evaporatory yielded 3.5 g (88%) of ethyl 6-hydroxyhexanoate as a colorless liquid, n^{20}D 1.4374. Distillation yielded 2.98 g (75%) of the material: bp 79° (0.7 mm); n^{20}D 1.4375 [lit.[24] bp 134° (15 mm)]; ir (neat) 3150–3750 (–OH), 1745 cm^{-1} (>C=O); nmr (CCl_4, TMS) δ 1.27 (t, 3, $-CH_3$), 1.0–2.0 [m, 6, $-(CH_2)_3-$], 2.28 [t, 2, $CH_2(C{=}O)O$], 3.53 (t, 2, $HOCH_2-$), 3.75 (s, 1, –OH), 4.17 (q, 2, $O{=}COCH_2-$).

H. Selective Reduction in the Presence of the Cyano Group.—Reduction of *p*-cyanobenzoic acid is representative. The experimental setup and the reaction conditions were the same as in the previous experiments (procedure B). *p*-Cyanobenzoic acid, 3.68 g (25 mmol), was suspended in 30 ml of THF (the acid has low solubility in THF) and to this at −15° 10.5 ml (25 mmol) of borane in THF was slowly added dropwise over a period of 20 min. The resulting mixture was stirred well and the ice–salt bath was allowed to equilibrate to room temperature (*ca.* 25°) slowly over a 12-hr period. Then the reaction mixture was worked up as described in the reduction of adipic acid monoethyl ester. Stripping off the solvent gave a pale yellowish, viscous oil. Distillation *in vacuo* gave 2.73 g (82%) of *p*-cyanobenzyl alcohol as a white solid: bp 108–109° (0.35 mm); mp 39–41° [lit.[25] bp 203° (53 mm), mp 41–42°]; nmr ($CDCl_3$, TMS) δ 3.6 (s, 1, –OH), 4.77 (s, 2, $-CH_2$), 7.6 (q, 4, aromatic).

(24) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

(25) J. N. Ashley, H. J. Barber, A. J. Ewins, G. Newbery, and A. D. H. Self, *ibid.*, 103 (1942).

Reduction of Formic Acid with Borane in THF. Isolation of Trimethoxyboroxine.—A typical reaction setup was assembled. Formic acid, 1.1412 g (24.8 mmol) dissolved in 5 ml of THF, was placed in the reaction flask. The flask was immersed in an ice bath and cooled to 0°. To this solution was added dropwise with stirring 10.4 ml (24.8 mmol) of borane in THF. There was evolved 23.6 mmol of hydrogen. The mixture was stirred vigorously for 1.5 hr at 25°. Analysis of a small aliquot of the reaction mixture indicated the absence of any residual hydride. Most of the THF was removed by distillation under nitrogen, yielding a colorless liquid, 1.58 g. Nmr examination of this material indicated a sharp singlet at δ 3.59 (from TMS) characteristic of trimethoxyboroxine (trimethoxyboroxine spectrum in Sadtler No. 9157 exhibits a sharp singlet at δ 3.59); methyl borate was found to exhibit a sharp singlet at δ 3.43 (Sadtler Spectrum No. 10916 for methyl borate exhibits a singlet at δ 3.43). The mixture had 27% of the THF by weight as determined by the integration of the protons of THF. Correcting for the amount of THF, the yield of the boroxine was 78%.

Registry No.—Borane, 13283-31-3; *o*-hydroxybenzyl alcohol, 90-01-7; *o*-iodobenzoic acid, 619-58-9; *o*-iodobenzyl alcohol, 5159-41-1; *p*-nitrophenylacetic acid, 104-03-0; *p*-nitrophenylethanol, 100-27-6; adipic acid monomethyl ester, 627-91-8; ethyl 6-hydroxyhexanoate, 5299-60-5; *p*-cyanobenzoic acid, 619-65-8; *p*-cyanobenzyl alcohol, 874-89-5; formic acid, 64-18-6; trimethoxyboroxine, 102-24-9.

Solvolyses of Axial and Equatorial Epimers of *trans*-2-Decalyl Tosylate and Their 6-Keto and 6-Keto $\Delta^{5(10)}$ Derivatives[1]

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The tosylates of *trans*-2(a and e)-decalols (**1a**-OTs and **1e**-OTs), 6-keto-*trans*-2(a and e)-decalols (**2a**-OTs and **2e**-OTs), and 6-keto-$\Delta^{5(10)}$-*trans*-2(a and e)-decalols (**3a**-OTs and **3e**-OTs) were solvolyzed in trifluoroacetic, formic, and acetic acids and ethanol. Rates in all the solvents and products in acetic acid were investigated. Product patterns from the axial and equatorial **2** tosylates were similar to those reported for the counterparts in the **1** system. Axial to equatorial relative reactivities of the tosylates in the **1** and **2** systems vary insignificantly with solvents being in the range of 3.0 to 5.0 at 50°. Those in the **3** system change from 0.89 in acetic acid and 0.90 in formic acid to 1.29 in ethanol. The greatly reduced ratios for the **3** system in the acids are ascribed to the fact that, while the rates for the axial tosylate are normal, those for the equatorial tosylate are enhanced owing to participation of the 5(10) double bond. The acetates produced from **3e**-OTs show an unusually low inversion–retention ratio, which is compatible with such participation.

Since the *trans*-decalin system is incapable of undergoing chair inversion, it is one of the models most conveniently used for the study of the relationship between conformation and reactivity of cyclohexane derivatives.[2] The higher reactivity of the axial over the equatorial tosylate in conformationally fixed cyclohexane derivatives has been investigated by several workers.[3-9] In the study of solvolyses of *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates, Winstein and Holness suggested steric acceleration arising from the axial conformation in the initial ground state.[3] Baker and his associates[7,8b] proposed the importance of participation of the β-axial hydrogen in the transition state in solvents of low nucleophilicity and high ionizing power. As an extension of our previous work,[10] we carried out the determination of solvolysis rates and products of the axial and equatorial epimers of *trans*-2-decalyl tosylate (**1**-OTs), 6-keto-*trans*-2-decalyl tosylate (**2**-OTs), and 6-keto-$\Delta^{5(10)}$-*trans*-decalyl tosylate (**3**-OTs) in trifluoroacetic, formic, and acetic acids and ethanol. Effects of solvents and the 5,10 double bond upon the relative reactivity of the epimeric tosylates are reported.[11]

Results

Preparations.—The axial and equatorial epimers of 6-keto-$\Delta^{5(10)}$-*trans*-decalin-2-ol (**3e**-OH, **3a**-OH) were

(1) Presented in part at the 23rd Symposium on Organic Reaction Mechanisms, Kobe, Japan, Oct 1972.

(2) (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, Chapter 8; (b) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morison, "Conformational Analysis," Interscience, New York, N. Y., 1965, Chapter 2.

(3) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

(4) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382, 1383 (1965).

(5) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southan, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968).

(6) K. Okamoto, S. Saito, and H. Shingu, *Bull. Chem. Soc. Jap.*, **42**, 3288, 3298 (1969).

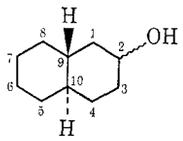
(7) R. Baker, J. Hudec, and K. L. Rabone, *Chem. Commun.*, 197 (1969).

(8) (a) R. Baker, J. Hudec, and K. L. Rabone, *J. Chem. Soc. B*, 1446 (1970); (b) R. Baker and K. L. Rabone, *ibid.*, 1598 (1970).

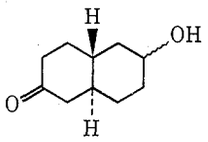
(9) I. Moritani, S. Nishida, and M. Murakami, *J. Amer. Chem. Soc.*, **81**, 3420 (1959).

(10) H. Tanida, S. Yamamoto, and K. Takeda, *J. Org. Chem.*, **38**, 2077 (1973).

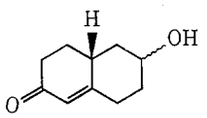
(11) All the compounds used in the present study are *dl* mixtures. For convenience, only one enantiomorph is shown in the figures and according to steroid convention, the hydrogen at C-9 is assigned the β orientation. The same convention was used in the previous work.[10]



1e-OH (equatorial OH)
1a-OH (axial OH)



2e-OH
2a-OH



3e-OH
3a-OH

synthesized from 6-methoxy-2-tetralol[12] by the procedure of Clarke and Martin.[13] The epimers of *trans*-decalin-2-ols (**1e**-OH, **1a**-OH) and 6-keto-*trans*-decalin-2-ols (**2e**-OH, **2a**-OH) were obtained from **3e**-OH and **3a**-OH by the methods described in the literatures.[13,14] Configurations at C_2 of these alcohols were determined by infrared and nmr spectra and vpc analyses.[14b] Each of the alcohols (**1**–**3**) used in the present study was shown by vpc to be over 99.0% pure. Treatment of the alcohols with *p*-toluenesulfonyl chloride in pyridine led to the tosylates (**1**-OTs–**3**-OTs), whose nmr spectral parameters and other physical constants are given in the Experimental Section.

Rates.—Acetolysis, formolysis, and trifluoroacetolysis were performed in buffered media (in the presence of 1.1 equiv of sodium salt of the respective acid), but ethanolysis was carried out without addition of base except in the case of **3**-OTs. Rates of formolysis, acetolysis, and ethanolysis were determined at several temperatures following the procedure described by Winstein and coworkers[10,15] using a potentiometer. Theoretical infinity values were obtained in all runs after about 10 half-lives at the reaction temperature. In each experiment the reaction was followed to 80% completion. The rates of trifluoroacetolysis were measured by a modification[10,16] of the spectrophotometric method advanced by Peterson and coworkers.[17] In trifluoroacetolysis the reaction was followed to 50% completion. The first-order rate constants were calculated by means of the least squares method with a FACOM 270-20 computer, the correlation coefficients of all the plots being 0.999 ± 0.001.

(12) W. Nagata, and T. Terasawa, *Chem. Pharm. Bull*, **9**, 267 (1961).

(13) R. L. Clarke and C. M. Martin, *J. Amer. Chem. Soc.*, **81**, 5716 (1959).

(14) (a) K. Takeda, and S. Yamamoto, *Chem. Pharm. Bull.*, **20**, 314 (1972); (b) *ibid.*, **20**, 1125 (1972).

(15) S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(16) Since the obtained infinity titers did not correspond to the theoretical values, the rates of trifluoroacetolysis were determined from the plots against time of log c_{OTs}, which were calculated according to the following equations,

$$A = c_{OTs}\epsilon_{OTs} + c_{PS}\epsilon_{PS} \quad (1)$$

$$c^{\circ}_{OTs} = c_{OTs} + c_{PS} \quad (2)$$

$$c_{OTs} = \frac{A - c_{OTs}\epsilon_{PS}}{\epsilon_{OTs} - \epsilon_{PS}} \quad (3)$$

where A is the absorbance at 273.2 mμ of an actual sample, c°_{OTs} is the initial concentration (moles/liter) of tosylate, c_{OTs} and c_{PS} are the concentration of tosylate and *p*-toluenesulfonic acid, respectively, and ϵ_{OTs} and ϵ_{PS} are the molar extinction coefficients at 273.2 mμ of tosylate and *p*-toluenesulfonic acid, respectively. See ref 10.

(17) P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, **87**, 5169 (1965).

The rate constants and activation parameters thus obtained are listed in Table I.

Acetolysis Products—A detailed analysis of solvolysis products from axial and equatorial *trans*-2-decalyl tosylates and some related tosylates has been reported;[18] so the present work deals with the products from the four tosylates, **2e**-, **2a**-, **3e**-, and **3a**-OTs. The tosylates were solvolyzed in glacial acetic acid buffered with 1.1 equiv of sodium acetate at 100.0° for about 10 half-lives. Olefins (products of elimination) and acetates (products of substitution) were separated by elution chromatography. The acetate fractions were identified by comparison of retention times on vpc with those of authentic samples,[14] and their yields were determined by vpc with internal standards. The olefin fractions were shown to be composed of the Δ^1 olefin and Δ^2 olefin by nmr and mass spectra and vpc analyses. However, these two olefins could not be completely separated by vpc analyses using several kinds of columns. Very small amounts of unknown products were observed but not identified. The results are summarized in Table II.

Discussion

The axial tosylate shows a higher reactivity than the equatorial epimer in the solvolysis of conformationally fixed cyclohexyl derivatives, although evidence has been presented that the tosylates react by different transition states.[18,19] The relative rate of the axial (cis) to the equatorial (trans) 4-*tert*-butylcyclohexyl tosylate at 50° is 3.90, 3.24, and 3.58 in ethanol, acetic acid, and formic acid, respectively.[3] That of *trans*-2-decalyl tosylate epimers (**1**-OTs) has been reported as 2.86[8b] (or 3.1[9]) at 75° in acetic acid and 5.55[8b] at 25° in formic acid. The axial–equatorial rate ratios (k_{ax}/k_{eq}) determined in the present work are listed in Table III. It is seen that the ratios for **1**-OTs are relatively insensitive to change in solvent from trifluoroacetic acid of high ionizing power and low nucleophilicity to formic acid, acetic acid, and then ethanol of low ionizing power and high nucleophilicity. These data would qualify Baker's suggestion[8b] that the extent of hydrogen participation is reflected in such changes in rate ratio, a conclusion which he arrived at from data in only two solvents, acetic and formic acids. From Table I, the differences in activation enthalpies and entropies between the axial and equatorial tosylates of **1**-OTs are −1.6 kcal/mol and −2.2 eu in trifluoroacetolysis, −2.0 kcal/mol and −3.0 eu in formolysis, −0.2 kcal/mol and 1.5 eu in acetolysis, and −1.4 kcal/mol and −1.4 eu in ethanolysis, respectively. The higher rate of the axial over the equatorial tosylate is thus attributable to the favorable difference in activation enthalpy, despite the unfavorable difference in activation entropy (except the entropy difference in acetolysis).

It was recently demonstrated that acetolysis of the monocyclic, conformationally unfixed cyclohexyl tosylate to form the substitution products occurs almost entirely by an inversion mechanism without rearrange-

(18) 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).

(19) (a) V. J. Shiner, Jr., and J. G. Jewett, *J. Amer. Chem. Soc.*, **86**, 945 (1964); (b) *ibid.*, **87**, 1382, 1383 (1965).

TABLE I

RATES AND ACTIVATION PARAMETERS IN SOLVOLYSES[a,b]

Compd	Solvent	Temp, °C	k_1, sec^{-1} [c]	$\Delta H^{\pm}$, kcal/mol[d]	$\Delta S^{\pm}$, eu[d]
1e-OTs	CF_3COOH[e]	25.0	1.19×10^{-4}	21.2 ± 0.2	−5.5 ± 0.6
		50.0	2.04×10^{-3}		
	HCOOH[f]	25.0	$(1.52 \pm 0.02) \times 10^{-5}$	24.4 ± 0.2	1.1 ± 0.5
		50.0	$(4.08 \pm 0.04) \times 10^{-4}$		
	CH_3COOH[e]	25.0	3.80×10^{-8}	26.7 ± 0.1	−2.8 ± 0.2
		50.0	1.35×10^{-6}		
	C_2H_5OH[e]	25.0	2.43×10^{-8}	25.2 ± 0.3	−8.8 ± 0.8
		50.0	7.26×10^{-7}		
1a-OTs	CF_3COOH	0.0	$(2.37 \pm 0.08) \times 10^{-5}$	19.6 ± 0.3	−7.7 ± 0.9
		15.0	$(1.59 \pm 0.02) \times 10^{-4}$		
		25.0	$(5.40 \pm 0.17) \times 10^{-4}$		
		25.0[b]	5.32×10^{-4}		
		50.0[b]	7.49×10^{-3}		
	HCOOH[f]	25.0	$(8.44 \pm 0.08) \times 10^{-5}$	22.4 ± 0.4	−1.9 ± 1.3
		50.0	$(1.78 \pm 0.08) \times 10^{-3}$		
	CH_3COOH	25.0[b]	1.18×10^{-7}	26.5 ± 0.1	−1.3 ± 0.3
		50.0[b]	4.07×10^{-6}		
		67.4	$(3.55 \pm 0.10) \times 10^{-5}$		
		80.1	$(1.49 \pm 0.07) \times 10^{-4}$		
		95.0	$(7.23 \pm 0.31) \times 10^{-4}$		
	C_2H_5OH	25.0[b]	1.30×10^{-7}	23.8 ± 0.5	−10.2 ± 1.2
		50.0[b]	3.16×10^{-6}		
		76.6	$(5.64 \pm 0.24) \times 10^{-5}$		
		90.0	$(2.16 \pm 0.04) \times 10^{-4}$		
		105.0	$(7.98 \pm 0.25) \times 10^{-4}$		
2e-OTs	CF_3COOH[e]	25.0	1.52×10^{-6}	22.7 ± 0.1	−8.9 ± 0.2
		50.0	3.20×10^{-5}		
	HCOOH	25.0[b]	1.57×10^{-6}	24.2	−3.8
		50.0	$(4.03 \pm 0.05) \times 10^{-5}$		
		70.0	$(3.86 \pm 0.17) \times 10^{-5}$		
	CH_3COOH[e]	25.0	4.73×10^{-9}	28.1 ± 0.3	−2.3 ± 0.9
		50.0	2.01×10^{-7}		
	C_2H_5OH[e]	25.0	1.81×10^{-8}	24.1 ± 0.06	−13.2 ± 0.1
		50.0	4.56×10^{-7}		
2a-OTs	CF_3COOH	25.0[b]	4.23×10^{-6}	22.7 ± 0.2	−7.0 ± 0.6
		40.0	$(2.76 \pm 0.06) \times 10^{-5}$		
		50.0	$(9.04 \pm 0.23) \times 10^{-5}$		
		50.0[b]	8.90×10^{-5}		
		70.0	$(7.38 \pm 0.06) \times 10^{-4}$		
	HCOOH	25.0[b]	5.03×10^{-6}	23.9	−2.7
		50.0	$(1.23 \pm 0.05) \times 10^{-4}$		
		70.0	$(1.14 \pm 0.08) \times 10^{-3}$		
	CH_3COOH	25.0[b]	2.26×10^{-8}	26.4 ± 0.4	−5.0 ± 1.1
		50.0[b]	7.61×10^{-7}		
		81.7	$(3.27 \pm 0.09) \times 10^{-5}$		
		95.0	$(1.36 \pm 0.12) \times 10^{-4}$		
		110.2	$(5.71 \pm 0.43) \times 10^{-4}$		
	C_2H_5OH	25.0[b]	1.08×10^{-7}	22.6 ± 0.3	−14.4 ± 0.8
		50.0[b]	2.26×10^{-6}		
		79.6	$(4.73 \pm 0.49) \times 10^{-5}$		
		95.0	$(1.95 \pm 0.10) \times 10^{-4}$		
		105.1	$(4.46 \pm 0.32) \times 10^{-4}$		
3e-OTs	HCOOH	50.0	$(2.65 \pm 0.08) \times 10^{-5}$	23.3	−7.6
		70.0	$(2.33 \pm 0.12) \times 10^{-4}$		
	CH_3COOH	50.0[b]	4.00×10^{-7}	25.3 ± 0.1	−9.8 ± 0.2
		100.1	$(9.04 \pm 0.25) \times 10^{-5}$		
		115.2	$(3.57 \pm 0.28) \times 10^{-4}$		
		130.0	$(1.22 \pm 0.05) \times 10^{-3}$		
	C_2H_5OH[g]	50.0[b]	4.74×10^{-7}	23.8 ± 0.3	−14.1 ± 0.8
		90.0	$(3.11 \pm 0.14) \times 10^{-5}$		
		105.1	$(1.24 \pm 0.08) \times 10^{-4}$		
		120.0	$(4.15 \pm 0.14) \times 10^{-4}$		
3a-OTs	HCOOH	50.0	$(2.39 \pm 0.09) \times 10^{-5}$	24.0	−5.4
		70.0	$(2.25 \pm 0.09) \times 10^{-4}$		
	CH_3COOH	50.0[b]	3.55×10^{-7}	26.6 ± 0.01	−6.0 ± 0.03
		94.5	$(6.04 \pm 0.29) \times 10^{-5}$		
		110.1	$(2.77 \pm 0.15) \times 10^{-4}$		
		125.1	$(1.07 \pm 0.04) \times 10^{-3}$		

TABLE I
(*Continued*)

Compd	Solvent	Temp, °C	k_1, sec^{-1} [c]	$\Delta H^{\pm}$, kcal/mol[d]	$\Delta S^{\pm}$, kcal/mol[d]
3a-OTs	C_2H_5OH[g]	50.0[b]	6.10×10^{-7}	23.9 ± 0.1	−13.2 ± 0.3
		90.0	$(4.12 \pm 0.33) \times 10^{-5}$		
		105.0	$(1.61 \pm 0.07) \times 10^{-4}$		
		120.0	$(5.58 \pm 0.23) \times 10^{-4}$		

[a] The concentrations of tosylates were 50 m*M* for trifluoroacetolyses, 20 m*M* for formolyses, and 1.0 m*M* for acetolyses and ethanolyses. Temperature deviation was ±0.03°. [b] Rates at 25 and 50° were calculated from observed rates. [c] Error limits for rate constants are 95% confidence limits [degree of freedom, $\phi = n - 2$ ($n = 10$)]. [d] With standard deviations. [e] Reference 10 gives the rates at 50°, from which the rates at 25° are calculated using the reported activation parameters. [f] Cited from ref 8b. [g] In the presence of 2,6-lutidine (2.0 m*M*).

TABLE II
PRODUCTS AND YIELDS[a] FROM ACETOLYSES AT 100.0°

Compd	Olefin, %[b]	Acetate, % 2α (eq)	Acetate, % 2β (ax)
1e-OTs[c]	64.0	2.2	33.3
1a-OTs[c]	86.4	7.8	4.0
2e-OTs	55.2	1.1	31.9
2a-OTs	78.2	10.2	3.5
3e-OTs	55.1	6.4	17.9
3a-OTs	63.9	21.5	5.8

[a] Based on theory. [b] Composed of Δ^1 and Δ^2 olefins. [c] Cited from ref 18.

TABLE III
AXIAL–EQUATORIAL RATE RATIOS (k_{ax}/k_{eq}) AT 50.0°

Compd	CF_3COOH	HCOOH	CH_3COOH	C_2H_5OH
1-OTs	3.67	4.36[a]	3.01	4.35
2-OTs	2.78	3.05	3.82	4.96
3-OTs		0.902	0.888	1.29

[a] Calculated from the rate data in ref 8b, where the ratio at 25° has been reported as 5.55.

TABLE IV
ELIMINATION/SUBSTITUTION RATIOS AND INVERSION/RETENTION RATIOS IN PRODUCTS OF ACETOLYSIS AT 100.0°

Compd	Elimination/ Substitution	Inversion/ Retention
1a-OTs[a]	7.23	1.95
2a-OTs	5.71	2.92
3a-OTs	2.34	3.71
cis-4-*tert*-Butylcyclohexyl OTs[a]	6.45	8.9
Cholestanyl a-OTs[b]	10.0	3.53
Δ^5-Cholestanyl a-OTs[b]	23.0	2.56
1e-OTs[a]	1.82	15.1
2e-OTs	1.67	29.5
3e-OTs	2.19	2.80
trans-4-*tert*-Butylcyclohexyl OTs[a]	3.61	48
Cholestanyl e-OTs[b]	1.45	31.3
Δ^5-Cholestanyl e-OTs[b]	1.71	176

[a] Cited from ref 5. [b] Cited from ref 8b.

ment (the solvent-assisted k_s mechanism).[20] On the other hand, according to the detailed product analysis by Whiting, *et al.*,[18] the substitution products from acetolysis of **1e**-OTs were the inverted acetate in 33.3% and the retained acetate in 2.2% yield, while those from **1a**-OTs were the inverted acetate in 7.8% and the retained acetate in 4.0% yields (presented in Table II). Similar products distributions were observed in the acetolyses of **2e**- and **2a**-OTs. The ratios of elimination products (olefins) to substitution products (acetates) and the ratios of inverted acetates to retained acetates, observed from **1**-, **2**-, and **3**-OTs and reported for some related conformationally fixed cyclohexyl tosylates, are listed in Table IV. There is accumulated evidence that the intermediates in the borderline solvolysis of secondary substrates are ion pairs, and not free carbonium ions.[21-23] Regarding the substitution stereochemistry in solvolysis, Sneen[21b] has recently proposed that inversion arises from the intimate ion pair, retention from the solvent-separated ion pair, and racemization from the dissociated ion. Good evidence for inversion may be the stereochemical studies with 2-octyl substrates[21a] and that for retention may be the kinetic and product studies on 2-adamantyl arenesulfonates in 70% aqueous ethanol with various arenesulfonate leaving groups.[23] By Sneen's argument, the large ratio of inversion to retention for **1e**-OTs (15.1) relative to that for **1a**-OTs (1.95) would mean a favorable reaction at the intimate ion-pair stage. Since it has been suggested that solvolysis of *trans*-4-*tert*-butylcyclohexyl tosylate[8b,18,19b] and **1e**-OTs[8b,18] takes place largely *via* nonchair (twist-boat) conformers and to some extent *via* the main, equatorial chair conformer, the formation of an incipient cationic center from any of these conformers would bring about flattening of the ring about the reaction site and, as a consequence, solvent participation from the back side resulting in inversion would be facilitated with reduction of the compression among the C_2 axial hydrogen and neighboring hydrogens (in particular, among the C_2 hydrogens and the C_1 and C_3 hydrogens in the nonchair conformer) at the expense of emerging bond-angle and torsional strains. Such an effect favorable for inversion is not obtained by the transition-state formation in the reactions of *cis*-4-*tert*-butylcyclohexyl tosylate[3,19] and **1a**-OTs,[18] which are considered to react *via* the axial chair conformer. In addition, solvent participation from the backside in this conformer would be disturbed by emerging compression among the solvent and the axial hydrogens at C_1 and C_3. The small inversion/retention ratio observed for **1a**-OTs may indicate competing substitutions on an intimate ion pair and a solvent-separated ion pair, effects specially favorable for either one of the substitutions being either absent or in a compensating balance with other, unfavorable factors.

In contrast to the above cases, the axial tosylate in the 3 system solvolyzes more slowly than the equa-

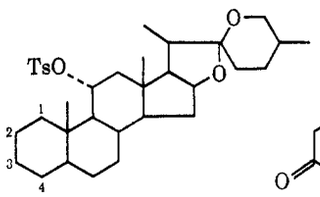
(20) (a) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972); (b) J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972).

(21) (a) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287, 292 (1965); (b) R. A. Sneen, *Accounts Chem. Res.*, **6**, 46 (1973), and references cited therein.

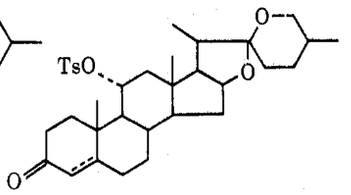
(22) V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969); V. J. Shiner, Jr., and W. Dowd, *ibid.*, **91**, 6528 (1969); V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *ibid.*, **91**, 7748 (1969); V. J. Shiner, Jr., and R. D. Fisher, *ibid.*, **93**, 2553 (1971).

(23) J. M. Harris, J. F. Fagan, F. A. Waden, and D. C. Clark, *Tetrahedron Lett.*, 3023 (1972).

torial epimer in formic and acetic acids. This reverse reactivity can be considered in two ways: (a) the rate of the axial tosylate is normal, but that of the equatorial one is unusually enhanced; (b) the rate of the axial tosylate is unusually retarded, but that of the equatorial one is normal. In a previous paper we reported the rates of acetolysis of A-ring substituted 11α-*p*-toluenesulfonyloxy steroidal sapogenins[24] and the rates of solvolyses of 6-substituted *trans*-decalyl-2α-*p*-toluenesulfonates in various solvents, and we showed, by linear correlation using the modified Hammett–Taft equation, that inductive effects are dominant in governing the rates. For example, transformation of 11α-tosyloxy-25D,5α-spirostan (**4**) into its 3-one derivative (**5**) and 4-en-3-one derivative (**6**) slows down the



4



5 and **6** ($\Delta^{4,5}$)

rate by factors of 0.19 and 3.9 $\times$ 10^{-2}, respectively, while the same transformation in the present systems (from **1** to **2** and **3**) decreases the rate by factors of 0.19 and 8.7 $\times$ 10^{-2}, respectively. This situation is summarized in Table V. It is seen from this table

TABLE V

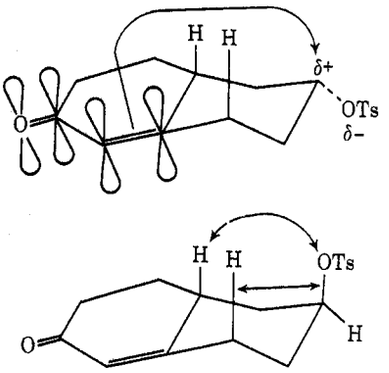
ACETOLYSIS RATES OF 2-DECALYL TOSYLATES (**1**, **2**, AND **3**) AT 65.0° [a] AND 11α-TOSYLOXY-25D,5α-SPIROSTAN DERIVATIVES (**4**, **5**, AND **6**) AT 65.4° [b]

Compd	ax-OTs	eq-OTs	ax-OTs	eq-OTs
1	26.6	8.96	1	1
2	4.95	1.46	0.19	0.16
3	2.31	2.38	8.7×10^{-2}	0.27
4		379		1
5		71.7		0.19
6		14.8		3.9×10^{-2}

[a] Rates at 65.0° were calculated from the observed rates in Table I. [b] The data at 65.4° are cited from our paper (ref 24).

that the relative rate of **3a**-OTs (8.7×10^{-2}) is normal, but that of **3e**-OTs (0.27) is unusually large. Further, when the observed rate of the equatorial epimer (4.00×10^{-7} sec^{-1} in Table I) is compared with that estimated by extrapolation of the reported Hammett–Taft linearity, $k_1 = 9.0 \times 10^{-8}$ sec^{-1} (at 50° in acetic acid), a rate enhancement in **3e**-OTs is seen. We propose that participation of the $\Delta^{5(10)}$ unsaturation from the back side of the leaving equatorial tosyloxy group is the main factor contributing to this enhancement. A molecular model indicates that the 1,3-diaxial interactions existing between the tosyloxy group at C_2 and the hydrogens at C_4 and C_9 in the **1** and **2** systems should be reduced slightly with introduction of the $\Delta^{5(10)}$ unsaturation as a result of the slight outward movements of the hydrogens at C_4 and C_9. This decrease in the 1,3-diaxial interactions should result in a decreased solvolysis rate for **3a**-OTs. In ethanol, however, just as with systems **1** and **2**, the

(24) K. Takeda, H. Tanida, and K. Horiki, *J. Org. Chem.*, **31**, 734 (1966).



axial tosylate **3a**-OTs is observed to be more active than the equatorial tosylate (k_{ax}/k_{eq} = 1.29 in Table III). It therefore seems difficult to explain this solvent effect upon relative reactivity in terms of 1,3-diaxial interaction, though it can be explained in terms of a decrease or absence of participation in the ethanolysis of **3e**-OTs, it being well established that neighboring group participation is not favored in a solvent of such high nucleophilicity and low ionization powder as ethanol.[25]

The ratios of inversion to retention in products (Table IV) from all the present axial tosylates (**1a**–**3a**) are normal. They are comparable to one another and to those for the reference compounds. The ratios for the two equatorial tosylates, **1e**-OTs and **2e**-OTs, are similarly normal, but **3e**-OTs is exceptional in that it shows a very low inversion/retention ratio (2.80). The increased yield of the retained acetate from **3e**-OTs can be regarded as a result of stereochemical control exerted by the $\Delta^{5(10)}$ double bond.

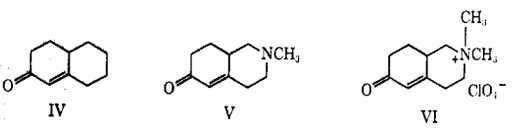
Experimental Section

Melting points were taken on a Yanagimoto melting point apparatus and are uncorrected. Nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as internal standard. Infrared spectra were measured on a Nippon Bunko DS201B spectrometer. Uv spectra were measured on a Hitachi EPS-032 and/or a Hitachi EPU-2A spectrometer. Vpc analyses were performed on a Hitachi gas chromatograph Model K53 equipped with a hydrogen frame ionization detector using the following columns: (A) 1 m $\times$ 3 mm stainless steel column packed with Carbowax 20M 5%, (B) 2 m $\times$ 3 mm Carbowax 20M 10%, and (C) 2 m $\times$ 3 mm DEGS 10%. Nitrogen was used as a carrier gas.

All the alcohols (1-OH–3-OH) used in the present study were synthesized from 6-methoxy-2-tetralol by methods described in a previous paper.[14] Each of the alcohols was shown by vpc analysis to be over 99.0% pure.

Preparation of *p*-Toluenesulfonates.—Tosylates (1-OTs–3-OTs) were prepared according to our previous paper,[10] in which

(25) In an ultraviolet study of the bicyclic ketones IV, V, and VI, which contain a quaternary nitrogen atom at a distance of about 3.1 Å from the α,β-unsaturated ketone group, E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959), observed that the absorption maximum for the π–π^* transi-



IV V VI

tion shifts to a shorter wavelength with increasing positive charge on the nitrogen atom (from compound IV to V to VI), while that for the n–π^* transition shifts to a longer wavelength. Although the mechanisms underlying the kinetic data and this ultraviolet data are, of course, different, it can be said that both the findings are based on long-range electrical effects operating from the $\Delta^{5(10)}$ double bond to the C_2 position.

nmr spectral parameters and other physical data are also given. Recrystallized from ether–*n*-hexane, ***trans*-2β-decalyl *p*-toluenesulfonate** (1a-OTs) has mp 107–108°; nmr ($CDCl_3$) δ 2.43, 7.55 (OTs), 4.80 (1 H, broad s, $W_{1/2}$ = 7 Hz, C_6 eq H); ir (KBr) 909, 1174, 1342 cm^{-1} (OTs); uv max (CH_3OH) 273.2 mμ (ε 445).

Anal. Calcd for $C_{17}H_{24}O_3S_1$: C, 66.20; H, 7.85; S, 10.39. Found: C, 65.95; H, 7.79; S, 10.58.

Recrystallized from ether, **6-keto-*trans*-2β-decalyl *p*-toluenesulfonate** (2a-OTs) has mp 102–103°; nmr ($CDCl_3$) δ 2.45, 7.57 (OTs), 4.86 (1 H, broad s, $W_{1/2}$ = 7 Hz, C_6 eq H); ir (KBr) 900, 1166, 1355 (OTs), 1715 cm^{-1} (C=O); uv max (CH_3OH) 273.2 mμ (ε 456).

Anal. Calcd for $C_{17}H_{22}O_4S_1$: C, 63.33; H, 6.87; S, 9.94. Found: C, 63.07; H, 6.96; S, 9.84.

Recrystallized from acetone-*n*-hexane, **6-keto-Δ$^{5(10)}$-*trans*-decalyl *p*-toluenesulfonate** (3e-OTs) has mp 100–101.0°; nmr ($CDCl_3$) δ 2.46, 7.58 (OTs), 4.67 (1 H, broad s, $W_{1/2} \cong$ 23 Hz, C_2 ax H), 5.83 (1 H, broad s, C_5 H); ir (KBr) 1625, 1673 cm^{-1} (α,β-unsaturated ketone).

Anal. Calcd for $C_{17}H_{20}O_4S_1$: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.45; H, 6.31; S, 9.90.

Recrystallized from acetone-*n*-pentane, **6-keto-Δ$^{5(10)}$-*cis*-decalyl *p*-toluenesulfonate** (3a-OTs) has mp 121–122°; nmr ($CDCl_3$) δ 2.46, 7.60 (OTs) 4.93 (1 H, broad s, $W_{1/2}$ = 8 Hz, C_2 eq H), 5.84 (1 H, t, J = 2 Hz, C_5H); ir (KBr) 1618, 1672 cm^{-1} (α,β-unsaturated ketone).

Anal. Calcd for $C_{17}H_{20}O_4S_1$: C, 63.73; H, 6.29; S, 10.01. Found: C, 63.79; H, 6.34; S, 9.86.

Kinetic Measurements.—The conditions and procedure for the solvolyses in trifluoroacetic acid, acetic acid, and ethanol were the same as previously reported.[10]

For formolysis, the tosylates were dissolved at a concentration of 20 mM in formic acid containing 22 mM sodium formate. The acid was purified by distillation with pure boric anhydride. Aliquots (1.0 ml) were distributed into tubes and sealed under nitrogen after freezing in Dry Ice–acetone. The tubes were placed in a constant-temperature bath and then successively withdrawn after appropriate intervals of time. The tubes were cooled and opened, and the contents were diluted with 10 ml of acetic acid. The solutions were titrated with 0.04 N perchloric acid in acetic acid using a Metrohm potentiograph E336A. Plots of log ($A_t - A_\infty$) *vs.* time, where A_∞ and A_t are titers at infinity and at given times, respectively, were uniformly linear. The slopes multiplied by −2.303 gave the pseudo-first-order rate constants.

Acetolysis Products.—The method employed was essentially the same as that described previously.[10] The olefin and acetate fractions were the separated by a small column of silica gel. The olefin fractions were collected, dried under reduced pressure, and weighed. The olefin fractions were shown to consist of the Δ^1 olefin and Δ^2 olefin by nmr and mass spectra and vpc analysis. The acetate fractions were collected and identified with authentic samples.[14] The yields of the acetates were determined by vpc with internal standards. Products and yields from the tosylates (1-OTs–3-OTs) are given in the Results and, in part, in the preceding paper.[10] The olefin fraction from **2a**-OTs showed nmr ($CDCl_3$) δ 5.5–5.7 (2 H, m, olefinic protons); mass spectrum m/e 150 (M^+). That from **3e**-OTs showed nmr ($CDCl_3$) δ 5.75 (1 H, broad s, C_5 H), 6.2–6.3 (2 H, m, olefinic protons); mass spectrum m/e 148 (M^+). That from **3a**-OTs showed nmr ($CDCl_3$) δ 5.75 (1 H, broad s, C_5 H), 6.2–6.3 (2 H, m, olefinic protons); mass spectrum m/e 148 (M^+).

Registry No.—**1a**, 5746-69-0; **1a**-OTs, 40429-90-1; **1e**, 36667-73-9; **1e**-OTs, 40429-92-3; **2a**, 36667-84-2; **2a**-OTs, 40429-94-5; **2e**, 39089-10-6; **2e**-OTs, 40429-96-7; **3a**, 40429-97-8; **3a**-OTs, 40429-98-9; **3e**, 40429-99-0; **3e**-OTs, 40550-47-8.

Formation of Endo Acetate in Acetolysis of a Fused *endo*-Norbornyl Brosylate *via* C-7 Participation[1,2]

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XII-OH, a new alcohol, was obtained in low yield by sodium amalgam reduction of the oxymercurials from endo,endo diene. Upon acetolysis, XII-OBs undergoes ~98% rearrangement *via* cation A to VI-OBs; no endo acetate XIII-OAc is formed. Acetolysis of the endo brosylate XIII-OBs results in 22.5% XIII-OAc, apparently *via* C-7 participation and cation C.

In continuance of studies in the bird-cage hydrocarbon system,[4] we reported[5] recently that acetolysis of exo brosylate VI-OBs produced 27% endo acetate VII-OAc *via* anchimerically unassisted solvolysis in competition with anchimerically assisted solvolysis. The endo brosylate VII-OBs produced 3% VII-OAc through 10% intimate ion pair return to and subsequent solvolysis of VI-OBs.[5] We now report the striking results of acetolysis of the related pair of brosylates XII-OBs and XIII-OBs, of which the most salient feature is formation of endo acetate XIII-OAc from endo brosylate XIII-OBs but not from exo brosylate XII-OBs.

Results and Discussion

XII-OH, a previously unknown alcohol,[4-6] and thus XIII-OH became accessible as a result of studies[7] of oxymercuration of endo,endo diene. Reaction of the diene[7,8] with mercuric acetate in acetic acid, treatment of the reaction mixture with aqueous sodium chloride, and reduction of the resultant solid mixture with sodium amalgam in water led to formation of *ca.* 62% bird-cage hydrocarbon, 5% residual unhydrolyzed acetates, 24% VI-OH, a trace of V-OH, and 9% XII-OH (Scheme I). Isolation of 98% pure XII-OH containing 2% V-OH was effected by chromatography of the crude product mixture on alumina. Final purification by gas chromatography, sublimation,

(1) Taken in part from the Ph.D. Thesis of Robert K. Howe, UCLA, Los Angeles, Calif., 1965.

(2) An extension of compound designations used previously[4] is employed herein for ease of cross reference between the papers of this series.

(3) Deceased November 23, 1969.

(4) L. deVries and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 5363 (1960).

(5) Robert K. Howe, Peter Carter, and S. Winstein, *J. Org. Chem.*, **37**, 1473 (1972).

(6) The alcohol with mp 72–73°, originally thought[4] to possess the XII-OH structure, has been shown[5] to be the endo epimer of VI-OH.

(7) K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

(8) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).