The compound was converted to a red dinitrophenylhydrazone, m.p. 140–142° dec.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29; N, 17.49. Found: C, 55.93; H, 6.29; N, 17.90.

The next largest v.p.c. peak was isolated and identified as *2-propylhexanal* on the basis of air oxidation to the carboxylic acid, with infrared peaks at 1700 and 3500–2300 cm.$^{-1}$ (broad) and a mass spectrum with ions at *m/e* 158 $(C_9H_{18}O_2)^+$, 116 $(BuCH{=}C(OH)_2)^+$, 102 $(PrCH{=}C(OH)_2)^+$, 73 ($^+CH_2{-}C{=}C(OH)_2$), and smaller fragments. The minor product was identified as di-*n*-butyl ketone by v.p.c. retention time.

B. Cycloheptenocyclopropenone. In an evacuated, sealed tube 3.66 g. (0.030 mole) of cycloheptenocyclopropenone was decomposed by immersion into a preheated oil bath at 250° for 30 min. On opening, the tube lost 0.40 g. (47% of theoretical, if CO; the CO was identified by infrared in a separate experiment); chromatography of the residue afforded 0.455 g. (16%) of *triscycloheptenobenzene*, m.p. 184–185°.

Anal. Calcd. for $C_{21}H_{30}$: C, 89.29; H, 10.71; mol. wt., 282. Found: C, 89.47; H, 10.48; mol. wt. (osmometer, CCl_4), 279.

The infrared spectrum showed absorption at 2920, 2860, and 1450 cm.$^{-1}$. In the n.m.r. there was a broad peak at τ 7.30 and another at 8.45 in a ratio of 2:3. The ultraviolet spectrum (95% EtOH) had λ_{max} 274 mμ (ϵ 262) and λ_{min} 253 mμ.

When 2.44 g. (0.020 mole) of cycloheptenocyclopropenone and 7.69 g. (0.020 mole) of tetracyclone were heated in a sealed, evacuated tube at 250° for 30 min., chromatography on alumina afforded (with hexane) 50 mg. (2.7%) of *triscycloheptenobenzene*. Elution with CCl_4 and benzene yielded 2.057 g. (22.8%) of *1,2-cyclohepteno-3,4,5,6-tetraphenylbenzene*, m.p. 215–217°.

Anal. Calcd. for $C_{35}H_{30}$: C, 93.29; H, 6.71; mol. wt., 450. Found: C, 93.65; H, 6.51; mol. wt. (osmometer, CCl_4), 435 ± 15.

The ultraviolet spectrum (isooctane) had λ_{max} 236 mμ (ϵ 42,000). The n.m.r. spectrum had peaks at τ 3.04 and 3.35 (20 protons), a multiplet at 7.35 (4 protons), and a multiplet at 8.30 (6 protons).

Elution with CH_2Cl_2 yielded 1.624 g. (21% recovered) of tetracyclone. Elution with $CHCl_3$ and ethyl acetate yielded 2.189 g. (21.5%) of a *1:1 adduct* of tetracyclone with the cyclopropenone, m.p. 214–216°.

Anal. Calcd. for $C_{37}H_{30}O_2$: C, 87.71; H, 5.97; mol. wt., 507. Found: C, 87.35; H, 5.89; mol. wt. (osmometer, CCl_4), 528.

In the infrared the compound had bands at 3080, 3058, 3030, 2925, 2855, 1763 (strong), 1670 (weak), 720, and 693 cm.$^{-1}$. The ultraviolet spectrum (EtOH) had $\lambda\lambda_{max}$ 345 mμ (ϵ 6900), 241 (30,000), and 206 (20,650), with a shoulder at 265. In the n.m.r., there was a multiplet at τ 3.01, one at 7.73, and a third at 8.49, with relative areas 43:8:12. The compound was recovered unchanged after 15 min. at 360°, or 14 hr. in refluxing (210°) nitrobenzene.

When 244 mg. of cycloheptenocyclopropenone was refluxed for 90 min. in 20 ml. of aqueous 10% KOH, 128 mg. (46%) of cycloheptene-1-carboxylic acid was obtained, m.p. 51–52°, identified by comparison with an authentic sample.[24] The n.m.r. spectrum had a one-proton triplet at τ 3 as well as signals in the aliphatic region.

C. Cycloundecenocyclopropenone. In an evacuated break-seal tube, 644 mg. of the cyclopropenone was kept for 30 min. at 210°. The gas was collected in an infrared cell, and it showed the typical CO peaks at 2165 and 2115 cm.$^{-1}$. The residue was filtered over Al_2O_3 with pentane, and then distilled to yield 502 mg. (93%) of cycloundecyne,[25] b.p. 102–105° (12 mm.), $n^{20}D$ 1.4876 (lit. $n^{20}D$ 1.4875). The infrared spectrum was identical with that reported, and the n.m.r. spectrum showed a narrow peak at τ 8.49 and a broad one at 7.95 in a ratio of 14:4.

(24) E. A. Brande, W. F. Forces, and E. A. Evans, *J. Chem. Soc.*, 2202 (1953).

(25) V. Prelog and V. Boarlund, *Helv. Chim. Acta*, **38**, 1776 (1955).

Small-Ring Compounds. XLIII. Formolysis of Substituted Allylcarbinyl Tosylates[1]

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Received November 13, 1964

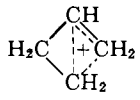
Rate accelerations have been measured as a function of methyl substitution in 3- and 4-positions and phenyl substitution at the 4-position in the formolysis of allylcarbinyl tosylate. The largest factor, 4.5 × 10^3, was observed for (γ,γ-dimethylallyl)carbinyl tosylate. The nature of the solvolytic transition state is discussed; the results are shown to be inconsistent with formation of classical carbonium ion intermediates.

(1) Supported in part by the National Science Foundation.

Numerous interconversion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives have been reported in the last 2 decades.[2] In reactions where carbonium ion intermediates can quite reasonably be assumed, cyclopropylcarbinyl and cyclobutyl derivatives are highly reactive and yield very similar

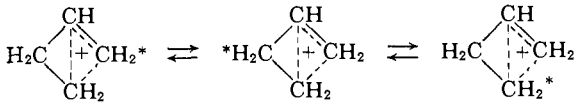
(2) For a general introduction, see R. Breslow in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963.

products.[3] The striking facility with which cyclopropylcarbinyl and cyclobutyl derivatives become interconverted in carbonium ion reactions combined with the high solvolytic reactivity of cyclopropylcarbinyl and cyclobutyl derivatives have led to the proposal that unsymmetrical bicyclic cations, termed bicyclobutonium ions (I), are the reaction intermediates.



I

The results of isotopic-labeling experiments in conjunction with the other findings can best be interpreted as resulting from a rapid but not instantaneous interconversion of the three possible methylene-labeled bicyclobutonium ions (Ia-c).[4-6] Each labeled ion would react with nucleophilic reagents to give the same proportions of cyclopropylcarbinyl, cyclobutyl, or allylcarbinyl derivatives with, of course, the possibility of the ^{14}C- or deuterium-labeled methylene group winding up in the different positions depending on whether or not the product arises from Ia, Ib, or Ic.



Ia Ib Ic

In support of this proposal, we have recently shown that formolysis of allylcarbinyl tosylate proceeds with rate enhancement to yield the same product distribution (after correction for product instability) as is observed from numerous reactions of cyclopropylcarbinyl or cyclobutyl derivatives.[7] Furthermore, the formolysis of 1,1-dideuterio-3-buten-1-yl tosylate was found to yield cyclopropylcarbinyl formate with the label statistically distributed among the three methylene groups.

In order to provide further evidence regarding the occurrence of bicyclobutonium ion intermediates in the formolysis of allylcarbinyl tosylate and to gain more detailed information on the structure and charge distribution in these species, the rates and products of solvolysis of several substituted allylcarbinyl tosylates have been investigated.

Results

Preliminary investigations indicated that the *p*-toluenesulfonic acid liberated in the solvolysis of allylcarbinyl tosylates in 98% formic acid catalyzed the addition of solvent to the disubstituted alkene bonds. After 30 min. at 40°, no vinyl proton absorption could be detected in the n.m.r. spectrum of a sample of (β-methylallyl)carbinyl tosylate in 98% formic acid. After several hours at 50° in 80% formic acid, the (β-methylallyl)carbinyl tosylate was only 30% solvolyzed but the absorption of the vinyl protons in the n.m.r. spectrum had decreased by more than 70%. In an attempt to avoid this difficulty, a mixture of 10% pyridine in formic acid was investigated as a possible solvent. Using this solvent, no evidence could be found for the undesirable side reactions that had occurred in the other solvents and the solvolysis showed clean first-order kinetics. No entirely satisfactory explanation of this unusual solvent behavior can be offered; however, suppression of the autoprotolysis of formic acid and/or ion-pair phenomena may well be responsible.

The rate of solvolysis of (β-methylallyl)carbinyl tosylate in 10% pyridine in formic acid was determined by the previously described n.m.r. technique.[7] In order to obtain the rate acceleration provided by a methyl group on the methinyl center, the rate of solvolysis of allylcarbinyl tosylate was also determined in 10% pyridine in formic acid. The results are given in Table I.

Solvolyses of *cis*- and *trans*-3-penten-1-yl tosylates were too fast to measure by the usual n.m.r. technique at 50°. For these two compounds, the n.m.r. tubes of the solutions of the tosylates in 10% pyridine in formic acid were placed in a variable temperature probe of a Varian V-4300B n.m.r. spectrometer. The probe temperature was controlled at 50.5 ± 0.5° with a heated nitrogen stream.[8] Spectra were taken continuously. The rates of solvolysis were then calculated by the previously described procedure.[7] The results are included in Table I.

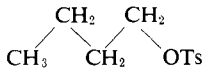
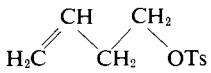
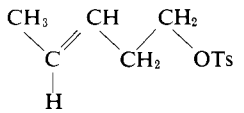
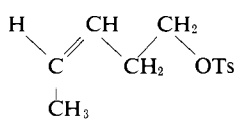
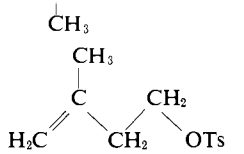
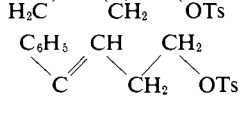
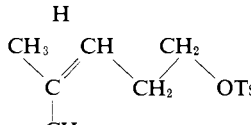
The rate of solvolysis of *trans*-4-phenyl-3-buten-1-yl tosylate in 98% formic acid was measured with the aid of an automatic titrator. The amount of base (sodium formate in formic acid) added to maintain a constant pH was plotted against time. The rate was determined from the usual plot of log $(a_\infty - x)/a_\infty$ *vs.* time; a_∞ = infinity titer; x = titer at time t. Rate constants determined in this fashion may be larger than the actual solvolytic rate constants if an internal rearrangement of the starting material to a much less reactive isomer is occurring. The observed rate constant is the sum of the solvolytic rate constant, k_s, and the rearrangement rate constant, k_r. The observed apparent infinity titer, $a_\infty^{obsd}/a_\infty^{calcd}$ divided by $[1 - (a_\infty^{obsd}/a_\infty^{calcd})]$, is then equal to k_s/k_r. The observed infinity titers for these compounds indicate $k_r << 0.2k_s$. An error as large as 20% in the observed rate constant would not affect the conclusions to be reached from the present studies.

The automatic titration procedure has the advantage that the solvent system does not change (except for the small amount of salt generated) during the course of the experiment. In addition, rate constants for reactions with half-lives of just a few minutes can also be conveniently determined. The rate of solvolysis of 4-methyl-3-penten-1-yl tosylate was determined by this procedure. In order to relate the results so obtained with those for the unsubstituted compound, the rate of formolysis of *trans*-3-penten-1-yl tosylate was also determined by this procedure. These results are summarized in Table I.

The products of formolysis of *cis*- and *trans*-3-penten-1-yl tosylate and (β-methylallyl)carbinyl tosylate in 10% pyridine in formic acid were determined. The

(3) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509 (1951).
(4) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, 81, 4390 (1959).
(5) E. Renk and J. D. Roberts, *ibid.*, 83, 878 (1961).
(6) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 11, 171 (1960).
(7) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, 86, 3773 (1964).
(8) The error indicates variation of the temperature during the experiment; the absolute temperature in the sample tube is accurate only to ±2°.

Table I. Solvolysis Rates of Substituted Allylcarbinyl Tosylates

Compound	Temp., °C.	Method[a]	$k_1 \times 10^4$	k_{rel}	k_{rel}
	50.3	A	0.0084[b,c]	0.27	(1)
	50	A	0.0136[d]	(1)	3.7
	50.3	A	0.031[b,c]		(3.7)
	50	C	2.9[d]	210	770
	50.1	B	4.6[b]	(210)	
	50.1	C	0.61[d]	45	165
	50	A	0.043[d]	3.3	12
	50.1	B	2.1[b]	96[e]	350
	49.9	B	100[b]	4500[e]	16500

[a] Methods A and C are by n.m.r.; B is by automatic titration; see Experimental section for details. [b] 98% formic acid. [c] Ref. 7. [d] 10% pyridine in 98% formic acid. [e] Based on *trans*-3-penten-1-yl tosylate as 210.

initial formolysis products were hydrolyzed with dilute sodium hydroxide and continuously extracted into ether. The resulting alcohols in the concentrated ether extract were analyzed by vapor phase chromatography on a 20-ft. 1,2,3-tris(2-cyanoethoxy)propane column at 120°. The stability of α-cyclopropylethanol, the product expected from the 3-penten-1-yl tosylates, was determined by subjecting it to the solvolysis conditions. The results are given in Table II. The products from the nitrous acid deamination of the corresponding amines are given for comparison in Table III.[9,10]

The ratio of 2-methylcyclobutanol to allylmethylcarbinol from the solvolysis of both *cis*-3-penten-1-yl and *trans*-3-penten-1-yl tosylate is about 0.7; the ratio obtained by subjecting α-cyclopropylethanol to the solvolysis conditions is 0.8. The ratios of 3-pentenol to allylmethylcarbinol from the solvolysis of both 3-penten-1-yl tosylates are about 2.4; the ratio obtained by subjecting α-cyclopropylethanol to the solvolysis conditions is also 2.4. This implies that the initial product from the solvolysis of both *cis*- and *trans*-3-penten-1-yl tosylate has the cyclopropylmethylcarbinyl structure.

The products from the deamination of the 3-penten-1-ylamines differ in two respects; (1) a high percentage of structurally unrearranged material is obtained; (2) a high percentage of hydride shift product is obtained. The unrearranged product in the amine deamination probably arises from a direct displacement reaction on the diazonium ion as was previously suggested.[11] The substituted allyl alcohols may result from hydride shifts in the initial "hot" (not completely solvated) carbonium ion produced by decomposition of the diazonium ion.

1-Methylcyclobutanol was the only cyclic product obtained from the solvolysis of (β-methylallyl)carbinyl tosylate. The very small amount of (β-methylallyl)-carbinol may result from a direct displacement reaction or from a secondary rearrangement. Again the rather different product mixture obtained upon deamination of (β-methylallyl)carbinylamine seems best explained by intervention of a direct displacement reaction on the diazonium ion accompanied by hydride shifts involving an initial hot carbonium ion.

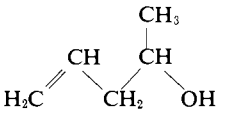
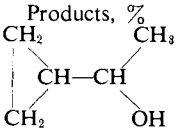
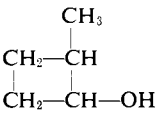
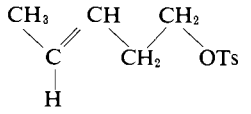
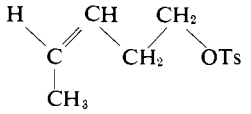
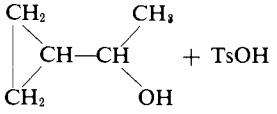
Discussion

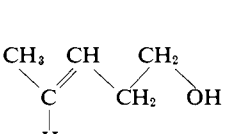
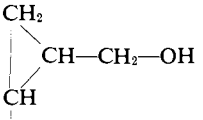
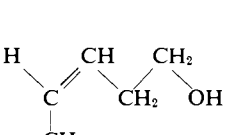
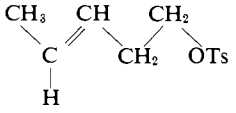
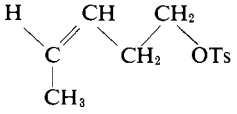
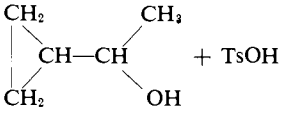
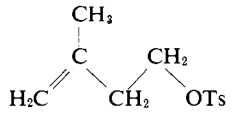
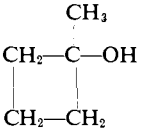
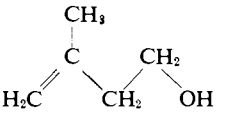
The observed rate accelerations require participation of the double bond electrons in the transition state of the rate-determining step in formolysis. A rate enhancement of 4500 by dimethyl substitution on a position three carbon atoms removed from the reaction center can hardly be explained through steric or inductive effects.

The rates of ethanolysis of several of these same compounds have recently been determined (Table IV).[12,13] Allylcarbinyl, *trans*-3-penten-1-yl, and *trans*-4-phenyl-3-buten-1-yl β-naphthalenesulfonates all solvolyze *slower* than their saturated analogs in absolute ethanol at 60°. 4-Methyl-3-penten-1-yl β-

(9) M. S. Silver, Ph.D. Thesis, California Institute of Technology, 1959.
(10) W. B. Kover, Ph.D. Thesis, California Institute of Technology, 1964.
(11) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, 83, 2719 (1961).
(12) M. Hanack and K. Görler, *Chem. Ber.*, 96, 2121 (1963).
(13) M. Hanack and H. J. Schneider, *Tetrahedron*, 20, 1863 (1964).

Table II. Formolysis Products of Substituted Allylcarbinyl Tosylates[a]

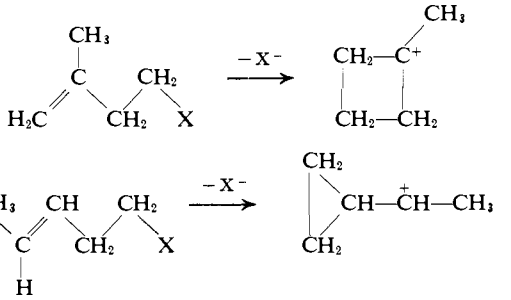
Compound	Products, %		
			
	6.9	69.5	4.6
	5.2	78.4	3.3
	20.1	...	15.8

Compound			
	13.3	1.7	4.0
	10.4	1.1	1.6
	48.5	*b*	*b*
	 96.7,		2.3

[a] In formic acid containing 10% pyridine. [b] Included in the 48.5% given for *trans*-3-penten-1-ol.

naphthalenesulfonate shows a rate enhancement of only 47.5 under the same conditions. It is clear that in the solvolysis of these substances, the mechanism is SN2-like in absolute ethanol and SN1-like in formic acid.

Any attempt to rationalize the rate effects on the basis of ionization of the allylcarbinyl derivatives to rearranged classical ions seems fruitless.[7] As part of such an explanation it would be required that the effect of γ-methyl substitution on the rate is the result of ionization to form a methylcyclobutyl cation while the effect of δ-methyl substitution would be the result of ionization to form a cyclopropylmethylcarbinyl cation. If this were true, then since γ-methyl substitution would lead to formation of a tertiary cyclobutyl cation and δ-methyl substitution to a more highly strained secondary cyclopropylcarbinyl cation, the rate enhancement of the γ-methyl substituent would be expected to be much larger than that for a δ-methyl substituent. The observed results are opposite to such a prediction; a γ-methyl group produces a threefold rate increase while a δ-methyl group produces more than a 200-fold increase.



Similarly, a δ-phenyl substitution would lead to formation of a benzylic cation if ionization were to occur to produce the rearranged cation. The cations derived from the δ-phenyl- and δ-methyl-substituted allylcarbinyl compounds would differ only in the nature

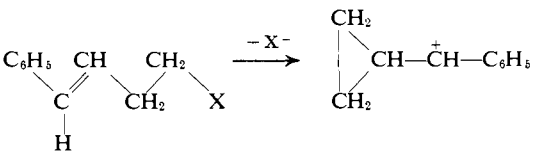
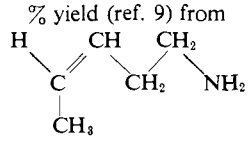
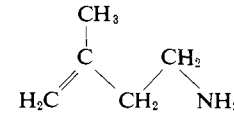
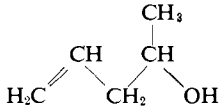
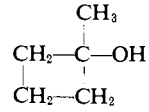
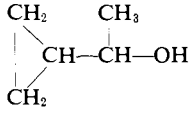
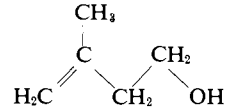
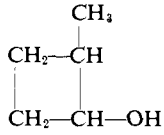
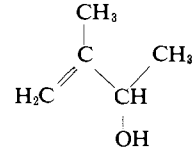
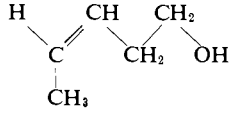
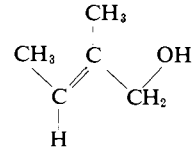
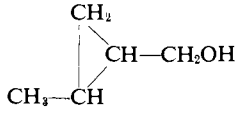
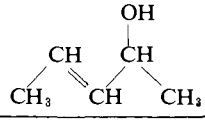


Table III. Products from the Amine–Nitrous Acid Reactions of Substituted Allylcarbinylamines

Alcohol formed	% yield (ref. 9) from 	Alcohol formed	% yield (ref. 10) from 
	0		59
	74		29
	0		6
	10		6
	0		
	16		

of the substituent on the carbonium ion center. Since a phenyl substituent on a developing cationic center normally produces much larger rate increase than a methyl substituent,[14] the rate of solvolysis of *trans*-4-phenyl-3-buten-1-yl tosylate would be predicted on this basis to be very much faster than the rate of solvolysis of *trans*-3-penten-1-yl tosylate. Again this prediction is not borne out; the phenyl-substituted compound solvolyzes more slowly by a factor of 2. This would, in part, also be the result of greater thermodynamic stability of the phenyl-substituted tosylate owing to conjugation of the phenyl group with the alkenic linkage.

Brown has suggested that "the cyclopropylcarbinyl cation is highly stabilized by some sort of electron release but that this stabilization has nothing to do with any bonding between the carbonium ion carbon and either the two carbons of the ring or with one of the three carbon–carbon bonds in the ring."[15] One might choose to explain the relative rate increases produced by γ-methyl and δ-methyl groups as resulting from ionization to produce substituted cyclopropylcarbinyl cations. However, a separate explanation would then be required to explain the relative rate increases for δ-methyl and δ-phenyl substitution.

(14) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.
(15) H. C. Brown, private communication.

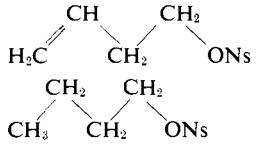
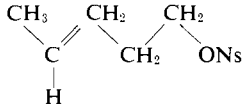
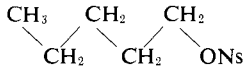
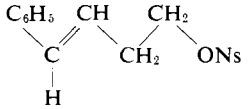
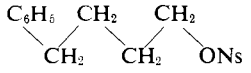
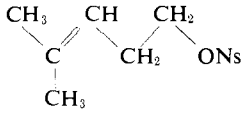
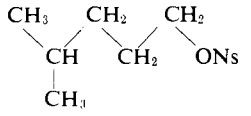
On the basis of intermediacy of bicyclobutonium ions in these solvolyses, it may seem at first glance surprising that methyl and phenyl substitution produces relatively small increases in the rates of solvolysis of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives. This marked insensitivity of the rate to substitution on any other but the α-carbon has also been observed in the solvolyses of other compounds where formation of nonclassical ions has been postulated.[16]

The observed substituent effects are not those expected if substituent effects on nonclassical ion formation were qualitatively the same as substituent effects on classical ion formation, there being only a proportionality factor corresponding to the degree of development of charge on the substituted carbon atom.

As evidence for this may be cited: first, the unusual deuterium isotope effects in solvolysis with cyclopropylcarbinyl and cyclobutyl derivatives[17]; and second, the relative effects of methyl and phenyl substituents on the

(16) (a) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246 (1964); (b) E. J. Corey and H. Uda, *ibid.*, **85**, 1788 (1963); (c) P. von R. Schleyer and D. C. Kleinfelter, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960, Abstracts, p. 43P; (d) R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3977 (1958); (e) R. A. Sneen, *ibid.*, **80**, 3982 (1958).
(17) (a) M. Nikoletič, S. Borčič, and D. E. Sunko, *Proc. Natl. Acad. Sci. U. S.*, **52**, 893 (1964); (b) S. Borčič, M. Nikoletič, and D. E. Sunko, *J. Am. Chem. Soc.*, **84**, 1615 (1962); (c) D. E. Sunko, personal communication.

Table IV. Ethanolysis of Substituted Allylcarbinyl β-Naphthalenesulfonates in Absolute Ethanol at 60°[a]

Compound	$k \times 10^6$, sec.$^{-1}$	Ratio
	4.8[b]	0.55
	8.7[b]	
	6.3	0.77
	8.2	
	6.7	0.90
	7.5	
	57.0[b]	47.5
	1.2[b]	

[a] Ref. 13. [b] Ref. 12.

cyclopropylcarbinyl and allylcarbinyl systems. For all of the available, reasonably comparable, compounds, methyl substitution on the ion produces greater rate enhancement than the phenyl substitution. This is quite at variance with the normal observation that phenyl groups provide much larger rate acceleration than methyl groups (thus trityl chloride solvolyzes 4.6×10^6 times faster than *t*-butyl chloride at 25° in 85% aqueous acetone).[18]

The reasonable explanation for these effects hinges critically on the mechanism of nonclassical electron delocalization. The orbitals involved in the cationic portion of the bicyclobutonium ion are not parallel and are probably not even pure p-orbitals.[19] Therefore, the resulting overlap and bonding will have both σ-type and π-type contributions. In order to understand what effect a methyl or a phenyl substituent at the different positions of the bicyclobutonium ion will have, one must first establish: (1) how much of the stability derives from σ-bonding and how much from π-bonding; and (2) the relative effectiveness with which the substituent stabilizes the ion by σ-bonding and π-bonding in this system.

One can estimate, using the model of Howden and Roberts,[19] that approximately 50% of the stabilization of I results from σ-type bonding. It is well established that a phenyl group withdraws electrons from σ-bonds inductively and either donates or supplies electrons to π-bonds by resonance. Therefore, a phenyl group will destabilize the cation inductively but stabilize it by π-interaction. Since the maximum stabilization by π-overlap, which requires the phenyl group to be in the nodal plane of the bonding molecular orbital, may not be possible, the π-interaction of a phenyl group with the bicyclobutonium ion electrons may be much reduced. Actually it appears as if the two effects nearly cancel in the systems studied in this work.

A methyl group is normally considered to stabilize a cationic center by inductive electron release through the σ-framework and by hyperconjugation through the π-framework. It seems possible that, if a phenyl group produces a relatively small degree of stabilization by π-interaction, then stabilization by the hyperconjugative effect might also be reduced from what is normally observed in methyl-substituted carbonium ions. This is consistent with the deuterium isotope effects recently reported for the solvolysis of cyclopropylmethylcarbinyl,[17c] 1-methylcyclobutyl, (1-methylcyclopropyl)carbinyl, and (2,2-dimethylcyclopropyl)carbinyl derivatives.[17]

The effect of a γ-methyl substituent compared to a δ-methyl substituent implies that the charge developed at the γ-position may be less than that developed at the δ-position in the solvolytic transition state. This situation is most easily understood if the solvolytic *transition state* coming from the open-chain compounds resembles a homoallylic ion. Formation of a bicyclobutonium ion from this transition state would then involve some structural reorganization with development of significant 1,4-interaction. It is not unreasonable to expect 1,3-interactions to be established before 1,4-interactions for formation of a bicyclobutonium ion from an open-chain tosylate since this would involve minimum structural reorganization. The relative amount of positive charge on the 3- and 4-carbon atoms in the transition state is dependent on the amount of 1,4-interaction; increasing 1,4-interaction increases the amount of charge on the 3-carbon with respect to the 4-carbon. The rate of solvolysis of (β-methylallyl)carbinyl tosylate indicates that the 1,4-interaction is relatively unimportant in the transition state even though the interaction must be large in the intermediate since only 1-methylcyclobutyl products are formed.

The relative rates of solvolysis of *cis*- and *trans*-3-penten-1-yl tosylates can also be explained on this basis. The electronic effects of the *cis*- and *trans*-methyl groups should be the same and produce the same rate enhancements. The *cis* compound solvolyzes slower because of steric interactions that develop as the homoallylic-like transition state is approached.

Solvolyses of substituted allylcarbinyl, cyclopropylcarbinyl, or cyclobutyl compounds yield predominantly α-substituted products. The product ratios are controlled by the way in which the substituent perturbs the energies of the transition states leading to the various products. This may, to some degree, reflect the way in which the substituent perturbs the charge distributions (and relative stabilities) of the possible nonclassical intermediates. For electron-donating substituents, the charge is expected to be most favorably located at the point of substitution and, where equilibration among the possible bicyclobutonium ions is rapid, formation of the α-substituted products is expected to be favored (at least where the products are stable).[9,10]

(18) Reference 14, p. 76.
(19) M. E. H. Howden and J. D. Roberts, *Tetrahedron*, 19, Suppl., 2, 403 (1963).

Experimental

Rates of Solvolysis of Allylcarbinyl Tosylates. Procedure A. Approximately 0.03 g. of the tosylate was placed in a 4.94-mm. o.d., thin-walled Pyrex tube. Approximately 1 ml. of solvent was added and the tubes were sealed. The sealed tubes were placed in a constant-temperature bath. For each measurement the tubes were removed from the oil bath and cooled to −10° in an ice–methanol bath. Immediately before measurement, the tubes were removed from the ice–methanol bath and placed in the probe of the Varian A-60 at 37°. Seven to ten spectra were taken of each sample for each measurement. After removal from the probe, the tubes were transferred back to the ice bath and then back to the constant-temperature bath. For each measurement, the tubes were out of the constant-temperature bath for 20 min. and were in the probe for 5 min.

Procedure B. A special Teflon cell cap was constructed to provide a sealed reaction vessel for the International Instruments difunctional recording titrator. The cap was sealed to the cell by means of an O-ring. The electrodes were introduced through O-ring seals. The stirrer was a section of a 1-ml. tuberculin syringe with a glass stirring blade attached to the bottom of the plunger. The stirrer was also introduced through an O-ring seal. The base and substrate were injected through rubber septums.

The glass electrodes were soaked in 98% formic acid for several days before use. After equilibration for 15 min., the electrodes showed no drift in pH reading over a 3-hr. period. Titration of *p*-toluenesulfonic acid with sodium formate in formic acid solution produced an apparent change of 2 pH units on going from excess acid to excess base. The inflection point on the titration curve was relatively flat.

For the rate studies, approximately 15 ml. of 98% formic acid was introduced into the thermostated cell and the system closed. After 15 min., the pH-stat was set to maintain the equilibrium pH. (This was not very reproducible.) The sample (~30 μl.) was injected through one of the rubber septums. The amount of base (5% sodium formate in formic acid) added to maintain a constant pH was plotted against time. The rates were determined from the usual plot of $\log (a_\infty - x)/a_\infty$ *vs.* time.

Procedure C. Approximately 0.03 g. of the tosylate was placed in a 4.94-mm. o.d., thin-walled Pyrex tube. Approximately 1 ml. of solvent was added and the tubes were sealed. The sealed tubes were immediately placed in the variable temperature probe of the HR-60. The probe temperature was controlled with a heated nitrogen stream. The rates of solvolysis were then determined as in procedure A.

Solvolysis Products of Allylcarbinyl Tosylates. A sample of the tosylate (~0.2 g.) was placed in a Pyrex tube (18 × 150 mm.), the solvent was added, and the tube was sealed and placed in a constant-temperature bath at 50°. After the specified length of time, the tube was removed from the bath, cooled in Dry Ice, and opened; the contents were poured into a 100-ml., round-bottomed flask. A 20% sodium hydroxide solution was added with cooling until a pH of 8 to 9 was obtained. The mixture was stirred at room temperature for 3 hr. and then continuously extracted with ether for 24 hr. The ether extract was dried over sodium sulfate and the volume reduced to ~5 ml. by removal of the ether through a 20-cm. Vigreux column. The residues were analyzed by v.p.c. on a 20-ft. 1,2,3-tris(2-cyanoethoxy)propane (TCEP) column at 120°. The analyses were calibrated by comparison with known mixtures of similar concentrations.

(β-Methylallyl)carbinyl Tosylate. A sample of crude (β-methylallyl)carbinol (prepared by Dr. W. B. Kover) was purified by preparative v.p.c. To 0.90 g. (0.0109 mole) of the carbinol in 4 g. of pyridine at 0° was added 1.92 g. (0.0108 mole) of *p*-toluenesulfonyl chloride. The mixture was allowed to stand for 1 day at 0° and then 2 hr. at room temperature. The mixture was then extracted with 75 ml. of petroleum ether (b.p. 60–70°). The petroleum ether extract was twice washed with 25 ml. of 1 *N* hydrochloric acid and once with 25 ml. of water. The ether extracts were dried over magnesium sulfate and the ether removed on the rotary evaporator. The residue was twice extracted into 10 ml. of petroleum ether (b.p. 30–40°). The petroleum ether was removed on a rotary evaporator. The product was flash distilled to give 1.7 g. of (β-methylallyl)carbinyl tosylate. This compound could not be obtained in crystalline form. Attempts to distill this compound fractionally led to decomposition. The n.m.r. spectrum (Figure 1) shows no absorption due to impurities. The measurement of the rate of solvolysis of this compound showed no deviation from linearity up to 60% solvolysis.

cis- and trans-3-Penten-1-ol. *cis-* and *trans*-3-penten-1-ol (K and K Laboratories) were separated by preparative v.p.c. on the Megachrom using four 12-ft. TCEP columns. The collected fractions were found to be 98% pure by v.p.c. analysis on a 6-ft. Carbowax column. The material assigned the *trans* structure had the characteristic infrared absorption band at 955 $cm.^{-1}$. The material assigned the *cis* structure had the characteristic absorption band at 690 $cm.^{-1}$.[20]

trans-3-Penten-1-yl Tosylate. To 0.90 g. (0.0105 mole) of *trans*-3-penten-1-ol in 4 g. of pyridine cooled to 0° was added 1.92 g. (0.0108 mole) of *p*-toluenesulfonyl chloride. The mixture was allowed to stand for 1 day at 0° and then for 2 hr. at room temperature. The mixture was extracted with 75 ml. of petroleum ether (b.p. 60–70°). The petroleum ether extract was washed twice with 25 ml. of 1 *N* hydrochloric acid and then with 25 ml. of water. The extracts were dried over magnesium sulfate and the solvent was removed on the rotary evaporator. The residue was twice extracted with 10 ml. of petroleum ether (b.p. 30–40°) and the petroleum ether removed on the rotary evaporator. Flash distillation of the residue gave 1.7 g. of *trans*-3-penten-1-yl tosylate, b.p. 140° (~1 mm.).

The n.m.r. spectrum of this compound (Figure 1) showed no absorption due to impurities. The measurement of the rate of solvolysis showed no deviation from linearity up to 85% solvolysis.

cis-3-Penten-1-yl Tosylate. The procedure was identical with that for the isomeric *trans* compound except that 0.50 g. (0.0058 mole) of *cis*-3-penten-1-ol was

(20) Koji Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

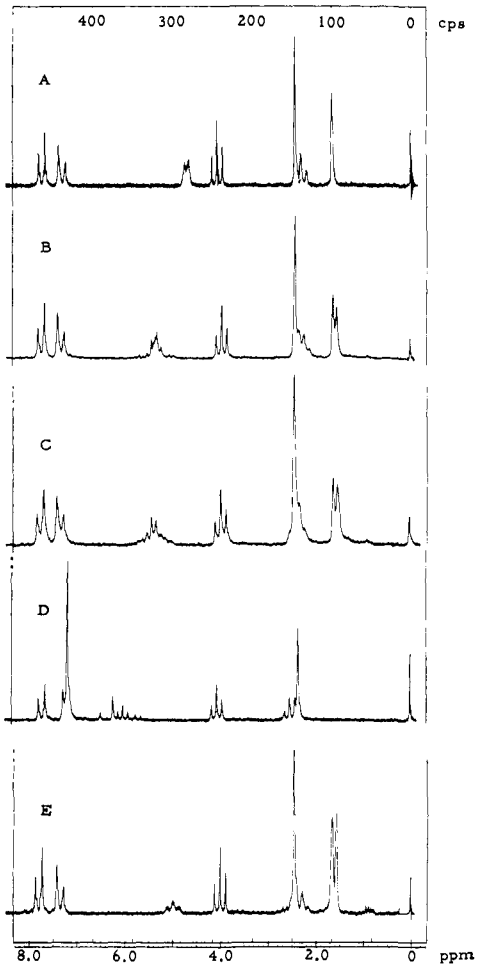


Figure 1. 60-M.c.p.s. H^1 nuclear magnetic resonance spectrum of (a) (β-methylallyl)carbinyl tosylate, (b) *trans*-3-penten-1-yl tosylate, (c) *cis*-3-penten-1-yl tosylate, (d) *trans*-4-phenyl-3-buten-1-yl tosylate, and (e) 4-methyl-3-penten-1-yl tosylate.

used with 1.06 g. (0.0059 mole) of *p*-toluenesulfonyl chloride. Bulb-to-bulb distillation gave 0.7 g. of *cis*-3-penten-1-yl tosylate, b.p. 140° (~1 mm.).

The n.m.r. spectrum of this compound (Figure 1) shows only one minor impurity peak at 0.9 p.p.m. The nature of this minor impurity is not known. The presence of this impurity did not interfere with the determination of the rate of solvolysis. The plot for the rate of solvolysis of this compound was linear up to 70% conversion.

4-Phenyl-3-buten-1-ol. In a 1-l. three-necked flask equipped with a stirrer, thermometer, and an addition funnel were placed 6.5 g. of magnesium and 400 ml. of freshly dried tetrahydrofuran. A Grignard reaction was started by adding 0.5 ml. of methyl iodide and heating to 50°. The solution was then cooled to 25° and a solution of 50.0 g. of freshly distilled β-styryl bromide in 100 ml. of tetrahydrofuran was added at such a rate to maintain the temperature at 30°. After the addition was complete, the mixture was heated at 50° for 5 min. and then cooled to 20°. To the cooled solution was added 20 g. of ethylene oxide in 100 ml. of tetrahydrofuran. The solution was stirred for 30 min. and then hydrolyzed with saturated ammonium chloride solution. The solution was filtered and the residue washed with two 50-ml. portions of tetrahydrofuran. The filtrate was evaporated on the rotary evaporator. The residue was distilled through a 5-cm. Vigreux column. After a low-boiling forerun, 24.8 g. of material, b.p. 142° (12 mm.), was obtained. This distillate was redistilled through a 20-cm. wire-spiral column to give 20.2 g. (55% yield) of 4-phenyl-3-buten-1-ol, b.p. 99–103° (2 mm.). The n.m.r. spectrum of the compound was consistent with the assigned structure.

The *cis* and *trans* isomers were separated by preparative v.p.c. on the Autoprep using a 20-ft. S.E.-30 column at 170°. The structural assignment was based on analysis of infrared spectra of the 650–1000-cm.$^{-1}$ region.[21]

trans-4-Phenyl-3-buten-1-yl Tosylate. To 0.90 g. (0.0061 mole) of *trans*-4-phenyl-3-buten-1-ol in 4 g. of pyridine cooled to 0° was added 1.1 g. (0.0062 mole) of *p*-toluenesulfonyl chloride. The mixture was allowed to stand at 0° for 1 day and then at room temperature for 2 hr. The solution was diluted with 100 ml. of petroleum ether (b.p. 30–40°) and then twice extracted with 25 ml. of 1 *N* hydrochloric acid and 25 ml. of water. The petroleum ether solution was dried over magnesium sulfate and evaporated on the rotary evaporator. The residue was twice extracted into the minimal amount of petroleum ether (b.p. 30–40°) and the ether removed on the rotary evaporator. Low-temperature recrystallization from 50:50 ether–petroleum ether gave white crystals. Three fractions of m.p. 49.8–51.2°, 50.2–51.4°, and 42.2–45.4°, respectively, were obtained by successive recrystallization. The n.m.r. spectra of the first two fractions were consistent with the assigned structure.

Since the n.m.r. spectrum of the second fraction (Figure 1) showed no detectable absorptions due to impurities, this fraction was used for determination of the solvolytic rate constant. The rate of solvolysis of this compound showed no deviation from linearity up to 75% solvolysis.

4-Methyl-3-penten-1-ol. To 2.5 g. of lithium aluminum hydride in 200 ml. of ether was added a solution of 6.0 g. of 4-methyl-3-pentenoic acid (prepared by Dr. C. Rüchardt) in 50 ml. of ether over a 2-hr. period. The solution was stirred an additional hour after the addition was complete and then hydrolyzed with saturated ammonium chloride solution. The ether layer was decanted off and the residue washed twice with ether. The combined ether fractions were dried over sodium sulfate and the ether removed on the rotary evaporator. The residue was distilled through a 5-cm. Vigreux column to give 4.18 g. of 4-methyl-3-penten-1-ol, b.p. 88–90° (60 mm.). The 4-methyl-3-penten-1-ol was further purified by preparative v.p.c. on the Megachrom using eight 6-ft. TCEP columns.

4-Methyl-3-penten-1-yl Tosylate. To 1.05 g. (0.0105 mole) of 4-methyl-3-penten-1-ol in 4 g. of pyridine cooled to 0° was added 1.92 g. (0.0108 mole) of *p*-toluenesulfonyl chloride. The mixture was allowed to stand for 1 day at 0° and then 2 hr. at room temperature. The mixture was extracted with 75 ml. of petroleum ether (b.p. 60–70°). The petroleum ether extract was washed twice with 25 ml. of 1 *N* hydrochloric acid and then with 25 ml. of water. The

(21) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

extract was dried over magnesium sulfate and the solvent was removed on the rotary evaporator. The residue was twice dissolved in 10 ml. of petroleum ether (b.p. 30–40°) and the petroleum ether removed on the rotary evaporator. Attempts to distill a portion of the residue at reduced pressure led to decomposition. The remainder of the residue was heated at ~50° under reduced pressure for 5 min. and gave 1.5 g. of 4-methyl-3-penten-1-yl tosylate.

This compound could not be obtained in crystalline form. The purity was established by examination of the nuclear magnetic resonance spectroscopy. The n.m.r. spectrum (Figure 1) shows only one minor absorption due to an impurity at 0.9 p.p.m. The absence of other absorptions which could be ascribed to impurities and the location of the resonance suggests that it may be due to a high-boiling hydrocarbon. An equivalent quantity of petroleum ether was evaporated to dryness (1 hr. at ~50° and 20 mm.) on the rotary evaporator and the flask rinsed with 1 ml. of ethanol-free chloroform. The n.m.r. spectrum of the chloroform solution showed an absorption at 0.9 p.p.m. (The same absorption was detected in the n.m.r. spectrum of *cis*-3-penten-1-yl tosylate.)

The high reactivity of 4-methyl-3-penten-1-yl tosylate made the measurement of the rate of solvolysis somewhat difficult. (The half-life is less than 1 min. at 50° in 98% formic acid.) However, the absence of any detectable deviation from linearity in the rate of solvolysis further substantiates its purity.

Nuclear Magnetic Resonance Spectroscopy. Studies of 1,1,4,4-Tetrafluoro-1,3-alkadienes[1]

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1,1,4,4-Tetrafluoro-1,3-butadiene is indicated by dipole moment studies to exist in the s-trans conformation. The ^{19}F–^{19}F spin–spin coupling constants for this compound are surprisingly similar to those of bis-4,5-(difluoromethylene)cyclohexene and perfluoro-1,2-dimethylenecyclobutane, both of which substances have their double bonds held in s-cis configurations. The results are related to the mechanism of transmission of fluorine–fluorine spin–spin interactions and are inconsistent with a predominance of a "through-space" mechanism of coupling.

Introduction

The conformational *s-cis–s-trans* equilibria of 1,3-butadienes have been investigated by a number of techniques. Detailed studies of the infrared and Raman spectra and extensive calorimetric measurements have indicated that 1,3-butadiene exists predominantly (at least 96%) in the *s-trans* form at room temperature.[2-5] Substituted butadienes have received less attention. Microwave studies of 2,3-dimethyl-1,3-butadiene, isoprene, and fluoroprene provide no evidence for the presence of more than a few per cent of the *s-cis* form.[6,7] 2,3-Di-*t*-butyl-1,3-butadiene has been reported to exist in a non-*transoid* conformation as a result of steric interactions of the bulky *t*-butyl groups.[8]

From the intensities of ultraviolet absorptions, it has been concluded that the double bonds in 2,4-dimethyl-1,3-pentadiene and 2-chloro-4-methyl-1,3-pentadiene deviate some 50° from planar, while with 1,1,-4,4-tetrachloro-1,3-butadiene the favored conformation is >70° from planar.[9] Infrared and Raman studies indicate that chloroprene, 2,3-dichloro-1,3-butadiene, and isoprene exist predominantly in the *s-trans* form while hexachloro-1,3-butadiene has a preferred nonplanar conformation.[10] From analysis of the infrared and Raman spectra and the polarization ratios of the stronger Raman lines of hexafluoro-1,3-butadiene, Nielsen and Albright concluded that "the spectral data are inconsistent with the assumption of molecular symmetry C_{2h} (*trans* form) but can be interpreted satisfactorily on the basis of symmetry C_{2v} (*cis* form)."[11]

The report by Anderson, Putnam, and Sharkey[12] that the 40-Mc.p.s. fluorine nuclear magnetic resonance of 1,1,4,4-tetrafluoro-1,3-butadiene (I) exhibits a broad (~160 c.p.s.) but unresolvable band which at temperatures of −80 to −120° sharpens somewhat suggests the possibility that conformational equilibrium between the *s-trans* form (Ia) and *s-cis* form (Ib) might be only slowly established, the broad band being the result of slow exchange of the fluorine nuclei between magnetically nonequivalent environments in Ia

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