Solvents of Low Nucleophilicity. XII. Triple-Bond Participation in the Acetolysis, Formolysis, and Trifluoroacetolysis of 6-Heptyn-2-yl Tosylate and 6-Octyn-2-yl Tosylate[1]

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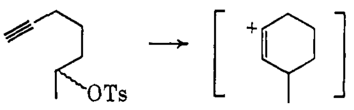
Abstract: 6-Heptyn-2-yl tosylate and 6-octyn-2-yl tosylate were prepared and solvolyzed. Analysis of the reaction rates and of the products agreed in showing that triple-bond participation occurred in competition with normal solvolysis, and that the proportion of reaction occurring *via* a participation path increased as the solvent was varied in the sequence acetic acid, formic acid, and trifluoroacetic acid. 6-Octyn-2-yl tosylate did *not* exhibit an extremely strong tendency to solvolyze *via* a linear vinyl cationic transition state or intermediate (in which the cationic carbon is exocyclic to a five-membered ring) in competition with reaction *via* a bent cation (in which the cationic carbon is part of a six-membered ring). Accordingly the transition state for solvolysis does not resemble a vinyl cation but instead may resemble a bridged ion. The results of the trifluoroacetolysis of 6-hepten-2-yl tosylate indicated that triple-bond participation occurred somewhat more readily than double-bond participation.

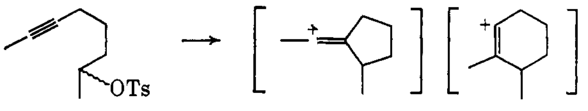
Double-bond participation has been extensively studied in the development of modern carbonium ion chemistry, homoallylic participation having received particular emphasis. The cholesteryl and norbornenyl systems are classic examples.[2] Participation of more remote double bonds also has received attenuation. The studies of 5-hexen-1-yl nosylate[3] are relevant to the present study, as are subsequent papers from Johnson's group.[4]

Triple-bond participation was, in contrast, reported only recently in papers by Hanack and coworkers in which "homopropargyl" participation in the solvolysis of 3-pentyn-1-yl nosylate was studied,[5] and in our preliminary communication in which participation of the remote triple bond of 6-heptyn-2-yl tosylate upon trifluoroacetolysis was reported.[6] Participation by the remote triple bond in the acetolysis of 6-phenyl-5-hexyn-1-yl brosylate has also been reported recently.[7]



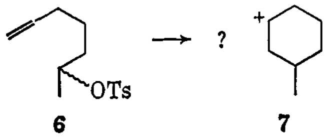
1 2 (1)

In the present full paper we report the solvolysis of 6-heptyn-2-yl tosylate (1) in the solvents acetic acid, formic acid, and trifluoroacetic acid, a sequence of solvents known to exhibit an increasing tendency to promote participation (in the order listed).[8] In these reactions the intermediacy of the secondary vinyl cation 2 may be envisioned (eq 1). Similarly, we have studied the solvolysis of 6-octyn-2-yl tosylate (3). As elaborated in the Discussion section, we were particularly attracted by the idea that hybridization considerations would lead to a strong preference for the formation (eq 2) of a linear, secondary, vinyl cationic intermediate, 4, in which the cationic center is exocyclic to a five-membered ring, as compared to a bent, secondary, vinyl cation, 5 (eq 2), in which the cationic site is incorporated in a six-membered ring. As will be described, our somewhat surprising results have led us to propose substantial modifications of the simple mechanisms of eq 1 and 2.



3 4 5 (2)

In addition to the above-mentioned studies, we carried out the solvolysis of 6-hepten-2-yl tosylate (6) in order to assess the comparative participation tendency of remote double and triple bonds (*cf.* eq 1 and 3).



6 7 (3)

Results

Syntheses and Rates. The desired tosylates, 6-heptyn-2-yl tosylate, 6-octyn-2-yl tosylate, and 6-hepten-2-yl tosylate, were synthesized as described in the Experimental Section and outlined in Scheme I. The rates of solvolyses, given in Table I, were measured as described in the Experimental Section.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(2) (a) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948); (b) J. D. Roberts, W. Bennet, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(3) (a) W. S. Johnson, D. M. Barley, R. A. Bell, and R. Owajang, *J. Am. Chem. Soc.*, **86**, 1959 (1964); (b) P. D. Bartlett, *Ann.*, **653**, 45 (1962); (c) P. D. Bartlett, W. D. Clossen, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965).

(4) W. S. Johnson, M. F. Semmelhack, M. U. S. Sultanbawa, and L. A. Dolak, *ibid.*, **90**, 2996 (1968), and earlier papers.

(5) (a) M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Letters*, 875 (1965); (b) M. Hanack and I. Herterich, *ibid.*, 3847 (1966); (c) M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967).

(6) P. E. Peterson and R. J. Kamat, *J. Am. Chem. Soc.*, **88**, 3152 (1966).

(7) W. D. Closson and S. A. Roman, *Tetrahedron Letters*, 6015 (1966).

(8) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Am. Chem. Soc.*, **89**, 5902 (1967).

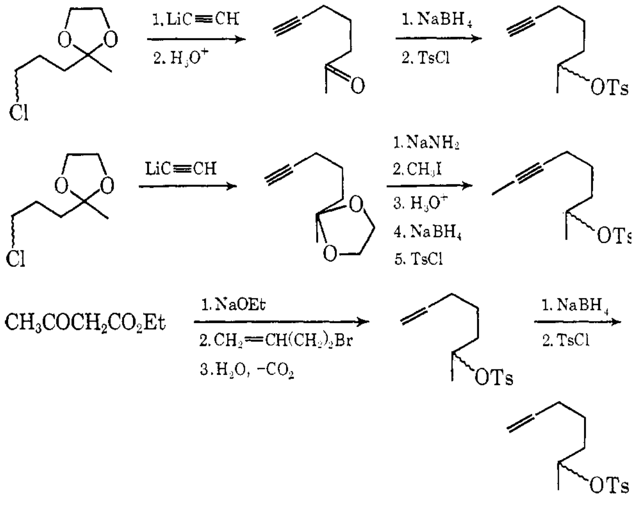
Table I. Rates of Solvolysis of Tosylates

Tosylate	10^5k, sec^{-1} CF_3CO_2H[a]	HCO_2H[b]	CH_3CO_2H[c]
2-Pentyl	19.0[d]	5.35[d]	4.8[e]
6-Heptyn-2-yl	26.6	2.66	3.18
6-Octyn-2-yl	302[f]	9.85	9.71
6-Hepten-2-yl	27.5		

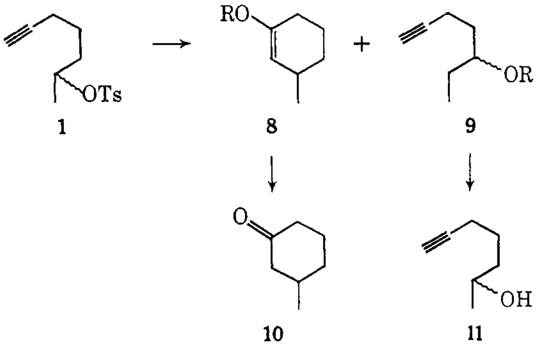
[a] Solvolysis at 25.0 ± 0.05° of a solution 0.05 *M* in tosylate and 0.125 *M* in sodium trifluoroacetate, except as noted. [b] Solvolysis at 25.0° of a solution 0.1 *M* in tosylate and 0.125 *M* in sodium formate. [c] For solvolysis at 70.0° of a solution 0.1 *M* in tosylate and 0.118 *M* in sodium acetate. [d] Data from P. E. Peterson, R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965). [e] Estimated from data in Peterson, *et al.*, footnote *d.* [f] From nmr data; 0.1 *M* tosylate, 0.125 *M* sodium trifluoroacetate, 25 ± 0.5°.

Products. The identification of the somewhat complex mixtures of solvolysis products was facilitated by the fortunate circumstance that cyclized substitution products hydrolyze to ketones whereas the "normal" solvolysis products yield alcohols. The first formed products and the ketones or alcohols obtained from them are shown in Schemes II and III. The formation of the rearranged vinyl tosylates, **12** and **13**, is of particular interest in the solvolysis of 6-octyn-2-yl tosylate. Yields of the various products determined by a combination of gas chromatographic and other procedures are given in Tables II and III.

Scheme I. Synthesis of Tosylates

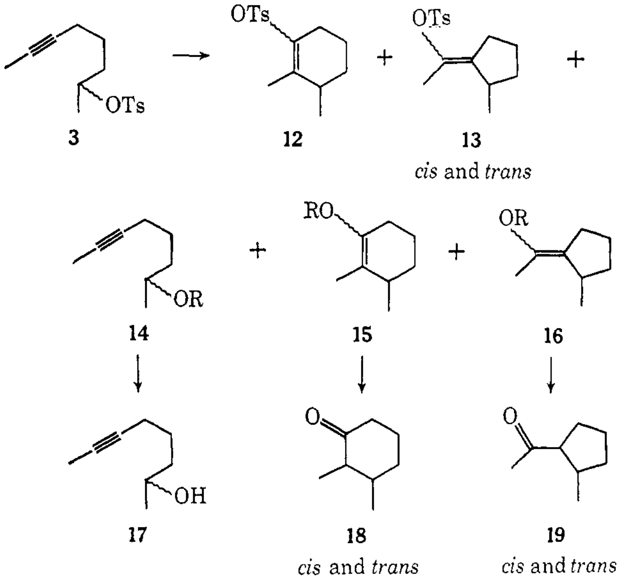


Scheme II. Products Derived from 6-Heptyn-2-yl Tosylate



The use of a basic fore column and a flame detector,[9] described previously, was again extremely advantageous, in that the dilute solution of products obtained in the course of a rate determination could be analyzed by direct injection, obviating problems of selective loss during work-up. In some of the analyses, hydrolysis occurred in the fore column, allowing the direct determination of hydrolysis products to be made.

Scheme III. Products Derived from 6-Octyn-2-yl Tosylate



The vinyl tosylates, **12** and **13**, were analyzed by their reduction with sodium in ammonia to a mixture of

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(9) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

Table II. Solvolysis Products of 6-Heptyn-2-yl Tosylate (*cf.* Scheme II)

Solvent	Ref	Elimination, %[a]	Cyclic 8, %	Cyclic 10, %	Acyclic 9, %	Acyclic 11, %	DNP, %[b]
CF_3CO_2H	*c*	7		91		2	89
	d		88	9	3		
HCO_2H	*c*	22		40	35	3	
	e			49	51		40
CH_3CO_2H	*c*	19	13	14	52	2	
	d		30	2	66	2	
	e			26		74	30

[a] Based on the uncorrected area of early gc peak or peaks. [b] Yield of crude 2,4-dinitrophenylhydrazone obtained from an aliquot. [c] Gas chromatographic analysis of the acid solution from reaction of 0.1 *M* tosylate, 0.125 *M* NaOR. [d] Analysis of the distillate from a preparative solvolysis, no base fore column. [e] Analysis of the hydrolyzed, distilled products.

Table III. Solvolysis Products of 6-Octyn-2-yl Tosylate (*cf.* Scheme III)[a]

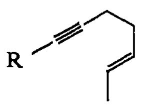
Solvent	Ref	Elimination, %[a]	6-ring 18, %	5-ring 19, %	Acyclic 14, %	Acyclic 17, %
CF_3CO_2H	*b*	0	23	78		
	c		13	87		
	d		8	92		
HCO_2H	*e*	6	28	50	11	5
	f		30	52	11	7
CH_3CO_2H	*e, g*	20	60		20	
	h		36	47	17	

[a] See footnotes, Table II, for procedures. [b] Analysis of volatile products, acid solution, 51% yield, the remaining 49% being vinyl tosylates. [c] Ketones from sodium-ammonia cleavage of vinyl tosylates. [d] Ketones from trifluoroacetolysis of vinyl tosylates. [e] Analysis of acid solution. [f] Analysis of distillate. [g] The 11% of rearranged tosylate was not analyzed. [h] Analysis of hydrolyzed products.

alcohols and ketones, followed by oxidation to the ketones **18** and **19**. Alternatively the vinyl tosylates were converted to ketones by prolonged reaction with trifluoroacetic acid, probably *via* an addition–elimination sequence.[10] The results of the two analyses (footnotes *c* and *d*, Table III) are in fair agreement in indicating the percentage of five-membered ring to be slightly higher (~90%) in the tosylate product than in the trifluoroacetate product (78%).

Discussion

Origin of Products. Before we consider the interpretation of our results in terms of neighboring group participation it is appropriate to examine the possible formation in our solvolyses of secondary reaction products arising by addition of acid solvents to the elimination products **20**, **21**, and **22**, which may be formed from the tosylates **1** and **3**. We presume that cyclized products of elimination, arising *via* participation, are not to be expected, since they would be allenes, or other strained species. The alkene tosylate **6** may be presumed possibly to give cyclic olefinic products in addition to olefins analogous to **20**, **21**, and **22**.



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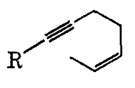

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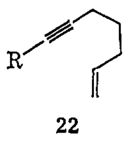

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R = H or CH_3

In several instances the formation of major amounts of secondary reaction products in our solvolyses may be ruled out by consideration of reaction rates, etc. For example, the "methylated" tosylate **3** undergoes trifluoroacetolysis 16 times faster than 2-pentyl tosylate (*cf.* Table I). Since it is clear from this result that neighboring group participation is the only major reaction path, and since this path does not lead to elimination, the observed products may be identified with confidence as the primary solvolysis products. As will be noted later, analysis of rates similarly shows that formolysis of **3** involves predominantly participation. Furthermore addition of formic acid–sodium formate to unbranched alkenes would be so slow[11] as to give minimal amounts of addition products under solvolysis conditions, unless the alkenes (or alkynes) should be unusually reactive owing to neighboring group participation. However the comparison studies available to date indicate that additions to alkenes occur with less neighboring group participation than solvolyses of tosylates.[8] Extraordinary enhancement of reactivity of enynes or dienes is, accordingly, unlikely. We conclude that the above-mentioned formolysis probably is not complicated by the occurrence of secondary addition reactions. A similar conclusion holds with even more certainty for acetolysis of **3**.

Similar considerations, which again make use of the per cent of participation, to be estimated below, indicate that we have observed predominantly the primary products of solvolysis of the "unmethylated" alkyne tosylate, **1**, in each of the three solvents.

In contrast, the trifluoroacetolysis products of 6-hepten-2-yl tosylate (given in the Experimental Section) very possibly do consist in part of the products of secondary addition reactions of trifluoroacetic acid to first formed alkenes. Nevertheless, we shall see that the rates and products both establish that triple-bond participation was more facile than double-bond participation in our study.

Finally, we note that we may rule out important contributions from reaction paths involving addition of trifluoroacetic acid to the triple bonds of our alkyne tosylates, followed by solvolysis with participation of the vinyl trifluoroacetate double bond.[12] Examination of the known rates of addition of trifluoroacetic acid to alkynes containing electronegative substituents showed them to be slower at 60° than the solvolyses at 25° reported here.[13]

Quantitative Assessment of Neighboring Group Participation. The rate constants, k, which we observed may, as is customary,[14] be dissected into the components k_Δ, the rate constant for reaction involving neighboring participation, and k_s, the rate constant for solvolysis without participation. The k_s value is obtained from that of 2-pentyl tosylate, a saturated methylalkylcarbinyl tosylate, by application of a factor which corrects for the inductive effect of the neighboring group. The magnitude of the correction may, in principle, be assessed by application of the Hammett–Taft equation, $\log k_X/k_H = \rho\sigma_I$, where k_X and k_H are rate constants for substituted and unsubstituted compounds, respectively. We note that the k_X values are, by assumption, the desired k_s values, and they are so designated in the following discussion and in the tables.

The required reaction parameters (ρ values) applicable to 5-substituted 2-pentyl tosylate solvolyses in the various solvents are derived from data obtained in the earlier comprehensive study where attenuation plots were used to separate inductive and participation effects of chlorine and fluorine.[8] We start with the ρ_I values derived from rates of 4-chloro-2-butyl tosylate solvolysis,[8] −5.36, −4.49, and −2.71, for the solvents trifluoroacetic acid, formic acid, and acetic acid, respectively.[8] The factors by which these values should be attenuated to give ρ_I values for the 5-substituted 2-pentyl series were reported to be 0.62, 0.56, and 0.35, respectively.[8] (These values were derived from data for solvolyses thought to involve no neighboring group participation.) The resulting ρ_I values, applicable to 5-substituted 2-pentyl tosylates, are given in Table IV, along with the other data to be discussed later.

Table IV. Predicted Inductive Rate Depressions for Alkyne Tosylates

Solvent	ρ_I	"Predicted" k_H/k_s (σ_I = 0.29)	Alternate k_H/k_s (σ_I = 0.22)
CF_3CO_2H	−3.32	9.18	5.38
HCO_2H	−2.51	5.35	3.57
CH_3CO_2H	−0.94	1.87	1.61

The choice of a σ_I value for the groups $CH_3C{\equiv}C$– and $HC{\equiv}C$– (which are presumed to have identical

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[10] P. E. Peterson and J. M. Indelicato, *J. Am. Chem. Soc.*, **90**, 6515 (1968).

[11] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[12] *Cf.* H. R. Ward and D. W. Sherman, Jr., *ibid.*, **89**, 1963 (1967); **90**, 3812 (1968).

[13] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

[14] For another example, see R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

σ_I values) is a source of some difficulty. The σ^* value used by Kreevoy,[15] 1.3, must be attenuated since it is applicable to a triple bond which is one carbon atom closer to the reaction center than are the other substituents listed in commonly used tables of σ_I values.[16,17] But should we again use a solvent-dependent attenuation factor? Here we presume that we should not, since the studies[8] from which ρ values were taken was referenced to standard, tabulated σ_I values. Accordingly we estimate σ_I for the triple bond using an "average" attenuation factor of 0.5 and a conversion factor (σ^* to σ_I) of 0.45, to get $\sigma_I = 0.29$.[18,19] The resulting "predicted" k_H/k_s values are given in Table IV.[19] However, the reliability of the prediction is subjected to some doubt, as a consequence of our observation that substituent effects of *alkyl groups*, containing only carbon and hydrogen, seem to fall off extremely rapidly with distance, leading to special "ρ_I alkyl" values.[8] Might the triple bond, which also contains only carbon and hydrogen, also exhibit only a small substituent effect when it is remote from the reaction site? Information bearing on this point is provided by the inductive rate depression exhibited in the formolysis of 7-nonyn-2-yl tosylate, where the triple bond may be too remote to participate. The observed k_H/k_X value, 1.62,[20] along with the applicable ρ_I value of -1.40, leads to the σ_I value, 0.15, for the triple bond. (Here the ρ_I value has been obtained by regarding 7-octyn-2-yl tosylate as a terminally substituted 2-hexyl tosylate; the previously discussed ρ_I value, -2.51, applicable to substituted 2-pentyl tosylate solvolyses, was attenuated by the factor 0.56.)

For the calculation of estimated values of k_Δ and k_s we have used the value $\sigma_I = 0.22$, the average of the somewhat diverse values obtained by attenuation and by the solvolytic experiment. We may bear in mind, however, that the logarithmic scale of σ_I values leads to substantial variation in calculated k_H/k_s values with modest variations in σ_I. The range of values to be expected is illustrated in the last column of Table IV where k_H/k_s values derived from the σ_I value, 0.22, are listed for comparison with values based on the "predicted" σ_I value of 0.29.

We turn now to a comparison of the various expected k_H/k_s values with the experimentally determined k_H/k_T ratios given in Table V. Here k_H is the rate constant for solvolysis of 2-pentyl tosylate,[21] and k_T (for k_{total}) values are our experimentally determined rate constants. The inclusion of a participation process, not immediately obvious from inspection of "raw" rate constants, is now seen to be probable in the formolysis (and possibly acetolysis) of 6-heptyn-2-yl tosylate.

Table V. Quantities Derived from Rates of Solvolysis; Per Cent Cyclization

Tosylate	Solvent	k_H/k_T	k_Δ/k_s[a]	100· (k_Δ/k_T)	Cyclization, %[b]
6-Heptyn-2-yl	CF_3CO_2H	0.714	6.5	87	91
	HCO_2H	2.01	0.77	44	40
	CH_3CO_2H	1.50	0.073	6.8	27
6-Octyn-2-yl	CF_3CO_2H	0.0629	84	98.8	~100
	HCO_2H	0.543	5.6	85	78
	CH_3CO_2H	0.495	2.3	70	60
6-Hepten-2-yl	CF_3CO_2H	0.691	1.1[c] 2.1[d]		

[a] Based on $\sigma_I = 0.22$. [b] From Tables II and III. Elimination products are presumed to be acyclic (see text). [c] Based on $\sigma_I = 0.05$. [d] Based on $\sigma_I = 0.10$.

Further algebraic manipulation yields quantitative estimates of k_Δ/k_s (Table V) based on the "alternate" k_H/k_s values of Table IV. (The equation $k_\Delta/k_s = \{[(k_H/k_s)/(k_H/k_T)] - 1\}$ has been used.)

Again following the treatment developed particularly by Winstein's group, we recall that the postulate that participation leads to cyclic products, and that normal solvolysis gives acyclic products, leads to an expression for the expected per centcy clization, $100[k_\Delta/(k_\Delta + k_s)]$ (*cf.* ref 14). The last two columns of Table IV give these predicted values of per cent cyclization and the observed values. Good agreement is found, except in the case of the acetolysis data, where the small magnitude of both inductive and participation effects, as well as the use of k_H values which were determined in another laboratory, leads to a relatively large uncertainty in the calculations.

Linear and Bent Vinyl Cations. As mentioned in the introductory section, the cyclic products obtained from solvolysis of 6-octyn-2-yl tosylate (*cf.* Table III) are not exclusively those containing a five-membered ring, which would be derived from the linear vinyl cation, although five-membered rings predominate. Inspection of Table III does suggest that there is a slight trend for five-membered rings to be formed increasingly as the the solvent changes in the sequence acetic acid, formic acid, trifluoroacetic acid. Similarly, rates of reaction (Table I) are only moderately larger (in terms of kilocalories/mole of activation energy) for 6-octyn-2-yl tosylate, which may form a linear secondary vinyl cation (eq 2), compared to those of 6-heptyn-2-yl tosylate, for which formation of the linear cation is excluded (because it would be primary).

These results may be contrasted with a calculated estimate of 77 kcal for the energy difference between a linear and bent vinyl cation! This value represents the energy required to promote "one-third of an electron" from an s to a p orbital.[22] Other factors

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(15) M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1608 (1959).

(16) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964).

(17) Since it is the $\rho\sigma_I$ product which is measured experimentally, attenuation to compensate for varying distance between the substituent and the reaction site may be applied either to ρ or to σ_I. In our papers ρ is attenuated unless the available σ_I value was not scaled to a distance comparable to that at which, to use a specific example, σ_I for Cl is approximately 0.47.

(18) For a brief review of the origin of σ_I and σ^* notations see P. E. Peterson and G. Thompson, *J. Org. Chem.*, **33**, 968 (1968); *cf.* also ref 16.

(19) The estimated k_H/k_s value, 17.5 (instead of 9.18), of our earlier communication was obtained by use of the attenuation factor 0.65 instead of 0.5 to obtain σ_I.

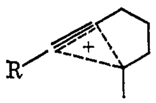
(20) We are indebted to Mr. Manuel Ajo for furnishing this value.

(21) See footnote *d*, Table I.

(22) (a) The cationic carbon of the linear cation forms two bonds involving sp orbitals and one π bond involving a p orbital. The assumption that an average of one electron per bond belongs to the cationic carbon leads us to the conclusion that there are two electrons of 50% or one-half s character each and one pure p electron. The bent cation differs in having two electrons of one-third s character each, and a pure p electron. The s orbital of the bent cation accordingly may be considered to contain two-thirds of an electron, whereas it is considered to contain one electron for the linear cation. Ground-state ionization potentials for carbon 2s and 2p orbitals differ by $21.01 - 11.27 = 9.74$ eV, resulting in the estimated energy difference of 3.25 eV (77 kcal) for the two cations (*cf.* ref 22b). A presumably more appropriate value is the even larger energy difference between the "didiπ" and "trtrπ" promotion energies from ref 22b, 4.006 eV. These values

besides hybridization energy may, of course, contribute to the ease of cyclization of the tosylates we studied (steric effects, torsional strain, etc.). Nevertheless hybridization effects are so large that they would be expected to predominate. *The clear conclusion seems to be that the transition states for solvolysis of the tosylates 1 and 3 bear almost no resemblance to linear and bent vinyl cations.*

Under the circumstances, one can almost picture the stampede to suggest a bridged ion transition state or intermediate, **23**, in which the triple bond solvates the developing cationic carbon without bending appreciably even in those instances where a six-membered ring, bent at the presumed cationic carbon, is ultimately formed. We do, in fact, tentatively suggest such a formulation, but we would emphasize that several aspects of our results, described below, are accommodated within the framework of the bridged ion hypothesis only with some modification of our intuitive expectations. If a bridged intermediate is indeed formed in the rate-determining step, it appears remarkable that its seemingly most likely fate, collapse in a product-determining step to a vinyl cationic species, appears to be ruled out by the absence of a strong preference for five-membered ring formation. This observation implies that bond formation to the nucleophile occurs during collapse of any bridged species. One is tempted to postulate a concerted reaction in which the nucleophile enters as the tosylate group leaves. Clearly this concept fails, however, since the formation of rearranged vinyl tosylates would not be explained. The formation of these tosylates in the trifluoroacetolysis and acetolysis of 6-octyn-2-yl tosylate implies that the tosylate anion separates completely from its original site, presumably with Walden inversion at C-2 induced by the solvating triple-bond electrons, wanders a remarkable distance across the "face" of the ion, and finally is selectively taken up as the ion collapses, in competition with the solvent molecules which are present. It seems surprising that, although the relatively modest rate accelerations and the inferred absence of bending in the bridged ion imply that the solvation of the carbonium ion at C-2 by the triple bond is relatively weak (not far advanced toward σ bond formation), the stability conferred by bridging is enough to prevent reaction of solvent molecules at C-2 during the time the tosylate group is moving.[23]



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R = H, CH_3

In summary, hybridization considerations seem to preclude the direct formation of a rearranged vinyl cationic intermediate during triple-bond participation, whereas the ultimate formation of rearranged tosylates **1** and **3** seems to require an intermediate having somewhat unexpected properties. We note, finally, that our study has no direct bearing on the possible existence of bridged σ bond systems which are at the heart of the nonclassical ion controversy.

Double- and Triple-Bond Participation. We turn now, with new perspective, to a comparison of double- and triple-bond participation. Since 6-hepten-2-yl tosylate solvolyzes (Table I) at a rate comparable to that of 6-heptyn-2-yl tosylate, it is clear that participation will again be evident only if we allow for the inductive effect of the double bond. Using the reported[16] σ_I value for the double bond of 0.05 leads to $k_H/k_s = 1.47$ whereas a value of 0.1 leads to 2.15. The later σ_I value was chosen to be half the triple-bond σ_I value. Based on these values and the experimental rate, the k_Δ/k_s values are 1.13 or 2.11. The difficulty of distinguishing the primary solvolysis products has been mentioned. Nevertheless it is a good guess that the 48% of the *cis*- and *trans*-3-methylcyclohexanol products arises predominantly *via* solvolysis with participation and that the 16% of 6-hepten-2-ol, plus some of the 28% of elimination products, arises from normal solvolysis. Comparison of this analysis of data pertaining to rates and products with that pertaining to 6-heptyn-2-yl tosylate leads to the conclusion that the tendency of the triple bond to participate slightly exceeded that of the double bond in our study. The reactivity of double and triple bonds toward the addition of trifluoroacetic acid[13] has likewise been found to be similar although double bonds were found usually to be slightly more reactive in the latter instances. The absence of special constraints on triple-bond participation arising from a preferred linear hybridization of vinyl cations is further emphasized by this experimental comparison with double-bond participation.

Experimental Section

Rates. Rates of trifluoroacetolyses of 6-heptyn-2-yl and 6-octyn-2-yl tosylate were measured by the ultraviolet spectrophotometric method described previously for solvolysis of unsubstituted 2-alkyl tosylates.[21] The rate of trifluoroacetolysis of 6-octyn-2-yl tosylate (0.14 *M* tosylate, 0.15 *M* sodium trifluoroacetate) was followed by nmr as a function of time, by observing the decrease in peak height of the doublet due to the methyl group on the carbon atom bearing the tosyl group. The rate for 6-heptyn-2-yl tosylate also could be followed by observing the decrease in the peak height of the singlet due to the methyl group on the benzene ring of the tosylate since the methyl singlets of alkyl tosylate and of the species presumed to be tosylate anion have different chemical shifts. Acetolyses were followed by the usual method involving perchloric acid in acetic acid as the titrant and brom phenol blue as an indicator. Formolyses were followed by quenching 3-ml aliquots of the solution in 20 ml of glacial acetic acid and titrating with perchloric acid in acetic acid, using brom phenol blue as an indicator. Further details are given in the footnotes of Table I.

Tosylates and Alcohols. Tosylates were prepared from the alcohols by the previously used procedure.[21] The alcohols and intermediates in their preparation and various synthetic reference samples of the products of solvolyses were distilled through spinning-band columns. All compounds gave the expected nmr and

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compare with a value of 28.9 kcal obtained by an extended Hückel molecular orbital calculation for the parent vinyl cation, $H_2C{=}CH^+$ (P. E. Peterson and P. Coffey, unpublished work). (b) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[23] (a) We are indebted to Professor W. D. Closson for a preprint [S. A. Roman and W. D. Closson, *J. Am. Chem. Soc.*, **91**, 1701 (1969)] in which the possibility of forming "hot" cationic intermediates in participation reactions is pointed out, the excitation energy being derived from conversion of a π bond to a σ bond. This concept may help in explaining the lack of selectivity in five- and six-membered ring formation upon collapse of a bridged ion in our reactions. The selective uptake of tosylate anions is conventionally regarded as a characteristic of a relatively stable ion, however. Accordingly, only time can tell whether the hot-ion hypothesis contributes to the understanding of ion-pair rearrangements. Professor Closson has also pointed out that bonds to sp-hybridized carbon have relatively small bending force constants, permitting a modest degree of bending without sacrifice of appreciable energy. For references see (b) L. K. Montgomery and L. Applegate, *J. Am. Chem. Soc.*, **89**, 2952 (1967).

infrared spectra. The purity of the various products was checked by gas chromatographic analyses, using F & M 609 or Hewlett-Packard 5750 instruments. Analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

The Dioxolane of 5-Chloro-2-pentanone. A mixture of 5-chloro-2-pentanone (122 g, 1.02 mol), ethylene glycol (63 g, 1.02 mol), and benzene (200 ml) was refluxed in the presence of *p*-toluenesulfonic acid (100 mg), and the water was separated azeotropically. Neutralization of the acid, followed by distillation, gave the desired product (127 g, 76%, bp 63° (2–3 mm)).

6-Heptyn-2-one. The dioxolane of 5-chloro-2-pentanone (44 g, 0.268 mol) was allowed to react with a slurry of lithium acetylide ethylenediamine complex (24.6 g, 0.268 mol) in dried (calcium hydride) dimethyl sulfoxide (100 ml) under constant stirring at 0–10°, over a period of 40 min. (A longer reaction time reduces the yield.) The unreacted lithium acetylide was decomposed by hydrochloric acid (6 *M*), and the reaction mixture was diluted with an excess of water (200 ml). After the usual work-up, distillation gave the desired product, 13 g, 44%, bp 88° (40–41 mm) (lit.[24] 82–85° (41 mm); 2,4-dinitrophenylhydrazone, mp 115° (lit.[24] 118–119°).

6-Heptyn-2-ol. 6-Heptyn-2-one (11.0 g, 0.1 mol) was reduced with sodium borohydride (1.57 g, 0.042 mol) in an alkaline methanolic solution to give 6-heptyn-2-ol (7.64 g, 67%, bp 75–77° (12 mm)).

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 74.97; H, 10.88.

6-Heptyn-2-yl Acetate. 6-Heptyn-2-ol (500 mg, 4.5 mmol) was esterified to give 6-heptyn-2-yl acetate (440 mg, 64%) using acetic anhydride (766 mg, 8.92 mmol).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.30; H, 9.28.

6-Heptyn-2-yl Formate. 6-Heptyn-2-ol (500 mg, 4.5 mmol) was heated (oil bath temperature, 60–70°) with formic acid (10.3 g, 22.3 mmol) for 4 hr. Ether extraction, followed by distillation, gave 6-heptyn-2-yl formate (280 mg, 44%).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.65; H, 8.63. Found: C, 68.65; H, 8.80.

6-Octyn-2-one. The reaction of the dioxolane of 5-chloro-2-pentanone (45.7 g, 0.278 mol) with lithium acetylide ethylenediamine complex (26.0 g, 0.278 mol) in dimethyl sulfoxide at 0–10°, followed by the decomposition of the unreacted lithium acetylide with an ice–water mixture, usual work-up, and distillation, gave the dioxolane of 6-heptyn-2-one (22.1 g, 51%), bp 71° (5 mm).

The dioxolane of 6-heptyn-2-one (22.1 g, 0.143 mol) was alkylated with methyl iodide (22.8 g, 0.16 mol) in liquid ammonia in the presence of sodium amide, prepared from 3.3 g of sodium, as described in the literature.[25] The reaction mixture, after ammonia had been removed, was acidified with hydrochloric acid (6 *M*) and stirred at room temperature to hydrolyze the ketal. Ether extraction followed by distillation gave the desired ketone (9.4 g, 53%), bp 75° (4.5 mm).

Anal. Calcd for $C_8H_{12}O_2$: C, 77.42; H, 9.72. Found: C, 77.24; H, 9.72.

6-Octyn-2-ol. Reduction of 6-octyn-2-one (6.19 g, 4.9 mmol) with sodium borohydride (790 mg, 2.8 mmol) gave 6-octyn-2-ol (4.76 g, 76%), bp 92° (10–11 mm).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.90; H, 10.79.

6-Octyn-2-yl Acetate. The preparation on a microscale from 6-octyn-2-ol was similar to that of 6-heptyn-2-yl acetate.

6-Octyn-2-yl Formate. The preparation from 6-octyn-2-ol was similar to that of 6-heptyn-2-yl formate.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.12; H, 9.24. Found: C, 69.98; H, 9.24.

4-Chloro-1-pentyl Acetate. Tetrahydro-2-methylfuran was allowed to react with acetyl chloride as described briefly in the literature[26] to give 4-chloro-1-pentyl acetate. To an ice-cooled stirred mixture of powdered, anhydrous aluminum chloride (77.5 g, 0.6 mol), acetyl chloride (280 g, 3.3 mol), and petroleum ether (bp 30–60°, 500 ml), placed in a three-necked flask, tetrahydro-2-methylfuran (258 g, 3.0 mol) was added dropwise, over a period of 6 hr; the reaction mixture was brought to room temperature and was poured on crushed ice. Ether extraction, followed by distillation, gave the desired product (237 g, 48%), bp 76–77° (8 mm), which contained a few per cent (less than 5) of 5-chloro-2-pentyl acetate.

4-Chloro-1-pentanol. 4-Chloro-1-pentyl acetate (57.6 g, 0.35 mol) was refluxed with methanol (140 ml) and hydrochloric acid (35 ml) for 1 hr (a longer reflux reduces the yield) to give 4-chloro-1-pentanol (33.8 g, 79%), bp 66–67° (11 mm) (lit.[26] 77–79° (11 mm)).

1-Bromo-4-chloropentane. From the reaction,[27] at room temperature (5 hr), of 4-chloro-1-pentanol (57.0 g, 0.46 mol) with phosphorus tribromide (50.5 g, 0.187 mol) there was obtained 1-bromo-4-chloropentane (62.0 g, 71%), bp 68–70° (10–11 mm).

Anal. Calcd for $C_5H_{10}BrCl$: C, 33.23; H, 5.56. Found: C, 33.23; H, 5.39.

1-Acetyl-1-carbethoxy-2-methylcyclopentane. From alkylation[28] of ethyl acetoacetate (15.0 g, 0.115 mol) with 1-bromo-4-chloropentane (20.0 g, 0.107 mol) in the presence of 1 equiv of sodium ethoxide in absolute ethanol, there was obtained the desired cyclic product (9.0 g, 46%), bp 67° (1.7–2 mm). (One equivalent of sodium ethoxide was used because cyclization was not anticipated.)

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.66; H, 9.09. Found: C, 66.66; H, 9.14.

1-Acetyl-2-methylcyclopentane. 1-Acetyl-1-carbethoxy-2-methylcyclopentane (8.66 g, 0.0437 mol) was refluxed with sodium hydroxide (1.75 g, 0.0437 mol) in ethylene glycol and water for 3 days. The reaction mixture was then acidified with hydrochloric acid and refluxed for 1 hr. After the usual work-up, distillation gave 1-acetyl-2-methylcyclopentane (2.8 g, 51%), bp 64° (15–17 mm), from which the presumed *trans*-2,4-dinitrophenylhydrazone, mp 109° (lit.[29] 106°), was obtained. A gas chromatographic analysis on 10% 1,2,3-tris-2-cyanoethoxypropane and Carbowax 20M columns at 125° showed an impurity (3.6%), which was ascribed to the *cis* isomer.

Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.18. Found: C, 76.21; H, 11.30.

Anal. Calcd for $C_{14}H_{18}N_4O_4$: C, 54.90; H, 5.88; N, 18.30. Found: C, 54.70; H, 5.91; N, 18.25.

2,3-Dimethylcyclohexanone. An isomeric mixture of 2,3-dimethylcyclohexanol[30] (6.65 g, 0.052 mol) was oxidized in the presence of ether with chromic acid, made from $Na_2Cr_2O_7 \cdot 2H_2O$ (5.3 g, 0.0178 mol), 98% sulfuric acid (6.97 g, 0.071 mol), and water (15 ml), according to the procedure reported by Brown and Garg,[31] to give an isomeric mixture of 2,3-dimethylcyclohexanone (4.0 g, 61%), bp 58° (8 mm) (75% *cis*, 25% *trans*);[32] *trans*-2,4-dinitrophenylhydrazone, mp 149.8°. Attempts to collect the *cis* isomer gave material containing some *trans* isomer, probably arising from epimerization.

Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.18. Found: C, 76.15; H, 11.13.

Anal. Calcd for $C_{14}H_{18}N_4O_4$: C, 54.90; H, 5.88; N, 18.30. Found: C, 54.70; H, 5.90; N, 18.20.

3-Carbethoxy-6-hepten-2-one. An alkylation of ethyl acetoacetate (48.0 g, 0.370 mol) with 4-bromo-1-butene (50.0 g, 0.370 mol) in the presence of sodium ethoxide, made from metallic sodium (8.50 g) and absolute ethanol (100 ml), gave 3-carbethoxy-6-hepten-2-one (39.0 g, 57%), 180–181° (10 mm) (lit.[27b] 103–105° (10 mm)).

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(25) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

(26) C. S. Kadyrov and J. P. Tsukeranif, *Chem. Abstr.*, **56**, 4602 (1962).

(27) (a) Mov'Gol, *Zh. Obshch. Khim.*, **22**, 2132 (1952); (b) G. Allen, Ph.D. Thesis, St. Louis University, 1963.

(28) For the general procedure see C. S. Marvel and F. D. Hager, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1944, p 248.

(29) P. F. Casals, *Bull. Soc. Chim. France*, 261 (1963).

(30) Obtained from rhodium-catalyzed hydrogenation of 2,3-dimethylphenol. We thank Dr. Jordan J. Bloomfield for this sample.

(31) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961).

(32) This assignment is based on the following observations. The gas chromatographic analysis of the resulting ketone showed the isomeric ratio to be (in the order of elution) 25 to 75. The sulfuric acid (96%) treatment of the same ketone for 10 min at room temperature, followed by pentane extraction, washing free of acid, and gas chromatographic analysis of the pentane solution on the 6-ft, 10% 1,2,3-tris-2-cyanoethoxypropane column at 125°, showed the isomer distribution to be reversed to 76 and 24%. The larger peak having a shorter gas chromatographic retention time is ascribed to the *trans* isomer on the basis that, at equilibrium, the "diequatorial" isomer should predominate. A similar ratio was observed when the ketone, obtained from the oxidation of corresponding alcohol, was analyzed (glpc) using a basic fore section (26% K_2CO_3, 9% Carbowax 20M, and 65% neutral Firebrick) on TCEP column, indicating the isomerization of the ketone by the basic fore column.

6-Hepten-2-one. 3-Carbethoxy-6-hepten-2-one (39.0 g, 0.212 mol) was refluxed with sodium hydroxide (8.4 g, 0.212 mol) in aqueous methanol (90:30) for 6 hr. After the usual work-up and distillation, there was obtained 6-hepten-2-one (18.2 g, 76.4%), bp 76–78° (60 mm) (lit.[27b] 74–75° (55 mm)).

6-Hepten-2-ol. 6-Hepten-2-one (17.0 g, 0.151 mol) was reduced with sodium borohydride (2.38 g, 0.063 mol) to give 6-hepten-2-ol (13.5 g, 78%), bp 89–92° (61 mm).

Anal. Calcd for $C_7H_{14}O$: C, 73.68; H, 12.28. Found: C, 73.74; H, 12.44.

Product Studies. Products of tosylate solvolyses were identified by comparing their gas chromatographic retention times with those of the corresponding compounds, which were synthesized independently. In selected instances the cyclic ketones were converted into 2,4-dinitrophenylhydrazone derivatives, and no depression in mixture melting point was observed.

Trifluoroacetolyses. 6-Heptyn-2-yl tosylate was allowed to solvolyze, to obtain material for gas chromatographic analyses, in 10 ml of trifluoroacetic acid (0.125 *M* in $NaO_2C_2F_3$) at 25° for ten half-lives. The products of solvolysis were identified by direct injection of the acid solution on the columns. The columns and temperatures were: silicone rubber UCW 98 at 80°, Carbowax 20M at 115°, and silicone oil Dow Corning 550 to 120°. Each column was fitted with a small basic fore section[9,32] during the analyses. The product distribution is shown in Table II.

6-Heptyn-2-yl tosylate (6.0 g, 0.022 mol) was allowed to solvolyze (on a larger scale than described above) in 100 ml of trifluoroacetic acid (0.25 *M* in $NaO_2C_2F_3$). After the acid was removed under vacuum, the reaction mixture was worked up with an ice water and sodium carbonate mixture to give 2.8 g of the distilled product, bp 80–85° (93 mm). The distillate was analyzed by gas chromatography (Table II); 2,4-dinitrophenylhydrazone, mp 142.1°, not depressed in a mixture melting point with the derivative of 3-methylcyclohexanone.

Anal. Calcd for $C_9H_{11}O_2F_3$: C, 51.90; H, 5.29. Found: C, 51.40; H, 5.50.

Trifluoroacetolysis of 6-Octyn-2-yl Tosylate. 6-Octyn-2-yl tosylate (0.12 mmol) was allowed to solvolyze in trifluoroacetic acid (0.5 ml, 0.25 *M* in $NaO_2C_2F_3$) in an nmr tube. Based on the heights of the methyl peak of the *p*-toluenesulfonate anion and that of the tosylate ester, 41–43% of the original tosylate had rearranged to vinyl tosylates (Scheme III) after completion of the reaction (10 min).

Gas Chromatographic Analysis of the Trifluoroacetolysis of 6-Octyn-2-yl Tosylate. 6-Octyn-2-yl tosylate (60 mg, 0.21 mmol) was allowed to solvolyze in trifluoroacetic acid (2 ml, 0.25 *M* in $NaO_2C_2F_3$). The acid solution was then analyzed gas chromatographically using a 1,2,3-tris-2-cyanoethoxypropane column at 125°. (The removable injection port liner was packed with basic fore-column material and kept at room temperature.) A comparison was made with a standard solution of 2,3-dimethylcyclohexanone and 1-acetyl-2-methylcyclopentane. The analysis corresponded to a 64% yield of ketones derived from cyclic trifluoroacetates. The product also can be analyzed on silicone rubber UCW 98 at 85° or Carbowax 20M columns at 125°.

In a reaction carried on a larger scale than described above (6-octyn-2-yl tosylate, 6.0 g, 0.0215 mol, in trifluoroacetic acid, 94 ml, 0.25 *M* $NaO_2C_2F_3$), there was obtained 5.1 g of the crude product, which gave 2.0 g of volatile product. The *trans*-2,3-dimethylcyclohexanone and *trans*-1-acetyl-2-methylcyclopentane were separated by preparative gas chromatography; 2,4-dinitrophenylhydrazone of *trans*-2,3-dimethylcyclohexanone, mp 149.8° (no depression in mixture melting point); 2,4-dinitrophenylhydrazone of *trans*-1-acetyl-2-methylcyclopentane, mp 109° (no depression in mixture melting point). The *cis* isomers of the ketones could not be successfully collected.

The crude vinyl tosylates (1.5 g, 5.36 mmol, containing less than 2% cyclic ketones) were allowed to react with metallic sodium (1.05 g) in liquid ammonia (30 ml) for 3 hr.[33] After the usual work-up, a crude product (977 mg) was isolated and oxidized with chromic acid.[31] The oxidation products (200 mg, 29%) were found to be 1-acetyl-2-methylcyclopentane (86.6%) and 2,3-dimethylcyclohexanone (13.4%). In the same way 1-cyclohexenyl tosylate[34] (1 g, 3.95 mmol) was allowed to react with metallic sodium in liquid ammonia to give a mixture of products (200 mg), which were identified as toluene, cyclohexanol, and cyclohexanone from their gas chromatographic retention times. A known 2,4-dinitrophenylhydrazone showed no depression in mixture melting point with that of cyclohexanone; mp 159.6–160°.

Trifluoroacetolysis of the Crude Rearranged Tosylate at 60°. The crude rearranged tosylate, 292 mg, containing 1-acetyl-2-methylcyclopentane (3.5%) and 2,3-dimethylcyclohexanone (3.1%) by gas chromatography, was allowed to react with trifluoroacetic acid (10 ml, 0.25 *M* $NaO_2C_2F_3$) at 60° for 3 hr. The products were identified as 1-acetyl-2-methylcyclopentane (91.6%) and 2,3-dimethylcyclohexanone (8.4%), after correcting for the amount of the ketones present in the starting material.

Formolyses. Formolyses of 6-heptyn-2-yl and 6-octyn-2-yl tosylates were carried out in the same way as described above. Analyses of the products of formolyses were carried out gas chromatographically, using a basic fore section.[9] Cyclic vinyl formates were hydrolyzed completely to the corresponding ketones, but the secondary formates were only partially hydrolyzed to the corresponding alcohols. The products of formolyses of 6-heptyn-2-yl tosylate (0.1 *M* in tosylate, 0.125 *M* in NaO_2CH) are given in Table II. The tosylate (5.0 g, 0.0188 mol) gave 1.8 g of the products which were hydrolyzed and analyzed gas chromatographically (Table II).

The products of formolysis of 6-octyn-2-yl tosylate (0.1 *M* in tosylate, 0.125 *M* in NaO_2CH) are shown in Table III. The tosylate (5.0 g, 0.0178 mol) gave 2.3 g of the distilled material.

Acetolyses. The products of acetolyses of 6-heptyn-2-yl and 6-octyn-2-yl tosylates were analyzed gas chromatographically using a basic fore section.[9] The cyclic vinyl acetates and secondary acetates were found to be more stable on the basic fore section than the corresponding formates and trifluoroacetates. The cyclic vinyl acetates from 6-octyn-2-yl tosylate could not be well resolved on the columns such as 1,2,3-tris-2-cyanoethoxypropane, Carbowax 20M, and silicone rubber UCW 98. The products of acetolyses of 6-octyn-2-yl tosylate, however, were hydrolyzed to give a resolvable mixture of products.

The distribution of the products of acetolysis of 6-heptyn-2-yl tosylate (0.1 *M* in tosylate, 0.125 *M* in $NaO_2C_2H_3$), is shown in Table II. The tosylate (6.0 g, 0.023 mol) gave 2.3 g of the distilled products (Table II). The products of acetolysis (1.0 g, 0.006 mol) were hydrolyzed to give 350 mg (48%) of products, as shown in Table II.

Acetolysis of 6-octyn-2-yl tosylate gave 10–12% of the rearranged tosylate according to nmr analysis. The gas chromatographic analysis from dilute solution showed the product distribution given in Table III. The tosylate (7.0 g, 0.025 mol) gave 2.3 g of the distilled products. The acetolysis products (1.2 g, 0.007 mol) were hydrolyzed to give 512 mg (68%) of products as shown in Table III.

Trifluoroacetolysis of 6-Hepten-2-yl Tosylate. The products of trifluoroacetolysis of 6-hepten-2-yl tosylate from a dilute solution (0.177 *M* in tosylate, 0.25 *M* in $NaO_2C_2F_3$ allowed to react for 450 min, ten half-lives) were analyzed as described above. The columns used were Carbowax 20M at 80° and 1,2,3-tris-2-cyanoethoxypropane at 80°. The products were, elimination products (28%), 3-methylcyclohexanols, *cis* and *trans* (48%), 6-hepten-2-ol (16%), and an unknown (8%), possibly 6-hepten-3-ol, arising from an elimination reaction of the tosylate followed by an addition of trifluoroacetic acid.

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(33) D. B. Denney and Goldstein, *J. Org. Chem.*, **21**, 479 (1956).

(34) 1-Cyclohexenyl tosylate was supplied by J. M. Indelicato.