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Addition, Substitution, Rearrangement, and Elimination in Allylic Systems

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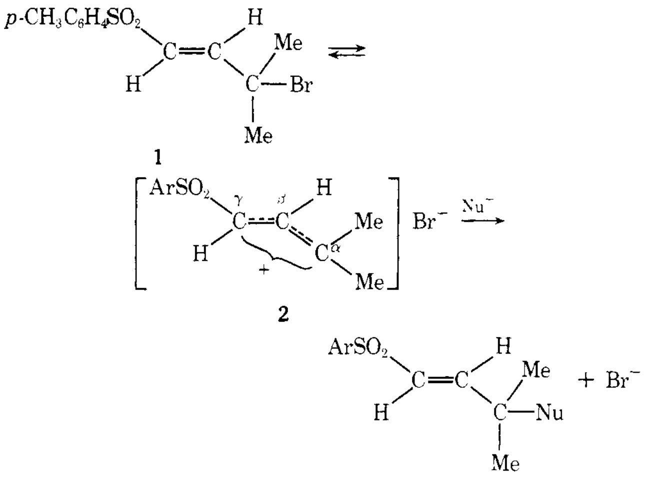
Abstract: Methanol adds to the double bond of tertiary allylic bromide **1**, $ArSO_2CH{=}CHC(CH_3)_2Br$, when **1** is treated with NaOMe-MeOH at 25°. This Michael adduct does not rearrange to the methoxide substitution product of **1** (OMe replaces Br). The SN2′-SNi′ route to SN2-type substitution products of **1** was also ruled out. Reaction of **1** with thiophenoxide salts under carefully controlled conditions did give the SN2′-type product, $ArSO_2CH(SPh)CH{=}C(CH_3)_2$, and this did undergo SNi′ rearrangement under ionizing conditions. The product formed in the SNi′-type rearrangement was, however, $PhSCH{=}CHC(CH_3)_2SO_2Ar$, an isomer of the SN2-type substitution product. Reaction of **1** with $NaNO_2$ in DMF gave a high yield of SN2-type substitution product. An analog of **1** in which the two methyl groups were replaced by a cyclohexyl group (**11**) was found to react principally by elimination under all conditions (Table I). Both sodium thiophenoxide and potassium thioacetate were found to be more effective in methanol at promoting elimination from **11** than was sodium methoxide. It is concluded that the greater reactivity of the sulfur nucleophiles is associated with their greater affinity for the cation of an ion-pair intermediate. The reactions are given the mechanistic classification ion-pair E2, $(E2)_{ip}$. The reaction of **11** with sodium methoxide was shown to be first order in methoxide concentration.

In previous papers we have shown that tertiary allylic bromide **1** displays unique properties in reacting with nucleophiles.[2] For example, **1**, unlike most tertiary bromides, gives substantial amounts of SN2-type substitution products with many weakly basic nucleophiles. Furthermore, the reactions in several instances have been shown to be first order in nucleophile.[2a] This unusual behavior has been attributed to the combined presence of the electron-withdrawing $ArSO_2$ group and the C=C bond. The $ArSO_2$ group apparently inhibits ion-pair dissociation but does not stop ion-pair formation. The allylic system in **1** allows sufficient delocalization of the positive charge in the cation of the ion pair to inhibit elimination. As a consequence, weakly basic nucleophiles are able to react at the cationic α-carbon atom in the ion-pair intermediate (**2**) to effect SN2-type substitution reactions giving **3**. The present paper presents a more detailed product study for reactions of certain nucleophiles with **1**, and reports results with an analogous tertiary allylic cyclohexyl bromide (**11**) wherein the tendency toward elimination is greatly enhanced.



1

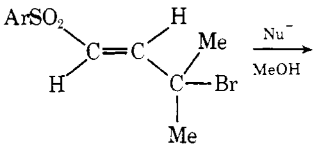
2

3

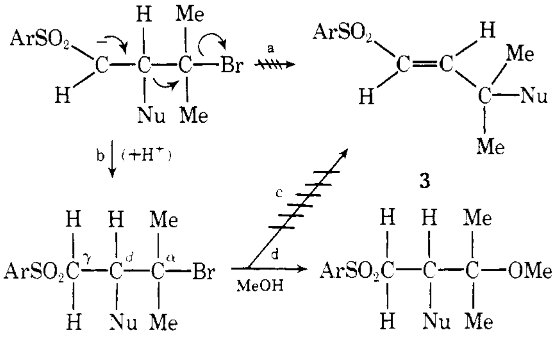
Results and Discussion

Michael Addition. Since SN2-type reactions at tertiary carbon atoms are rare,[2a] one must be on the alert for other pathways leading to the observed substitution products (**3**). Several mechanisms involving Michael-type addition can be imagined which might give **3** (*e.g.*, paths a and c).

Reaction of bromide **1** with NaOMe in MeOH at 25° gives an 89% yield of Michael adduct **4** (Nu = OMe). This shows that path b is much preferred to path a. Conceivably the Nu group in adduct **4** could initiate neighboring group participation, possibly aided by simultaneous loss of a proton from the γ-carbon atom, to displace Br and give the SN2-type product **3** (Nu = OMe). Alternatively, the C-Br bond in adduct **4** might dissociate to a C^+Br^- ion pair, and Nu could migrate to the electrophilic center thus produced; simultaneous or subsequent loss of a proton from the γ-carbon atom would give **3**. In practice, neither of these c pathways was realized.[3] Instead adduct **4** underwent methanolysis on refluxing for 27 hr to form 42% of the dimethoxy compound (**5**, Nu = OCH_3) and 58% of the diene derived from **4** by loss of HBr and HOMe. These results rule out the paths a and c for the (observed) formation of **3** (Nu = OCH_3) by treatment of bromide **1** with methanol or methanol containing small amounts of sodium methoxide. They also argue against a Michael-type addition pathway as a reasonable alternative to SN2-type displacement for the formation of **3** from **1**.



1



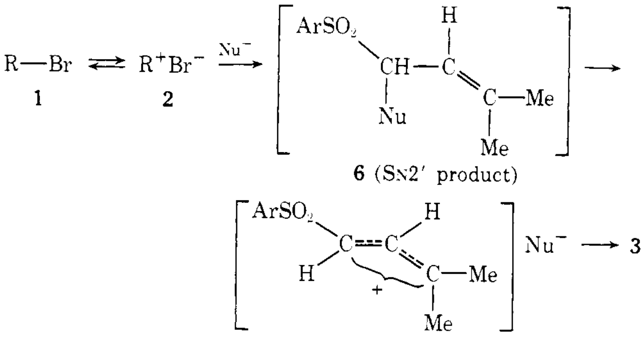
3

4

5 (plus diene)

The formation of a Michael adduct from allylic bromide **1** is easily discernible by the disappearance of nmr signals for alkenic protons. Products of this type are formed in only small amounts, if at all, with most nucleophiles that we have studied under the conditions we have used.[2] One exception, in addition to NaOMe, is the observation of a Michael product in substantial yield from the reaction of **1** with potassium thioacetate in MeOH at 25°.

SN2'-SNi' Reactions. Another possible route from tertiary allylic bromide **1** to SN2-type substitution products (**3**) involves: (a) dissociation of the C-Br bond in **1** to ion-pair **2**, (b) attachment of Nu$^-$ to the γ-carbon atom of the allylic cation of ion-pair **2** to give **6** (in effect, an SN2' substitution), (c) dissociation of Nu$^-$ from this SN2' product (**6**) to form a new ion pair (**6a**), and (d) collapse of **6a** to the SN2-type product **3**.



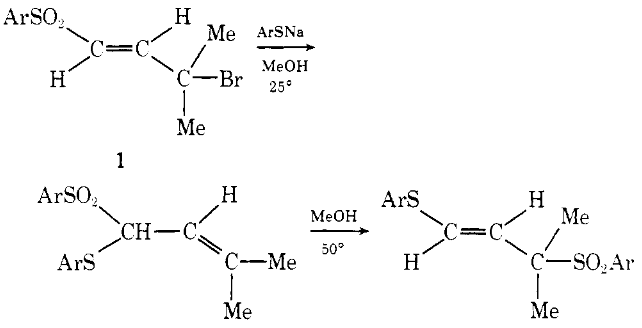
1 2

6 (SN2' product)

6a

Steps (c) and (d) constitute an SNi' rearrangement. We have argued previously that SNi' rearrangement of the SN2' product **6** to **3** is unlikely since **6** should be more stable than the SN2-type product (**3**). In addition, we have excluded this path for the reaction of $PhSO_2Na$ with **1** in DMF.[2b] Additional study of the reaction of thiophenoxide salts with bromide **1** has now allowed us to rule this out as a general pathway.

Reaction of bromide **1** with potassium thiophenoxide in refluxing methanol has been reported to give some SN2-type product, but the major product was that formed from elimination, followed by Michael addition ("elimination-addition product").[2b] We have found that the course of the reaction of **1** with thiophenoxide salts is markedly dependent on the experimental conditions used. Reaction of bromide **1** with triethylammonium *p*-bromothiophenoxide in benzene at 25° for 3 days gave a 79% yield of the SN2'-type product (**6**, Nu = SAr), together with 21% of the SN2-type product (**3**, Nu = SAr). A similar result was obtained at 25° with triethylammonium thiophenoxide in benzene or with potassium thiophenoxide in methanol. Product **6** was stable in benzene at 50°, but underwent slow SNi' rearrangement in MeOH under these conditions to give **7**. The rearrangement was catalyzed by silica in benzene and by alumina in benzene or chloroform. SNi' rearrangement also occurred on melting.



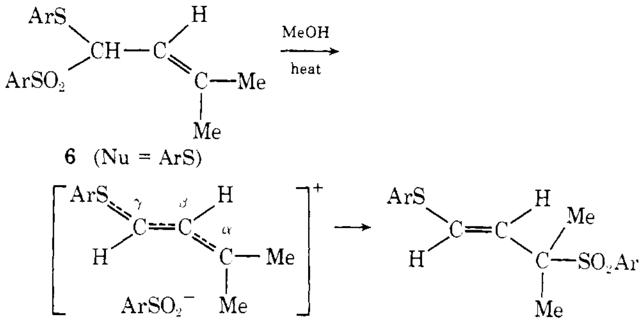
1

6 (Nu = SAr)
(plus 20% of 3 with
Nu = SAr)

7

Buffering in MeOH of PhSNa with PhSH reduced the amount of elimination reaction observed with **1** at higher temperatures.[2b] Under these conditions a reaction at 50° for 4.5 hr gave 25% of SN2-type product, 25% of SN2'-type product, 27% of SN2'-SNi' rearrangement product, and 10% of elimination-addition product (analysis by nmr).

We believe that SN2'-type product (**6**) arises by attachment of ArS$^-$ at the γ position of the cation in ion-pair **2**. Rearrangement of **6** involves dissociation of $ArSO_2^-$ to give ion-pair **6a**, wherein the cation is strongly stabilized by the ArS and Me groups, and recombination of $ArSO_2^-$ with the cation at the α position to give **7**.



6 (Nu = ArS)

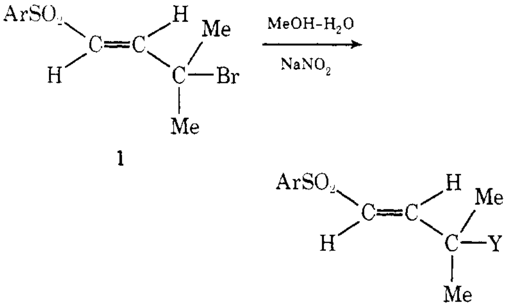
6a (Nu$^-$ = $ArSO_2^-$)

7

The rearrangement of **6** to **7** is no doubt reversible, but **7** is probably favored at equilibrium. (This assumes that the stabilizing effect of ArS on C=C is greater than that of two methyl groups.) Rearrangement of **6** to **7**, rather than to **3**, can be rationalized since dissociation of ArS$^-$ from **6** would yield a much less stable cation, and the rearrangement product (**3**), formed by attachment of ArS$^-$ to the α-carbon atom of this cation, should *not* be favored at equilibrium. ($ArSO_2$ in **3** destabilizes the C=C bond whereas the two Me groups in **6** are stabilizing.) In any event, it is clear that formation of the SN2-type product **3** (Nu = SAr) from bromide **1** and ArS$^-$ does not occur *via* an SN2'-SNi' route (**1** → **6** → **3**) since SNi' rearrangement of **6** gives **7** and not **3**. Since the preferential migration of $ArSO_2$, rather than Nu, would be expected, for the same reason, from other SN2'-type products (**6**), it follows that the SN2'-SNi' pathway is excluded for most, if not all, reactions of nucleophiles with bromide **1** to give SN2-type products (**3**).

These results suggest that reaction of bromide **1** with thiophenoxide salts is a reaction between two sets of ion pairs, ArS^-M^+ and R^+Br^-. For example, the PhS^- ion in PhS^-Na^+ has three choices in reacting with the allylic cation R^+ of R^+Br^- (**2**): (1) attachment at the α-carbon atom (SN2-type substitution), (2) attachment at the γ-carbon atom (SN2′-type substitution), or (3) abstraction of a proton from one of the methyl groups (E2-type elimination). Evidently these three pathways differ but little in their free energies of activation. At 25° in MeOH with PhSK, path 2 predominates over path 1. At 50° with PhSNa-PhSH, path 3 competes to some extent with path 2, and at 65° with PhSK, path 3 has apparently completely replaced path 2. It seems likely that the nature of the cation, as well as the temperature and solvent, may influence the path chosen.

Reactions with Sodium Nitrite. Reaction of **1** with sodium nitrite in DMF at 25° for 45 hr gave an essentially quantitative yield of the corresponding tertiary nitro SN2-type product (**3** with Nu = NO_2). No reaction was observed with sodium nitrite in methanol at 25°, even after 65 hr. At 50° in 60% MeOH reaction did occur with the results indicated. (The nitrite was not isolated as such; see the Experimental Section.)



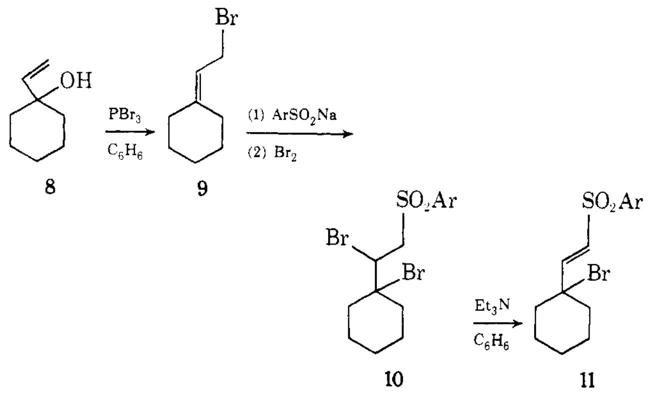
Y	%
OMe	33
OH	22
NO_2	20
ONO	25

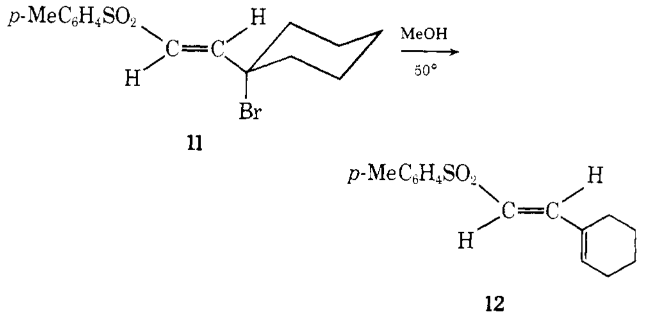
The mixture of products formed in aqueous methanol is consistent with dissociation of **1** to ion-pair **2** and competition between MeOH, H_2O, and NO_2^- for the cation in **2**. Comparison with similar data[2a] obtained with N_3^- shows that 0.02 M N_3^- competes about as well with MeOH-H_2O as does 0.5 M NO_2^-.[5] Furthermore, lithium azide is far more reactive in MeOH toward **1** than is sodium nitrite.

Formation of an SN2-type product by reaction of nitrite ion with a tertiary halide is unusual.[6] The success of the reaction in the present instance can be attributed to the reduced steric effects in the allylic tertiary system **1**, as compared to a *tert*-butyl system, and to delocalization of the positive charge into the allylic system of the cation in ion-pair **2**, thus making the methyl groups less subject to deprotonation.[7]

Elimination Reactions. Although tertiary bromide **1** gives high yields of SN2-type substitution products with several weakly basic nucleophiles in MeOH or DMF, it is also highly susceptible to elimination reactions. For example, elimination is the main result when **1** is treated with unbuffered PhSK or with piperidine in refluxing methanol.[2b] Also, we find that even at 25° with piperidine in MeOH elimination occurs to the exclusion of substitution (the elimination-addition product is formed). In order to obtain additional information concerning the elimination pathway an analog of **1** in which the two methyl groups were replaced by a cyclohexyl group was synthesized, using the route worked out previously for **1**.[2b]

As expected, this tertiary allylic bromide (**11**) exhibited a much greater tendency to undergo elimination than did **1**. For example, methanolysis of **11** at 50° gave diene **12** as the only detectable product, whereas, methanolysis of **1** at 50° gives *ca.* 80% of the methyl ether (**3**, Nu = OMe) and 20% of elimination product (diene).[2b] The rate of methanolysis of **11** is considerably slower than for **1**.





The reactions of **11** with nucleophiles under various conditions are summarized in Table I.

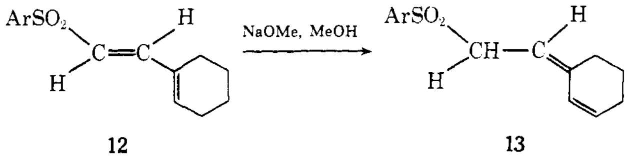
Table I. Reactions of 1-(1-Bromocyclohexyl)-2-*p*-tolylsulfonylethene (**11**) with Nucleophiles (Nu)[a]

Nu	Sol	T, °C	t, hr	Products, %[b] **11**	 **12**	 Other
MeOH	MeOH	50	24	82	18	0
MeOH	MeOH	65	16	33	67	0
NaOMe	MeOH	25	20	48	32	19[c]
NaOMe	MeOH	50	3	0	~70[d]	~10[c]
$C_6H_{10}NH$	MeOH	50	24	0	~100[e]	0
CH_3COSNa	MeOH	25	1	60	40	0
CH_3CO_2Na	MeOH	25	30	100	0	0
$(H_2N)_2C{=}S$	MeOH	25	20	80	~20	0
PhSNa	MeOH	25	20	0	100[e]	0
LiN_3	MeOH	50	6	35	35	30[f]
LiN_3	MeOH	50	30	0	70	25[f,g]
KSCN	MeOH	50	12	35	60–65[h]	0
LiN_3	DMF	25	24	0	>95	0
LiN_3	Me_2CO	25	98	17	65	17[f,g]
Et_3N	CH_2Cl_2	50	47	0	100	0

[a] The concentration of **11** was generally *ca.* 0.05 M and that of Nu 0.5 M. [b] Analysis by nmr: in most instances 90% or more of the products could be accounted for. [c] Michael addition product. [d] Rearranged diene; see text. [e] A mixture of about 50% diene **12** and 1,4-addition product. [f] SN2-type product. [g] Some decomposition of the azide product appears to have occurred. [h] Less than 5% of SN2-type product is formed.

One is impressed on examination of Table I with the great proclivity of **11** to undergo elimination. Even lithium azide, which gives essentially quantitative yields of substitution products with **1** in either MeOH or DMF,[2b] reacts with **11** mainly by elimination (>50% in MeOH; >95% in DMF). This propensity for elimination is not caused by facilitation of concerted E2 reactions in the cyclohexyl system, relative to the acyclic system, since the reactions of **11** with MeOH and with LiN_3 in MeOH, which give elimination, are considerably *slower* than the corresponding reactions with **1**, which give substitution.

With weakly basic nucleophiles (MeOH, CH_3COSNa, $(H_2N)_2CS$, LiN_3, KSCN), diene **12** was obtained as such, but with PhSK in MeOH or piperidine in MeOH, the product was a mixture of **12** and 1,4-Michael adduct. With NaOMe in MeOH a slow rearrangement of **12** to the isomeric diene **13** occurred.



12 **13**

A study of the kinetics of dehydrobromination of bromide **11** to diene **12** by NaOMe in MeOH is summarized in Table II.

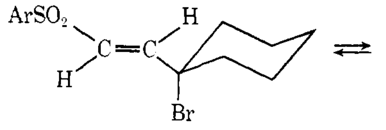
Table II. Kinetics of Dehydrobromination of **11** by Sodium Methoxide in Methanol at 50°[a]

[NaOMe]	10^4k,[b] sec^{-1}	10^4k,[c] sec^{-1}	10^3k_2,[d] M^{-1} sec^{-1}
1.219×10^{-1}	9.10	8.35	6.86
1.219×10^{-1}	9.05	8.24	6.76
6.095×10^{-2}	4.66	4.31	7.07

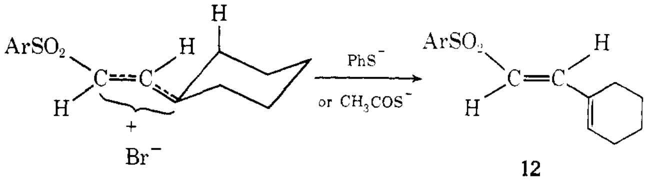
[a] Determined spectrophotometrically at 286 nm; 1.3×10^{-4} *M* substrate. [b] Pseudo-first-order constant determined using the infinity absorption. [c] Pseudo-first-order constant determined by the Guggenheim method. [d] Second-order constant calculated from the Guggenheim constants. (See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 2nd ed, 1961, p 49, for a discussion of the Guggenheim method.)

The rate determination was subject to some error due to slow rearrangement of diene **12** to its isomer **13**, which has a somewhat different absorption at 286 nm. This error should be minimized in the constants determined by the Guggenheim method.

Relative Effect of Oxygen and Sulfur Nucleophiles. Comparison of the yields of diene **12** produced by the reaction of various nucleophiles with bromide **11** in MeOH shows that sulfur nucleophiles are much more effective at promoting elimination than are oxygen nucleophiles. The observation that potassium thioacetate in methanol gives 40% of elimination product in 1 hr at 25° whereas under comparable conditions sodium acetate, a stronger base, shows no reaction whatsoever in 30 hr is particularly striking. Even more impressive is the fact that potassium thioacetate causes about as much elimination in 1 hr as sodium methoxide does in 20 hr. Sodium thiophenoxide in MeOH is also clearly more effective in promoting elimination than is sodium methoxide. These results are in agreement with a number of earlier studies which have shown that PhS^- (or RS^-) has a greater ability than MeO^- to promote elimination from cyclohexyl halides (or tosylates) and from tertiary halides in protic media.[9] Recent studies indicate that PhS^- has a considerably greater affinity for cations than does MeO^- (the N_+ values in MeOH are 10.7 and 7.5, respectively[5b]). It appears reasonable, therefore, to expect PhS^- or CH_3COS^- to be better able than MeO^- to attack the cation of ion-pair **11a** and to abstract a proton from the β position of the cyclohexyl group therein. It is possible that the rate of interchange of ion-pair partners may play a role here, since there is some evidence for the existence of thiol salts in methanol as ion pairs.[10] Since the methoxide-initiated elimination with bromide **11** is first order in sodium methoxide (Table II), it seems probable that this will be true also for the reactions of PhSNa and CH_3COSK with **11.** On this basis these eliminations may be classified as E2 reactions, but a more proper designation would be ion-pair-E2 mechanism, $(E2)_{ip}$.[2,11]



11



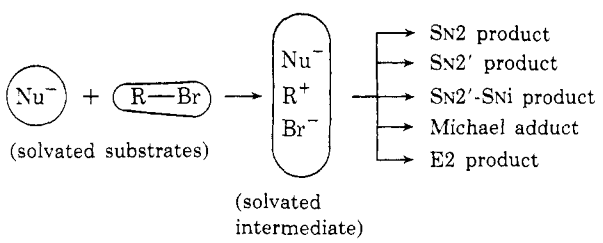
11a **12**

Comparison of the rate of methoxide-initiated elimination from bromide **11** with that of ethoxide-initiated elimination from cyclohexyl bromide (or cyclohexyl tosylate)[9a,9d] shows that k_2^E for **11** is over ten times larger. If our conclusion that oxygen and sulfur nucleophiles are reacting with **11** by ion-pair mechanisms is accepted, it follows that this mechanism is also likely for the reaction of oxygen and sulfur nucleophiles with cyclohexyl halides and tosylates.[9] On the other hand, if one adopts the usually assumed concerted type mechanism for the latter,[9] one is forced to conclude, in view of the slower rates, that the concerted E2 mechanism has less driving force than the ion-pair-E2 mechanism.

As we have pointed out previously,[11] the ion-pair mechanism also appears likely for dehydrohalogenations initiated by oxygen and sulfur nucleophiles on simple tertiary halides, such as *tert*-pentyl halides, since these substrates are much more prone to C–Br bond dissociation than are bromides **1** and **11** (*t*-BuBr undergoes methanolysis in 60% aqueous methanol at a rate over 1000 times that of bromide **1,** which is, in turn, more reactive than **11**). The ion-pair mechanism has been considered for the reactions of *t*-BuSK with *tert*-pentyl halides, *t*-$C_5H_{11}X$, in *t*-BuOH at 55° but has been rejected on the grounds that the change in orientation in alkene formation with a change in the nature of the leaving group (31% of 1-alkene with X = Cl, 26% with X = Br, and 21% with X = I) is similar to that observed for the reaction of (secondary) 2-pentyl halides reacting with NaOEt in EtOH, a reaction "which is almost certainly E2."[9c] We find this circumstantial evidence against the ion-pair mechanism unconvincing, particularly since, for reasons just given, we believe that the reaction of (secondary) cyclohexyl bromide (or tosylate) with alkoxide ions is also likely to occur by an ion-pair-E2 mechanism.

The ion-pair-E2, $(E2)_{ip}$, mechanism is also applicable in dipolar aprotic media.[11] Formation of diene **12** in the reaction of bromide **11** with LiN_3 in DMF probably proceeds by this mechanism. In this connection it is interesting to note that bromide **1** was recovered quantitatively after a 50-hr reflux in benzene (ϵ 2.3), whereas about 40% of diene was formed (60% recovery of **1**) during a 50-hr reflux in acetonitrile (ϵ 38), and 25% of diene was formed (75% recovery **1**) during a 44-hr reflux in *t*-BuOH (ϵ 11). Dissociation to an ion pair in the more polar solvents and deprotonation of the cation by its anionic partner provides a likely reaction path under these conditions.

Alternative Ion-Pair Mechanism. We have assumed in discussing the reactions of tertiary allylic bromides **1** and **11** (RBr) with nucleophiles that reaction occurs by attack of the nucleophile on a preformed ion pair (present in equilibrium with the covalent substrate). An alternative representation, which is in many respects more attractive, is to assume that ionization of the C–Br bond is aided by entrance of RBr into the solvent shell of the nucleophile (ion-pair formation by nucleophilic assistance). This mechanism, which assumes that solvation plays the major role in making and breaking bonds, and therefore the major role in dictating product formation, provides an economical representation for the wide variation in product formation observed in these allylic systems. A discussion of the possible general application of this mechanism to SN2-type substitution reactions will be given in the final paper in this series.[12]



Experimental Section

2-Bromo-2-methyl-3-methoxy-4-*p*-tolylsulfonylbutane (4, Nu = OCH_3). A solution containing 606 mg (2 mmol) of 1^{2b} and 46 mg (2 mmol) of NaOMe in 15 ml of MeOH was allowed to stand for 12 hr at 20–25° and then concentrated under reduced pressure. The residue was dissolved in 30 ml of CH_2Cl_2, washed, dried, and evaporated. The crystalline residue was crystallized from MeOH: 89% yield, mp 103–104°. An analytical sample was prepared by chromatography over silica gel: nmr ($CDCl_3$) δ 1.55 and 1.62 (d, 6 H), 2.45 (s, 3 H), 3.52 (s, 3 H), 3.18 and 3.52 (d, 2 H, J = 14.2 Hz), 3.75 (m, 1 H), 7.33, 7.80 (d, 4 H).

Anal. Calcd for $C_{19}H_{19}BrO_3S$: C, 46.57; H, 5.71. Found: C, 46.58; H, 5.74.

4-(*p*-Tolylsulfonyl)-4-*p*-bromophenylthio-2-methyl-2-butene (6). A solution containing 909 mg of **1** (3 mmol), 856 mg (4.5 mmol) of *p*-bromothiophenol, and 450 mg (4.5 mmol) of triethylamine in 30 ml of benzene was allowed to stand at 20–25° for 5 days under nitrogen. The residue obtained after washing (10% Na_2CO_3, then 1 *M* HCl), drying (Na_2SO_4), and evaporating consisted of a 3:1 mixture of **6** and **3** (Nu = *p*-BrC_6H_4S). It was washed with hexane (6 × 5 ml) and crystallized from MeOH and finally from hexane to give 160 mg of **6**, mp 83–84°: nmr ($CDCl_3$) δ 1.41 (d, 3 H, J = 0.9 Hz), 1.71 (d, 3 H, J = 1.3 Hz), 2.47 (s, 3 H), 4.83, 5.05 (2 H, J = 10.5 Hz), 7.1–7.8 (m, 8 H).

Anal. Calcd. for $C_{18}H_{19}BrO_2S$: C, 52.54; H, 4.65. Found: C, 52.61; H, 4.70.

3-*p*-Tolylsulfonyl-3-methyl-1-*p*-bromophenylthio-1-butene (7). Preparation of crude **6** from 4.85 mmol of **1** was performed as described above. A 1.87-g sample of this material was chromatographed on 45 g of SiO_2 using benzene as an eluent. Crystallization of the residues obtained on evaporation from methanol gave 200 mg of **7**, mp 139–140°: nmr ($CDCl_3$) δ 1.45 (s, 6 H), 2.46 (3 H), 5.80, 6.15 (2 H, J = 15 Hz), 7–7.8 (m, 8 H).

Anal. Calcd for $C_{18}H_{19}BrO_2S_2$: C, 52.54; H, 4.65. Found: C, 52.37; H, 4.65.

Reaction of 1 with Sodium Thiophenoxide in MeOH at 50°. Nmr analysis was made possible by the separate appearance of alkenic peaks at δ 4.92 and 5.07 (J = 10.6 Hz) for **6**; 5.84 and 6.20 (J = 15 Hz) for **7**, and 5.80 and 6.97 (J = 14.7 Hz) for **3** (Nu = SPh).

1-*p*-Tolylsulfonyl-3-methyl-3-nitro-1-butene (3, Nu = NO_2). A mixture of 303 mg (1 mmol) of **1**, 690 mg (10 mmol) of sodium nitrite, and 20 ml of DMF was kept at 25° for 44 hr. Water (100 ml) was added and the solution was extracted with ether (7 × 25 ml). The extracts were washed with brine, dried (Na_2SO_4), and evaporated to leave a residue (92%), which slowly crystallized. A sample crystallized from 1:5 benzene-hexane melted at 84°: ir (Nujol) ν_{NO_2} 1545 and 1350 cm^{-1}; nmr ($CDCl_3$) δ 1.63 (s, 3 H), 2.21 (s, 6 H), 5.2, 5.7 (d, 2 H), 7.8 (s, 4 H).

Anal. Calcd for $C_{12}H_{15}NO_4S$: C, 53.51; H, 5.61; N, 5.20. Found: C, 53.73; H, 5.60; N, 5.04.

The reaction of **1** with $NaNO_2$ in 60% MeOH gave (nmr analysis) 33% of tertiary methyl ether (**3**, Nu = OCH_3), 47% of tertiary alcohol (**3**, Nu = OH), and 20% of tertiary nitro compound (**3**, Nu = NO_2). Assuming that the ratio of ether to alcohol will be the same here as in the solvolysis of **1** in 60% MeOH, 25% of the alcohol obtained is derived from hydrolysis of tertiary nitrile (**3**, Nu = ONO).

2-*p*-Tolylsulfonylethylidenecyclohexane. 2-Bromoethylidenecyclohexane was prepared from 12.6 g (100 mmol) of 1-vinylcyclohexanol (**8**)[13] in benzene (25 ml) by slow addition of 10.8 g (40 mmol) of PBr_3 in benzene (25 ml) (temperature maintained at 40–45°). After an additional hour the benzene was washed (iced water, saturated $NaHCO_3$, brine) and dried (Na_2SO_4). Distillation gave 21 g (85%) of bromide **9**, bp 36–37° (0.2 mm) (lit.[14] bp 57° (0.9 mm)). The bromide (11 g, 58 mmol) was added with stirring to a suspension of 21 g of sodium *p*-toluenesulfinate suspended in 70 ml of 100% EtOH. After standing overnight, the mixture was heated at reflux for 2 hr, the solvent was removed, and 200 ml of water was added. Extraction with CH_2Cl_2 (2 × 10 ml) gave, on evaporation, a residue which was crystallized from hexane (100 ml) to give 7.54 g of material. Additional crystallizations from methanol gave material melting at 72°: nmr ($CDCl_3$) δ 1.1–2.2 (m, 10 H), 2.2 (s, 3 H), 3.78 (d, 2 H, J = 8 Hz), 5.05 (s, 1 H), 7.15–7.71 (pseudo d, 4 H).

Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62. Found: C, 68.10; H, 7.64.

A similar preparation from bromide **9** and $C_7H_7SO_2Na$ in DMF gave 40% of sulfone, mp 69–71°.

1-(1-Bromocyclohexyl)-1-bromo-2-*p*-tolylsulfonylethane (10). A solution of 5.28 g (20 mmol) of 2-*p*-tolylsulfonylethylidenecyclohexane in 50 ml of CH_2Cl_2 was cooled to −78° and treated dropwise with 10 ml of a CH_2Cl_2 solution containing 3.60 g (20 mmol) of bromine. After 10 min the cooling bath was removed, the solution was evaporated in the cold at reduced pressure, and the residue was taken up in 30 ml of methanol. The solid (5.89 g, 70%) obtained on concentration was used for dehydrobromination to **11**.

An analytical sample was obtained by crystallization from methanol (mp 156–157°) and then from benzene, mp 160.5–161.5°: nmr ($CDCl_3$) δ 1.3–2.0 (m, 10 H), 2.42 (s, 3 H, H_A 3.70, H_B 4.17, H_X 4.48, J_{AB} = −15.4, J_{AX} = 8.6, J_{BX} = 1.5 Hz), 7.28 and 7.74 (4 H).

Anal. Calcd for $C_{15}H_{20}Br_2O_2S$: C, 42.47; H, 4.75. Found: C, 42.41; H, 4.68.

1-(1-Bromocyclohexyl)-2-*p*-tolylsulfonylethene (11). The 5.89-g sample of dibromide **10** prepared above was treated with 1.53 g (15.3 mmol) of triethylamine in 110 ml of benzene. After 6 hr at 25° the solution was washed (1 *N* HCl; brine), dried (Na_2SO_4), and evaporated. The residue (4.5 g, 90%) was crystallized from MeOH to give 68% (overall) of **11**, mp 134°: nmr ($CDCl_3$) δ 1.2–2.3 (m, 10 H), 2.45 (s, 3 H), 6.05, 7.05 (AB system, J = 14.2 Hz), 7.25, 7.75 (aromatic AA′BB′ system); uv, λ_{max} (MeOH) 237 nm (log ϵ 4.19).

Anal. Calcd for $C_{15}H_{19}BrO_2S$: C, 52.50; H, 5.58. Found: C, 52.34; H, 5.77.

1-(1-Cyclohexenyl)-2-*p*-tolylsulfonylethene (12). A solution of 680 mg (2 mmol) of **11** in 10 ml of CH_2Cl_2 containing 2 g (20 mmol) of Et_3N was heated at 50° for 47 hr. After processing, an analytical sample was obtained by crystallization from hexane, mp 93–94°: nmr ($CDCl_3$) δ 1.6–1.8 (m, 4 H), 1.8–2.3 (m, 4 H), 2.3 (s, 3 H), 6.17 (t, 1 H), 6.12 and 7.15 (AB system, J = 14.5 Hz), 7.35, 7.75 (aromatic AA′BB′); uv, λ_{max} (MeOH) 262 nm (log ϵ 4.48).

Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.66; H, 6.92. Found: C, 68.48; H, 6.91.

Reactions of 11 with Nucleophiles. Bromide **11** (303 mg, 1 mmol) was dissolved in 10 or 20 ml of solvent, a 10 mmol quantity of nucleophile was added, and the solution was kept in a thermostated bath at the indicated temperature for the time designated (Table I). The solvent was evaporated (water added first to DMF) and the residue extracted with CH_2Cl_2 (5 × 50 ml). After washing with brine (2 × 50 ml), the extract was dried and evaporated. The composition of the residue was determined by nmr (Table I).

Purification of Potassium Thioacetate. The commercial product was dissolved in a minimum amount of MeOH and the solution decolorized with charcoal. Twice the volume of ether was added to the filtrate and the precipitate was collected. This procedure was repeated twice. The colorless crystalline material thus obtained was crystallized from methanol by cooling to −10°.

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References and Notes

(1) NATO Postdoctoral Research Fellow, 1972–1973.

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

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(5) Azide ion is known to have a greater nucleophilicity toward cations than do most other anions; see (a) C. G. Swain, C. B. Scott, and K. H. Lohmann, *J. Amer. Chem. Soc.*, **75**, 136 (1963); (b) C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972).

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(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-$NO_2C_6H_4CMe_2X$. 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-$C_7H_7SO_2CH{=}CHCMe_2Br$ (**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