conformationally homogeneous *cis*-3-methyl and *trans*-4-*t*-butyl compounds; in fact, however, its rate is palpably lower (Table VI, entries 11, 1, and 3).

The Kinetic Method of Conformational Analysis. The lack of constancy of the reaction rates in a series of conformationally analogous 3-, 4- and 3,5-substituted compounds, such as 1–10 (Table VI) or 15–19 (Table VII), raises, of course, serious questions regarding the kinetic method of conformational analysis. In this method it is necessary to assume that k_a and k_e for cyclohexyl-X are the same as those for a conformationally homogeneous alkylcyclohexyl-X which serves as a conformational model. The present work shows that the choice of an appropriate model is insecure; others[57] have experienced similar difficulties. For example, it has already been shown that, using acetylation data for cyclohexanol and its *cis*- and *trans*-4-*t*-butyl homologs, one obtains a reasonable value (0.56 kcal/mole) for the conformational energy of hydroxyl. However, were one to choose *cis,cis*- and *trans,trans*-3,5-dimethylcyclohexanol as conformationally homogeneous models (and such a choice would appear entirely reasonable), the conformational equilibrium constant of hydroxyl would be calculated to be $K = (3.37 - 8.60)/(8.60 - 13.1) = 1.16$, whence $\Delta G°_{OH} = 0.1$ kcal/mole, a manifestly erroneous value which disagrees with everything else in the literature. Looking at it in another way, the lack of constancy of "k_e" and "k_a" in conformationally rigid models makes it impossible to assert which of the various values, if any, apply to the monosubstituted, conformationally heterogeneous system.

In view of these severe problems, it is quite surprising that the kinetic method has given as good results as it has: several conformational energy values determined by the kinetic method are in very good agreement with values obtained by other, theoretically more firmly based methods.[3,4] The agreement is excellent for hydroxyl, carbethoxyl, and tosyl[58] and only slightly less good for amino and bromine;[59] on the other hand, clear-cut failures have occurred for carboxyl and acetate.[59] It must be concluded either that whatever success the kinetic method has had is entirely accidental or (and we are more inclined to this second view) that, perhaps fortuitously, the *cis*- and *trans*-4-*t*-butyl compounds originally used as conformational models in virtually all the studies so far completed do serve the purpose and give useful results, whereas other conceivable conformational models do not. If this is so, it would mean that the 4-*t*-butyl compounds are more free of polar and steric difficulties and simulate whatever distortions occur in the ground and transition states of the monosubstituted compounds better than do other conformationally homogeneous compounds. In any case, it would be well to view the kinetic method with reserve and to use it only when other methods are not readily available.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant 266-A.

(57) J. Sicher, personal communication; J. Krupička, J. Sicher, J. Závada, and M. Tichý to be submitted; V. J. Shiner and J. Jewett, *J. Am. Chem. Soc.*, **87**, 1382, 1383 (1965); W. H. Saunders and K. T. Finley, *ibid.*, **87**, 1384 (1965); see also ref 16 and 23. These investigations deal with more limited series of compounds than those studied in the present work.

(58) Two out of three determinations in the case of tosyl. The third one[5] is in major disagreement.

(59) See ref 3, pp 436–444.

Chemistry of Cyclopropanols. IV. The Solvolysis of Cyclopropyl Tosylates[1,2]

C. H. DePuy,[3] L. G. Schnack, and J. W. Hausser

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa. *Received February 19, 1966*

Abstract: The rates of acetolysis of a series of 1- and 2-arylcyclopropyl tosylates have been determined. Solvolysis proceeds with *simultaneous* ring opening, leading directly to arylallyl cations. This transformation is postulated to be highly stereospecific, with substituents *trans* to the leaving group rotating *outward* and those *cis* to the leaving group rotating *inward*. This hypothesis is used to explain a number of cases of previously anomalous reactivities among halonorcaranes.

Although it has been known for many years that cyclopropyl compounds undergo nucleophilic substitution reactions only with the greatest reluctance,[4] there are few quantitative data available with which to draw detailed conclusions about the mechanism by which, if suitably forced, reactions do occur. In fact, the only pertinent study is that of Roberts and Chambers[5] who showed that the acetolysis of cyclopropyl tosylate leads, at 170°, to allyl acetate at a rate 2×10^{-5} times that of cyclohexyl tosylate. Recent synthetic methods developed in our laboratories for a

(1) Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

(2) A preliminary account of a portion of this work has been reported: C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965).

(3) Address correspondence to Department of Chemistry, University of Colorado, Boulder, Colo. 80302.

(4) G. Gustavson, *J. Pract. Chem.*, [2] **43**, 396 (1891).

(5) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

Table I. Rate Constants for the Acetolysis of 1-Arylcyclopropyl Tosylates[a]

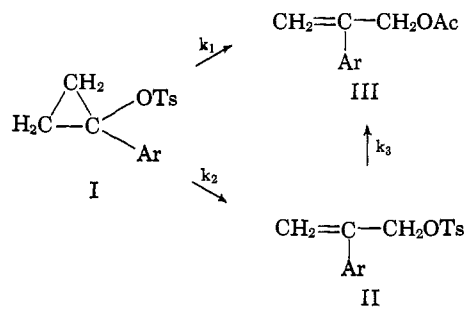
Substituents[b]	Temp, °C	$(k_1 + k_2) \times 10^4$,[c] sec^{-1}	$k_1 \times 10^4$,[c] sec^{-1}	$k_3 \times 10^4$,[c] sec^{-1}
p-CH_3	30	0.560 ± 0.01	0.176 ± 0.007	
	50	6.40 ± 0.11	2.19 ± 0.06	
	108.4	1890[d]	741[d]	4.59 ± 0.09
H	50		0.0545 ± 0.0008	
	59.7	0.881 ± 0.012		
	70.5		0.531 ± 0.011	
	80.5	7.87 ± 0.05		
	108.4	101[d]	19.3[d]	3.97 ± 0.04
m-Cl	108.4	3.86 ± 0.10	0.832 ± 0.014	2.83 ± 0.05
m-CF_3	108.4	1.71 ± 0.06	0.294 ± 0.014	2.40 ± 0.10

[a] In dry 0.04 *M* sodium acetate–acetic acid solution. [b] In the aromatic ring. [c] Each rate constant is the average of two or more kinetic runs. [d] Calculated from the data at lower temperature.

variety of cyclopropanols[6] has led us to an investigation of the mechanism of solvolysis of cyclopropyl tosylates, and the results are reported in this paper.

Results and Discussion

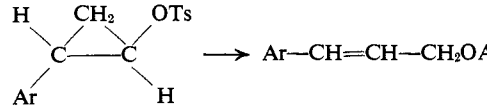
1-Arylcyclopropyl *p*-toluenesulfonates readily undergo solvolysis in dry acetic acid–sodium acetate solution according to the scheme shown in eq 1. The progress of the reaction can be followed spectrophotometrically, by observing the appearance of the styrene chromophore, and this measures the rate of appearance



(1)

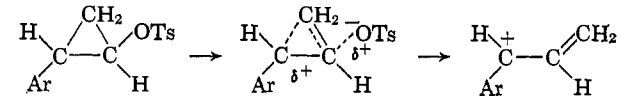
of II + III. If the rate is followed titrimetrically, the initial rate is that of the formation of III, while the final rate approaches that of the solvolysis of II. By appropriate analysis, k_1, k_2, and k_3 can be determined individually. These values are collected in Table I.

The solvolysis of *trans*-2-arylcyclopropyl tosylates is more straightforward (eq 2), since any rearranged tosylate formed by internal return is more reactive than the starting acetate and does not accumulate. As a consequence, the spectrophotometric and titrimetric rates are identical, and are reported in Table II. Under the conditions of the solvolysis the various cinnamyl acetates are equilibrated[7] so that the formation only of the conjugated isomers is not significant.



(2)

The fact that 2- and 3-arylallyl acetates are the solvolysis products is not a result of further transformations of initially formed cyclopropyl acetates, for both 1- and 2-phenylcyclopropyl acetate are stable to the reaction conditions. A diligent search for these products by gas chromatographic analysis failed to reveal their presence. The accelerating effect of a 2-aryl group (Table II) is, we feel, tied in with this observation. Since both a *cis*- and *trans*-2-phenyl group increases the rate of solvolysis of cyclopropyl tosylate, the formation of a phenonium ion in the transition state is ruled out and another source of the acceleration must be sought. A reasonable one is a ring opening *concerted* with solvolysis so that a partial positive charge is generated on the benzyl carbon in the transition state (IV). Support for this



IV

postulate is found in the Hammett ρ values for the solvolysis, collected in Table III. The large value of ρ observed in the 2-aryl system is fully in accord with the suggested transition state.

Table II. Rate Constants for the Acetolysis of 2-Arylcyclopropyl Tosylates[a]

Substituent[b]	Temp, °C	k_4[c] $\times 10^4$, sec^{-1}
cis-2-Phenyl	123.4[d]	0.083 ± 0.001
	146.8[d]	0.882 ± 0.03
trans-2-Phenyl	108.8[d]	0.305 ± 0.012
	109.3[e]	0.321 ± 0.002
	128.1[d]	2.22 ± 0.02
trans-*p*-Tolyl	109.3[d]	0.747 ± 0.028
trans-*m*-Tolyl	109.3[d]	0.656 ± 0.011
trans-*m*-Chlorophenyl	109.3[d]	0.0538 ± 0.0001

[a] In 0.04 *M* sodium acetate–acetic acid solution. [b] In the aryl ring of 2-arylcyclopropyl tosylates. [c] Each rate constant is the average of two or more kinetic runs. [d] Determined titrimetrically. [e] Determined spectrophotometrically.

Table III. Hammett Correlations of Rates of Solvolysis of Arylcyclopropyl Tosylates[c]

Cyclopropyl tosylate	Rate constant	ρ (at 108°)
trans-2-Aryl	k_4	−1.75 ± 0.25[a]
		−2.35 ± 0.15[b]
1-Aryl	k_1	−4.31 ± 0.05[a]
	k_2	−3.94 ± 0.02[a]

[a] Using σ^+. [b] Using σ. [c] It is interesting to note here that the ρ for the solvolysis of the 2-phenylallyl tosylates was found to be −0.4.

(6) C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, 29, 2813 (1964).
(7) F. A. Braude, D. W. Turner, and E. S. Waight, *J. Chem. Soc.*, 2396 (1958).

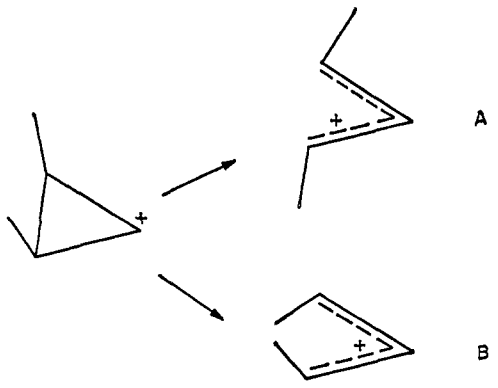


Figure 1.

The transformation from a cyclopropyl to an allyl system is a complicated one, and it is improper to consider a cyclopropyl and an allyl cation as resonance hybrids of one another. In their elegant recent theory, Woodward and Hoffmann[8] have considered the case of a cyclopropyl cation undergoing an electrocyclic transformation. The substituent groups were predicted to move in opposite directions (disrotatory), either both *inward* (giving cation B, Figure 1) or both *outward* (giving cation A, Figure 1). The results reported in this paper have shown that a cyclopropyl cation is not an intermediate in the solvolysis of cyclopropyl tosylate, but that ring opening proceeds simultaneously with breaking of the C–X bond. As a consequence, we were led independently to the hypothesis that *the direction of rotation of the groups R depends upon the stereochemistry of the leaving group X.* In particular, as the C–X bond begins to break, the carbons will rotate so as to bring the electrons of the C-2–C-3 bond to the back face of the C-1–X bond. The net effect will be that groups *trans* to the leaving group will rotate *outward*, those *cis* will rotate *inward*, as shown in Figure 2.

In this picture some C-2–C-3 bonding is retained in the transition state, which may gain stability from its resemblance to the cyclopropenyl cation, *i.e.*, it contains a cyclic system of two electrons in three π orbitals. Olah[9] has recently emphasized the possible importance of such structures (IV) as contributing to the abnormal shielding of the 2 proton in the nmr spectrum of allyl cations. This hypothesis also has the advantage of offering a ready explanation for the fact that while cyclopropyl cations rearrange readily, cyclopropyl anions and radicals seldom do. In the latter two species the transition state would not have the advantage of this "aromatic" character.

The idea of a preferred *inward* rotation of a *cis* R group accounts for the slower rate of solvolysis of *cis*- than *trans*-2-phenylcyclopropyl tosylate, since in the former case the more sterically hindered *cis*-cinnamyl cation should be the initial product. More striking differences are found in fused ring systems, and the hypothesis accounts for a number of anomalous results previously recorded in the literature. Thus Schweizer and Parham[10] have prepared the *exo* and *endo* isomers

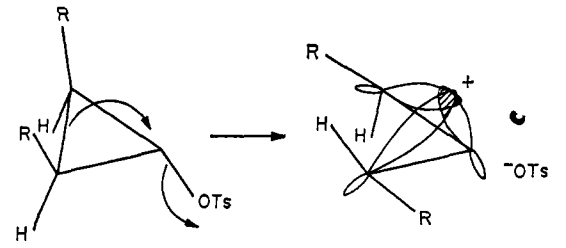
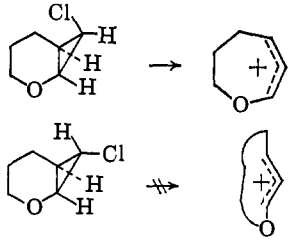


Figure 2.

shown, by addition of chlorocarbene to dihydropyran. One isomer readily rearranges while the other is stable to heating in quinoline at 175°. The *endo* isomer, in



our view, should rearrange easily to the highly stable ion shown by inward rotation of the two *cis* groups. In the *exo* isomer outward rotation of the *trans* groups is prevented and a concerted ring opening is forbidden. This reverses the assignment previously suggested by Schweizer and Parham. In the latter case a cyclopropyl cation may have to be formed first, and such systems may be suitable for an investigation of this hitherto unavailable species. Other examples of stereospecific rearrangements are those of Skell and Sandler[11] and of Cristol, Sequeira, and DePuy.[12]

Experimental Section

2-Phenylcyclopropanols. These alcohols were prepared by the method already reported[6] which involves the addition of ethyl diazoacetate to the appropriately substituted styrene, separation of the ethyl *cis*- and *trans*-2-arylcyclopropanecarboxylates by distillation, conversion to the methyl ketones, and Baeyer–Villiger oxidation to the *trans*-2-arylcyclopropyl acetates. Reaction with methyllithium produced the free alcohols.

2-Arylcyclopropyl *p*-toluenesulfonates were prepared by the method of Tipson.[13]

trans-**2-Phenylcyclopropyl *p*-toluenesulfonate** had mp 63.5–64°. *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** had mp 53–54°. *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** had mp 57–58°. *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** had mp 62.5–63°. *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** had mp 46–47°. *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. These alcohols were prepared, by the method already described,[6] from 1,3-dichloroacetone by reaction with the appropriate aryl Grignard reagent and ring closure with ethylmagnesium bromide and ferric chloride.

1-Arylcyclopropyl *p*-toluenesulfonates were prepared by Tipson's procedure.[13]

(8) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(9) G. A. Olah and M. B. Comisarow, *ibid.*, **86**, 5682 (1964).
(10) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960).
(11) P. S. Skell and S. R. Sandler, *ibid.*, **80**, 2024 (1958).
(12) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).
(13) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

1-Phenylcyclopropyl *p*-toluenesulfonate had mp 75–75.5°. *Anal.* Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.65; H, 5.49.

1-*p*-Methylphenylcyclopropyl *p*-toluenesulfonate had mp 87.5–88°. *Anal.* Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.16; H, 6.09.

1-*m*-Chlorophenylcyclopropyl *p*-toluenesulfonate had mp 56–57°. *Anal.* Calcd for $C_{16}H_{15}ClO_3S$: C, 59.53; H, 4.68. Found: C, 59.53; H, 4.67.

1-*m*-Trifluoromethylphenylcyclopropyl *p*-toluenesulfonate had mp 31.5–32.5°. *Anal.* Calcd for $C_{17}H_{15}F_3O_3S$: C, 57.30; H, 4.24. Found: C, 57.55; H, 4.94.

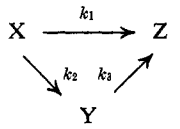
Kinetic Procedures. All of the *p*-toluenesulfonates were recrystallized several times immediately before use. For the kinetics followed by ultraviolet spectroscopy the *p*-toluenesulfonate was weighed and placed in a 25-ml volumetric flask in a constant temperature bath. A sodium acetate solution was prepared by dissolving anhydrous sodium acetate in acetic acid which had been refluxed for 4 hr with acetic anhydride and then distilled through a 4-ft packed column. This solution was maintained at the bath temperature until it was added to the tosylate. It was then added until it appeared at the surface of the bath in the neck of the volumetric flask. The flask was stoppered, removed from the bath, inverted twice for mixing, and replaced immediately. Two-milliliter aliquots were withdrawn at timed intervals and diluted 1:100 with 95% ethanol which 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 hr on samples kept at room temperature gave less than a 3% change, which indicated that the temperature differential and solvent change were effective in quenching the reactions. The infinity points were not recorded until after at least 8 half-lives. The first-order rate constants were calculated by using the equation

$$k = \frac{2.303}{t} \log \frac{(A - A_0)}{(A - A_t)}$$

At least two runs were made on each compound at each temperature.

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 buret 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 only 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. The first-order rate equation was again used to calculate the rate constant. A plot of $\log (a/(a - x))$ *vs.* 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-2-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 $d[X]/dt = -(k_1 + k_2)[X]$, $d[Y]/dt = -k_3[Y] + k_2[X]$, and $d[Z]/dt = k_1[X] + k_3[Y]$. These may be solved to give

$$(b - k_3)^{-1}(e^{-k3^t} - e^{-bt})k_1 - Z/a + k_3(b - k_3)^{-1}e^{-bt} - b(-k_3)^{-1}e^{-k_3t} + 1 = 0$$

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.