inversion mechanism without rearrangement (k_s). The experiment does not differentiate between direct displacement and displacement on an intimate ion pair. Formolysis gives a mixture of inversion and hydride-shift mechanisms, and trifluoroacetolysis gives almost entirely hydride shift. It is noteworthy that no retention mechanism is observed. Cleavage of the C–OTs bond (or break-up of the ion pair) must occur with either solvent (k_s) or hydride (k_Δ) assistance. There is no evidence for a free carbonium ion (k_c) at the 1 position, even in trifluoroacetic acid. The cyclohexyl system thus stands in sharp contrast to 2-adamantyl tosylate, the solvolysis of which is now considered to be the archetypal k_c process[10] and which gives a substitution product with predominantly retained stereochemistry.[11] Flattening deformations that can accommodate the trigonal bipyramidal k_s transition state in the cyclohexyl system are structually precluded in the 2-adamantyl system.

(10) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970).

(11) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(12) (a) NDEA Fellow, 1968–1971; NASA Trainee, 1971–1972; (b) NSF Trainee, 1968–1969.

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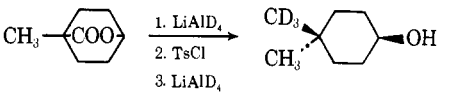
Stereochemistry and Mechanism of Acetolysis of 4,4-Dimethylcyclohexyl Tosylate

Sir:

While the solvolysis stereochemistry of a variety of conformationally fixed cyclohexyl sulfonates has been studied,[1] that of the mobile parent system has not yet been reported.[2] Such information is central to the questions of conformational reactivities and transition-state detail for this model displacement process.

Recently we presented[3] solvolysis rate data for 4,4-dimethylcyclohexyl tosylate relative to cyclohexyl tosylate, which indicated the geminate dimethyl reactant to be closely representative of the parent compound and served to rule out reaction of either substrate through a nonchair ground-state conformation. Here we report the products and stereochemistry of acetolysis of 4,4-dimethylcyclohexyl tosylate and related mechanistic observations.

Configurational analysis was based on the cis methyl-d_3 reactant, **1**, which provided for equivalent determination of both hydride-shifted and directly formed substitution products. (*Z*)-4-Methylcyclohexanol-*4-methyl-d*$_3$[4] (**2**) was synthesized from the lactone[5] **3** of (*Z*)-1-methyl-4-hydroxycyclohexanecarboxylic acid by lithium aluminum deuteride reduction, conversion[6] of the resulting diol[7] (mp 80.0–81.0°; bis-3,5-dinitrobenzoate, mp 146.0–147.0°) to the primary tosylate, and lithium aluminum deuteride reduction of the latter.



3 **2**

Acetolysis of 0.12 *M* 4,4-dimethylcyclohexyl tosylate (0.14 *M* sodium acetate, 1.0 wt% acetic anhydride) at 65° was found to produce essentially quantitatively a mixture of 83% olefin(s), 14.8% 4,4-dimethylcyclohexyl acetate, and 2.2% (13% of total acetates) 3,3-dimethylcyclohexyl acetate.[8] From 3,3-dimethylcyclohexyl tosylate[7,9] under the same conditions was obtained equally cleanly the same products in yields of 79, 2.7 (13% of total acetates), and 18.3%, respectively.

Simultaneous nmr configurational analysis of the acetates from labeled 4,4-dimethyl substrate **1** required resolution of the four ring-methyl singlets of the two unlabeled esters. This condition was not met in various solvents alone at 100 MHz, but was realized by complexation of the acetates with paramagnetic shift reagent Eu(fod)$_3$,[10] Figure 1A. From the labeled tosylate **1** only a single methyl peak was observed for each of the acetates, in both cases belonging to the position closer, *i.e.*, cis, to the complexing acetoxy group,[10,11] Figure 1B. This result corresponds to nonrearranging displacement (**4**) with complete inversion of configuration (±2%) and to hydride shift followed by solvent capture (**5**) at the face opposite the leaving group (±5%), *i.e.*, retention of configuration at the migration origin.

Further information was developed by treatment of the rate constants[3,6b] for cyclohexyl and 4,4-dimethylcyclohexyl tosylates in acetic and trifluoroacetic acids

(1) (a) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 77, 5562 (1955); (b) H. L. Goering and R. L. Reeves, *ibid.*, 78, 4931 (1956); (c) H. P. Fischer, C. A. Grob, and W. Schwarz, *Tetrahedron Lett.*, 25 (1962); (d) D. S. Noyce, B. N. Bastian, and R. S. Monson, *ibid.*, 863 (1962); (e) C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, 47, 1385 (1964); (f) C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Lett.*, 3405 (1965); (g) C. W. Jefford, D. T. Hill, and J. Gunsher, *J. Amer. Chem. Soc.*, 89, 6881 (1967); (h) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 298 (1968); (i) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968); (j) M. Panková, J. Sicher, M. Tichý, and M. C. Whiting, *ibid.*, 365 (1968); (k) R. Baker, J. Hudec, and K. L. Rabone, *Chem. Commun.*, 197 (1969); (l) D. S. Noyce, B. E. Johnston, and B. Weinstein, *J. Org. Chem.*, 34, 463 (1969); (m) D. S. Noyce, B. N. Bastian, P. T. S. Lau, R. S. Monson, and B. Weinstein, *ibid.*, 34, 1247 (1969); (n) K. Okamoto, S. Saitô, and H. Shingu, *Bull. Chem. Soc. Jap.*, 42, 3288, 3298 (1969); (o) J. A. Bone and M. C. Whiting, *Chem. Commun.*, 115 (1970).

(2) A complementary study is reported in the accompanying communication by J. B. Lambert, G. J. Putz, and C. E. Mixan (*J. Amer. Chem. Soc.*, 94, 5132 (1972)), to whom we are grateful for prior exchange and concurrent publication.

(3) J. E. Nordlander, J. M. Blank, and S. P. Jindal, *Tetrahedron Lett.*, 3477 (1969).

(4) Isotopic purity >99% by nmr and mass spectrometry.

(5) M. Rubin, D. Apotheker, and R. Lutmer, *Proc. Sci. Sect. Toilet Goods Ass., Suppl.*, 37, 24 (1962); *Chem. Abstr.*, 58, 11163h (1963).

(6) (a) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944); (b) H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, 78, 2735 (1956).

(7) Correct elemental analyses (±0.30%) were obtained for (unlabeled) new compounds (Galbraith Laboratories, Inc.).

(8) These results confirm the mechanistic similarity of 4,4-dimethylcyclohexyl to cyclohexyl tosylate, for whose acetolysis 85% elimination at 75° and substitution with 7% hydride shift at 50° (17% at 100°) have been reported. See J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, 73, 5034 (1951); T. N. Shatkina, E. V. Leont'eva, and A. O. Reutov, *Dokl. Akad. Nauk SSSR*, 177, 373 (1967) (incorrectly abstracted in *Chem. Abstr.*, 68, 86861v (1968)); see also *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2838 (1968).

(9) Mp 20–21°; prepared in the usual manner from 3,3-dimethylcyclohexanol (Chemical Samples Co.).

(10) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 93, 1522 (1971) (Norell Chemical Co.).

(11) Configuration 4 was assigned from the effect of shift reagent on the acetate of **2**, while **5** conforms to results with various model compounds. See (a) G. H. Wahl, Jr., and M. R. Peterson, Jr., *Chem. Commun.*, 1167, 1584 (1970); (b) J. Briggs, F. A. Hart, and G. P. Moss, *ibid.*, 1506 (1970); (c) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, 92, 5734 (1970); (d) P. Belanger, C. Freppel, D. Tizane, and J. C. Richer, *Chem. Commun.*, 266 (1971); (e) *Can. J. Chem.*, 49, 1985 (1971); (f) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, 93, 3281 (1971).

Table I. Stereochemistry of Nonrearranging Substitution in Acetolysis of Conformationally Fixed Cyclohexyl Sulfonates[a]

Tosylate	Conformation	Temp, °C	% simple substitution[b]	% inversion[c]	Ref
cis-4-*tert*-Butylcyclohexyl	Ax	100	8.7	91	1i
trans-4-*tert*-Butylcyclohexyl	Eq	100	19.6	98	1i
trans,trans-2-Decalyl	Ax	100	11.8	66[d]	1i
trans,cis-2-Decalyl	Eq	100	35.5	94[d]	1i
endo-3-Bicyclo[3.2.1]octyl	Ax	90	56.0	62	1g
exo-3-Bicyclo[3.2.1]octyl	Eq	90	64.2	100	1g
trans,cis-1-Decalyl	Ax	100	1.8	39	1i
trans,trans-1-Decalyl	Eq	100	46.7	67	1i
cis-2-Methyl-*cis*-4-tert-butylcyclohexyl	Ax	100	0.2	100	1i
trans-2-Methyl-*trans*-4-*tert*-butylcyclohexyl	Eq	100	17.1	81	1j
trans-2-Methyl-*cis*-4-*tert*-butylcyclohexyl	Ax	100	6.5	89	1j
cis-2-Methyl-*trans*-4-*tert*-butylcyclohexyl	Eq	100	0.5	80	1j
2-Adamantyl	Ax, eq[e]	100	100[f]	35[g]	1o

[a] Acetate buffer in all cases. [b] Yield of unrearranged acetates. [c] Remainder retention. [d] Includes undetermined amount of degenerate hydride-shift product. [e] Functional position common to two chair cyclohexane rings. [f] Slight rearrangement; M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969). [g] Interpolated from methyl derivatives.

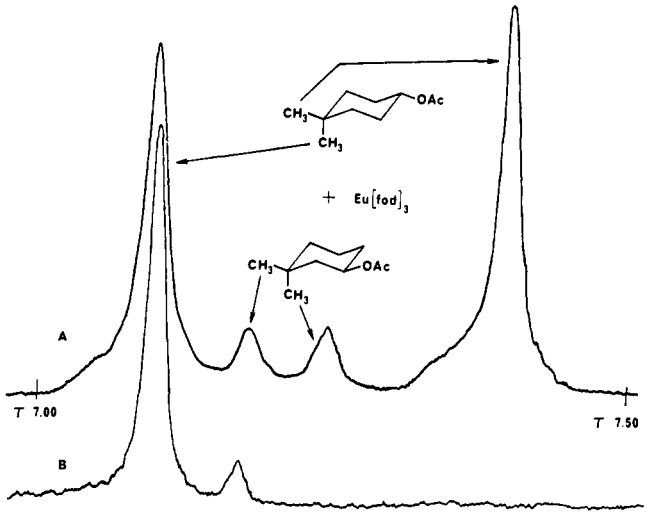
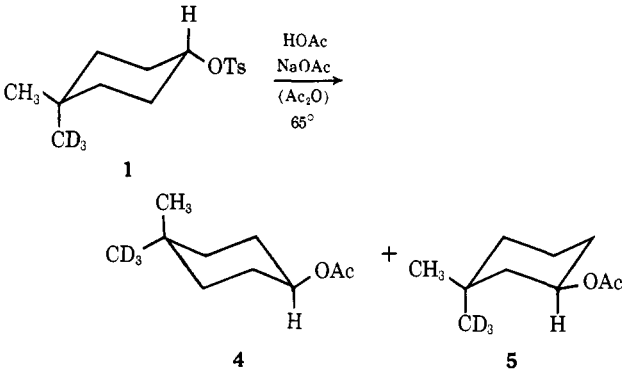


Figure 1. Geminate dimethyl pmr spectra at 100 MHz: (A) 4,4-dimethylcyclohexyl (87%) and 3,3-dimethylcyclohexyl (13%) acetates 2.6 *M* in carbon tetrachloride plus 0.10 *M* Eu(fod)$_3$; (B) acetates **4** and **5** from solvolysis of labeled tosylate **1**, same sample conditions.



with reference to those for 2-adamantyl tosylate as proposed by Schleyer, *et al.*,[12] as a minimal measure of nucleophilic solvent assistance to ionization.[13] Assistance factors $(k_s/k_c)_{HOAc}$ thus derived are cyclohexyl, 35, and 4,4-dimethylcyclohexyl, 30, values comparable to that for cyclopentyl, 93,[12d,14] and an order of magnitude less than for minimally hindered isopropyl, 560.[12c,d]

For the simple displacement process the total inversion of configuration and substantial solvent assistance factor indicate nucleophilic attack to be closely linked with substrate ionization, or possibly ion-pair dissociation.[15] The data are inconsistent with independent carbonium ion intermediates. Cyclohexyl is thus indicated to be closely related in acetolysis mechanism to 2-octyl tosylate, for which complete inversion in displacement *per se* has also been demonstrated.[16]

In the acetolysis of conformationally fixed cyclohexyl tosylates, axial and equatorial isomers are differentiated by displacement stereochemistry as shown in Table I. A higher proportion of direct substitution with inversion is found characteristically for equatorial isomers (exceptions in particularly substituted cases); for no axial reactant has <9% retention been observed.[17] On this basis, direct displacement in 4,4-dimethylcyclohexyl tosylate is indicated to proceed largely from the equatorial conformer.

Particularly marked is the stereochemical distinction between 4,4-dimethylcyclohexyl tosylate and 2-adamantyl tosylate, for which retention of configuration predominates.[10] This divergence must relate to transi-

(12) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); (d) professor Schleyer has advised us that the trifluoroacetolysis rate constant for 2-adamantyl tosylate at 25.0°[12c] should be modified to 8.98×10^{-4} sec^{-1}; (e) see also T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 992 (1972).

(13) It should be noted that k_s/k_c may include contributions from the solvent as base as well as nucleophile.

(14) J. E. Nordlander, R. R. Gruetzmacher, W. J. Kelly, and S. P. Jindal, manuscript in preparation.

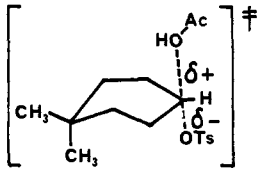
(15) (a) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.* 87, 287, 292 (1965); (b) R. A. Sneen and J. W. Larsen, *ibid.*, 88, 2593 (1966); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969); (d) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6031 (1969); (e) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93**, 4821 (1971).

(16) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, 87, 3682 (1965); (b) A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, 87, 3686 (1965).

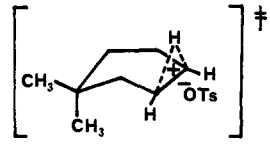
(17) Neglecting *cis*-2-methyl-*cis*-4-*tert*-butylcyclohexyl tosylate, which undergoes only 0.2% simple substitution.

tion states,[12] and may be understood if that for the monocyclic system is characterized by pronounced flattening of the ring about the reaction center, as in half-chair **6**.[18] Nucleophilic solvent participation would thus be facilitated through reduced compression with axial hydrogens at C-3 and C-5, at the expense of new but distributed bond-angle and torsional strains. Such distortion could not be accommodated by the 2-adamantyl framework.

The stereospecificity of substitution with hydride shift from **1** is in accord with hydride migration trans to tightly paired tosylate ion followed by displacement with inversion on the rearranged ion pair or recombined tosylate.[19] Maximum overlap in such rearrangements has been correlated with diaxial orientation of leaving and migrating groups,[20] but such a rule is compromised by the observation of hydride shift to the same extent (according to substitution products) from wholly equatorial 3,3-dimethylcyclohexyl tosylate as from the biconformational[21] 4,4-dimethylcyclohexyl reactant. We propose that hydride shift from the 3,3- and in part from the 4,4-dimethyl reactant may originate from the respective equatorial chair conformations, by ionization to a bridged half-chair transition state, such as **7**.[19]



6



7

The inversion attending acetolysis of tosylate **1** stands in marked contrast to the essentially complete retention observed by Streitwieser and Coverdale[22] for aqueous deamination of cyclohexylamine. Comment is reserved for a full paper.

Acknowledgment. Partial support of this work by National Science Foundation Grant No. GP-20732 is gratefully acknowledged.

(18) Such a structure would explain as well the isotope-effect pattern observed for acetolysis of cyclohexyl tosylate by W. H. Saunders, Jr., and K. T. Finley, *J. Amer. Chem. Soc.*, 87, 1384 (1965); see also V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, 87, 1383 (1965), and preceding papers.

(19) Compare ref 1i, j.

(20) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 227–229.

(21) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969), have measured the conformational free energy for tosyloxy as 0.515 kcal/mol (eq:ax = 79:21) in carbon disulfide at −80°; see F. R. Jensen and C. H. Bushweller, *Advan. Alicycl. Chem.*, 3, 139 (1971); see also ref 1a, and E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5995 (1957).

(22) A. Streitwieser, Jr., and C. E. Coverdale, *ibid.*, 81, 4275 (1959).

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Cholesteric Liquid-Crystal-Induced Circular Dichroism (LCICD) of Achiral Solutes. A Novel Spectroscopic Technique

Sir:

In our first report[1] of the induced circular dichroism of achiral solutes in cholesteric mesophases the experimentally observed sign of the LCICD bands, for the compounds studied up to that time, was always opposite to the sign of the reflective circular dichroism (CD) of the cholesteric pitch band. This observation seemed rather unusual since in natural and magnetic circular dichroism (MCD) bands of both positive and negative signs are commonly observed in multichromophoric systems.[2]

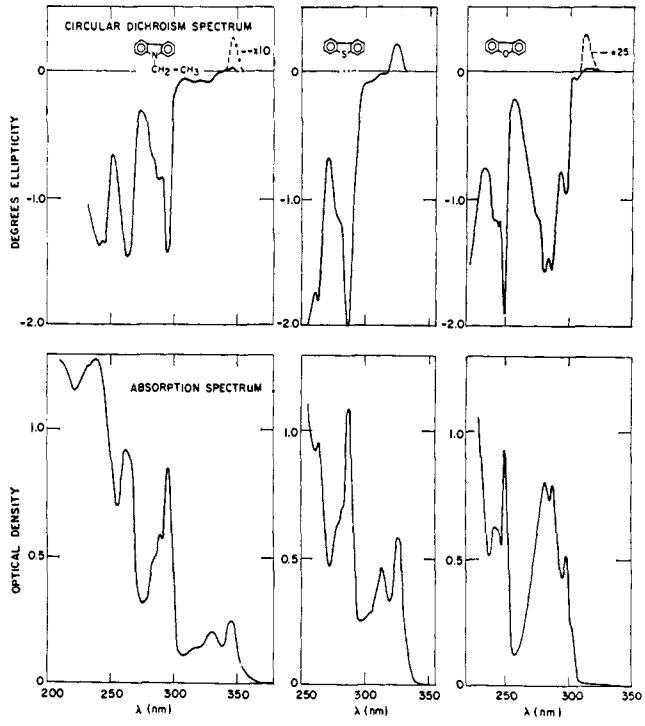
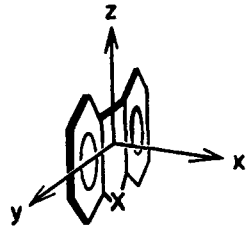


Figure 1. Cholesteric liquid-crystal-induced circular dichroism (LCICD) and absorption spectrum of *N*-ethylcarbazole, dibenzofuran, and dibenzothiophene (1.0 wt %) in 60/40 (wt%) cholesteryl chloride (CC)–cholesteryl nonanoate (CN) (right-handed helix) as ~5-μ film between 1 × $^1/_8$ in. quartz disks.

This communication presents the LCICD spectra of *N*-ethylcarbazole (I), dibenzothiophene (II), and dibenzofuran (III), which are known to possess $\pi \rightarrow \pi^*$ electronic transition moments, at wavelengths >200 nm, polarized along different molecular axes[3-5] as shown below, and indicates their spectroscopic significance.



Electronic Transition	Polarization (axis)
1 ($^1L_b \leftarrow {}^1A$)	*z*
2 ($^1L_a \leftarrow {}^1A$)	*y*
3 ($^1B_a \leftarrow {}^1A$)	*y*

Compd	X
I	NC_2H_5
II	S
III	O

The LCICD and absorption spectra of compounds I–III dissolved in a right-handed helicoidal cholesteric mesophase are presented in Figure 1, where a positive

(1) F. D. Saeva and J. J. Wysocki, *J. Amer. Chem. Soc.*, **93**, 5928 (1971).

(2) A. Moscowitz, *Proc. Roy. Soc., Ser. A*, **297**, 16 (1967).

(3) A. Bree and R. Zwarich, *J. Chem. Phys.*, **49**, 3355 (1968).

(4) H. Schutt and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **67**, 54 (1963).

(5) C. A. Pinkham and S. C. Wait, Jr., *J. Mol. Spectrosc.*, **27**, 326 (1968).