Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.29; H, 11.35; N, 8.51.

The perchlorate of form B was prepared in ethanol and was recrystallized from ethanol–ether as colorless needles, m.p. 117.5–118°, infrared maximum 3455 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{20}ClNO_5$: C, 44.60; H, 7.10; N, 5.19. Found: C, 44.47; H, 7.36; N, 5.24.

The picrate of form B was prepared from the pure base in absolute ethanol. After one recrystallization from ethanol, the picrate melted at 150–160°; after a second recrystallization with rapid cooling, at 151–152°; after a third recrystallization with slow cooling, at 150–160°. This behavior suggested that an ethanolate was being formed in the slow cooling process, and this idea was confirmed. Recrystallization of the material of original m.p. 151–152°, with very slow cooling, gave thick orange needles, m.p. 158.5–160°, which had the correct analysis for the picrate with one molecule of ethanol.

Anal. Calcd. for $C_{18}H_{28}N_4O_9$: C, 48.64; H, 6.35; N, 12.61. Found: C, 48.45; H, 6.35; N, 12.74.

The ethanolate of the picrate was converted to picrate by rapid cooling during crystallization as fine yellow needles, m.p. 151–152°.

Anal. Calcd. for $C_{16}H_{22}N_4O_8$: C, 48.24; H, 5.57; N, 14.07. Found: C, 48.55; H, 5.61; N, 13.97.

At no time during the recrystallization procedure was there any evidence of the presence of a trace of the isomeric picrate (form A), m.p. 156–156.5°. Form A picrate depressed the melting point of both form B picrate and form B picrate ethanolate.

Catalytic Hydrogenation of 10-Hydroxy-1-methyl-$\Delta^{1(9)}$-octahydroquinolinium Acetate.—A solution of 0.4 g. (2.4 mmoles) of 10-hydroxy-1-methyl-Δ^8-octahydroquinoline in 50 ml. of 5% aqueous acetic acid was reduced using 0.1 g. of 10% palladium-on-charcoal in a microhydrogenation apparatus. The theoretical volume of hydrogen was absorbed within 24 hours. The oily product was converted to the picrate, which, after one recrystallization from absolute ethanol, was observed to melt at 150–151°, yield 0.65 g. (68%). Admixture with 10-hydroxy-1-methyldecahydroquinoline (form B) picrate caused no depression in melting point.

Evaporation of the picrate mother liquor gave 80 mg. (8%) of the more soluble picrate of 10-hydroxy-1-methyldecahydroquinoline (form A) m.p. 156–156.5°, undepressed on admixture with this derivative.

Catalytic Hydrogenation of 10-Hydroxy-1-methyl-$\Delta^{1(9)}$-octahydroquinolinium Perchlorate.—The hydrogenation of 0.4 g. (0.5 mmole) of 10-hydroxy-1-methyl-$\Delta^{1(9)}$-octahydroquinolinium perchlorate in 50 ml. of absolute ethanol using 0.1 g. of 10% palladium-on-charcoal was completed in 10 minutes. The residue after removal of catalyst and ethanol was recrystallized from ethanol–ether, giving 0.27 g. (68%) of perchlorate, m.p. 115–116°. A second recrystallization raised the melting point to 116–118° and this salt did not depress the melting point of 10-hydroxy-1-methyldecahydroquinoline (form B) perchlorate. The mother liquor yielded 0.08 g. (20%) of 10-hydroxy-1-methyldecahydroquinoline (form A) perchlorate, m.p. 103–105°.

Acid Dehydration of 10-Hydroxy-1-methyldecahydroquinoline (Form A).—A solution of 0.1 g. (0.6 mmole) of 10-hydroxy-1-methyldecahydroquinoline (form A) in 10 ml. of concentrated hydrochloric acid was heated at the reflux temperature for 18 hours. The solution was cooled, basified with aqueous sodium hydroxide and extracted with ether. The oil remaining after removal of the ether was taken up in absolute ethanol and converted to the picrate. Recrystallization from ethanol gave fine orange needles, m.p. 123–124°, yield 0.15 g. (63%).

Anal. Calcd. for $C_{16}H_{20}N_4O_7$: C, 50.52; H, 5.30; N, 14.73. Found: C, 50.56; H, 5.62; N, 14.54.

From inspection of the 3 and 6 μ regions of the infrared spectrum of a Nujol mull of the picrate, it is indicated that this substance is most safely regarded as the derivative of a mixture of 1-methyloctahydroquinolines ($\Delta^{4(10)}$, $\Delta^{5(10)}$, Δ^9).

Catalytic Hydrogenation of 1-Methyloctahydroquinoline.—A solution of 84 mg. (0.5 mmole) of 1-methyloctahydroquinoline, prepared from 0.2 g. of the picrate described above, in 25 ml. of ethanol was hydrogenated using 0.05 g. of 10% palladium-on-charcoal. The product was converted to the picrate, m.p. 197–198°, yield 0.17 g. (85%), which was identified by direct comparison as *cis*-1-methyldecahydroquinoline picrate.

Acid Dehydration of 10-Hydroxy-1-methyldecahydroquinoline (Form B).—The treatment with concentrated hydrochloric acid was the same as that applied to form A. The product was converted to the picrate, orange needles, m.p. 123–124°, identical with the 1-methyloctahydroquinoline picrate described above, yield 18%. A considerable quantity of gummy material was formed which had no counterpart in the acid treatment of form A.

Formic Acid Reduction of 10-Hydroxy-1-methyl-Δ^8-octahydroquinoline.—The procedure of de Benneville and Macartney[31] was followed[6] in the formic acid reduction of 10-hydroxy-1-methyl-Δ^8-octahydroquinoline. A mixture of products was obtained from which only the picrate of 10-hydroxy-1-methyldecahydroquinoline (form A), m.p. 155–156°, could be isolated (5% yield) and identified.

(31) P. L. de Benneville and J. H. Macartney, THIS JOURNAL, **72**, 3073 (1950).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Elimination Reactions in Cyclic Systems. IV. *cis* and *trans* Eliminations in the Cyclohexane and Cyclopentane Series[1]

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cis-2-*p*-Tolylsulfonylcyclohexyl and *cis*-2-*p*-tolylsulfonylcyclopentyl *p*-toluenesulfonates have been synthesized. Elimination of *trans* groups on treatment with hydroxide ion was found to be favored in the cyclopentane series over the cyclohexane series by a factor of 3. This result is correlated with other data which show the greater ease of introducing a double bond into the cyclopentane ring system than into the cyclohexane ring system. The rate of *trans* elimination for the cyclohexane derivative was about 435 times as rapid as the corresponding *cis* elimination. In the cyclopentane series *trans* elimination is favored over *cis* elimination by a factor of 20. It is concluded that attainment of a planar four-centered transition state with the groups to be eliminated occupying *trans* positions is not nearly so important a factor in facilitating elimination in these systems where the hydrogen being eliminated is activated, as in some studied previously.

The much higher rates of *trans* elimination as compared to *cis* elimination observed for reactions in a number of cyclic systems[2-4] showed that the

(1) This investigation was supported by the Office of Naval Research under Contract No. N7onr-45007. The results were reported in a preliminary fashion in THIS JOURNAL, **76**, 4748 (1954).

(2) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(3) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951); E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

(4) D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

stereo relationship of the groups being eliminated may be the controlling factor in deciding the rate and course of such eliminations. Generalization of these results has led to the conclusion that the stereo relationship of the groups H– and –Y in a system H–C–C–Y is the dominant rate determining factor in elimination reactions

$$B:^- + H—C_\beta—C_\alpha—Y = B:H + C_\beta{=}C_\alpha + :Y^-$$

This view has found expression in the *E2 Rule*,[5] which says that "..... the β-CH electrons, independently of the electrostatic situation, enter the C_α octet on the side remote from Y, because the repulsive energy between electron-pairs in the transition state can thus be minimized: the result is *anti*-elimination, independently of the structural details of the system." However, in the previous three papers in this series[6-8] it was shown that an increase in the acidity of the H–C bond, caused by the presence of an electron-withdrawing group on C_β, may be more effective in directing the course of an elimination than is the stereo relationship of H– to –Y. For example, *trans*-2-(*p*-tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate (I) reacted with hydroxide ion by *cis* elimination to give 1-*p*-tolylsulfonyl-1-cyclohexene rather than by *trans* elimination to give 3-*p*-tolylsulfonyl-1-cyclohexene. Synthesis of *cis*-2-(*p*-tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate (II) and the corresponding *cis*-cyclopentane derivative IV has now made possible a comparison of the rate at which *cis* and *trans* eliminations occur in this type of cyclic system.

The reduction of 2-substituted cyclohexanones often gives good yields of *cis*-2-substituted cyclohexanols, and Noyce and Denney[9] have shown that this is true for lithium aluminum hydride reductions if steric hindrance around the carbonyl group is sufficiently great. Since there is evidence that the sulfonyl group may produce a large steric effect,[10] we decided to investigate the reduction of 2-*p*-tolylsulfonylcyclohexanone with lithium aluminum hydride. The 2-*p*-tolylsulfonylcyclohexanone required for the study was obtained readily by the reaction of the sodium salt of *p*-thiocresol with 2-chlorocyclohexanone and oxidation of the sulfide thus obtained to the sulfone using 30% hydrogen peroxide. Reduction of the resulting β-ketosulfone with lithium aluminum hydride was unsuccessful, probably because removal of a proton from the active methylene group occurs rapidly to give an anion which is reduced with difficulty. However, reduction with sodium borohydride in cold aqueous methanol was found to give a good yield of the desired *cis* isomer. A similar series of reactions was used to prepare *cis*-2-*p*-tolylsulfonylcyclopentanol. In one experiment in which the sodium borohydride reduction of 2-*p*-tolylsulfonylcyclohexanone was carried out at steam-bath temperature and hydrochloric acid added to the hot solution, reduction to *p*-tolylsulfonylcyclohexane occurred in 66% yield.

(5) C. K. Ingold, "Structure and Mechanism of Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 467.
(6) F. G. Bordwell and R. J. Kern, THIS JOURNAL, **77**, 1141 (1955).
(7) F. G. Bordwell and M. L. Peterson, *ibid.*, **77**, 1145 (1955).
(8) J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955).
(9) D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950).
(10) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951).

The *p*-toluenesulfonate esters (II and IV, respectively) of *cis*-2-*p*-tolylsulfonylcyclohexanol and *cis*-2-*p*-tolylsulfonylcyclopentanol were prepared in the manner described for the corresponding *trans* isomers (I and III, respectively).[6]

The infrared spectra of chloroform solutions of I and II were very similar as were also those of III and IV. The major differences occurred in the region between 9.5 and 15 μ and at 7.6 μ.

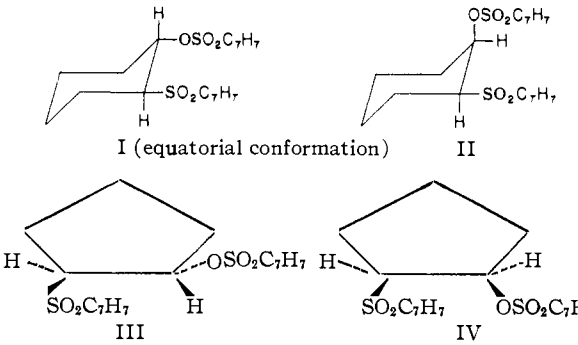
The rates of the *trans* eliminations occurring on treatment of II, IV or an open-chain analog, 1-(*p*-tolylsulfonyl)-2-propyl *p*-toluenesulfonate (V), with hydroxide ion were too rapid to measure by the titrimetric method used for I and III.[6] They were determined, therefore, by direct measurement using the steady-state method recently developed by Pearson and Piette.[11] The rate for III was determined both by the steady-state method and by a conductometric method. The reaction of I with hydroxide ion was too slow to be determined by the steady-state method. The rate measured conductometrically agreed well with a value obtained by extrapolation of the data from runs determined titrimetrically[6] in solutions containing more dioxane. The rates of reaction of I-V with hydroxide ion are summarized in Table I. The values given, except that for I, were obtained by the steady-state method.

TABLE I

RATES OF REACTION OF I–V WITH HYDROXIDE ION IN 50% DIOXANE AT 25°

p-Toluenesulfonate	Type of elimination	*K* (l. mole^{-1} sec.$^{-1}$)	Relative rates
I, *trans*-2-(*p*-Tolylsulfonyl)-cyclohexyl	*cis*	0.0348[a]	1
II, *cis*-2-(*p*-Tolylsulfonyl)-cyclohexyl	*trans*	15.1	434
III, *trans*-2-(*p*-Tolylsulfonyl)-cyclopentyl	*cis*	2.17[b]	62.6
IV, *cis*-2-(*p*-Tolylsulfonyl)-cyclopentyl	*trans*	43.4	1240
V, 1-(*p*-Tolylsulfonyl)-2-propyl	*trans*	184	5270

[a] Determined conductometrically. The value of the rate constant as determined by an extrapolation from the data of Bordwell and Kern[6] is 0.034 l. mole^{-1} sec.$^{-1}$. [b] A value of 2.07 l. mole^{-1} sec.$^{-1}$ was obtained by a conductometric method.



I (equatorial conformation) II

III IV

The data in Table I show that *trans* elimination is favored in the cyclopentane series as compared

(11) R. G. Pearson and L. Piette, *ibid.*, **76**, 3087 (1954).

to the cyclohexane series by a factor of 3-fold. The greater ease of *trans* elimination in the cyclopentane *vs.* the cyclohexane series appears to be a general phenomenon. It has been observed by Owen and Saharia[12] for the reaction of hydroxide ion with *cis*-monotoluene-*p*-sulfonates of cycloalkane-1,2-diols to give cycloalkanones (factor of 9.3-fold) and for the elimination of bromine from *trans*-cycloalkane dibromides[13] (factor of 4-fold).

cis-Elimination is also favored in the cyclopentane series, the factor being about 60 from our data (Table I) and about 140 with these compounds in a solvent richer in dioxane.[6]

It is interesting to note that *trans* elimination occurs more rapidly in the cyclopentane series despite the fact that a planar four-centered transition state for elimination is more easily achieved in the cyclohexane series. However, since there is evidence that cyclopentane rings tend to be nonplanar with one of the five carbons out of the plane of the ring,[14] it should be possible for cyclopentane derivatives, such as IV, to acquire this transition state with but little distortion of the ring.

The greater rate of elimination reactions in the cyclopentane series is most likely associated with the partial relief of strain[15] resulting from a reduction in the number of opposed hydrogens or other groups as the cyclopentane ring is converted to a cyclopentene ring.[16] This factor is probably responsible for the apparent general rule that *it is easier to introduce a double bond into a five-membered ring than into a six-membered ring.*[6,12,13] The 240-fold greater rate of removal of a proton from the active methylene group of 2-carbethoxycyclopentanone than from that of 2-carbethoxycyclohexanone[17] can be taken as another example of the operation of this rule. The 1.7 kcal. lower heat of hydrogenation of cyclopentene as compared to cyclohexene[18] also illustrates the rule.

According to this view introduction of a double bond (endo or exo) has a stabilizing influence on a five-membered carbon ring, but not on a six-membered ring. This is essentially the position taken by Brown, Brewster and Schechter,[19] except that they have emphasized the greater stability of an endo over an exo double bond in the cyclohexane series and the reverse for the cyclopentane series. Actually, the evidence is not convincing for the greater stability of an exo *vs.* an endo double bond in the cyclopentane series, since in all the examples cited[19] the exo double bond structure is also favored either by conjugation or because it is the more highly substituted double bond.[20] A better test of the tendency for exo *vs.* endo double bonds to form in cyclopentane systems can be made by observing the behavior of 1-alkylcyclopentanols on dehydration. According to data in the literature dehydration of 1-methyl- or 1-ethylcyclopentanol by a variety of methods always gives preponderant amounts of the 1-alkylcyclopentene.[21] Even the dehydration of 1-isopropylcyclopentanol, where formation of an exo double bond is favored by virtue of its being more highly substituted, is reported to give chiefly 1-isopropylcyclopentene.[22] It is difficult to arrive at a definite conclusion from the limited amount of evidence available, but it appears likely that, contrary to the previous hypothesis,[19] cyclopentane derivatives with endo double bonds are at least as stable as those with comparable exo double bonds.[23]

The factors of 435 favoring *trans* over *cis* elimination in the cyclohexane series and 20 favoring *trans* over *cis* elimination in the cyclopentane series are much smaller than might have been anticipated from the work of Cristol[3] and of Barton.[4] Even if these differences are due entirely to facilitation of the *trans* elimination by virtue of a favorable path *via* a planar four-centered transition state,[4] this factor is not very great in these systems. The much less prominent role played by the stereochemistry in our system is undoubtedly associated with the greater acidity of the H–C bond due to its activation by the α-sulfonyl group. A more detailed discussion of this point will be given in the next paper in this series.[24]

The fact that *trans* elimination is favored over *cis* elimination to a greater degree in the cyclohexane series than in the cyclopentane series may be explained by the greater ease with which the cyclohexane system can acquire a planar four-centered transition state. Inasmuch as eliminations are *faster* in the cyclopentane series than in the cyclohexane series, this is probably not the only factor involved, but it is not easy to assess the relative importance of other influences.

Experimental[25]

2-(*p*-Tolylmercapto)-cyclohexanone.—To a solution of 38.2 g. (0.305 mole) of *p*-thiocresol and 18.0 g. (0.32 g.) of potassium hydroxide in 50 ml. of water at 0°, there was added 39.9 g. (0.30 mole) of 2-chlorocyclohexanone. After

(12) L. N. Owen and G. S. Saharia, *J. Chem. Soc.*, 2582 (1953). In this paper the authors also point out an instance of *cis* elimination with an activated H–C bond taking precedence over a possible *trans* elimination involving a non-activated hydrogen.[6-8]

(13) J. Weinstock, S. Iglowitz and F. G. Bordwell, unpublished data.

(14) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947).

(15) Referred to by H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951), as I-strain.

(16) The conversion of *trans*-2-chlorocyclopentanol to cyclopentene oxide also results in a reduction of the number of these oppositions and the 12-fold greater rate of ring closure to form cyclopentene oxide than to form cyclohexene oxide from the corresponding *trans*-chlorohydrins [see F. V. Brutcher, Jr., and T. Roberts, Abstracts of the Cincinnati Meeting of the American Chemical Society, April, 1955, p. 39N] can also be attributed to this factor.

(17) R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

(18) G. B. Kistiakowsky and co-workers, *ibid.*, **58**, 137 (1936); **59**, 831 (1937).

(19) H. C. Brown, J. H. Brewster and H. Schechter, *ibid.*, **76**, 467 (1954).

(20) The heats of hydrogenation of alkenes have been shown to decrease with increased substitution, see ref. 18.

(21) See, for example, O. Wallach and K. von Martins, *Ann.*, **365**, 276 (1909); G. Chavanne and P. Becker, *Bull. soc. chim. Belg.*, **36**, 593 (1927).

(22) H. Meerwein, *Ann.*, **405**, 155 (1914).

(23) The small per cent. enol form of 2-carbethoxycyclopentanone as compared to 2-carbethoxycyclohexanone[19] does not constitute evidence for superiority of an exo double bond, since the cyclopentanone derivative resembles open-chain analogs in this respect. See J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932); G. Schwartzenbach, M. Zimmerman and V. Prelog, *Helv. chim. Acta*, **34**, 1954 (1951).

(24) J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **78**, 3473 (1956).

(25) Analyses were by Miss H. Beck. Melting points and boiling points are uncorrected.

stirring the mixture 1 hr. in the cold and 1 hr. on a steam-bath, cold water was added and the suspension extracted with benzene. Removal of the solvent from the benzene layer and distillation of the residual oil gave 55.9 (83.7%) of a light yellow oil, b.p. 138° at 0.2 mm., $n^{25}D$ 1.5713.

Anal. Calcd. for $C_{13}H_{16}SO$: C, 70.87; H, 7.32. Found: C, 70.97, 70.15; H, 7.10, 7.15.

2-(*p*-Tolylsulfonyl)-cyclohexanone.—A solution of 22.2 g. (0.1 mole) of 2-(*p*-tolylmercapto)-cyclohexanone in 100 ml. of glacial acetic acid was treated with 50 ml. of 30% hydrogen peroxide with cooling to keep the solution near room temperature. After standing overnight, water was added, and 22.4 g. (88%) of white crystals, m.p. 76–80°, came out of solution. On further dilution an additional 3.5 g. of product of the same melting point was obtained to give an almost quantitative yield of product. This product was identical with that obtained by Kern[26] (m.p. 81°) by the oxidation of 2-(*p*-tolylsulfonyl)-cyclohexanol with chromium trioxide and with that obtained by treating 2-chlorocyclohexanone with sodium *p*-toluenesulfinate in aqueous ethanol under reflux.

***cis*-2-(*p*-Tolylsulfonyl)-cyclohexanol.**—A solution of 13.0 g. (0.051 mole) of 2-(*p*-tolylsulfonyl)-cyclohexanone in 30 ml. of methanol and a solution of 2.5 g. of sodium borohydride in 20 ml. of methanol were chilled in an ice-bath and slowly mixed. After standing for 1 hr. at 0° and 1 hr. at room temperature, the reaction mixture was filtered and then water added to precipitate the product. On cooling 9.65 g. (74%) of white crystals, m.p. 92–97°, was obtained. Three recrystallizations from benzene–hexane gave needles, m.p. 94–97°. The infrared spectrum of this compound was somewhat similar to that of *trans*-2-(*p*-tolylsulfonyl)-cyclohexanol, the major differences being in the region between 8 and 15 μ.

Anal. Calcd. for $C_{13}H_{18}SO_3$: C, 61.39; H, 7.13. Found: C, 61.75; H, 7.04.

***cis*-2-(*p*-Tolylsulfonyl)-cyclohexyl *p*-Toluenesulfonate.**—A solution of 11.7 g. (0.046 mole) of *cis*-2-(*p*-tolylsulfonyl)-cyclohexanol and 11.0 g. (0.058 mole) of *p*-toluenesulfonyl chloride in 17 ml. of dry pyridine was allowed to stand for 3 days in a cold room at 9°. The reaction mixture was treated with 150 ml. of cold 4 *N* hydrochloric acid in an ice-bath and then quickly extracted with benzene. On removal of the solvent from the benzene layer under vacuum, adding methanol and chilling, 6.45 g. (34%) of white crystals, m.p. 119–124.5°, was obtained in the first crop. This was dissolved in benzene, treated with activated silica and diluted with hexane to give white crystals, m.p. 121.5–124.5°. Recrystallization from benzene–hexane gave white crystals, m.p. 119–124°.

Anal. Calcd. for $C_{26}H_{24}O_5S_2$: C, 58.80; H, 5.92. Found: C, 59.05; H, 5.68.

2-(*p*-Tolylmercapto)-cyclopentanone.—This compound was prepared from 2-chlorocyclopentanone in the same manner as described for the corresponding cyclohexanone derivative. The product was obtained in 80% yield as a yellow oil, b.p. 129° at 0.3 mm., $n^{25}D$ 1.5750.

Anal. Calcd. for $C_{12}H_{14}SO$: C, 69.88; H, 6.84. Found: C, 69.89; H, 6.57.

***cis*-2-(*p*-Tolylsulfonyl)-cyclopentanol.**—A solution of 20.8 g. (0.1 mole) of 2-(*p*-tolylmercapto)-cyclopentanone in 100 ml. of glacial acetic acid was treated with 50 ml. of 30% hydrogen peroxide at 0°. After 1 hr. the solution was allowed to come to room temperature, and after 12 hr. water was added and the mixture extracted with benzene. Removal of the solvent from the benzene layer under vacuum gave 16.7 g. (71%) of a yellow oil, $n^{25}D$ 1.5496, which did not crystallize. This product was then directly reduced with 1.9 g. of sodium borohydride in a methanol–water solution at 0°. Filtration of the reaction mixture followed by removal of the solvent gave an oil which crystallized on standing to give a white product, m.p. 56–64°. Recrystallization from hexane and from an acetic acid–water mixture gave white crystals, m.p. 64–68.5°.

Anal. Calcd. for $C_{12}H_{16}SO_3$: C, 59.97; H, 6.71. Found: C, 59.89; H, 6.63.

***cis*-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-Toluenesulfonate.**—A solution of 4.5 g. (0.0187 mole) of *cis*-2-(*p*-tolylsulfonyl)-cyclopentanol and 4.5 g. (0.0236 mole) of *p*-toluenesulfonyl chloride in 15 ml. of dry pyridine was allowed to stand at 9° for 40 hr. The reaction mixture was poured into cold dilute hydrochloric acid and quickly extracted with chloroform. Removal of the solvent from the chloroform layer under vacuum and addition of methanol gave 4.8 g. (65%) of white crystals, m.p. 95–106°. Recrystallization from methanol gave 3.7 g. of white crystals, m.p. 100–106°. Treatment of this product with Darco in methanol gave 3.4 g. of white crystals, m.p. 133.5–136.5°; recrystallization from ethanol gave white needles, m.p. 134–137°.

Anal. Calcd. for $C_{19}H_{22}S_2O_5$: C, 57.84; H, 5.62. Found: C, 58.47, 58.46; H, 5.76, 5.41.

1-(*p*-Tolylsulfonyl)-2-propanol.—This was prepared by a modification of the procedure of Culvenor, Davies and Savige.[27] A solution of 10 g. (0.172 mole) of propylene oxide and 26.7 g. (0.150 mole) of sodium *p*-toluenesulfinate in 200 ml. of aqueous 1 *N* sodium dihydrogen phosphate was heated on a steam-bath for 18 hr., the cooled reaction mixture extracted with benzene and the benzene layer concentrated under vacuum. This gave 22.3 g. (72%) of a product, m.p. 64–73°, which on two recrystallizations from benzene gave white crystals, m.p. 77–78°; reported m.p. 77–78°.[27]

1-(*p*-Tolylsulfonyl)-2-propyl *p*-Toluenesulfonate.—A solution of 4.7 g. (0.022 mole) of 1-(*p*-tolylsulfonyl)-2-propanol and 5 g. (0.0254 mole) of *p*-toluenesulfonyl chloride in 20 ml. of dry pyridine was allowed to stand at 9° for 56 hr. The reaction mixture was then treated with 50 ml. of cold 6 *N* hydrochloric acid and immediately extracted with benzene. The benzene layer was washed, filtered and concentrated under vacuum. Addition of methanol and cooling overnight gave 5.45 g. (67%) of white crystals, m.p. 82–86°, which on recrystallization from methanol and then from a benzene–hexane mixture gave white crystals, m.p. 84–85°.

Anal. Calcd. for $C_{17}H_{20}S_2O_5$: C, 55.41; H, 5.47. Found: C, 56.05; H, 5.42.

***trans*-2-(*p*-Tolylmercapto)-cyclohexanol.**—A solution of 4.4 g. (0.11 mole) of sodium hydroxide and 12.42 g. (0.10 mole) of *p*-thiocresol in 15 ml. of 33% aqueous ethanol was treated with 13.4 g. (0.10 mole) of *trans*-2-chlorocyclohexanol at room temperature and then heated on a steam-bath for 0.5 hr. On cooling the reaction mixture, extracting with benzene, removing the solvent from the washed benzene layer under vacuum and distilling the residue, there was obtained 16.25 g. (73.5%) of a product, b.p. 146.2–146.7° at 1.5 mm., $n^{25}D$ 1.5730. On seeding with authentic *trans*-2-(*p*-tolylmercapto)-cyclohexanol[6] the product crystallized to a solid, m.p. 40–43°, undepressed by admixture with an authentic sample[6] of *trans*-2-(*p*-tolylmercapto)-cyclohexanol.

***trans*-2-(*p*-Tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate** and its cyclopentyl analog were prepared by the method of Bordwell and Kern.[6]

Cyclohexyl-*p*-tolylsulfone.—A solution of 4.4 g. (0.0175 mole) of 2-(*p*-tolylsulfonyl)-cyclohexanone and 1 g. (0.025 mole) of sodium borohydride in 90% methanol was refluxed for 2 hr. on a steam-bath. Then 10 ml. of 6 *N* hydrochloric acid was added, the refluxing continued for 45 minutes, an additional 15 ml. of 6 *N* hydrochloric acid added and the refluxing continued 30 more minutes. Chilling the solution obtained by adding water to filtered reaction mixture gave 2.75 g. (66%) of a white product, m.p. 82–85°. Recrystallization from an ethanol–water mixture gave white crystals, m.p. 84–86°, undepressed by admixture with an authentic sample prepared by R. J. Kern[26] by hydrogenation of 3-(*p*-tolylsulfonyl)-cyclohexene.

Kinetic Measurements.—The method used was patterned after that of Pearson and Piette.[11]

Apparatus.—The anode consisted of a platinum foil electrode placed in a tube containing the carboxylate ion-exchange resin *Permutit H* in the form of its potassium salt. The bottom of the tube was sealed with a diaphragm consisting of a disk of the cation permeable membrane *Amberplex-C-1* held in place by a perforated screw cap. The cathode consisted of a circular 20 mm. band of platinum gauze to which a platinum connecting wire was soldered. The cathode was fastened to the anode tube so that the two electrodes were concentric with the bottom of the anode tube just below the top of the cathode. The assembly was

(26) R. J. Kern, Ph.D. Thesis, Northwestern University, 1952.

(27) C. C. J. Culvenor, W. Davies and W. E. Savige, *J. Chem. Soc.*, 2198 (1949).

placed into the kinetic solution so that the bottom of the anode tube was immersed about five millimeters. Both anolyte and catholyte were 0.1 N in potassium chloride. A 120 volt source of direct current was used with sufficient resistance in the line so that the current could be varied between 15 and 100 milliamperes and held constant to 0.1 during a run. The pH of the kinetic solutions were determined with a Beckman Model G pH meter using a saturated calomel and a Beckman Type E glass electrode. The pH meter was set before use with a pH 9 Beckman buffer. During the course of each run the solution was stirred with a small motor-driven stirrer. The best results were obtained using a 250-ml. beaker as the reaction cell. Sufficient temperature control was obtained by immersing the reaction beaker into a large beaker containing water at 25° and by equilibrating the solutions at 25° before starting the runs.

Method.—One hundred ml. of a 50% by volume aqueous dioxane solution 5×10^{-3} molar in the sulfone tosylate and 0.1 molar in potassium chloride was equilibrated at 25° and poured into the reaction beaker of the apparatus. The various electrodes were adjusted so that turning on the electrolysis current momentarily did not cause the pH meter needle to jump due to a field effect. It was found that the field effect was lowered by the presence of sufficient potassium chloride in the catholyte and by separating the electrolysis and pH electrodes as far as possible. The run was started by adjusting the resistance to give the desired current and then turning on the current and starting the stopwatch simultaneously. When the rate of change of pH with time became very small, the system was assumed to be at the steady state.

Calibration of pH Readings.—It was found that the hydroxide ion concentration could not be calculated from the pH reading by the relationship $-\log[OH^-] = pK_w - p$H where pK_w equals 16.09 at 25° in 50% by volume dioxane–water.[28] A correction factor was obtained by preparing solutions of known concentration of potassium hydroxide and measuring their pH. It was found that

$$-\log [OH^-] = pK_w - (p\text{H} + 1.13)$$

The validity of this correction was established by determining the rate of hydrolysis of ethyl acetate in 50% dioxane–water using this method and also by determining the rate of elimination of III both by this method and by a method independent of pH. The data are given in Table II.

TABLE II

VERIFICATION OF pH CORRECTION

	Rate found by the steady-state method, l. mole^{-1} sec.$^{-1}$	Check method, l. mole^{-1} sec.$^{-1}$
Ethyl acetate	5.75×10^{-2}	6.14×10^{-2}[a]
hydrolysis		6.32×10^{-2}[b]
Elimination from III	2.17	2.07[c]

[a] E. J. Salmi and R. Korte, *Ann. Acad. Sci. Fenn.*, Series A, **54**, No. 12 (1940). [b] P. M. Nair and S. V. Anantakrishman, *Proc. Ind. Acad. Sci.*, **32A**, 187 (1950). [c] The change in conductance with time of a 50% dioxane–water solution 5×10^{-3} molar in III and about 5×10^{-4} molar in sodium hydroxide was determined. The first-order rate constant was 9.83×10^{-3} sec.$^{-1}$. Division of this by 4.75×10^{-3} (the average concentration of III during the run) gave 2.07 l. mole^{-1} sec.$^{-1}$ for the second-order constant. In this pseudo first-order rate determination the hydroxide ion concentration does not enter into the calculation.

(28) Calculated from the data of H. S. Harned and C. D. Fallon, THIS JOURNAL, **61**, 2374 (1939).

Calculations.—The equations

$$u = k[OH^-][S_0 - ut]$$
$$u = I/(F)(v)$$

where S_0 is the initial substrate concentration, t the time in seconds, I the current in amperes, F the faraday and V the volume of the kinetic solution in liters, as derived by Pearson and Piette,[11] were used to calculate the rate constants. Consecutive runs were made on the same solution by letting S_0 for the second run equal $(S_0 - ut)$ for the first run. The results are summarized in Table III.

TABLE III

HYDROXIDE RATES DETERMINED BY THE STEADY-STATE METHOD IN WATER AT 25°

Compound	S_0 (moles/l.)	t (sec.)	I (ma.)	pH	k l. (mole^{-1} sec.$^{-1}$)
Ethyl acetate	9.85×10^{-2}	390	0.0280	11.67	5.79×10^{-2}
	9.74×10^{-2}	180	.0700	12.08	5.71×10^{-2}
				Av.	5.75×10^{-2}
II	5.00×10^{-3}	240	.0154	10.32	15.10
	4.62×10^{-3}	210	.0237	10.56	15.06
				Av.	15.1
III	5.00×10^{-3}	210	.0285	11.44	2.24
	4.38×10^{-3}	210	.0330	11.61	2.10
				Av.	2.17
IV	5.00×10^{-3}	300	.0195	10.00	41.8
	4.40×10^{-3}	210	.0330	10.28	44.5
	3.68×10^{-3}	180	.0750	10.85	44.0
				Av.	43.4
V	4.41×10^{-3}	210	.0300	9.61	185
	3.76×10^{-3}	180	.0600	10.07	183
				Av.	184
I[a]					3.48×10^{-2}

[a] Direct conductometric determination.

Compound I reacted too slowly to be studied by this method. At the end of the usual periods of time the pH calculated by assuming no disappearance of hydroxide ion by reaction with the substrate was approximately that found by applying the usual correction to the pH meter reading. The rate of this reaction was determined by conductance as a second-order reaction with both reactants 5×10^{-3} molar. A plot of $R/(R - R_\infty)$ against time gave a line whose slope was 2.515×10^{-4} sec.$^{-1}$ and whose intercept was 1.300. The second-order constant therefore is 3.48×10^{-2} l. mole^{-1} sec.$^{-1}$.

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