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 Aliquots were withdrawn with an automatic pipette and quenched in 10 ml of 0.5 *M* sulfuric acid in aqueous acetone.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 The infinity titer was the average of at least four titrations (±2%) of samples withdrawn after 10–12 half-lives.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.

Acknowledgment. This work was supported in part by the National Science Foundation (GP-29539X) and in part by the Mobil Research Foundation.

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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 with azide ion by different mechanisms. An ion-pair-S$_N$2 mechanism was assigned to **3**. Further comparisons of the reactivity of primary system **1** and tertiary system **3** have now been made, and further differences have been noted. Their relative behavior has been explored with respect to: (a) effect of nucleophile structure on the rate, (b) products formed with various types of nucleophiles, and (c) effect of changing the leaving group on the rate. Some comparisons have been made with the corresponding secondary halide, **2**.

Results

The rates of reaction of primary, secondary, and tertiary halides, **1a, 1b, 2b,** and **3b,** with sodium or lithium azide and with aniline were followed by titration of the released halide ion with silver nitrate. The reactions of mesylates **1c** and **3c** with neutral nucleophiles were followed by measuring the solution conductance as a function of time. All of these experiments were performed under pseudo-first-order conditions with concentrations of substrate of the order of 2 × 10^{-3} M and at least a 12-fold excess of nucleophile. Least-squares analysis gave good first-order lines to at least 4 half-lives under proper conditions.

Reactions of primary chloride **1a** with azide in methanol or aqueous methanol and of primary bromide **1b** with azide in methanol did not obey a first-order rate law. Plots of log (C_∞/C_i) *vs.* time showed definite curvature, and the calculated rate after *ca.* 40% reaction was much less than the initial rate of reaction. This deviant behavior was corrected by buffering the solutions with 2 mol % (based on [RX]) of a mixture of mono- and dibasic potassium phosphate. Under these conditions good first-order behavior was observed to at least 4 half-lives. We believe that the behavior of **1a** and **1b** in nonbuffered media is caused by liberation of a small amount of a strong base (MeO^- or HO^-) *via* an addition reaction; the liberated base then catalyzes tautomerization of the substrate.[3]

$$\underset{\textbf{1a or 1b}}{PhSO_2CH{=\!=}CHCH_2X} + N_3^- + MeOH \rightleftharpoons PhSO_2CH_2CH(N_3)CH_2X + MeO^-$$

$$PhSO_2CH{=\!=}CHCH_2X \xrightleftharpoons{[MeO^-]} PhSO_2CH_2CH{=\!=}CHX$$

This interpretation is strengthened by the observation of clean pseudo-first-order kinetics in the reactions of tertiary bromide **3b** with LiN_3 and of primary halides **1a** or **1b** with aniline under similar conditions. With **3b** tautomerism is not possible and in the reactions of **1a** and **1b** with aniline addition of $PhNH_2$ will not generate lyate ion.

Rate data for reactions of **1** and **3** with LiN_3 in DMF are summarized in Table I. Similar data for reactions of **1, 2,** and **3** with lithium azide, aniline, and thiourea in MeOH and in 60% MeOH are given in Tables II and III.

The values reported in Tables I-III are an average of at least three kinetic runs and at least two nucleophile concentrations. The observed second-order values were determined to a precision of at least 5%. The best second-order constants were obtained when constant ionic strength was maintained with lithium perchlorate. Numerical estimates of the magnitude of salt effects were obtained by use of the Winstein equation,[4] $k_2^{obsd} = k_2(1 + b[salt])$.

Table I. Second-Order Rate Constants for the Reaction of $ArSO_2CH{=\!=}CHCR_1R_2X$ with Lithium Azide in Dimethylformamide

RX	R$_1$	R$_2$	X	T, °C	μ^a	10^3k_2,^{b} M^{-1} sec^{-1}
1a	H	H	Cl	0	0.04	3.5
1a	H	H	Cl	25	0.00	54.5^c
1b	H	H	Br	0	0.04	>2000
3a	CH_3	CH_3	Cl	50	0.30	0.67
3a	CH_3	CH_3	Cl	25	0.00	0.31^d
3b	CH_3	CH_3	Br	20	0.30	10.9
3b	CH_3	CH_3	Br	40	0.30	53.5^e
3b	CH_3	CH_3	Br	50	0.30	110
3b-d_6	CD_3	CD_3	Br	50	0.30	95.6
3b	CH_3	CH_3	Br	50	0.00	344^f

[a] Constant ionic strength maintained with $LiClO_4$. [b] The rates at μ = 0.30 are observed whereas those at 0.00 are those obtained by extrapolating to zero salt concentration using the Winstein salt equation. [c] b = −3.1 in the Winstein equation. [d] Calculated using E_a (the value for **3b**) and k^{Br}/k^{Cl} = 164 (ratio at 50°). [e] At 0.08 M LiN_3 k_{obsd} was not affected by light, dark, or saturation of the solvent with air. [f] b = −4.7 in the Winstein equation.[3]

Table II. Rates of Reaction of $ArSO_2CH{=\!=}CHR_1R_2X^a$ with Nucleophiles in Methanol at 50°

RX	Nu	R$_1$	R$_2$	X	μ^b	10^4k_2, M^{-1} sec^{-1}
1b	LiN_3	H	H	Br	0.30	262^c
1b	LiN_3	H	H	Br	0.04	326
1b	$PhNH_2$	H	H	Br		16.5
1c	$PhNH_2$	H	H	OMs		5.83
1b	$S{=\!=}C(NH_2)_2$	H	H	Br		468^d
1c	$S{=\!=}C(NH_2)_2$	H	H	OMs		74.6
2b	LiN_3	H	CH_3	Br	0.30	90.9
2b	LiN_3	H	CH_3	Br		96.0
2b	$PhNH_2$	H	CH_3	Br		2.04
3b	LiN_3	CH_3	CH_3	Br	0.30	9.01^{e,f}
3b-d_6	LiN_3	CD_3	CD_3	Br	0.30	7.5
3b	LiN_3	CH_3	CH_3	Br	0.10	8.7
3b	$PhNH_2$	CH_3	CH_3	Br		0.23
3b	$S{=\!=}C(NH_2)_2$	CH_3	CH_3	Br		0.18^g
3c	LiN_3	CH_3	CH_3	OMs		2320^h

[a] For **1** and **2**, Ar = C_6H_5; for **3**, Ar = p-$CH_3C_6H_4$. [b] Ionic strength maintained by adding $LiClO_4$. [c] At 25° (μ = 0.30) k = 21.5 × 10^{-4} M sec^{-1}. [d] F. G. Bordwell, P. E. Sokol, and J. D. Spainhour, *J. Amer. Chem. Soc.*, **82**, 2881 (1960). [e] At 25° (μ = 0.30) k = 0.65 × 10^{-4} M^{-1} sec^{-1}. [f] No appreciable change in the rate was observed: (1) under protection from light, (2) with degassed solvent, (3) with solvent saturated with air, or (4) on addition of 20 mol % (based on **3b**) of galvinoxyl. [g] Calculated from the rate in 60% MeOH assuming a solvent effect comparable to that observed for aniline (*i.e.*, 6.6-fold rate decrease). [h] Calculated from product data obtained at 25° and k_S at 50° (see text).

The rate of reaction of tertiary mesylate **3c** with LiN_3 was too fast for convenient measurement in methanol. A value for k_N could be estimated, however, from the product data determined as for tertiary bromide **3b**.[2] A plot of the product ratios $[RN_3]/[ROSol]$ *vs.* $[N_3^-]$ for azide concentrations of 0.00, 0.0524, 0.1095, 0.2190, and 0.3260 gave a line (Figure 1) with a correlation coefficient (r) of 0.9997 (the zero point was given a weight of 3 in the least-squares plot) with a slope = 4.86 ± 0.04; $k_N = 4.86 \times k_S = 1.73 \times 10^{-2}$ M^{-1} sec^{-1} at 25° (2.32 × 10^{-1} M^{-1} sec^{-1} at 50°). The inert salt effects on the individual rate components (k_N and k_S) were not explicitly determined; however, in view of the observed linear correlation of products with azide concentration and the small inert salt effects observed for reactions of the corresponding tertiary bromide, **3b**, in methanolic solvents,[2] the error in k_N should not be large. From these data k_N/k_S = 122 in MeOH at 25°.

Discussion

Table IV presents a comparison of: (a) the relative reactivities of primary system **1** and tertiary system **3** toward various nucleophiles, (b) the types of products formed from **1** and **3** with certain nucleophiles, and (c) leaving group effects for **1** and **3**.

Relative Nucleophilicities. Examination of Table IV reveals some marked differences between **1** and **3** in responses toward azide ion, relative to other nucleophiles, in MeOH

Table III. Rates of Reaction of $ArSO_2CH{=}CHCR_1R_2X^a$ with Nucleophiles (Nu) in 60% MeOH–H_2O at 50°

RX	Nu	R_1	R_2	X	μ^b	10^4k_2, M^{-1} sec^{-1}
1a	LiN_3	H	H	Cl	0.30	9.9
1b	LiN_3	H	H	Br	0.30	451
1b	LiN_3	H	H	Br	0.04	512^c
1b	$PhNH_2$	H	H	Br		91.9
2b	LiN_3	H	CH_3	Br	0.30	206
3b	LiN_3	CH_3	CH_3	Br	0.30	62.2^d
3b-d_6	LiN_3	CH_3	CH_3	Br	0.30	42.1
3b	LiN_3	CH_3	CH_3	Br		58.5^d
3b	$PhNH_2$	CH_3	CH_3	Br		1.52^e
3b	$S{=}C(NH_2)_2$	CH_3	CH_3	Br		1.22^f

[a] For **1** and **2**, Ar = C_6H_5; for **3**, Ar = p-$CH_3C_6H_4$. [b] Constant ionic strength maintained with $LiClO_4$. [c] Rates at 25 and 37.4° (μ = 0.04) were 51.3×10^{-4} and 164×10^{-4} M^{-1} sec^{-1}, respectively. [d] Reference 2b. [e] Determined from a plot of k_{obsd} *vs.* $[PhNH_2]$ (r = 0.998). [f] Determined from a plot of k_{obsd} *vs.* $[S{=}C(NH_2)_2]$ (r = 0.985).

Table IV. Comparison of Nucleophilic Displacements at Primary and Tertiary Carbon Atoms

No.	Mechanistic probe	Relative response to mechanistic probe of $ArSO_2CH{=}CHCH_2X^a$	Relative response to mechanistic probe of $ArSO_2CH{=}CHCMe_2X^b$
(1)	$k^{N_3^-}/k^{SC(NH_2)_2}$ (in 60% MeOH)	0.67	51
(2)	$k^{N_3^-}/k^{SCN^-}$ (in MeOH)	0.16^c	10^d
(3)	$k^{N_3^-}/k^{NO_2^-}$ (in 60% MeOH)	2.7^e	$>15^f$
(4)	$k^{N_3^-}/k^{PhNH_2}$ (in MeOH)	20	38
(5)	$k^{N_3^-}/k^{PhNH_2}$ (in 60% MeOH)	5.6	39
(6)	Product with KSCN (in MeOH)	>98% RSCN	40% RNCS
(7)	Product with PhSNa (in MeOH)	S_N2^g	S_N2' $(80\%)^h$
(8)	$k_{N_3^-}{}^{Br}/k_{N_3^-}{}^{Cl}$ (in DMF)	570	164
(9)	$k_{Nu}{}^{OMs}/k_{Nu}{}^{Br}$ (in MeOH)	*ca.* 0.2^i	260^j

[a] $ArSO_2$ = $PhSO_2$, X = Br, unless otherwise noted. [b] $ArSO_2$ = p-$CH_3C_6H_4SO_2$, X = Br, unless otherwise noted. [c] For MeBr in H_2O; for MeI in MeOH the value is 0.15. [d] Based on product analysis; >98% RN_3 plus <2% ROMe as compared to 43% (RSCN + RNCS) plus 53% ROMe. [e] For MeI in MeOH. [f] Based on product analysis. [g] Unpublished result of J. Weinstock. [h] Reference 12. [i] Based on the behavior of **1** with $PhNH_2$ and $S{=}C(NH_2)_2$. [j] Based on the reaction of **3** with LiN_3.

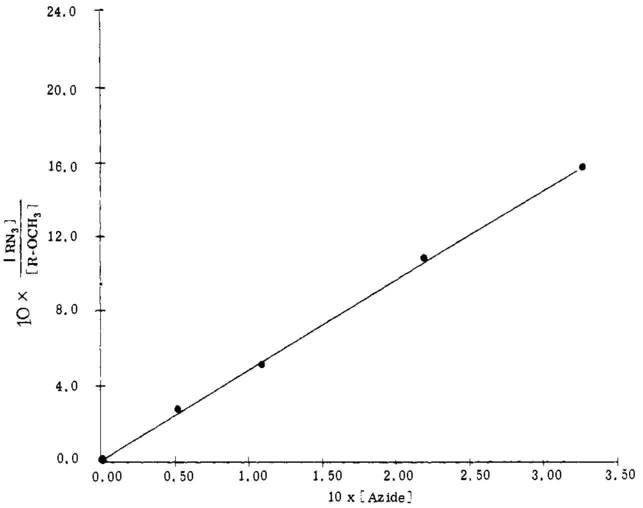


Figure 1. Plot of $[RN_3]/[ROCH_3]$ *vs.* $[LiN_3]$ for 3-mesyloxy-3-methyl-1-p-tolylsulfonyl-1-butene (**3c**) in methanol at 25°.

or 60% MeOH. The tertiary bromide (**3b**) is more reactive toward azide ion than toward thiourea, thiocyanate ion, or aniline. On the other hand, primary bromide **1b** is less reactive toward azide ion than toward thiourea in 60% MeOH. Relative reactivities of **1b** toward azide ion and thiocyanate ion were not measured, but for MeBr in water[5a] and MeI in MeOH[5b] the order of reactivity with N_3^- and SCN^- is known to be opposite to that observed with **3**.

$$ArSO_2CH{=}CHCR_2Br + Nu^- \longrightarrow ArSO_2CH{=}CHCR_2Nu + Br^-$$

For **1** (R = H): $N_3^- < S{=}C(NH_2)_2$; KSCN gives exclusively $ArSO_2CH{=}CHCH_2SCN$. For **3** (R = H): $N_3^- > S{=}C(NH_2)_2$; KSCN gives some $ArSO_2CH{=}CHCMe_2NCS$.

High reactivity appears to be characteristic of reactions of azide ion with cationic species. An early study by Swain, Scott, and Lohmann showed that azide ion was about 10^5 times more reactive than water toward the trityl cation, and that it was also more reactive than AcO^-, Cl^-, $PhNH_2$, HO^-, SCN^-, or $S_2O_3^{2-}$.[6] Ritchie has shown that this high reactivity holds also for other stable cations.[7] In his studies azide ion was shown to be at least $10^{5.4}$ times more reactive than water toward cations and 10^8 times more reactive than MeOH toward cations. In MeOH relative reactivities toward stable cations (N_+ values) are: 3.8 for $C_6H_5SO_2^-$, 5.9 for CN^-, 7.5 for CH_3O^-, 8.5 for N_3^-, and 10.7 for $C_6H_5S^-$.

The data in Table IV demonstrating an unusual preference for azide ion relative to other nucleophiles in the reactions of tertiary bromide **3b** appear to be best interpreted in terms of reaction of **3b** *via* a cationic intermediate. On the other hand, the behavior of **1b** is typical of that of a primary bromide. Thus **1b** follows the example of MeBr[5a] and MeI[5b] in being more reactive toward thiourea than toward azide ion, but it behaves like **3b** (and MeI) in being more reactive toward azide ion than toward aniline.

The response of $k^{N_3^-}/k^{PhNH_2}$ on changing from MeOH to 60% MeOH is different for **1b** and **3b**. For **1b** this ratio decreases from 20 to 5.6 as the ionizing power of the solvent increases. This is not unexpected since the rates of S_N2 reactions between two neutral substrates (*i.e.*, **1b** and $PhNH_2$) are known to increase with increased solvent ionizing power,[8] whereas that between a negatively charged nucleophile and neutral substrate may either increase or decrease.[2] For **1b** the aniline rate increases by 5.5-fold and the azide rate by 1.7-fold; for **3b** the aniline rate increased by 6.6-fold, but this is matched by a 6.9-fold increase in azide rate. As has been pointed out previously,[2] this large increase in azide rate is contrary to the Hughes-Ingold qualitative solvation rule and is further evidence for a reaction involving a cationic intermediate or transition state.

Variations in Product Types. The formation of appreciable quantities of isothiocyanate products in the reaction of mesylate **3c** and bromide **3b** with potassium thiocyanate in MeOH and acetone under conditions of kinetically controlled product formation is further evidence for an ion-pair-S_N2 mechanism for these tertiary substrates. Reaction of bromide **3b** with KSCN in MeOH for 16 hr at reflux gave an even smaller [RSCN]:[RNCS] ratio (0.3:1.0) than for mesylate **3c**. Some RSCN → RNCS rearrangement may have occurred under these conditions, although no isomerization of p-$MeC_6H_4SO_2CH{=}CHCMe_2SCN$ was detected after 24 hr in MeOH at 50°. (Isomerization in refluxing acetonitrile required *ca.* 60 hr for completion.) Primary and secondary bromides are known to react with KSCN to give essentially 100% RSCN products.[10] Primary and secondary bromides **1b** and **2b** follow this pattern. On the other hand, the behavior of **3b** (and **3c**) resembles that of t-BuCl, which reacts with KSCN in water at 38° to give [RSCN]:[RNCS] = 2.5:1.0;[11] it is also reminiscent of the behavior of the ion pair (p-MeC_6H_4)CH^+SCN^-, which undergoes internal return to give (p-MeC_6H_4)$_2CHNCS$.[10]

The ambident ion NO_2^- behaves somewhat differently than the SCN^- ion with **3b.** In 60% MeOH about equal amounts of RNO_2 and RONO products appear to be formed,[12] which is expected for a reaction involving cationic intermediate or transition state,[13] but in DMF the product is essentially all RNO_2, and it is formed in high yield.[12]

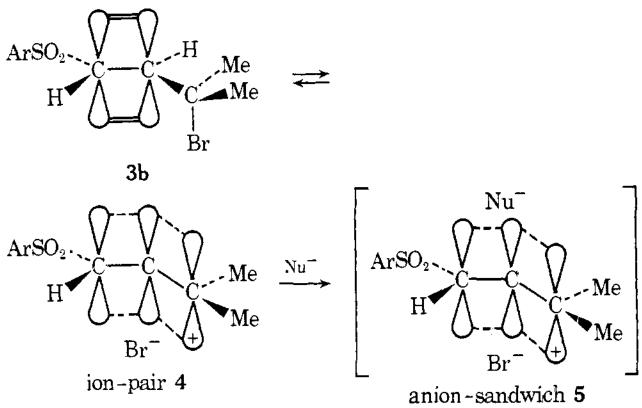
With PhSNa-PhSH in MeOH at 50° **3b** initially gives about 25% of the SN2 product, 10% of the elimination product, and 50% of the SN2′ product.[12] (The SN2′ product undergoes partial SNi′ rearrangement under these conditions.[12]) In contrast, **1b** gives essentially 100% of the SN2 product. Once again we have evidence for reactions of **3b** and **1b** occurring by different mechanisms. The formation of both SN2 and SN2′ products from **3b** appears to be best explained by assuming a competitive attack at the α- and γ-carbon atoms of a cationic intermediate.[12]

Leaving Group Effects. The large k^{Br}/k^{Cl} ratio (570) for **1** in DMF (Table IV) is typical behavior for primary halides in dipolar aprotic solvents (k^{Br}/k^{Cl} is 178 for EtX reacting with LiCl in acetone[14] and 250 for the reaction of N_3^- with MeX in DMF[15]). The effect with tertiary halide **3** with LiN_3 in DMF is also large (164). On the other hand, the k^{OMs}/k^{Br} ratios in protic solvents are dramatically different for **1** and **3.** The k^{OMs}/k^{Br} ratio of less than one for **1** reacting with LiN_3 in MeOH is typical for strong nucleophiles reacting with a primary system.[16] The k^{OMs}/k^{Br} ratio of 260 for LiN_3 reacting with **3** in MeOH is, on the other hand, the reverse of the order usually observed in SN2 reactions. A ratio greater than one is, instead, typical of SN1 and E1 reactions,[15] and indeed the ratio for **3** approaches these in magnitude.[17]

Relative Rates. Comparisons of relative rates for primary, secondary, and tertiary bromides, **1b, 2b,** and **3b,** can be made from the data presented in Tables I-III. The large primary:tertiary ratio for **1b** *vs.* **3b** in DMF (>1500) is of the same order of magnitude as that observed by Cook and Parker for $Et_4N^+N_3^-$ reacting with MeBr *vs.* t-BuBr in DMF (2.5×10^4 at 25°).[19] Examination of Table II shows that in MeOH the primary:tertiary ratio for **1b** *vs.* **3b** reacting with N_3^- is much compressed (29:1.0), and the primary:secondary ratio (**1b** *vs.* **2b**) is also small (2.9:1.0).[20] The primary:secondary ratio is also somewhat smaller than usual for reaction of **1b** *vs.* **2b** with aniline (8.9; see Table III). These small primary:secondary ratios may be due to lesser steric hindrance toward nucleophilic attack in these allylic systems. The small primary:tertiary ratio of **1b** *vs.* **3b** toward N_3^- in MeOH conceivably could also be explained in this way, but in view of the extensive evidence for ion pairs in reactions of **3b** we believe that this is more likely due to a mechanistic change. The primary:tertiary ratio is somewhat larger for the reaction of **1b** and **3b** with aniline in MeOH (72) and is substantially larger for the reaction of **1b** and **3b** with thiourea (2600; see Table II).

Evidence for an Ion-Pair-SN2 Mechanism. The evidence summarized in Table IV for greater ionic character in the reactions of nucleophiles with tertiary bromide **3b,** as compared to the corresponding primary bromide **1b** or aliphatic primary bromides, appears to be best accommodated by assuming that **3b** is reacting by an ion-pair-SN2 mechanism. The possible existence of a mechanism wherein the rate-limiting step is attack by a nucleophile on an ion pair, which is in equilibrium with a covalent substrate, has been recognized for some time.[21,22] This mechanism is indistinguishable in kinetic order from the classical SN2 mechanism wherein the nucleophile attacks the covalent substrate. From a kinetic analysis of the reaction of azide ion with 2-octyl mesylate in 30% aqueous dioxane, a "borderline" kinetic region, Sneen and Larsen claim to have identified an ion-pair intermediate and to have established the ion-pair-SN2 mechanism as a reality.[23,24] Similar evidence has been presented for a number of other borderline systems,[24] and Sneen has suggested that this mechanism should be extended to include *all* SN2 reactions. The kinetic analysis of Sneen depends, however, on an interpretation of salt effects, and Schleyer and his students have shown that an alternative interpretation is possible, which makes the data consistent with a classical SN2 mechanism.[25,26]

Our evidence for an ion-pair intermediate in the reactions of nucleophiles with tertiary bromide **3b** is circumstantial. It depends on a comparison of the behavior of **3b** in these reactions, on the one hand, with those of the corresponding primary bromide **1b** (or simple aliphatic primary halides), and, on the other hand, with those of t-BuBr. The primary systems can be looked on as models for the classical SN2 mechanism and the tertiary aliphatic system as a model for a classical SN1 mechanism. In the previous paper[2] we presented evidence to show that tertiary bromide **3b** responded differently than primary bromide **1b** in four different kinetic tests toward azide in that it showed: (a) a smaller (accelerating) solvent effect in changing from MeOH to DMF and a larger accelerating solvent effect in changing from MeOH to 60% MeOH, (b) an appreciable β-deuterium isotope effect (1.2-fold retardation), (c) an apparent negative Taft ρ^* rather than a positive Taft ρ^*, and (d) a positive salt effect in both MeOH and 60% MeOH, rather than a negative one. All of these differences point to much greater ionic character for the reactions of **3b** than for **1b** or ordinary aliphatic primary halides. In this paper we have presented further evidence which leads to the same conclusion, namely we have observed: (a) a greater reactivity for **3b** toward N_3^- than toward $S{=}C(NH_2)_2$ of KSCN, as contrasted to a reversed order of reactivity for **1b,** (b) formation of appreciable quantities of RNCS for reactions of bromide **3b** or mesylate **3c** with KSCN under conditions where **1b** gave only RSCN, (c) formation of a preponderance of SN2′ product from **3b** and PhSNa under conditions where **1b** gave only SN2 prouct, and (d) a large $k_{Nu^-}{}^{OMs}/k_{Nu^-}{}^{Br}$ ratio for **3** reacting with N_3^- as compared to an inverse ratio for **1** reacting with $PhNH_2$ or $S{=}C(NH_2)_2$. These studies have provided abundant evidence to show that tertiary allylic bromide **3b** reacts with nucleophiles by a different mechanism than does the corresponding primary bromide **1b,** or other primary bromides. On the other hand, the characteristics of the reactions of tertiary bromide **3b** with nucleophiles resemble those of *tert*-butyl bromide with nucleophiles or protic solvents in the following respects: (1) a positive response to increasing the ionizing power of the protic solvent, (2) a positive kinetic salt effect, (3) a substantial rate-retarding β-deuterium isotope effect, (4) a negative Taft ρ^*, (5) a high reactivity toward N_3^- relative to other nucleophiles, (6) formation of some RNCS in reactions with KSCN in protic solvents, and (7) a much lower reactivity with respect to that of the corresponding mesylate. Yet **3b** differs from t-BuBr in two important respects. First, it is much more susceptible to attack by nucleophiles than by protic solvents, which leads to a difference in kinetics, *i.e.,* reactions in protic solvents are first order in nucleophile for **3b** as compared to zero order in nucleophile for t-BuBr. Second, although **3b** resembles t-BuBr in giving principally elimination products with strongly basic nucleophiles, it differs from t-BuBr in giving high yields of substitution products with weakly basic nucleophiles.[27] The evidence points, then, to a modified ionic-type mechanism for **3b** similar to that which is generally accepted for t-BuBr. One representation, which has a number of attractive features, is to assume the formation of an ion-sandwich intermediate (*e.g.*, **5**).[28] Intermediate **5** could be formed by attack of a nucleophile on a preformed ion-pair intermediate (**4**),[23,24] or could be formed by direct nucleophilic attack on **3b.**



3b

ion-pair **4**

anion-sandwich **5**

This mechanism differs from that generally accepted for t-BuBr with respect to the role of the nucleophile (Nu$^-$). For t-BuBr the intimate ion pair, analogous to **4**, is believed to dissociate readily, and attack by Nu$^-$ occurs *after* the rate-limiting step. For **3b** attack of Nu$^-$ is pictured as occurring either on ion-pair **4** or on **3b** (to form **5** directly). In either event the nucleophile is involved in the rate-limiting step. The differing behavior of **3b** arises from replacement of one methyl group in t-BuBr by an ArSO$_2$CH=CH group. This changes both the electronic and steric behavior of the bromide. The presence of the strongly electron-withdrawing ArSO$_2$ group greatly retards ionization of the C–Br bond (the hydrolysis rate for **3b** is *ca.* 10^5 slower than for t-BuBr and *ca.* 10^{11} slower than for the parent allylic bromide, HCH=CHC(Br)Me$_2$[29]). At the same time the presence of the -CH=CH- group allows some delocalization of the positive charge from the α-carbon atom in **4** or **5** (as shown) and lessens the build-up of positive charge in the methyl groups. Substitution of ArSO$_2$CH=CH for CH$_3$ also decreases steric hindrance to attack of the α-carbon atom by the nucleophile. The result of a smaller positive charge on the methyl groups and lesser steric hindrance accounts for the greater tendency of **3b** *vs.* t-BuBr to undergo S$_N$2-type, rather than E2-type, reactions.

Acknowledgment. This work was supported by the National Science Foundation (GP-29539X). We wish to express our appreciation to Professor P. v. R. Schleyer for many helpful suggestions with respect to the interpretation of the data presented in this series of papers.

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