found to be 95% 1-*t*-butylcyclohexene and 5% 3-*t*-butylcyclohexene.

When a sample of 3-*t*-butylcyclohexene was heated with phosphoric acid at 130–160° for 2 hr. the composition of the recovered binary mixture was 6% 1-*t*-butylcyclohexene and 94% 3-*t*-butylcyclohexene. These experiments demonstrate that the *t*-butylcyclohexenes are isomerized to only a slight extent under the conditions of the dehydration.

Infrared Analysis. A. ***cis*- and *trans*-2-*t*-Butylcyclohexanols.**—The relative transmittances at 9.47 μ (*trans*) and 10.34 μ (*cis*) were measured for synthetic mixtures of *cis*- and *trans*-alcohols (0.4 *M* solutions in CS_2, using 0.1-mm. cells). The compositions of unknown mixtures were read from a plot of the transmittance ratio against percentage composition.

B. **1- and 3-*t*-Butylcyclohexene.**—Compositions of unknown mixtures of the olefins were determined by comparison of the absorption intensities at 9.67 μ (1-isomer) and 10.02 μ (3-isomer) with those of synthetic mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

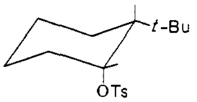
The Solvolysis of *cis*- and *trans*-2-*t*-Butylcyclohexyl *p*-Toluenesulfonate[1,2]

BY HARLAN L. GOERING AND RICHARD L. REEVES[3]

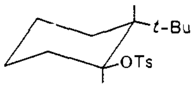
RECEIVED APRIL 30, 1956

The kinetics and products of solvolysis of *cis*- and *trans*-2-*t*-butylcyclohexyl *p*-toluenesulfonate in acetic acid and in ethanol have been investigated. The *cis* (*axial*) isomer is ethanolyzed 5 times faster (30°) and acetolyzed 2 times faster (50°) than the *trans* (*equatorial*) isomer. Both isomers are solvolyzed considerably faster than cyclohexyl *p*-toluenesulfonate; *e.g.*, the *trans* isomer is ethanolyzed 300 times faster (30°) and acetolyzed 240 times faster (50°) than cyclohexyl *p*-toluenesulfonate. The high reactivity of the isomeric 2-*t*-butylcyclohexyl *p*-toluenesulfonates as compared to cyclohexyl and the isomeric 3- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates is attributed to steric acceleration. Only elimination products were isolated from the ethanolysis experiments. The *cis* (*axial*) isomer is converted to 1-*t*-butylcyclohexene and the *trans* (*equatorial*) isomer gives 53% 1- and 47% 3-*t*-butylcyclohexene. Acetolysis of both isomers gives 87–90% olefin together with 2-*t*-butylcyclohexyl acetate. The olefin from the *cis* isomer is 1-*t*-butylcyclohexene; that from the *trans* isomer is 82–86% 1-*t*-butyl- and 14-18% 3-*t*-butylcyclohexene. The acetates were isolated in yields too low for accurately determining the configurational compositions. No evidence was obtained for rearranged solvolysis products.

As pointed out in the previous paper[4] the isomeric 2-*t*-butylcyclohexanols, like the 3- and 4-*t*-butylcyclohexanols,[5] are presumably conformationally homogeneous with the *t*-butyl group in an equatorial position. Thus in the isomeric 2-*t*-butylcyclohexyl *p*-toluenesulfonates the tosyl group is *axial* in the *cis* isomer I and *equatorial* in the *trans* isomer II as illustrated below. In order to obtain information concerning the effect of the position of the leaving group, *i.e.*, *axial* or *equatorial*, on the rates and products of solvolysis we have investigated the products and relative rates of ethanolysis and acetolysis of *cis* I and *trans* 2-*t*-butylcyclohexyl *p*-toluenesulfonate II. This information is also of interest for comparison with the recently reported[5] rates and products of solvolysis of the diastereoisomeric 3- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates.



I



II

Results of Kinetic Experiments.—The results of the pertinent kinetic experiments are summarized in Table I. The first-order rate constants (calculated by use of the integrated equation for a first-order reaction) were steady over the ranges that the reactions were followed (to 95% completion in some cases) for both acetolysis and ethanolysis. Most of the first-order constants (*k*) given in Table I are average values and mean deviations of two or more independent kinetic experiments. In each kinetic experiment six or more values of the rate constant were determined from appropriately spaced titrations during the reactions. As shown in Table I acetolyses of the isomeric tosylates in the presence of sodium acetate (initial concentration 0.2 *M*) are first-order and the rate is increased only slightly over that observed in the ab-

TABLE I

RATES OF ACETOLYSIS AND ETHANOLYSIS OF *cis*- AND *trans*-2-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE

Tosylate	Temp., °C.	[ROTs] 10^2 *m*	[Lyate ion]^a 10^2 *M*	n^b	10^5k^c sec.$^{-1}$
			Acetolysis		
cis	20.11	3–4		2	0.92 ± 0.04
cis	30.12	2–4		4	3.66 ± 0.06
cis	50.03	4.78		1	44.2 ± 1.0
cis	30.12	3–5	19.92	2	4.68 ± 0.10
trans	20.11	3–5		4	0.350 ± 0.012
trans	30.12	4.91		1	1.48 ± 0.04
trans	50.03	3–5		2	21.0 ± 0.2
trans	30.12	3–5	19.92	2	1.78 ± 0.00
			Ethanolysis		
cis	29.99	5.73		1	2.84 ± 0.02
cis	29.99	2–3	29.86	2	3.89 ± .01
trans	29.99	4		3	0.57 ± .01
trans	29.99	3–5	29.86	2	0.83 ± .02

[a] Lyate ion supplied as the sodium salt. [b] Number of independent kinetic experiments. [c] Where more than one independent kinetic experiment was carried out the reported constants are average values for the separate experiments and the mean deviation; where only one kinetic experiment was carried out the reported constant is the average of 7–11 values determined during the reaction, and the mean deviation.

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(1) This work was supported in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(2) Abstracted from the doctoral dissertation of Richard L. Reeves, University of Wisconsin, 1954.

(3) Socony-Vacuum Oil Co. Fellow, 1953–1954.

(4) H. L. Goering, R. L. Reeves and H. H. Espy, THIS JOURNAL, **78**, 4926 (1956).

(5) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

sence of added acetate ion. Similarly the addition of sodium ethoxide (initial concentration 0.3 *M*) does not affect the order of ethanolysis of either isomer and results in only a small increase in rate. A kinetic experiment which demonstrates the first-order behavior of the solvolysis of the *axial* (*cis*) tosylate in ethanol containing 0.3 *M* sodium ethoxide is included in the Experimental section.

Results of Product-isolation Experiments.—The products resulting from the solvolysis of the isomeric 2-*t*-butylcyclohexyl *p*-toluenesulfonates in ethanol (0.2 *N* $NaOC_2H_5$) and acetic acid (0.2 *N* NaOAc) at 50° were investigated. In these experiments the lyate-ion salt was present in slight excess (so initially formed products would survive) and the products were isolated after 10 half-lives. As shown in Table I the reactions are cleanly first order under the conditions of these experiments, *i.e.*, at a lyate-ion concentration of 0.2 *N*. The results of these experiments are presented in Table II.

TABLE II

PRODUCTS ISOLATED FROM SOLVOLYSIS OF *cis*- AND *trans*-2-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE AT 50°

p-Toluenesulfonate	Yield of olefin,[b] %	% olefin compn. 1-*t*-butylcyclohexene	Yield acetate,[c] %
	Acetolysis[a]		
cis	88	100	4.6
cis	90	100	1
trans	89	86	11
trans[d]	87	82	
	Ethanolysis[e]		
cis	52	100	
trans	95	53	

[a] Acetolyses were carried out in the presence of excess sodium acetate (*ca.* 0.2 *N* NaOAc). [b] In all experiments the isolated olefin was 1-*t*-butylcyclohexene or a binary mixture of 1- and 3-*t*-butylcyclohexene. [c] The acetate consisted substantially of *cis*- and *trans*-2-*t*-butylcyclohexyl acetate; however, an unidentified impurity was present (presumably in small amounts); see footnote 6. [d] This experiment was carried out at 30°. [e] Only elimination products were isolated from the ethanolyses.

The solvolysis products were isolated by extraction followed by chromatography, a method which enables isolation of the products in good yields. Control experiments showed that (a) the products are stable under the conditions of the reactions and isolation and (b) fractionation during the isolation is slight and probably not significant.

As shown in Table II acetolysis results primarily in elimination together with lesser amounts of substitution. There was no evidence for the formation of rearranged products. The infrared spectrum of the olefin resulting from ethanolysis and acetolysis corresponded in detail to that of 1-*t*-butylcyclohexene or a binary mixture of 1- and 3-*t*-butylcyclohexene. The compositions of the binary mixtures were determined by infrared analysis.[4] The infrared spectra of the acetates isolated from the acetolyses were very similar to those of authentic binary mixtures of *cis*- and *trans*-2-*t*-butylcyclohexyl acetate; however, the spectra revealed the presence of an impurity. The quantity of acetate isolated was too small for separation of the impurity. Because of interference from the impurity and because some acetate could possibly be formed by esterification of alcohol which might contaminate the *p*-toluenesulfonate, the observed configurational composition[6] of the acetate fractions are not considered reliable. As indicated in Table II only elimination products were isolated from the ethanolysis of the isomeric *p*-toluenesulfonates (I and II). The high yield of olefin obtained from the *trans*-*p*-toluenesulfonate suggests that other products (*e.g.*, rearranged, cleavage and substitution) are formed in low yield if at all.

Discussion of Results.—As shown in Table I the *cis* (*axial*) isomer I solvolyzes faster than the *trans* (*equatorial*) isomer II by factors of about 2 in acetic acid and 5 in ethanol. The rates and activation parameters of solvolysis of I and II are compared with those of other alkylcyclohexyl *p*-toluenesulfonates, including the conformationally homogeneous 3- and 4-*t*-butylcyclohexyl *p*-toluenesulfonates,[5] in Table III.

It is interesting to note that the *axial–equatorial* ratios included in Table III are similar for the three pairs of *t*-butylcyclohexyl *p*-toluenesulfonates. However, the 2-*t*-butyl *p*-toluenesulfonates are substantially more reactive than the 3- and 4-*t*-butyl isomers. Thus the *axial* (*cis*) 2-*t*-butyl isomer is about 90 times more reactive than the *axial* 3- or 4-*t*-butyl isomer and the *equatorial* (*trans*) 2-*t*-butyl isomer is about 145 times more reactive than the *equatorial* 3- or 4-*t*-butyl isomer.

TABLE III

COMPARISON OF RATES AND ACTIVATION PARAMETERS FOR ACETOLYSIS AND ETHANOLYSIS OF ALKYLCYCLOHEXYL *p*-TOLUENESULFONATES

Cyclohexyl OTs	10^5k, sec.$^{-1}$	Rel. rate[a]	(a/e)[b]	$\Delta H^{\ddagger}$,[c] kcal./mole	$\Delta S^{\ddagger}$,[c] e.u.
		Acetolysis 50°			
cis-2-*t*-Butyl	44.2	242	2.1	23.8 ± 0.4	−0.5 ± 1.3
trans-2-*t*-Butyl	21.0	115		25.2 ± .4	2.4 ± 1.2
trans-3-*t*-Butyl[d]	0.510	2.79	3.6	26.6	−0.6
cis-3-*t*-Butyl[d]	.142	.78		27.5	− .5
cis-4-*t*-Butyl[d]	.479	2.62	3.2	26.7	− .5
trans-4-*t*-Butyl[d]	.148	.81		28.1	1.7
cis-Neomenthyl[e]	10.1	55		24.6	−0.7
trans-Menthyl[e]	0.130	.71		29.9	7.1
Cyclohexyl[d]	0.183	(1.00)		27	−1.1
		Ethanolysis 30°			
	10^7k				
cis-2-*t*-Butyl	284	303	5.4		
trans-2-*t*-Butyl	57	61			
cis-4-*t*-Butyl[d]	3.18	3.4	4.9		
trans-4-*t*-Butyl[d]	0.652	.70			
Cyclohexyl[d]	0.937	(1.00)			

[a] Rate of solvolysis relative to that of cyclohexyl *p*-toluenesulfonate. [b] Ratio of rate of axial isomer to that of corresponding equatorial isomer for pairs of epimers that are conformationally homogeneous. [c] Activation parameters for *cis*- and *trans*-2-*t*-butylcyclohexyl *p*-toluenesulfonate are for 30°; for other compounds activation parameters are given at different temperatures (50–100°). [d] Data for this compound taken from reference 5. [e] Extrapolated from data at other temperatures reported in reference 8.

It appears that the greater reactivity of the 2-*t*-butyl isomers is primarily due to steric acceleration.[7] Scale models indicate that the 2-*t*-butyl-

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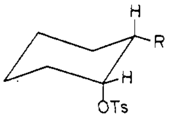
(6) The apparent configurational compositions of the acetates were found to be: 92% *cis*-acetate from the *cis*-*p*-toluenesulfonate I and 53% *cis*-acetate from the *trans*-*p*-toluenesulfonate.

(7) (a) H. C. Brown and H. L. Berneis, THIS JOURNAL, **75**, 10 (1953); (b) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

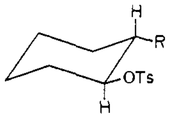
cyclohexyl system, unlike the 3- and 4-*t*-butylcyclohexyl systems, is quite congested and rotation of the *t*-butyl and tosylate groups is restricted. The restriction of rotation (B-strain)[7b] in the 2-*t*-butylcyclohexyl system is very similar to that in the dimethylneopentylcarbinyl system which in turn is an abnormally reactive tertiary system, presumably because of steric acceleration.[7]

It has been suggested[5] that the slightly greater reactivity of the *axial* than *equatorial* isomers in the 3- and 4-*t*-butylcyclohexyl system is at least partly due to steric acceleration. It appears that the same arguments apply to the 2-*t*-butylcyclohexyl system. Since the *t*-butyl and tosylate groups are equidistant in *cis*- and *trans*-2-*t*-butylcyclohexyl *p*-toluenesulfonate, it would appear that the additional steric crowding in this system as compared to the 3- and 4-*t*-butylcyclohexyl systems would be the same for the *axial* and *equatorial* isomers. If in addition the polar effect of the *equatorial* *t*-butyl group is the same in both diastereoisomers the rates of solvolysis of the 2-*t*-butyl system would be expected to be greater than those of the 3- and 4-position isomers (steric acceleration), but the *axial–equatorial* ratio might be expected to be substantially the same as is in fact the case.

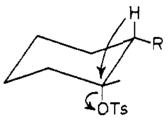
The constancy of the *axial–equatorial* ratio for the three pairs of *t*-butylcyclohexyl toluenesulfonates is of considerable interest in view of the much greater spread in rates of solvolysis of other pairs of isomeric 2-alkylcyclohexyl toluenesulfonates (III). For example, when R is isopropyl the *cis* isomer IIIa is about 80 times more reactive than the *trans* isomer IIIb (*cf.* menthyl and neomenthyl toluenesulfonate[8] (Table III)). Similarly when R is methyl the *cis* isomer IIIa is about 100 times more reactive than the *trans* isomer IIIb.[5] In the last two cases, *i.e.*, R = isopropyl or methyl, the epimers are not conformationally pure, but tend to have the conformations indicated below. The fact that the isomers (especially the *cis* isomer IIIa) are not conformationally homogeneous is not responsible for the large difference in rates and indeed tends to lower the difference.[5]



IIIa



IIIb



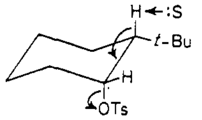
IV

The greater reactivity of IIIa than IIIb when R is methyl or isopropyl has been attributed[5,8] to hydrogen participation (IV) in the rate-determining ionization; such participation being possible in the axial isomer IIIa but not in the equatorial isomer IIIb. *cis*-2-*t*-Butylcyclohexyl *p*-toluenesulfonate (I) also has the required geometry for hydrogen participation; however, if such participation is involved it is not manifested by a detectable increase in solvolytic reactivity.

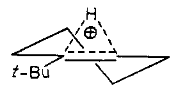
The reason for a large *axial–equatorial* ratio for III when R is methyl or isopropyl (*ca.* 80–100) and a small ratio when R is *t*-butyl (*ca.* 3) is not clear. It is difficult to see why hydrogen participation should result in increased reactivity with an adjacent equatorial methyl or isopropyl group but not with a *t*-butyl group. It seems unlikely that hydrogen participation is less important with a *t*-butyl group than with a smaller group because of the larger reactivity of the former due to steric acceleration. Presumably steric acceleration decreases $\Delta F^{\ddagger}$ (and increases the rate) by raising the free energy level of the reactant. Hydrogen participation, on the other hand, would presumably facilitate the rate-determining ionization by lowering the energy level of the transition state. Thus it would appear that hydrogen participation or steric acceleration would not be obscured by the presence of the other.

The preponderant formation of olefin in the acetolysis of *cis*- and *trans*-2-*t*-butylcyclohexyl *p*-toluenesulfonate parallels previous observations[5,9] that acetolysis of cyclohexyl *p*-toluenesulfonate results primarily in elimination. The formation of different products from the two isomers (Table II) shows that the products are not derived entirely from a dissociated 2-*t*-butylcyclohexyl cation (as would be required according to the E_1 and S_N1 mechanisms in their simplest forms[10]) since this intermediate would be common to both isomers.

It is interesting that in both ethanolysis and acetolysis the *axial* tosylate I gives 1-*t*-butylcyclohexene (one of the two possible *trans*-elimination products) as the only elimination product, whereas the *equatorial* isomer gives a mixture of 1- and 3-*t*-butylcyclohexene. This is similar to the observation that menthyl *p*-toluenesulfonate gives a mixture of Δ^2- and Δ^3-menthene on solvolysis in ethanol or acetic acid, whereas neomenthyl *p*-toluenesulfonate gives Δ^3-menthene exclusively.[8] With *axial* 2-*t*-butylcyclohexyl *p*-toluenesulfonate, *trans* elimination with the observed orientation would be expected for (a) an E_2-type elimination involving nucleophilic participation by the solvent (S:) as illustrated by V, or (b) an E_1-type elimination involving the bridged ion VI or rearranged 1-*t*-butylcyclohexyl cation as the only intermediate, *i.e.*, hydrogen participation. As in the case of the dehydration of the 2-*t*-butylcyclohexyl alcohols,[4] there was no evidence for the formation of rearranged (*e.g.*, ring-contracted) products or cleavage products (*e.g.*, isobutene and cyclohexene) in the solvolysis of the isomeric *p*-toluenesulfonates.



V



VI

As discussed above, the kinetic studies do not provide evidence for hydrogen participation in the solvolysis of the axial isomer. Similarly the kinetic studies do not provide evidence for a concerted elimination (V). That nucleophilic participation by the solvent evidently is not important in the rate-determining step is indicated by (a) the greater

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[8] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

[9] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 8.

rate of acetolysis than ethanolysis,[11] and (b) the observation that the inclusion of 0.2 to 0.2 M lyate ion in acetolysis and ethanolysis results in only a slight increase in rate which can be attributed to a salt effect. On the other hand, it would appear that the conversion of the *axial* tosylate to 1-*t*-butylcyclohexene probably occurs by one of these two processes. It appears unlikely that a dissociated 2-*t*-butylcyclohexyl cation is involved since this presumably is the intermediate in the solvolyses of the *equatorial* isomer which gives different products.

It is interesting to note that *axial* 4-*t*-butylcyclohexyl *p*-toluenesulfonate, unlike the *axial* 2-isomer, reacts largely by a second-order process in ethanol containing 0.065 M $NaOC_2H_5$[5] (the inclusion of 0.065 M ethoxide results in about a 6-fold increase in rate). This fact is not inconsistent with our observation that the ethanolysis of the 2-*axial* isomer I in the presence of 0.3 M $NaOC_2H_5$ is cleanly first-order. Indeed, if it is assumed that the 2-*axial* isomer undergoes a second-order reaction with ethoxide ion not significantly faster than do the 3- and 4-*axial* isomers, it is clear that steric acceleration has raised the rate of solvolysis of the *axial* 2-*t*-butyl isomer to the point where the second-order reaction would not be expected to compete under the present conditions.

Experimental

Materials.—The acetates and *p*-toluenesulfonates of *cis*- and *trans*-2-*t*-butylcyclohexanol and 1- and 3-*t*-butylcyclohexene used in the present work are described in the previous paper.[4]

Rate Measurements.—The temperatures of the thermostats used in the present work were 20.11, 30.12 and 50.03°. Temperature fluctuations were <0.02° and all concentrations are given for 20°. For each kinetic experiment the reaction mixture was distributed in ampules and in general six or more well-spaced points were obtained in addition to the "zero-time" point (determined after temperature equilibration) and "infinity" titer (determined in duplicate). During each run aliquots were measured at the same temperature (usually 20°) with calibrated 5-ml. pipets and 5-ml. microburets were used for the titrations. Specific first-order rate constants were calculated from the observed titers by use of the integrated equation for a first-order reaction.

A. **Acetolysis.**—Anhydrous acetic acid was prepared by refluxing reagent grade glacial acetic acid, minimum assay, 99.5%, with the calculated amount of acetic anhydride. Aliquots were delivered into an equal volume of chilled acetic acid to quench the reaction and rapidly titrated with a standard 0.05 N solution[12] of sodium acetate in acetic acid to the slowly fading (several minutes) brom phenol blue end-point.[12] Because the end-point is more readily reproduced when approached from the acid side, when the solvolysis was carried out in the presence of acetate ion, aliquots were delivered into a slight excess of standard *p*-toluenesulfonic acid in acetic acid and the resulting solution was titrated in the usual manner. The values of the specific rate constants for duplicate runs (different initial concentration) were within 4% and the average deviation of the constants (usually six) within a run from the mean was usually <2%. No trends in the rate constants were observed in any of the experiments. Typical solvolysis equivalents determined from the initial concentration of 2-*t*-butylcyclohexyl *p*-toluenesulfonate and infinity titer are 173.2 and 171.7 (172.20 calcd.).

B. **Ethanolysis.**—The solvolyses of the *p*-toluenesulfonates in absolute ethanol[13] were followed by periodic titration of aliquots with a standard 0.05 N solution of sodium methoxide in methanol to the brom thymol blue end-point. The preparation of the standard solutions and similar titrations have been described previously.[14] As in the case of acetolysis, the rate constants were reproducible and showed no significant trends. Except for the solvolyses in the presence of a high concentration of ethoxide ion the average deviation of the rate constants (at least six) within a run from the mean was about 1%. An experiment which illustrates the first-order nature of the ethanolysis of *cis*-2-*t*-butylcyclohexyl *p*-toluenesulfonate in the presence of 0.3 N sodium ethoxide is summarized in Table IV.

TABLE IV

SOLVOLYSIS OF *cis*-2-*t*-BUTYLCYCLOHEXYL *p*-TOLUENESULFONATE AT 30° IN ABSOLUTE ETHANOL CONTAINING 0.2986 N SODIUM ETHOXIDE

Time, 10^3 sec.	[ROTs], 10^2 M	10^5k, sec.$^{-1}$
0	3.15	..
2.49	2.91	3.2
8.10	2.33	3.7
10.68	2.10	3.8
15.27	1.71	4.0
21.45	1.34	4.0
27.87	1.05	3.9
37.83	0.74	3.8
42.21	0.64	3.8

Product-isolation Experiments. A. **Acetolysis.**—For the product studies *ca.* 0.2 N 2-*t*-butylcyclohexyl *p*-toluenesulfonate and a slight excess of sodium acetate in glacial acetic acid were thermostated at 50° for at least 10 half-lives. The organic products were isolated from the acetic acid by diluting with three volumes of water and extracting the resulting solution thoroughly (continuous extractor) with freshly distilled petroleum ether (b.p. 40–60°). After extracting with water and sodium carbonate solution the dried (magnesium sulfate) petroleum ether solution was concentrated with an efficient fractionating column and the concentrated solution was passed through a chromatography column packed with Alcoa activated alumina. The material was eluted first with petroleum ether which selectively and completely removed the olefins and then with benzene which eluted the acetates.

The petroleum ether was removed from the olefin fraction with an efficient fractionating column and in every case the infrared spectrum showed this material to be 1-*t*-butylcyclohexene or a mixture of 1- and 3-*t*-butylcyclohexene. The composition of the binary mixture was determined by infrared analysis.[4] When a synthetic equimolar mixture of pure 1- and 3-*t*-butylcyclohexene[4] was isolated from an acetic acid solution by the above method the composition of the olefin recovered in nearly quantitative yield was found to be 54% 1- and 46% 3-*t*-butylcyclohexene. When pure 3-*t*-butylcyclohexene was subjected to the conditions of the acetolysis, *i.e.*, heating in acetic acid containing 0.2 M sodium acetate at 50° for four days, the recovered olefin had an infrared spectrum indistinguishable from that of pure 3-*t*-butylcyclohexene. These experiments demonstrate that the products are stable under the conditions of the solvolysis and isolation and that fractionation of the olefin fraction during the isolation is insignificant.

The infrared spectrum of the acetate fraction was essentially a composite of the spectra of pure *cis*- and *trans*-2-*t*-butylcyclohexyl acetate[4]; however, the spectrum revealed the presence of an impurity (evidently present in very small amounts). Because of the small quantities of acetate isolated from the solvolysis (*e.g.*, 0.5 g.) no attempt was made to separate the acetates from the impurity. The configurational composition of the acetate fraction was esti-

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[11] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

[12] S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[13] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 359.

[14] H. L. Goering and A. B. Olson, THIS JOURNAL, **75**, 5853 (1953).

mated from the absorption at 9.61 μ (*trans* isomer) and 9.85 μ[15] (*cis* isomer) by the method described for analyzing mixtures of 1- and 3-*t*-butylcyclohexene. The acetate isolated from the acetolysis of the *trans*-toluenesulfonate II was found to be 53% *cis*-acetate and that obtained from the *cis*-toluenesulfonate I was found to be 92% *cis*-acetate. Because of the impurity in the acetate fraction the accuracy of these determinations is uncertain. Moreover it is possible that some of the acetate results from esterification of small amounts of 2-*t*-butylcyclohexanol which may have been present in some of the samples of *p*-toluenesulfonate that were solvolyzed.

The reaction products were carefully examined with provisions for trapping gaseous products; however, cleavage products, *e.g.*, cyclohexene and isobutene, or rearranged products were not present in detectable quantities.

B. **Ethanolysis.**—A solution of 7.34 g. (0.024 mole) of *trans*-*p*-toluenesulfonate II in 190 ml. of 0.13 *N* sodium ethoxide in absolute ethanol was heated to 50° for 18 hours (about 10 half-lives). The products were extracted and isolated by the same procedure used for the acetolyses. The 3.1 g. (95%) of olefin was found to be an apparently pure binary mixture of 1- and 3-*t*-butylcyclohexene consisting of 53% of the 1-isomer. The products resulting from the solvolysis of the *cis*-*p*-toluenesulfonate II were examined in the same way. There was no evidence for the formation of rearrangement or cleavage products.

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[15] The spectrum of *cis*-2-butylcyclohexyl acetate has a strong band at 10.4 μ (not present in the spectrum of the *trans* isomer); however, the impurity interfered with the absorption at this wave length.

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The Application of Taft's Equation to Polar Effects in Solvolyses

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The Taft equation, $\log (k/k_0) = \sigma^*\rho^*$, is applied to several solvolytic systems with satisfactory results. Driving forces for anchimeric assistance are derived from the correlations.

One criterion for neighboring group participation in solvolytic reactions is an enhancement of rate over that expected in the absence of participation.[1]

The application of this criterion requires a good estimate of the unassisted solvolysis rate. One elegant approach is that of Winstein, Grunwald and Ingraham,[2,3] who compared the acetolysis rates of *cis*- and *trans*-2-substituted cyclohexyl brosylates. Participation is geometrically impossible for the *cis* cases; hence, the solvolysis rates of the *cis* compounds may be taken as approximations to the unassisted rates of the *trans* isomers. Excesses of rates over these estimates are then attributable to anchimeric[1] assistance. Conformation effects are known to be significant in alkyl cyclohexyl systems[4]; however, the fact that the acetolysis rates of *cis*- and *trans*-1,2-di-*p*-bromobenzenesulfonoxycyclohexane, in which participation does not occur, differ by a factor of only 1.12,[2] suggests that dipole interactions tend to cancel the differences due to axial and equatorial configurations in those cases in which the 2-substituent is highly polar. In other systems, Winstein and Grunwald[5] have used calculations based on simple electrostatic principles to estimate polar effects on solvolysis rates. The method requires a number of approximations and cannot be applied to alkyl or aryl substituents. The wide utility of Taft's polar substituent constants, σ^*,[6] (which are an extension of Branch and Calvin's[7] earlier concept of inductive parameters) suggests an application to solvolytic systems. Sufficient data are available for a test in several solvolytic systems of Taft's equation: $\log (k/k_0) = \sigma^*\rho^*$.

The literature contains much rate data on the solvolyses of secondary carbinyl sulfonic esters in acetic acid. Using the data in Table I, the reactivities of the secondary alkyl and *cis*-2-substituted

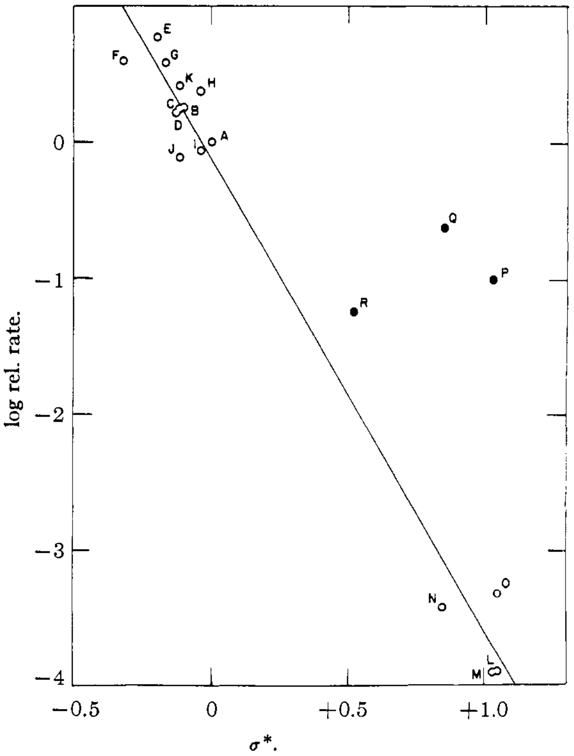

Fig. 1.—Correlation of secondary carbinyl sulfonate acetolysis rates with polar substituent constants, σ^*. The least squares line is based on the open circles. Closed circles refer to compounds which involve anchimeric assistance. Letters refer to compounds in Table I.

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(1) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

(2) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(3) E. Grunwald, *ibid.*, **73**, 5458 (1951).

(4) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(5) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

(6) R. W. Taft, Jr., *ibid.*, (a) **74**, 2729 (1952); (b) **74**, 3120 (1952); (c) **75**, 4231 (1953); (d) **75**, 4534 (1953); (e) **75**, 4538 (1953).

(7) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 201.