solute-induced water structuring especially when the salts of high carbon number are compared to alkali metal bromides. The self-consistency of this picture suggests the reasonable question, "How would analogous measurements compare in another solvent?" Being unaware of published results which could provide an answer, we measured $\Delta C_{p_2}^\circ$ for tetra-*n*-butylammonium bromide in ethanol. Some of the results are displayed in Table VII and differ dramatically from those for the aqueous systems in Table V.

Table VII. Molal Heat of Solution of Tetra-*n*-butylammonium Bromide in Ethanol as a Function of Temperature and Concentration[a]

8°		22.3°		40.3°	
$M \times 10^3$	Kcal/mol	$M \times 10^3$	Kcal/mol	$M \times 10^3$	Kcal/mol
3.14	+4.50	2.50	+4.64	4.62	+4.52
6.45	+4.59	4.20	+4.69	7.02	+4.89
8.83	+4.82	6.14	+4.93	9.86	+4.93
11.2	+4.61	8.68	+4.70	12.6	+4.99
14.2	+4.70	10.7	+4.96	16.4	+4.79
17.8	+4.71	12.9	+5.05	19.4	+5.02

[a] These are representative values taken at the extremes and the middle of our temperature range. Approximately 40 similar results were obtained at 8, 17.4, 17.5, 22.7, 32.2, 32.6, and 40.0°.

First, and most important, we note the small temperature dependence of $\Delta \bar{H}_s$ for solution of this salt in ethanol compared to that in water the apparent least squares average for $\Delta C_{p_2}^\circ$ being 10.2 ± 2.3 cal/mol deg in the former case against 176 in the latter. It is also clear that molal heats of solution of this salt in ethanol are far more dependent on concentration than they are in water. The same is found for $\Delta C_{p_2}^\circ$ since the temperature coefficient for the most dilute solutions in Table VII are clearly less temperature dependent than are those for the most concentrated. Decreasingly exothermic heats in response to increasing concentration are commonly a symptom of solute–solute interactions. In view of the absence of such a phenomenon in water, we attribute its appearance in ethanol to ion pairing. No enthalpies of ion pairing are known for cases such as this although Kay[18] reports very small temperature coefficients for ion pairing constants in methanol.

Applying Evans[19] value of $K_{assoc} = 75$ for tetra-*n*-butylammonium bromide in ethanol at 22° to the present case, we may calculate that 14% of the ions at our lowest solute concentration (2.5×10^{-3} *M*) are paired. At the same temperature, 38% of the ions at the highest concentration (1.3×10^{-2} *M*) are paired. The less exothermic heat of solution at higher concentration is reasonable if we accept the proposition that bromide ions which are tightly paired are poorer hydrogen-bond acceptors than are dissociated ones.

Several suggestions could be made for the positive sign of $\Delta C_{p_2}^\circ$ in ethanol. (1) Ethanol has some residual solute-induced structure (like that of water) which is temperature dependent. (2) At low temperatures the free bromide ions are better solvated through hydrogen bonding than at higher temperatures so that a temperature increase favors contact ion pairing. (3) The dielectric constant of ethanol, like most other solvents, has a negative temperature coefficient. This favors ion pairing at higher temperatures and more concentrated solutions are most sensitive to the effect. The latter explanation seems most reasonable to us.

(18) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69** 4208 (1965).
(19) D. F. Evans and P. Gardam, *ibid.*, **72**, 3281 (1968).

Homoallenic Participation. III. The Effect of a 2-Methyl Group

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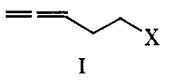
Abstract: The preparation and acetolysis of 2-methyl-3,4-pentadien-1-yl tosylate (IIIb) and model compound 2-methyl-1-pentyl tosylate are reported. Compound IIIb undergoes acetolysis with accompanying return-rearrangement to the same rearranged tosylate afforded by 4,5-hexadien-2-yl tosylate (X). Both III band X yield essentially identical product mixtures, suggesting that both solvolyze through the same ion (manifold). The rates of acetolysis were followed titrimetrically; IIIb was found to solvolyze ~40 times faster than the model compound at 85°, and about one-fourth as fast as X. The results are discussed in the context of neighboring group participation.

Several recent publications, by our group[1] and others,[2–7] have shown that a β-allenic system (I) exhibits the same versatiiity in promoting solvolytic reactions (homoallenic participation) as does a similarly located double bond (homoallylic participation). Our

(1) (a) T. L. Jacobs and R. S. Macomber, *Tetrahedron Lett.*, 4877 (1967); (b) *J. Amer. Chem. Soc.*, **91**, 4824 (1969).
(2) (a) R. S. Bly, A. R. Ballentine, and S. U. Koock, *ibid.*, **89**, 6993 (1967); (b) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969).
(3) R. Garry and R. Vessiere, *Bull. Soc. Chim. Fr.*, 1542 (1968).
(4) (a) M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2511 (1969); (b) *ibid.*, 2515 (1969); (c) *ibid.*, 3699 (1969); (d) C. Santelli-Rouvier, P. Archer, and M. Bertrand, *C. R. Acad. Sci., Paris, Ser. C*, **269**, 252 (1969).
(5) A preliminary report by Bertrand and Santelli[6] suggested that homoallenic participation in the hydrolysis of optically active 4,5-hexadien-2-yl tosylate proceeds with a high degree of stereospecificity to yield rearranged products, while unrearranged alcohol arises from a classical SN1 process. They also found[4a,c] that acetolysis of the same compound led to unrearranged acetate with some retained activity.

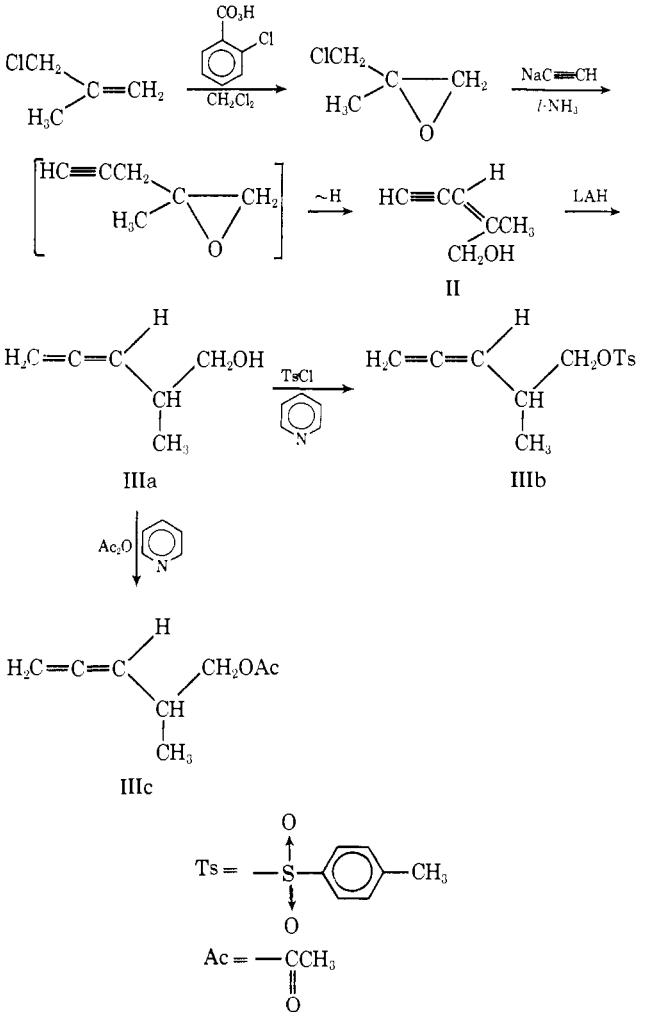


I

work has included a series of compounds I, with varying substituents at one or more of the four available positions, all studied under a fixed set of conditions.[8] We now wish to present data for the acetolysis of 2-methyl-3,4-pentadien-1-yl tosylate (IIIb), an important addition to the work in the area.

Syntheses. Allenic alcohol IIIa, a new compound, was prepared as shown in Scheme I. One isomer of enynol II predominates to the extent of >98%, inferred from its shoulderless ultraviolet absorption at 225 nm (log ϵ 4.11), its pmr spectrum (Experimental Section), and its homogeneity during glpc analysis. By analogy with a series of similar enynols[1b] where both cis and trans isomers are formed, we feel the uv absorption corresponds more closely to the value expected for the cis compound (225 ± 2 nm) than trans (233 ± 2 nm). The succeeding reduction and derivative preparations were similar to the preparations of analogous compounds.[1]

Scheme I



Results and Discussion

In contrast to some other workers in this area, we have felt that solvolysis results are best interpreted when comparisons are made with suitable model compounds, as opposed to direct comparisons between β-allenic systems. Thus 2-methyl-1-pentyl tosylate (IV) was chosen as a compound which should simulate the solvolytic behavior of IIIc in the absence of homoallenic participation.

The model compound IV underwent clean first-order acetolysis[8] with rate constants shown in Table I.

Table I. Titrimetric First-Order Rate Constants for Tosylate Acetolyses

Compd	T, °C[a]	k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
IV	65.0[b]	1.50×10^{-7}	26.65	−11.2
	85.0	$(1.45 \pm 0.003) \times 10^{-6}$		
	100.0	$(6.81 \pm 0.04) \times 10^{-6}$		
IIIb[c,d]	65.0	$(7.35 \pm 0.19) \times 10^{-6}$	24.08	−11.1
	85.0	$(5.78 \pm 0.13) \times 10^{-5}$		
	100.0	$(2.33 \pm 0.04) \times 10^{-4}$		

[a] ±0.05°. [b] Extrapolated using a value of 27.32 kcal/mol for E_a. [c] Rearranges during acetolysis to a more reactive tosylate. See text. [d] E_a = 24.75 ± 0.02 kcal/mol.

Immediately striking is the fact that IV undergoes acetolysis less than half as fast as *n*-pentyl tosylate.[1b] This is evidence that both solvolyze primarily by a k_s (*vide infra*) pathway which responds to steric requirements of substitution α to the reacting atom. No evidence was found for the rearrangement of IV to a different tosylate during solvolysis.

The acetolysis products of IV are also informative (eq 1 and Table II). Not only were the unrearranged

Table II. Acetolysis Products of 2-Methyl-1-pentyl Tosylate at 100° [a]

Product	$\tau_{1/2}$,[b] %	$4\tau_{1/2}$, %
V	42	34
VI	15	10
VII	15	9
VIII	28	47

[a] Measured as crude glpc peak areas. [b] $\tau_{1/2}$ = 1.1×10^5 sec.

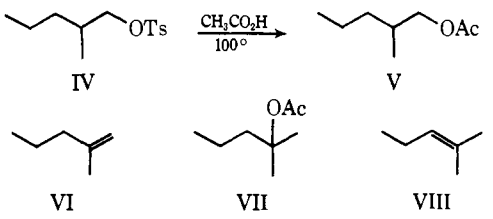
acetate V and derived olefin 2-methyl-1-pentene (VI) observed, but also 2-methyl-2-pentyl acetate (VII) and 2-methyl-2-pentene (VIII), products formally arising from 1,2-hydride shift. As expected, tertiary acetate VII slowly eliminated acetic acid under the acetolysis conditions yielding, after 0.8 half-lives at 100°, 17% VI and 21% VIII. Under similar conditions VI gave 7% VIII and 19% VII. Both V and VIII are stable under these conditions. Thus the yields of rearranged products VII and VIII are substantially greater than can be explained by *in situ* rearrangements of V and VI. These facts, coupled with the observation that no products were found which would have arisen from 1,2-

Our finding[1b] that this system undergoes extensive rearrangement–return during acetolysis was not taken into account by these authors. They feel[7] that their lower substrate concentrations precluded formation of rearranged tosylate by a mass-law effect; this conclusion was a result of their observation of strict first-order behavior at these lower concentrations.

(6) M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968).

(7) M. Santelli, private communication.

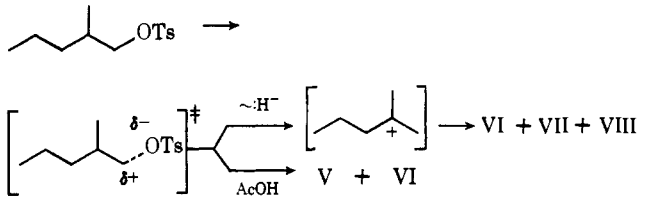
(8) Acetolysis in dry acetic acid containing 1 equiv of anhydrous sodium acetate and 1% acetic anhydride. Many authors use the term "buffered acetic acid" to describe this system, but it should be recalled that acetate ion serves as a strong base rather than a true buffer.



(1)

methyl migration (*e.g.*, 3-hexyl acetate and derived olefins), lead us to the interpretation shown in Scheme II. Solvent participation has been reduced due to the

Scheme II

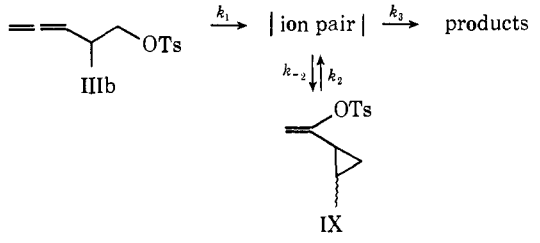


α-methyl group, and as a result hydride transfer becomes competitive to the extent of ~50%.

The acetolysis of IIIb was unfortunately far more complex. Plots of ln (C_0/C_t) *vs.* time for the acetolysis at 65, 85, and 100° all had a common feature: *the value of the integrated rate constant increased significantly throughout the solvolyses.* For example, the integrated rate constant for IIIb at 85° increased from a value of 3.3×10^{-5} sec^{-1} at 10% reaction to 5.7×10^{-5} at 95% reaction (Figure 1). In spite of this, the data could be analyzed in typical least-squares fashion to yield slopes with less than 3% probable error (Table I), although it should be obvious that these rate constants are, at best, approximations of the true rate of substrate disappearance.

We interpret this behavior in terms of rearrangement of the initial tosylate to a comparably reactive tosylate (IX), which then solvolyzes exclusively through the same ion pair which led to its formation (Scheme III). Return to rearranged tosylate (k_{-2}) must be considerably greater than k_3 to account for the accumulation of observable amounts of rearranged tosylate (*vide infra*).

Scheme III



At this point it is important to reconsider the acetolysis of 4,5-hexadien-2-yl tosylate (X) (differing from IIIb only in the location of the methyl group) which rearranges to a *less* reactive tosylate during solvolysis.[1b,5] The pmr spectrum of the rearranged tosylate from X is identical with the rearranged species from IIIb, hence our assignment. Our estimate[1b] for the rate of acetolysis of the rearranged tosylate at 65° (6.5×10^{-6} sec^{-1}) is very close to the rate constant for IIIb (7.35×10^{-6}, Table I), as would be expected if IX were indeed the product and rate-determining species in both systems.

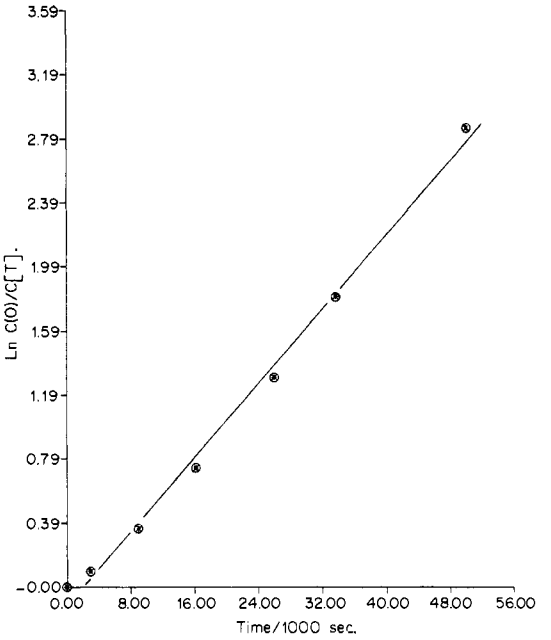
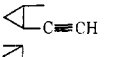
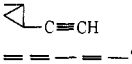
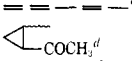
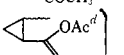
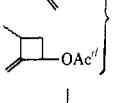
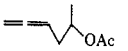
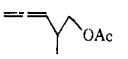


Figure 1. First-order plot for acetolysis of IIIb at 85°. The least-squares line is also shown.

If IIIb and X both rearrange to the same compound, then do the solvolyses proceed through the same intermediate(s)? A product study answers this question affirmatively (Table III). Not only are the major products found in very similar amounts, but even the minor products (<~10%) match very closely. Perhaps most striking is the fact that unrearranged acetate IIIc is present only at the 1% level, although it is stable under the reaction and separation conditions. The small differences in the percentages of products probably arise from the longer reaction periods required for acetolysis of IIIb compared to X.

Thus it is apparent that both compounds IIIb and X undergo acetolysis through the same ion (or ion manifold). Since both also rearrange to the same tosylate, it too must be involved in product determination. (Ex-

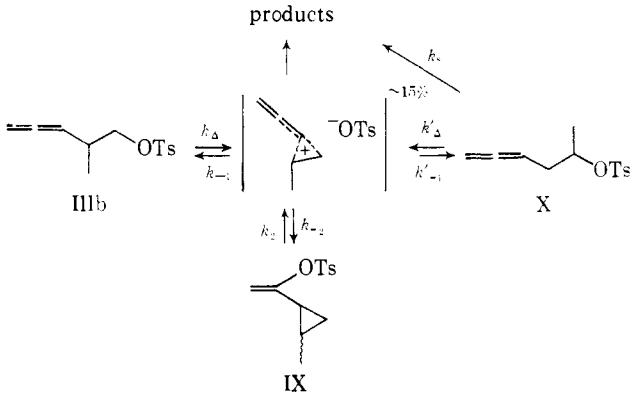
Table III. Acetolysis Product Percentages[a] from IIIb and X at 85°

Product	IIIb[b] $\tau_{1/2}$	IIIb[b] $7\tau_{1/2}$	X[c] $\tau_{1/2}$	X[c] $6.5\tau_{1/2}$
	17	6	17	9
	27	14	13	14
 [d]	3	3	9	7
 [d]	10	24	5	16
 [d]	9	14	8	7
	34	49	47	49
	~1	~1	~1	~1

[a] Measured as crude glpc peak areas; see Experimental Section. [b] $\tau_{1/2} \approx 12{,}000$ sec. [c] $\tau_{1/2} \approx 7000$ sec. [d] cis and trans isomers.

periments are underway to isolate pure rearranged tosylate and investigate its solvolytic properties.) We feel the most economical interpretation of our results is that shown in Scheme IV.[9]

Scheme IV



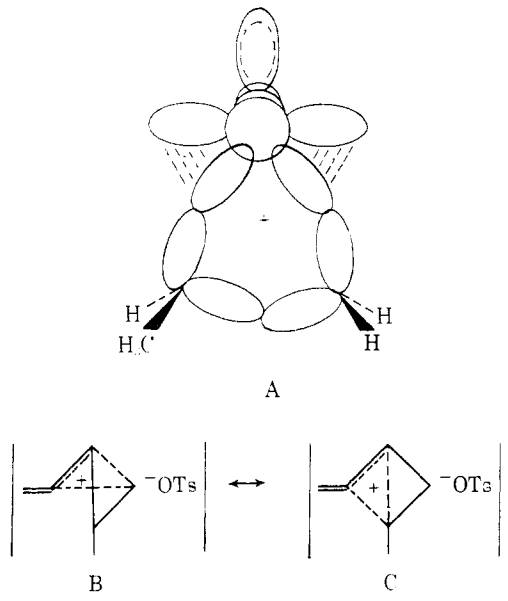
Since the yield of 4,5-hexadien-2-yl acetate is slightly greater for X than IIIb and since only *ca.* 1% IIIc is formed from IIIb, we conclude that the k_s pathway (*vide infra*) is unimportant in the IIIb system and only slightly important (~15%) for X.[10] Both yield the same ion in the k_Δ pathway, although X does so faster due to the lability of the secondary C–X bond. The stabilized nature of the intermediate is suggested not only on the basis of similar products in both cases, but also because IIIb undergoes acetolysis approximately 40 times as fast as the model compound, indicating a fair degree of stabilization in the transition state leading to the (first) intermediate. This stabilization of transition state is further verified by the observation that X undergoes acetolysis at 65° less than five times as fast ($k = 3.41 \times 10^{-5}$)[1b] as IIIb, a rather remarkable situation considering that X is a secondary tosylate while IIIb is primary.[11] Whether the indicated ion pair is trapped directly by nucleophiles, or whether it opens to "classical" ions first, is not possible to answer at this point.

To complete our previous analysis[1b] on the effect of substitution on homoallenic participation, we calculate a value for k_Δ ($= k_t - k_{model}$) of 7.2×10^{-6} for IIIb at 65°. This value is 21 times[12] k_Δ for 3,4-pentadienyl tosylate (XI). Thus on our relative scale[1b] a 2-methyl group aids the k_Δ pathway by a factor of 21 compared to the unsubstituted system, while the same group retards k_s solvolysis by 50%. Finally, it is interesting to compare the effect on k_Δ of a single methyl group at C_2 with a *gem*-dimethyl group.[1b] The latter increases k_Δ by a factor of 270, only slightly less (due to saturation effects) than $(21)^2$.

Conclusion

These results further confirm our earlier conclusions[1b] regarding homoallenic participation. Although the exact role, if any, of the more remote double bond is not clear, the 3,4-double bond can and does become intimately involved with developing positive charge at C_1. The extent of this interaction depends heavily on the alkyl substitution of I, as would be anticipated for a species where charge delocalization is significant. There is ample evidence, both here and before,[1b] that C_1 and C_2 can attain pseudoequivalence, and that positive charge is heavily felt there, as well as at C_3. The fate of the intermediate ion pair is similarly determined by the substitution pattern: a *gem*-dimethyl group at C_2 causes opening to a stable tertiary cation; a methyl group at C_3 favors formation of a methylene cyclobutyl allylic cation; absence of substitution (or alkyl groups at C_5) renders the cyclopropyl carbinyl-like cation[9] the most stable accessible species. A methyl group at C_1 or C_2 still favors formation of the cyclopropyl carbinyl-like cation, but in these cases the methyl group causes an increase in the tendency toward ion-pair return. The intermediate ion pair may undergo substitution at C_1 or C_2 (whichever is methyl bearing) to yield allenic ester, or at C_3 or C_4 to yield cyclobutyl or cyclopropyl esters (the latter yielding ketones). Elimination may also take place: loss of a proton from C_2 or C_1 yields allenic olefins, but apparently more favorable is loss of a C_5 proton leading of cyclopropyl acetylenes. The decrease in per cent

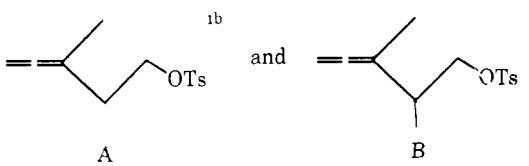
(9) We feel the indicated ion pair (a bisected cyclopropyl–carbinyl cation), which is shorthand for orbital representation A, is the *best hybrid* for resonance structures B and C. This type of structure has also been invoked in the solvolyses of related vinyl cyclopropyl systems: D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 92, 229 (1970). One referee feels this represents a significant change from our earlier preference for bicyclobutonium-type structures for the intermediate ion pairs. The principle difference between the two representations is the exact position of the orbital connecting C_1 (or C_2) with the 3,4 π system. If overlap takes place exclusively with an orbital on C_3 (as shown in A) a cyclopropyl–carbinyl cation results. If the same orbital on C_1 (or C_2) is shifted somewhat more toward the middle of the 3,4 π bond a bicyclobutonium-type structure (as in B or C) results. We emphasize that A is our choice for the best *overall* representation for contributing *resonance forms* B and C.



(10) Two independent solvolysis pathways for X are also kinetically implied by the *decrease* in integrated rate constant with time. If X solvolyzed exclusively *via* the k_Δ' route, it would exhibit the same behavior as IIIb.

(11) Another leveling factor between IIIb and X could be that k_{-1}' (Scheme IV) is still an effective quench for the intermediate ion pair, while k_{-1} is not.

(12) Although they report no such return–rearrangements, Bertrand and Santelli[4c] report kinetic data for compounds A and B where



$k_B/k_A = 14.5$ at 70°. The ratio between IIIb to XI (which have the same relationship as B to A) is ~10.5 at 65°. This indicates the lower reliability of direct comparisons between allenic substrates.

acetylene with time (Table III) suggests that formation of this type of product is sensitive to the amount of lyate ion remaining. It is also significant that at no time has simple methyl or hydride migration been observed in these systems; these processes must be of considerably higher energy than homoallenic participation.

Recent work by Sneen and coworkers[13] suggests that direct "SN2 attack" by external nucleophile is exceptional, and that an ion-pair mechanism better explains the results in the systems studied. If one extrapolates from these conclusions, it is perhaps better to conceive of neighboring group participation during carbonium ion formation not as *nucleophilic attack* by (σ, π, or n) electron pairs on the leaving group-bearing atom, but rather as electrophilic addition by the developing cationic center to whatever source of "loose" electron pairs the molecule can supply.[14] In the absence of "classical stabilization," as reactivity increases and the activated complex more and more resembles starting material, C–X bond heterolysis and G–C bond formation (G denotes the neighboring group) become more and more synchronous.[15] The propensity for a group to participate in carbonium ion formation is determined by its basicity toward $C^{\delta+}$ rather than its nucleophilicity toward C–X.

Regardless of which viewpoint one adopts, there may be another factor in solvolysis mechanisms which may help to explain very low k_Δ/k_s ratios in systems where neighboring group participation is stereochemically but not kinetically implied. Participation, for which the appearance of *any* rearranged primary product is *prima facie* evidence, can occur during or after ionization. Whether or not the group exerts a kinetic effect (anchimeric assistance) depends on exactly which step is rate limiting: ionization (formation of the ion pair), dissociation, or rearrangement.[13,16] The usual method of assessing a kinetic effect is the comparison of substrate rates with measurements on a similarly constituted model compound (*e.g.*, IIIb and IV), with allowances for inductive influences of the absent group. Confining our attention to compounds where ionization is rate limiting, the molecule can solvolyze by two principle mechanisms:[17] anchimerically assisted (k_Δ) and solvent assisted (k_s),[18] the relative importances of which are determined by the difference in activation energies. Although there should be *relatively* little conformational dependence for the k_s pathway, it is obvious that only a small fraction of the total number of conformations render the k_Δ route feasible. If, then, one-tenth of the conformations permit intramolecular assistance, then some fraction of this 10%, depending on the relative energies of the two pathways (100% if k_Δ is greater than k_s, ~50% if $k_\Delta = k_s$), should be subtracted from all conformations to give that fraction disposed toward the k_s route. The value chosen for k_s of the substrate should not be the observed solvolysis rate of the model compound, but rather 90% of the model compound rate (if k_Δ is greater than k_s). This should yield an adjusted k_Δ/k_s ratio which would be a more accurate measure of the relative importance of both pathways.

(13) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 91, 362, 6031 (1969).

(14) For similar interpretations, see P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, 1545 (1969), and J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(15) W. G. Dauben and J. L. Chitwood, *J. Amer. Chem. Soc.*, 92, 1624 (1970).

(16) V. J. Shiner and W. Dowd, *ibid.*, 91, 6528, 7748 (1969).

(17) J. M. Harris, F. L. Schadt, C. J. Lancelot, and P. von R. Schleyer, *ibid.*, 7508 (1969), and other papers in the series.

(18) Sneen's work[13] requires that only one solvent-assisted "classical" pathway is operative (k_s), and it is not a composite of SN1 and SN2 processes. For significant recent advances in understanding the importance of the k_s route, see P. von R. Schleyer, *et al.*, *ibid.*, 92, 2538, 2540, 2542, 3789 (1970).

Experimental Section

General. Unless otherwise noted, experimental procedures were similar to those previously described.[1b] Gas chromatography was carried out on a Hewlett-Packard Model 700-231 instrument fitted with a 6 ft × 1/8 in. column packed with 10% UCON W68 on 80/100 Chromosorb. Usual analytical conditions were column temperature, 90°; injection block, 100°; carrier gas flow rate, 30 cc/min. Ultraviolet spectra were recorded on a Cary Model 12 while infrared spectra were determined with a Perkin-Elmer Model 700. Pmr spectra were run on a Varian T-60, with samples in carbon tetrachloride containing 1% TMS. Boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Epoxidation of Methallyl Chloride. To a magnetically stirred suspension of 81.2 g (0.400 mol) of 85% *m*-chloroperbenzoic acid in 900 ml of methylene chloride at ambient temperature was added 41.6 g (0.460 mol) of methallyl chloride. The reaction is exothermic and was cooled as necessary to prevent reflux. After addition was complete (30 min), the solution was allowed to stir at ambient temperature for 40 hr. Excess peracid was destroyed with 10% sodium sulfite solution, until a starch–iodide test was negative. The resulting mixture was filtered, the solid was washed with 50 ml of methylene chloride, and the combined filtrate and washings were washed seven times with 10% sodium carbonate (until the extracts were colorless), once with saturated sodium chloride solution, and dried over molecular sieves. Most of the solvent was carefully removed at 300 mm and 25°, and the residue was distilled to yield 33.2 g (78%) of the epoxide, bp 58–60° (90 mm) (lit.[19] bp 51° (55 mm)). Glpc showed one peak at 1.4 min; pmr δ 1.40 (S, 3 H), 2.60 (S, 2 H), 3.42 (AB quartet, 2 H).[20]

2-Methyl-2-penten-4-yn-1-ol (II). A solution of ~1.39 mol of sodium amide in 900 ml of liquid ammonia was prepared, using the usual method.[1b] To this was added gaseous acetylene, freed from acetone by passage through sulfuric acid traps, until the solution became dark grey (about 6 hr at 100 ml/min). To this solution, at −78°, was added 32.0 g (0.30 mol) of the epoxide. The solution was stirred for 3 days at temperatures between −78 and −33°. Ammonium chloride (81 g, 1.5 mol) was cautiously added, then the ammonia was allowed to evaporate (~20 hr). Ether (400 ml) was added, followed by 600 ml of water. The ether was separated (with some difficulty due to an emulsion interface), then the aqueous phase was extracted with an additional 300 ml of ether. The combined ether solutions were washed twice with saturated sodium chloride solution, then dried over sieves at −20°. Removal of solvent and two distillations yielded 9.6 g (33%) of enynol as a clear colorless liquid, bp 59–60° (4.3 mm). Glpc showed two peaks 2.8 min (1%), 3.2 min (99%); ir 3100–3700 cm^{-1} (broad, O–H), 3320 (≡CH), 2140 (C≡C), 1640 (C=C); pmr δ 5.57 (symmetrical m, 1 H), 4.1 (broad s, 3 H), 3.08 (d, J = 2.5, 1 H), 1.90 (s, 3 H); uv (methanol) λ_{max} 225 nm (log ϵ 4.11). Owing to the high rate of polymerization of II a satisfactory analysis could not be obtained.

2-Methyl-3,4-pentadienol (IIIa). To a suspension of 4.0 g (0.11 mol) of lithium aluminum hydride in 400 ml of dry ether was added a solution of 9.6 g (0.10 mol) of enynol II in 20 ml of dry ether. The resulting suspension was gently refluxed for 6 hr during which time the solid material coagulated making stirring difficult. The mixture was carefully hydrolyzed with water and enough 1 *N* sulfuric acid was added to dissolve the basic solids. The ether was separated and the aqueous phase extracted with a total of 150 ml of ether. The combined ether phases were washed with saturated sodium chloride solution and dried over sieves at −20°. Removal of solvent and careful spinning band distillation yielded 5.2 g (53%) of the allenic alcohol, a clear, colorless liquid, bp 49.5–50.5° (9 mm). Glpc showed a major peak at 2.3 min, and another

(19) V. I. Isagulyants and V. V. Baleshova, *Chem. Abstr.*, 55, 18694*b* (1961).

(20) Owing to the neighboring asymmetric carbon atom.

peak (3%) at 2.1 min. The latter is most likely a conjugated isomer of IIIa, the tosylate of which is considerably less reactive than IIIb, judging by infinity titers: ir 3300 cm^{-1} (broad, OH), 1945 (C=C=C); pmr[21] δ 5.1 (d of triplets, 1 H), 4.7 (d of doublets, with fine structure, 2 H), 4.07 (s, 1 H), 3.40 (d of doublets, 2 H),[20,21] 2.3 (m, 1 H), 1.00 (d, J = 6.7, 3 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.42; H, 10.27. Found: C, 73.43; H, 10.09.

2-Methyl-3,4-pentadienyl Acetate (IIIc). A solution of 360 mg (3.7 mmol) of IIIa and 420 mg (41 mmol) of acetic anhydride in 3 ml of dry pyridine was heated to 95° for 5 hr. Work-up as usual[1b] afforded 440 mg of the crude acetate, containing ~3% of the conjugated isomer. Microdistillation (bp 69° (18 mm)) did not increase its purity: ir 1948 cm^{-1} (C=C=C), 1739 (C=O) pmr[21] δ 5.1 (d of triplets, 1 H), 4.7 (d of doublets with fine structure, 2 H), 3.9 (d of doublets, 2 H),[20,21] 2.6 (m, 1 H), 1.98 (s, 3 H), 1.09 (d, J = 7, 3 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.15; H, 8.79.

2-Methyl-3,4-pentadienyl tosylate (IIIb) was prepared in 86% yield by the reaction of 1.47 g (15 mmol) of IIIa and 3.2 g (17 mmol) of tosyl chloride in 20 ml of dry pyridine. The product was a clear colorless oil which could not be crystallized. Evacuation at 0.02 mm and ambient temperature for 24 hr left analytically pure material: ir 1950 cm^{-1} (C=C=C), 1600 (aromatic C=C), 1380 ($-SO_2-$); pmr[21] δ 7.74 (d, J = 8, 2 H), 7.33 (d, J = 8, 2 H), 5.0 (d of triplets, 1 H), 4.65 (d of doublets with fine structure, 2 H), 3.85 (d of doublets, 2 H), 2.4 (m containing s at 2.41, 4 H), 0.98 (d, J = 7, 3 H).

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39. Found: C, 62.10; H, 6.39.

2-Methyl-1-pentyl tosylate (IV) was prepared in 92% yield by the reaction of 2-methyl-1-pentanol with a 5% excess of tosyl chloride in pyridine: ir 1600 cm^{-1} (aromatic C=C), 1385 ($-SO_2-$); pmr δ 7.76 (d, J = 8, 2 H), 7.33 (d, J = 8, 2 H), 3.81 (d, J = 6, 2 H), 2.42 (s, 3 H), 0.7–2.0 (complex envelope containing apparent d, J = 6, at 0.82, 11 H).

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.92; H, 7.87. Found: C, 60.81; H, 7.87.

2-Methyl-1-pentyl Acetate (V). Treatment of 2-methyl-1-pentanol with a 10% excess of acetic anhydride in pyridine (8.5 hr at 95°) afforded, upon work-up, an 82% yield of the desired acetate: bp 160° (lit.[22] bp 162°); pmr δ 3.87 (d of doublets, 2 H),[20] 1.98 (s, 3 H), 0.8–1.6 (m, containing apparent d, J = 6, at 0.98, 11 H); ir 1730 cm^{-1} (C=O).

2-Methyl-2-pentyl Acetate (VIII). A solution of 1.0 g of 2-methyl-1-pentene (VI) and 3 drops of concentrated sulfuric acid in 8 ml of dry acetic acid was stirred at ambient temperature for 20 hr. At this point glpc indicated ~50% conversion to the Markovnikov ester, with accompanying rearrangement of the remaining olefin to 2-methyl-2-pentene (VIII). The solution was poured onto an equal volume of cold water and extracted with a total of 10 ml of pentane. This was washed with 10% aqueous sodium carbonate to pH 8, then with saturated sodium chloride solution, and finally dried over molecular sieves at −20°. Removal of solvent left 0.40 g of the tertiary acetate, >98% pure by glpc: bp 139° (lit.[23] 142°); pmr δ 1.87 (s, 3 H), 0.7–1.9 (m, containing ~6 H singlet at 1.40, 13 H); ir 1725 cm^{-1} (C=O).

Acetolysis of IV. The exact procedure for analysis of acetolysis products has been outlined earlier.[1b] Aliquots were removed at timed intervals from a solution of 2.5 mmol in 25 ml of acetolysis solvent.[8] These were dissolved in an equal volume of water and extracted with pentane, which was washed once with 10% aqueous sodium carbonate and dried. These solutions were analyzed with the Ucon oil column (initial conditions: column, 35°; injection block, 104°; detector block, 112°; flow rate, 30 cc/min) for 3 min and then programmed to 100° at 30°/min. Under these conditions the retention times of the significant products were VI, 2.0 min; VIII, 2.3 min; VII, 7.5 min; V, 8.8 min. Traces of two esters comprising <1% of the reaction mixture were also observed. The results are given in Table II. After analysis, the pentane solution from the aliquot removed after one half-life was evaporated under reduced pressure, and the resulting oil analyzed by pmr. Only unrearranged IV was in evidence, showing, as expected, that return to rearranged tosylate was not occurring.

Stability of Products from IV under Acetolysis Conditions. Small amounts (~0.1 g) of V, VI, and VII were separately dissolved in ~5 ml of acetolysis solvent and heated to 100° for 0.8 half-life. These were treated in the same manner as the original acetolysis products and analyzed by glpc. Results are given in the text.

Acetolysis of IIIb. Using the procedure outlined for IV, IIIb was subjected to acetolysis conditions and the products were analyzed on an 8 ft × 1/8 in. column containing 12% silicon oil 550 on 80–100 Chromosorb W (initial conditions: column, 35°; injector block, 95°; flow rate, 30 cc/min) for 2 min and then programmed to 100° at 10°/min. The retention times of the products were compared directly with those from X. Retention times were also compared on the Ucon oil column. The relative ratios listed in Table III represent averages of several analyses. The precision is estimated to be 0.5%. Although the percentages varied slightly with exact work-up conditions, the trends in going from τ 1 to 6 are real, as verified by independent runs. Products were isolated by preparative glpc on a Ucon 50 HB 2000 column. Components 1–4 were not identified in our previous study.[1b]

The first component had retention time (rt) 2.2 min, *cis*-2-methylcyclopropylacetylene (cis on the basis of its apparent tendency to yield the second component); ir 3325 (≡CH), 3030 (cyclopropyl CH), 2150 (C≡C).

The second component had rt 2.6, *trans*-2-methylcyclopropylacetylene; ir 3320 (≡CH), 3030 (cyclopropyl CH), 2155 (C≡C); pmr (TMS) δ 1.75 (m containing d, 2 H), 1.3–0.6 (m, 5 H), 0.4 (m, 1 H).

The third and fourth components had rt 3.3 and 3.5 (not completely resolved). Judging from retention times and an ir absorption at 1935 cm^{-1} these are allenic hydrocarbons, probably *cis*- and *trans*-2,4,5-hexatriene.

The fifth and sixth components had rt 6.4 and 6.5 (not well resolved), a mixture of *cis*- and *trans*-2-methylcyclopropyl methyl ketone; ir 3025 (cyclopropyl CH), 1690 (C=O); pmr (TMS) δ 2.17 and 2.20 (singlets), 1.4–2.0 (m), 0.6–1.3 (m).

The seventh, eighth, and ninth components had rt 8.9, 9.0, and 9.3, a mixture of 1-(2-methylcyclopropyl)-1-acetoxyethylene (both isomers) and *trans*- and *cis*-3-methyl-2-methylenecyclobutyl acetate in the ratio 1:3:1.

The tenth component had rt 9.8, 4,5-hexadien-2-yl acetate, by comparison with authentic material.[1b]

The eleventh component had rt 10.1, 2-methyl-3,4-pentadien-1-yl acetate (IIIc) by comparison with a sample of IIIc prepared directly from IIIa (*vide supra*).

Identity of Rearranged Tosylate. The pentane solution of acetolysate isolated after one half-life was evaporated to near dryness at 0.025 mm, leaving only tosylates. The pmr spectrum showed, in addition to unrearranged IIIb, about 15% of the same rearranged tosylate described earlier.[1b]

Kinetics Determinations. Acetolysis rate measurements were carried out as previously described,[1b] except that 3-ml aliquots were used, and methyl violet 2B was employed as indicator. Owing to the presence of 3% of an unreactive isomeric tosylate in IIIb (*vide supra*) the infinity titer method was used in the rate constant calculations, which were carried out on an IBM 360/65 computer with the aid of a CalComp plotter (Figure 1).

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(21) The pmr spectra of IIIa, b, and c are of special interest and will be discussed separately: R. Macomber, *J. Org. Chem.*, in press.

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