Substituent Effects on Cyclobutyl and Cyclopropylcarbinyl Cations

Kenneth B. Wiberg,* David Shobe, and Gordon L. Nelson

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511

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Abstract: The acetolyses of 3-substituted cyclobutyl tosylates (X = Ar, Cl, and OEt) were examined giving rate constants and product distributions. With the alkyl- and aryl-substituted compounds, the rate-determining step leads to the formation of a bridged cyclobutyl cation which then rearranges to a cyclopropylcarbinyl/homoallyl ion. The value of ρ for the solvolysis of the 3-aryl derivatives was −1.5, suggesting some charge transfer to the 3-position. The 3-chlorocyclobutyl tosylates react to give only the inverted 3-chlorocyclobutyl acetates. The 3-ethoxy derivatives give ~1:1 mixtures of the corresponding acetates. Further information concerning these reactions was obtained via ab initio MO calculations at the MP2/6-31G* theoretical level. They showed that except for the silyl substituents, all of the other 3-substituents led to a decrease in energy on rearrangement to the corresponding cyclopropylcarbinyl ion. The latter was found to have considerable homoallyl cation character when substituted at the 2-position. All of the results are in accord with the hypothesis that the rate-determining step with X = alkyl or aryl is the formation of a bridged cyclobutyl cation that is a transition state for a stereospecific rearrangement to the corresponding cyclopropylcarbinyl ion. The reaction products are then formed from the latter ion.

Introduction

The cyclobutyl/cyclopropylcarbinyl system[1] has been of continuing interest from the early studies of the *i*-cholesteryl system[2] and the suggestion of a nonclassical bicyclobutonium ion[3] to the recent ab initio calculations[4] and solid-state NMR and IR studies.[5] Both the calculations at the MP2/6-31G* level and the experimental data now agree that the cyclobutyl cation has a bicyclobutonium ion structure with a strong cross-ring interaction and that the delocalized cyclopropylcarbinyl cation has essentially the same energy. The barrier to interconversion between these ions is low, and the interconversion is stereospecific.[6] In the unsubstituted series, the open homoallyl cation has a relatively high energy and does not need to be considered.

One might expect to find significant substituent effects on a closely balanced system of this type. Electron-withdrawing substituents at the 3-position of cyclobutyl derivatives should destabilize the bicyclobutonium ion and retard solvolysis. 3-Substituents that may stabilize carbocations would have their major effect on the stability of the ring-opened homoallyl cation, and it may have the lower energy in this case. An electron-releasing substituent at the 2-position should stabilize the corresponding cyclopropylcarbinyl cation and might be expected to lead to only cyclopropylcarbinyl derivatives.

A number of these compounds have been studied experimentally. Lillien, Reynolds, and Handloser[7] examined the solvolysis of *cis*- and *trans*-3-isopropylcyclobutyl brosylates in aqueous acetone and found the cis isomer to be one-sixth as reactive as cyclobutyl brosylate, whereas the trans isomer had about the same reactivity as the latter. The products were similar to those they previously found in the deamination of the corresponding amines,[8] with the cis isomer giving mainly cyclopropyl isopropyl carbinol and the trans isomer giving mainly (*trans*-2-isopropylcyclopropyl)carbinol. Some of the homoallyl and cyclobutyl alcohols also were found. Schleyer, LePerchec, and Raber[9] examined the solvolysis of the isomeric 3-*tert*-butylcyclobutyl tosylates in aqueous acetone. The cis isomer was 17.5 times less reactive than the trans isomer, and the latter was 7 times less reactive than cyclobutyl tosylate. The corresponding (2-*tert*-butylcyclopropyl)carbinyl dinitrobenzoates also were studied, and it was found that the pair of cis isomers gave essentially the same products, mainly 2,3-dimethylhex-5-en-2-ol formed from the homoallyl ion via a neopentyl rearrangement. The pair of trans isomers also gave essentially the same products, mainly (*trans*-2-*tert*-butylcyclopropyl)carbinol. The results suggest common intermediates for the product-forming steps. The acetolysis of the corresponding tosylates was examined by Rhodes and Becker who found a similar reactivity pattern.[10]

Bly and Vyas[11] have examined the acetolysis of 3,3- and 2,2-dimethylcyclobutyl tosylates. The 3,3-dimethyl compound was less reactive than cyclobutyl tosylate and gave only homoallylic acetates and dienes. The 2,2-dimethyl compound was quite different, being 400 times as reactive as cyclobutyl tosylate and giving cyclopropyldimethylcarbinyl acetate as the major product. The deamination of both (*cis*-(and *trans*)-2-methylcyclobutyl)-amines gave cyclopropylmethylcarbinol as the sole product.[12] The

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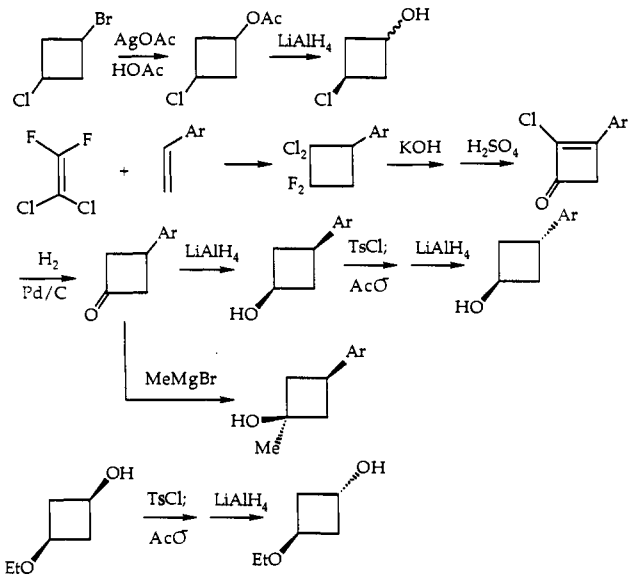
Scheme I



3,3-dimethyl and 3,3-diphenyl tosylates were studied by Michejda and Comnick,[13] and a marked rate reduction was found with the diphenyl derivative. The 3-ethoxycyclobutyl tosylates were found to be less reactive in hydrolysis than cyclobutyl tosylate.[14]

A series of 2,2,4,4-tetramethylcyclobutyl tosylates with methyl or hydroxy groups in the 3-position also have been studied.[15] However, in view of the rate acceleration afforded by 2-alkyl groups and the possibility of steric interactions between the substituents and the alkyl groups, it is difficult to interpret these results, and they will not be further considered in this report.

In all of these cases, there is the problem of separating transition-state effects and product-forming effects. It appeared that more experimental data would be helpful. Therefore, a number of additional compounds were examined. A preliminary account of the experimental study has been presented.[16]

Results and Discussion

Experimental Studies. The substituted cyclobutanols were prepared as shown in Scheme I. They were converted to the tosylates, and their solvolyses were studied in dry acetic acid containing enough sodium acetate to neutralize the acid formed. The extent of reaction was determined by titration of aliquots of the reaction solution, and good first-order kinetics were found. The rate constants are summarized in Table I. The products of the solvolysis were determined by diluting the acetic acid with water and extracting the products with carbon tetrachloride. The products were analyzed by GC and NMR spectroscopy and are summarized in Scheme II. The relative rates of solvolysis are given in Table II.

The solvolysis of the 3-arylcyclobutyl tosylates proceeded slowly, even though only homoallyl products were formed. Since the phenyl-substituted homoallyl ions should be relatively stable, the formation of these ions in the rate-determining step should lead to marked rate acceleration. Therefore, in this case, it appears likely that rearrangement to the homoallyl ion occurs after the rate-determining step for the solvolysis. The less stable trans isomer was the more reactive in each case, and the cis isomers were considerably less reactive than cyclobutyl tosylate.

A Hammett σ/ρ plot gave a slope of -1.56 (ρ) for the cis isomers, suggesting some charge transfer to the 3-carbon in the rate-determining step (Figure 1). The trans isomers gave essentially

Table I. Rates of Acetolysis of the Cyclobutyl Tosylates

compound	T (°C)	$k \times 10^5$ (s^{-1})	ΔH^*	ΔS^*	k_{cis}/k_{trans}
cyclobutyl	74.8	54.2	23.8	−5	
	50.0	3.58			
cis-3-*p*-tolyl	110.0	10.1 ± 0.1	28.2	−4	1/72
	131.0	73.1 ± 1.9			
trans-3-*p*-tolyl	60.4	3.87	25.5	−2	
	74.8	19.9 ± 0.3			
cis-3-phenyl	110.0	5.82 ± 0.15	27.4	−7	1/76
	118.9	13.9			
	131.0	39.8 ± 1.0			
trans-3-phenyl	74.8	11.5 ± 0.4	25.9	−2	
	93.7	83.4 ± 0.1			
cis-3-*p*-chlorophenyl	110.0	2.42 ± 0.03	27.4	−9	1/71
	131.0	16.6 ± 0.4			
trans-3-*p*-chlorophenyl	74.8	4.69 ± 0.19	26.0	−4	
	93.7	34.4 ± 0.2			
cis-3-*m*-chlorophenyl	116.6	2.92 ± 0.04	28.6	−7	
	129.9	10.2 ± 0.3			
cis-3-*tert*-butyl[10]	75.0	1.5	26.9	−3	1/16
	85.0	4.89			
	95.0	13.2			
trans-3-*tert*-butyl[10]	75.0	24.3			
cis-3-ethoxy	131.0	3.81 ± 0.16	25.5	−16	1/12
	152.6	20.1 ± 0.5			
trans-3-ethoxy	100.1	3.15 ± 0.04			
cis-3-chloro	154.5	0.88	26.8	−20	1/3
	156.3	1.05			
	180.9	6.08 ± 0.10			
trans-3-chloro	155.2	2.91 ± 0.06	27.8	−15	
	182.5	21.9 ± 1.0			
cis-2-methyl	30.0	8.35 ± 0.08	21.3	−7	3/1
	44.7	46.9			
	50.0	78.6 ± 1.9			
trans-2-methyl	30.0	2.34	22.1	−7	
	50.0	24.1 ± 0.8			
3-pentyl tosylate	65.1	4.15 ± 0.05	24.6	−6	
	80.0	20.3 ± 0.2			

the same slope. In order to have a model for a field effect responding to a localized charge at C1, we have examined the acetolyses of some 1-methyl-substituted tosylates (Table III). The tertiary cation formed on ionization should help to localize the charge, although it has been found that the 1-methylcyclobutyl cation is nonplanar.[17] Thus, even here, some cross-ring interaction appears to be present. The rate constants are given in Table III and lead to a ρ value of -0.97. It should be noted that the products in this case were again homoallylic acetates and no cyclobutyl acetates were found. It is also possible to correlate the rates of reaction of the chloro-, ethoxy-, phenyl-, and *tert*-butyl-substituted compounds with the field-effect parameter F.[18] The correlation is, at best, fair ($r^2 = 0.87$), and the unsubstituted compound falls well off the correlation line. Here, the slope is -5 (Figure 2), again indicating a significant positive charge at C3 in the transition state. The data do suggest charge transfer to the 3-position but do not give much information as to its magnitude.

The 3-*tert*-butylcyclobutyl tosylates were also less reactive in acetolysis than cyclobutyl tosylate, with the trans isomer 0.45 times as reactive and the cis isomer 0.027 times as reactive.[10] These results are similar to those reported for the solvolysis of the *tert*-butyl and isopropyl derivatives in aqueous acetone. *cis*-2-Methylcyclobutyl tosylate was found to be considerably more reactive than cyclobutyl tosylate, and this appears to be generally true with 2-alkyl-substituted compounds.[11,12]

The 3-ethoxycyclobutyl tosylates were quite unreactive, and both isomers gave about the same 1:1 mixture of 3-ethoxycyclobutanols as the product. The reactions of the 3-chlorocyclobutyl tosylates were unusual in that they were remarkably slow and gave the corresponding acetates with inversion of configuration. The reactions gave good first-order kinetics

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(17) Saunders, M.; Krause, N. *J. Am. Chem. Soc.* **1988**, *110*, 8050.
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Scheme II. Products of Acetolysis

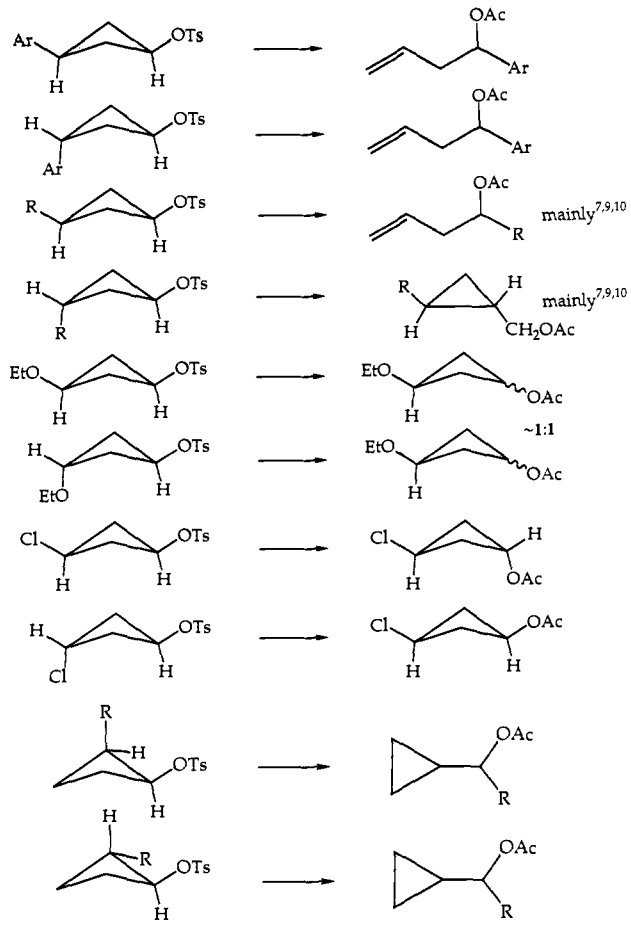

Table II. Relative Rates of Acetolysis of the Cyclobutyl Tosylates at 100 °C

compound	k_{rel}	compound	k_{rel}
2,2-dimethyl	400	*cis-tert*-butyl	0.04
cis-2-methyl	17	3,3-dimethyl	0.037
trans-2-vinyl	6.0	*trans*-3-ethoxy	0.005
trans-2-methyl	5.5	*cis*-3-phenyl	0.0037
cyclobutyl	1.0	3,3-diphenyl	0.0007
trans-3-*tert*-butyl	0.64	cis-3-ethoxy	0.0004
trans-3-phenyl	0.26	*trans*-3-chloro	0.00003
3-pentyl tosylate	0.24	*cis*-3-chloro	0.000016

through 85% reaction, indicating that they occurred by displacement by acetic acid rather than by acetate ion (0.036 M).

The principal results from the experimental data are as follows.

1. The 3-alkyl-substituted cyclobutyl derivatives give mixtures of cyclobutyl, cyclopropylcarbinyl, and homoallyl products,[7,9,10] and in this way, they are similar to cyclobutyl itself. The trans isomers are more reactive than the cis isomers, but at least part of the difference may be accounted for by the higher energy of the trans isomer. Alkyl groups retard the reaction despite the usual assumption that they are electron-releasing groups. The cis isomers give largely homoallyl products whereas the trans isomers give largely cyclopropylcarbinyl products. These products are usually the same as those formed from the corresponding cyclopropylcarbinyl derivatives, indicating that the cyclopropylcarbinyl cations are the product-forming ions. Although alkyl groups should stabilize the rearranged ions (see below), they lead to rate retardation, suggesting that the cyclopropylcarbinyl ions are not formed in the rate-determining step. Rate retardation by alkyl groups also has been found in the solvolysis of 4-alkylbicyclo[2.2.2]octyl-1-*p*-nitrobenzenesulfonates[19] and has been attributed to steric hindrance of solvation in the transition

(19) Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793.

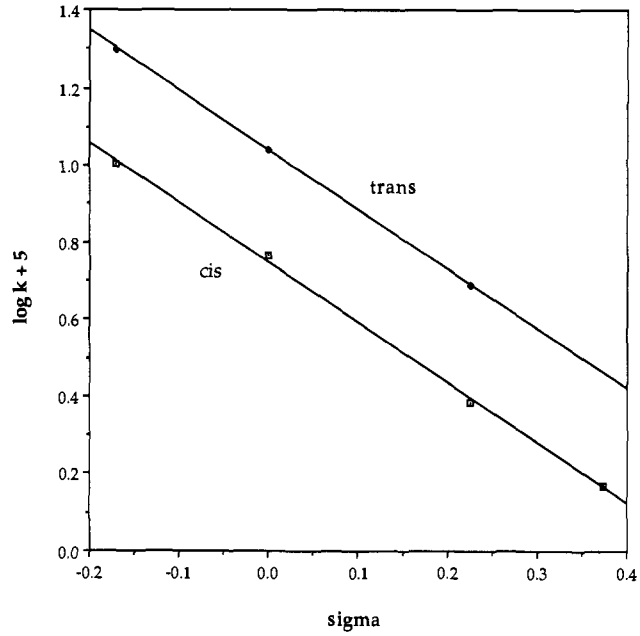

Figure 1. Correlation of log k with the Hammett σ values for the *cis*-3-arylcyclobutyl tosylates (slope = −1.56; r^2 = 0.999) and for the trans tosylates (slope = −1.54; r^2 = 1.000).

Table III. Rates of Acetolysis of the 3-Substituted 1-Methylcyclobutyl Tosylates

substituent	T (°C)	$k \times 10^5$ (s^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
cis-3-phenyl	30.0	6.59 ± 0.03	23.3	−7
	49.9	76.3 ± 0.8		
cis-*p*-chlorophenyl	50.0	51.4		
cis-*m*-chlorophenyl	30.0	2.28 ± 0.03	24.4	−8
	49.9	29.6 ± 0.1		

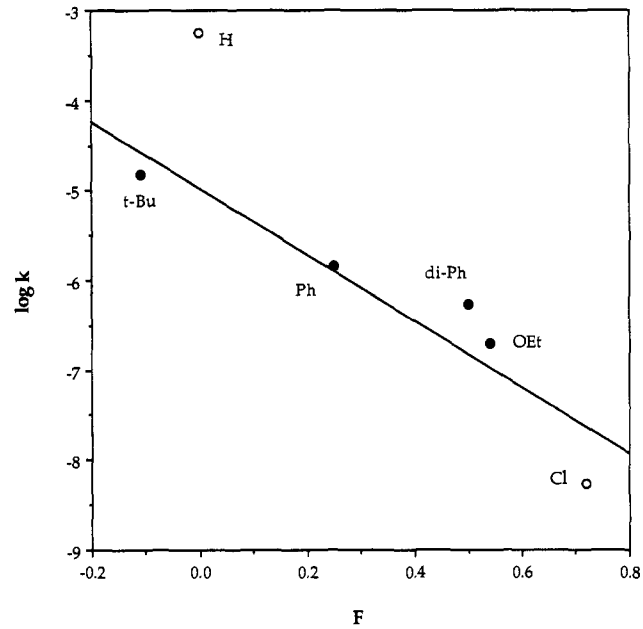

Figure 2. Correlation of log k with the field-effect parameter F using the points indicated by solid circles. The slope is −4.9; r^2 = 0.87.

state leading to the cationic intermediate.[20] The cyclobutyl system should be an even better candidate for steric hindrance to solvation at C3.

2. In contrast to the 3-alkyl-substituted derivatives, 2-alkylcyclobutyl tosylates are more reactive than cyclobutyl tosylate and they give alkylcyclopropylcarbinyl derivatives as products. The increased rate of reaction suggests, in these cases, that

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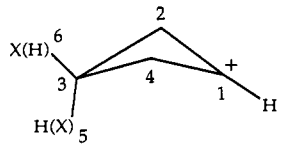
Table IV. Structures of the Cyclobutyl Cations, MP2/6-31G*



X[a]	r(1,2)[b]	r(2,3)	r(1,3)	∠135	∠136
H	1.425	1.649	1.650	110.95	133.15
endo CH_3	1.421	1.670	1.650	117.29	126.72
exo CH_3	1.425	1.643	1.691	104.72	142.26
endo Cl	1.425	1.664	1.652	115.45	130.32
exo Cl	1.427	1.643	1.736	106.18	142.55
endo HO	1.422	1.688	1.646	120.31	128.39
exo HO	1.424	1.656	1.775	106.62	144.40
endo SiH_3	1.422	1.674	1.642	116.14	126.79
exo SiH_3	1.435	1.613	1.638	104.66	145.60

[a] Position 5 is endo, and 6 is exo. [b] Distances are given in Å and angles in degrees.

rearrangement to the cyclopropylcarbinyl ion occurs in the rate-determining step.

3. The 3-aryl-substituted cyclobutyl derivatives give only homoallyl products. The homoallyl ion should be quite stable because it is aryl stabilized. Nevertheless, aryl groups retard the reaction, with the cis isomer about 70 times less reactive than the trans. If rearrangement to a homoallyl ion occurred in the rate-determining step, one might reasonably expect significant rate acceleration. Therefore, it is likely that the transition state for solvolysis has essentially the cyclobutyl cation structure. The ρ value for the reaction of the cis isomers was −1.55. α-Methyl substitution reduced the ρ value to −0.97.

4. The 3-ethoxy compounds had very low reactivity and led to ~1:1 mixtures of *cis*- and *trans*-3-ethoxycyclobutyl acetates. This product ratio is similar to that found in the deamination of the (3-ethoxycyclobutyl)amines.[21]

5. The 3-chloro compounds were 10^{-5} as reactive as cyclobutyl tosylate. The acetolysis gave the inverted acetates.

Computational Studies. It is often difficult to establish the details of solvolytic reactions using only experimental data. In the case of cyclopropylcarbinyl and cyclobutyl derivatives, the formation of a mixture of homoallyl, cyclopropylcarbinyl, and cyclobutyl products could result from a single cationic intermediate that may be attacked at different sites by a nucleophile or may involve two or more rapidly equilibrating ions. The theoretical calculations have shown that the cyclobutyl and cyclopropylcarbinyl cations have essentially the same energy and have only a small barrier (~2 kcal/mol) for interconversion.[4] The rearrangement has been shown to be stereospecific.[6] Recent low-temperature NMR and IR studies have confirmed the results of the computational studies.[5]

We have applied the same computational procedure to the study of the ions that may be involved in the present study. The structures and energies of a series of 3-substituted cyclobutanes and cyclobutyl cations were obtained at the MP2/6-31G* level of theory, which has been found to be satisfactory for the parent ion. The structures are summarized in Table IV, and the calculated energies are given in Table V. With the exception of the exo CH_3 and exo SiH_3 cases, the cyclobutyl cation structure was a transition state for rearrangement to a more stable ion. The course of the reactions was followed computationally, and the data for the final ions which had the cyclopropylcarbinyl cation structure also are given in Table V. The other substituted cyclopropylcarbinyl ions also were studied.

The structures of the bicyclobutonium ions are interesting. The C–C bonds adjacent to the cationic center are quite short, suggesting significant double-bond character, and do not vary much with changes in substituents. The more distant C–C bonds are rather long and are more sensitive to changes in substituents.

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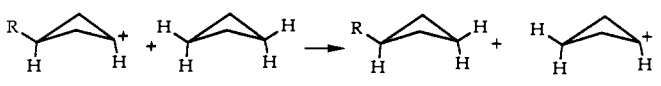
Table V. Calculated Energies of the Cyclobutanes, Cyclobutyl Cations, and Cyclopropylcarbinyl Ions

compound	HF/6-31G*	MP2/6-31G*	ZPE[c]
Substituted Cyclobutanes			
cyclobutane	−156.09703	−156.63706	66.7
endo-3-methyl	−195.13312	−195.81055	83.4
exo-3-methyl	−195.13465	−195.81219	83.4
endo-3-chloro	−615.00195	−615.68112	61.4
exo-3-chloro	−615.00475	−615.68442	61.5
endo-3-hydroxy		−231.66591	69.6[a]
exo-3-hydroxy	−230.95067	−231.67068	69.6
endo-3-silyl	−446.17104	−446.80250	75.6
endo-3-silyl	−446.17172	−446.80310	75.6
Substituted Cyclobutyl Cations			
cyclobutyl	−155.22381	−155.74766	59.1
1-methyl[b]	−194.27557	−194.93674	74.5
endo-3-methyl[b]	−194.26361	−194.92626	76.0
exo-3-methyl	−194.26153	−194.92318	76.2
endo-3-chloro[b]	−614.10221	−614.76843	53.6
exo-3-chloro[b]	−614.09375	−614.75592	53.4
endo-3-hydroxy[b]	−230.05791	−230.76445	61.5
exo-3-hydroxy[b]	−230.05255	−230.74869	60.5
endo-3-silyl[b]	−445.30232	−445.91849	68.2
exo-3-silyl	−445.31515	−445.93286	69.1
Cyclopropylcarbinyl Ions			
cyclopropylcarbinyl	−155.22778	−155.74471	58.4
1-methyl	−194.26758	−194.92555	75.2
cis-2-methyl	−194.27345	−194.92682	75.4
trans-2-methyl	−194.27645	−194.93060	75.5
endo-α-methyl	−194.28108	−194.93461	75.6
exo-α-methyl	−194.28455	−194.93740	75.5
cis-2-chloro	−614.11114	−614.77275	53.3
trans-2-chloro	−614.11345	−614.77633	53.3
cis-2-hydroxy	−230.10736	−230.79898	62.1
trans-2-hydroxy	−230.10761	−230.79951	62.1
cis-2-silyl	−445.30603	−445.91362	67.8
trans-2-silyl	−445.30992	−445.91792	67.9
Methylcyclopropane Derivatives			
methylcyclopropane	−156.09593	−156.63676	65.8
cis-1,2-dimethyl	−195.13048	−195.80878	82.8
trans-1,2-dimethyl	−195.13284	−195.81086	82.7
cis-2-chloro-1-methyl	−614.99564	−615.67650	60.7
trans-2-chloro-1-methyl	−614.99710	−615.67742	60.6
cis-2-hydroxy-1-methyl	−230.94390	−231.66442	68.8
trans-2-hydroxy-1-methyl	−230.94441	−231.66460	68.7
cis-2-silyl-1-methyl	−446.17254	−446.80486	75.0
trans-2-silyl-1-methyl	−446.17481	−446.80690	75.0

[a] At the RHF/6-31G* level, the endo hydroxycyclobutane inverted, giving the exo conformer. It was a stationary point at MP2/6-31G*. The zero-point energy was assumed to be the same as for the exo conformer. [b] The MP2/6-31G* calculations found these ions to be transition states for rearrangement to the corresponding cyclopropylcarbinyl cations. [c] The zero-point energies were obtained from HF/6-31G* frequency calculations and were scaled by 0.893.

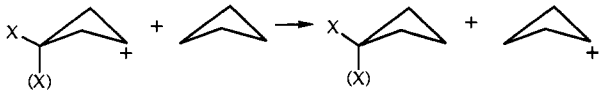
In each case, the ions with endo substituents have greater C–C bond lengths than those with exo substituents. The cross-ring distance also is sensitive to substituents, being quite long for X = Cl or HO, the cases that lead to the smallest rates of acetolysis.

One way in which to examine the substituent effect on the ions is to calculate the hydride-transfer energies for the reactions.



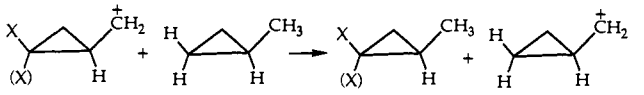
These energies are given in Table VI. It can be seen that an exo 3-methyl group is predicted to have little effect on the relative energies and that an endo 3-methyl group appears to stabilize the substituted cyclobutyl cation. This is in accord with the experimental observations that the endo 3-alkyl-substituted tosylates are more reactive than the exo 3-substituted counterparts. The experimental observation that both types of compounds are a little less reactive than cyclobutyl tosylate itself and that the decrease in reactivity is correlated with the size of the substituent

Table VI. Calculated Hydride-Transfer Energies for the Cyclobutanes, MP2/6-31G* with ZPE Correction



X	ΔH	X	ΔH
endo CH_3	3.1	endo OH	−7.1
exo CH_3	−0.1	exo OH	−18.9
endo Cl	−14.4	endo SiH_3	3.1
exo Cl	−24.0	exo SiH_3	10.9

Table VII. Calculated Rearrangement Energies, MP2/6-31G* with ZPE Correction



X	ΔH	X	ΔH
H	1.2	endo 3-HO	−21.4
endo 3-CH_3	−3.2	exo 3-HO	−30.0
exo 3-CH_3	−3.1	endo 3-SiH_3	0.0
endo 3-Cl	−5.3	exo 3-SiH_3	10.8
exo 3-Cl	−10.7	1-CH_3	7.7

suggests that steric hindrance to solvation at the 3-position may be involved, reducing the reactivity of both epimers.[20,22]

With the 3-hydroxy and 3-chloro substituents, there is a strong preference for the unsubstituted ion over the 3-substituted ions. This is in accord with their markedly reduced reactivity. On the other hand, a 3-silyl group leads to marked stabilization of the substituted cyclobutyl cation, and one might predict that the 3-silylcyclobutyl tosylates would undergo solvolysis remarkably rapidly.

The simplest explanation for the products formed from the 3-alkyl-substituted cyclobutyl tosylates is that they rearrange to form the corresponding cyclopropylcarbinyl cation and that the products are formed from these ions. This is in accord with the observation that the 3-*tert*-butyl derivatives and the corresponding (2-*tert*-butylcyclopropyl)carbinyl derivatives gave the same product distribution that did not include any cyclobutyl products.[9] Similar observations have been made with the corresponding isopropyl derivatives.[7,8] The energies of the cyclopropylcarbinyl cations are given in Table V. The rearrangement energies for going from the cyclobutyl cation to the cyclopropylcarbinyl cation are given in Table VII.

With X = H, both types of ions are minima on the potential energy surface and the difference in energy is quite small. An alkyl substituent leads to a preference for the cyclopropylcarbinyl ion, in good accord with the experimental observations. Similarly, one would predict that a 3-phenyl substituent would lead to a decrease in energy on going to the homoallyl/cyclopropylcarbinyl ion, and although rearranged products are formed, the rate of solvolysis is retarded. These data strongly suggest that for alkyl- and aryl-substituted compounds, the initial ionization process is one that leads to the cyclobutyl cation rather than directly forming the more stable cyclopropylcarbinyl cation. Both the hydroxy and chloro substituents lead to a large decrease in energy on going to the cyclopropylcarbinyl ion. The experimental observation that only cyclobutyl products are formed indicates that a free cyclobutyl cation is not formed in these cases. Here, it is likely that a tight ion-pair-stabilized ion is the product-forming species with the 3-ethoxycyclobutyl tosylates which give a mixture of *cis*- and *trans*-3-ethoxycyclobutyl acetates as products.

Only in the case of a silyl substituent is the substituted cyclobutyl cation predicted to be more stable than the corresponding cyclopropylcarbinyl cation, and even here, it is only the exo SiH_3 group that is effective. For the endo SiH_3 group, both of the possible C_s-symmetric rotamers about the C–Si bond for the cyclobutyl cation are transition states. They differ in energy by less than 0.1 kcal/mol. The data contained in the tables are for the lower energy rotamer. Following the imaginary frequency eigenvector downwards leads not to the trans SiH_3-substituted cyclopropylcarbinyl cation shown in the tables but rather to an intermediate geometry shown in Figure 3. Although this ion is 0.5 kcal/mol lower in energy than the cyclopropylcarbinyl cation and is thus the global minimum for the endo/trans SiH_3 system, it was not further investigated because it was not comparable to the other ions.

(22) Steric hindrance to rearrangement also has been suggested as the origin of the rate-retardation effect of alkyl substituents.[7] However, in view of the markedly reduced rates of reaction of the phenyl-substituted compounds whereas they should strongly stabilize the developing cyclopropylcarbinyl/homoallyl ion, this seems to be a less likely possibility.

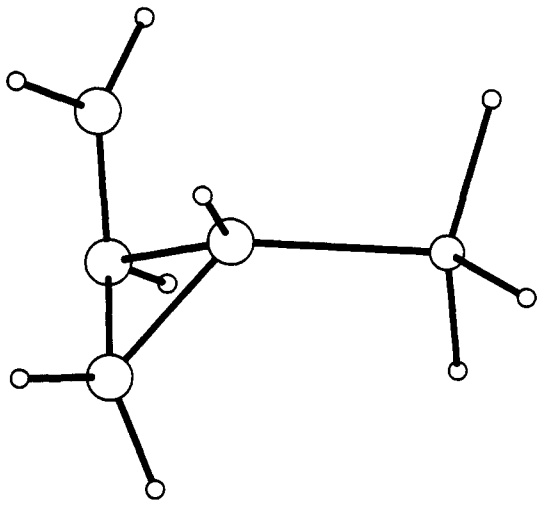
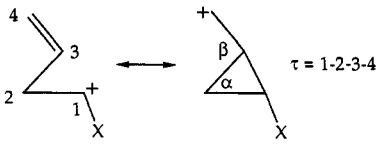


Figure 3. Calculated structure of the ion formed from the endo 3-silyl-substituted cyclobutyl cation.

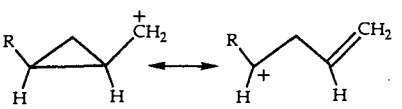
Table VIII. Structures of the Cyclopropylcarbinyl/Homoallyl Ions, MP2/6-31G*



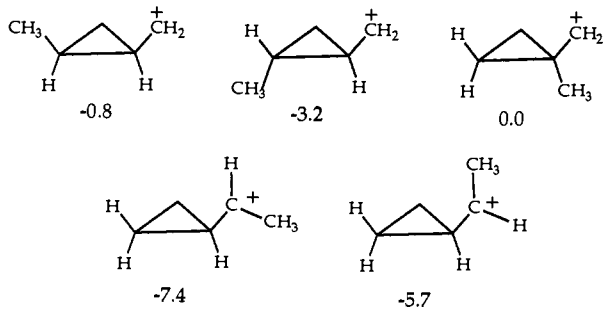
X	$r(1,2)^a$	$r(1,3)$	$r(2,3)$	$r(3,4)$	α	β	τ
H	1.415	1.646	1.646	1.356	64.5	116.5	103.7
cis CH_3	1.425	1.784	1.573	1.354	72.9	122.2	91.8
trans CH_3	1.435	1.771	1.552	1.358	72.6	121.7	85.1
cis OH	1.452	2.209	1.535	1.341	95.4	121.8	80.3
trans OH	1.453	2.159	1.534	1.343	92.6	122.2	86.8
cis Cl	1.426	1.870	1.559	1.353	77.4	122.3	89.8
trans Cl	1.436	1.828	1.546	1.358	75.6	122.2	84.7
cis SiH_3	1.423	1.628	1.675	1.357	62.8	112.2	114.3
trans SiH_3	1.427	1.690	1.595	1.358	67.7	119.5	94.5

[a] Distances are given in Å and angles in degrees.

The structures of the 2-substituted cyclopropylcarbinyl cations are interesting (Table VIII). The cyclopropane ring is no longer symmetrical, but rather, the structure appears to have considerable homoallyl character. This is not surprising since the corresponding homoallyl cation canonical structure will be stabilized by an alkyl substituent. With a strong conjugating substituent such as a phenyl, the homoallyl structure might be expected to be stabilized over the cyclopropylcarbinyl structure, and indeed, only homoallyl products were found.



The relative energies (kcal/mol) of the five methyl-substituted cyclopropylcarbinyl cations are interesting:



Methyl substitution at the 1-position is the least effective in stabilizing the positive charge. As expected, the two secondary ions are the more stable ions, and the less sterically encumbered exo isomer is the more stable of the two. Substitution at the trans 2-position is half as effective in stabilizing the ion as is α substitution. This stabilizing effect is a result of the stabilization of the homoallyl component of the ion.

The effect of the other substituents on the energy of the cyclopropylcarbinyl cation may be examined using hydride-transfer reactions in the same way as for the cyclobutyl cations above (Table IX). The energies of the cyclopropylcarbinyl ions and of the corresponding substituted methylcyclopropanes are given in Table V. It might first be noted that the calculated difference in energy between *cis*- and *trans*-1,2-dimethylcyclopropane (1.3 kcal/mol) is in good agreement with our experimental data for 1,2-diethylcyclopropane.[23] The methyl-substituted compounds prefer to have the methyl group attached to the cyclopropylcarbinyl ion so that it may help stabilize the homoallyl component of the ion. This is seen in the calculated geometry of the ion where the C1–C3 bond is lengthened and the C2–C3 bond is shortened with respect to the unsubstituted ion.

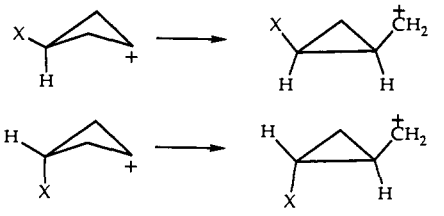
A chlorine has the opposite effect. It clearly destabilizes the cyclopropylcarbinyl cation and prefers to be on the uncharged species. This is in good accord with the observation that a 2-chloro substituent reduced the rate of solvolysis of cyclopropylcarbinyl derivatives.[24] Nevertheless, it still leads to a markedly unsymmetrical ion. On the other hand, a hydroxy group leads to marked stabilization of the cyclopropylcarbinyl/homoallyl ion which now has mainly homoallyl character (note the very long C1–C3 distance). A silyl group was different in that it had little effect on the energy of the ion, leading to a very small hydride-transfer energy. The ion is now relatively symmetrical, and this is especially true with the cis silyl group.

Charge Distribution. We were interested in examining the charge distributions in the ions in order to determine to what extent charge is transferred to the 3-position in the cyclobutyl cations. The effect of the 3-aryl substituents suggests some charge transfer, but it does not provide an estimate of the magnitude.

The question was examined in two ways. First, we have made use of Bader's theory of atoms in molecules[25] that allows one to calculate the electron population at each atom via direct integration of the charge density within well-defined atomic regions. The results are summarized in Table X. The most striking observation is that on going from the substituted cyclobutane to the corresponding bicyclobutonium ion, the charge is found largely on the hydrogens and the C3 carbon gains charge density. This may at first seem surprising, but it can readily be checked by calculating the difference in charges between the bicyclobutonium ion and a cyclobutyl radical having the same geometry. A plot of this charge difference is shown in Figure 4. It is obvious that the hydrogens bear most of the charge and that C3 does indeed gain charge density. It should be noted that the hydrogens at C2 and C4 also suffer considerable loss of charge

(23) Wiberg, K. B.; Lupton, E. C.; Wasserman, D. J.; deMeijere, A.; Kass, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1740.
(24) Robinson, G. C. *J. Org. Chem.* **1969**, *34*, 2517.
(25) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*; Clarendon Press: Oxford, 1990.

Table IX. Calculated Hydride-Transfer Energies for the Methylcyclopropanes, MP2/6-31G* with ZPE Correction



X	ΔH	X	ΔH
cis-2-methyl	6.3	*cis*-2-hydroxy	16.0
trans-2-methyl	7.2	*trans*-2-hydroxy	16.1
cis-2-chloro	−7.3	*cis*-2-silyl	0.3
trans-2-chloro	−5.8	*trans*-2-silyl	1.6

Table X. Atomic Charges for the Cyclobutanes and Bicyclobutonium Ions

substituent	compound	C1	H[a]	C3	X	H
H	neutral	−0.039	0.020	−0.039	0.020	0.020
	cation	−0.002	0.184	−0.158	0.233	0.184
endo CH_3	neutral	−0.042	0.020	0.022	−0.007	0.010
	cation	−0.014	0.173	−0.128	0.239	0.208
exo CH_3	neutral	−0.039	0.021	0.026	−0.010	0.013
	cation	0.009	0.175	−0.105	0.278	0.151
endo OH	neutral	−0.051	0.013	0.529	−0.557	0.040
	cation	−0.030	0.166	0.573	−0.494	0.240
exo OH	neutral	−0.045	0.028	0.550	−0.571	0.042
	cation	0.026	0.183	0.571	−0.428	0.185
endo Cl	neutral	−0.036	0.042	0.075	−0.272	0.064
	cation	−0.008	0.197	−0.012	−0.032	0.248
exo Cl	neutral	−0.041	0.031	0.085	−0.277	0.037
	cation	0.024	0.187	0.024	−0.001	0.190
endo SiH_3	neutral	−0.037	0.028	−0.763	0.702	0.033
	cation	−0.014	0.172	−0.725	0.817	0.218
exo SiH_3	neutral	−0.032	0.024	−0.770	0.705	0.035
	cation	−0.012	0.176	−0.642	0.826[b]	0.162

[a] The endo C1 hydrogen for the neutral compounds. The exo hydrogens have essentially the same charge. [b] This atom did not integrate satisfactorily, and the value was obtained by difference.

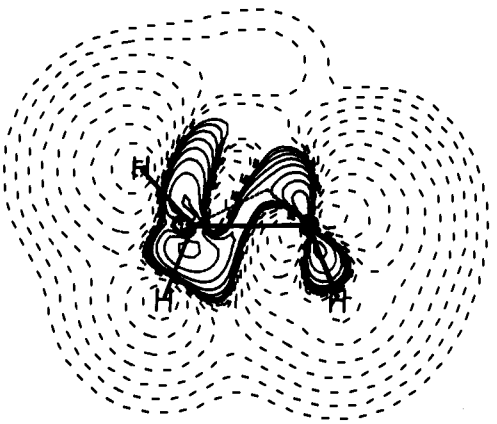


Figure 4. Charge density difference plot for the HC3 ··· C1H plane of the cyclobutyl radical minus the cyclobutyl cation, both at the latter geometry. Dashed lines indicate regions in which charge density was removed on going to the cation, and solid lines indicate regions in which there is increased charge density in the cation.

density. In the case of the bicyclobutonium ion, these hydrogens have atomic charges of 0.170 and 0.161 e. The changes in charge density on going from the radical to the cation (i.e., loss of charge by hydrogens and gain by carbons) appear to be quite general.[26]

In each case, the change in charge at C1 is surprisingly small, corresponding to the loss of only 0.02–0.07 e. The attached hydrogen loses 0.15 e in all cases. The main differences are seen at C3. An exo hydrogen loses 0.18–0.20 e whereas an endo

(26) Wiberg, K. B.; Schleyer, P. v. R. To be published.

hydrogen loses 0.13–0.16 e. C3 gains population on going to the cation for all substituents except SiH_3, and the effect is largest when a hydrogen occupies the exo position. With CH_3 or Cl as the substituent, it loses ~0.25 e on going to the cation, and when the substituent is OH or SiH_3, it loses ~0.12 e. The difference between the exo and endo substituents is relatively small.

It is difficult to put the substituent effect on the charges in perspective at the present time because there are so few other examples with which they may be compared.

Conclusions

Both the experimental data and the theoretical calculations are in agreement with the hypothesis that the solvolysis of the 3-alkyl- and 3-aryl-substituted cyclobutyl tosylates leads in the rate-determining step to a bridged cyclobutyl cation which then rearranges to the corresponding cyclopropylcarbinyl cation. The latter has a structure between that of the symmetrical parent ion and a homoallyl ion. The products are in most cases derived from these ions. Rate retardation by 3-alkyl groups probably results from steric hindrance to solvation at C3.

The cis 2-substituted cyclopropylcarbinyl cations usually lead to homoallyl products whereas the trans 2-substituted ions usually lead to cyclopropylcarbinyl products. In this connection, it is worth noting that the difference in calculated energy between the cis and trans 2-methyl-substituted ions is 2.4 kcal/mol, and it would be expected to increase with larger alkyl groups. It appears that the more sterically constrained cyclopropylcarbinyl ions react to give mainly homoallyl products, whereas the more stable ions react mainly to give cyclopropylcarbinyl products.

Strongly electron-withdrawing groups such as Cl and RO retard the reaction and give only cyclobutyl products. Calculations for these derivatives also indicate a considerable cross-ring interaction in the corresponding cyclobutyl cations and again find that the rearranged cyclopropylcarbinyl ion has the lower energy. The lack of rearrangement shows that free cyclobutyl cations are not formed in the reactions of these compounds, and it is likely that relatively tight ion pairs are the product-forming species with X = OEt.

Cyclopropylcarbinyl and homoallyl ions were found to be a single species, whose geometry was strongly controlled by the substituents.

Experimental Section[27]

3-Chlorocyclobutanol. A mixture of 96.0 g (0.566 mol) of 1-bromo-3-chlorocyclobutane[28] and 145 g (0.856 mol) of silver acetate in 500 mL of glacial acetic acid was stirred at reflux for 48 h. The flask was wrapped to exclude light. The mixture was cooled, the solids were filtered by suction, and the filtrate was distilled at 30 mmHg giving 49.6 g (59%) of 3-chlorocyclobutyl acetate. To 17 g (0.45 mol) of lithium aluminum hydride in 500 mL of dry ether in a 1-L flask was added 49 g (0.33 mol) of 3-chlorocyclobutyl acetate in 100 mL of ether dropwise with stirring. The mixture was stirred for 1 h. Water was added, the ether layer was separated, and the solvent was distilled. The residue was distilled giving 21.8 g (62%) of 3-chlorocyclobutanol, bp 85–95 °C at 20 Torr. This was a mixture of the cis and trans isomers in a ratio of 60–40 as shown by VPC on a 15-ft 20M-Carbowax on 45–60 Anakrom column at 196 °C. The two isomers were separated by preparative VPC.

***trans*-3-Chlorocyclobutyl Tosylate.** To 2.00 g (0.010 mol) of tosyl chloride in 10 mL of pyridine was added 1.11 g (0.0094 mol) of *trans*-3-chlorocyclobutanol. The solution was allowed to stand at room temperature for 1 h and at −1 °C for 24 h. The pyridine solution was diluted with 50 mL of water and extracted with 50–50 ether–pentane, and the combined extracts were washed twice with 1 N hydrochloric acid, once with 10% sodium carbonate, and once with a saturated sodium chloride solution. After being dried over magnesium sulfate, the solvent was removed under reduced pressure. The crude oil was recrystallized from ether–pentane affording a solid with mp 39.0–39.5 °C. Anal. Calcd for $C_{11}H_{13}SO_3Cl$: C, 50.65; H, 5.02; Cl, 13.61. Found: C, 50.74; H, 4.89; Cl, 13.46.

***cis*-3-Chlorocyclobutyl Tosylate.** To 2.2 g (0.0115 mol) of tosyl chloride in 10 mL of pyridine was added 1.14 g (0.0107 mol) of *cis*-3-chlorocyclobutanol. The reaction was carried out as described above. Recrystallization yielded 2.45 g (87%) of tosylate, mp 57.0–57.5 °C. Anal. Calcd for $C_{11}H_{13}SO_3Cl$: C, 50.65; H, 5.02; Cl, 13.61. Found: C, 50.81; H, 4.92; Cl, 13.45.

***cis*-3-Phenylcyclobutanols.** To a Carius combustion tube were added 10.0 g (0.096 mol) of styrene and 12.4 g (0.093 mol) of difluorodichloroethylene. The tube was sealed and heated in a tube furnace for 43 h at 112 °C. The tube was opened. Vacuum distillation afforded 13.6 g (62%) of product, bp 83–88 °C at 2 Torr (lit.[29] bp 78–82 °C at 1 Torr). The substituted styrenes gave the following yields: *p*-Cl, 65%, bp 110–114 °C at 2.5 Torr; *m*-Cl, 52%, bp 107–112 °C at 2 Torr; *p*-Me, 48%, bp 92–95 °C at 1 Torr; and *m*-Br, 66%, bp 112–117 °C at 1.5 Torr.

To a solution of 4.0 g of potassium hydroxide in 30 mL of 95% ethanol was added 13.6 g (0.056 mol) of 2,2-dichloro-3,3-difluoro-1-phenylcyclobutane with stirring. The mixture was allowed to stir for 1 h and then allowed to stand for 20 h at room temperature. The mixture was poured into 60 mL of water and extracted four times with ether. The combined ether extracts were dried over magnesium sulfate and distilled to remove ether. Distillation of the residue afforded 9.5 g (83%) of 1,1-difluoro-2-chloro-3-phenyl-2-cyclobutene, bp 73–75 °C at 2 Torr (lit.[29] bp 66–67 °C at 1 Torr). For the *p*-Cl, *m*-Cl, *m*-Br, and *p*-Me derivatives, the oil or solid obtained here was used directly in the next step.

To 5 mL of concentrated sulfuric acid was added 9.5 g (0.047 mol) of 1,1-difluoro-2-chloro-3-phenyl-2-cyclobutene. The mixture was heated on a steam bath for 2 min, 50 mL of concentrated sulfuric acid was added, and heating was continued for 15 min. The mixture was added slowly to 2 L of ice. 2-Chloro-3-phenylcyclobut-2-enone was collected by suction filtration and dried under vacuum overnight. Recrystallization once from 50–50 ether–pentane yielded 6.6 g (78%) of product, mp 66.0–67.0 °C (lit.[29] mp 67.8–69.2 °C).

The *p*-Cl, *m*-Cl, *m*-Br, and *p*-Me derivatives afforded yields of 77%, 65%, 60%, and 77%, respectively. The melting points were 158–159, 83–84, 87.0–87.5, and 40.5–41.0 °C, respectively.

To 7.1 g (0.0394 mol) of 2-chloro-3-phenylcyclobut-2-enone in a Parr shaker were added 3.6 g of sodium acetate, 100 mL of methanol, and 0.2 g of Pd/C catalyst. Hydrogenation resulted in the uptake of 0.8 mol of hydrogen. The mixture was filtered, poured into water, and extracted three times with ether. The combined ether extracts were dried over magnesium sulfate, and the ether was removed under reduced pressure affording 5.6 g (96%) of 3-phenylcyclobutanone.

This material was reduced with 2.0 g of lithium aluminum hydride (excess) in 150 mL of ether. Hydrochloric acid (0.1 N) was added, and the ether was separated. The aqueous layer was extracted three times with ether. The combined ether extracts were dried over magnesium sulfate, and the ether was evaporated. Vacuum distillation afforded 4.6 g (80%) of *cis*-3-phenylcyclobutanol, bp 90–95 °C at 0.6 Torr (lit.[29] bp 80–84 °C at 1 Torr).

For the substituted phenyl derivatives, the yields were as follows (compound, ketone, alcohol, boiling point of alcohol): *p*-Cl, 85%, 86%, bp 108–115 °C at 1 Torr; *m*-Cl, 80%, 80%, bp 110–120 °C at 1.5 Torr; and *p*-Me, 75%, 99% (crude), VPC separated. For the *m*-bromo derivative, considerable hydrogenolysis of the C–Br bond occurred.

***cis*-3-Phenylcyclobutyl Tosylates.** Tosylates were prepared from the above alcohols by the following methods.

To 6.0 g (0.0315 mol) of tosyl chloride in 20 mL of pyridine was added 4.6 g (0.031 mol) of *cis*-3-phenylcyclobutanol. The solution was allowed to stand at room temperature overnight. The mixture was added to water and extracted twice with ether, and the extracts were washed in turn with 1 N hydrochloric acid, 1 N sodium bicarbonate, and saturated sodium chloride solutions. Evaporation of ether yielded 6.4 g (68%) of the tosylate as an oil which resisted recrystallization but which had no extraneous peaks in the NMR.

To a solution of 5.3 g (0.0358 mol) of *cis*-3-phenylcyclobutanol in 100 mL of ether was added 16 mL of 2.25 M *n*-butyllithium. Stirring was maintained for 15 min at room temperature. To this solution was added 6.8 g (0.0358 mol) of tosyl chloride in 25 mL of ether. The solution was stirred for 20 h at room temperature. Water (50 mL) was added, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the ether was removed under reduced pressure affording 9.9 g (91%) of *cis*-3-phenylcyclobutyl tosylate. Analytical data are as follows.

(27) The ^1H NMR spectra of all of the compounds are available in the Ph.D. Thesis of G.L.N., Yale University, New Haven, CT, 1970.

(28) Wiberg, K. B.; Lampman, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 4429.

(29) Manatt, S. L.; Vogel, M.; Knutson, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2645.

***cis*-3-(*p*-Tolylphenyl)cyclobutyl tosylate**: mp 63–64 °C. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.31; H, 6.38. Found: C, 68.16; H, 6.24.

***cis*-3-(*m*-Chlorophenyl)cyclobutyl tosylate**: oil. Anal. Calcd for $C_{17}H_{17}O_3SCl$: C, 65.76; H, 6.07. Found: C, 65.68; H, 6.19.

***cis*-3-(*p*-Chlorophenyl)cyclobutyl tosylate**: oil. Anal. Calcd for $C_{17}H_{17}O_3SCl$: C, 65.76; H. 6.07. Found: C, 65.70; H, 6.31.

***trans*-3-Phenylcyclobutyl Tosylate.** To 8.0 g (0.097 mol) of sodium acetate in 75 mL of dimethylformamide was added 4.5 g (0.015 mol) of *cis*-3-phenylcyclobutyl tosylate. The mixture was allowed to stir at 120 °C for 20 h. The cooled mixture was added to water and extracted twice with ether. The combined ether extracts were dried over magnesium sulfate. Ether was removed under reduced pressure affording 3.0 g of crude acetate. VPC on a 10-ft 20M-Carbowax column gave 1.0 g of pure trans acetate. The acetate was reduced with 0.5 g of lithium aluminum hydride in 50 mL of ether. Acid workup and ether removal yielded 0.6 g of *trans*-3-phenylcyclobutanol. The trans tosylate was prepared from 0.8 g of tosyl chloride and 0.6 g of *trans*-3-phenylcyclobutanol in 10 mL of pyridine. Workup as for the cis isomer afforded an oil which was used without further purification. The NMR and IR spectra were consistent with *trans*-3-phenylcyclobutyl tosylate.

The *p*-chloro and *p*-methyl derivatives were prepared in like manner. Analytical data are as follows.

***trans*-3-Phenylcyclobutyl tosylate**: oil. Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.53; H, 5.99. Found: C, 67.34; H, 5.82.

***trans*-3-(*p*-Chlorophenyl)cyclobutyl tosylate**: oil. Anal. Calcd for $C_{17}H_{17}O_3SCl$: C, 60.61; H, 5.08. Found: C, 60.41; H, 5.22.

***trans*-3-(*p*-Tolylphenyl)cyclobutyl tosylate**: oil. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.31; H, 6.38. Found: C, 68.16; H, 6.24.

***cis*-3-Ethoxycyclobutyl Tosylate.** To 8.3 g (0.0436 mol) of tosyl chloride in 50 mL of pyridine was added 5.0 g (0.0431 mol) of *cis*-3-ethoxycyclobutanol[30] Workup as for *cis*-3-phenylcyclobutyl tosylate afforded an oil which was used without further purification.

***trans*-3-Ethoxycyclobutyl Tosylate.** To 3.2 g (0.0126 mol) of *cis*-3-ethoxycyclobutyl tosylate in 50 mL of dimethylformamide was added 5 g (0.061 mol) of sodium acetate. The mixture was allowed to stir at 120 °C for 20 h. Workup as for *trans*-3-phenylcyclobutyl acetate afforded *trans*-3-ethoxycyclobutyl acetate. The crude acetate was purified by VPC on a 15-ft 20M-Carbowax column. Lithium aluminum hydride reduction of the pure acetate afforded 0.35 g of *trans*-3-ethoxycyclobutanol.

The tosylate was prepared by the pyridine method as above. Workup afforded an oil which was used without further purification.

1-Methyl-*cis*-3-phenylcyclobutanol. To a solution of 20 mL of 2.15 M methylmagnesium chloride in 50 mL of dry ether was added dropwise 5.0 g (0.0342 mol) of 3-phenylcyclobutanone in 25 mL of ether under a nitrogen atmosphere. Stirring was maintained for 2 h. 1 N sulfuric acid was added slowly. The ether layer was separated and the aqueous layer extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the ether was removed under reduced pressure. Vacuum distillation of the residue afforded 4.4 g (79%) of the alcohol, bp 89–92 °C at 0.4 Torr.

The *p*-chlorophenyl and *m*-chlorophenyl derivatives were prepared in like manner.

1-Methyl-*cis*-3-phenylcyclobutyl Tosylate. A 250-mL three-neck flask was fitted with a mechanical stirrer, a nitrogen inlet, an addition funnel, and a condenser. To the flask was added 4.4 g (0.0272 mol) of 1-methyl-*cis*-3-phenylcyclobutanol in 125 mL of dry ether. To the ice-cooled mixture was added 13 mL of 2.25 M *n*-butyllithium in hexane by means of a syringe. The mixture was stirred for 15 min. Then, 5.3 g (0.0279 mol) of tosyl chloride in 50 mL of ether was added. The solution was stirred at 0 °C for 5 h; 50 mL of water was added and the ether layer separated. The aqueous layer was extracted with ether, and the combined extracts were dried over anhydrous potassium carbonate. The ether was removed under reduced pressure and the residue recrystallized from petroleum ether.

The *p*-chloro and *m*-chloro derivatives were prepared in like manner. The analytical data are as follows.

1-Methyl-*cis*-3-phenylcyclobutyl tosylate: mp 48–49 °C. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.35; H, 6.33; S, 10.13. Found: C, 68.11; H, 6.50; S, 9.98.

1-Methyl-*cis*-3-(*p*-chlorophenyl)cyclobutyl tosylate: mp 56–57 °C. Anal. Calcd for $C_{18}H_{19}O_3SCl$: C, 61.61; H, 5.45. Found: C, 61.36; H, 5.59.

1-Methyl-*cis*-3-(*m*-chlorophenyl)cyclobutyl tosylate: mp 60–61 °C. Anal. Calcd for $C_{18}H_{19}O_3SCl$: C, 61.62; H, 5.45. Found: C, 61.75; H, 5.61.

2-Methylcyclobutyl Tosylates. 2-Methylcyclobutanol was obtained by the acid-catalyzed isomerization of 1-vinylcyclopropanol followed by lithium aluminum hydride reduction.[31] VPC on a 28-ft 20M-Carbowax column on Anakrom 70–80 ABS at 150 °C showed the mixture to be 70% cis and 30% trans. Pure material was obtained by preparative VPC. Tosylates were prepared from the pure alcohols by the method previously described for *cis*-3-phenylcyclobutyl tosylate (*n*-butyllithium method). The oils obtained on workup were used directly without purification. The NMR spectra showed no rearrangement. Some unreacted alcohol was present in each case, however.

Kinetic Investigations. The integrated first-order rate expression $k = 1/t(\ln(a/a - x))$ was used for the calculation of the rate constants. The slope of the best straight line was determined using a least-squares analysis. Where possible, at least two determinations were used for each tosylate at each temperature. The rate constants agreed to within 5%.

The acetic acid used in the kinetic runs was prepared by heating 99.8% acetic acid (6.5 L) to reflux overnight with an excess of acetic anhydride (180 g). The resulting solution was 0.05 N in acetic anhydride.

Standard potassium acetate solution was prepared by dissolving weighed quantities of Mallinckrodt Analytical anhydrous potassium carbonate in measured volumes of acetic acid. Titrant solutions of *p*-toluenesulfonic acid were prepared by dissolving approximately weighed quantities of Fisher Certified Reagent *p*-toluenesulfonic acid monohydride in acetic acid. They were standardized with the standard potassium acetate solution.

The sodium acetate buffer solutions used in the kinetic runs were prepared by treating weighed quantities of sodium carbonate in acetic acid with the calculated amount of acetic anhydride necessary to destroy the liberated water. The concentrations of these solutions were determined by titrating with the *p*-toluenesulfonic acid solutions.

Method A. The tosylate was weighed in a 50-mL volumetric flask. The flask was filled to the line at room temperature with ~0.03 M sodium acetate solution and the solution thoroughly mixed. The volumetric flask was placed in a constant-temperature bath and allowed to equilibrate for 10 min before the first point was taken.

For each point, 3 mL of solution was removed using a pipette. The solution was delivered into a 10-mL Erlenmeyer flask containing 2 drops of a saturated solution of bromophenyl blue indicator in acetic acid and 3 mL of carbon tetrachloride. The carbon tetrachloride quenched the reaction. Time was recorded when the initial drop hit the carbon tetrachloride solution.

The excess sodium acetate was titrated using the *p*-toluenesulfonic acid solution delivered from a 5-mL Koch microburette. The end point was a change from pale yellow to nearly colorless. The experimental infinity titration was taken after 10 half-lives.

Method B. This method was used for runs above 100 °C. As in method A, the tosylates were weighed in a volumetric flask and then sodium acetate buffer was added. Aliquots (3.5 mL) were removed, and each was sealed in an ampoule. The ampoules were placed together in a wire basket, which was immersed in a thermostated constant-temperature bath. After immersion, the ampoules were allowed to equilibrate for 15 min. They were removed one at a time with tongs. The reaction was quenched by placing the ampoule in cold water. Time was recorded on immersion. Three-milliliter samples were withdrawn from the opened ampoules and titrated with the *p*-toluenesulfonic acid solution.

Product Studies. A solution of 0.15 g of the tosylate in 25 mL of the sodium acetate–acetic acid buffer solution was allowed to remain at the appropriate temperature for several half-lives. The solution was diluted with water and extracted with carbon tetrachloride. The dried carbon tetrachloride solution was analyzed by NMR to determine the nature of the products and by GC to determine the relative amounts of the products. The acetates that could be formed as products either were obtained in the course of the preparation of the alcohols (see above) or were prepared from the alcohols. The NMR spectra of the authentic acetates were used in identifying the reactions products. In no case were internal return products (rearranged tosylates) found as products.

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(31) Silver, M. S.; Caserio, M. C.; Rice, H. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 3675.