diazonium-containing species was still present. This was assumed to be the *E* ether. Decomposition of this *E* ether was investigated, and the rate of reaction was found to be dependent on the base concentration. Rate constants for the decomposition of *E* ethers derived from compounds **1h** and **1j** are in Table IV.

The assumption that the residual diazonium-containing species was the *E* ether is justified by the following observations. For the *Z* ether of compound **1h** the observed rate increased by only 17% as the base concentration was increased from 0.05 to 0.20 M (24% for compound **1j**). For the residual *E* ether of compound **1h** a corresponding increase in base concentration resulted in a 230% increase in rate (258% for compound **1j**).

Thus the decomposition of the *Z* ether of compound **1h** occurs predominantly by the base-independent mechanism (93% at 0.1 M MeO^-), but for the *E* ether the predominant mechanism is the base-dependent one. This presumably results from the much slower rate of ionization of the *E* ether, precluding reaction by the base-independent mechanism for that isomer.

On comparing the total rates of decomposition of *Z* and *E* ethers of compound **1h**, we find that at 0.05 M MeO^- the *Z* ether reacts 26 times faster than the *E* ether (mainly because of the contribution of the base independent reaction for the *Z* ether). Thus, it is reasonable to expect that all of the *Z* ether could have decomposed while the *E* ether was still present. For compound **1j** the *Z* ether decomposed 20 times faster than the *E* ether at 0.05 M MeO^-.

The second-order rate constant, however, for the reaction by the base-dependent mechanism is only approximately twice as fast for the *Z* ether as for the *E* ether. This difference in rate for the decomposition of the corresponding *Z* and *E* ethers by the base-dependent mechanism probably stems from ground-state energy differences of the two isomers. It is well-known that *E* ethers are thermodynamically more stable than their *Z* isomers.[1] Therefore, the large differences in ionization rates of (*Z*)- and (*E*)-arylazo alkyl ethers[9] [10^5 for (4-nitrophenyl)azo methyl ethers] do not arise merely from ground-state energy differences. These differences probably arise from stereoelectronic factors.[10] Ionization of the *Z* ether is assisted by the availability of a trans lone pair on the α-nitrogen whereas in the *E* ether the lone pair on the α-nitrogen is cis to the leaving group.

Synthesis and Characterization of the *E* Ether of Compound 1h. To confirm that we were in fact observing the reaction of an (*E*)-arylazo methyl ether for compounds **1h** and **1j**, we prepared a sample of (*E*)-arylazo methyl ether from compound **1h** by methylation of the silver diazotate obtained from 2-nitro-4-(trifluoromethyl)benzenediazonium salt.[1] The product obtained from this reaction was very unstable and was not obtained in a pure form. Its presence as the major reaction product was confirmed by a combination of proton and ^{13}C NMR spectroscopy and mass spectrometry. Furthermore, when the decomposition of this material was studied, the azo dye obtained on coupling with *N*-(1-naphthalenyl)ethylenediamine had the same absorbance maximum (520 nm) as that obtained from both the *Z* and *E* ethers prepared in situ.

Proton and ^{13}C NMR data for 2-nitro-4-(trifluoromethyl)benzenediazonium salt and its (*E*)- and (*Z*)-methyl ethers are given in Table V. Proton chemical shifts for the synthetic *E* ether and for *Z* ether prepared in situ are very similar but show large shifts compared to those of the diazonium salt. Proton chemical shifts were assigned from a consideration of substituent effects and observed coupling. In all cases H_A was observed as a singlet, while H_B and H_C exhibited ortho splitting (J_{BC} = 8 Hz). H_C for the diazonium salt had a large downfield shift due to deshielding by the charged diazonio group. In the azo ethers the downfield doublet was assigned to H_B (para to nitro group) while the other doublet was assigned to H_C (meta to nitro group).

Carbon-13 chemical shifts were assigned by observation of C–F splitting for C-3 and for C-5 with the CF_3 group at C-4. A singlet was observed for C-6 and for the methyl carbon in all cases. The coupling constant observed between the CF_3 group and the ortho carbons (i.e., C-3 and C-5) was 3.66 Hz. This is consistent with previously observed coupling constants for other compounds containing a trifluoromethyl substituent.[11] Resonances due to C-3 and C-5 were assigned after consideration of the downfield shift caused by a nitro group situated para to a particular carbon and the upfield shift caused by an ortho nitro group.[12]

The largest change in the ^{13}C NMR spectrum on neutralization of the positive charge of the diazonio group was for C-6, as expected. Smaller changes in chemical shift were observed for C-3 and C-5. Interestingly, on comparison of the (*Z*)- and (*E*)-methyl ethers, the chemical shift for C-6 was at higher field for the *E* ether while for

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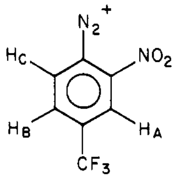
(9) Broxton, T. J.; Stray, A. C. *J. Org. Chem.* **1980**, *45*, 2409.

(10) Deslongchamps, P. *Pure Appl. Chem.* **1975**, *43*, 351; *Tetrahedron* **1975**, *31*, 2463; *Heterocycles* **1977**, *7*, 1271.

(11) Shehan, P. Honours Thesis, La Trobe University, Bundoora, Victoria, Australia, 1980.

(12) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley: New York, 1972.

Table V. Proton and Carbon-13 NMR Data for the 2-Nitro-4-(trifluoromethyl)benzenediazonium Salt and Its (*Z*)- and (*E*)-Methyl Ethers



	chemical shifts[a] (coupling constants, Hz)							
	^1H				^{13}C			
compd	H_A[b]	H_B[b]	H_C	OMe	C_3	C_5	C_6	methyl
ArN_2^+	9.14 (s)	8.87 (d, $J = 8$)	9.44 (d, $J = 8$)		126.2[f]	134.7[f]	139.2 (s)	
Z ether[c]	8.50 (s)	8.18 (d, $J = 8$)	7.97 (d, $J = 8$)	*e*	121.1[f]	132.1 (s)	127.9 (s)	57.8
E ether[d]	8.40 (s)	8.15 (d, $J = 8$)	7.71 (d, $J = 8$)	4.27 (s)	122.1[f]	130.1[f]	125.6 (s)	59.0

[a] In parts per million relative to Me_4Si (δ). [b] Meta splitting not observed in spectrum. [c] *Z* ether generated in situ by the addition of $MeO^-/MeOH$ to ArN_2^+ in acetone-d_6. [d] Reaction product dissolved in acetone-d_6. Additional ^{13}C resonances due to impurities were observed at 127.6 and 122.2 ppm. [e] OMe resonance obscured by MeOH. [f] C–F splitting ($J = 3.66$ Hz) observed in these resonances.

Table VI. Rate Constants for the Decomposition of *Z* Ethers Derived from Diazonium Salts 1l and 1m in the Presence of Thiophenolate Ions in Basic Alcoholic Solvents at 10 °C

	$10^6 k_{obsd}$	
[NaSPh], M	**1l**[a]	**1m**[b]
0.01		2160
0.02		3600
0.03		4890
0.04		6780
0.05	578	
0.075	720	
0.10	886	
0.125	1100	
0.15	1279	

[a] 4-SO_2Me compound in ethanol at 0.05 M NaOEt. From a plot of k_{obsd} against [NaSPh]: slope (k_2 for PhS^-) = 7.04×10^{-3} L mol^{-1} s^{-1}; intercept (k_{obsd} for EtO^-) = 200×10^{-6} s^{-1}. Expected rate at 0.05 M EtO^- = 228×10^{-6} s^{-1}. $k_2(PhS^-)/k_2(EtO^-) = 1.5$. [b] 4-$NO_2$ compound in methanol at 0.05 M NaOMe. From a plot of k_{obsd} against [NaSPh]: slope (k_2 for PhS^-) = 1.51×10^{-1} L mol^{-1} s^{-1}; intercept (k_{obsd} for MeO^-) = 500×10^{-6} s^{-1}. Expected rate at 0.05 M MeO^- = 491×10^{-6} s^{-1}. $k_2(PhS^-)/k_2(MeO^-) = 15.3$.

the methyl carbon it was at a higher field for the *Z* ether. A similar effect has been observed previously for the C-6 and cyanide carbons of (*E*)- and (*Z*)-cinnamonitriles.[13] This analogy was in fact used by us to assign the resonance at δ 125.6 to C-6 for the *E* ether and that at δ 127.6 to an impurity.

The rate of decomposition of this (*E*)-arylazo methyl ether was very similar to that obtained for the *E* ether generated in situ (Table IV). Also, the rate of decomposition was first order in [OMe^-] in both cases (Table IV).

Thus it seems reasonable that we have observed the direct decomposition (i.e., without prior ionization) of the (*E*)-arylazo alkyl ether for compounds **1h** and **1j**.

Reaction in the Presence of Thiophenolate Ions. Since electron transfer to the *Z* ether is postulated in the rate-determining step, it was thought that a better electron donor than an alkoxide ion (e.g., thiophenolate ion) should increase the rate of decomposition. Rate constants for the decomposition of compounds **1l** and **1m** in the presence of thiophenolate ions in basic ethanol and methanol, respectively, are given in Table VI. If the observed rate is plotted against [$C_6H_5S^-$], the second-order rate constant for the thiophenolate ion reaction is obtained from the slope while the intercept corresponds to the alkoxide rate at the base concentration used. For compound **1l** in ethanol, thiophenolate was found to react 1.5 times faster than ethoxide ion while for compound **1m** in methanol, thiophenolate reacts 15 times faster than methoxide ion. Thus the order of electron-transfer ability is $PhS^- > EtO^- > MeO^-$.

Scheme III. Suggested Mechanism for Base-Independent Reaction in CH_3OH

$$ArN{=}NOCH_3 \rightleftharpoons ArN_2^+ + OCH_3^- \qquad (7)$$

$$ArN_2^+ + OCH_3^- \longrightarrow ArN_2\cdot + CH_3O\cdot \qquad (8)$$

$$ArN_2\cdot \longrightarrow Ar\cdot + N_2 \qquad (9)$$

$$Ar\cdot + CH_3OH \longrightarrow \cdot CH_2OH + ArH \qquad (5)$$

$$2\dot{C}H_2OH \longrightarrow HOCH_2CH_2OH \qquad (6)$$

Mechanism of the Base-Independent Reaction. In summary, the base-independent mechanism is important for compounds that do not carry many strong electron-withdrawing substituents. Although the rate of reaction does not correlate well with either σ or σ^+, there is a definite trend to faster rate as the electron-donating power of subsitituents is increased ($\rho = -2.0$ in ethanol and -4.1 in methanol). In fact, the magnitude of the Hammett ρ value for the base-independent reaction in methanol (-4.1) is very similar to a literature value[2] for the ionization of (*Z*)-arylazo methyl ethers in methanol (-4.3). This suggests that the rate-determining step for the base-independent mechanism involves ionization of the (*Z*)-arylazo alkyl ether and that decomposition occurs on the free diazonium ion. This conclusion is also supported by the solvent effect on the rate of reaction for the base-independent mechanism (for compound **1e**, reaction in methanol occurs 16 times faster than in ethanol) and the fact that the observed decomposition rate is slower than the ionization rate (Table III).

Reaction of compound **1l** in EtOD gave nitrobenzene containing negligible (<3%) deuterium.[4] This indicates the intermediacy of aryl radicals. It has been shown that reaction of compound **1d** in methanol gives a lower yield of nitrobenzene when the reaction is carried out under an oxygen atmosphere (24.2%) than when it is carried out under a nitrogen atmosphere (56.6%).[14] This also indi-

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(13) Butt, G. Master of Science Thesis, La Trobe University, Bundoora, Victoria, Australia, 1981.

(14) Broxton, T. J.; Bunnett, J. F., unpublished observations.

cates the intermediacy of aryl radicals. The above kinetic data would seem to rule out the possibility that the rate-determining step for the base-independent reaction is homolytic cleavage of the *Z* ether to give free radicals. A mechanism that is consistent with these observations (Scheme III) involves electron transfer to the free diazonium ion from alkoxide ion (step 8).

The observed rate of decomposition of compound **1a** was not affected if the reaction mixture was bubbled with oxygen ($k_{obsd} = 3.56 \times 10^{-3}$ s^{-1} at 0.05 M ethoxide ion; cf. $k_{obsd} = 3.67 \times 10^{-3}$ s^{-1} at 0.05 M ethoxide ion in the normal reaction). This eliminates the possibility of a chain reaction for the base-independent reaction.

The rate-determining step is the ionization of the *Z* ether (step 7), and this leads to the observed substituent and solvent effects. The observed decomposition rate is less than the ionization rate because of partitioning of the free diazonium salt between reformation of the *Z* ether and acceptance of an electron. As the electron-withdrawing nature of the substituent is increased, the rate of ionization is reduced, but the acceptance of an electron by the free diazonium ion becomes more favorable. This results in a smaller ρ value in EtOH for decomposition (−2.0) than for ionization (−4.7) and in the considerable scatter of points in the Hammett plot for decomposition by the base-independent mechanism for compounds **1f,h,j**.

One further point that requires some comment is our conclusion that neither the base-dependent nor the base-independent mechanism of dediazoniation is a chain process. Chain processes have previously been reported for reactions in basic methanolic solution. For example, the radical-induced deiodination of aryl iodides in basic methanol is formulated as a chain process.[15] One possible reason why dediazoniation of the substituted 2-nitrobenzenediazonium salts in basic methanol is not a chain process is that the product of the reaction is a substituted nitrobenzene. It has previously been shown that the radical-induced deiodination of aryl iodides in basic methanol is inhibited very effectively by the addition of nitrobenzene.[15] Furthermore, chain processes in basic methanol depend on the efficient conversion of hydroxymethyl radicals into the formaldehyde radical anion. This results in the production of a better electron-transfer agent to carry the chain and also in the production of a radical species that is less prone to dimerization than the hydroxymethyl radical. To achieve this conversion efficiently, it has been shown that at least 2 M NaOMe is required.[15] In this work the highest [NaOMe] used was 0.2 M.

Experimental Section

Materials. Anilines. 2-Nitro-, 2-nitro-4-phenoxy-, 4-methyl-2-nitro-, 4-chloro-2-nitro-, 5-chloro-2-nitro-, and 2-nitro-4-(trifluoromethyl)anilines were available from previous work.[3] 2,4-Dinitroaniline was commercially available (Aldrich). 2-Nitro-4-methanesulfonylaniline [mp 197 °C (lit.[16] mp 200 °C)] was prepared from chlorobenzene by methanesulfonylation[17] ($MeSO_2Cl/AlCl_3$), nitration[18] (KNO_3/H_2SO_4), and amination (aqueous NH_3/CuCl/EtOH). 4-Benzoyl-2-nitroaniline [mp 137–139 °C (lit.[19] 135 °C)] was prepared by amination of 4-chloro-3-nitrobenzophenone (aqueous NH_3/CuCl/EtOH) at 150 °C in a sealed tube. 4-Cyano-2-nitroaniline [mp 159–160 °C (lit.[20] mp 162–163 °C)] was prepared from *p*-chloroaniline by diazotization[21a] ($HCl/NaNO_2$/0 °C), Sandmeyer reaction[21b] (KCN/CuCN), nitration[22] (fuming $HNO_3/HClO_4$), and amination[20] (pyridine/pyrollidine). 2-Nitro-5-(trifluoromethyl)aniline [mp 98–99 °C (lit.[23] mp 101 °C)] was prepared from 3-amino-1-(trifluoromethyl)benzene by acetylation (NEt_3/Ac_2O), nitration (fuming $HNO_3/HOAc/H_2SO_4$), hydrolysis (HCl), and steam distillation.[23] Its identity was confirmed by the production of *p*-nitro(trifluoromethyl)benzene upon dediazoniation (MeO^-/MeOH).

Diazonium Salts. With one exception, the required diazonium salts were prepared by the diazotization ($NaNO_2/HBF_4$) of the corresponding anilines as described by Bunnett.[5] The diazonium salt from 4-cyano-2-nitroaniline was prepared by the method of Doyle and Bryker.[24] (*Z*)-Arylazo alkyl ethers were prepared in situ by mixing precooled (10 °C) solutions of diazonium and alkoxide ions. [(*E*)-2-Nitro-4-(trifluoromethyl)phenyl]azo methyl ether was prepared from silver diazotate by methylation with methyl iodide.[1] Although this compound could not be isolated in a pure form, the following evidence suggests that it is the major product of the above reaction. A mass spectrum (JEOL JMS-D 100 operating at 25 °C) was obtained. Although no molecular ion was detected, a peak at *m*/*e* 218 which could be attributed to the breakdown product, the free diazonium ion, was seen. High-resolution measurements confirmed this conclusion: mol wt 218.0186; $C_7H_3F_3N_3O_2$ requires 218.0177. A sample of the free diazonium ion was not volatile enough to give a mass spectrum at 25 °C. It was necessary to heat this sample to 300 °C before a mass spectrum was detected. Thus the peak at *m*/*e* 218 in the mass spectrum of the reaction product must come from some component containing the diazonium function and having greater volatility than the free diazonium salt. This was most likely the (*E*)-arylazo methyl ether.

The proton and ^{13}C NMR spectra of the reaction product were compared to those of the free diazonium ion and the product formed initially on basification of the free diazonium ion (the *Z* ether). Proton spectra were determined at 90 MHz by using a Perkin-Elmer R32 NMR spectrometer.

Carbon-13 spectra were recorded by using a JEOL FX-200 NMR spectrometer and a pulse interval such that the carbon atoms bearing hydrogen dominated the spectrum.

The chemical shifts and coupling constants observed in these spectra are given in Table V. The ^{13}C spectra of the free diazonium ion and of the *Z* ether generated in situ were reasonably clean, but the spectrum of the *E* ether showed the presence of aromatic impurities.

Alcoholic solvents were dried by treatment with magnesium alkylate.[21c]

Kinetics. Decomposition rates of the *Z* and *E* ethers in alcoholic solvents were measured by a sampling technique using *N*-(1-naphthalenyl)ethylenediammine (NED) as described previously.[1,3] Rates of the base-dependent (k_2) and base-independent (k_1) reactions were obtained, respectively, from the slope and the intercept of plots of the observed rate against the [base]. Rate constants for reactions in the presence of thiophenolate ions were obtained in the same way except that thiophenol was added to the premixed diazonium and alkoxide ion solutions. Second-order rate constants for the thiophenolate reaction and observed rates for the alkoxide ion reaction were obtained, respectively, from the slope and the intercept of a plot of the observed rate against the thiophenolate concentration (see footnotes to Table VI).

Product Studies. The required diazonium salt (0.2 g) was dissolved in the basic alcoholic solvent (e.g., MeO^-/MeOD or EtO^-/EtOD). The mixture was stirred for 16 h at room temperature, poured onto ice, acidified, and extracted (Et_2O). The extract was washed (H_2O), dried ($MgSO_4$), and concentrated to approximately 1 mL. The products were analyzed by GC/MS with a 6-ft glass column containing 3% OV-1 on Gas Chrom Q. For compound **1m** the deuterium content of the dediazoniation

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[15] Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 6712.

[16] Lavrischchev, V.; Plakidin, V. L.; Kretov, A. E., *Zh. Obshch. Khim.* **1960**, *30*, 3064; *Chem. Abstr.* **1961**, *55*, 18647c.

[17] Truce, W. E.; Vriesen, C. W. *J. Am. Chem. Soc.* **1953**, *75*, 5032.

[18] Heppolette, R. L.; Lantzke, I. R.; Miller, J. *Aust. J. Chem.* **1956**, *9*, 299.

[19] Schöpff, M. *Ber.* **1891**, *24*, 3772.

[20] Lipke, B. *Z. Chem.* **1970**, *10*, 463.

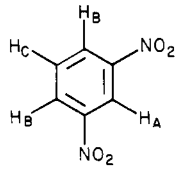
[21] Vogel, A. I. "Textbook of Practical Organic Chemistry", 3rd ed.; Longmans, Green and Co.: London, 1961: (a) p 600, (b) pp 607–8, (c) pp 167–9.

[22] Hammond, G. S.; Douglas, K. J. *J. Am. Chem. Soc.* **1959**, *81*, 1184.

[23] Rouche, H. *Bull. Cl. Sci., Acad. R. Belg.* **1927**, *13*, 346; *C. R. Hebd. Seances Acad. Sci.* **1927**, *185*, 1817. *Chem. Abstr.* **1928**, *22*, 2149.

[24] Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572.

product 3 increased with time. By NMR studies it was possible



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to show that the exchange was occurring at H_A and not at a H_B, the site vacated by the diazonium group.

For authentic *m*-dinitrobenzene: ^{1}H NMR δ 9.1 (1 H, H_A, t, J_{AB} = 2 Hz (meta)), 8.7 (2 H, H_B, dd, J_{BC} = 8 Hz (ortho), J_{AB} = 2 Hz (meta)), 7.95 (1 H, H_C, t, J_{BC} = 8 Hz (ortho)). After 10 min in the presence of 0.5 M EtO^-/EtOD, the integral for H_A had decreased by 50%, and if left overnight, the signal due to H_A disappeared completely. No change in the relative intensity of the signals due to H_B and H_C was observed. Thus H/D exchange occurs at H_A (the hydrogen on carbon 3 of the original diazonium salt). No deuterium incorporation at H_B could be detected. GC/MS confirmed the incorporation of 50% of one D in the product from **1m** after 10 min in 0.5 M EtO^-/EtOD.

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Registry No. (*Z*)-**1a** (R = Et), 71099-75-7; (*Z*)-**1b** (R = Et), 71099-76-8; (*Z*)-**1c** (R = Et), 71099-77-9; (*Z*)-**1d** (R = Et), 62375-92-2; (*Z*)-**1d** (R = Me), 62375-91-1; (*Z*)-**1e** (R = Et), 71099-79-1; (*Z*)-**1e** (R = Me), 81536-33-6; (*Z*)-**1f** (R = Et), 71099-80-4; (*Z*)-**1f** (R = Me), 81536-34-7; (*Z*)-**1g** (R = Me), 81536-35-8; (*Z*)-**1h** (R = Et), 71099-81-5; (*Z*)-**1h** (R = Me), 81536-36-9; (*E*)-**1h** (R = Me), 81536-37-0; (*Z*)-**1j** (R = Et), 81536-38-1; (*Z*)-**1j** (R = Me), 81536-39-2; (*E*)-**1j** (R = Me), 81536-40-5; (*Z*)-**1k** (R = Et), 81536-41-6; (*Z*)-**1l** (R = Et), 81536-42-7; (*Z*)-**1l** (R = Me), 81536-43-8; (*Z*)-**1m** (R = Et), 81536-44-9; (*Z*)-**1m** (R = Me), 81536-45-0; 2-nitro-4-(trifluoromethyl)benzenediazonium ion, 81536-46-1.

Lithium Perchlorate as a Reagent for Synthesis of Covalently Bonded Organic Perchlorates via Electrophilic Additions of Halogens and Nitronium Tetrafluoroborate to Olefins

N. S. Zefirov,* A. S. Koz'min, V. V. Zhdankin, A. V. Nikulin, and N. V. Zyk

Department of Chemistry, Moscow State University, Moscow 117234 USSR

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The reaction of a series of olefins with chlorine and bromine in the presence of a large excess of lithium perchlorate in ether gave 1,2-halo perchlorates together with the corresponding 1,2-dihalides. Analogous reactions of NO_2BF_4 in the presence of $LiClO_4$ in methylene chloride or ethyl acetate with monoolefins gave 1,2-nitro perchlorates. Norbornadiene reacted with a NO_2BF_4/$LiClO_4$ system to give two isomeric nitro perchlorates of nortricyclenic structure. Several synthetic and mechanistic aspects of this new reaction of electrophilic perchloration of olefins are discussed.

The influence of added salts on the rates and even the modes of organic reactions is of both fundamental and applied interest.[1,2] For example, salt effects can provide valuable information about the mechanism because rate changes can be used to determine the charge distribution in the transition state.[1] If the added salt should not interfere in the reaction by capturing any intermediates, the salts of perchloric acid usually can be used to meet this requirement due to the very weak nucleophilicity of perchlorate ions. For example, the addition of perchlorates to reaction media is commonly used to maintain a constant ionic strength in buffer-catalysis studies. Anodic oxidation is often performed in the presence of the salts of perchloric acid.[3] The addition of perchlorates produces a rate acceleration, and the rate constant is directly proportional to the salt concentration (normal salt effect).[4]

However, the additon of perchlorates, e.g., $LiClO_4$, sometimes induces a number of interesting chemical effects.[5,6] Studies of salt effects due to the addition of $LiClO_4$ have proved to be extremely successful in investigations of ion-pair phenomena in solvolysis.[6] A special salt effect characterized by Winstein et al.[5] led to the proposal that at least two types of ion pairs were present in many solvolyses. Anhydrous solutions of $LiClO_4$ in solvents of low ionizing capacity exhibit a significant acceleration of processes which proceed via carbocationic-like intermediates.[7,8] For example, epoxides undergo facile rearrangements when perchlorate salts are present.[7] This promotion appears to be due to electrostatic effects.[7c] Catalysis by ionic aggregates of $LiClO_4$ in diethyl ether is also clearly documented.[8]

The rates of electrophilic addition reactions often have been measured in the presence of added lithium per-

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(1) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; Chapters 7 and 9.

(2) Gordon, J. E. "The Organic Chemistry of Electrolyte Solutions"; Wiley: New York, 1975; Chapter 3.

(3) Baizer, M. M, Ed. "Organic Electrochemistry"; Marcell Dekker: New York, 1973; Section C.

(4) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763–7. Winstein, S.; Friedrich, E. C.; Smith, S. *Ibid.* **1964**, *86*, 305–7.

(5) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2767–70. Winstein, S.; Clippinger, E. *Ibid.* **1956**, *78*, 2784–8. Winstein, S.; Klinedinst, P. E.; Robinson, G. C. *Ibid.* **1961**, *83*, 885–95. Winstein, S.; Appel, B. R. *Ibid.* **1964**, *86*, 2718–20, 2720–1.

(6) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Szwarz, M., Ed., Wiley: New York, 1974; Vol. 2. Beletskaya, I. P. *Usp. Khim.* **1975**, 2205–48.

(7) (a) Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4193–4. (b) Battistini, C.; Crotti, P.; Ferretti, M.; Macchia, F. *J. Org. Chem.* **1977**, *42*, 4067–71. (c) Pocker, Y.; Ronald, B. P. *J. Am. Chem. Soc.* **1980**, *102*, 5311–6.

(8) Pocker, Y.; Buchholz, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 2075–84; **1971**, *93*, 2905–9. Pocker, Y.; Ellsworth, D. L. *Ibid.* **1977**, *99*, 2276–84, 2284–93.

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