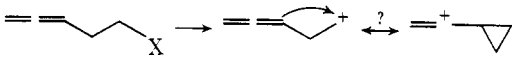
Homoallenic Participation. IV. Confirmation of the Involvement of a Vinylcyclopropyl Compound[1]

Thomas Von Lehman and Roger S. Macomber*

Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received July 11, 1974*

Abstract: Previous results from the acetolysis of 4,5-hexadien-2-yl tosylate (**1**) and 2-methyl-3,4-pentadienyl tosylate (**3**)[3] have implicated a third isomeric tosylate as being common to both solvolyses. This compound was believed to be 1-(2-methylcyclopropyl)-1-tosyloxyethylene (**2**) on the basis of limited spectral evidence, as well as the kinetic behavior of **1** and **3**, and the nature of their solvolysis products. Vinyl tosylate **2** has now been independently synthesized and its acetolysis behavior determined. The solvolysis products from **2** match closely those from **1** and **3**, although the percentage of products possessing a cyclopropyl skeleton is greatest in the case of **2**. Unlike **1** and **3**, compound **2** solvolyzes in a strictly linear first-order fashion, and the rate constant for its disappearance agrees well with the value calculated to explain the kinetic behavior of **1** and **3**. We conclude that **2** is intimately involved in the solvolyses of **1** and **3**, and that all three compounds react *via* the same intermediate manifold.

The widely explored phenomenon of homoallylic participation in solvolysis stimulated several groups of investigators to study the effects of a similarly located allenic system—homoallenic participation. One impetus for these studies derived from a desire to assess the relative importance of vinyl cation resonance forms, which are absent in the case of normal homoallylic participation. It was found

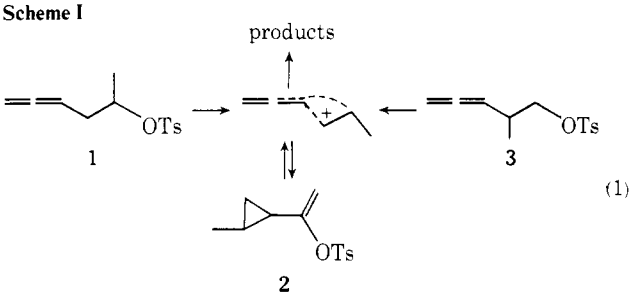


that the β-allenic linkage exhibited a versatility for involvement in solvolyses comparable to that of a simple double bond, and product studies supported the hypothesis that considerable positive charge existed at the incipient vinyl carbon.[2,3] Nearly all of the β-allenic compounds investigated yielded substantial amounts of products diagnostic of the intervention of the β-π bond and, with two exceptions, all exhibited well-behaved first-order titrimetric kinetics which were accelerated by comparison with saturated model compounds. Notably different was the behavior of 4,5-hexadien-2-yl tosylate (**1**).[3a,4] Although the acetolysis products from **1**[3a] suggested that *at least*[5] half of the product mixture arose *via* homoallenic participation, the stage of the reaction at which this participation took place was less clear owing to the ambiguous kinetic behavior of **1**.[3a,7] A typical "first-order" plot of the titrimetrically monitored liberation of *p*-toluenesulfonic acid during the acetolysis of **1**[8] shows marked negative curvature (a monotonic decrease in the instantaneous rate constant with time), evidence that return of **1** to a kinetically less reactive isomeric tosylate was competitive with solvolysis.[3a,9] The rearranged tosylate, which accumulated during the course of the reaction, was isolated in impure form and tentatively identified[3a] as 1-(2-methylcyclopropyl)-1-tosyloxyethylene (**2**) on the basis of its spectral properties, the anticipated lower reactivity of **2** compared with that of **1**, and the nature of the products from **1**.

The possibility then became apparent that if **1** indeed ionized to give a cyclopropylcarbinyl-like cation, the isomeric 2-methyl-3,4-pentadienyl tosylate **3** should enter the same intermediate manifold upon ionization (Scheme I).

To explore this possibility, **3** was prepared and its solvolytic behavior examined.[3b] As predicted, the products arising from **3** matched those from **1**, although there was a slight product spread. Equally interesting, however, was its kinetic behavior. In contrast to **1**, compound **3** exhibited a continuously *increasing* integrated titrimetric rate constant (positive curvature in the "first-order" plot).[10] This implied that

Scheme I

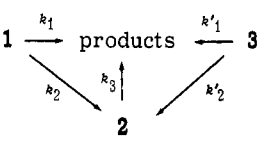


(1)

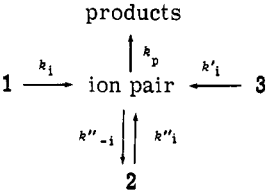
3, like **1**, was solvolyzing (at least in part) through a rearranged tosylate, one which was *more* reactive than **3**.[9] Two observations were especially significant here.[3b] The pmr spectrum of unreacted **3** included absorptions which resembled those of the unsolvolyzed tosylate mixture isolated from the acetolysis of **1**, and the major acetolysis product from **3** was *rearranged* 4,5-hexadien-2-yl acetate, the same major product isolated from the acetolysis of **1**. Only a trace of unrearranged acetate was formed, indicating that the k_s process[5] was negligible in the case of **3**. The most economical interpretation of these findings was that **1** and **3** were both solvolyzing and simultaneously rearranging to a common isomeric tosylate (**2**) *via* the same intermediate manifold, as shown in Schemes I and II.

Scheme II

(a)



(b) (equivalent to (a))[9]



During this period, Bergman and coworkers had begun to attack the problem from the other extreme by examining the solvolytic behavior of several vinylcyclopropyl iodides and their isomeric allenic counterparts. In an elegant series of papers,[11] they found that vinylcyclopropyl iodides similar to **2** reacted with silver ion readily, a reaction characteristic

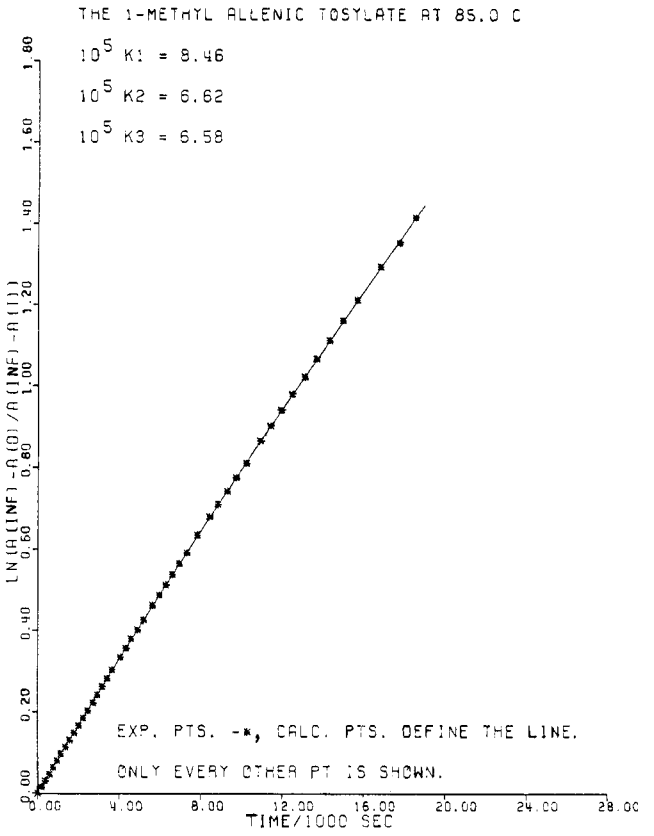


Figure 1. Nonlinear acetolysis of **1** at 85°, experimental and calculated.

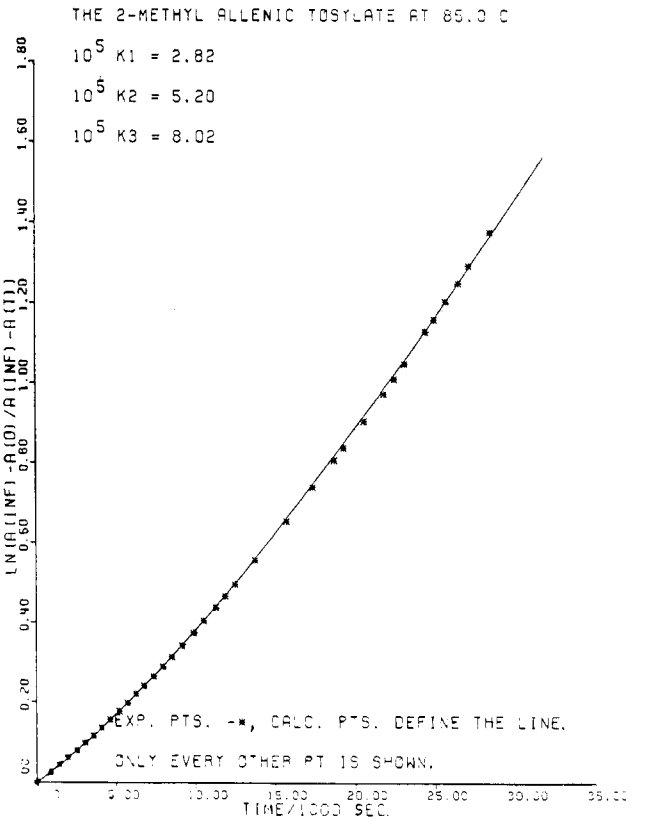
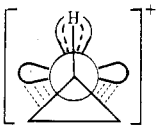


Figure 2. Nonlinear acetolysis of **3** at 85°, experimental and calculated.

of activated halides. Moreover, when comparisons were made between the silver-"catalyzed" and uncatalyzed solvolyses of the vinyl systems with their allenic isomers, the same products were isolated from both, although there was a not-surprising product spread favoring unrearranged products. These authors concluded that the first solvolytic intermediate in both cases was the same, one with vinylcyclopropylcarbinyl skeleton **4.**



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Results

Before further meaningful conclusions could be made about the kinetic relationships between **1, 2,** and **3,** the previously graphically estimated[3] rate constants for Scheme IIa had to be more accurately determined. With the exact equations governing such triangular kinetic schemes,[9] a nonlinear least-squares program was written to extract the values of k_1, k_2, and k_3 from the best fit of experimental kinetic data to eq 1.[9,12] In order to minimize errors in the determination of rate constants by nonlinear curve fitting, it was desirable to input many more data points than were available from the titrimetric ampoule method previously employed. Since it has been demonstrated[13] that conductometric rate constant determinations exactly parallel titrimetric determinations but conveniently allow acquisition of many more data points, we have now adopted this method while retaining the original solvent system, dry acetic acid containing a slight excess of acetate ion.

$$\ln\left(\frac{[\mathrm{HOTs}]_\infty}{[\mathrm{HOTs}]_\infty - [\mathrm{HOTs}]_t}\right) = \ln\left[\frac{k_1 + k_2 - k_3}{k_2 e^{-k_3 t} + (k_1 - k_3)e^{(k_1+k_2)t}}\right] \quad (1)$$

The acetolyses of **1** and **3** were reinvestigated using the conductometric method. As can be seen from Figures 1 and 2, the kinetic trends previously observed[3] in titrimetric runs were equally obvious from conductometric data. Moreover, the number of points in each run (*ca.* 100) facilitated ready convergence to well-defined values of k_1, k_2, and k_3 for both compounds (Table I). Agreement between the calculated points (shown by the lines in Figures 1 and 2) and the experimental points (shown by asterisks) was clearly excellent; the two sets of data were generally superimposed.

Although several conclusions from this data will be described below, two observations are important at this point. If Scheme IIa is to be valid for these systems, the value of k_3 calculated for **1** should match the value of k_3 for **3** under a given set of conditions. The agreement, as can be seen from Table I, is reasonably good, the difference ranging from 18% at 85° to 32% at 100°. It is also seen that the k_3 value calculated for **3** is uniformly larger than k_3 calculated for **1.** Even more worrisome was the physically unlikely *decrease* in k_2 for **1** while *raising* the temperature from 93 to 100°. Interpretations of these observations will be discussed below.

Thus, even under careful scrutiny, the kinetic evidence continued to implicate a third isomeric tosylate with reactivity intermediate to **1** and **3.** Could **2** be synthesized and its involvement unambiguously demonstrated?

Synthesis of 2

Few general methods of preparing vinyl tosylates are known.[14] However, Bergman had reported[11b] that the reaction of 1-cyclopropyl-1-iodoethylene with silver tosylate in acetonitrile provided in low yield the highly unstable vinyl

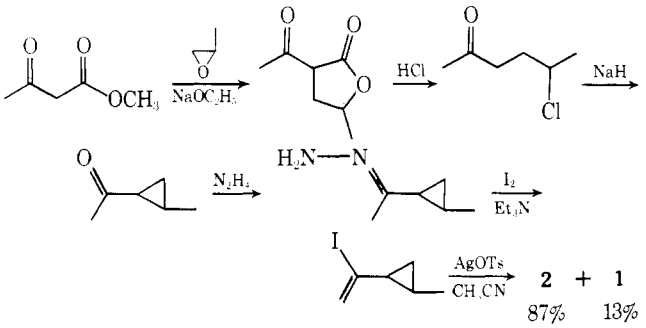
Table I. Rate Constants for Scheme IIa[a]

Compd	Temp ± 0.05, °C	$k_1 \times 10^5$, sec	$k_2 \times 10^5$, sec	$k_3 \times 10^5$, sec
1[b]	85.00	8.46(1)	6.6(6)	6.58(9)
		[8.55(1)]	[10.9(2)]	[7.00(1)]
	93.00	18.2(7)	27(1)	11.7(1)
	100.00	35.2(1)	16(2)	19(1)
		[37.4(4)]	[104(5)]	[28.9(0)]
3[c]	85.00	2.82(0)	5.20(1)	8.02(1)
		[2.63(4)]	[7.2(1)]	[7.00(1)]
	93.00	6.80(1)	11(1)	18(1)
		[6.68(1)]	[16.0(0)]	[15.6(0)]
	100.00	14.3(0)	17.0(0)	31.4(0)
		[13.6(1)]	[22.7(3)]	[28.9(0)]

[a] Extracted from nonlinear least-squares fit of conductimetric data to eq 1. Quoted uncertainties are standard deviations computed during least-squares refinement,[12] and are given in parentheses: 8.46(1) = 8.46 ± 0.01; this notation is used throughout the paper. Bracketed values use the experimentally determined k_3 values. See text. [b] Previously estimated values (65°) were $k_1 = 1.45 \times 10^{-5}$ and $k_3 = 0.65 \times 10^{-5}$ sec^{-1}. Extrapolation of the data in this table to 65° gives $k_1 = 1.07 \times 10^{-5}$ and $k_3 = 1.32 \times 10^{-5}$ sec^{-1}. [c] Previously estimated[3b] values (85°) were $k_1 = 3.3 \times 10^{-5}$ and $k_3 = 7.4 \times 10^{-5}$ sec^{-1}.

tosylate. We have explored this avenue toward **2**, and although the reaction is complex, we have been able to isolate **2** in reasonable yield. The entire sequence is shown in Scheme III.[15] There are several important aspects of

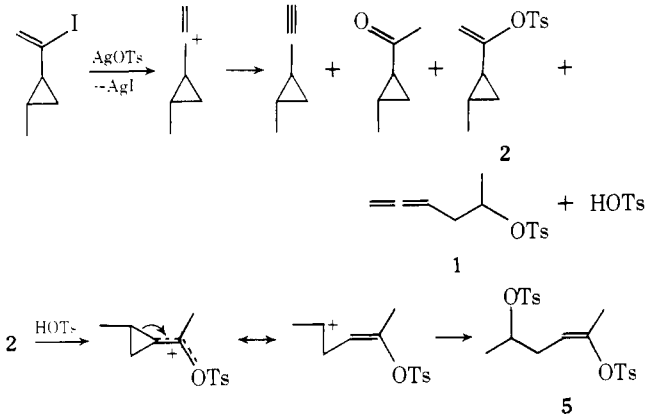
Scheme III



Scheme III that deserve comment. One fundamental question regards the stereochemistry of the cyclopropyl ketone-forming ring closure. In our hands, one isomer predominated to the extent of 95% by glc. Roberts and coworkers[16] reported that the trans ketone displayed a medium ir band at 1322 cm^{-1}, while the cis ketone absorbed at 1128 cm^{-1}. The ir spectrum of our product exhibited only the band at 1322 cm^{-1}. Moreover, the melting point of the 2,4-DNP derivative of our ketone matched that reported for the trans isomer. Even on treatment with sodium hydride, the composition of the mixture was unchanged, confirming the predominance of the more thermodynamically stable isomer. Thus, we feel the ketone is 95% trans, and this stereochemistry persists to the iodide (91% trans by glc).

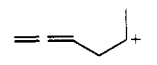
Our initial attempts to carry out the last step were so discouraging that we nearly abandoned the procedure. Although silver iodide was rapidly produced during the reaction, many products were formed, and attempts to isolate them by column chromatography led only to unstable oils. But of this myriad of products, three were immediately recognizable: 2-methylcyclopropylacetylene, 2-methylcyclopropyl methyl ketone (both predominantly trans), and tosylate **1**! The ketone was produced even when all reactants were scrupulously dried.[11b] The appearance of **1** under these conditions further indicated the intimate involvement of the allenic system with its isomeric vinylcyclopropyl counterpart under ionizing conditions and suggests that return to **1** during acetolysis was at least possible. But most

Scheme IV



informative was the isolation and characterization of ditosylate **5**, which presumably arises as shown in Scheme IV. This observation suggested that if the *p*-toluenesulfonic acid liberated during the reaction could be rapidly neutralized by some base (mild enough not to promote acetylene formation), perhaps **2** would survive the reaction. Indeed by carrying out the reaction at 0° in the presence of suspended sodium bicarbonate, **2** could be isolated (as an oil) in *ca.* 50% yield. All attempts to crystallize and thereby purify the product have so far failed. Although column chromatography afforded material which was stable for days at room temperature, and which gave satisfactory elemental analysis, it was clear from tlc, pmr, and quantitative ir that there remained 13% of **1** in the otherwise pure **2.** It was possible to free **2** from **1** by difficult and painstaking preparative tlc, but the product remained an oil and refused to crystallize.

The question of the stereochemistry of **2** is less easily handled. Four lines of evidence suggest that the product is predominantly trans. First, unless the (presumed) vinylcyclopropyl cation resulting from attack of Ag^+ on the iodide reversibly opens to an allenic (resonance?) form (such as secondary ion **6**), the stereochemical integrity of the cyclo-



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propane (trans in the precursor iodide) should be retained. Tlc shows only one spot. The pmr spectrum, while complex, nonetheless shows only *one* AB quartet for the vinyl protons and one set of tosylate resonances, even upon addition of the paramagnetic shift reagent Eu(fod)$_3$. (It has been previously observed[3] that relatively subtle structural variations in tosylates can give rise to small but observable changes in the position of the tosylate methyl resonance.) The kinetic behavior (*vide infra*) is consistent only with a pure compound or a mixture whose components all solvolyze at nearly (±5%) the same rate. Finally, treatment of **2** or its precursor iodide with potassium *tert*-butoxide gives the cyclopropylacetylene with trans/cis ratios of 86:14 and 88:12, respectively. We thus feel that the evidence supports the conclusion that **2** is ≥86% trans.

Once obtained, compound **2** was compared with the rearranged tosylates isolated from **1** and **3.** The positions and intensities of absorptions in the pmr spectrum of authentic **2** matched with those from rearranged **1,** although the vinyl AB quartet present in the spectrum of synthetic **2** appeared as a less structured multiplet in the spectrum of the rearranged material. This could be attributed to smaller trans/cis ratios in the rearranged tosylate, and evidence for this can be adduced from the acetolysis products (*vide infra*). Confirmation that the unsolvolyzed tosylate from **1** contained **2** came from tlc, which exhibit a spot of R_f identical

Table II. Acetolysis Products from 1, 3, and 2 at 85.0°[a]

	1		3		2[b]	
Component/half-lives[c]	1.63	4.38	1.10	3.00	0.76	2.23
1	9.3(4)	8.7(4)	6.5(5)	8.5(1)	14.5(1)	11.0(3)
2	7.3(2)	8.4(4)	13(1)	16(1)	8.0(2)	7.0(2)
3	1.0(2)	1.4(2)	T	T	T	T
4	2.1(2)	1.4(2)	T	T	T	T
5	2.1(5)	3(5)	2.4(2)	3(1)	34.6(6)	39.2(2)
6	5(1)	12(1)	7(1)	13(1)	T	T
7	1.2(2)	T	1.5(3)	0.6(1)	T	T
8	0.6(1)	T	1.6(2)	0.6(1)	T	T
9	0.7(1)	T	1.5(2)	1.2(5)	T	T
10	T	T	2.2(3)	1.5(5)	T	T
11	7(2)	1.2(2)	4.5(5)	1.5(5)	2.3(3)	2.8(1)
12	4.2(5)	4.7(2)	8.5(1)	6.0(5)	6.9(3)	7.8(3)
13	3.6(5)	2.3(2)	5(1)	3.0(1)	4.4(9)	4.8(7)
14	54(1)	55(1)	39(2)	40(2)	29.2(7)	27.4(1)
15	T	T	3.6(5)	1.9(2)	T	T
16	0.6(2)	T	3.6(5)	1.9(2)	T	T

[a] Determined by glc as described in Experimental Section. Each entry represents an average of two separate runs, each multiply analyzed. Errors are average deviations; 9.3(4) = 9.3 ± 0.4%. T is a detectable trace ≤0.5%, and these account for sums <100%. [b] See ref 18. [c] For 1 and 3, the number of half-lives = $0.69/(k_1 + k_2)$ (Table I). For 2, it equals $0.69/k$.

with that of the synthetic material.

The situation with **3** was unfortunately more complex. Because rearranged **3** solvolyzed considerably more rapidly than **3** itself (Table I), unreacted tosylate reisolated after 1 titrimetric half-life was >75% unrearranged **3**; *i.e.*, as expected there was very little accumulation of rearranged material. From the nmr comparison, it became clear that at least half of the *rearranged* tosylate was **1**, as evidenced by the methyl doublet at δ 1.24.[17] Unfortunately it is difficult to estimate the amount of **2** in the rearranged tosylate, for its resonances fall exactly among those of **1** and **3**. Tlc again came to the rescue. Unreacted tosylate from **3** clearly showed a spot with R_f characteristics identical with that of **2**. Addition of authentic **2** to the mixture only increased the intensity of the spot.

Thus we have shown conclusively that **1** rearranges to **2** upon solvolysis, and **3** yields both **1** and **2**, the latter observation suggesting that *at least* one additional pathway (**3** → **1**) is needed in Scheme II.

Solvolysis Results

The acetolysis of **2** under the previously described conditions[3] led to the complex mixture of *ca.* 16 products shown in Table II.[18] To maximize the internal consistency of comparisons with the product mixtures from **1** and **3**, the latter were redetermined under isolation and separation conditions *identical* with those for **2**. Extreme attention was given to the reproducibility of these determinations. With the exception of the vinylcyclopropyl acetate (which reacts with solvent to give ketone),[11] the products seem to be stable to the reaction and separation conditions, as shown in the table by the constancy of percentage with time.

Two points are immediately obvious: virtually all of the products formed during the acetolysis of **1** and **3** were also formed from **2**, and a major product in all three cases was 4,5-hexadien-2-yl acetate (**14**). It is thus unambiguously clear that the product-determining intermediate (or intermediate manifold) is common to all three systems. The most obvious difference between the product mixture from **2** and those from **1** and **3** is the greater percentage of (unrearranged) cyclopropyl products from **2**. While **3** must undergo <4% direct displacement by solvent, approximately ⅓ (15%) of the acetate **14** from **1** could arise *via* a k_s pathway. Similarly, the considerably greater percentage of cyclopropyl ketones (components **5** and **6**) from **2** can be rationalized not only by the instability of the related enol acetate (*vide supra*) but also by a similar, nonionization reaction of **2**. Another significant difference lies in the trans/cis ratio of the cyclopropyl products from **2** *vs.* **1** and **3**. While **1** and **3** yield mixtures of the cyclopropyl acetylene (components **1** and **2**) where the ratio is in the range 1.0–0.5, **2** provides considerably more trans than cis. In fact, the ratio parallels the 86:14 stereoratio originally present in the starting tosylate. Similarly, the trans/cis ratio of cyclopropyl ketone from **1** and **3** ranges from 0.4 to 0.2, while **2** yields nearly exclusively the trans ketone. The logical conclusion is that solvolysis of *trans*-**2** leads (*via* a trans intermediate) to *trans*-cyclopropyl products, while cis tosylate yields exclusively cis products, with no crossover (*via* opening to **6**). Further, it suggests that the trans/cis ratio of acetylene and ketone is diagnostic of the relative amounts of the cis and trans solvolytic intermediates, a ratio near 9:7 for **1** and 1:2 for **3**. These conclusions complement the finding[2b,19] that hydrolysis of optically active **1** leads to active cis and trans ketones and racemic 4,5-hexadien-2-ol.

The data in Table I provided accurate predictions for the acetolysis rate constants for **2** at various temperatures, assuming it was indeed the missing link. Compound **2** solvolyzed in a strictly first-order linear fashion through as many as 4 half-lives (Figure 3). The acetolysis rate constants at several temperatures, determined using the conductometric method described above, are listed in Table III.[20] Furthermore, a sample of tlc-purified **2** (free of **1**) was reisolated after partial acetolysis and found to contain no detectable amount of any rearranged tosylate.

A comparison of the experimental acetolysis rate con-

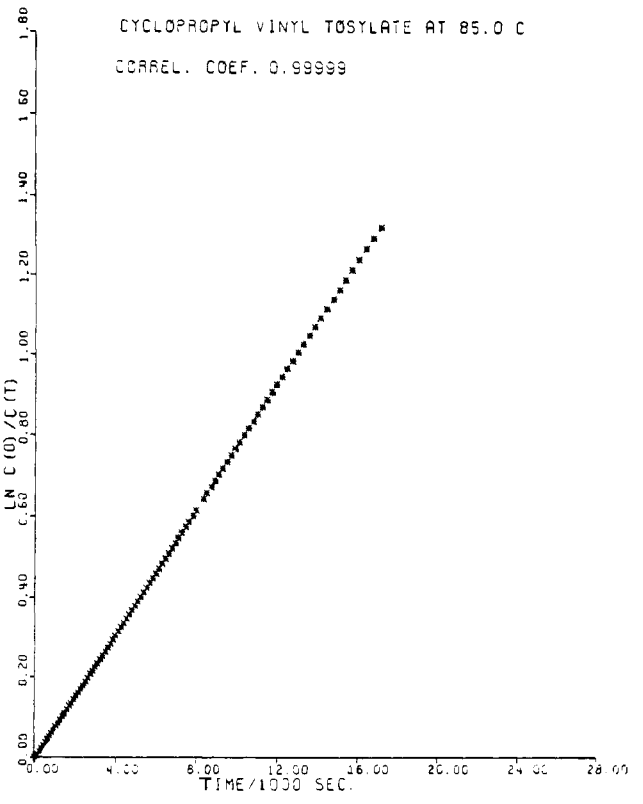


Figure 3. Linear acetolysis of **2** at 85°.

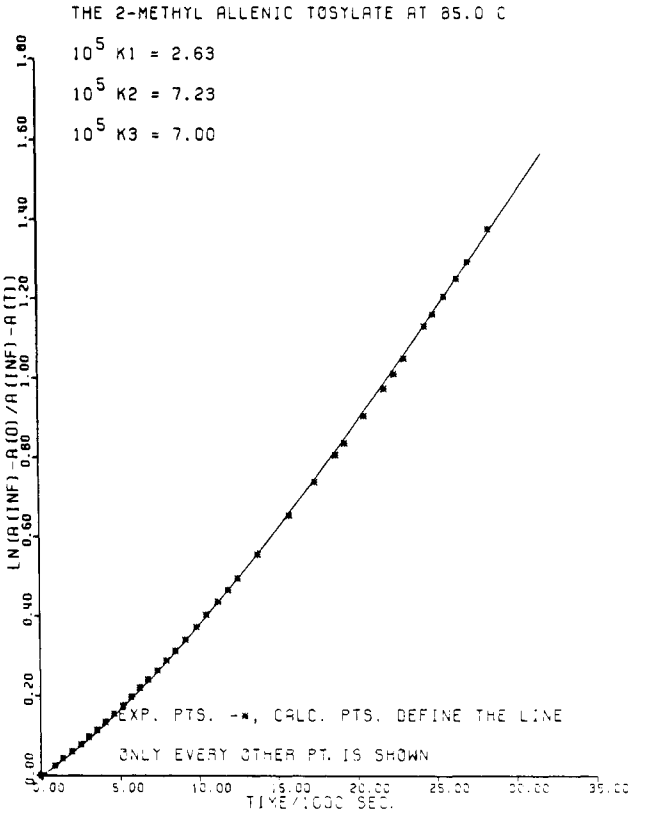


Figure 4. Nonlinear acetolysis of **3**, with calculated line using fixed value of k_3.

stants for **2** with the predicted values of k_3 (Table I) can now be made. Notice that, at all temperatures studied, the experimental value falls between the k_3 value for **1** and the k_3 value for **3**, always lying closer to the latter.

While it is tempting to dismiss these relatively small differences between experimental and predicted rate constants and pronounce the agreement as excellent, we were aware that the differences exceeded experimental errors and calculated standard deviations by a fair margin. The capricious change in k_2 with increasing temperature (*vide supra*) also suggested that the nonlinear program may be converging on some local minimum rather than the absolute minimum. Even though the experimental *vs.* calculated agreement in nonlinear runs was visually excellent (Figures 1 and 2), we decided to calculate best values of k_1 and k_2 for **1** and **3** using the acetolysis rate for **2** as k_3. Indeed, this leads to a slightly improved fit of the acetolysis data for **1** and **3** and yields more realistic values of k_2, as shown by the bracketed values in Table I. (See Figure 4.)

Cursory examination of these "best" values for k_1, k_2, and k_3 shows why the kinetic behavior of **1** and **3** is so complex. At any given temperature, all three rate constants differ by less than a factor of 2. As required by the observed sign of curvature in the kinetic plots,[9] $k_1 > k_3$ for **1**, and $k_1 < k_3$ for **3**. More significant is a comparison of the lower limits of the ionization rates, as given by $(k_1 + k_2)$ for **1** and **3** and k_3 for **2**. For example, at 85°, **1**, **2**, and **3** disappear at rates of 19.5×10^{-5}, 7.00×10^{-5}, and 9.8×10^{-5} sec^{-1}, respectively. Thus, the relative rates of disappearance (and the relative rates of ionization, assuming comparable amounts of return *without* rearrangement) are 2.79, 1.00, and 1.40 for **1**, **2**, and **3**, respectively. This confirms that **3**, a primary tosylate, is greatly accelerated over its saturated counterpart,[3b] **2** is greatly accelerated over its noncyclopropyl counterpart, and that **1** is typically reactive for a secondary tosylate.[3a] It also shows that the stabilizing influence of the β-allenic system in **3** is comparable to the influence of a cyclopropane on an incipient vinyl cation.

Table III. Conductometric Acetolysis Rate Constants for **2**[a-c]

Temp ± 0.02, °C	$k \times 10^5$, sec	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
85.00	7.00(1)		
93.00	15.6(0)	24.4(3)	13.6(2)
100.00	28.9(0)		

[a] Quoted uncertainties are standard errors. Correlation coefficients for these determinations exceeded 0.9999. [b] Arrhenius activation energy = 25.1(3) kcal/mol.[20] [c] Extrapolated rate constant at 65.0° = 8.8×10^{-6} sec^{-1}. Previously estimated[3] value: 6.5×10^{-6} sec^{-1}.

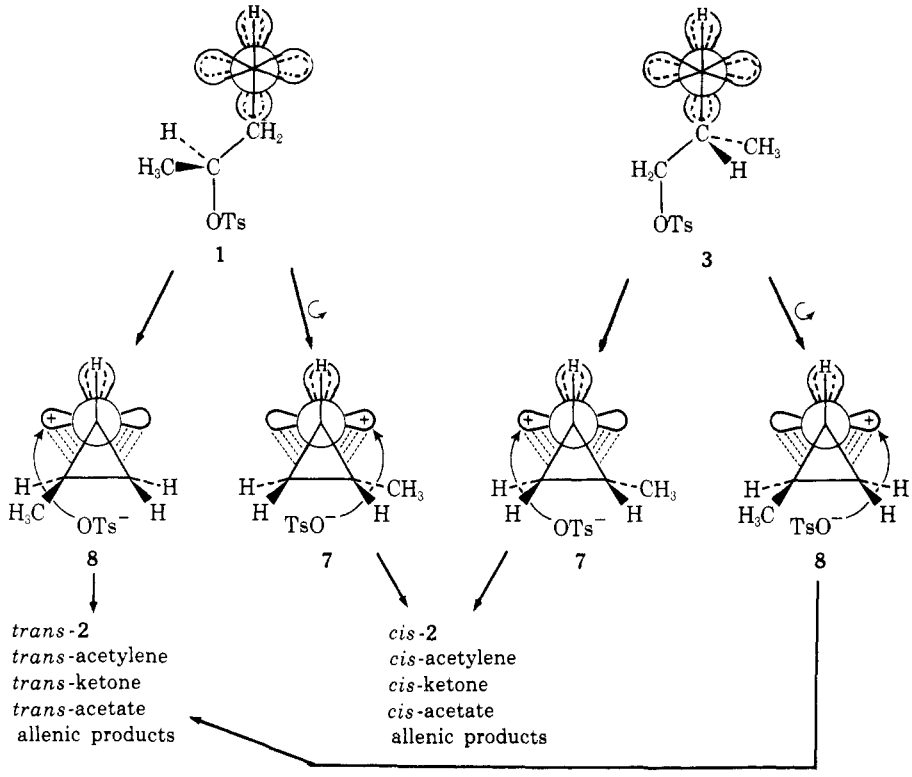
Discussion

While the preponderance of evidence, both from product and kinetic studies, proves that **2** is intimately involved in the solvolyses of **1** and **3**, we would suggest several reasons for some of the minor incongruities pointed out above. For example, why was there a product spread, especially in the case of cis/trans ratios of cyclopropyl products? Why did **1** return to **2**, **3** return to **1** and **2**, but **2** return to neither **1** or **3**? Why is the agreement between predicted and observed rate constants not perfect?

It is possible that **2** has available to it other reaction pathways than heterolytic solvolysis (*e.g.*, E2 elimination to the acetylene) which may account for some of the product spread. Similarly, the direct elimination of *p*-toluenesulfonic acid from **1** to give trienes seems not to occur with **2** or **3** (Table I). However, even if the experimental rate of acetolysis of **2** is a composite of several (pseudo) first-order steps, the *same* composite value should be calculated during nonlinear curve fitting.

The most likely cause of the small disagreement between calculated and experimental values of k_3 is the different cis/trans ratios of **2** depending on whether **1**, **3**, or authentic **2** is the starting material. If **3** rearranged to predominantly

Scheme V

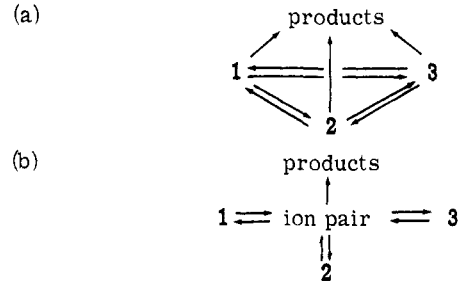


trans-**2**, (like authentic **2**), their k_3 values should be comparable, as is the case. If **1** gave rearranged **2** somewhat richer in the cis isomer, *and* if the cis isomer solvolyzed more slowly than the trans, k_3 calculated for **1** would be less than k_3 measured for **2**. But should **1** and **3** return to **2** with different cis/trans ratios?

Allenic tosylates **1** and **3** can undergo participation through a number of rotational conformations, leading ultimately to mixtures of products derived from both *cis*- and *trans*-cyclopropylcarbinyl ions **7** and **8**, as is indeed observed (Scheme V). But if one starts with isomerically pure *trans*-**2**, and if the intermediate resulting from heterolytic cleavage is ion **8**, only *trans*-cyclopropyl-containing products should be observed (in addition to allenic and cyclobutyl products). Although we have not made quantitative studies of the rates of cis $\rightleftarrows$ trans isomerization for the cyclopropyl ketones and acetylenes, our product studies (Table II) do suggest that the trans/cis ratio for these products isolated from the acetolysis products from **2** matches the ratio found when **2** or its precursor iodide is treated with potassium *tert*-butoxide (*vide supra*). The conclusion based on these results is inescapable: *cis*-**2** yields exclusively *cis*-cyclopropyl-containing products, while *trans*-**2** yields only trans products, and that there is no crossover of the type **8** $\rightleftarrows$ **6** $\rightleftarrows$ **7**. If this is true, there seems to be no reason to invoke any carbonium ion intermediates other than **7** and **8**, which can *both* be formed from **1** or **3**, but which can only be formed independently from *cis*- and *trans*-**2**, respectively. Attack by solvent on these ions (or more probably ion pairs) yields cyclopropyl products if approach comes from the vinyl end, or allenic products if attack takes place at C_2 or C_3 of the ring. From the observation that ionization of **3** leads to both **1** and **2**[17] and products with their carbon skeleton, one can infer that the charge distribution in **7** and **8** is somewhat unsymmetrical, residing mostly on C_2 of the ring and the vinyl sp carbon. This can account for the facility with which **1** and **3** return to **2**, but it is still puzzling why other similarly constituted allenic tosylates give no evidence of such behavior.[2,3] Further, the difference in the cis/trans ratio of cyclopropyl acetylenes from **3** compared with **1** may reflect preferential closure of **3** to **7** and **1** to **8**.

Since the **2** formed during acetolysis of **1** and **3** is actually a cis-trans mixture, and the two geometrical isomers may solvolyze at somewhat different rates, and since **3** yields some **1** in addition to **2**, Scheme II is not a totally accurate depiction of the mechanistic relationship between **1**, **2**, and **3**. One is tempted to over-generalize Scheme II to tetrahedral kinetic Scheme VIa, with the implicit assumption that **1**, **2**, and **3** *all* yield *exactly* the same ion pair manifold, as shown by equivalent Scheme VIb. Unfortunately the number of variables now approaches the ridiculous, and certainly with so many adjustable parameters *any* kinetic behavior could be fit. We have considered some of the reasonable simplified versions of Scheme VI, but none is any more satisfactory. This leads us to believe that perhaps **1**, **2**, and **3** don't all ionize to a *single* ion pair, but rather to ion pairs that differ in the position of the tosylate counterion (as shown in Scheme V). This may also account for differences in product distribution, and to the facility of return *vs.* product formation.[21] It seems not unreasonable that movement of the counterion to other electrophilic sites in the carbonium ion should be slower than its reattachment so that interconversion of the ion-pairs (differing in counterion location but not carbonium ion structure) will be kinetically significant. If this argument is true, then it fol-

Scheme VI



lows that product spreads, as observed here and in many similar systems, could result not only from the usually invoked k_s component (which should be negligible for **2** and **3**) but also from a directing influence of the counterion (*via* hydrogen bonding) toward the original point of attachment. Only if counterion migration within the ion pair is rapid by comparison with solvent trapping will the product spread be minimized.

If such a counterion effect is important, it might be possible to influence the migration of the counterion through the operation of something resembling the special salt effect.[22] Preliminary studies show that addition of small amounts of lithium perchlorate to acetolysis solutions of **1** significantly enhance the rate of acid formation and decrease the amount of cyclopropyl product. Further studies are underway.

Conclusions

Based on the evidence presented here and before,[3] there is no doubt that **2** (both cis and trans) is the missing link in the acetolysis of **1** and **3**. That the acetolysis rate of **2** quite accurately explains the behavior of **1** and **3** indicates that Scheme I is nearly, but not totally consistent with the actual mechanistic relationships involved. Finally, our data suggests that indeed a single *type* of intermediate is common to all three acetolyses, and this is best represented[3,11] as a vinylcyclopropylcarbinyl ion (**7** and **8**). The ion not only accounts for the product mixtures from all three tosylates but also for the accelerated kinetics, most dramatic in the case of **3**.[3b] The exact position of the counterion may influence the reactivity of the ion-pair intermediates.

Experimental Section

General. Instruments used were: for nmr, Varian A-60 and T-60 (spectra referred to internal TMS); for ir, Perkin-Elmer Models 700 and 337; for ms, Hitachi RMU-7; for analytical gc, Hewlett-Packard Model 700 (TC detection) equipped with matching 13 ft × ⅛ in. aluminum columns packed with 18% DC Silicon Oil 550 on 80–100 Chromosorb W, AW-DMCS. The acetolysis products were separated under the following conditions: injection port 130°, helium flow rate 30 cc/min, initial column temperature 30° (4 min) then programmed to 150°, 0.5°/min. Melting points (oil bath) and boiling points are uncorrected. Elemental analyses were performed by Chemalytics, Tempe, Ariz.

2-Methylcyclopropyl methyl ketone was prepared by the published route,[15] bp 62° (80 mm) [lit.[15] 66° (91 mm)]. Glc of this product on squalene, didecyl phthalate, and TCEP columns showed two isomers in the ratio 95:5. Spectral data: pmr[23a] τ 7.87 (S, 3 H), 8.4 (M, 1 H), 8.8 (M, 5 H), 9.4 (M, 1 H); ir[23a] 2960 (C–H), 1710 cm^{-1} (C=O). A 2,4-DNP derivative of the ketone had mp 100° (lit.[16] for the trans ketone, 95°).

2-Methylcyclopropyl Methyl Ketone Hydrazone. A solution of 15.0 g (0.154 mol) of the ketone, 30.4 g (0.604 mol) of hydrazine hydrate, and ~20 ml of ethanol was stirred 19 hr at ambient temperature. The reaction mixture was poured into 40 ml of saturated aqueous sodium chloride (hereafter brine) and extracted with a total of 100 ml of ether. The ether solution was washed with 40 ml of brine and dried over anhydrous magnesium sulfate. Removal of solvent and residual ethanol yielded 12.2 g (71%) of the crude hydrazone as a clear colorless liquid. Spectral data was: pmr[23a] τ 8.20 (S, 3 H), 8.47 (S, 2 H), 8.9 (M, 6 H), 9.5 (M, 1 H); ir[23a] 3400 (N–H), 2950 (C–H), 1625 cm^{-1} (C=N).

1-(2-Methylcyclopropyl)-1-iodoethylene was prepared using the general procedure of Barton, *et al.*[24] In a 500-ml flask, 8.10 g (0.072 mol) of the crude hydrazone and 80 ml of triethylamine were dissolved in 200 ml of tetrahydrofuran (THF). While this solution was stirred in an ice bath, a solution of 35.0 g (0.14 mol) of iodine in 130 ml of THF was added dropwise until a red color persisted. Sodium thiosulfate (0.5 g in 100 ml water) was added and then the reaction mixture was poured into 1000 ml of ice water. This was extracted with a total of 160 ml of pentane. The combined pentane solutions were washed with 500 ml of ice water, two 80-ml portions of 1 *N* HCl, 250 ml of saturated aqueous sodium bicarbonate, and 250 ml of water. Removal of the pentane solvent at 1 atm, then bulb-to-bulb distillation of the residue at 2 mm yielded 3.4 g (23%) of the vinyl iodide as a clear colorless liquid (~10% ketone). Spectral data: pmr[23a] τ 4.04 (perturbed d, J = 1 Hz, 1 H), 4.39 (perturbed d, J = 1 Hz, 1 H),[25] 8.6–9.2 (broad m containing d, J = 2, Hz, 6 H), 9.2–9.6 (M, 1 H); ir[23a] 1650 (C=C–I), 3090 and 3030 cm^{-1} (C=C–H and cyclopropyl C–H).

1-(2-Methylcyclopropyl)-1-tosyloxyethylene (2). A solution of 14.0 g (50 mmol) silver tosylate in 125 ml of dry acetonitrile was filtered to remove a slight amount of insoluble material (Ag_2O) and was cooled to 0° in a nitrogen-purged 250-ml flask with drying tube attached. To this, 11 g (50 mmol) of the vinyl iodide (containing ~10% of the ketone) was added at once together with 1 g of sodium bicarbonate. The mixture was stirred at 0° for 10 hr and filtered and 1 g of sodium bicarbonate added to the filtrate, which was then stirred for an additional hour. No more precipitation of silver iodide was observed; lithium bromide (1.0 g) was added and the reaction mixture shaken well, causing precipitation of some unreacted silver ion. The solution was filtered and the solvent evaporated at ambient temperature (20 mm) to a volume of 15 ml. This was diluted to a volume of 50 ml using dry chloroform. There was immediate precipitation of additional silver salt. The solution was filtered, washed with 50 ml of water, and dried over magnesium sulfate. Removal of solvent at ambient temperature (1 mm) yielded 7.2 g (57%) of the vinyl tosylate as a light yellow oil. Tlc (silica gel, two elutions with benzene) indicated the presence of **5** (R_f 0.22) and **1** (R_f 0.38) as well as **2** (R_f 0.46). The amount of **5** could be estimated at ~2–3% from the tlc, but a more accurate measurement of the amount of **1** was needed for acetolysis data. A Beer's law study was undertaken using the 1950 cm^{-1} allenic stretching band in the ir spectrum of **1**. From the intensity of this peak in the ir spectrum of **2**, it was determined that **1** constituted 13% of the oil used in most of the preparative acetolysis studies, with corrections made for the presence of **1**. Column chromatography with silica gel or alumina did not provide an adequate separation of **2** from its impurities but in fact caused rearrangements to **1** and **5** (*vide infra*). The vinyl tosylate could be best separated from its impurities by preparative tlc. A 20 × 20 cm plate with a 2-mm coating of silica gel (Brinkman P-254 and 366) was spotted with 100 mg of **2** and eluted twice with benzene. Recovery of the proper fraction yielded 70 mg of a very light yellow oil which was >95% **2** with ~4% ditosylate **5**. This material was used for kinetic runs. If kept away from moisture, the vinyl tosylate was stable for several days at ambient temperature. Any contact with moist air caused decomposition and rearrangement to **1** and **5** within several hours. Spectral data: pmr[23b] τ 2.23 (perturbed d, J = 8 Hz, 2 H), 2.67 (perturbed d, J = 8 Hz, 2 H), 5.38 (d, J = 2.2 Hz, 1 H), 5.50 (d, J = 2.2 Hz, 1 H),[25] 7.57 (S, 3 H), 8.5–9.3 (broad m containing d, 6 H), 9.3–9.6 (M, 1 H); ir[23b] 3080 (C=CH), 2950 (-CH), 1650 (C=CO), 1605 cm^{-1} (aromatic C=C); mass spec M$^+$ (70 eV), *m/e* 252.

Anal.[26] Calcd for $C_{13}H_{16}O_3S$: C, 61.89; H, 6.39. Found: C, 61.03; H, 6.22.

Identification of Ditosylate 5. When the reaction described above between silver tosylate and the vinyl iodide was carried out at ambient temperature without addition of sodium bicarbonate, 7.5 g (59% yield) of a brown oil was obtained. Tlc of the oil showed three components, the largest of which crystallized upon addition of a small amount of anhydrous ether. The other two components were found to be **2** and **1**. The brown crystals were recrystallized from ether–pentane, but a wide melting point indicated the compound was not pure. A 10-g silica gel column was prepared, and 0.5 g of the crystals was eluted through the column with carbon tetrachloride. The white crystals so obtained were recrystallized from ether–pentane until a sharp melting point (66–67°) was attained. Compound **5** was identified as the ditosylate by the spectral data: pmr[23b] τ 2.15 (perturbed d, J = 8 Hz, 4 H), 2.61 (perturbed d, J = 8 Hz, 4 H), 5.1 (M, 1 H), 5.5 (M, 1 H), 7.55 (S, 6 H), 7.8 (M, 2 H), 8.24 (broad S, 3 H), 8.82 (d, J = 6 Hz, 3 H); ir[23b] 1695 cm^{-1} (C=CO), 1605 (aromatic C=C); mass spec M$^+$ (70 eV), *m/e* 424.

Anal. Calcd for $C_{20}H_{24}O_6S_2$: C, 56.58; H, 5.70. Found: C, 56.63; H, 5.59.

Identification of Rearranged Tosylate from Preparation of 2 as 1. A 10 g silica gel column was prepared and a solution of 0.5 g of vinyl tosylate **2** in minimal carbon tetrachloride (CCl_4) was eluted

through the column using CCl_4 as eluent. Noticeable decomposition of material occurred on the column during elution.[27] Only one fraction was collected, and tlc indicated that the fraction was a mixture of the rearranged tosylate and ditosylate **5.** The ditosylate was separated from the rearranged tosylate by recrystallization from CCl_4–pentane. The rearranged tosylate was recovered by evaporation of recrystallization solvent and identified as **1** by its pmr and ir spectra, which were identical with those reported for 4,5-hexadien-2-yl tosylate.[3a]

Preparative Acetolyses and Product Determinations. Exactly the same procedure was used in the cases of **1, 2,** and **3.** The tosylate (630 mg, 2.5 mmol) was dissolved in enough acetolysis solvent (dry acetic acid containing 0.11 *M* sodium acetate and 1% acetic anhydride)[3] to make 25.00 ml. The solution was shaken vigorously then divided into four equal volumes which were sealed in ampoules. These were placed in an oil bath thermostated to 85.0 ± 0.05°. After the appropriate interval, two ampoules were removed and separately processed as follows. After quenching the tube in ice-water, its contents were poured onto 6.0 g of ice-water slurry in a 30-ml separatory funnel. Once the ice had melted, the solution was extracted with 4 × 1.5 ml of ether–pentane (1:1 v/v).[28] The combined organic extracts were washed once with 2.0 ml of 5% (w/w) aqueous sodium bicarbonate then dried over molecular sieve at −10°. The two solutions were then each analyzed three times, and the results were averaged yielding the data in Table II. It should be noted that, although the silicon oil column provided better separation of the *ca.* 16 components than any of the 12 other liquid phases investigated, some of the components were not well resolved from their neighbors. As a result, to obtain precise (reproducible) percentages, a Du Pont analog curve resolving computer was used to measure the relative areas of incompletely separated peak. This data, in combination with disk integration, provided the precisions given in Table II.

To confirm product identities,[3] the produced mixture was subjected to gc–mass spec. All assignments were fully corroborated.[29] During the analysis, it was discovered that **2** yielded minor amounts of *ca.* five "products" of higher retention time than the products from **1** or **3.** These were subsequently found by mass spec to have molecular weight (246) indicative of dimers of $H_3CC_6H_4S$, and they are not included in Table II. No diacetates (*m/e* 200) were detected among these later eluting products.

Test for Return of 2. A sample of 0.097 g (0.38 mmol) of tlc-purified **2** was dissolved in 5 ml of acetolysis solvent (*vide infra*) and heated at 85° for 7100 sec (~1 $\tau_{1/2}$). Work-up as usual (*vide supra*) and removal of all volatile material at 0.2 mm yielded a slightly yellow oil whose pmr spectrum was identical with that of the starting material. Also the ir displayed no absorption at 1950 cm^{-1} indicating the absence of **1** (<1%), and tlc showed only one spot.

Kinetic Determinations. Conductance measurements were taken with an M-D Mini-Cell,[13] attached by shielded cables to a Beckman RC-18 conductivity bridge and immersed in a nonconducting oil bath with temperature regulation of ±0.01°. All manipulation of the cell outside the bath were carried out in a moisture- and oxygen-free glove box. The cell was conditioned as previously described.[13]

The solvent for kinetics determinations was prepared by dissolving 29.4 mg of potassium acetate in 250 ml of freshly distilled glacial acetic acid containing 1% (v/v) acetic anhydride. This provided a solution 1.2×10^{-3} *M* in acetate ion. In a given run, *ca.* 6 mg of the tosylate (25 μmol) was dissolved in enough of the above solvent to bring the volume to 25.00 ml. After conditioning with the solution, the cell was charged with 3.0 ml of the solution. The cell was then placed in the bath and agitated at *ca.* 80 cycles/min. After 3 min required for thermal equilibration, the first reading was taken and the clock started. The conductance decreased with time as acetate ion was consumed. Between 80 and 100 data points were collected over 3 half-lives. Infinity and drift values were taken as previously described.[13]

The experimental data were analyzed in a first-order fashion and reduced to the usual form

$$\ln\left[\frac{L_\infty - L_0}{L_\infty - L_t}\right] = \ln\left(\frac{[\mathrm{HOTs}]_\infty - [\mathrm{HOTs}]_0}{[\mathrm{HOTs}]_\infty - [\mathrm{HOTs}]_t}\right)$$

L = specific conductance

This was done with a Fortran IV program[30] run on an IBM 370-168 computer. Sample graphical output from this program is shown in Figure 3. For compounds **1** and **3,** their nonlinear acetolyses were analyzed as described in the text.

Acknowledgment. This work was supported by a Frederick Gardner Cottrell Grant from Research Corporation. T.V.L. expresses his gratitude for a NDEA Fellowship.

References and Notes

(1) The results are taken from the Ph.D. thesis of T.V.L., University of Cincinnati, 1974. They were presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, Abstract ORGN-122.

(2) (a) M. Hanack and J. Haffner, *Tetrahedron Lett.*, 2191 (1964); (b) M. Santelli and M. Bertrand, *Tetrahedron,* **30,** 227, 235, 243, 251, 257 (1974), and earlier papers in the series; (c) R. Garry and R. Vessiere, *Bull. Soc. Chem. Fr.,* 1542 (1968); (d) R. S. Bly and S. U. Koock, *J. Amer. Chem. Soc.,* **91,** 3292, 3299 (1969).

(3) (a) T. L. Jacobs and R. S. Macomber, *J. Amer. Chem. Soc.,* **91,** 4824 (1969); (b) R. S. Macomber, *ibid.,* **92,** 7101 (1970).

(4) This system has also been investigated by Santelli and Bertrand,[2b] but they do not report any unexceptional kinetic behavior; see note 5 of ref 3b. Their product studies have generally been carried out in aqueous solvents and, while similar, they were not identical with our results with dry acetic acid containing sodium acetate.

(5) Throughout this work, the usual assumption has been made that two independent solvolytic pathways compete: the k_s (solvent assisted) pathway[6] and the k_Δ (intramolecularly assisted) pathway. If the acetolysis rate constant for a given allenic compound significantly exceeds that of its saturated counterpart, the difference has been attributed to the operation of the k_Δ mechanism. Further it has been assumed that, product instabilities notwithstanding, the k_s pathway can lead only to unrearranged products (including derived elimination products), while the k_Δ process can yield rearranged and/or unrearranged products, depending on the relative energies of the transition states leading to them.

(6) Such kinetic dissections and rate–product correlations are, of course, common. See, for example, D. J. Raber, J. M. Harris, and P. R. Schleyer, *J. Amer. Chem. Soc.,* **93,** 4829 (1971), and references therein.

(7) There is some evidence [V. J. Shiner and W. Dowd, *J. Amer. Chem. Soc.,* **91,** 6528, 7748 (1969); W. M. Schubert and P. H. LeFevre, *ibid.,* **94,** 1639 (1972)] that accelerated reaction rates due to neighboring-group participation (NGP) can be explained in two fundamentally different ways. They may be due to anchimeric assistance, involvement of the internal nucleophile *during* ionization thereby lowering its transition-state energy, or they may be due to more effective partitioning of the ion (pair) *after* it has been formed. This view has recently been questioned by Schleyer, *et al., ibid.,* **96,** 1970 (1974). To our way of thinking,[3b] the term NGP covers both categories, for the neighboring group *is* involved in both, regardless of the exact stage of the reaction.

(8) See R. S. Macomber, Ph.D. Thesis, University of California at Los Angeles, 1968, Figure II-A, p 28; *Diss. Abstr.,* **29,** 4101B (1969).

(9) The mathematical details of such return rearrangement during solvolysis can be found in R. S. Macomber, *J. Org. Chem.,* **36,** 2182 (1971); **38,** 2568 (1973).

(10) For example, see Figure 1, ref 3b.

(11) (a) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.,* **93,** 1941, 1953 (1971); (b) S. A. Sherrod and R. G. Bergman, *ibid.,* **93,** 1925 (1971).

(12) This program, written in Fortran IV, iteratively minimizes the sum of squares of the differences between experimental values of $\ln\{[\mathrm{HOTs}]_\infty/([\mathrm{HOTs}]_\infty - [\mathrm{HOTs}]_t)\}$ and values calculated from eq 1. The computational method has been described by K. J. Johnson, "Numerical Methods in Chemistry," University of Pittsburgh Press, Pittsburgh, Pa., 1971. A listing of the program, which will be supplied upon request, appears in the Ph.D. thesis of T.V.L., University of Cincinnati, 1974.

(13) R. N. McDonald and G. E. Davis, *J. Org. Chem.,* **38,** 138 (1973).

(14) For an excellent review on the subject of vinyl cations, including the preparation of their precursors, see P. J. Stang, *Progr. Phys. Org. Chem.,* **10,** 276 (1973).

(15) The steps leading to the cyclopropyl ketone have been previously described: S. W. Cannon, A. A. Santelli, and P. Sheenian, *J. Amer. Chem. Soc.,* **81,** 1660 (1959).

(16) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.,* **89,** 1404 (1967).

(17) The presence of **1** in the rearranged tosylate from **3** escaped our detection earlier.[3b]

(18) The products were identified by comparison with earlier results,[3] and checked by gc–mass spec. In the case of **2,** but not **1** or **3,** several higher molecular-weight "products" were observed and found to be tolylsulfur compounds and are not included in the tabulation. See Experimental Section.

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

(20) The relevant activation equations are $d \ln k/d(1/T) \equiv -E_a/R$, $\Delta H^\ddagger = E_a - RT$, $\Delta G^\ddagger = -RT \ln (kh/kT)$, $\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T$.

(21) Over the recent past, several workers have invoked counterion position control of solvolytic reactions; see, for example, C. J. Collins, *et al., J. Amer. Chem. Soc.,* **94,** 899 (1972); W. L. Dilling and J. A. Alford, *ibid.,* **96,** 3615 (1974). NOTE ADDED IN PROOF: Stereochemical evidence supporting the involvement of ion pairs in solvolyses of vinyl triflates has recently been described: T. C. Clark and R. G. Bergman, *ibid.,* **96,** 7934 (1974), and references therein.

(22) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, **76**, 2597 (1954).
(23) (a) Carbon tetrachloride solution; (b) deuteriochloroform for pmr, chloroform for ir.
(24) D. H. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).
(25) These two absorptions actually constitute a AB pattern.
(26) Analysis believed to be low due to presence of ~4% **5**.
(27) The vinyl tosylate was found to decompose and rearrange whenever eluted through a silica gel column, the extent of which depended on the eluent and time spent on the column. The rearrangement yielded varying amounts of **1** and **5**.
(28) Pentane alone had been used previously.[3] Since there was some indication[11] that cyclopropyl ketones were not effectively measured under the previous conditions, it was hoped that the ether would be more effective. Since the present results agree quite well with the previous ones,[3] we conclude indeed that our percentages of ketones are accurate as well as precise.
(29) The identification of the first component as *cis*-acetylene and the second component as *trans*-acetylene as reported in ref 3 is now believed to have been in error. We have found that treatment of 90% *trans*-1-(2-methylcyclopropyl)-1-iodoethylene yields 90% of this first component acetylene. This would indicate that the first component acetylene should be trans and not cis, as reported previously.
(30) A listing of this program, which will be supplied on request, appears in the Ph.D. thesis of T.V.L., University of Cincinnati, 1974.

Stable Carbocations. CLXXX.[1] ^{13}C and ^{1}H Nuclear Magnetic Resonance Spectroscopic Study of Phenyl-, Methyl-, and Cyclopropyl-Substituted Alkenyl (Allyl) Cations. Further Studies of the Trend of Charge Distribution and the Relative Delocalization Afforded by Phenyl, Methyl, and Cyclopropyl Groups

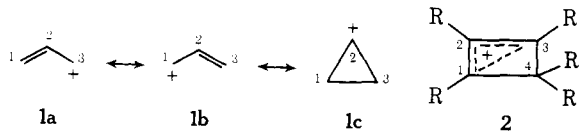
George A. Olah* and Robert J. Spear[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received August 30, 1974*

Abstract: Two series of methyl-, cyclopropyl-, and phenyl-substituted alkenyl (allyl) cations have been studied by ^{13}C NMR and ^{1}H NMR spectroscopy under stable-ion conditions. The 1,3-substituted alkenyl cations (**3a–f**) exclusively adopt the trans,trans conformation and exhibit strong charge delocalization between C_1 and C_3, whereas the charge in the 1,1-substituted alkenyl cations (**4a, 4b,** and **4d–f**) is substantially higher at C_1, the tertiary carbon. 1,3 overlap does not appear to contribute significantly to the total ion structure. In **3a–f,** the relative charge delocalization afforded by the substituents is cPr $\gtrsim$ Ph $\gg$ CH_3. It is suggested that the steric crowding inherent in tertiary carbenium ions and the subsequent disruption of resonance stabilization may lead to a different relative order for change delocalization in tertiary carbenium ions. A neighboring-group deshielding of carbenium ion centers by cyclopropyl groups was detected in addition to the normal α-substituent effect and opposing the shielding from charge delocalization, and this must be taken into consideration when comparing charge delocalization trends in carbocations.

Alkenyl cations (often called allyl cations) are the simplest conjugatively stabilized carbocations and have been the subject of many theoretical and experimental studies. The generation of alkenyl cations under stable-ion conditions can be achieved by a wide range of experimental procedures, including ionization of allylic alcohols and halides, ionization of cyclopropyl halides and alcohols, and hydride abstraction from alkenes. The earlier literature (to late 1965) on alkenyl cations generated under stable-ion conditions has been reviewed by Deno.[3]

The distribution of charge in alkenyl cations has been a subject of some controversy, particularly regarding the importance of 1,3 overlap (**1c**) relative to the two classical resonance structures **1a** and **1b**.[4,5] Recent molecular-orbital calculations have suggested that 1,3 overlap is not significant for acyclic alkenyl cations.[6] There is convincing experimental evidence that cyclobutenyl cations (**2**), where the



1a **1b** **1c** **2**

proximity of C_1 and C_3 permits greater overlap between the π orbitals on these carbon atoms, have strong 1,3 overlap.[4] Our recent observation of the parent cyclobutenyl cation (**2**, R = H) indicates very strong 1,3 overlap in this species resulting in comparable charge density at C_1, C_2, and C_3 and thus the truly "homocyclopropenyl cation" nature of this ion.[7] The charge distribution will clearly be dependent upon the substituents at C_1, C_2, and C_3, and the relative delocalization afforded by the substituents should give additional insight into charge distributions in these systems.

The factors which affect carbon-13 chemical shifts are currently being critically examined in many laboratories, including ours, and at the present time, it appears that although carbon-13 chemical shifts cannot be directly equated with charge densities, they do reflect the trend of charge densities at carbon atoms of similar hybridization and substitution.[1,8] Proton chemical shifts, which indirectly reflect the charge density at the carbon to which the proton is attached, are useful indications of charge distribution in carbocations, but the dependence of ^{1}H NMR shifts on a number of additional factors which are of comparable magnitude to the charge dependence can lead only to qualitative results. Although these same additional factors affect ^{13}C NMR shifts, they are of small magnitude relative to the total chemical shifts involved. Carbon chemical shifts therefore appear to be the most reliable tool for studies of charge distribution in carbocations.

Although the ^{1}H NMR spectra of a large number of alkenyl[3,9,10] and cycloalkenyl[3,4a,5,10] cations have been re-