1965

Solvolyses of cyclopropyl p-toluenesulfonates

Larry Gene Schnack
Iowa State University

SOLVOLYSES OF CYCLOPROPYL p-TOLUENESULFONATES

by

Larry Gene Schnack

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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INTRODUCTION

Often the object of a study or a series of studies is to detect trends in the data so that the overall picture may lead to predictions and give reasons for the regularity or irregularity in these tendencies. Those studies which prove to be at an extreme end of a trend are sometimes the most valuable but are often those which are the most difficult to undertake. For example, any consideration of ring compounds should find the cyclopropyl analog at the extreme end of any trend as the smallest member to consider.

One of the most important and interesting tools of the Organic chemist has been the solvolysis reaction. Many chemical predictions are presently being made on the basis of relative rates and product distributions in these reactions. However, not until the recent availability of various substituted cyclopropanols has the three membered ring been made amenable to an extensive study in this area.

The purpose of this paper is to report the results of a kinetic study of the solvolyses of a variety of substituted cyclopropyl p-toluenesulfonates and to propose a reasonable mechanism and transition state for the reaction. These results, along with other available data, will be used to

describe the stereochemistry of the ring opening process in cyclopropyl compounds. This in turn will be used to predict the stereochemistry of some molecules whose stereochemistry is at present unknown.

HISTORICAL

The solvolysis reaction, which has long been one of the Organic chemists most illuminating tools, can be defined as a displacement reaction,

$$SOH + R\text{-}Y \longrightarrow R\text{-}OS + HY,$$

in which a bond between an atom in R and one in Y is replaced by a bond between an atom of a solvent molecule, SOH, and an atom in R. A portion of the substrate, R, may undergo rearrangement during the solvolysis process. This type of reaction has for years been described by the symbols SN1 and SN2 introduced by Hughes, Ingold and Patel.[1] These symbols more correctly represent the reaction mechanism. The SN1 mechanism is a unimolecular nucleophilic substitution,

$$R\text{-}X \rightleftharpoons R^{+} \qquad X^{-} \xrightarrow{SOH} \text{products},$$

unimolecular because the transition state involves only one molecule and nucleophilic substitution because the group which does the substituting, SOH, is a nucleophile and more specifically in solvolyses, a nucleophilic solvent molecule.

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[1]E. D. Hughes, C. K. Ingold and C. S. Patel, J. Chem. Soc., 526 (1933).

The SN2 mechanism can be defined in an exactly analogous manner.

By studying the solvolysis reaction it has been possible to gain insight into such diverse areas as structural effects on mechanism, electronic factors in transition states, solvent effects on reaction rates, the nucleophilicity of various solvent molecules, migratory aptitudes of adjacent groups, and neighboring group effects on rates. Streitweiser has written an excellent review article[2] on the solvolysis reaction, which was reprinted with a short supplement as a text.[3] A more recent book[4] on the solvolysis mechanism discusses the thermodynamic aspects of the reaction. Because of these excellent reviews no attempt will be made here to rewrite or even review the material from these texts. Instead, the more recent papers which relate more closely to, and are necessary in the discussion of, the present work will be reviewed.

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[2]A. Streitweiser, Jr., Chem. Rev., 56, 571 (1956).

[3]A. Streitweiser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill Book Co., Inc., New York, N.Y., 1962.

[4]E. R. Thornton, "Solvolysis Mechanisms", The Ronald Press Company, New York, N.Y., 1964.

As early as 1891 Gustavson[5] reported the extreme unwillingness of cyclopropyl compounds to undergo nucleophilic substitution. Cyclopropyl chloride, when treated with potassium hydroxide and silver ion in ethanol, gave only a 6.16% yield of silver chloride after seven hours at 100°C. This was shown to be comparable to the rate of reaction of 1-chloropropene under similar conditions. Perkin[6] has also discussed the reluctance of small ring compounds to undergo nucleophilic substitution.

Recently, more qualitative studies have been carried out on the cyclopropyl system. Roberts and Chambers[7] solvolyzed some cycloalkyl p-toluenesulfonates in dry acetic acid at 60°C. and found that the cyclobutyl and cyclopentyl p-toluenesulfonates solvolyzed 14 and 15 times faster, respectively, than cyclohexyl p-toluenesulfonate. However, the cyclopropyl p-toluenesulfonate solvolyzed with a relative rate of 2×10^{-5} that of the cyclohexyl p-toluenesulfonate. The solvolysis of the cyclopropyl compound required a

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[5] G. Gustavson, J. prakt. Chem., (2) 43, 396 (1891).

[6] W. H. Perkin, Jr., J. Chem. Soc., 65, 950 (1894).

[7] J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951).

temperature of 170°C. and the product was reported to be exclusively allyl acetate. While this rate appears to be quite slow, it can be argued[8] that this apparent lack of reactivity is deceiving. Cyclopropyl p-toluenesulfonate, with 60° internal angles, reacts almost 100 times faster than 7-norbornyl p-toluenesulfonate, with a 98.3° angle at the reaction site. The solvolysis of cyclopropyl derivates may, therefore, be anchimerically assisted[9] (accelerated by neighboring group participation[10]), since angle strain has an important bearing on the interpretation of solvolytic reactivities. Its influence, in fact, is demonstrated by the acetolysis at 25°C. of 2-adamantyl, 7-norbornyl, and cyclohexyl p-toluenesulfonates which give rates of 3.25×10^{-9}, 6.36×10^{-15}, and 4.88×10^{-8} sec.$^{-1}$, respectively. Thus, an increase in angle strain in passing from a tetrahedral ground state to a quasi-trigonal transition state is of primary importance in determining rate differences in these systems.

Recently, a more qualitative comparison of solvolysis

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[8] P. Schleyer and R. D. Nicholas, J. Am. Chem. Soc., 83, 182 (1961).

[9] S. Winstein, J. Am. Chem. Soc., 81, 6523, 6524 (1959).

[10] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, J. Am. Chem. Soc., 75, 147 (1953).

rates has been made possible via the introduction of semi-empirical relationships for calculating these rates.[11,12] Foote[11] prepared the first correlation between the acetolysis rates of many arenesulfonates, $R'RCHOSO_2Ar$, and the infrared carbonyl stretching frequencies of the corresponding ketones, $RCOR'$. The correlation was limited to saturated secondary arenesulfonates with two types specifically excluded: (1) compounds in which ground state eclipsing interactions are relieved in the solvolytic transition state (for example, cyclopentyl and endo-2-norbornyl[13] derivatives), and (2) compounds which have been shown to undergo anchimerically accelerated solvolysis (for example, exo-2-norboryl[13] and cyclobutyl[14] derivatives).

The equation,

$$\log k = -0.132(\nu - 1720),$$

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[11] C. S. Foote, J. Am. Chem. Soc., 86, 1853 (1964).

[12] P. Schleyer, J. Am. Chem. Soc., 86, 1854 (1964).

[13] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, J. Am. Chem. Soc., 74, 1127 (1952).

[14] H. C. Brown and G. Ham, J. Am. Chem. Soc., 78, 2735 (1956).

where k = the relative rate of acetolysis of cyclohexyl p-toluenesulfonate at 25°C., and ν = the carbonyl stretching frequency in cm.$^{-1}$, results from a least squares line through a plot of log k versus ν. Applying this equation to the acetolysis of cyclopropyl tosylate at 25°C. one would predict $k = 10^{-12.5}$. The observed relative rate at this temperature is $10^{-5.32}$. The $10^{7.2}$ factor between the two values is accorded by Foote to the sum of rate enhancements from anchimeric acceleration and steric effects (other than those of internal angle strain).

Schleyer's semiempirical correlation[15] related solvolysis rates by considering the effects of bond angle strain, torsional strain, and nonbonded interaction strain. The equation,

$$\log k = (1715-\nu)/8 + 1.32\sum_i(1 + \cos 3\phi_i) +$$

$$(\text{GS-TS strain})/1.36 + \text{inductive term},$$

is proposed. The carbonyl stretching frequency, ν, the average smaller torsional angle around each of the C-C bonds adjacent to the p-toluenesulfonate group, ϕ, ground state

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[15]P. Schleyer, J. Am. Chem. Soc., 86, 1854 (1964).

strain, GS, transition state strain, TS, and the rate relative to cyclohexyl p-toluenesulfonate, k, all appear in the equation. The bond angle strain term, $(1715-\nu)/8$, followed naturally from Foote's arguments involving changes in the hybridization on carbon. The next term, the torsional strain term, results from a consideration of the amount of eclipsing in the ground state. Thus, if total eclipsing by both groups adjacent to the carbon containing the p-toluenesulfonate group occurs ($\phi_1 = 0$ and $\phi_2 = 0$), as it does in cyclopropyl p-toluenesulfonate, the maximum value 5.3 is attained by the torsional strain term. This would correspond to a rate enhancement of $10^{5.3}$ over a compound such as cyclohexyl p-toluenesulfonate where $\phi_1 = 60^\circ$ and $\phi_2 = 60^\circ$. The non-bonded interaction strain term has a relatively small effect on the rate constant. The effect was evaluated by estimating ground state interactions of the p-toluenesulfonate group from conformational analogies or from experimental values and then deciding to what extent this nonbonded strain is decreased (or increased) in going to the transition state. One of the larger values, 0.95, for this term is given to endo-2-norbornyl p-toluenesulfonate from a non-bonded interaction of

1.3 kcal.[16]

For cyclopropyl p-toluenesulfonate $\nu = 1815$[17], ϕ_i = 0,0 and (GS-TS) = 0. Thus, by using Schleyer's equation the relative rate of acetolysis of cyclopropyl p-toluenesulfonate at 25°C can be calculated to be $10^{-7.2}$. This is almost 100 times slower than the relative rate actually observed, $10^{-5.3}$. It is interesting to recall here that the only product of the acetolysis was reported to be allyl acetate. This perhaps suggests an unusual or nonclassical transition state.

One of the more important, colorful, and closely followed chemical discussions, recently, has been over the legitimacy of invoking so-called non-classical ions for representing transition states of various reactions. Of special interest because of its relationship to possible intermediates to be discussed in this paper is the three-

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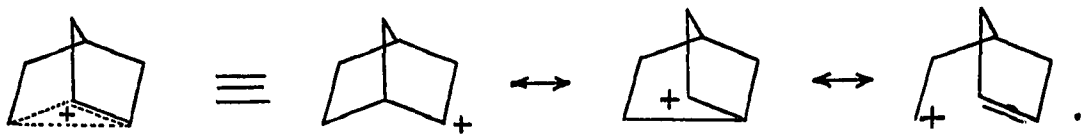
[16]C. F. Wilcox, Jr., M. Sexton and M. F. Wilcox, J. Org. Chem., 28, 1079 (1963).

[17]W. B. DeMore, H. D. Pritchard and N. Davidson, J. Am. Chem. Soc., 81, 5878 (1959).

centered non-classical norbornyl cation proposed[18,19,20] for the solvolysis of some norbornyl derivatives,



Three major categories of evidence have been used to justify the non-classical norbornyl cation's existence: (1) unusually fast rates, attributed to the formation of a highly stabilized cation[19]; (2) high exo/endo solvolytic rate ratios, attributed to carbon participation in the exo, but not in the endo derivative[20]; and (3) exo substitution, even in norbornyl derivatives containing gem-dimethyl groups in the 7-position, attributed to shielding of the endo direction

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[18]T. P. Neville, E. de Salas and C. L. Wilson, J. Chem. Soc., 1188 (1939).

[19]F. Brown, E. D. Hughes, C. K. Ingold and J. F. Smith, Nature, 168, 64 (1951).

[20]S. Winstein and D. Trifan, J. Am. Chem. Soc., 74, 1147, 1154 (1952).

by the non-classical bond.[21] Brown[22], however, has pressed strongly for a critical re-examination of the concept. Recently, in a series of communications[23,24] Brown has attacked the three categories of evidence in turn. Winstein, however, has since published a rebuttal.[25] Thus, acceptance or rejection of the non-classical cation in this system is still very much undecided.

Recently, Olah[26], in one of a series of papers on stable carbonium ions, has reported direct observation of the allyl and 2-methylallyl cations by using nuclear magnetic resonance techniques. It was reported that a surprisingly large amount of deshielding is experienced by the 2-proton in the allyl

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[21] S. Winstein and D. Trifan, J. Am. Chem. Soc., 74, 1147, 1154 (1952).

[22] H. C. Brown, "The Transition State", Special Publication No. 16, The Chemical Society, London, pp. 140-158, 174-178. 1962.

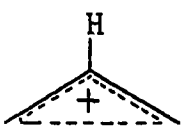
[23] H. C. Brown, J. Am. Chem. Soc., 86, 1246, 1247, 1248 (1964).

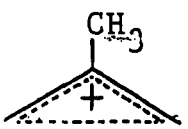
[24] H. C. Brown, J. Am. Chem. Soc., 86, 5003, 5004, 5006, 5007, 5008, 5010 (1964).

[25] S. Winstein, J. Am. Chem. Soc., 87, 376, 378, 379, 381 (1965).

[26] G. A. Olah and M. B. Comisaraw, J. Am. Chem. Soc., 86, 5682 (1964).

cation and by the 2-methyl protons in the 2-methylallyl cation. This observed deshielding, along with the quantum mechanical calculations of electron distribution of the allyl cation[27,28], indicate a strong contribution of 1,3-π-interactions. The following non-classical structures were suggested:





A three-centered non-classical cation should most appropriately appear as an intermediate or in the transition state of at least some cyclopropane reactions if it is to exist elsewhere. As pointed out earlier in this paper, however, cyclopropyl compounds have a great reluctance to undergo charge build up. Thus, it was rather surprising when Pettit[29] in an attempt to make the perinaphthenylium ion by

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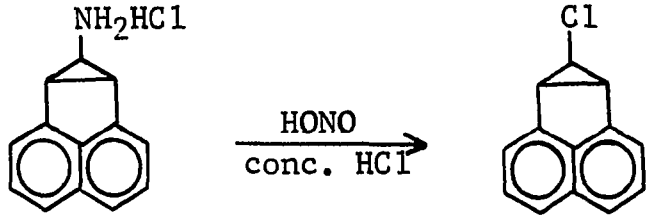
[27] D. M. Hirst and J. W. Linnett, J. Chem. Soc., 1035 (1962).

[28] M. Simonetta and E. Heibronner, Theoret. Chim. Acta (Berlin), 2, 228 (1964).

[29] R. Pettit, J. Am. Chem. Soc., 82, 1972 (1960).

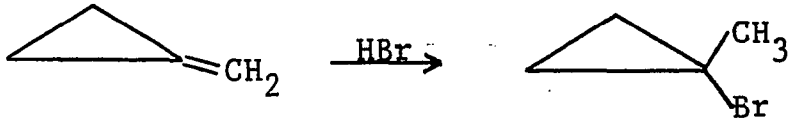
reacting 3'-amino-1:2-cyclopropanoacepaphthene with nitrous acid in concentrated hydrochloric acid isolated the corresponding chloride (eq. 1). Pettit rationalized this result



(1)

by an SNi mechanism since a carbonium ion most likely would have rearranged to the very stable perinaphthenylium ion.

Another anamolous result appeared recently in the low temperature addition of hydrogen bromide to methylene cyclopropane.[30] The only product of the reaction is reported to be 1-bromo-1-methylcyclopropane (eq. 2). In the same study,



(2)

however, the addition of hypobromous acid to methylene cyclo-

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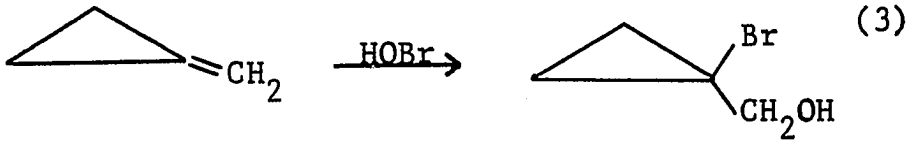
[30] B. C. Anderson, J. Org. Chem., 27, 2720 (1962).

propane was reported to give 1-bromocyclopropyl carbinol, the expected product for an ionic addition if a positive charge on methyl is more stable than on cyclopropane (eq. 3). Therefore, it seems reasonable in view of what has been



(3)

reported that the hydrogen bromide proceeds via some mechanism other than ionic.

Cyclopropane again demonstrated its reluctance to take on a positive charge when cyclopropyl bromide failed to react with potassium iodide in acetone even at 100°C., conditions which are generally considered forcing.[31]

The existence of the cyclopropyl carbonium ion, or even appreciable positive charge in the ring, has never been

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[31] J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951).

clearly demonstrated. The recent availability[32,33,34] of various substituted cyclopropanols, which could be converted to the corresponding p-toluenesulfonates, made an investigation of the electronic and steric effects in the solvolysis of cyclopropyl p-toluenesulfonates very promising. The possibility of demonstrating a cyclopropyl carbonium ion also seemed more likely than before. DePuy and Hausser[35] solvolyzed the p-toluenesulfonates of cis-2-phenylcyclopropanol, trans-2-phenylcyclopropanol, 1-methylcyclopropanol, and 1-phenylcyclopropanol. The rates of solvolysis of these compounds in dry acetic acid were determined by titrating the p-toluenesulfonic acid liberated. The 1-phenylcyclopropyl p-toluenesulfonate solvolysis rate was followed by nuclear magnetic resonance spectroscopy. The 1-substituted cyclopropyl p-toluenesulfonates were shown by nuclear mag-

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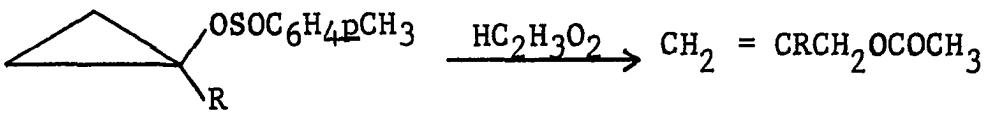
[32] C. H. DePuy, L. R. Mahoney and K. L. Eilers, J. Org. Chem., 26, 3616 (1961).

[33] C. H. DePuy, G. M. Dappen and R. A. Klein, J. Org. Chem., 27, 3742 (1962).

[34] C. H. DePuy, G. M. Dappen, K. L. Eilers and R. A. Klein, J. Org. Chem., 29, 2813 (1964).

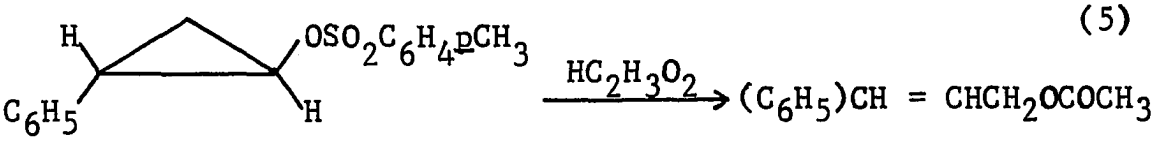
[35] C. H. DePuy and J. W. Hausser, Ames, Iowa. Private communication. 1962.

netic resonance spectroscopy to yield the corresponding 2-substituted allyl acetates (eq. 4). Both the cis- and trans-2-phenylcyclopropyl p-toluenesulfonates formed cinnamyl



(4)

acetate on solvolysis (eq. 5). When the 1-phenylcyclopropyl p-toluenesulfonate was solvolyzed for 15 minutes at 90°C in



(5)

dry acetic acetic it gave 67.5% of 2-phenylallyl p-toluenesulfonate and 32.5% of 2-phenylallyl acetate (eq. 6). The 2-phenylallyl p-toluenesulfonate was described as being a product of ion pair return.[36] The corresponding cyclopropyl

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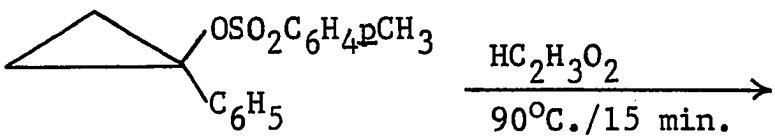
[36] S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, J. Am. Chem. Soc., 76, 2597 (1954).



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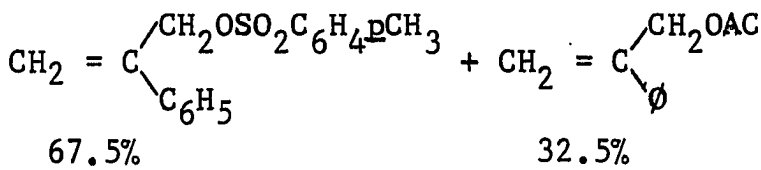

acetates were shown to be stable to the reaction conditions, but attempts to isolate and identify these acetates from the solvolysis products were unsuccessful by both nuclear magnetic resonance spectroscopy and vapor phase chromatographic techniques. A possible special salt effect[37] was investigated, but only a normal salt effect was shown to be present. The reactions were shown to follow first order kinetics. The rates of solvolysis in dry acetic acid at 123°C. relative to the unsubstituted compound were 21.5, 304, 340 and 112,000 for the p-toluenesulfonates of cis-2-phenylcyclopropanol, trans-2-phenylcyclopropanol, 1-methylcyclopropanol and 1-phenylcyclopropanol, respectively (Table 1).

A better look at the transition state in cyclopropyl

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[37] S. Winstein and G. C. Robinson, J. Am. Chem. Soc., 80, 169 (1958).

Table 1. Rates and thermodynamic data for the solvolyses of some cyclopropyl p-toluenesulfonates in 0.04M $NaC_2H_3O_2/HC_2H_3O_2$

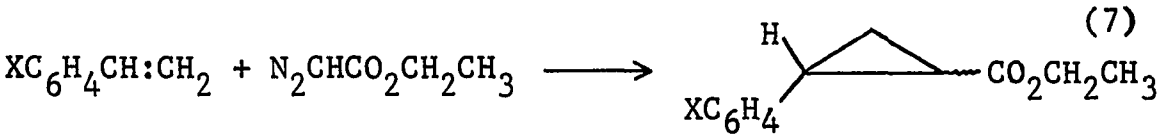
Compound[a]	Temp. (°C.)	Rate x 10^5 ($sec.^{-1}$)	ΔH^* (kcal/mole)	ΔS^* e.u.
cis-2-phenyl	123.4	0.831 ± 0.01	32.6	-0.1
	146.8	8.82		
trans-2-phenyl	101	1.28 ± 0.01		
	123	11.8 ± 0.2	30.6	-1.6
1-phenyl	49.85	2.66 ± 0.04	24.0	-5.2
	65.15	16.3 ± 0.1		
1-methyl	121.9	12.4 ± 0.2		

[a]Substituent is that of cyclopropyl p-toluenesulfonate.

p-toluenesulfonate acetolysis was undertaken by studying substituent effects. The rest of this paper will report the results of that study.

RESULTS AND DISCUSSION

The arylcyclopropyl p-toluenesulfonates used in this study were prepared by the methods described by DePuy.[38,39] The synthesis of the 2-arylcyclopropyl p-toluenesulfonates requires an appropriately substituted styrene and ethyl diazoacetate as starting materials (eq. 7). The resulting



(7)

cis and trans esters were best separated by distillation through a four foot jacketed packed column. The pure isomers were amenable to the normal saponification methods. The acids were treated with slightly less than two equivalents of methyllithium, as determined by titration, to give the corresponding ketones in yields as high as 90% (eq. 8). If the titration procedure were deleted and an excess of methyl-

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[38] C. H. DePuy, L. R. Mahoney and K. L. Eilers, J. Org. Chem., 26, 3616 (1961).

[39] C. H. DePuy, G. M. Dappen, K. L. Eilers and R. A. Klein, J. Org. Chem., 29, 2813 (1964).

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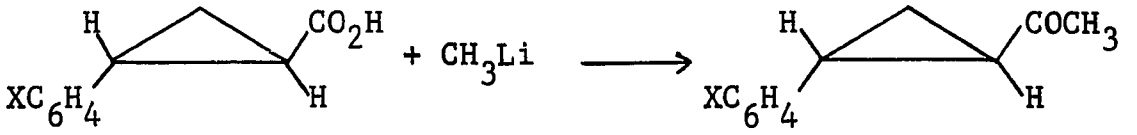
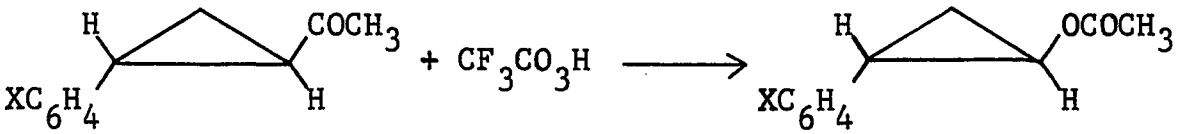
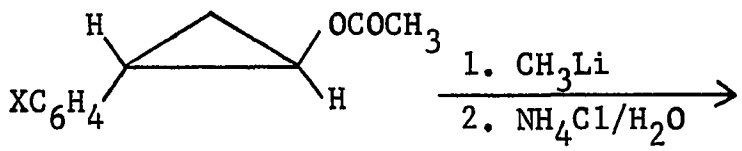


lithium used, the yields were lessened considerably by the production of the corresponding cyclopropyl dimethyl carbinols. The ketones were converted to the acetates by reaction with peroxytrifluoroacetic acid (eq. 9). The acetates were

(9)



readily reduced to the alcohols by methyllithium. Titration of the methyllithium solution was unnecessary, but continued exposure to the strongly basic solutions was avoided. The work-up was accomplished by adding the etheral solution of the methyllithium reaction to a saturated aqueous ammonium chloride solution (eq. 10). The p-toluenesulfonates were prepared in pyridine by reacting the alcohols with p-toluenesulfonyl chloride at -5°C. (eq. 11). The resulting compounds were stored at room temperature and could be kept indefinitely without decomposition. The p-toluenesulfonates of cis-2-



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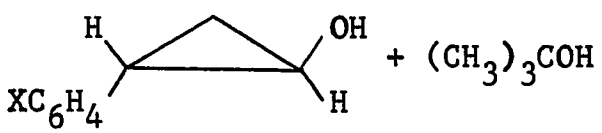

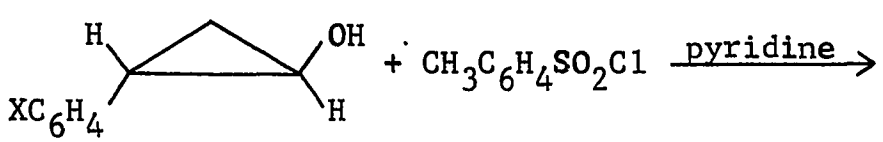

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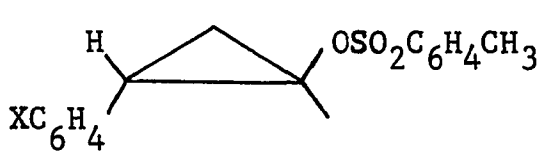
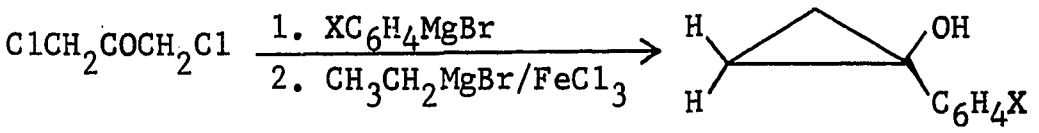


phenylcyclopropanol, trans-2-phenylcyclopropanol, trans-2-m-methylphenylcyclopropanol, trans-2-p-methylphenylcyclopropanol, trans-2-m-chlorophenylcyclopropanol were obtained.

The 1-arylcyclopropanols* were prepared by reacting 1,3-dichloroacetone with the appropriate aryl Grignard reagent and ring closure was accomplished with ethyl magnesium bromide and ferric chloride (eq. 12). The p-toluene-



(12)

sulfonates of 1-p-methylphenylcyclopropanol, 1-phenylcyclopropanol, 1-m-chlorophenylcyclopropanol and 1-m-trifluoromethylphenylcyclopropanol were prepared by the same procedure as described for the 2-arylcyclopropanols (eq. 11).

The 2-arylcyclopropyl p-toluenesulfonates were solvolyzed in dry acetic acid containing excess sodium acetate at 109°C. The only product isolated from the reaction mixture during the solvolysis of the cis- and trans-2-phenylcyclopropyl p-toluenesulfonate was trans-cinnamyl acetate. If the other two acetates, cis-cinnamyl and 3-phenylprop-1-en-3-yl acetate, are formed during the solvolyses they are probably equilibrated with the more stable trans-cinnamyl acetate as

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*R. A. Klein kindly provided these alcohols for this study.

described by Braude.[40,41,42,43] The rates of solvolysis were followed by using ultraviolet spectroscopy which more specifically gave the rate of appearance of the cinnamyl moiety. The rates all followed first order kinetics. Since cinnamyl p-toluenesulfonate and cinnamyl acetate would both absorb in the ultraviolet spectrum and since cinnamyl p-toluenesulfonate could be formed before or during the formation of the cinnamyl acetate, the rate of solvolysis of trans-2-phenylcyclopropyl p-toluenesulfonate was monitored by titrating the p-toluenesulfonic acid produced. The two rates, as seen in Table 2, were essentially equal. This demonstrated that the p-toluenesulfonic acid was formed at the same rate as the trans-2-phenylcyclopropyl p-toluenesulfonate disappeared, assuming a cinnamyl moiety is produced each time a cyclopropyl moiety disappears. This leaves three possibilities: (1) ring opening and loss of p-toluene-

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[40]E. A. Braude, E. R. H. Jones and E. S. Stern, J. Chem. Soc., 396 (1946).

[41]E. A. Braude, E. R. H. Jones and E. S. Stern, ibid., 1087 (1947).

[42]E. A. Braude, J. S. Fawcett and D. D. E. Newman, J. Chem. Soc., 793 (1950).

[43]E. A. Braude, D. W. Turner and E. S. Waight, J. Chem. Soc., 2396, 2404 (1958).

Table 2. Solvolyses of 2-arylcyclopropyl p-toluenesulfonates in dry 0.04M $NaC_2H_3O_2/HC_2H_3O_2$

Substituent[a]	Temp. (°C.)	Method[b]	Rate constant x 10^5 ($sec.^{-1}$)[c]
2-p-CH_3	109.33	UV	7.47 ± 0.28
2-m-CH_3	109.33	UV	6.56 ± 0.11
2-H	109.33	UV	3.21 ± 0.02
2-H	108.85	Titr	3.05 ± 0.12
2-H	128.12	Titr	22.2 ± 0.2
2-m-Cl	109.33	UV	0.538 ± 0.010
2-H[d]	123	Titr	0.835 ± 0.026

[a]Substituent is that of the aryl group in trans-2-arylcyclopropyl p-toluenesulfonate, except d.

[b]UV if the rate of solvolysis was followed by ultraviolet spectroscopy and Titr if the rate was followed by titrating p-toluenesulfonic acid.

[c]Each rate constant is the average of two or more kinetic determinations.

[d]cis-2-phenylcyclopropyl p-toluenesulfonate.

sulfonate ion are simultaneous, (2) ring opening to the cinnamyl p-toluenesulfonate is followed by a very rapid solvolysis to cinnamyl acetate, or (3) both of the above situations may be occurring, in part, at the same time.

These possibilities were better differentiated in the 1-arylcyclopropyl p-toluenesulfonate system.

The 1-arylcyclopropyl p-toluenesulfonates were also solvolyzed in dry acetic acid. The first order rate constants as determined by following the reaction by utilizing ultraviolet spectroscopy are given in Table 3.

Table 3. The solvolyses of 1-arylcyclopropyl p-toluenesulfonates in dry 0.04M $NaC_2H_3O_2/HC_2H_3O_2$ as followed by ultraviolet spectroscopy

Substituent[a]	Temp. (°C.)	Rate constant x 10^4 (sec.$^{-}$)[b]
p-CH_3	30.30	0.560 ± 0.010
	50.10	6.40 ± 0.11
	108.24	1890[c]
H	59.67	0.881 ± 0.012
	80.46	7.87 ± 0.05
	108.24	101[c]
m-Cl	108.24	3.86 ± 0.10
m-CF_3	108.24	1.71 ± 0.06

[a]Substituent is that of the aryl group of 1-arylcyclopropyl p-toluenesulfonate.

[b]Each rate constant is the average of two or more kinetic determinations.

[c]Calculated from the data at lower temperatures.

When the solvolyses of 1-phenylcyclopropyl and 1-*p*-methylphenylcyclopropyl *p*-toluenesulfonates were monitored by titration in order to follow the rate of appearance of *p*-toluenesulfonic acid the rate constants decreased steadily over the last 80% of the reaction. On the other hand, titration over the first 15% of the reaction showed the rate of acid formation followed first order kinetics, k_1, Table 4. The last 75% of the reaction produced the acid at a much slower rate but again followed first order kinetics, k_3, Table 4. This, along with the magnitude of these rate constants (k_1, Table 4) relative to those obtained by ultraviolet spectroscopy (Table 3), indicate that these 1-arylcyclopropyl *p*-toluenesulfonates solvolyze by two pathways, one pathway forming *p*-toluenesulfonic acid directly, or at least relatively rapidly, the other by way of an intermediate which solvolyzes much more slowly to produce the *p*-toluenesulfonic acid. Since 2-phenylallyl *p*-toluenesulfonate has already been identified as one of the solvolysis products, it is most likely the intermediate in question. The postulated scheme is outlined in eq. 13. The *m*-chloro- and *m*-trifluoromethylphenylcyclopropyl *p*-toluenesulfonates, on the other hand, showed steadily <u>increasing</u> rate constants over the entire reaction. This indicates that k_1 and k_3 of

Table 4. Solvolyses of the 1-arylcyclopropyl p-toluenesulfonates in dry acetic acid

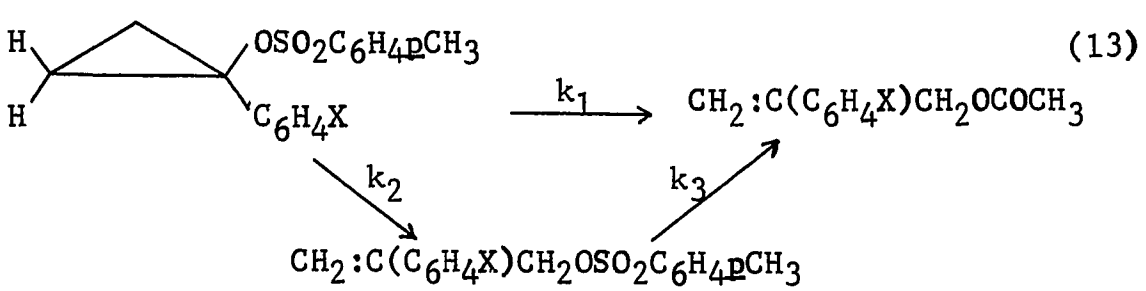
Substituent[a]	Temp. (°C.)	k as defined in eq. 13	Rate constant x 10^4 ($sec.^{-1}$)[b]
p-CH_3	30.02	k_1	0.176 ± 0.007
	50.11	k_1	2.19 ± 0.06
	108.54	k_1	741[c]
	108.54	k_3	4.59 ± 0.09
-H	50.11	k_1	0.0545 ± 0.0008
	70.52	k_1	0.531 ± 0.011
	108.54	k_1	19.3[c]
	108.54	k_3	3.97 ± 0.04
m-Cl	108.54	k_1	0.832 ± 0.014[d]
	108.54	k_3	2.83 ± 0.05[d]
m-CF_3	108.54	k_1	0.294 ± 0.014[d]
	108.54	k_3	2.40 ± 0.10[d]

[a]Substituent of the aryl group of 1-arylcyclopropyl p-toluenesulfonate.

[b]Each rate constant is the average of two or more kinetic determinations.

[c]Calculated from data at lower temperatures.

[d]Calculated as described in the text.



(13)

the two simultaneous pathways to p-toluenesulfonic acid are comparable in magnitude. In order to solve for these rate constants, the three rate equations 14, 15 and 16

$$dX/dt = -(k_1 + k_2)X \tag{14}$$

$$dY/dt = -k_3Y + k_2X \tag{15}$$

$$dZ/dt = k_1X + k_3Y \tag{16}$$

(where X, Y and Z are the concentrations of 1-arylcyclopropyl p-toluenesulfonate, 2-arylallyl p-toluenesulfonate and 2-arylallyl acetate,* respectively) for the two pathways were solved.

Integration of eq. 14 gives eq. 17

$$\ln(a/X) = (k_1 + k_2)t \tag{17}$$

(where a = initial concentration of X). Substitution of eq. 17 into eq. 15 and integration gives eq. 18.

$$Y = ak_2(k_1 + k_2 - k_3)^{-1}(e^{-k_3t} - e^{-(k_1 + k_2)t}) \tag{18}$$

Finally, substitution of eq. 18 into eq. 16 and integration

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*The term Z also represents the concentration of p-toluenesulfonic acid.

gives eq. 19,

$$(b - k_3)^{-1}(e^{-k_3t} - e^{-bt})k_1 - Z/a + k_3(b - k_3)^{-1}e^{-bt} - b(b - k_3)^{-1}e^{-k_3t} + 1=0 \quad (19)$$

(where $b = k_1 + k_2$). The b, then, represents the rate constant as computed from the ultraviolet spectroscopy results at 108.24°C., Table 3. A range for the rate constant, k_3, for the production of p-toluenesulfonic acid from the 2-arylallyl p-toluenesulfonate was obtained by using numbers of the same magnitude as those obtained directly from the solvolysis of the 1-phenylcyclopropyl and 1-methylphenylcyclopropyl p-toluenesulfonates, Table 4, lines 4 and 8. The p-toluenesulfonic acid concentration, Z, was then measured for a series of times, t, and the IBM 7074 computer was used to evaluate both the coefficients of k_1 and the sums of the remaining four terms, plot these pairs of values and fit a straight line through the origin and the resulting points by the method of least squares. The slope of the line, k_1, and a root mean square error term was also computed. It can be seen in Table 5, which gives the values from a typical run, how k_3 and the root mean square error term varied together. The results of these estimations are given in Table 4, lines

Table 5. Estimation of k_1[a] and k_3[a] for a typical solvolysis run for 1-m-chlorophenylcyclopropyl p-toluenesulfonate

$k_3 \times 10^4$[a] (estimated)	$k_1 \times 10^5$[a] (computed)	Root mean square error $\times 10^5$
3.05	7.33	0.24
3.00	7.53	.20
2.95	7.76	.18
2.90	7.98	.15
2.85	8.20	.14
2.80	8.43	.14
2.70	8.88	.18
2.60	9.32	.23

[a]This rate constant is as defined by eq. 13.

9-12.

A comparison of all of the rates under discussion was made by using the Hammett equation, $\log(k/ko) = \rho\sigma^+$ and plotting -log k versus σ^+ so that the slope ρ may be determined. The solvolyses of the 1-arylcyclopropyl p-toluenesulfonates fit σ^+ better than σ. Since the σ^+ values are obtained from reactions where the benzylic carbon atom is the site of positive charge build up, the solvolyses of the 1-arylcyclopropyl p-toluenesulfonates should also have a charge build up at the benzylic carbon atom in the transition state. The magnitude of this charge build up is reflected in

the value of ρ. The solvolyses of the 2-arylcyclopropyl p-toluenesulfonates, where the predominate charge build should be alpha to the benzylic carbon atom, should fit σ since these values are obtained from reactions where the reaction site is alpha to the benzylic carbon atom, e.g. the ionization of various substituted benzoic acids. All of the solvolyses are plotted on σ^+, Figure 1, so that a more direct comparison of the ρ values may be obtained. Table 6, however, includes the ρ values from both the σ^+ and σ plots.

A ρ value of -4.31 for the 1-arylcyclopropyl p-toluenesulfonates going directly to 2-arylallyl acetate is indicative of considerable positive charge being localized on the benzylic carbon atom. A ρ value of -3.94 may be calculated for the ring opening of the 1-arylcyclopropyl p-toluenesulfonates to yield the 2-arylallyl p-toluenesulfonates. These two values, being large, negative and of the same magnitude suggest a transition state very similar for the two processes. The ρ of -1.75 for the solvolysis of the 2-arylcyclopropyl p-toluenesulfonates suggests a transition state with less positive charge localized on the benzylic carbon, but not necessarily less charge in the cyclopropyl moeity. In considering transition states for all of the

Figure 1. Hammett plots for the solvolysis in acetic acid of: ○, 1-arylcyclopropyl p-toluenesulfonates as followed by ultraviolet spectroscopy (ρ = -3.98); □, 1-arylcyclopropyl p-toluenesulfonates as followed by titration (ρ = -4.31); ‡, 2-arylallyl p-toluenesulfonate (ρ = -0.37); and Δ, trans-2-arylcyclopropyl p-toluenesulfonate (ρ = -1.75)

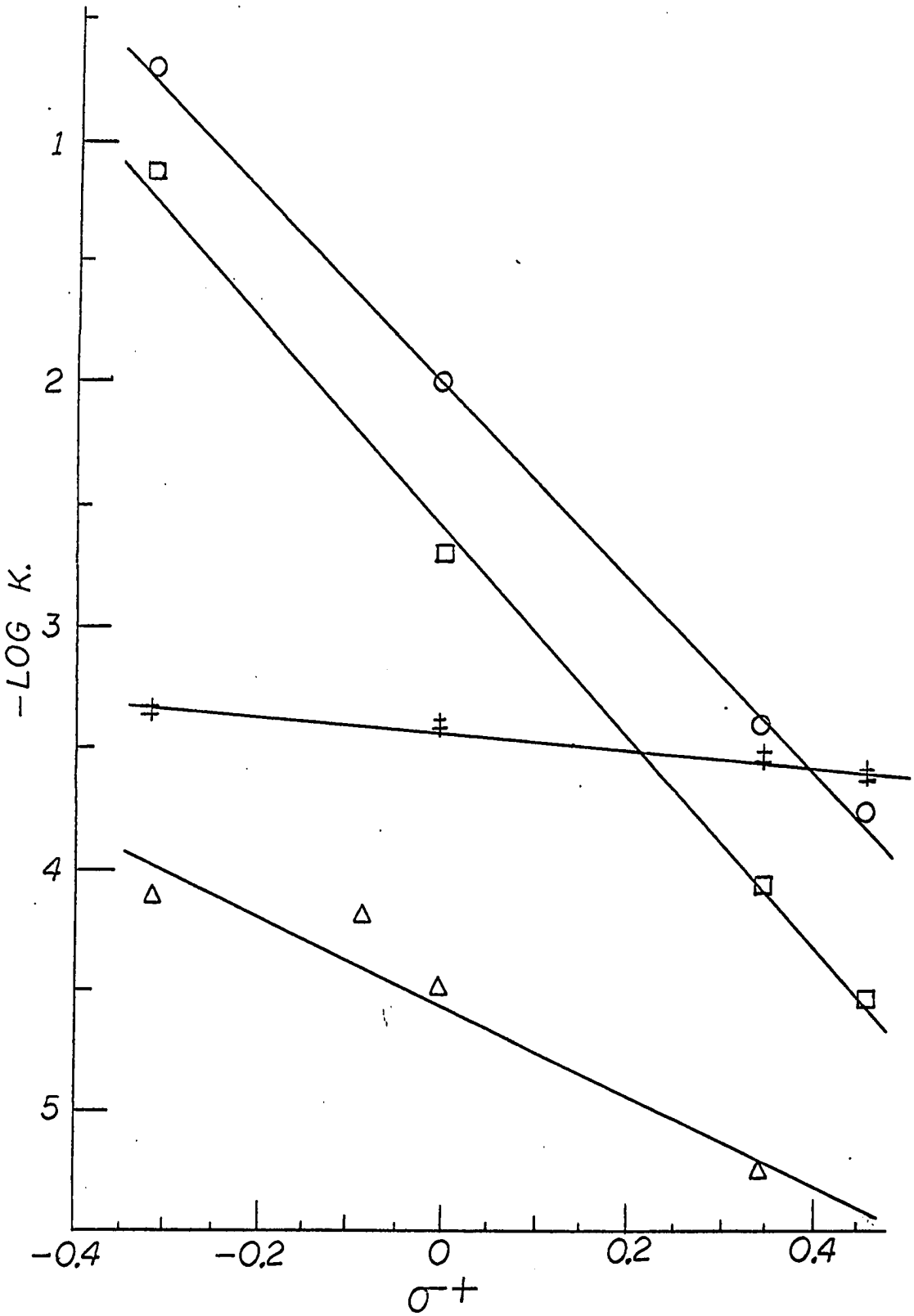

1
2
3
4
5
-LOG K.
-0.4
-0.2
0
0.2
0.4
σ+

Table 6. Hammett correlations of rates for the solvolyses of the arylcyclopropyl p-toluenesulfonates

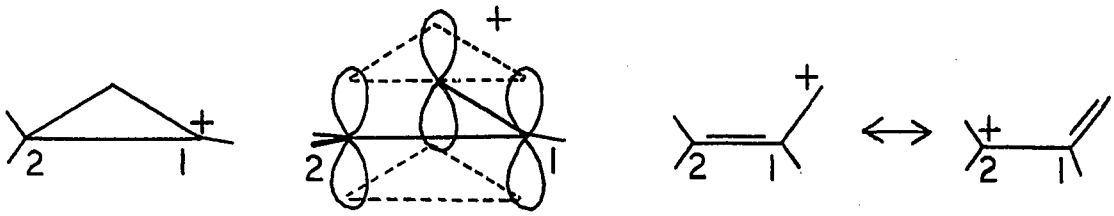
Compounds[a]	k as defined in eq. 13	ρ (at 108°C.)
trans-2-aryl		-1.75 ± 0.25[b]
trans-2-aryl		-2.35 ± 0.15[c]
1-aryl	$k_1 + k_2$	-3.98 ± 0.02
1-aryl	k_1	-4.31 ± 0.05
1-aryl	k_2	-3.94 ± 0.02
1-aryl	k_3	-0.37 ± 0.05[b]
1-aryl	k_3	-0.45 ± 0.02[c]

[a]Substituents of cyclopropyl p-toluenesulfonate.

[b]Using σ^+.

[c]Using σ.

solvolyses under discussion, one finds three ways in which the transition state can vary: (1) the nearness of the p-toluenesulfonate to the cyclopropyl moiety; (2) the structure of the positive portion in the transition state; or (3) both of the afore mentioned variations may be invoked simultaneously. Two classical (I and III) and one non-classical (II) carbonium ions can be considered. The non-classical structure can be realized by overlapping three p like atomic orbitals, one on each carbon, and allowing two electrons to move freely through the overlapping orbitals. The proximity



I II III

of the p-toluenesulfonate half in the transition state may determine the quantity of positive charge contained in any of the ions depicted. If the transition state is identical to I, the ρ for the solvolysis of the 2-arylcyclopropyl p-toluenesulfonates should be negligible compared to the ρ for the solvolysis of the 1-arylcyclopropyl p-toluenesulfonates. The ρ for the solvolysis of the 1-arylcyclopropyl p-toluenesulfonates should be negligible, on the other hand, if III were the best representation of the transition state. If one assumes complete freedom for delocalization of the electrons in the overlapping orbitals of II, then the ρ's for the two sets of solvolysis reactions under consideration would be equal. A transition state, then, between I and II with the proximity of the p-toluenesulfonate fixed can be used to describe the rate differences. It should be pointed out, however, that neither the structure of the positively charged moiety nor the proximity of the p-toluenesulfonate

ion need be identical in every solvolysis being considered.

Variations in the structure of the transition state and in the proximity of the p-toluenesulfonate from reaction to reaction should be regular. For example, in the case of structure, as the σ^+ value increases the transition state should approach structure II. In fact, extension of the Hammett plots predicts the 2-arylcyclopropyl p-toluenesulfonate and 1-arylcyclopropyl p-toluenesulfonate with a σ^+ of +1.35, will solvolyze at the same rate. The transition state for both of these hypothetical compounds could be described by the non-classical structure II. Likewise, the distance of the p-toluenesulfonate ion from the positively charged moiety in the transition state should increase as σ^+ decreases. The fact that a greater percentage of the 1-p-methylphenylcyclopropyl p-toluenesulfonate solvolyzes directly to the corresponding allyl acetate than 1-m-chlorophenylcyclopropyl p-toluenesulfonate substantiates this argument.

A transition state between I and II with the appropriate variances as described above best fits the results. The activation parameters, Table 7, also help to describe this as the transition state. The additional fact that the trans-2-phenylcyclopropyl p-toluenesulfonate solvolyzes about 16 times faster than the cis-2-phenylcyclopropyl p-toluene-

Table 7. Activation parameters for the solvolysis of some arylcyclopropyl p-toluenesulfonates in acetic acid

Compound[a]	k as defined by eq. 13	ΔH^{*b} (kcal/mole)	ΔS^{*b} (e.u.)
1-phenyl	$k_1 + k_2$	24.0 ± 0.2	-5.2 ± 0.7
1-phenyl	k_1	24.0 ± 0.4	-8.5 ± 1.0
1-p-methylphenyl	$k_1 + k_2$	23.3 ± 0.3	-1 ± 1
1-p-methylphenyl	k_1	23.8 ± 0.7	-2 ± 2
trans-2-phenyl		30.7 ± 0.2	-0.5 ± 0.2

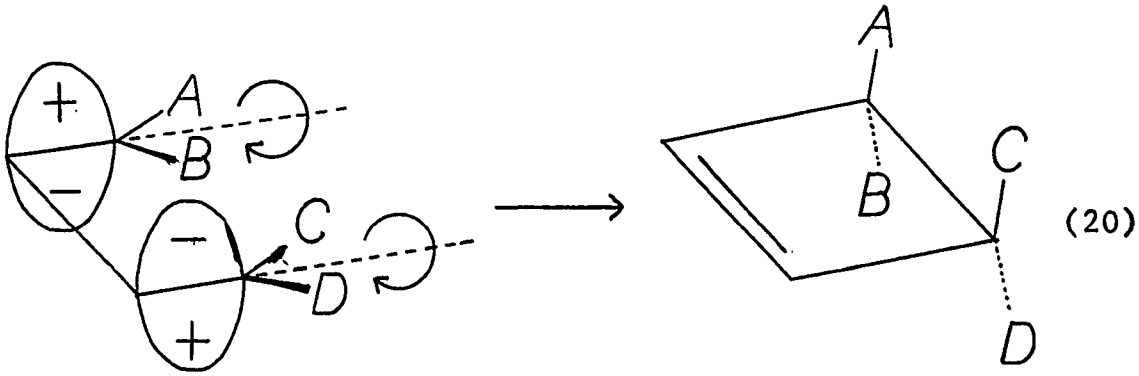
[a]Substituent given is that of cyclopropyl p-toluenesulfonate.

[b]Calculated at 50°C.

sulfonate at 108°C. can be used, along with the arguments which follow, to substantiate and even to describe the mechanism of the formation of the transition state depicted.

Since the solvolyses of all of the cyclopropyl p-toluenesulfonates under consideration produce ring opened products, then the system fits that of an electrocyclic transformation as defined, recently, by Woodward and

Hoffmann.[44] Their hypothesis suggests that the steric course of electrocyclic transformations is determined by the symmetry of the highest occupied molecular orbital of the open-chain partner in these changes. For example, in the case of butadiene the symmetry of the highest occupied ground-state orbital is such that a terminal bonding interaction requires overlap of orbital envelopes on opposite faces of the system, attainable only by conrotatory displacements, (eq. 20). On the other hand, in the case of



(20)

hexatriene, terminal bonding interaction within ground-state molecules requires overlap of orbital envelopes on the same face of the system, attainable only by disrotatory displacements (eq. 21). It should be noted that the fixed geometrical

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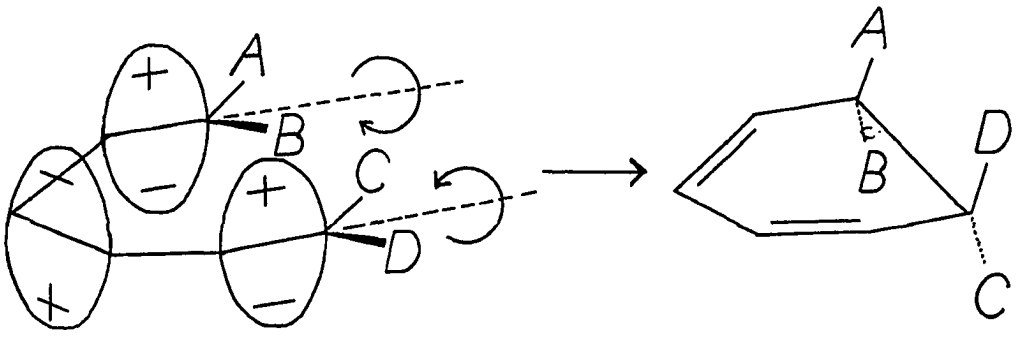
[44] R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).

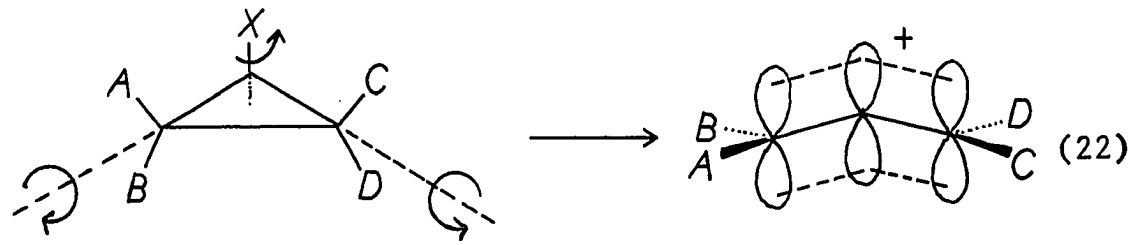


(21)

isomerism in the open-chain systems is related to rigid tetrahedral isomerism in the cyclic compounds.

The above examples can be extended so that the discussion for butadiene fits any system containing 4n π-electrons and, therefore, undergoes conrotatory displacements and that for hexatriene fits any system containing 4n + 2 π-electrons and, thus, undergoes disrotatory displacements. These arguments also apply to the converse process, the ring opening. Thus, for the ring opening of a cyclopropyl cation to the corresponding allyl cation containing 2 π-electrons (4n + 2, where n = 0), the isomerization must be a disrotatory displacement. There are two disrotatory displacements to consider (eq. 22 and eq. 23).

It can be argued, further, that as the C-X bond is breaking and the positive charge is developing on the side of the carbon remote from X, eq. 24, the ring opening should



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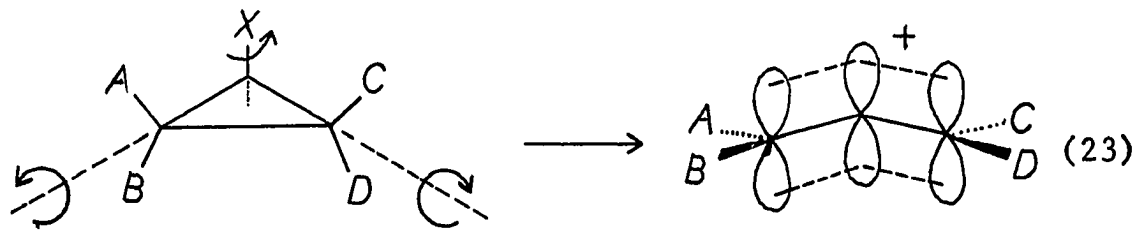

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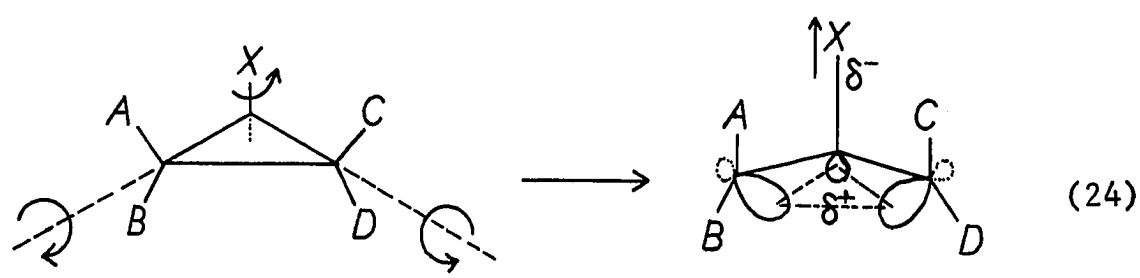

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favor the process described by eq. 22 and redrawn in eq. 24. Only by this process, as seen in the product of eq. 24, can the system begin to delocalize the developing positive charge, namely, by overlapping the lower lobe of the developing p atomic orbital. This would argue, then, that when cis-2-phenylcyclopropyl p-toluenesulfonate (X = p-toluenesulfonate, A = phenyl and B = C = D = hydrogen) undergoes ring

opening the bulky phenyl group, A, and the adjacent hydrogen, C, would be moving toward one another as the transition state was approached (eq. 24). This process would cause serious steric interactions which would not be present in the corresponding trans-compound (X = p-toluenesulfonate, B = phenyl and A = C = D = hydrogen) where the bulky phenyl, B, would be moving away from its cis hydrogen, D (eq. 24).

More conclusive evidence for the above arguments should be forthcoming as the problems below are explained. For example, Schweizer and Parham[45] have prepared the two isomers of 2-oxa-7-chloronorcarane and reported that one of the isomers ring opens at 140°C. in quinoline to yield oxa-2,4-cycloheptadiene while the other isomer does not ring open even at 175°C. in quinoline. They tentatively assign the latter isomer the endo configuration. The arguments above, however, predict the exo isomer to be that one which does not ring open. If the exo isomer were to ring open as described above and represented in eq. 25, a trans double bond would be forming in a seven membered ring which is an impossible structure. On the other hand, the endo isomer can ring open

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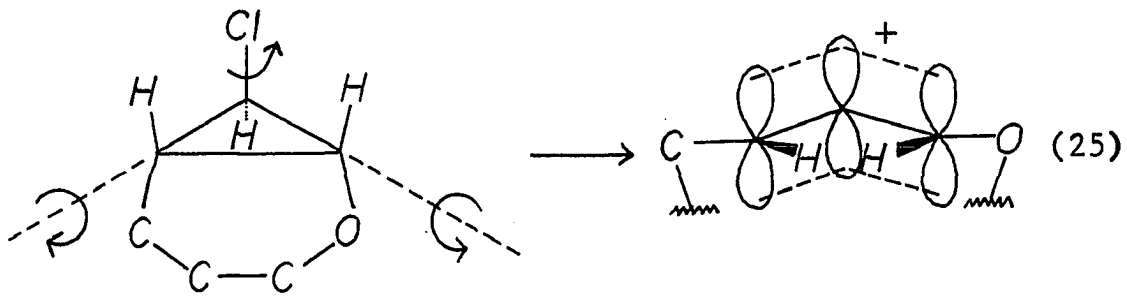
[45] E. E. Schweizer and W. E. Parham, J. Am. Chem. Soc., 82, 4085 (1960).



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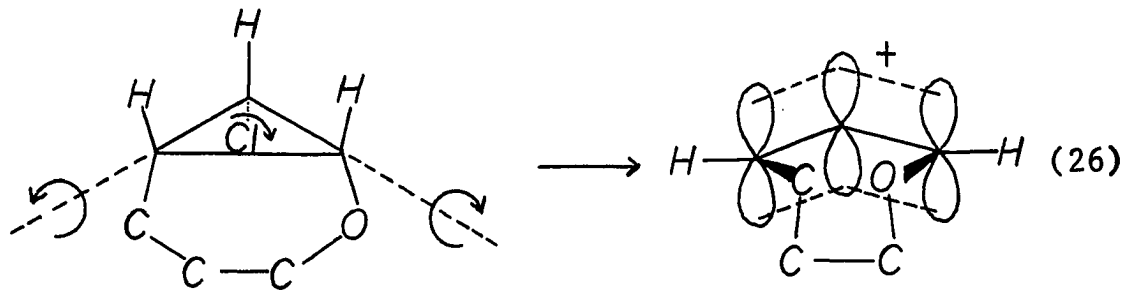
by rotating the bonds of the ring inward as shown in eq. 26 to yield the reported product. Thus, the endo isomer should



(26)

finally be identified as that isomer which forms oxa-2,4-cycloheptadiene when heated at 140°C. in quinoline.

Skell and Sander[46] report a similar case involving the two isomeric 2-bromo-2-chlorobicyclo [4,1,0] heptanes. The

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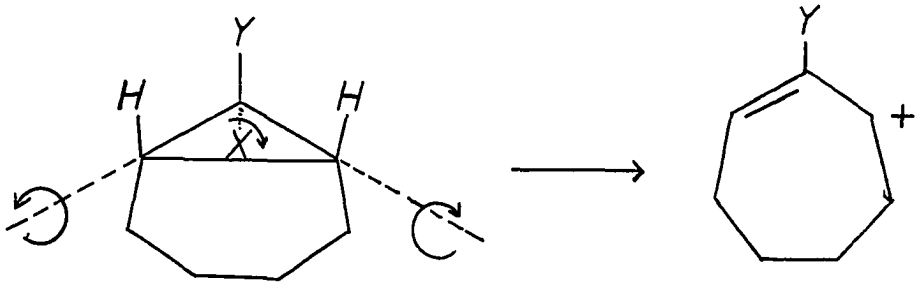
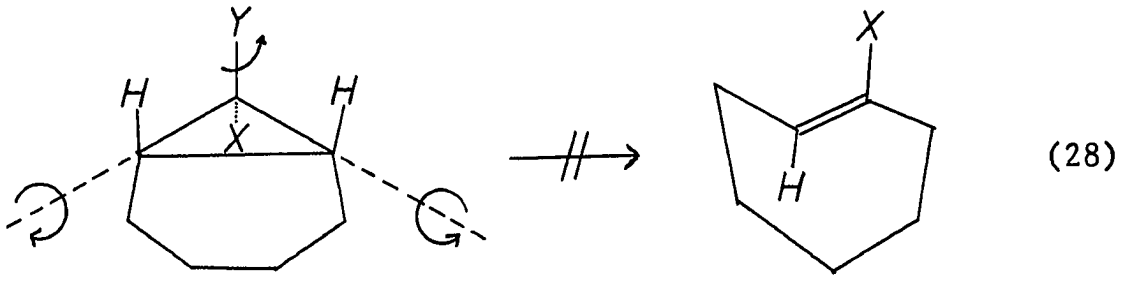
[46] P. S. Skell and S. R. Sandler, J. Am. Chem. Soc., 80, 2024 (1958).

two isomers react quite differently when treated with silver ion in ethanol. One isomer loses chloride ion at the same rate as 2,2-dichlorobicyclo [4,1,0] heptane to form 2-bromo-2-cycloheptenol. The other isomer loses bromide ion at the same rate as 2,2-dibromobicyclo [4,1,0] heptane to form 2-chloro-2-cycloheptenol.* Unfortunately, the two isomers have not been distinguishable. The arguments above predict, however, that the endo group must be the leaving group in the reaction because the carbon-carbon bond undergoing cleavage must break outward as in eq. 27, rather than as in eq. 28, due to the constraints placed on the system by the six membered ring.



(27)

*Skell reported analogous results for the two isomeric 2-bromo-2-chlorobicyclo [3,1,0] hexanes but Winstein has since reported that these compounds had already rearranged.



(28)

This work, then, in an attempt to formulate a mechanism and transition state for the solvolyses of arylcyclopropyl p-toluenesulfonates has extended the ideas stimulated by the original objectives to making some rather bold predictions concerning the compounds of Skell and Parham above. The effect of these predictions on future determinations of stereochemistry should be apparent.

EXPERIMENTAL

All melting points and boiling points are uncorrected and given in degrees Centigrade. Pressure is given in millimeters of mercury. The melting points were taken on a Fischer-Johns Melting Point Apparatus. The ultraviolet spectra were measured on a Beckman DK-2A spectrophotometer using 95% ethanol as the solvent and reference. The infrared spectra were measured either on a Perkin-Elmer model 21 or a Perkin-Elmer Infra-Cord and characteristic peaks are given after IR in microns. The intensity of these peaks are designated as broad (b), moderate (m), strong (s), and very strong (vs). The nuclear magnetic resonance spectra were measured on a Varian HR-60 spectrometer using carbon tetrachloride as the solvent and tetramethylsilane (TMS) as an internal standard. The spectral data are given after NMR and are in ppm downfield from TMS. The multiplicity of these peaks is indicated by singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The proton ratio is given in parentheses following and in the same order as the chemical shifts. Chromatographic separations were carried out on a Perkin-Elmer Vapor Fractometer model 154 utilizing a one meter column of Ucon LB550X on 60/80 mesh Regular W Chrom-

sorb. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Syntheses

Ethyl 2-phenylcyclopropyl carboxylate[47]

A two-liter three-necked round bottom flask was fitted with an addition funnel, a stirrer, and an air condenser containing a thermometer which extended into the reaction vessel. A constant flow of nitrogen was allowed to purge the system. Two hundred grams (1.92 moles) of styrene (Aldrich Chem. Co., Inc.) was brought to reflux and an additional 100 g. (0.96 mole) of styrene mixed with 220 g. (1.92 moles) of ethyl diazoacetate[48] at 0° was added at such a rate as to maintain brisk nitrogen evolution. The reaction is very exothermic, however, if methylene chloride, unknowingly left in the diazoacetate, is not swept out of the system periodically the temperature may drop below 135° and cause the nitrogen evolution to stop. When the solution regains reflux conditions the reaction may yield nitrogen in explosive proportions. After approximately four hours nitrogen evolution

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[47]A. Burger and W. L. Yost, J. Am. Chem. Soc., 70, 2198 (1948).

[48]Org. Syn. Coll. Vol. 2, 310 (1943).

stopped. The excess styrene was removed by a water aspirator. Continued distillation of the dark red residue at 85-105° (0.3 mm) gave 250 g (69%) of ethyl *cis*- and *trans*-2-phenylcyclopropyl carboxylates. Analysis of this mixture by gas phase chromatography at 174° indicated a 38/62 *cis* to *trans* mixture by area comparison.

Ethyl 2-arylcyclopropyl carboxylates

The preparation of the ethyl 2-arylcyclopropyl carboxylates paralleled that of ethyl 2-phenylcyclopropyl carboxylate, except the mixture of appropriately substituted styrene and ethyl diazoacetate at 0° were added to refluxing xylene. Obtained in this manner were:

Ethyl 2-*m*-chlorophenylcyclopropyl carboxylates (39/61 *cis* to *trans*) b.p. 80-140° (0.2 mm), 93.3 g (82%), and

Ethyl 2-*p*-methylphenylcyclopropyl carboxylates (40/60 *cis* to *trans*) b.p. 75-100° (0.2 mm), 67.5 g (78%).

Separation of ethyl cis- and trans-2-arylcyclopropyl carboxylates

Separation of the stereoisomers was effected by use of a four foot jacketed packed distillation column from Todd Scientific. Fractions ranging from one to three grams were collected. The distillation was monitored by gas phase chromatography. A representative distillation, that of

81.7 g of ethyl 2-m-chlorophenylcyclopropyl carboxylate, is described in Table 8.

Table 8. Separation of ethyl cis- and trans-2-m-chlorophenylcyclopropyl carboxylate

Fraction	Weight (grams)	Temperature	Composition
1 and 2	4.58	78- 83° (0.2 mm)	10% cis
3-12	23.24	96- 99° (0.2 mm)	>99% cis
13	1.49	100-102° (0.2 mm)	75/25 cis to trans
14	2.31	104-107° (0.2 mm)	55/50 cis to trans
15	2.43	108-110° (0.2 mm)	25/75 cis to trans
16-18	37.22	111-115° (0.2 mm)	>99% trans
residue	5	---	---

Ethyl cis-2-phenylcyclopropyl carboxylate, b.p. 70-74° (0.2 mm). NMR 0.92(t), 1.31(m), 1.76(m), 2.38(broad quintet), 3.79(q), and 7.15(m); (3:2:1:1:2:5).

Ethyl trans-2-phenylcyclopropyl carboxylate, b.p. 79-82° (0.2 mm). NMR 1.26(t), 1.70(m), 2.42(finely split octet), 4.10(q), and 7.10(m); (3:3:1:2:5).

Ethyl cis-2-p-methylphenylcyclopropyl carboxylate, b.p. 78-82°(0.2 mm). NMR 0.93(t), 1.60(m), 2.24(s), 2.36(broad multiplet), 3.80(q), and 7.00(m); (3:3:3:1:2:4).

Ethyl trans-2-p-methylphenylcyclopropyl carboxylate, b.p. 83-88° (0.2 mm). NMR 1.22(t), 1.44(m), 2.25(s), 2.38 (finely split octet), 4.07(q), and 6.92(m); (3:3:3:1:2:4).

Ethyl cis-2-m-chlorophenylcyclopropyl carboxylate, b.p. 93-97° (0.2 mm). NMR 0.97(t), 1.60(m), 2.44(broad quartet), 3.82(q), and 7.10(m); (3:3:1:2:4).

Ethyl trans-2-m-chlorophenylcyclopropyl carboxylate, b.p. 109-114° (0.2 mm). NMR 1.29(t), 1.35(m), 2.49(finely split octet), 4.20(q), and 7.32(m); (3:3:1:2:4).

2-Arylcyclopropyl carboxylic acids

The 2-arylcyclopropyl carboxylic acids were all prepared by the general procedure described in detail for trans-2-phenylcyclopropyl carboxylic acid.

Ninety-eight grams (0.516 mole) of ethyl trans-2-phenylcyclopropyl carboxylate was dissolved in 360 ml of 95% ethanol and 240 ml of water. To this solution was added 40 g (1.03 moles) of sodium hydroxide pellets and the solution heated at reflux for approximately 10 hours. The ethanol was removed under vacuum on a Rinco rotary evaporator, ice was added to bring the solution to 0°, and concentrated hydro-

chloric acid was added until the solution was very acidic. The white heavy solid which formed was filtered, air-dried, and dissolved in hot petroleum ether (b.p. 60-70°). Crystallization and recrystallization from the same solvent gave 84 g (100%) of trans-2-phenylcyclopropyl carboxylic acid, m.p. 91-92° (lit.[49] m.p. 93.0°). NMR 1.59(m), 2.60(finely split octet), 7.19(m), and 11.91(s); (3:1:5:1).

cis-2-Phenylcyclopropyl carboxylic acid, m.p. 106-108° (lit.[49] m.p. 106-107°). NMR 1.59(m), 2.54(broad quartet), 7.06(s), and 11.43(s); (3:1:5:1).

trans-2-m-Chlorophenylcyclopropyl carboxylic acid, m.p. 104.5-106°. IR 3.41(b) and 5.90(vs); NMR 1.57(m), 2.52 (finely split octet), 7.08(m), and 12.1(s); (3:1:4:1).

trans-2-p-methylphenylcyclopropyl carboxylic acid, m.p. 120.5-121.5°. NMR 1.55(m), 2.28(s), 2.54(finely split octet), 6.96(m), and 12.3(s).

trans-2-m-Methylphenylcyclopropyl carboxylic acid,* m.p. 73-74°. IR 3.42(b), 5.93(vs), 12.90(vs), 13.33(m), 14.12(m), 14.36(s), and 14.92(m); NMR 1.62(m), 2.31(s), 2.57

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[49]A. Burger and W. L. Yost, J. Am. Chem. Soc., 70, 2198 (1948).

*Prepared by G. F. Morris from a mixture of m- and p-methylstyrenes by a procedure identical to the foregoing.

(finely split octet), and 7.06(m); (3:3:1:4).

trans-2-Arylcyclopropyl methyl ketones

The trans-2-arylcyclopropyl methyl ketones were all prepared by the general procedure described in detail for trans-2-phenylcyclopropyl methyl ketone which is a modification of Tegner's procedure.[50]

To a stirred two phase solution of 60 g (0.37 mole) of trans-2-phenylcyclopropyl carboxylic acid in 400 ml. of anhydrous ether were added dropwise 780 ml of 0.93N (0.725 mole) of an ethereal methyl lithium solution. The resulting solution was allowed to stir for 2 hours and then added carefully with stirring to 500 ml of a saturated aqueous ammonium chloride solution. The water layer was separated and washed once with ether. The combined ether layers was washed twice with 100 ml of saturated aqueous ammonium chloride solution, twice with 100 ml of distilled water, and dried over anhydrous magnesium sulfate. The ether was removed at reduced pressure on a Rinco. Distillation of the residue gave 39.8 g (63%) of trans-2-phenylcyclopropyl methyl ketone, b.p. 70-72° (0.2 mm). IR 3.30(m) and 5.91(vs); NMR 1.37(m), 2.06(m), 2.18(s), 2.39(finely split octet), and 7.12(m); (2:1:3:1:5).

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[50] C. Tegner, Acta. Chem. Scand., 6, 782 (1952).

cis-2-Phenylcyclopropyl methyl ketone, b.p. 62-64° (0.2 mm). IR 3.35(m) and 5.92(vs); NMR 1.12(m), 1.72(m), 1.81(s), 2.29(m), and 7.10(m); (2:1:3:1:5).

trans-2-m-Chlorophenylcyclopropyl methyl ketone, b.p. 92-96° (0.2 mm). IR 3.38(m), 5.89(vs), and 6.30(m); NMR 1.36(m), 2.05(m), 2.22(s), 2.38(finely split octet), and 7.03 (m); (2:1:3:1:4).

trans-2-p-Methylphenylcyclopropyl methyl ketone, b.p. 81-89° (0.36 mm). NMR 1.31(m), 2.04(m), 2.18(s), 2.28(s), 2.36(finely split octet), and 6.93(m); (2:1:3:3:1:4).

trans-2-m-Methylphenylcyclopropyl methyl ketone, b.p. 83-88° (0.28 mm). NMR 1.35(m), 2.04(m), 2.16(s), 2.26(s), 2.33(finely split octet), and 6.89(m); (2:1:3:3:1:4).

trans-2-Arylcyclopropyl acetate

The trans-2-arylcyclopropyl acetates were all prepared by the general procedure described in detail for trans-2-phenylcyclopropyl acetate. The procedure is that of Emmons and Lucas.[51]

Trifluoroacetic anhydride (110 g, 0.524 mole) was added with stirring to 100 ml. of methylene chloride maintained at

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[51]W. D. Emmons and G. B. Lucas, J. Am. Chem. Soc., 77, 2287 (1955).

0°. Fourteen milliliters (0.524 mole) of 90% hydrogen peroxide were then added in 3 portions, waiting after each addition until the mixture became homogeneous. The resulting solution was then added dropwise to an ice cold solution of 30.5 g (0.190 mole) of trans-2-phenylcyclopropyl methyl ketone in 200 ml. of methylene chloride in which 135 g of disodium hydrogen phosphate had been slurried. After the addition, the resulting mixture was heated at reflux for one hour, cooled, and the solids removed by filtration. The filter cake was washed thoroughly with methylene chloride (3 x 100 ml). The combined methylene chloride solution was washed with saturated aqueous sodium bicarbonate until free of acid. The solution was then washed three times with 100 ml of water and dried over anhydrous magnesium sulfate. The methylene chloride was removed by distillation at atmospheric pressure. Continued distillation at 76-78° (0.35 mm) gave 20.3 g (61%) of trans-2-phenylcyclopropyl acetate. NMR 1.16(m), 1.92(s), 2.12(m), 4.11(m), and 7.11(m); (2:3:1:1:5).

cis-2-Phenylcyclopropyl acetate, b.p. 62-65° (0.2 mm). IR 5.70(s) and 5.86(s).

trans-2-m-Chlorophenylcyclopropyl acetate, b.p. 88-95° (0.2 mm). IR 5.74(vs) and 6.30(s). NMR 1.22(m), 1.98(s), 2.10(m), 4.08(m), and 7.06(m); (2:3:1:1:4).

trans-2-p-methylphenylcyclopropyl acetate, b.p. 81-84° (0.2 mm). IR 5.60(m) and 5.71(s). NMR 1.15(m), 1.97(s), 2.12(m), 2.26(s), 4.06(m), and 6.95(m); (2:3:1:3:1:4).

trans-2-m-methylphenylcyclopropyl acetate, 84-87° (0.2 mm). NMR 1.32(m), 1.94(s), 2.18(m), 2.33(s), 4.08(m), and 6.96(m); (2:3:1:3:1:4).

trans-2-Arylcyclopropanols

The trans-2-arylcyclopropanols were all prepared by the general procedure described in detail for trans-2-phenylcyclopropanol which is that of DePuy, et al.[52]

To a stirred solution of 20.3 g (0.115 mole) of trans-2-phenylcyclopropyl acetate in 250 ml of ether was added dropwise 350 ml of 1.10N methyl lithium (0.384 mole). The solution was allowed to stir 1 hour after the addition and then was added slowly to 400 ml of saturated aqueous ammonium chloride to which 20 ml of 1.2N hydrochloric acid had been added. The ethereal layer was then separated, washed three times with 100 ml of water, and dried over anhydrous magnesium sulfate. The ether was removed by distillation at atmospheric pressure. Continued distillation of the residue

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[52]C. H. DePuy, G. M. Dappen, K. L. Eilers and R. A. Klein, J. Org. Chem., 29, 2813 (1964).

gave 13.1 g (85%) of trans-2-phenylcyclopropanol, b.p. 76-78° (0.4 mm). NMR 1.00(m), 1.97(heptet), 3.43(m), 4.32(s), and 7.03(m); (2:1:1:1:5).

cis-2-Phenylcyclopropanol, b.p. 62-65° (0.2 mm). NMR 1.02(m), 1.03(s), 1.94(m), 3.45(m), and 7.15(m); (2:1:1:1:5).

trans-2-m-Chlorophenylcyclopropanol, b.p. 91-95° (0.2 mm). IR 2.99(b) and 6.23(m). NMR 1.04(m), 1.95(heptet), 3.42(m), 4.00(s), and 6.87(m); (2:1:1:1:4).

trans-2-p-Methylphenylcyclopropanol, b.p. 82-84° (0.2 mm). IR 3.01(b) and 6.54(s). NMR 1.04(m), 1.92(m), 2.24(s), 3.35(m), 4.75(s), and 6.85(m); (2:1:3:1:1:4).

trans-2-m-Methylphenylcyclopanol, b.p. 88-92° (0.45 mm). NMR 1.00(m), 1.94(m), 2.26(s), 3.38(m), 4.01(s), and 6.84(m); (2:1:3:1:1:4).

trans-2-Arylcyclopropyl p-toluenesulfonates

The trans-2-arylcyclopropyl p-toluenesulfonates were all prepared by the general procedure described in detail for trans-2-phenylcyclopropyl p-toluenesulfonates which is that of Tipson.[53] The compounds with higher positive sigma constants were allowed to stay in the refrigerator for longer periods of time to complete the tosylation reaction.

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[53] R. S. Tipson, J. Org. Chem., 9, 235 (1944).

Three grams (0.0224 mole) of trans-2-phenylcyclopropanol was dissolved in 30 ml. of pyridine (previously distilled from barium oxide) and cooled to -5° in an ice-salt bath. To the cold solution was added 6.4 g (0.0336 mole) of p-toluenesulfonyl chloride and the resulting solution swirled periodically for 1 hour at -5°. The solution was then placed in a freezer at -25° for approximately 30 hours. It was then poured into 200 ml of ice-water. This mixture was allowed to stand for 1 hour with occasional scratching of the beaker with a stirring rod. Crystals formed slowly. The mixture was filtered, the crystals washed with 50 ml of pentane, and recrystallized twice from ether-pentane to give 4.6 g (71%) of trans-2-phenylcyclopropyl p-toluenesulfonate, m.p. 63.5-64°. IR (kBr) 3.28(m), 6.22(m), 6.26(m), 9.81(m), 12.82(vs), 13.33(vs), 13.45(vs), 14.17(m), and 14.36(vs). NMR 1.17(m), 2.13(m), 2.42(s), 3.85(m), and 7.25(m); (2:1:3:1:9). Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.53; H, 5.60; S, 11.15.

cis-2-Phenylcyclopropyl p-toluenesulfonate, m.p. 53-54°. NMR 1.18(m), 2.00(m), 2.37(s), 4.16(m), and 7.26(m); (2:1:3:1:9). Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.68; H, 5.37; S, 11.11.

trans-2-m-methylphenylcyclopropyl p-toluenesulfonate,

m.p. 57-58°. IR (kBr) 3.43(m), 6.26(m), 9.81(m), 12.36(vs), 13.13(vs), 14.18(m), and 14.36(m). NMR 1.21(m), 2.07(m), 2.28(s), 2.44(s), 3.84(m), and 7.25(m); (2:1:3:3:1:8). Anal. Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.40; H, 5.96; S, 10.65.

trans-2-p-Methylphenylcyclopropyl p-toluenesulfonate, m.p. 62.5-63°. IR (kBr) 3.31(m), 3.43(m), 6.26(m), 9.81(m), 12.40(vs), 13.13(vs), and 14.17(m). NMR 1.08(m), 2.02(m), 2.20(s), 2.36(s), 3.71(m), and 7.28(m); (2:1:3:3:1:8). Anal. Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60. Found: C, 67.44; H, 5.95; S, 10.69.

trans-2-m-Chlorophenylcyclopropyl p-toluenesulfonate, m.p. 46-47°. IR (kBr) 3.27(m), 3.92(m), 6.26(s), 9.81(m), 13.05(vs), 14.22(m), 14.43(s), and 14.65(s). NMR 1.26(m), 2.08(m), 2.44(s), 3.84(m), and 7.28(m); (2:1:3:1:8). Anal. Calcd. for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68; S, 9.93; Cl, 10.98. Found: C, 59.44; H, 4.43; S, 9.96; Cl, 11.11.

1-Arylcyclopropanols

The 1-arylcyclopropanols were prepared by R. A. Klein by the procedure of DePuy, Dappen, and Klein.[54]

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[54]C. H. DePuy, G. M. Dappen and R. A. Klein, J. Org. Chem. 27, 3742 (1962).

1-Arylcyclopropyl p-toluenesulfonates

The 1-arylcyclopropyl p-toluenesulfonates were prepared by the method of Tipson.[55]

1-Phenylcyclopropyl p-toluenesulfonate, m.p. 75-75.5°. NMR 1.08(m), 1.60(m), 2.33(s), and 7.19(m); (2:2:3:9).

1-p-Methylphenylcyclopropyl p-toluenesulfonate, m.p. 85.5-86.5°. NMR 1.05(m), 1.55(m), 2.28(s), 2.34(s), and 7.14(m); (2:2:3:3:8).

1-m-Chlorophenylcyclopropyl p-toluenesulfonate, m.p. 56-57°. NMR 1.11(m), 1.64(m), 2.37(s), and 7.26(m); (2:2:3:8).

1-m-Trifluoromethylphenylcyclopropyl p-toluenesulfonate, m.p. 31.5-32.5°. NMR 1.15(m), 1.67(m), 2.31(s), and 7.26(m); (2:2:3:8).

Kinetic Procedures and Data

For the kinetics followed by ultraviolet spectroscopy the p-toluenesulfonate was weighed and placed in a 25 ml volumetric flask in a constant temperature bath. A sodium acetate solution, prepared by dissolving anhydrous sodium acetate in acetic acid which had been refluxed for four

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[55] R. S. Tipson, J. Org. Chem., 9, 235 (1944).

hours with acetic anhydride and then distilled through a four foot packed column, was maintained at the bath temperature until it was added to the tosylate. The sodium acetate solution was added until it appeared at the surface of the bath in the neck of the volumetric flask. The flask was then stoppered, removed from the bath, inverted twice for mixing, and then replaced immediately. Two milliliter aliquots were withdrawn at timed intervals and diluted 1 to 100 with 95% ethanol. The ethanol was kept at 0° for those solvolyses which were run at 50° or below. The ultraviolet spectra were recorded as soon as practical. However, spectra repeated after 10 hours on samples kept at room temperature gave less than a 3% change which indicated the temperature differential and solvent change were effective in quenching the reactions. The infinity points were not recorded until after at least eight half lives. The first order rate constants were calculated by using the equation,

$$k = \frac{2.303}{t} \log \frac{(A_{\infty} - A_0)}{(A_{\infty} - A_t)} .$$

The constants were checked by using an IBM 7074 computer to plot the log term versus time and fit a straight line through these points by using the method of least squares. At least

two runs were made on each compound at each temperature and one of these is here included as a table. See Tables 9 to 19.

Table 9. Rate of solvolysis of 1-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 30.30°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^5 (sec.$^{-1}$)
0	0.147	--	--
315	.160	0.00767	5.61
1,200	.195	.02904	5.57
2,400	.240	.05816	5.58
3,600	.279	.08507	5.44
5,400	.339	.13004	5.54
7,200	.394	.17579	5.62
9,600	.455	.23291	5.59
12,000	.511	.29291	5.62
15,600	.582	.38326	5.66
32,940	.767	.78404	5.48
∞	.889	--	--
Average rate constant			5.57 ± 0.05[b]

[a] 0.0575 g of p-toluenesulfonate was used.

[b] Average of two runs = 5.60 ± 0.10 x 10^{-5} sec.$^{-1}$.

Table 10. Rate of solvolysis of 1-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 50.10°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^4 (sec.$^{-1}$)
0	0.136	--	--
150	.184	0.03981	6.11
302	.228	.07982	6.08
720	.339	.20096	6.42
1,080	.418	.31390	6.69
1,500	.474	.41656	6.39
1,920	.527	.54288	6.51
2,400	.564	.65960	6.33
3,120	.612	.88145	6.51
3,840	.638	1.0760	6.45
∞	.684	--	--
Average rate constant			6.39 ± 0.14[b]

[a]0.0501 g of p-toluenesulfonate was used.

[b]Average of two runs = 6.40 ± 0.11 x 10^{-4} sec.$^{-1}$.

Table 11. Rate of solvolysis of 1-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 59.67°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^5 (sec.$^{-1}$)
0	0.136	--	--
240	.147	0.00844	8.10
1,380	.198	.04983	8.31
2,160	.233	.08071	8.60
3,300	.275	.12091	8.44
5,100	.337	.18803	8.49
8,000	.440	.32927	9.48
14,400	.545	.54521	8.72
∞	.708	--	--
Average rate constant			8.59 ± 0.29[b]

[a]0.0592 g of p-toluenesulfonate was used.

[b]Average of three runs = 8.81 ± 0.12 x 10^{-5} sec.$^{-1}$.

Table 12. Rate of solvolysis of 1-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 80.46°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^4 (sec.$^{-1}$)
0	0.117	--	--
360	.217	0.1137	7.28
540	.262	.1766	7.53
720	.304	.2448	7.83
960	.350	.3343	8.02
1,200	.384	.4148	7.96
1,680	.438	.5806	7.78
2,400	.485	.8180	7.85
∞	.551	--	--
Average rate constant			7.75 ± 0.21[b]

[a]0.0653 g of p-toluenesulfonate was used.

[b]Average of two runs = 7.87 ± 0.05 x 10^{-4} sec.$^{-1}$.

Table 13. Rate of solvolysis of 1-m-chlorophenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.24°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k \times 10^4$ (sec.$^{-1}$)
0	0.223	--	--
488	.313	0.0797	3.76
719	.355	.1225	3.92
1,080	.416	.1934	4.12
1,501	.474	.2736	4.20
2,042	.525	.3589	4.05
2,698	.577	.4675	3.99
4,081	.645	.6693	3.78
5,190	.679	.8215	3.64
∞	.760	--	--
Average rate constant			3.93 ± 0.16[b]

[a] 0.0500 g of p-toluenesulfonate was used.

[b] Average of two runs = $3.86 \pm 0.10 \times 10^{-4}$ sec.$^{-1}$.

Table 14. Rate of solvolysis of 1-m-trifluoromethylphenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.54°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^4 (sec.$^{-1}$)
0	0.079	--	--
360	.100	.0277	1.77
683	.115	.0486	1.64
1,198	.139	.0843	1.62
1,721	.164	.1249	1.67
2,455	.200	.1910	1.79
3,297	.227	.2482	1.73
4,942	.276	.3761	1.75
7,530	.325	.5584	1.71
10,728	.364	.7911	1.70
∞	.419	--	--
Average rate constant			1.71 ± 0.06[b]

[a] 0.0444 g of p-toluenesulfonate was used.

[b] Average of two runs = 1.71 ± 0.04 x 10^{-4} sec.$^{-1}$.

Table 15. Rate of solvolysis of trans-2-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 109.33°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k \times 10^5$ (sec.$^{-1}$)
0	0.034	--	--
768	.063	.02326	6.97
2,280	.123	.07575	7.65
5,748	.232	.19119	7.66
7,518	.281	.25511	7.81
9,456	.326	.32347	7.88
13,146	.388	.43972	7.70
19,002	.464	.64470	7.81
27,330	.510	.84198	7.09
∞	.590	--	--
Average rate constant			7.57 ± 0.27[b]

[a] 0.0182 g of p-toluenesulfonate was used.

[b] Average of two runs = $7.47 \pm 0.28 \times 10^{-5}$ sec.$^{-1}$.

Table 16. Rate of solvolysis of trans-2-m-methylphenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2$/$HC_2H_3O_2$ at 109.33°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^5 (sec.$^{-1}$)
0	.038	--	--[b]
774	.063	.01829	5.44
2,670	.135	.07575	6.53
4,404	.193	.12829	6.71
7,032	.269	.20844	6.82
11,028	.359	.32763	6.84
14,136	.406	.40589	6.61
18,864	.466	.53205	6.49
25,800	.515	.67188	6.00
∞	.644	--	--[b]
Average rate constant for 7 points[b]			6.57 ± 0.20[c]

[a] 0.0205 g of p-toluenesulfonate was used.

[b] Points not used in the average.

[c] Average of two runs 6.56 ± 0.11 x 10^{-5} sec.$^{-1}$.

Table 17. Rate of solvolysis of trans-2-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 109.33°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^5 (sec.$^{-1}$)
0	0.056	--	--
3,492	.109	0.04594	3.03
6,066	.143	.07819	2.97
11,170	.211	.15092	3.11
17,800	.295	.26173	3.47
25,370	.354	.36090	3.28
35,110	.417	.49991	3.28
∞	.584	--	--
Average rate constant			3.19 ± 0.15[b]

[a] 0.0200 g of p-toluenesulfonate was used.

[b] Average of two runs = 3.21 ± 0.10 x 10^{-5} sec.$^{-1}$.

Table 18. Rate of solvolysis of trans-2-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 128.12°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	k x 10^4 ($sec.^{-1}$)
0	0.093	--	--
443	.145	0.03885	2.02
688	.173	.06176	2.07
1,007	.205	.08951	2.05
1,289	.240	.12204	2.18
1,655	.268	.14994	2.09
2,070	.308	.19319	2.15
2,551	.347	.23996	2.17
3,075	.387	.29381	2.20
3,690	.419	.34228	2.14
4,350	.459	.41164	2.18
∞	.690	--	--
Average rate constant			2.14 ± 0.04

[a] 0.0558 g of p-toluenesulfonate was dissolved in 50 ml. of solution and divided equally into ampules.

Table 19. Rate of solvolysis of trans-2-m-chlorophenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2$/$HC_2H_3O_2$ at 109.33°

Time (sec.)	Absorbance	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k \times 10^6$ (sec.$^{-1}$)
0	.047	--	--
22,840	.114	0.05351	5.39
52,410	.179	.11260	4.95
84,750	.264	.20442	5.55
137,490	.361	.34033	5.70
167,960	.395	.40020	5.49
389,220	.563	.96954	5.74
∞	.625	--	--
Average rate constant			5.47 ± 0.20[b]

[a] 0.0227 g of p-toluenesulfonate was used.

[b] Average of two runs = $5.38 \pm 0.10 \times 10^{-6}$ sec.$^{-1}$.

For the kinetics which were followed by titration the p-toluenesulfonate was placed in a 100 ml beaker which was mounted in the constant temperature bath, with a glass rod stirrer, nitrogen inlet tube and burette tip extending to the surface of the liquid. Approximately 10 ml of acetic acid and 2 drops of methyl violet were added. When the indicator turned green a sodium acetate solution which was kept at bath temperature was used to titrate the entire solution to

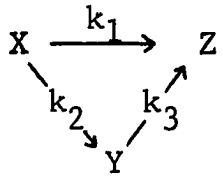
the disappearance of the green tinge and the time was recorded at the end of the titration. This procedure was repeated as many as 15 times. The advantage of this method was that a relatively small amount of p-toluenesulfonate was needed to follow the first 10% of the reaction. Dissolving the p-toluenesulfonate in acetic acid in a 25 ml. volumetric flask, removing aliquots, and titrating at room temperature gave the same result within experimental error. At temperatures above 70° the rate constants were determined exclusively by the latter method since the indicator seemed to turn grey when used in the bath at these higher temperatures. The p-toluenesulfonate solution was divided and placed in sealed ampoules for runs made above 110°. At least two runs were made on each compound at each temperature and one is included as a table. See Tables 21 to 31. The first order rate equation,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} ,$$

was used to calculate the rate constant. A plot of log (a/a-x) versus time gave a straight line segment in the first 15% reaction. The 1-m-trifluoromethylphenylcyclopropyl p-toluenesulfonate and the 1-m-chlorophenylcyclopropyl p-

toluenesulfonate at 108.54°, however, gave a curved line with a tangent which was increasing at such a rate that no straight portions could be used for rate constants. This indicated that the rate of solvolysis of the 1-arylcyclopropyl p-toluenesulfonate was comparable to that of the corresponding 2-aryl-3-propenyl p-toluenesulfonate. Lines were drawn tangent to the curve near zero time for several runs and the slopes ranged from 5.8×10^{-5} sec.$^{-1}$ to 8.5×10^{-5} sec.$^{-1}$ for the 1-m-trifluoromethylphenylcyclopropyl p-toluenesulfonate and from 2.5×10^{-5} sec.$^{-1}$ to 3.5×10^{-5} sec.$^{-1}$ for the 1-m-chlorophenylcyclopropyl p-toluenesulfonate.

The three differential equations which can be written for a system such as:



are $dX/dt = -(k_1 + k_2)X$, $dY/dt = -k_3Y + k_2X$, and $dZ/dt = k_1X + k_3Y$. These may be solved to give

$$(b-k_3)^{-1}(e^{-k_3t} - e^{-bt})k_1 - Z/a +$$

$$k_3(b-k_3)^{-1}e^{-bt} - b(b-k_3)^{-1}e^{-k_3t} + 1 = 0$$

where $b = k_1 + k_2$, Z = concentration of species Z at time t, and a = initial concentration of species X. The IBM 7074 computer was used to evaluate both the coefficient of k_1 and the sum of the remaining four terms, plot these two values for a set of Z's and t's, and fit a straight line through the origin and resulting points by the method of least squares. Since a range for k_3 was known from the solvolyses of 2-phenyl-3-propenyl p-toluenesulfonate and 2-p-methylphenyl-3-propenyl p-toluenesulfonate several first approximations for k_3 could be submitted. Results of two typical runs are given in Tables 20 and 21. Table 20 utilized the data from Table 30 and the data from Table 31 was used for Table 21. The values which best fit the equation are given as footnotes in Tables 30 and 31.

Table 20. Evaluation of k_1 and k_3 for the solvolysis of 1-m-chlorophenylcyclopropyl p-toluenesulfonate in acetic acid

$k_3 \times 10^4$ used	Calculated $k_1 \times 10^5$	Root mean square error $\times 10^5$
3.05	7.33	0.24
3.00	7.53	.20
2.95	7.76	.18
2.90	7.98	.15
2.85	8.20	.14
2.80	8.43	.14
2.70	8.88	.18
2.60	9.32	.23

Table 21. Evaluation of k_1 and k_3 for the solvolysis of 1-m-trifluoromethylphenylcyclopropyl p-toluenesulfonate in acetic acid

$k_3 \times 10^4$ used	Calculated $k_1 \times 10^5$	Root mean square error $\times 10^5$
2.10	3.98	.18
2.20	3.67	.15
2.30	3.36	.13
2.40	3.05	.14
2.50	2.74	.16
2.60	2.44	.21

Table 22. Rate of solvolysis of trans-2-phenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}N $NaC_2H_3O_2/HC_2H_3O_2$ at 108.85°

Time (sec.)	ml. $NaC_2H_3O_2$[b]$/HC_2H_3O_2$	$\log \frac{a}{a-x}$	$kx10^5$ (sec.$^{-1}$)
1,194	0.322	.01626	3.14
2,478	.590	.03027	2.81
4,284	1.098	.05814	3.13
5,970	1.534	.08357	3.22
8,220	1.976	.11097	3.11
11,060	2.500	.14586	3.04
19,940	3.824	.24899	2.88
Average rate constant			3.05 ± 0.12

[a]0.2504 g of p-toluenesulfonate was dissolved in 50 ml of solution and 5 ml aliquots withdrawn.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M and concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

Table 23. Rate of solvolysis of trans-2-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408N $NaC_2H_3O_2/HC_2H_3O_2$ at 128.12°

Time (sec.)	ml. $NaC_2H_3O_2$[b]$/HC_2H_3O_2$	$\log \frac{a}{a-x}$	$kx10^4$ (sec.$^{-1}$)
551	0.980	0.05362	2.24
676	1.182	.06554	2.23
852	1.433	.08083	2.18
1,032	1.723	.09919	2.21
1,293	2.097	.12408	2.21
1,571	2.505	.15297	2.24
1,871	2.890	.18210	2.24
2,231	3.270	.21292	2.20
2,651	3.748	.25507	2.22
3,131	4.188	.29785	2.19
3,611	4.635	.34611	2.21
4,271	5.170	.41196	2.22
4,958	5.645	.48017	2.23
5,883	6.160	.56869	2.23
∞	8.438	--	--
Average rate constant			2.22 ± 0.02

[a]0.6027 g of p-toluenesulfonate was dissolved in 50 ml of solution and divided equally among 15 ampoules.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908x10^{-3}M$ and concentration of $HC1O_4/HC_2H_3O_2 = 0.0406M$.

Table 24. Rate of solvolysis of 1-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}M $NaC_2H_3O_2/HC_2H_3O_2$ at 30.02°

Time (sec.)	ml. $NaC_2H_3O_2$[b]/$HC_2H_3O_2$	$\log \frac{a}{a-x}$	$kx10^5$ (sec.$^{-1}$)
348	0.053	0.00308	2.04[c]
600	.067	.00440	1.69
888	.096	.00715	1.85
1,200	.106	.00811	1.56
1,584	.140	.01136	1.65
2,040	.172	.01444	1.63
2,910	.251	.02215	1.75
4,500	.348	.03180	1.63
7,260	.550	.05263	1.67
10,080	.753	.07461	1.70
13,500	.945	.09648	1.65
20,700	1.215	.12292	1.37[c]
33,900	1.585	.17853	1.21[c]
86,400	1.957	.23447	0.62[c]
Average rate constant for 10 points[c]			1.68 ± 0.06[d]

[a]0.1391 g of p-toluenesulfonate was dissolved in 50 ml of solution.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M, concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[c]Points not included in average rate.

[d]Average of three runs = $1.76 \pm 0.07 \times 10^{-5}$ sec.$^{-1}$.

Table 25. Rate of solvolysis of 1-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}M $NaC_2H_3O_2/HC_2H_3O_2$ at 50.11°

Time (sec.)	ml $NaC_2H_3O_2$[b]$/HC_2H_3O_2$	log $\frac{a}{a-x}$	$kx10^4$ (sec.$^{-1}$)
157	0.192	0.0125	2.31
235	.324	.0205	2.01
295	.452	.0283	2.21
349	.551	.0345	2.28
415	.644	.0404	2.24
481	.744	.0468	2.24
547	.842	.0532	2.24
625	.940	.0597	2.20
721	1.104	.0708	2.26
823	1.222	.0789	2.21
895	1.341	.0873	2.25
1,045	1.506	.0992	2.19
1,213	1.664	.1108	2.10[c]
1,423	1.828	.1233	2.00[c]
1,705	2.068	.1422	1.92[c]
2,215	2.330	.1639	1.70[c]
2,887	2.624	.1896	1.51[c]
3,385	2.798	.2055	1.40[c]
4,165	2.988	.2236	1.24[c]
6,925	3.218	.2465	0.82[c]
Average rate constant for 12 points[c]			2.22 ± 0.05[d]

[a]0.0224 g of p-toluenesulfonate was dissolved in 50 ml of solution.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M, concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[c]Points not included in average rate.

[d]Average of two runs = $2.19 \pm 0.06 \times 10^{-4}$ sec.$^{-1}$.

Table 26. Rate of solvolysis of 1-p-methylphenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.54°

Time (sec.)[b]	ml $NaC_2H_3O_2$[c]/$HC_2H_3O_2$	log $\frac{a}{a-x}$[d]	$kx10^4$ (sec.$^{-1}$)
0	1.900	0	--
252	2.210	.04476	4.09
452	2.520	.09468	4.81
688	2.780	.14148	4.73
986	3.075	.20152	4.71
1,288	3.300	.25363	4.54
1,654	3.610	.33751	4.70
2,369	4.000	.47302	4.59
3,176	4.280	.60550	4.39
∞	5.065	--	--
Average rate constant			4.68 ± 0.08[e]

[a] 0.1853 g of p-toluenesulfonate was dissolved in approximately 25 ml of solution and 2 ml aliquots withdrawn.

[b] 68 sec. have been subtracted from each time.

[c] Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M and concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[d] 0.20421 has been subtracted from each log term.

[e] Average of two runs = $4.59 \pm 0.09 \times 10^{-4}$ sec.$^{-1}$.

Table 27. Rate of solvolysis of 1-phenylcyclopropyl p-toluenesulfonate[a] in acetic acid at 50.11°

Time (sec.)	ml $NaC_2H_3O_2$[b]/$HC_2H_3O_2$	$\log \frac{a}{a-x}$	k x10^6 ($sec.^{-1}$)
1,972	0.120	0.00421	4.92
3,160	.222	.00781	5.69
4,894	.358	.01269	5.97
8,852	.608	.02176	5.72
10,900	.768	.02770	5.85
13,400	.888	.03219	5.53
16,640	1.108	.04056	5.61
20,140	1.248	.04597	5.01
Average rate constant			5.54 ± 0.29[c]

[a]0.0355 g of p-toluenesulfonate was used.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2$ = 9.908x10^{-3}N.

[c]Average rate constant from two runs = 5.45 ± 0.08x10^{-6} $sec.^{-1}$.

Table 28. Rate of solvolysis of 1-phenylcyclopropyl p-toluenesulfonate[a] in acetic acid at 70.52°

Time (sec.)	ml $NaC_2H_3O_2$[b]/$HC_2H_3O_2$	$\log \frac{a}{a-x}$	$kx10^5$ ($sec.^{-1}$)
528	0.280	.01151	5.02
948	.471	.01960	4.76
1,302	.658	.02762	4.88
1,620	.896	.03807	5.41
1,986	1.094	.04695	5.44
2,466	1.276	.05396	5.04
2,874	1.528	.06708	5.37
3,330	1.718	.07618	5.27
3,912	1.868	.08353	4.92
Average rage constant			5.12 ± 0.22[c]

[a] 0.0305 g of p-toluenesulfonate was used.

[b] Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908x10^{-3}M$.

[c] Average of two runs = $5.31 \pm 0.11 \times 10^{-5}$ $sec.^{-1}$.

Table 29. Rate of solvolysis of 1-phenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.54°

Time (sec.)[b]	ml $NaC_2H_3O_2$[c]/$HC_2H_3O_2$	log $\frac{a}{a-x}$[d]	$kx10^4$ (sec.$^{-1}$)
0	1.820	0	--
485	2.510	.08501	4.03
884	2.990	.15581	3.86
1,571	3.660	.27910	4.09
2,174	4.065	.37516	3.98
2,665	4.380	.46804	4.04
3,220	4.610	.55112	3.94
∞	5.701	--	--
Average rate constant			3.99 ± 0.06[e]

[a] 0.2036 g of p-toluenesulfonate was dissolved in approximately 25 ml of solution and 2 ml aliquots withdrawn.

[b] 430 sec. have been subtracted from each time.

[c] Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M and concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[d] 0.16699 has been subtracted from each log term.

[e] Average of two runs = $3.97 \pm 0.04 \times 10^{-4}$ sec.$^{-1}$.

Table 30. Rate of solvolysis of 1-m-chlorophenylcyclopropyl p-toluenesulfonate[a] in 9.908×10^{-3}M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.54°

Time (sec.)	ml $NaC_2H_3O_2$[b]$/HC_2H_3O_2$	$\log \frac{a}{a-x}$	k[c]
373	0.131	0.01308	
881	.375	.03853	
1,104	.511	.05339	
1,486	.718	.07703	
2,231	1.158	.13201	
3,227	1.678	.20748	
3,938	2.018	.26502	
4,849	2.438	.34856	
∞	4.418	--	

[a]0.1738 g of p-toluenesulfonate was dissolved in approximately 25 ml of solution and 2 ml aliquots withdrawn.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M and concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[c]The best fit to equation gave $8.32 \pm 0.14 \times 10^{-5}$ sec.$^{-1}$ with rate constant for the solvolysis of the allyl p-toluenesulfonate = $2.83 \pm 0.05 \times 10^{-4}$ sec.$^{-1}$.

Table 31. Rate of solvolysis of 1-m-trifluoromethylcyclopropyl p-toluenesulfonate[a] in 9.908M $NaC_2H_3O_2/HC_2H_3O_2$ at 108.54°

Time (sec.)	ml $NaC_2H_3O_2$[b]$/HC_2H_3O_2$	log $\frac{a}{a-x}$	k[c]
532	0.058	0.00644	
1,411	.248	.02822	
1,958	.400	.04647	
2,959	.670	.08091	
3,616	.870	.10830	
5,223	1.365	.18461	
7,021	1.835	.27206	
9,323	2.325	.38701	
∞	3.942	--	

[a]0.1712 g of p-toluenesulfonate was dissolved in approximately 25 ml of solution and 2 ml aliquots were withdrawn.

[b]Concentration of $NaC_2H_3O_2/HC_2H_3O_2 = 9.908 \times 10^{-3}$M and concentration of $HClO_4/HC_2H_3O_2 = 9.948 \times 10^{-3}$M.

[c]The best fit to equation gave $2.94 \pm 0.14 \times 10^{-5}$ sec.$^{-1}$ with rate constant for the solvolysis of the allyl p-toluenesulfonate = $2.40 \pm 0.10 \times 10^{-4}$ sec.$^{-1}$.

Table 32. Rate of solvolysis of cis-2-phenylcyclopropyl p-toluenesulfonate[a] in 0.0408M $NaC_2H_3O_2/HC_2H_3O_2$ at 123.4°

Time (sec.)	ml $NaC_2H_3O_2/HC_2H_3O_2$[b]	$\log \frac{a}{a-x}$	$kx10^6$ ($sec.^{-1}$)
10,800	1.65	0.0473	10.08[d]
27,980	2.11	.1029	8.47
39,600	2.36	.1364	7.93
54,000	2.71	.1881	8.02
86,400	3.41	.3148	8.39
113,100	3.88	.4268	8.69
172,800	4.45	.6186	8.24
259,200	4.92	.8843	7.86
∞	5.32[c]	--	--
Average rate constant for 7 points			8.23 ± 0.27[e]

[a]Concentration of p-toluenesulfonate = 0.0348M.

[b]Concentration of $HClO_4$ = 0.0507M.

[c]Calculated infinity = 5.48.

[d]Point not used in average rate.

[e]Average rate constant from three runs = $8.31 \pm 0.10 \times 10^{-6}$ $sec.^{-1}$.

SUMMARY

The p-toluenesulfonates of cis and trans-2-phenylcyclopropanol, trans-2-m-methylphenylcyclopropanol, trans-2-p-methylphenylcyclopropanol, trans-2-m-chlorophenylcyclopropanol, 1-phenylcyclopropanol, 1-p-methylphenylcyclopropanol, 1-m-chlorophenylcyclopropanol and 1-m-trifluoromethylphenylcyclopropanol were prepared and solvolyzed in dry acetic acid. The solvolyses were followed both by ultraviolet spectroscopy and by titration of the p-toluenesulfonic acid produced. The p-toluenesulfonates were shown to solvolyze by way of two simultaneous pathways. One pathway goes directly to the appropriately substituted allyl acetate and the other by way of the appropriately substituted allyl p-toluenesulfonate.

The Hammett ρ value for the solvolyses of the 1-arylcyclopropyl p-toluenesulfonates to form the acetates directly was -4.31 and for the pathway forming ring opened p-toluenesulfonate, -3.94. The solvolyses of the aryl substituted allyl p-toluenesulfonates was shown to have a Hammett ρ value of -0.37. A Hammett ρ value of -1.75 was obtained for the solvolyses of the 2-arylcyclopropyl p-toluenesulfonates.

A description of the mechanism and transition state

consistent with the results was given. With this and an extension of the descriptions of the stereochemistry of electrocyclic transformations of Woodward and Hoffmann, the stereochemistry of the ring opening process in cyclopropyl compounds was described. This information was used to predict the stereochemistry of at least two compounds whose stereochemistry is as yet unknown.

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ACKNOWLEDGMENTS

The author gratefully acknowledges the encouragement, patience and guidance which Dr. C. H. DePuy gave throughout the course of this work and especially in his helpful criticism of this paper.

The author is also indebted to his wife, Carol, for bearing with him and encouraging him throughout his college career; to his parents, for their encouragement and understanding; and to the members of the DePuy group for providing a stimulating and intellectual atmosphere.

Special thanks are also due to Dr. G. F. Morris for many helpful discussions and many hours of consultation.