Apparatus and Method.—A Perkin–Elmer model 21 double beam spectrometer was employed for the spectra determinations. A 1.0-mm. microcell with sodium chloride windows was used for the sample solutions and a 1.0-mm. cell with sodium chloride windows was used as the reference cell. The solvent used in the spectra, tetrachloroethylene, was of spectral grade (courtesy Carwin Co.), b.p. 121°. After calibration and checking the I_0 line, solvent was run against solvent; no observable uncompensated absorption took place in the region of carbonyl absorption. The spectra of the compound was then scanned slowly (concentrations ranged from 0.0082 M to 0.0183 M, see legend of Figs. 1 and 2) with the resolution set at 960. Spectra were also taken with changed gear ratios; an attempt was made to measure the area of the expanded curves by use of a planimeter but in several cases overlapping bands made the determinations questionable. This method was therefore abandoned and the "base-line" density method was employed to determine the intensity of the carbonyl absorption bands. In practice, a base-line was drawn as nearly parallel to the I_0 line (*i.e.*, solvent *vs.* solvent) as possible; the difference between the absorbance at the band maximum and absorbance at the point where a vertical line through the maximum crosses the base-line was determined. This figure was divided by the molar concentrations (given in Figs. 1 and 2) to give the base line density (intensity/mole). The base line densities so determined are recorded in Table I.

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[Contribution from the Institute of Scientific and Industrial Research, Osaka University]

The Effect of Conformation on Reactivity. I. Acetolysis of the *trans*-Decalyl *p*-Toluenesulfonates; 1,3-Diaxial Interactions as a Factor in the Chemical Behavior of Decalyl Derivatives

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The rates of acetolysis of 1-axial, 1-equatorial, 2-axial and 2-equatorial *trans*-decalyl tosylates were measured in order to determine the effects of the conformations on the reactivities of these compounds. The relative reactivity was observed to decrease in the order: 1-axial $\gg$ 2-axial > 2-equatorial > 1-equatorial. The increased rate of solvolysis of the 2-axial to the 2-equatorial derivative, 3:1, is attributed to 1,3-diaxial interactions. The larger effect observed in comparing the 1-axial to the 2-axial, 9:1, is attributed to increased 1,3-diaxial interactions. The rates of solvolysis of the tosylates correlate well with earlier data on the rates of hydrolysis of the corresponding decalyl hydrogen succinates. It is concluded that the fixed conformation of the decalyl system provides a valuable tool for quantitative studies of the effect of conformation on chemical behavior.

It is of considerable interest to correlate the reactivity of cyclohexane derivatives with their conformations. Since the electronic effects of both axial and equatorial bonds in such molecules should be quite similar, significant differences in reactivity must arise from conformational effects.[1] Detailed knowledge of the relationship between conformation and reactivity is important for the full understanding of the chemical behavior of many natural products, such as the steroids and triterpenes, whose structures are based on the cyclohexane system.

A major difficulty in studying relative reactivities of isolated axial and equatorial bonds in simple cyclohexane derivatives is the ready interconversion of the two types of bonds in these compounds. For example, according to Kojima and Yoshino[2] and Larnaudie,[3] *trans*-1,2-dichloro- and *trans*-1,4-dibromocyclohexane are present in solution as an equilibrium mixture of the equatorial–equatorial and axial–axial conformations.

Recently, Winstein and Holness[4] have attempted to circumvent this difficulty by working with the *cis*- and *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonates. They postulate that in these derivatives the bulky *t*-butyl group would prefer to occupy the equatorial position and thereby prevents the interconversion of the cyclohexane ring into the alternate conformation. The observed rate ratio of *cis*- to *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate, 2.7, has been attributed to the steric strain arising from the axial conformation of the tosyl group in the *cis* derivative.

The *trans*- decalin system appears to possess real advantages for the study of conformational effects. In this system the two rings cannot be joined through axial–axial bonds. Consequently, no rotary isomerization can occur and the conformations can be assigned on the basis of the structure of the molecules. Hückel observed differences in the reactivities of the *trans*-1- and 2-decalyl *p*-toluenesulfonates.[5] Accordingly, we undertook to obtain precise quantitative data on the acetolysis of these derivatives.

Results

The rate of acetolysis were determined at several temperatures following the procedure described by Winstein and co-workers.[6]

The reactions followed first-order kinetics. Data for a typical kinetic study are shown in Table I. In the case of the *trans-trans*-1- and *trans-trans*-2-derivatives it was noted that the reaction rate is not influenced by the presence of potassium acetate.

The rate constants at several temperatures gave excellent plots of log k vs. $1/T$. Heats and entropies of activation were calculated using the equation given by Eyring.[7] The results are summarized in Table II.

The solvolysis of *trans-cis*-1-decalyl tosylate pro-

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[1] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

[2] K. Kojima and T. Yoshino, This Journal, **75**, 166 (1953).

[3] M. Larnaudie, *Compt. rend.*, **236**, 909 (1953).

[4] S. Winstein and N. J. Holness, This Journal, **77**, 5562 (1955).

[5] W. Hückel, *Ber.*, **77**, 805 (1944).

[6] S. Winstein, E. Grunwald and L. L. Ingraham, This Journal, **70**, 812, 821 (1948).

[7] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, p. 196

TABLE I

REPRESENTATIVE KINETIC DATA FOR THE ACETOLYSIS OF *trans-trans*-2-DECALYL *p*-TOLUENESULFONATE AT 89.78°

$[\text{Tosylate}]_0 = 0.0178\ M;\ [\text{KOAc}]_0 = 0.0196\ M$

Time, sec.	$HClO_4$, ml.	$10^4\ k_1$, sec. $^{-1}$
0	3.848	..
900	2.963	3.26
1200	2.724	3.25
1500	2.498	3.27
1800	2.305	3.25
2100	2.133	3.23
2400	1.956	3.26
2700	1.801	3.28
3000	1.665	3.29
3300	1.558	3.25
∞	0.365	..
	Mean	3.26 ± 0.01

TABLE II

RATE CONSTANTS AND DERIVED DATA FOR THE ACETOLYSIS OF *trans*-1- AND 2-DECALYL *p*-TOLUENESULFONATE

Decalyl *p*-toluene-sulfonate	Conformation	Temp., °C.	$10^5\ k$, sec. $^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
trans-trans-1	1 e	104.58	30.6 ± 0.3		
		103.71	28.4 ± .3		
		90.26	6.36 ± .06		
		90.18	6.38 ± .06		
		75.52	1.10 ± .02		
		75.42	1.12 ± .01		
		75.0	1.05	29.2	−2.2
trans-cis-1	1 a	75.52	59.3 ± 0.4		
		75.0	54.9	25.3	+1.0
		74.97	53.6 ± 0.7		
		60.13	10.2 ± .2		
		59.94	10.0 ± .06		
		45.15	1.62 ± .008		
trans-cis-2	2 e	104.50	52.2 ± 0.5		
		103.60	50.1 ± .7		
		90.18	11.8 ± .15		
		90.09	11.7 ± .1		
		75.52	2.14 ± .03		
		75.07	1.95 ± .01		
		75.0	1.99	28.5	−1.6
trans-trans-2	2 a	90.20	35.4 ± 0.2		
		89.78	32.6 ± .1		
		75.51	6.61 ± .03		
		75.0	6.19	27.8	−1.8
		74.78	5.97 ± .05		
		60.09	1.01 ± .008		
		59.48	0.883 ± .09		

duces an olefin in a yield of 90%, the remainder being the acetate. The infrared spectrum of this olefin was identical with that reported by Cope[8] for $\Delta^{1,9}$-octalin, but not for $\Delta^{9,10}$-octalin.[9] Therefore, the olefin is $\Delta^{1,9}$-octalin as shown in Fig. 1.

Discussion

The value of 3.1 for the difference in rates between *trans*-2-axial and 2-equatorial decalyl *p*-toluenesulfonates corresponds closely to the value of 2.7[4] observed for the isomers of 4-*t*-butylcyclohexyl *p*-toluenesulfonates and the value of 3.3[4] observed for the corresponding 3-derivatives. These results reveal a consistent increase in reactivity of the derivatives with the tosyl group in the axial position.

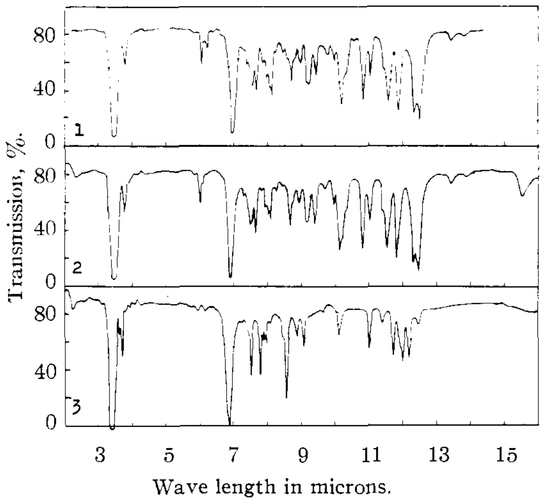

Fig. 1.—Infrared absorption spectra: curve 1, the olefin obtained by the acetolysis of *trans-cis*-1-decalyl *p*-toluenesulfonate; curve 2, $\Delta^{1,9}$-octalin[8]; curve 3, $\Delta^{9,10}$-octalin.[8]

The increase in the reactivity of the axial tosylcyclohexane derivatives has been attributed to steric strain arising from the interaction of the tosyl group and the two axial (3-) hydrogen atoms.[4] Relief of such strain should sterically assist the ionization stage.[10] Examination of the molecular models indicates that such 1,3-diaxial interactions should also be present in the *trans*-2-decalyl tosylates. The similarity in the effect upon the rate provides additional support for the proposed explanation.

trans-cis-1-Decalyl *p*-toluenesulfonate (1-axial) solvolyzed at a rate much greater than that exhibited by the corresponding 2-axial derivative. We propose that this increase arises from the presence of three 1,3-diaxial interactions (Table III). The increase is relatively large (axial-1/axial-2 is 9:1). At first sight it is surprising that an increase in the 1,3-diaxial interactions from two to three should result in such a relatively large increase in solvolysis rate.

The magnitude of the increase can be rationalized in two ways. The large increase can be interpreted in terms of an unusually large increase in steric strain resulting from the favorable geometrical arrangement of the three 1,3-diaxial interactions. Alternatively, the large increase in rate might be attributed to participation of the hydrogen atom in the 9-position. Let us consider this latter possibility.

In this explanation, ionization would proceed to give not the anticipated secondary ion I, but with rearrangement to give the more stable tertiary carbonium ion II. The transition state would

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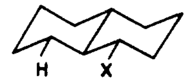
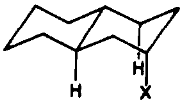
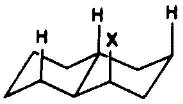
[8] A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3594 (1955).

[9] Cope indicated that a band of 12.2 μ is one of the characteristic bands for $\Delta^{9,10}$-octalin. However, this band is absent from the spectrum of the olefin obtained.

[10] H. C. Brown, *Science*, **103**, 385 (1946); H. C. Brown and I. Moritani, THIS JOURNAL, **77**, 3623 (1955).

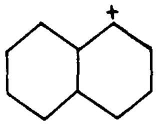
TABLE III

RELATIONSHIP BETWEEN 1,3-DIAXIAL INTERACTIONS AND RELATIVE REACTIVITY IN *trans*-DECALYL DERIVATIVES

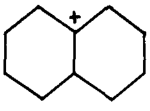
Decalyl derivative	Conformation	1,3-Diaxial interactions (X-H)	Relative rate of acetolysis of tosylate at 75.0°	Relative rate hydrolysis of H-succinates at 60°[a]
trans-cis-2		0	1.0	1.0
trans-trans-1		0 to 1	0.5	0.22
trans-trans-2		2	3.1	0.14
trans-cis-1		3	27.6	0.012

[a] Ref. 13.

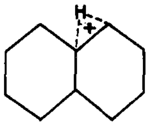
then be the partially rearranged ion III,[11] with



I



II



III

somewhat increased stability because of the greater capacity of the tertiary carbon atom to accommodate the developing positive charge.

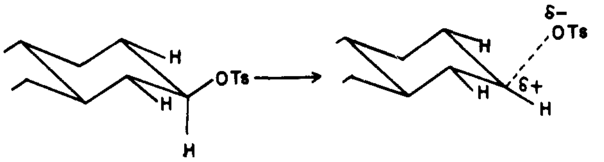
If the ionization proceeded to the formation of the more stable tertiary ion II, the olefin formed in the reaction would be expected to be predominantly the $\Delta^{9,10}$-octalin, which is known to be thermodynamically more stable than $\Delta^{1,9}$-octalin.[12] However, the olefin formed in our experiments was clearly pure $\Delta^{1,9}$-octalin with the $\Delta^{9,10}$-derivative clearly absent. If we are to attribute the enhanced rate to hydrogen participation, we are forced to postulate that the reaction proceeds to a transition state which is partially rearranged to the more stable tertiary carbonium ion, but on continuing along the reaction path the bridged ion collapses to the less stable secondary ion II. This interpretation appears highly forced and improbable. Consequently, we prefer to attribute the relatively large increase in rate to the steric strain arising from the three 1,3-diaxial interactions.

In the *trans-trans*-2-derivative, the two 1,3-diaxial interactions are situated stereochemically such that the steric interactions could be reduced by a minor movement of the tosyl group away from the axial hydrogen atoms in the plane defined by the carbon–oxygen bond and the 2- and 4-carbon atoms (Table III). However, the three 1,3-diaxial interactions in the *trans-cis*-1 derivative surround the tosyl group on three sides (Table III). To shift the tosyl group away from the three 1,3-diaxial interactions would require a severe distortion of the ring system.

Summing up these arguments, it appears more reasonable to attribute the enhanced rate of the *trans-cis*-1-derivative to 1,3-diaxial interactions and not to participation of the 9-hydrogen.

There is now considerable evidence as to the importance of 1,3-diaxial interactions on the rates of reactions of cyclohexane derivatives. In the *trans-trans*-1-derivative (Table III) there occurs a 1,8-diequatorial interaction which appears to be related geometrically to the 1,3-diaxial interactions under discussion. Nevertheless, no increase in solvolysis rate is observed. Indeed, the tosylate solvolyzes at 0.5 the rate of the *trans-cis*-2 derivative, which has no 1,3-diaxial interactions. It must be concluded either that 1,8-diequatorial interactions are far less effective than 1,3-diaxial interactions, or that some other factor intervenes to mask the effect of the 1,8-diequatorial interactions.

A possible factor of this kind is the following. In the course of forming the carbonium ion from the 2-decalyl derivative IV, the carbon–hydrogen bond originally in the axial conformation moves into opposition with the two β-equatorial bonds (V). However, in the 1-decalyl derivative VI, this carbon–hydrogen bond moves into opposition with one β-carbon–hydrogen bond with one β-carbon–carbon bond. If the energy requirements to bring the carbon–hydrogen bond into opposition with the carbon–carbon bond are the larger, this would provide a simple explanation for the small decrease in rate observed for the *trans-trans*-1.

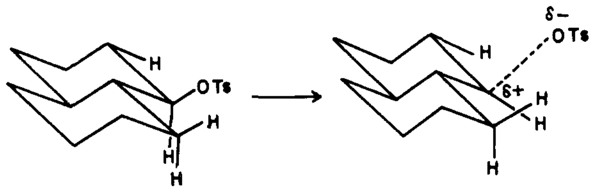


IV

2-equatorial

V

(transition state)



VI

1-equatorial

VII

(transition state)

In the case of the *trans-trans*-2- and the *trans-cis*-1-decalyl tosylates, we have attributed the observed increase in rates to an increase in steric strain, arising from two and three 1,3-diaxial interactions, respectively. These strains should be present in other derivatives and should be reflected

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(11) This representation is similar to that discussed by Winstein and co-workers in numerous papers in THIS JOURNAL, but we do not ascribe any stabilization to the bridging phenomenon itself. All attempts to observe enhancement of rates in systems where the rearrangement does not lead to a more stable carbonium ion have failed; S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952); J. D. Roberts, W. Bennett, R. E. McMahon and B. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943; H. C. Brown and Y. Okamoto, *ibid.*, **77**, 3619 (1955).

(12) W. Huckel and H. Naab, *Ann.*, **502**, 148 (1933).

in their chemical behavior. It is gratifying to observe that the *trans-trans*-2-decalyl hydrogen succinate exhibits a decreased rate of hydrolysis (0.14) as compared with the reference compound, *trans-cis*-2 (1.00).[13] Likewise, the marked increase in the rate of solvolysis of the *trans-cis*-1-decalyl tosylate is matched by a very sharp decrease in the relative rate of hydrolysis of the corresponding hydrogen succinate (0.012). This observation argues strongly for our conclusion that hydrogen participation is not a major factor in the fast rate exhibited by the *trans-cis*-1-decalyl tosylate.

In the case of the *cis-trans*-1-decalyl tosylate we attributed the slow rate to the necessity of bringing the axial carbon–hydrogen bond into opposition with the β-carbon–carbon bond during the ionization stage. We suggested that this overcomes the relatively small increase that would otherwise be anticipated on the basis of the steric interactions with the 8-hydrogen. The above effect should be a factor only in ionization reactions. Consequently, it is gratifying that the alkaline hydrolysis of the hydrogen succinate is normal, exhibiting a small decrease in the relative rate (0.22), corresponding to the small steric effect of the 8-position. These results are summarized in Table III.

In conclusion, it appears that the decalyl systems offers real advantages in the quantitative study of conformation effects.

Experimental

***trans-trans-* and *trans-cis*-1-Decalol.**—1-Decalol, b.p. 126–128° at 20 mm., was prepared by the hydrogenation of α-naphthol, m.p. 94–96°, over Raney nickel,[14] and converted into 1-decalone, b.p. 125–132° at 20 mm., by chromic acid oxidation.[15] Treatment with sodium methoxide in methanol yielded *trans*-1-decalone, b.p. 92–95° at 8 mm., m.p. 32°, m.p. of oxime, 168°.[16] It was reduced by lithium aluminum hydride in ether to *trans-trans*-1-decalol, m.p. 59° (lit.[15] 63°), in 94% yield. *trans*-1-Decalone was converted into *trans-cis*-1-decalol, m.p. 42–46° (lit.[15] 49°), in 75% yield by hydrogenation over platinum black in acetic acid solution containing a trace of hydrochloric acid. The product was purified by preparation and recrystallization of the oxalate, m.p. 142°.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 72.80; H, 9.52.

***trans-trans-* and *trans-cis*-2-Decalol.**—For the preparation of 2-decalol, the metal-catalyzed reduction of β-naphthol gives chiefly the *cis* isomer.[17] Therefore, the method utilized by van Tamelen and co-workers[18] was followed.

Cyclohexanone was converted into 2-N,N-dimethylaminomethylcyclohexane[19] (b.p. 98–99° at 13 mm.) in a yield of 44%. 2-N,N-Dimethylaminomethylcyclohexanone was treated with methyl iodide, followed by the sodium salt of acetocetic ester. The product, 2-keto-$\Delta^{1,9}$-octalin[20] (b.p. 110–120° at 15 mm., $n^{20}D$ 1.5211), was obtained in 70% yield. The 2,4-dinitrophenylhydrazone melted at 170° (lit.[20] 168°). The 2-keto-$\Delta^{1,9}$-octalin was reduced by lithium in liquid ammonia to *trans*-2-decalone[18] (b.p. 115–117° at 17 mm., $n^{17.5}D$ 1.4864) in 52% yield; m.p. of semicarbazone, 191.5–192.5° (lit.[18] 192–192.5°).

trans-cis-2-Decalol, b.p. 112–115° at 15 mm., m.p. 68–72° (lit.[15] m.p. 75°), was obtained in 75% yield by reduction of *trans*-2-decalone with lithium aluminum hydride. *trans-trans*-2-Decalol, b.p. 94–98° at 5 mm., m.p. 52° (lit.[15] m.p. 53°), was obtained in 74% yield by reduction over platinum black and hydrochloric acid.

***trans*-Decalyl *p*-Toluenesulfonates.**—Since the alcohols are highly soluble in organic solvents, they are difficult to purify by recrystallization.[21] Consequently, we were content to synthesize the *p*-toluenesulfonates[22] and to recrystallize these from ligroin to constant m.p. Only in the case of the *trans-cis*-1-decalyl tosylate, the ester proved to be too unstable to purify in this way, so that the alcohol was purified through the oxalate as mentioned earlier.

MELTING POINTS AND THE ANALYTICAL DATA OF *trans*-DECALYL *p*-TOLUENESULFONATES

Decalyl tosylate	M.p., °C.	M.p. (lit.)[15] °C.	Analyses, %[a] C	H
trans-trans-1	97–98	98	66.07	7.90
trans-cis-1	70–71	72	66.21	7.98
trans-trans-2	110–111	111	66.22	7.85
trans-cis-2	62.5–63	63	66.50	7.71

[a] Calcd. for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84.

Acetolysis of Decalyl Tosylates.—The method employed was essentially the same as that described by Winstein and his co-workers.[6]

The indicators used were brom phenol blue and α-naphtholbenzoin. A saturated solution of the former in acetic acid and a 1% solution of the latter in acetic acid were used; the latter gives a brownish-red color in a basic solution and a green one in an acidic solution.

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SAKAI, OSAKA, JAPAN

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(13) W. Hückel, *Ber.*, **67A**, 129 (1934); W. Hückel, H. Haveloss, K. Kumetat, D. Ullmann and W. Doll, *Ann.*, **533**, 128 (1937).

(14) D. M. Musser and H. Adkins, THIS JOURNAL, **60**, 664 (1938).

(15) W. Hückel, *Ann.*, **441**, 31 (1925).

(16) A. C. Cope, R. J. Cotter and G. G. Roller, THIS JOURNAL, **77**, 3599 (1955).

(17) R. P. Linstead, W. E. Doering, S. B. Davis and R. R. Whetstone, *ibid.*, **64**, 1985 (1942).

(18) E. E. van Tamelen and W. C. Proost, Jr., *ibid.*, **76**, 3634 (1954).

(19) C. Mannich and R. Braun, *Ber.*, **53**, 1874 (1920).

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(21) W. Hückel, R. Danneel, A. Gross and H. Naab, *Ann.*, **502**, 104 (1933).

(22) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).