(2) (a) F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 2119 (1972); (b) *ibid.*, **94**, 5829 (1972).

(3) The initially formed Michael carbanion might be expected to initiate an intramolecular displacement to give a cyclopropane derivative.[4] Products of this type have never been observed in reactions of **1**.

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(6) H. O. Larson, "The Chemistry of the Nitro and Nitroso Compounds," H. Feuer, Ed., Interscience, New York, N.Y., 1969, p 330, reports that "use of *tert*-butyl halides with sodium nitrite for the preparation of nitro compounds is worthless."

(7) N. Kornblum has shown that SN2-type substitution products also can be obtained from reactions of nucleophiles with a somewhat analogous tertiary halide system, $p\text{-}NO_2C_6H_4CMe_2X$. Here, however, the substitution is usually accomplished by an anion-radical mechanism.[8] Evidence that our substitutions are not of this type will be given in subsequent papers.

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Formation of an Ion-Pair Intermediate in an SN2-Type Reaction

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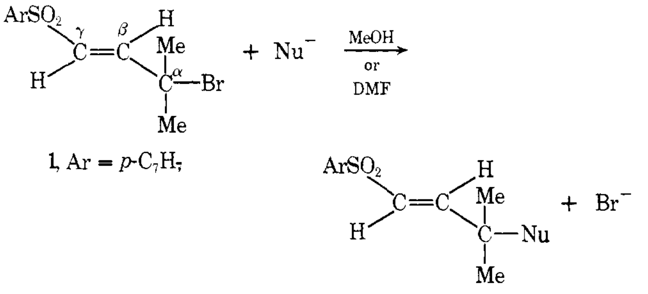
Abstract: With lithium azide $p\text{-}C_7H_7SO_2CH{=}CHCMe_2Br$ (**1**) undergoes second-order substitution in DMF or MeOH. A second-order component for the rate was demonstrated also in 60% MeOH by both kinetic analysis and product analysis. The close correspondence between the $k^{N_3^-}/k^{Sol}$ ratio in 60% MeOH as derived from kinetic analysis (2180) with that derived from product analysis (2150) shows that the rate-controlling and product-controlling steps are the same. In MeOH the selectivity of azide over solvent was about twice as great as in 60% MeOH. The rate for **1** reacting with LiN_3 increases on increasing the polarity of the protic medium by addition of water or salt to a much greater extent than is true for the same reaction with the corresponding primary bromide, $ArSO_2CH{=}CHCH_2Br$. The $k_{N_3^-}{}^{DMF}/k_{N_3^-}{}^{MeOH}$ ratio is appreciably smaller for tertiary bromide **1** (*ca.* 122) than for SN2 reactions of primary bromides (10^3-10^4). Changing the substituent Y in $YCH{=}CHCMe_2Br$ from H to $ArSO_2$ causes a marked retardation in rate in a reaction with azide (negative ρ^*) whereas a similar change for $YCH{=}CHCH_2Br$ reacting with $S{=}C(NH_2)_2$ or KI causes an opposite change (positive ρ^*). These observations, together with a substantial β-deuterium isotope effect for the reaction of **1** with lithium azide in 60% MeOH, are consistent with an ion-pair-SN2 mechanism for reactions of **1** with nucleophiles in protic solvents.

Azide ion has proved to be particularly useful in studying substitutions at carbon since it displays high nucleophilicity toward both primary substrates (*e.g.*, toward MeBr log (k^N/k^{H_2O}) = 4.0[2] and toward MeI log (k^N/k^{MeOH}) = 5.78[3]) and cations.[4,5] In 80% acetone a linear relationship between log (k^N/k^{H_2O}) and log k_0 has been observed for *t*-BuCl and other highly reactive chlorides ($H_2C{=}CHCMe_2Cl$, Ph_3CCl, etc.) which appear to react without nucleophilic assistance (Lim mechanism) in solvents of high-ionizing power.[6] Less reactive substrates, including 2-octyl mesylate and $H_2C{=}CHCHMeCl$, fail to fit the correlation, being much more selective than expected.[6] On the other hand, the selectivity–reactivity correlation can be extended to a number of other substrates believed to be reacting without nucleophilic assistance.[7] Ritchie has shown that stable cations, regardless of structure and reactivity, exhibit the same *relative reactivity* (N_+ value) toward azide ion *vs.* solvent in a number of solvents. (The N_+ for N_3^- in H_2O is >5.4, for N_3^- in MeOH it is 8.5, and for N_3^- in DMSO it is 10.5).[5] It appears likely, therefore, that if "free" cations (as distinct from ion pairs) were produced in solvolyses in 80% acetone they would show the *same* selectivity toward N_3^- *vs.* H_2O. The differing selectivities observed for N_3^- *vs.* H_2O in this medium of relatively poor ionizing power (Y = −0.637 compared to 3.493 for water) is probably a consequence of a blend of selectivities of different kinds of ion pairs rather than being characteristic of the stability of free cations, as was formerly supposed.[6] Nevertheless, the reactivity–selectivity correlation still can provide useful mechanistic information. It seems likely that the k^N/k^{H_2O} ratio will change in some characteristic manner for unhindered substrates as one changes from SN2-type reactions with extensive nucleophilic participation, to reactions involving ion-pair intermediates of various types, and finally to free cations.

In solvents like 80% acetone, azide ion often accelerates the rate for substrates of intermediate susceptibility to ionization, or sometimes even those of high reactivity, to an extent greater than anticipated for a salt effect. For example, with the highly reactive tertiary allylic chloride, $H_2C{=}CHCMe_2Cl$ azide appears to introduce a second-order component into the rate ($k_2 \cong 42\ M^{-1}\ sec^{-1}$ at 32°).[8] This observation, together with the observation of 100% inversion for the reaction of the azide and of solvent with substrates exhibiting "borderline" solvolytic behavior, and a detailed kinetic analysis of the latter systems has led Sneen to conclude that in these situations the solvent and azide (or other nucleophile) are competing for an intimate ion-pair intermediate.[9] Sneen has further suggested that this ion-pair mechanism can accommodate *all* substitutions at saturated carbon.[9,10]

Schleyer and his students have shown that for *i*-PrOTs and 2-Oct-OBs substrates the rate-controlling and product-controlling steps are the same for reactions of azide in 80% EtOH, whereas for adamantyl systems they are not.[7] Schleyer suggests that competitive nucleophilic solvent and azide attack on *either* the covalent substrate or the tight ion pairs derived therefrom can account for their kinetic data and also for Sneen's kinetic data.[11]

In previous papers we have shown that tertiary allylic bromide **1** undergoes SN2-type substitution reactions with a variety of weakly basic nucleophiles.[12] As a result of applying a number of types of mechanistic probes it was concluded in a preliminary report that the reactions were occurring by an ion-pair-SN2 mechanism rather than a classical SN2 mechanism,[13] In this and the two succeeding papers we present the details of this study.



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Results

Second-Order Substitution Reactions. The rate of reaction of bromide **1** with lithium azide was determined under pseudo-first-order conditions and constant ionic strength in methanol, aqueous methanol, or dimethylformamide (DMF) solutions using at least a 12-fold excess of azide ion. For reactions in methanol and DMF, division of the pseudo-first-order rate constants by the nucleophile concentrations (three or more in the range 0.03 to 0.30 *M*) gave second-order constants independent of azide concentration. These results are summarized in Table I; rates for chloride **1a** with lithium azide in DMF are included for comparison.

Table I. Second-Order Coefficients for the Reaction of p-$C_7H_7SO_2CH{=}CHC(Me)_2Br$, **1** (and Chloride **1a**), with Lithium Azide

RX	Solvent	T, °C	μ^a	10^5k_2,[b] M^{-1} sec^{-1}
1	MeOH	25	0.30	6.48
1	MeOH	50	0.10	87
1	MeOH	50	0.30	90 (±1)[c]
1a	60% MeOH–H_2O	50	0.30	19.9
1	60% MeOH–H_2O	50		585 (±3)[d,e]
1	60% MeOH–H_2O	50	0.30	622 (±1)[c,f]
1a	DMF	25	0.30	10[g]
1a	DMF	50	0.30	67
1	DMF	20	0.0	3400[h]
1	DMF	20	0.30	1090
1	DMF	40	0.30	5350
1	DMF	50	0.30	11000

[a] Total of [LiN_3] plus [$LiClO_4$]; substrate concentrations were *ca.* 2×10^{-3} *M* and LiN_3 concentrations were at least 12-fold larger. [b] Precise to within ±5% unless otherwise noted. [c] The rate was unaffected by addition of 10 mol % (based on **1**) of galvinoxyl, or by protection of the reaction from light with aluminum foil, or by using degassed methanol, or by saturating the methanol with air. [d] No $LiClO_4$ added; salt concentration varied from 0.04 to 0.13 *M* during the runs. [e] Obtained using eq 1 (r = 0,999). [f] Obtained using eq 1 (r = 0.9999). [g] Extrapolated from the rate at 50° using E_a for **1** (14.5 kcal/mol) and k_{Br}/k_{Cl} measured at 50°. [h] Extrapolated rate at zero salt concentration using eq 2 (r = 0.99).

In 60% methanol–water the second-order coefficients calculated in the usual way were *not* independent of azide concentration but, instead, decreased monotonically with increasing azide concentration. The data in Table II for the reaction of bromide **1** with lithium azide in the presence of $LiClO_4$ (0.3 *M* total salt concentration) are typical. A reasonably constant coefficient could be obtained using eq 1,

Table II. Pseudo-First-Order ($k_{obsd}{}^1$); Second-Order ($k_{obsd}{}^2$), and Calculated (eq 2) Second-Order ($k_N{}^2$) Rate Constants for the Reaction of 3-Bromo-3-methyl-1-*p*-tolylsulfonyl-1-butene (**1**) with Lithium Azide in 60% (v/v) MeOH–H_2O at 50° and Ionic Strength 0.30[a]

10[LiN_3]	$10^4k_{obsd}{}^1$, sec^{-1}	$10^3k_{obsd}{}^2$,[b] M^{-1} sec^{-1}	$10^4k_N{}^2$,[c] M^{-1} sec^{-1}
0.00	1.03[d]		
0.00	1.22		
0.60	5.04	8.39	63.7
0.80	6.21	7.77	62.4
1.0	7.44	7.44	62.2
1.2	8.75	7.29	62.8
1.4	9.92	7.09	62.1
1.6	11.17	6.98	62.2

[a] Anhydrous $LiClO_4$ was used to maintain constant ionic strength [b] $k_{obsd}{}^2 = k_{obsd}/[LiN_3]$. [c] $k_N{}^2 = (k_{obsd}{}^1 - k_S)/[LiN_3]$, where k_S is the rate in the absence of nucleophile (0.3 *M* $LiClO_4$ present). [d] Rate in the absence of $LiClO_4$.

$$k_N = (k_{obsd} - k_S)/[N] \text{ or } k_{obsd} = k_N[N] + k_S \qquad (1)$$

where k_N is the true second-order constant, k_{obsd} is the observed pseudo-first-order constant, and k_S is the observed solvolysis rate constant in the absence of azide, but in the presence of 0.3 *M* $LiClO_4$. This equation assumes that the observed rate is the sum of a nucleophile-dependent rate and an azide-independent rate. Equation 1 predicts a linear relationship between k_{obsd} and [N], the slope being k_N and the intercept k_S. The data in Table II are depicted graphically in Figure 1. The least-squares slope, k_N, is 6.22 ± 0.01 × 10^{-1} M^{-1} sec^{-1} with a correlation coefficient (r) of 0.9999.[14] The other second-order coefficients in 60% MeOH–H_2O recorded in Table I were obtained similarly.

Since in the reaction of bromide **1** with LiN_3 in 60% MeOH both the azide product (**2a,** Nu = N_3) and the solvolysis products (**2b,** Nu = OMe or OH) were formed in appreciable quantities, the kinetic analysis could be checked by a product analysis. According to eq 1 the product ratio, [**2a**]/[**2b**], is determined only by the ratio $k_N[LiN_3]/k_S$. In other words, a plot of the ratio [**2a**]/[**2b**] *vs.* [LiN_3] should be a straight line with a slope of k_N/k_S. The product ratios for bromide **1** with varying azide concentration are summarized in Table III and are represented graphically in Figure 2. A good linear correlation was observed (r = 0.99).

Table III. Product Distributions from Reactions of Bromide **1** with Varying Concentrations of Sodium Azide in 60% (v/v) MeOH–H_2O

10[NaN_3]	[RN_3]/ [R-O-Sol][a,b]	10[NaN_3]	[RN_3]/ [R-O-Sol][a,b]
0.000	0.00	0.520	2.7
0.208	0.86	0.785	3.7
0.311	1.4	1.04	5.2
0.415	1.9		

[a] Product data based on nmr integration of the geminal methyl group resonances of RN_3 and R-O-Sol (*i.e.*, either ROH and $ROCH_3$). [b] In the least-squares analysis of the data each point was given unit weight except for the zero azide points which were given a weight of three.

The relative rates of reaction of bromide **1** (or an intermediate derived therefrom) with azide ion *vs.* solvent defines a *selectivity coefficient.* The ratio of second-order rate constants, $k_N/(k_S/[S])$, is 2180 ([S] = solvent concentration = 43 *M*), which is in good agreement with the selectivity coefficient of 2150 obtained from the product data.

Small positive salt effects (*ca.* 3% increase from 0.1 to 0.3 *M* $LiClO_4$) were observed for the reactions of **1** with

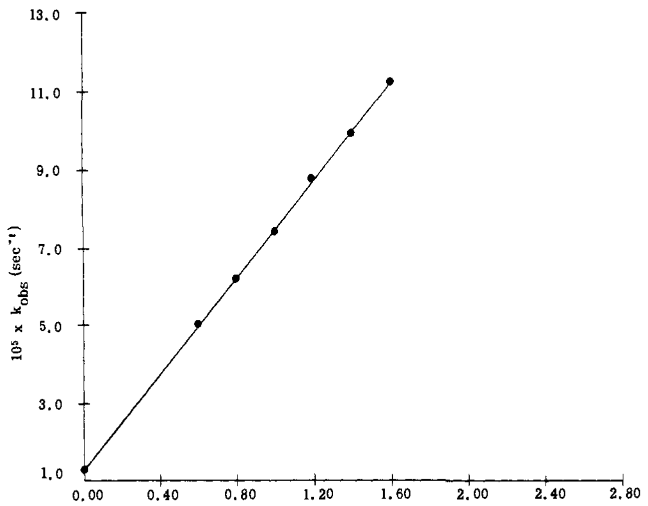

Figure 1. Plot of k_{obsd} *vs.* [LiN_3] for 3-bromo-3-methyl-1-*p*-tolysulfonyl-1-butene (**1**) in 60% (v/v) methanol-water at 50° and ionic strength of 0.3 *M*.

lithium azide in methanol and 60% methanol, but a large negative salt effect (*ca.* 300% decrease from 0.0 to 0.3 *M* $LiClO_4$) was observed in DMF (Table IV). The rate at zero salt concentration for the reaction of DMF at 20° was calculated from the data using the Winstein equation for salt effects,[15] where k_{obsd} is the second-order rate constant at a given salt concentration, k_0 is the second-order constant obtained by extrapolation to zero salt concentration, and *b* is a constant varying with the sensitivity of the system to salt effects. Linear regression analysis of data where the lithium azide concentration was fixed and the total salt concentration was varied by addition of lithium perchlorate (from 0.02 to 0.14) yielded $b = -4.7$ ($r = 0.99$); see Table IV.

$$k_{obsd} = k_0(1 + b[\text{total salt}]) \qquad (2)$$

Table IV. The Effect of Added Lithium Perchlorate on the Rate of Reaction of Bromide **1** with Lithium Azide in DMF at 20°

$10^2[LiN_3]$, *M*	10^2[total salt],[a] *M*	10^4k_1, sec^{-1}	10^2k_2,[b] M^{-1} sec^{-1}
3.56	3.56	10.5	2.85
3.56	5.47	8.72	2.45
3.56	7.52	7.56	2.12
3.56	9.47	6.54	1.84
3.56	11.4	5.89	1.65
6.44	30.0	6.74	1.05
13.44	30.0	14.7	1.10
13.68	30.0	15.7	1.12

[a] [LiN_3] + [$LiClO_4$]. [b] The rate at zero salt concentration is $3.4 \pm 0.1 \times 10^{-2}$; *b* is −4.7 ($r = 0.99$) calculated using eq 2.

Discussion

In the preliminary account of this work we demonstrated that in reactions with nucleophilic solvents and nucleophiles, **1** exhibits borderline behavior, *i.e.*, it responds to some mechanistic probes in a manner expected for an ionization mechanism, but to others in a manner expected for an SN2 reaction.[13] It was concluded that reactions with solvents and nucleophiles were occurring generally by attack on the α-carbon atom of the cation of an ion-pair intermediate formed in a preequilibrium step. Evidence was presented to show that formation of **2** from **1** did not occur: (a) by elimination followed by addition, (b) by attack of Nu^- at the γ-carbon atom (SN2′) followed by its rearrangement to the α-carbon atom (SNi′), or (c) by an anion-radical substitution mechanism.[12,16] Since then, further evidence against the SN2′-SNi′ pathway has been obtained, a mechanism whereby Nu^- undergoes Michael addition to the β-carbon atom followed by migration to the α-carbon atom has been shown to be unlikely, and evidence for an analogous ion-pair-E2 mechanism for reactions of a tertiary allylic cyclohexyl analog of **1** has been obtained.[17]

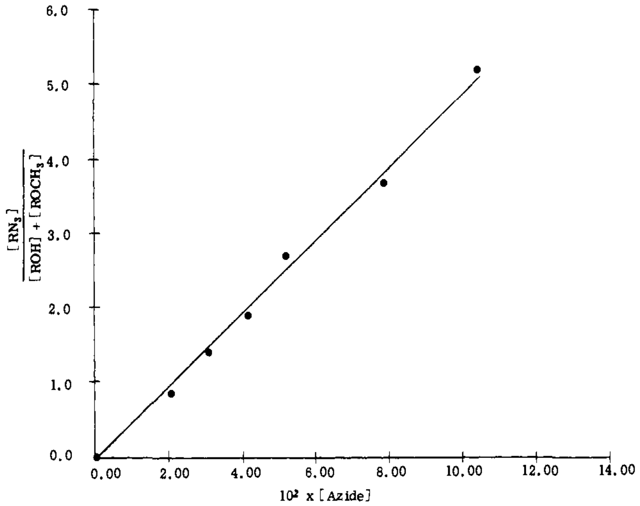

Figure 2. Plot of [RN_3]/{[ROH] + [$ROCH_3$]} *vs.* [NaN_3] for 3-bromo-3-methyl-1-*p*-tolylsulfonyl-1-butene (**1**) in 60% methanol-water (v/v) at 50°.

In this paper we compare the behavior of tertiary bromide **1** with that of the corresponding primary bromide, $ArSO_2CH{=}CHCH_2Br$, with respect to: (a) kinetics in MeOH, 60% MeOH, and DMF, (b) relative sensitivity to nucleophilicity and solvent ionizing power, (c) solvent and salt effects, and (d) structure-reactivity relationships (Table V).

Table V. Comparison of Nucleophilic Substitution with $ArSO_2CH{=}CHCH_2Br$ and $ArSO_2CH{=}CHCMe_2Br$ (**1**)

Mechanistic probe	Relative response to mechanistic probe of $ArSO_2CH{=}CHCH_2Br$	 $ArSO_2CH{=}CHCMe_2Br$
Kinetic order with LiN_3	2nd (DMF) 2nd (MeOH)	2nd (DMF) 2nd (MeOH) Mixed (60% MeOH)[a]
k^{rel} (LiN_3 in MeOH)	29[b]	(1.0)
k^{rel} (LiN_3 in DMF)	>1500	(1.0)
k^{DMF}/k^{MeOH} (with LiN_3)	*ca.* 10^4	122
$k^{60\%\ MeOH}/k^{MeOH}$ (with LiN_3)	1.7	6.9
Kinetic salt effect on $k_{N_3^-}$ ($LiClO_4$ in MeOH or 60% MeOH)	Negative[c]	Positive
β-Deuterium isotope effect (LiN_3 in 60% MeOH)	Negligible[d]	1.22-Fold retardation per CD_3 group[c,e]

[a] First order in LiN_3 and pseudo first order in solvent. [b] The rate for the corresponding secondary bromide is 2.9 times slower. [c] See F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **97**, 127 (1975), Tables II and III for the data. [d] Judging from the behavior of other primary substrates. [e] In MeOH the α-CD_3 effect is 1.10 and in DMF it is 1.07,

Kinetics in Aqueous Methanol. The solvolysis rate for **1** is of a comparable order of magnitude to that for isopropyl bromide or isopropyl tosylate, Furthermore, the reaction of **1** with azide ion in 60% MeOH resembles that of *i*-PrOTs in 80% EtOH[7] in that the rate-controlling and product-controlling steps are the same. (With **1** $k_N/k_S = 2180$ from kinetic analysis and 2150 from product analysis.) This could mean that azide ion and solvent are competing with one an-other for a common intermediate, presumably an ion pair. Azide competes more successfully in pure MeOH, where $k_N/k_S = 6000$ (from a comparison of k_N in Table I with the methanolysis rate), than in 60% MeOH. This could be due to a higher nucleophilicity of azide ion in MeOH than in 60% MeOH, but this cannot be the whole story since k_N is actually 6.9 times greater in 60% MeOH. The attack by solvent nucleophiles on **1** is facilitated even more than that by azide ion by virtue of this solvent change (27-fold). Since water is probably a slightly weaker nucleophile than methanol, the faster rate in aqueous MeOH does not appear to be caused by increased nucleophilicity, but rather by a greater susceptibility of **1** to attack by solvent nucleophiles in a solvent of greater ionizing power. This could mean that more than one kind of ion pair is present.

Relative Sensitivities of Primary and Tertiary Bromides to Nucleophilicity and Ionizing Power. A change from a protic to a dipolar aprotic solvent is known to markedly enhance the rates of SN2 reactions of anions with primary alkyl halides by virtue of an increased nucleophilicity of the anion caused by desolvation.[18] Judging from the reactions of PhSNa with *n*-BuBr, *i*-PrBr, and *t*-BuBr, these effects become progressively smaller in going from primary to secondary to tertiary bromides.[18] The ratios of rates for primary *vs.* tertiary bromides, $ArSO_2CH{=}CHCR_2Br$ (R = H or Me), reacting with azide are: >1500:(1.0) in DMF, 29:(1.0) in MeOH, 7.1:(1.0) in 60% MeOH, and 2.4:(1.0) in H_2O (calcd). The decrease in this ratio appears to be caused on the one hand by a higher sensitivity of the primary bromide to azide nucleophilicity, which decreases as N_3^- becomes more strongly solvated, and on the other hand by a higher sensitivity of the tertiary bromide to solvent ionizing power, which increases markedly from DMF to MeOH to H_2O. The tertiary bromide is sensitive to nucleophilicity, but much less so than the primary bromide, as may be seen by the increased rates for DMF *vs.* MeOH (122 for **1** as compared to *ca.* 10^4 for the primary bromide).

Solvent and Salt Effects. The Hughes-Ingold solvation rule predicts that rates for SN2 reactions involving negatively charged nucleophiles and neutral substrates will be retarded in protic solvents by a change to a solvent with greater ionizing power.[19] This qualitative rule holds in many instances, but there also appear to be numerous exceptions. The rule holds for *i*-PrBr reacting with lyate ion in aqueous alcohol,[19] for CH_3I reacting with SCN^-, Br^-, or I^-,[18] for CH_3Br reacting with I^-, and for methyl tosylate reacting with SCN^- and N_3^- (changes from MeOH to H_2O)[18] but fails to hold for CH_3Br or CH_3I reacting with Cl^-, for *n*-BuBr reaction with N_3^- (changes from MeOH to H_2O)[18] or for $ArSO_2CH{=}CHCH_2Br$ or **1** reacting with N_3^- (changes from MeOH to 60% MeOH, Table V). In terms of Grunwald-Winstein m values, adherence to the rule corresponds to a small negative m value while violation of the rule corresponds to a small positive m value. For $ArSO_2CH{=}CHCH_2Br$, *n*-BuBr, and **1** m values calculated from the data cited are 0.09, 0.18, and 0.32, respectively. The latter value is comparable to the m values for solvents reacting with most primary bromides.

Both **1** and the corresponding primary chloride[20] show comparable negative salt effects in reacting with LiN_3 in DMF ($b = -4.7$ and -3.1, respectively). This appears to be typical of SN2 reactions in dipolar aprotic solvents and is presumably caused by increased aggregation of LiN_3 as the salt concentration increases. In MeOH and 60% MeOH tertiary bromide **1** and $ArCH{=}CHCH_2Br$ exhibit *opposite* salt effects (Table V). This constitutes further evidence for a difference in mechanism, but the effects are small.

Structure-Reactivity Relationships. Effect of an Arenesulfonyl Group. Comparison shows that tertiary allylic bromide **1** undergoes solvolysis at a rate *ca.* 1400 times slower than that of *t*-BuBr in 60% MeOH-H_2O and *ca.* 10^{10} slower than that of $H_2C{=}CHCMe_2Br$ in 80% EtOH-H_2O.[21] These rate differences would be expanded to *ca.* 10^4 and *ca.* 10^{11}, respectively, if comparisons were made in water.[21] It is clear that introduction of the $ArSO_2$ group has retarded the solvolysis rate of **1** to the point where it behaves more like an ordinary secondary bromide than a tertiary allylic bromide. The rate of reaction of **1** with azide ion has also been greatly retarded, judging from a comparison of our rate data with that reported by Sneen.[8] Using the Grunwald-Winstein mY relationship a rough estimate indicates that in 80% acetone at 32° the rate constant for **1a**, $ArSO_2CH{=}CHCMe_2Cl$, reacting with azide ion in 80% acetone will be about $3 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$. This value is about 10^7 smaller that the second-order rate constant estimated by Sneen for reaction of $H_2C{=}CHCMe_2Cl$ with azide under these conditions.[8] This strong rate-retarding effect of the $ArSO_2$ group contrasts sharply with its effect on the reactivity of primary allylic halides reacting with nucleophiles. Thus, for $ArSO_2CH{=}CHCH_2X$ *vs.* $H_2C{=}CHCH_2X$ reacting with thiourea in MeOH the $ArSO_2$ group causes a 2.8 to 4.8 *acceleration* in rate with X = Cl, Br, or I.[22] A similar accelerating effect has been observed in the reaction of $ArSO_2CH{=}CHCH_2Cl$ (or $N{\equiv}CCH{=}CHCH_2Cl$) *vs.* $H_2C{=}CHCH_2Cl$ with potassium iodide in acetone.[23] The reactions of the primary halides, $ArSO_2CH{=}CHCH_2X$, with nucleophiles therefore have positive Taft ρ^* values. This is not surprising, since the Hammett ρ for reactions of nucleophiles with the analogous benzyl halides are often slightly positive.[24] On the other hand, the reaction of tertiary chloride **1** with azide appears to have a strongly negative ρ^*. This negative ρ^* is consistent with a reversible ionization step for **1** preceding attack by azide ion.

β-Deuterium-Isotope Effects.[25] Both α- and β-deuterium-isotope effects for direct displacements on primary systems are near unity. For $^{131}I^-$ exchange on CH_3I in MeOH the CD_3 effect was 1.05,[26] and for hydrolysis of various ethyl substrates (CD_3CH_2X) the CD_3 effects averaged 1.03.[27] The effect of 1.22 per CD_3 for **1** reacting with azide ion in 60% MeOH is in the range observed for hydrolysis of isopropyl substrates (1.20),[26] and the effects in MeOH and DMF are also larger than those expected for an SN2 reaction. The data point to a mechanism involving ionization as part of the rate-controlling process. We conclude from the above results that reactions of **1** with aqueous alcoholic solvents and azide nucleophile are consistent with a mechanism involving formation of an ion-pair intermediate. Additional discussion of mechanism will be presented in the next two papers in this series.[20,21]

Experimental Section

Chemicals. The methanol was freshly opened B & A anhydrous reagent grade used without further purification. Absolute ethanol was purified by the method of Lund and Bjerrum.[28] The aqueous alcohol solvents were prepared by mixing the alcohols (v/v) with the appropriate amounts of distilled, deionized water. Reagent grade DMF was purified by treatment with barium oxide, distilled at reduced pressure, and then stored over Linde 4A molecular sieves for at least 1 week prior to use. The latter treatment was essential to remove the last traces of dimethylamine contaminant. Sodium azide was recrystallized from ethanol. Lithium azide was Eastman reagent grade used without purification, as was the anhydrous lithium perchlorate. All salts were stored over P_2O_5.

Kinetic Procedure. The nucleophile and lithium perchlorate (when they were used) were precisely weighed into 50 (or 100) ml screw-cap volumetric flasks and *ca.* 95% of the solvent was added. The solution was made up to volume after equilibration in a constant temperature bath (±0.02°) for at least 1 hour. A preweighed sample of **1** was then added (to make *ca.* 2×10^{-3} *M* solution of halide) and the solution was thoroughly mixed. Aliquots were withdrawn with an automatic pipette and quenched in 10 ml of 0.5 *M* sulfuric acid in aqueous acetone. The time at which the sample was half quenched was recorded. The samples were titrated immediately with 2.82×10^{-3} *M* silver nitrate using a Sargent Model D Autotitrator. The infinity titer was the average of at least four titrations (±2%) of samples withdrawn after 10-12 half-lives. First-order rate constants were obtained by simple linear regression analysis of the ln $(V_\infty - V_i)$ *vs.* time data. In all cases the first-order plots were strictly linear to at least 4 half-lives. Second-order constants were calculated by division of the pseudo-first-order constants by the nucleophile concentration (at least two different concentrations) when applicable, or by linear regression analysis of the pseudo-first-order constant and nucleophile concentration data (eq 1).

Product Distribution. The distribution of solvolysis and substitution products resulting from the reaction of **1** with sodium azide in 60% aqueous methanol (v/v) was determined by integration of the geminal methyl resonances of the components using a Varian A60 spectrometer. The gem-methyl resonances of the alcohol, the methyl ether, and azide were previously determined to be 1.35, 1.28, and 1.40 τ, respectively.[12] The reactions were performed under pseudo-first-order conditions with a large excess of sodium azide at the reflux point of the solvent. After 18 hr the reaction mixtures were poured into a saline solution and extracted with four portions of chloroform. The chloroform was dried using sodium sulfate and concentrated *in vacuo.* The residue was taken up in chloroform-*d*, and the nmr spectra were measured.

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Further Evidence for the Formation of an Ion-Pair Intermediate in an SN2-Type Reaction[1a]

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Abstract: The rates of reaction of primary bromide $ArSO_2CH{=}CHCH_2Br$ (**1b**) reacting with lithium azide in DMF and MeOH have been compared to those of tertiary bromide $ArSO_2CH{=}CHCMe_2Br$ (**3b**). Rate and product comparisons for **1b** and **3b** were also made with KSCN in MeOH, $S{=}C(NH_2)_2$ in 60% MeOH, and $PhNH_2$ in MeOH and 60% MeOH. Leaving group effects were determined where Br in **1b** and **3b** is replaced by Cl and OMs (methanesulfonate). Striking differences in the behavior of **1b** and **3b** were observed in some of these comparisons, and it is concluded that **1b** and **3b** are reacting with nucleophiles by different mechanisms. The behavior of **3b** in reactions with nucleophiles in protic solvent is shown to resemble in many respects that of *t*-BuBr. The reactions of **3b** are interpreted in terms of an ion-pair-SN2 mechanism.

In the previous paper both primary allylic halide **1**, $ArSO_2CH{=}CHCH_2X$, and tertiary allylic halide **3**, $ArSO_2CH{=}CHCMe_2X$, were shown to undergo SN2-type substitution reactions with azide ion, but the rates of these reactions were found to be affected differently by: (a) solvent effects, (b) substituent effects, and (c) β-deuterium isotope effects.[2] Changing the solvent from MeOH to DMF evoked a much greater rate-accelerating response from primary halide **1** than from tertiary halide **3**, whereas the opposite was true when the solvent was changed from MeOH to 60% MeOH. Comparison of the rates for $ArSO_2CH{=}CHCH_2X$ *vs.* $HCH{=}CHCH_2X$ reacting with nucleophiles showed that the $ArSO_2$ group caused a mild accelerating effect, whereas for the tertiary system ($ArSO_2CH{=}CHCMe_2X$ *vs.* $HCH{=}CHCMe_2X$) the $ArSO_2$ group caused a strong retarding effect. For tertiary halide **3** reacting with azide ion an appreciable β-deuterium isotope effect was observed, whereas primary halides, like **1**, are known to exhibit negligible isotope effects in reactions with nucleophiles. It was concluded that **1** and **3** were reacting