Cyclopropylcarbinyl *p*-Toluenesulfonate Solvolysis. III. 1-*p*-Anisyl Substituent Effect[1]

DONALD D. ROBERTS

Department of Chemistry, Louisiana Polytechnic Institute, Ruston, Louisiana 71270

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Solvolysis rates of 1-*p*-anisylcyclopropylcarbinyl tosylate (**6**) have been determined in a series of solvents of varying ionizing strength. The solvolysis of **6** relative to cyclopropylcarbinyl tosylate (**1**) is only slightly accelerated. The solvolytic reactivity of allylcarbinyl tosylate, the homoallylic isomer of **1**, demonstrates a similar insensitivity to substitution at the 3 position. In addition, both the cyclopropylcarbinyl and allylcarbinyl series yield the same cyclobutyl solvolysis products. The implications of this solvolytic behavior are discussed in terms of similar neighboring-group participation in the transition state. An analysis of the partitioning of the activation parameters lends further support to the transition-state speculation.

The work reported in this series of papers[2] has clearly established that cyclopropylcarbinyl tosylate (**1**) suffers solvolysis without responding to 1-ring substitution. Various explanations have been advanced to explain this unpredicted result.[3] These explanations tend to rationalize the apparent insensitivity of a phenyl substituent to charge development on a neighboring carbon in terms of a balance between the rate accelerating conjugative effect and the rate-retarding inductive effect. More specifically, it has been argued that (1) the geometry of the reacting molecular orbitals in the transition state is unfavorable to maximization of the phenyl ring conjugative effect while the inductive effect is stereoelectronically independent and (2) the orbitals involved in the cationic portion of the transition state structure promote a bonding intermediate between σ and π types resulting in a near balance of the phenyl group electron-donating effect (conjugatively *via* π interaction) and the electron-withdrawing effect (inductively *via* σ interaction).

A related explanation[2a,b] was also advanced where it was suggested that extension of the delocalized charge structure to include both the phenyl π bond and the cyclopropane τ bond network was prohibited because of unfavorable orbital geometry. It was further suggested, based principally upon product structure and to a lesser extent upon solvent effect studies, that a transition-state structure was favored where the charge was localized at the methinyl carbon.

As a further test of these explanations, the solvolytic reactivity of 1-*p*-anisylcyclopropylcarbinyl tosylate was investigated. The greatly enhanced ability of a *p*-anisyl group to assist ionization is well established;[4-6] therefore, it is to be expected that the *p*-anisyl substituent would be a significantly more sensitive probe for charge distribution in the transition state than the phenyl substituent.

(1) This work was supported in part by the Petroleum Research Fund of the American Chemical Society. This support is gratefully acknowledged.

(2) (a) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964); (b) D. D. Roberts, *ibid.*, **30**, 23 (1965); (c) D. D. Roberts, *ibid.*, **31**, 2000 (1966).

(3) (a) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 4; (b) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965); (c) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (d) M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967); (e) Z. Majerski, M. Nikoletic, S. Borcic, and D. E. Sunko, *ibid.*, **23**, 661 (1967); (f) C. D. Ritchie in "Carbonium Ions," G. A. Olah and P. R. Schleyer, Ed., Interscience Publishers, Inc., New York, N. Y.

(4) For example *p*-methoxyneophyl tosylate suffers acetolysis 118 times faster than neophyl tosylate[5] and 2-*p*-anisyl-2-propyl chloride undergoes solvolysis about 3400 times faster than 2-phenyl-2-propyl chloride.[6]

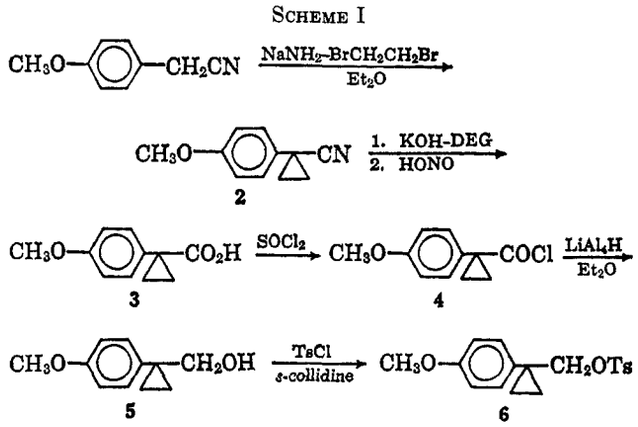
(5) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 618 (1961).

(6) H. C. Brown, and Y. Okamoto, *ibid.*, **79**, 1914 (1957).

Synthetic Procedures and Experimental Results

The synthesis of 1-*p*-anisylcyclopropylcarbinyl tosylate was accomplished as shown in Scheme I. The

SCHEME I



preparation of **2** by the method employed for the synthesis of 1-phenylcyclopropylcarbonitrile was attended with difficulty; only trace quantities of 1-*p*-anisylcyclopropylcarbonitrile were obtained. Modification of the reaction conditions, based upon the extensive alkylation work of Hauser, *et al.*,[7] gave **2** in 45% yield. The remaining compounds, **3**-**6**, were obtained in high yield by the procedure[2a] developed for the preparation of 1-phenylcyclopropylcarbinyl tosylate.

The kinetic data are summarized in Table I. Each of these esters was allowed to solvolyze in the indicated solvent and the course of reaction was followed by titrating the liberated *p*-toluenesulfonic acid. All reactions were strictly first order in *p*-toluenesulfonate up to at least 80% conversion and furnished, within experimental error,[8] 100% of the theoretical amount of acid present. That 1-ring-substituted cyclopropylcarbinyl tosylates solvolyze by a SN1-type mechanism has been well established[2b] and evidence[9] has also been presented in support of a SN1 mechanism for the formolysis of allylcarbinyl tosylate (**7**). The use of formic acid, 0.08 *N* in lithium formate, should introduce less than 5% SN2 reaction of the tosylate with formate ion, based on the study of Roberts.[9]

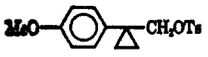
(7) For example, see C. R. Hauser and W. R. Bracken, *J. Amer. Chem. Soc.*, **78**, 494 (1956).

(8) The solvolysis of 3-phenyl-3-buten-1-yl tosylate at 80° liberated 87% of theoretical amount of acid after 20 half-lives. The *p*-toluenesulfonic acid catalyzed addition of solvent to the disubstituted alkene bond[3b] would lead to the less reactive saturated ester.

(9) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

TABLE I

SUMMARY OF SOLVOLYSIS RATES FOR ORGANIC TOSYLATES

Compound	Solvent	Temp, °C	k_1,[a] 10^5 sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
	AcOH	15.0	18	19.9	−6.3
		20.0	33		
		25.0	62		
		30.0	106		
	Sulfolane[b]	30.0	8.3	19.5	−13.1
		40.0	22		
		50.0	68		
	EtOH	20.0	8.0	22.0	−2.1
		30.0	29		
		40.0	95		
	DMSO[c]	20.0	20	17.9	−14.5
		30.0	59		
		40.0	147		
CH_2=$CHCH_2CH_2OTs$	HCO_2H[d]	50.0	0.35	23.2	−11.9
		60.0	1.00		
		70.0	3.20		
		80.0	8.00		
CH_2=$CPhCH_2CH_2OTs$	HCO_2H[d]	50.0	2.0	20.8	−15.9
		60.0	5.8		
		70.0	14.0		
		80.0	20.0[e]		

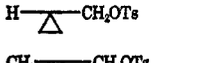
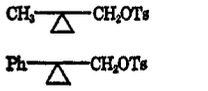
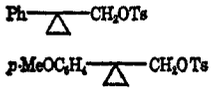
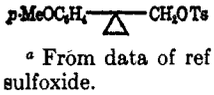
[a] The uncertainties varied from 0.6 to 1.6 standard deviation units from the mean. [b] Tetramethylene sulfone. [c] Dimethyl sulfoxide. [d] Contained 0.08 *N* HCO_2Li. [e] Value not included in activation parameter calculations.

Discussion

Table II compares the relative rates of several selected tosylates in carboxylic acid solvents. It is readily apparent that *p*-anisyl substitution at the 1-ring position has substantially no greater influence than

TABLE II

RELATIVE ACETOLYSIS RATES AT 30°[a]

Compound	AcOH	Sulfolane[b]	EtOH	DMSO[c]
	1.0	1.0	1.0	1.0
	4.9		4.0	
	2.0	8.5	0.8	1.1
	3.1	13.7	2.5	3.0

[a] From data of ref 2. [b] Tetramethylene sulfone. [c] Dimethyl sulfoxide.

phenyl on the solvolytic reactivity of cyclopropylcarbinyl tosylate. The finding is even more marked when one notes the small variation of the relative rates over the range of solvents. This result clearly rules out any significant localization of charge at the methinyl carbon in the transition state and implies that the transition state must have little resemblance to the 1-arylcyclobutyl cationic intermediate suggested by the exclusive formation of ring-expanded products.

Furthermore, in view of the near insensitivity of the solvolysis rate to effects of substituents varying over a wide range of charge stabilizing ability,[10-12] to argue that the absence of substituent effect for all three groups is due to a balance in the rate-retarding and rate-accelerating interaction mechanisms would seem to be too coincidental.

For the limiting type of solvolysis reactions of unsubstituted cyclopropylcarbinyl derivatives, a single transition-state structure, similar to the bicyclobutonium ion, accounts for both the kinetic and product distribution data.[13] On the other hand, with substituted cyclopropylcarbinyl derivatives, the kinetic and product distribution data[2,3b-e] support considerable structural reorganization between the transition state and the cationic intermediate eventually captured by solvent.

In this connection, it is interesting to examine the influence of substitution on the solvolytic reactivity of allylcarbinyl tosylate. The small rate-accelerating effect of a γ-methyl group (see Table III) relative to a δ-methyl group, as noted by Roberts and Servis,[3b] implies less charge development at the γ position in the transition state,[14] and is compatible with a homoallyl-like[15] transition-state structure. Consistent with this proposed transition state is the finding of this study that a γ-phenyl substituent compared to a δ-phenyl substituent exerts a similar small rate-accelerating effect on the solvolytic reactivity of allylcarbinyl tosylate.

TABLE III

RELATIVE FORMOLYSIS RATES AT 50°

Compound	$k_1 \times 10^4$, sec^{-1}	k_{rel}
CH_2=$CHCH_2CH_2OTs$	0.035	1.0
	0.031[a]	
	0.014[b]	
CH_2=$C(Me)CH_2CH_2OTs$	0.043[b]	3.3
CH_3CH=$CHCH_2CH_2OTs$	0.61[b]	45
CH_2=$C(Ph)CH_2CH_2OTs$	0.20	5.7
$PhCH$=$CHCH_2CH_2OTs$	2.1[a]	96

[a] Taken from data in ref 3b, determined in 98% formic acid. [b] Taken from data in ref 3b, determined in 98% formic acid containing 10% pyridine.

Although the homoallyl-like transition state satisfactorily accommodates the kinetic data, the almost exclusively ring-expanded products from the formolysis of both 3-methyl and 3-phenyl-3-buten-1-yl tosylates (see Table IV) demand that the cationic intermediate, captured by the solvent, involve appreciable 1,4 interaction with concomitant localization of charge at the methinyl carbon. These structural requirements are conveniently illustrated by Figure 1. The intervening intermediate(s) I represents a structural reorganization continuum varying from predominantly 1,3 interaction (T_1) to predominantly 1,4 interaction (T_2).

Failure of the solvent to capture effectively an intermediate with 1,3-interaction geometry supports the presence of the currently recognized,[16] stepwise

$$ROTs \rightleftharpoons \underset{a}{R^+OTs^-} \rightleftharpoons \underset{b}{R^+ + OTs^-}$$

ionization mechanism. With bridged ions, the back side of the initially formed ion pair, a, is protected, in addition to the front side; consequently, to the extent that poorly dissociated ionic intermediates intervene between the two transition states, progress along the reaction coordinate to T_2 is more favorable than reaction with solvent.

(10) The relative solvolysis rates of primary tosylates[6,11] $R(Me)_2CCH_2OTs$ for the R groups are Me (1.0), Ph (460), *p*-anisyl (54,000); and for the related tertiary series,[6,12] $R(Me)_2CCl$, are Me (1.0), Ph (620), *p*-anisyl 2×10^6.

(11) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 113 (1952).

(12) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(13) For a review, see ref 3f.

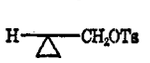
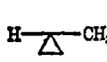
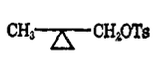
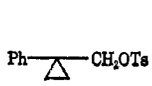
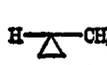
(14) However, see ref 3b and 3d for a discussion concerning the extension of substituent effects in classical ion formation to nonclassical ion formation.

(15) S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.*, **81**, 4399 (1959).

(16) S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, *ibid.*, **83**, 4986 (1961).

TABLE IV

SOLVOLYSIS PRODUCTS

Compound	Solvent	Products		
	AcOH[a]	 71%	 24%	CH_2=$CHCH_2CH_2OAc$ 8%
	AcOH[b]		 100%	
	AcOH[c]		 100%	
CH_2=$CHCH_2CH_2OTs$	HCO_2H[d,e]	 45%	 45%	CH_2=$CHCH_2CH_2OH$ 10%
CH_2=$C(Me)CH_2CH_2OTs$	HCO_2H[d,f]		 96.7%	CH_2=$C(Me)CH_2CH_2OH$ 2.3%
CH_2=$C(Ph)CH_2CH_2OTs$	HCO_2H[d]		 >97%	

[a] Taken from data in ref 2a. [b] Taken from data in ref 2c. [c] From data of ref 21. [d] Formate ester hydrolyzed to alcohol. [e] Taken from data of ref 9. [f] Taken from data of ref 3b.

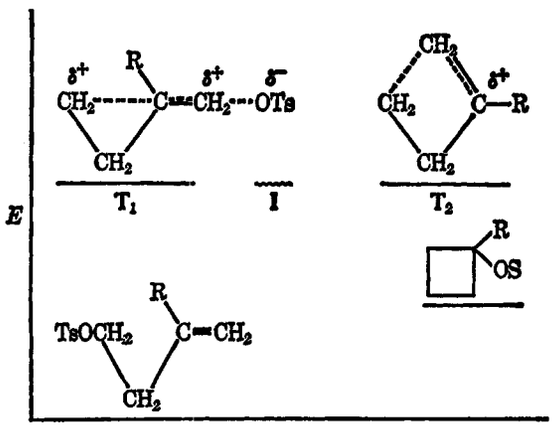
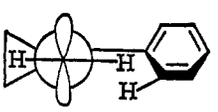


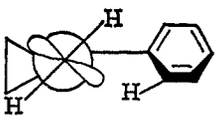
Figure 1.

The effects of 1-ring substitution in the cyclopropylcarbinyl series parallel the effects of similar structural change in the allylcarbinyl series. This correlation between the two series of homoallylic isomers suggests that the effects of 1-ring substitution in the cyclopropylcarbinyl tosylates may be explained by a reaction mechanism similar to that shown in Figure 1. Again, the transition-state structure is stabilized by homoallyl-like neighboring-group assistance. Then, further progress along the reaction coordinate with consequent greater structure reorganization and localization of charge at the methinyl carbon leads to the cationic intermediate eventually captured by solvent (see Table IV).

An examination of framework molecular orbital models of the 1-phenylcyclopropylcarbonium ion gives further support to the speculation that the character of the transition state is influenced by substitution. If the conformation with the phenyl plane bisecting the three-membered ring is energetically most favorable,[17] then symmetrical homoallylic interaction (8) is accompanied by nonbonded steric strain between an *o*-hydrogen and a σ-hydrogen bond. The nonbonded steric strain, however, is relieved with unsymmetrical homoallylic interaction (9).



8

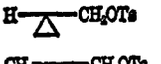
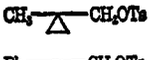
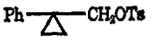
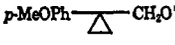


9

Finally, it is pointed out that, in a limiting type of solvolysis of cyclopropylcarbinyl tosylate, the partitioning of the activation parameters is greatly influenced by 1-ring substitution. The ΔS^* values for all of the 1-ring-substituted compounds recorded in Table V are within experimental error equal to -5.4 eu, contrasting with the -19-eu value for the unsubstituted compound. The fact that 1-ring substitution is distinguished from nonsubstitution by such an entropy change supports a transition state with significantly less molecular reorganization for the 1-ring-substituted compounds. The fact that the entropy value is not sensitive to the considerable steric bulk difference of the methyl and the *p*-anisyl group argues against the meaningful influence of steric hindrance to solvation.

TABLE V

SUMMARY OF ACTIVATION PARAMETERS FOR ACETOLYSIS REACTIONS OF ORGANIC TOSYLATES

Compound	ΔH^*, kcal/mol	ΔS^*, eu
	16.7	−19
	20.1	−5.2
	21.0	−4.2
	19.9	−6.3

Experimental Section

All boiling points are uncorrected for stem exposure. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using sodium chloride optics. A F & M Model 700 gas

(17) (a) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (b) G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965).

chromatographic instrument equipped with a hydrogen flame ionization detector was used for this work. All microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

1-p-Anisylcyclopropylcarbonitrile (2) was prepared several times. In a typical run, p-methoxyphenylacetonitrile (Aldrich Chem. Co., 14.7 g, 0.1 mol) was added all at once to a stirred suspension of sodium amide (8.6 g, 0.22 mol) in 200 ml of dry ether. After stirring for 2 hr at reflux temperature, 300 ml of dry ether was added followed by the rapid addition of ethylene bromide (18.8 g, 0.1 mol). The brown mixture was stirred at reflux temperature for 20 hr; then 200 ml of crushed ice was added. The flocculent precipitate was filtered out and the filtrate was washed twice with cold, dilute HCl (100-ml portions), three times with cold water (75-ml portions), dried (Na_2SO_4), concentrated, and distilled giving 8.0 g (45%) of the nitrile **2**: bp 112–113° (0.1 mm); $n^{25}D$ 1.5400; ir (neat) 950 cm^{-1} (cyclopropane ring[18]). The glpc retention times (GE SE-30 on Celite, 180°) of **2** and p-methoxyphenylacetonitrile were different.

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.41; N, 8.10. Found: C, 76.20; H, 6.40; N, 8.22.

1-p-Anisylcyclopropanecarboxylic Acid (3).—A solution of the nitrile, **2** (41 g, 0.24 mol), in 50 ml of diethylene glycol was added to a solution of potassium hydroxide (85%, 16.5 g, 0.25 mol) in 100 ml of diethylene glycol and refluxed for 3 days. After cooling, it was poured into cold, dilute HCl. The precipitated organic acid was separated by filtration and stirred with dilute HONO (generated by slow addition of aqueous NaONO to dilute HCl) for 1 hr. The resulting organic acid was collected by filtration, washed with water, and air dried to yield 40.0 g (87%) of crude acid (mp 120–124°). Four recrystallizations from 1:1 alcohol–water gave the analytical sample of the acid **3**, mp 129–130°.

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.72; H, 6.30. Found: C, 68.78; H, 6.45.

1-p-Anisylcyclopropylcarbonyl Chloride (4).—A solution of **3** (40.0 g, 0.21 mol) and 100 ml of thionyl chloride was refluxed for 3 hours. Distillation yielded 39.1 g (88%) of the chloride **4**: bp 106–107° (0.2 mm); $n^{25}D$ 1.5475; ir (neat), 1775 (acid chloride C=O), 960 cm^{-1} (cyclopropane ring[18]).

Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.76; H, 5.22; Cl, 16.80. Found: C, 63.02; H, 5.32; Cl, 16.68.

1-p-Anisylcyclopropylcarbinol (5) was prepared in 95% yield by lithium aluminum hydride reduction of **4**. Recrystallization from hexane yielded the pure alcohol **5**: mp 40–41°; ir (CCl_4), 3300 (OH), 1026 cm^{-1} (primary alcohol C–O).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.18; H, 7.92. Found: C, 73.85; H, 7.81.

1-p-Anisylcyclopropylcarbinyl p-toluenesulfonate (6) was prepared several times. In a typical run, 3.5 g (17 mmol) of recrystallized p-toluenesulfonyl chloride was added in 10 min to a solution of **5** in 10 ml of purified s-collidine maintained at 0° by an ice–water bath. After standing 20 min at 0°, the tan paste was hydrolyzed by rapid addition of 40 ml of cold, dilute HCl. The resulting ester was collected by filtration and washed several times with cold, dilute HCl, followed by water, and recrystallized from petroleum ether (bp 39.7–57°)–ethyl acetate to give the tosylate **6**: mp 53° dec; ir (CCl_4), 1358 (νSO_2 asymmetric), 1172 cm^{-1} (ν^{SO_2}, symmetric). The purity calculated from infinity titers of the solvolyses was 100% of theoretical (the tosylate was too unstable for combustion analysis).

Allylcarbinyl p-Toluenesulfonate (7).—Lithium aluminum hydride reduction of 15.0 g of 3-butenoic acid gave 8.0 g (63%) of allylcarbinol, bp 112–113° (lit.[9] bp 110–113°). The reaction of 1.46 g of allylcarbinol with 4.2 g of p-toluenesulfonyl chloride in s-collidine gave 2.5 g of the tosylate **7**: bp 139–140° (1.0 mm) [lit.[9] bp 150° (~6 mm)]; ir (neat) 1610 (C=C), 1360 (ν^{SO_2}, asymmetric), 1175 (ν^{SO_2}, symmetric), 900 cm^{-1} (CH_2=).

3-Phenyl-3-buten-1-ol was prepared in 30% yield by published procedure:[19] bp 82° (0.1 mm); $n^{20}D$ 1.5580 [lit.[19] bp 130–131° (13 mm); $n^{20}D$ 1.5581]; ir (neat) 3330 (OH), 1630 (C=C), 1045 (RCH_2OH), 890 cm^{-1} (CH_2=). Analysis by glpc revealed the presence of only trace quantities of 3-phenyl-2-buten-1-ol.

3-Phenyl-3-buten-1-yl p-Toluenesulfonate.—To 2.96 g (20 mmol) of 3-phenyl-3-buten-1-ol in 15 ml of s-collidine cooled to 0° was added 4.19 g (22 mol) of p-toluenesulfonyl chloride. The mixture was allowed to stand at 3° for 1 day then hydrolyzed with 40 ml of cold, 3 *N* HCl. The precipitated oil was taken up in 40 ml of methylene chloride, washed twice with cold, dilute HCl (40-ml portions) and twice with cold water (40-ml portions), dried (Na_2SO_4–$NaHCO_3$), and concentrated to yield an oil. The crude ester was dissolved in hot petroleum ether (bp 39.7–57°) and cooled to −78°. The solvent was removed from the precipitated ester by decantation and flash distillation under reduced pressure (*ca.* 0.1 mm) to yield 5.0 of an oil. The purities, calculated from infinity titers of the formolyses, ranged from 93 to 96%. The infrared spectrum [ν^{SO_2} (asymmetric) 1360 cm^{-1} and ν^{SO_2} (symmetric) 1177 cm^{-1}] was consistent with the assigned structure.

Rate measurements were accomplished by the usual technique.[2] The titrating solutions were, for reaction in sulfolane, ethanol, and dimethyl sulfoxide, 0.020 *N* sodium hydroxide and, for acetolysis and formolysis, 0.050 *N* sodium acetate in acetic acid. The indicators used were bromthymol blue and bromphenol blue, respectively. The end point in the formolyses was improved by diluting a 2-ml aliquot with 5 ml of purified dioxane and titrating to a bromcresol green end point.

Solvents.—Sulfolane was purified by redistillation just prior to use. Dimethyl sulfoxide was purified by drying over calcium hydride and distillation. Absolute ethanol was prepared according to the method of Fieser.[20] Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride. Formic acid solvent was dried over boric anhydride, decanted, and distilled from fresh anhydride.

Treatment of Kinetic Data.—The activation parameters were obtained by IBM 1620 computer regression analysis of ln (k/T) *vs.* 1/T.

Product Studies.—A solution (50 ml) of 3-phenyl-3-buten-1-yl tosylate (7 mmol) in formic acid containing lithium formate (12.5 mmol) was thermostated at 50° for 27 hr. The material was added to ice water (200 ml) and extracted three times with ether (50-ml portions). The ether extract was shaken with powdered sodium bicarbonate until neutral, dried (Na_2SO_4), and concentrated to yield 1.1 g (89%) of an oil. Analysis by glpc (6-ft sucrose acetate–isobutyrate column at 170°) revealed the presence of a single major peak accounting for more than 97% of the chromatogram area. The infrared spectrum had a strong carbonyl band at 1710 cm^{-1} and was transparent in the 1620–1650-cm^{-1} region. The formolysis product was hydrolyzed with dilute sodium hydroixde and extracted with ether. Analysis of the concentrated ether extract by glpc (sucrose acetate isobutyrate at 120°) revealed, other than trace peaks, a single product peak with a retention time identical with that of authentic 1-phenylcyclobutanol.[21]

Registry No.—**1**, 1015-45-8; **2**, 16728-00-0; **3**, 16728-01-1; **4**, 16728-02-2; **5**, 16728-03-3; **6**, 16728-4-4; **7**, 778-29-0; 3-phenyl-3-buten-1-yl p-toluenesulfonate, 16728-06-6.

(18) The characteristic cyclopropane ring absorption band at approximately 1025 cm^{-1} is obscured by a strong absorption band present in the spectrum of p-methoxyphenylacetonitrile. The latter compound is transparent in the 1000–850-cm^{-1} region.

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(20) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 285.

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