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SOLVOLYSIS OF 3-SUBSTITUTED CYCLOBUTYL TOSYLATES (1)

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Previous studies of cyclobutyl derivatives have suggested that marked steric and electronic effects should be noted in the solvolysis of 3-substituted cyclobutyl tosylates (2, 3, 4). The steric effect, which is noted with an equatorial 3-substituent, presumably arises from a change in geometry on going to the activated complex. Such a change in geometry would bring the substituent close to the axial hydrogens at C_2 and C_4. The electronic effect could arise either from a cross-ring interaction as is calculated for a cyclobutyl cation (3), or from changes in charge distribution resulting from rearrangement toward another ion (such as an allylcarbinyl cation). In order to further examine these interactions, we have studied the acetolyses of a series of 3-substituted cyclobutyl tosylates.

The cis-3-phenylcyclobutanols were prepared from the corresponding ketones (5) by lithium aluminum hydride reduction. Conversion to the tosylate followed by acetate ion displacement in dimethylformamide led to the trans-acetates. The 3-chlorocyclobutyl acetates were prepared by the reaction of 3-chlorocyclobutyl bromide (6) with silver acetate in acetic acid at the reflux temperature. trans-3-Ethoxycyclobutyl acetate was obtained by acetate ion displacement on the tosylate derived from cis-3-ethoxycyclobutanol (7). The displacement reactions gave predominantly the inverted acetate and proceeded in good yield.

The rates of acetolysis are summarized in Table I and relative rates are given in Table II. A plot of log k for the cis-3-phenyl derivatives (110°) against σ gave $\rho = -1.55$ and a similar plot for the trans-3-phenyl derivatives (75°) gave $\rho = -1.55$. In both cases the plots were quite satisfactory. The 3-phenyl derivatives gave largely allylcarbinyl products.

The 3-ethoxy and 3-chloro derivatives underwent reaction at markedly decreased rates. The 3-ethoxycyclobutyl tosylates gave mixtures of the two epimeric unrearranged acetates whereas the 3-chloro derivatives gave only the unrearranged acetate formed with inversion of configuration. The k_{trans}/k_{cis} ratios were markedly less than for the 3-phenyl derivatives. In the trans-series a plot of log k against the field effect parameter, F, (8) for the H, C_6H_5-, EtO- and Cl- substituents was linear and had a slope of -7.

The slope of -7 for the log k vs. F plot and the $\rho = 1.55$ found with the 3-phenyl derivatives are in good accord with each other. The ionization constants of the 3-phenylcyclobutanecarboxylic acids in 50% ethanol was correlated with σ by $\rho = 0.26$ (9). The ρ value for the ionization constants of the 3-substituted cyclobutanecarboxylic acids would be expected to be at least unity (10).

It is clear from these data that the activated complex cannot be described as being similar in structure to the allylcarbinyl cation. If it were, marked stabilization by phenyl, and especially by ethoxy, should be observed. However, these substituents retard the reaction, and the allylcarbinyl products are not formed in significant amount with a 3-ethoxy substituent. This is similar to the deamination of 3-ethoxycyclobutylamines in which the major products are the 3-ethoxycyclobutyl acetates (11). The observations also do not suggest any significant direct participation of the ethoxy group in the formation of the activated complex (12).

The 3-substituted compounds stand in marked contrast to the 2-alkylcyclobutyl derivatives which are much more reactive than cyclobutyl tosylate (13). Thus, 2-alkyl substituents are capable of stabilizing the charge developed in the activated complex. The difference in substituent effects for the two positions may be accommodated either by an activated complex resembling a cyclopropylcarbinyl cation or a puckered cyclobutyl cation. The former will lead to charge transfer to the 2-position but not the 3-position. CNDO calculations for the latter suggest that a trans-3-alkyl substituent should lead to a slightly increased charge at the cationic center whereas a 2-alkyl substituent should lead to a significantly decreased charge at this position. However, a cis-3-alkyl substituent also

Table I

Rates of Acetolysis of Cyclobutyl Tosylates

Compound	T	k(sec^{-1})	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
cis-3-p-Tolyl	110.0°	1.01×10^{-4}	28.2	- 4
	131.0°	7.35×10^{-4}		
cis-3-Phenyl	110.0°	5.84×10^{-5}	27.4	- 7
	118.9°	1.39×10^{-4}		
	131.0°	4.05×10^{-4}		
cis-3-p-Chlorophenyl	110.0°	2.42×10^{-5}	27.4	- 9
	131.0°	1.66×10^{-4}		
cis-3-Chloro	156.3°	1.13×10^{-5}	26.7	-20
	180.9°	6.20×10^{-5}		
	181.7°	6.68×10^{-5}		
cis-3-Ethoxy	131.0°	3.76×10^{-5}	25.6	-16
	152.6°	2.01×10^{-4}		
trans-3-p-Tolyl	74.8°	1.99×10^{-4}	25.5	- 2
	60.4°	3.87×10^{-5}		
trans-3-Phenyl	74.8°	1.10×10^{-4}	26.5	- 1
	93.7°	8.31×10^{-4}		
trans-3-p-Chlorophenyl	74.8°	4.87×10^{-5}	25.5	- 5
	93.7°	3.44×10^{-4}		
trans-3-Chloro	155.2°	2.83×10^{-5}	28.6	-13
	182.5°	2.28×10^{-4}		
trans-3-Ethoxy	100.1°	3.15×10^{-5}		
Cyclobutyl (13)	74.8	5.42×10^{-4}	23.8	- 5
	50.0	3.58×10^{-5}		

Table II

Relative Rates of Acetolysis

Compound	k_{rel}	k_{cis}/k_{trans}	Compound	k_{rel}	k_{cis}/k_{trans}
Cyclobutyl	1		cis-3-Chloro	1/50000	1/3
cis-3-p-Tolyl	1/250	1/77	trans-3-Chloro	1/15000	
trans-3-p-Tolyl	1/3		3,3-Dimethyl (15)	1/30	
cis-3-p-Phenyl	1/375	1/74	3,3-Diphenyl (15)	1/1000	
trans-3-p-Phenyl	1/5		3-Isopropyl (4)		1/6
cis-3-p-Chloro-phenyl	1/770	1/69	3-t-Butyl (16)		1/16
trans-3-p-Chloro-phenyl	1/11				
cis-3-Ethoxy	1/2300	1/12			
trans-3-Ethoxy	1/190				

should stabilize the positive charge.

The k_{cis}/k_{trans} ratios again indicate that a change in geometry occurs in the formation of the activated complex. Large groups such as phenyl and t-butyl give relatively large ratios whereas smaller groups such as methyl and isopropyl give small ratios. It may be noted that the effect with the 3, 3-diphenyl compound is approximately the product of the effects found for the cis- and trans-phenyl derivatives.

It then appears that significant geometrical change occurs in the formation of the activated complex, but that the bonding at the 3-position remains essentially of the σ -type so that no important π-interaction with phenyl or ethoxy is possible. The course of the reaction will be considered in further detail when we present the full data.

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