Tetrahedron Letters No.49, pp. 6107-6113, 1966. Pergamon Press Ltd.
Printed in Great Britain.

I. ACETOLYSIS STUDIES OF DI-, TETRA- AND HEXAMETHYLATED CYCLOPENTYL TOSYLATES

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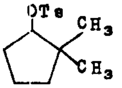
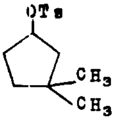
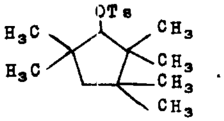
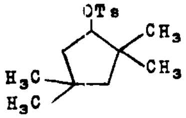
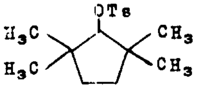
(Received 15 August 1966; in revised form 10 October 1966)

Brown and Chloupek (1) have reported that the introduction of α-methyl groups in a series of 1-chloro-1-methylcyclopentanes causes an increase in the ethanolysis rate (e.g., 1-chloro-1,2,2,5,5-pentamethylcyclopentane reacts 82 times faster than 1-chloro-1-methylcyclopentane). The increased solvolysis rates of the α-methyl substituted compounds in these tertiary systems have been rationalized in terms of increased ground state steric strain.

It was of interest to compare the acetolysis rates of a series of geminally polymethylated secondary cyclopentyl tosylates. We have compared the acetolysis behavior of 2,2-dimethyl-, 3,3-dimethyl-, 2,2,4,4-tetramethyl-, 2,2,5,5-tetramethyl- and 2,2,3,3,5,5-hexamethylcyclopentyl tosylates with that of cyclopentyl tosylate and in each case have found a small rate deceleration. In order to facilitate rate comparisons of the compounds studied, the acetolysis rates and their relative rates at 65° are tabulated in Table I.

TABLE I

RATE COMPARISONS OF THE METHYLATED CYCLOPENTYL TOSYLATES

TOSYLATE [a]	k (65°, sec.$^{-1}$ x 10^4)	REL. RATE
	2.07 [b]	1.0
	1.78	0.86
	1.68	0.81
	0.41	0.20
	0.32	0.15
	0.14	0.07

[a] Satisfactory spectroscopic and analytical data have been obtained for all new compounds.

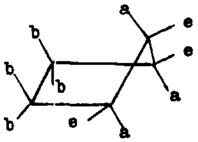
[b] This experimentally obtained value agrees well with the calculated value of 1.95 x 10^{-4} sec.$^{-1}$ from the data of H. C. Brown and G. Ham, J. Amer. Chem. Soc., 78, 2735 (1956).

It can be seen from the data of Table I that the tosylate undergoing the slowest solvolysis is the 2,2,5,5-tetramethylcyclopentyl tosylate (the reverse of the tertiary chlorides). Kinetic studies currently underway on the six-membered ring show that 2,2,6,6-tetramethylcyclohexyl mesylate undergoes acetolysis about 6 times faster than cyclohexyl mesylate.

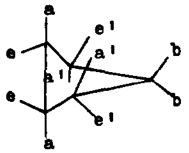
In our product studies, acetate percentages were calculated from micro-hydrogenation data and infrared analysis. Nmr analyses of the acetolysis products and vpc studies of the hydrogenated products were employed to ascertain the structures of the hydrocarbons. In the case of 3,3-dimethylcyclopentyl tosylate, the products consisted of 58% unrearranged acetate and 34% 1,1-dimethylcyclopentane (along with 8% unidentified hydrocarbon). The 2,2,4,4-tetramethylcyclopentyl tosylate yielded about 10-15% of an acetate component, 52% of 1,1,3,3-tetramethylcyclopentane, along with about 30% unidentified rearranged hydrocarbon. The product from 2,2,5,5-tetramethylcyclopentyl tosylate was readily identified as 1,2,3,3-tetramethylcyclopentene by nmr analysis (a trace amount of acetate was detectable in the infrared). Because of the small amounts of the 2,2,3,3,5,5-hexamethylcyclopentyl tosylate currently at hand, the products have not yet been determined. The acetolysis of cyclopentyl tosylate has been reported to yield 61% cyclopentyl acetate and 39% cyclopentene (2). Wilcox (3) has reported the product study of 2,2-dimethylcyclopentyl tosylate in 80% aqueous acetone as yielding about 70% methyl migrated olefins and 6% unidentified alcohol.

The highest acetate yields are obtained from cyclopentyl tosylate (61%) and 3,3-dimethylcyclopentyl tosylate (58%). Extrapolation of the data of Wilcox for the 2,2-dimethylcyclopentyl tosylate would indicate that less than 10% acetate would be formed in the acetolysis. This number also reflects the acetate composition of the products from the 2,2,4,4-tetramethylcyclopentyl tosylate. Finally, the formation of only trace amounts of acetate from the 2,2,5,5-tetramethyl system is certainly significant in these product comparisons.

The conformations of simple substituted cyclopentanes are difficult to specify because of the mobile pseudorotation characteristics of the five-membered ring. However, two major conformations for the cyclopentane ring (4) are usually considered - the envelope form (A) and the half-chair form (B).



A



B

The 3-methyl- and cis- and trans-3-t-butylcyclopentyl tosylates showed negligible kinetic differences compared to cyclopentyl tosylate (5). This lack of solvolytic discrimination was ascribed to the absence of non-bonded repulsive driving forces for both equatorial ester positions (cis- and trans-3-substituted esters could assume diequatorial conformations, A for the cis-isomer and B for the trans-isomer). The ethanolysis rates of cis- and trans-3-isopropylcyclopentyl tosylates have also been reported to be about the same as cyclopentyl tosylate at 40° (6).

Hückel and Mögle (7) have reported that a 2-methyl substituent cis to the toluenesulfonate group increases the rate over cyclopentyl tosylate by a factor of about two (alcoholysis). A trans-2-methyl group decreases the rate by about one-quarter (relative rates at 30°). The faster rate of the cis-isomer was explained by postulating a puckered conformation for the cyclopentane ring with a quasi-axial position of the tosylate group (8).

Meinwald (9) has solvolyzed the tosylates of the exo-and endo-isomers of cis-bicyclo(3.2.0)heptan-3-ol and trans-bicyclo (3.2.0) heptan-3-ol and found these compounds to undergo slower solvolysis than cyclopentyl tosylate. The trans compound solvolyzed about 55 times slower than cyclopentyl tosylate. It was suggested that in this compound the five-membered ring might exist in an extreme half-chair conformation and the non-bonded repulsions between the departing group and the neighboring hydrogens should be less than in the more nearly planar cyclopentane itself.

In the present study, if one considers 2,2,5,5-tetramethylcyclopentyl tosylate as adopting conformation A (tosylate group in an equatorial position), an axial-axial interaction of two methyl groups would occur. In conformation B an axial-quasi-axial interaction of two methyl groups would occur. If these non-bonded interactions were to be partially relieved at the transition state one might anticipate an increased solvolytic rate over that of cyclopentyl tosylate (an inductive increase should also operate in the methylated cases). Experimentally, the rate of cyclopentyl tosylate is found to be about 15 times faster than that of the 2,2,5,5-tetramethylcyclopentyl tosylate.

The effect of methyl participation is not considered to be of primary importance in these systems. It is suggested that two factors may be responsible for the rate decelerations: (a) non-bonded repulsions in the transition state greater than in the ground state (methyl-hydrogen partial eclipsing on carbons 2 and 3 and 5 and 4) and (b) a steric inhibition of effective solvation at the back side of the departing tosyloxy group at the transition state. The transition state in these secondary systems has a structure closer to the sp^2 carbonium ion, and orbital overlap with solvent would be important (10). That the latter factor is important is indicated by the trace amount of acetate found in the 2,2,5,5-tetramethylated system. Both of these factors would be expected to lower the solvolytic rate. In the series of tertiary cyclopentyl chlorides reported by Brown and Chloupek (1), non-bonded interactions in the ground state may outweigh non-bonded interactions in the transition state because of additional methyl group interaction with the adjacent methyl groups. Furthermore, in these cases the transition state is also less demanding for solvent participation because of favorable electronic stabilization.

The similarity in the rates of the 2,2-dimethyl- and 3,3-dimethylcyclopentyl tosylates (both slightly slower than cyclopentyl tosylate) is probably due to a net cancellation of factors a and b listed above. In the case of the transition state from the 3,3-dimethyl system, partial eclipsing of four C-H bonds with the geminal dimethyl group would occur, while in the 2,2-dimethyl system two C-H bonds are partially eclipsed in the same manner producing a net acceleration for the 2,2-dimethyl system. However, the effect of solvation is also important. The high acetate yield from the 3,3-dimethyl system suggests an unhindered tosylate group. This solvation factor would lead to a net retardation in the 2,2-dimethyl system. The similarity in the rates of 2,2,4,4-tetramethyl- and 2,2,5,5-tetramethylcyclopentyl tosylates might also be rationalized in this manner. The slightly higher rate of the 2,2,3,3,5,5-hexamethyl system compared to the 2,2,5,5-tetramethyl system might reflect partial release of non-bonded methyl-methyl interactions in the ground state of the first compound.

Further studies of the importance of the solvation factor in other highly alkylated cyclopentyl and cyclohexyl ring systems are nearing completion. These results will be reported shortly.

Acknowledgment.- The authors are indebted to the National Science Foundation (NSF Grant GP-5166) for financial support which made this work possible.

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