[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

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

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trans-2-(*p*-Tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate (II) was observed to undergo a *cis* E2 elimination reaction with hydroxide ion to give 1-*p*-tolylsulfonyl-1-cyclohexene rather than a *trans* elimination to give 3-*p*-tolylsulfonyl-1-cyclohexene. *trans*-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-toluenesulfonate underwent a *cis* E2 elimination under similar conditions at a rate about 140 times that observed for the cyclohexane analog. The preference for *cis* rather than *trans* elimination in these systems is ascribed to the influence of the *p*-tolylsulfonyl group, which greatly increases the acidity of the hydrogen being eliminated, and it is concluded that the effect of electron-withdrawing groups will generally overshadow opposing effects of steric configuration in dictating the course of elimination of a β-grouping. The effect of variation of the composition of the dioxane–water solvent on the rate was determined for II, and the rates were measured at several temperatures.

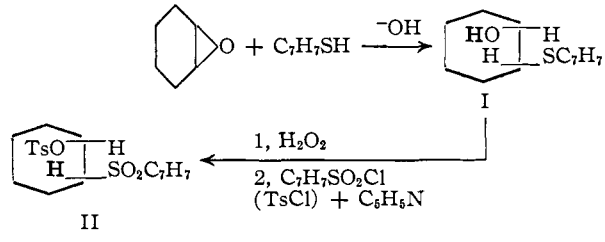
In recent years rather striking evidence has been presented to establish the preference for elimination of *trans* rather than *cis* groupings in cyclic systems. Hückel, Tappe and Legutke[3] found in the dehydrochlorination of menthyl and neomenthyl chlorides that a *trans* configuration for the hydrogen and chlorine atoms being eliminated was more important than the influence of an alkyl group in determining the course of the reaction (exception to the Saytzeff rule). Nevitt and Hammond[4] recently have come to a similar conclusion from the observation that *trans*-1,2-dimethyl-1-bromocyclohexane underwent dehydrobromination under E2 conditions to give exclusively 1,2-dimethylcyclohexene, whereas the *cis* isomer reacted under similar conditions at one-twelfth the rate giving chiefly 2-methylmethylenecyclohexane.

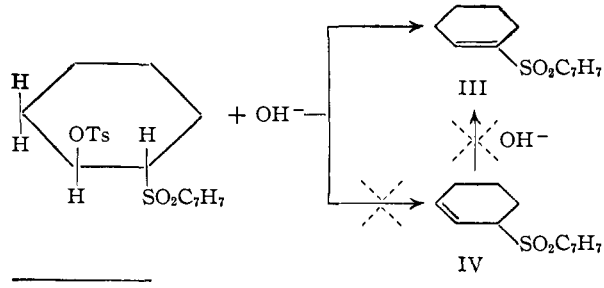
Barton and his co-workers[5] have presented evidence to show that iodide ion initiated eliminations of bromine from dibromides where all four atoms, Br–C–C–Br, involved in the reaction are in a single plane with the bromine atoms *trans* to one another are favored, since in certain cyclohexane systems "polar" (or "axial") *trans* eliminations (Br–C–C–Br all in one plane) were greatly favored over "equatorial" *trans* eliminations. Recent kinetic evidence on E2 eliminations with menthyl and neomenthyl chlorides[6] also supports this hypothesis.

Cristol, Hause and Meek[7] observed a very large factor favoring *trans* elimination in the dehydrochlorination of benzene hexachloride isomers. Their data showed that the activation energy for a *cis* elimination in a cyclic system may be 9–12 kcal. higher than for a comparable *trans* elimination; rate differences of the order of 10^4 were observed.

In view of the impressive collection of data showing the preference for elimination of *trans* groupings, we were intrigued by the observation[8] that the reaction of barium *trans*-2-bariosulfato-1-cyclopentanesulfonate with hydroxide ion gave barium 1-cyclopentene-1-sulfonate (*cis* elimination) rather than barium 2-cyclopentene-1-sulfonate (*trans* elimination). A kinetic investigation showed, however, that this and similar reactions were not simple E2 eliminations.[8] Since the preference for *cis* elimination seemed likely to reside in the increased acidity of the hydrogen alpha to the sulfonate group, we decided to prepare an analogous cyclic compound containing the *p*-tolylsulfonyl group ($-SO_2C_7H_7$) in place of the sulfonate group ($-SO_3^-$).

Synthesis of the desired compound, *trans*-2-(*p*-tolylsulfonyl)-cyclohexyl *p*-toluenesulfonate (II) was accomplished by the reaction of *p*-thiocresol with cyclohexene oxide in alkaline medium, oxidation of the resulting *trans*-2-hydroxycyclohexyl *p*-tolyl sulfide (I) to the sulfone with hydrogen peroxide, and conversion to the corresponding tosylate II. The *trans* opening of epoxide rings in reactions with nucleophilic reagents of this type has been firmly established, so the *trans* structure for I seems assured. Since the subsequent steps in the synthesis do not involve breaking of bonds to ring atoms, II also must have a *trans* structure.





(1) An account of this work was given at the Meeting of the American Chemical Society in Milwaukee, Wis., April, 1952 (p. 84K of Abstracts).

(2) Procter and Gamble Predoctoral Fellow, 1951–1952.

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

(4) T. D. Nevitt and G. S. Hammond, THIS JOURNAL, **76**, 4124 (1954).

(5) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951), and previous papers.

(6) E. D. Hughes, C. K. Ingold and J. B. Rose, *ibid.*, 3839 (1953).

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

(8) M. L. Peterson, Doctoral Dissertation, Northwestern University, June, 1951; see F. G. Bordwell and M. L. Peterson, THIS JOURNAL, **77**, 1145 (1955).

The reaction of II with hydroxide ion gave 1-*p*-tolylsulfonyl-1-cyclohexene (III) (*cis* elimination) rather than 3-*p*-tolylsulfonyl-1-cyclohexene (IV) (*trans* elimination). The reaction did not proceed by a *trans* elimination to give IV followed by a base-catalyzed rearrangement to III, since a synthetic sample of IV did not rearrange to III under the experimental conditions used for the elimination.

Synthesis of IV was accomplished by reaction of 3-bromocyclohexene (prepared from cyclohexene and N-bromosuccinimide) with *p*-thiocresol in basic medium and oxidation of the resulting 3-*p*-tolylthiocyclohexene to IV with hydrogen peroxide.

The structures of III and IV were further supported by reducing each by catalytic hydrogenation to *p*-tolylsulfonylcyclohexane. With methoxide ion in methanol solution both III and IV gave mixtures. A small amount of III was isolated from the mixture obtained from IV and methoxide, indicating that IV partially rearranges to III under these conditions, which establishes further the relationship of III and IV.

Reaction of cyclopentene oxide with *p*-thiocresol, oxidation of the resulting *trans*-2-hydroxycyclopentyl *p*-tolyl sulfide to the sulfone and conversion to the tosylate gave *trans*-2-(*p*-tolylsulfonyl)-cyclopentyl *p*-toluenesulfonate (V). Treatment of V with hydroxide ion also resulted in a *cis* elimination giving 1-*p*-tolylsulfonyl-1-cyclopentene (VI). Once again it was established that the reaction did not proceed by a *trans* elimination to give 3-*p*-tolylsulfonyl-1-cyclopentene followed by rearrangement to VI.

Compound VI gave an addition product when treated with piperidine in ethanol solution. The β,γ-isomer, 3-*p*-tolylsulfonyl-1-cyclopentene, failed to add piperidine as did both the α,β- and β,γ-unsaturated sulfones in the cyclohexane series.

The rate of the reaction of II with hydroxide ion was studied in aqueous dioxane solutions containing 55, 60, 70, 77.5 and 85% of dioxane, and at temperatures ranging from 0–40°.[9] The reactions were followed by measuring the consumption of hydroxide ion. Variation of the relative concentrations of hydroxide ion and tosylate II showed that the reaction was first order in each. The results of these experiments are summarized in the Experimental section.

The reaction of V with hydroxide ion was so much faster than that of II, that the rate could be studied conveniently by the method used for II only at 0° and in a solvent containing 70% or more of dioxane. In 70% dioxane at 0.2° for II $k_2 = 0.0042$ l. mole^{-1} sec.$^{-1}$, and for V, $k_2 = 0.55$ l. mole^{-1} sec.$^{-1}$.

The rate of reaction of II with hydroxide ion increased as the quantity of water in the solvent decreased. This is consistent with the generalizations made by Hughes and Ingold for the effect of solvent in this type of E2 reaction.[7b,10] The effect of temperature on the rate at various solvent concentrations was determined. Activation energies were obtained by plotting the rates *vs.* $1/T$, and the activation entropies were calculated using the equation[11]

$$\ln k_2 = \frac{kT}{h} + \frac{\Delta S^{\ddagger}}{R} - \frac{E_a - RT}{RT}$$

From the results summarized in Table I it appears that the change in rate is reflected chiefly in the entropy of activation. It is of interest to note that the values for the activation energy in *cis* eliminations with II are slightly less than those observed for *trans* elimination with hydroxide ion and the α-, γ-, δ- and ϵ-benzene hexachloride isomers (19.0, 20.4, 21.6 and 21.4),[7] and much less than the values of 31.0[7a] and 32.3[7b] given for the *cis* elimination of the β-isomer.

TABLE I

EFFECT OF SOLVENT ON THE RATES, ACTIVATION ENERGIES AND ENTROPIES IN THE REACTION OF II WITH HYDROXIDE ION

Dioxane, %	k_2 (avg.) at 20°, l. mole^{-1} sec.$^{-1}$	E_a, kcal./mole	$\Delta S^{\ddagger}$, e.u.
55	0.0224	17.4	−8.6
60	.0256	17.6	−7.4
70	.0388	17.4	−7.6
77.5	.0706	17.4	−6.3
85	.144	18.8	−0.2

Discussion

In the reactions described above and in the following paper[8] several examples are given in which preference is shown for the elimination of a group with an activated *cis* hydrogen rather than with a less acidic *trans* hydrogen in the same molecule. The presence of electron-attracting groups is known to have a profound influence on the rate and course of elimination reactions in open-chain compounds.[12] From the present data it appears that this effect in cyclic compounds may be a dominant one, completely overshadowing configuration effects, which may sometimes be very large.[7] Since the sulfonate group[8] is one of the weaker electron-attracting groups,[13] it is anticipated that stronger electron-attracting groups (NO_2, CN, COR, COOR, etc.) will, like the SO_3^- and $C_7H_7SO_2$ groups, exert complete control over the course of elimination reactions, when substituted in a position beta to the leaving group.[14]

The factor of about 140 favoring elimination in V over that in II is believed to reflect the relative ease of E2 elimination in cyclopentane and cyclohexane systems. This point will be treated more fully in a later paper in this series.

(9) Aqueous alkaline dioxane solutions were found to be unstable in the presence of light and air, an acidic impurity (presumably a hydroperoxide) being produced under these conditions (see Experimental section).

(10) See C. K. Ingold, "Structures and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 458.

(11) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 96.

(12) See reference 10, page 443.

(13) H. Zollinger, *Nature*, **172**, 257 (1953), has assigned a Hammett σ-value of +0.31 to the *m*-SO_3^- group.

(14) The chlorine atom (*m*-Cl, $\sigma = +0.37$) is apparently also a sufficiently strong electron-withdrawing group to effect *cis* elimination under some circumstances, since H. C. Stevens and O. Grummitt, THIS JOURNAL, **74**, 4876 (1952), have shown that *trans*-1,2-dichlorocyclohexane on dehydrochlorination with quinoline gave 47% of cyclohexadiene and 40% of 1-chlorocyclohexene. It is possible that the phenyl group (*m*-C_6H_5, $\sigma = +0.22$) also may promote *cis* elimination since the product formed from the reaction of hydroxide ion with the trimethyl-*trans*-2-phenylcyclohexylammonium ion is 1-phenylcyclohexene (R. T. Arnold and P. N. Richardson, *ibid.*, **76**, 3649 (1954)).

Experimental[15]

trans-2-Hydroxycyclohexyl *p*-Tolyl Sulfide (I).—Cyclohexene oxide[16] (9.8 g., 0.1 mole) was added slowly to a solution containing 4.4 g. (0.11 mole) of sodium hydroxide and 12.4 g. (0.1 mole) of *p*-thiocresol in 15 cc. of alcohol and 15 cc. of water. After stirring for 2 hours the mixture was poured into 300 cc. of water and the mixture extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate, decolorized with silica gel and charcoal, the solvent removed on the steam-bath. Distillation of the residue gave 17.2 g. of light straw-colored sirup, b.p. 116–118° (0.1 mm.), (171–172° (5 mm.)), $n^{20}D$ 1.5730. On crystallization from hexane 16.4 g. (74%) of a waxy solid melting at 43° was obtained.

Anal. Calcd. for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.35; H, 8.08.

trans-2-Hydroxycyclohexyl *p*-Tolyl Sulfone.—Fifteen grams (0.067 mole) of *trans*-2-hydroxycyclohexyl *p*-tolyl sulfide was dissolved in 40 cc. of glacial acetic acid, 30 cc. (0.26 mole) of 30% hydrogen peroxide was added, and the mixture heated at 85° for 2 hours. The mixture was poured into water, filtered, washed and dried to give 16.5 g. (95%) of colorless solid, m.p. 121–122°. An identical product was obtained in 40% yield from cyclohexene oxide and sodium *p*-toluenesulfinate using the directions of Culvenor, Davies and Heath.[17]

trans-2-(*p*-Tolylsulfonyl)-cyclohexyl *p*-Toluenesulfonate (II).—Seven and seven-tenths grams (0.03 mole) of *trans*-2-hydroxycyclohexyl *p*-tolyl sulfone was added to a solution of 9.3 (0.05 mole) of purified *p*-toluenesulfonyl chloride in 30 cc. of dry pyridine. The clear solution was allowed to stand at room temperature (at higher temperatures some elimination occurs) for one week, after which the liquid was decanted from the large crystals of pyridinium chloride into 250 cc. of water, and the resulting mixture extracted with chloroform. The chloroform solution was dried, treated with silica gel and the solvent removed by distillation. The residue was crystallized from benzene and hexane to give 9.3 g. (82%) of white crystals, m.p. 111–112°.

Anal. Calcd. for $C_{20}H_{24}O_5S_2$: C, 58.80; H, 5.92. Found: C, 58.66; H, 5.71.

1-(*p*-Tolylsulfonyl)-1-cyclohexene (III).—Five grams (0.012 mole) of II in 60 cc. of purified dioxane and 5 cc. of 5 *N* sodium hydroxide were heated with occasional swirling on a steam-bath for one hour. The mixture was poured into 350 cc. of water, neutralized with hydrochloric acid and extracted with chloroform. This extract was washed with water, dried over calcium chloride and the chloroform removed by distillation. Crystallization of the residue from hexane gave 2.4 g. (80%) of product, m.p. 82–83°.

Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.04; H, 6.82. Found: C, 65.94; H, 6.65.

3-(*p*-Tolylthio)-cyclohexene.—3-Bromocyclohexene was prepared by the method of Ziegler[18]; it was observed that pure dry reagents are necessary for a successful preparation. To a solution of 1.4 g. (0.035 mole) of sodium hydroxide and 4.2 g. (0.034 mole) of *p*-thiocresol in 10 cc. of water and 20 cc. of ethanol was added 5.5 g. (0.034 mole) of 3-bromocyclohexene, $n^{20}D$ 1.5298. After stirring for 2 hours the mixture was poured into cold water and extracted with chloroform. The chloroform was removed and the residue distilled to give 4.4 g. (64%) of a viscous liquid, b.p. 142° (3 mm.), $n^{20}D$ 1.5834.

Anal. Calcd. for $C_{13}H_{16}S$: C, 76.43; H, 7.89. Found: C, 76.48; H, 7.88.

3-*p*-(Tolylsulfonyl)-1-cyclohexene (IV).—Six grams (0.03 mole) of 3-*p*-tolylthio-1-cyclohexene was dissolved in 50 cc. of glacial acetic acid and 12 cc. of 30% hydrogen peroxide added at 5°. After standing overnight the mixture was poured into water and extracted with chloroform. The chloroform extract was washed with 5% sodium bicarbonate solution, then with dilute sodium bisulfite solution, and finally with water. A negative test with acidified potassium iodide solution was obtained on the last washing. After drying over calcium chloride and removing the chloroform the residue was crystallized from hexane. The yield of product, m.p. 62–63°, was 5 g. (80%).

Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.04; H, 6.82. Found: C, 66.29; H, 6.96.

Attempted Rearrangement of IV to III.—A 0.61-g. sample of IV was allowed to stand for 4 hours at 30° in a 0.02 *M* solution of sodium hydroxide in 75% dioxane. The solution was neutralized with hydrochloric acid, and the solvent removed under reduced pressure. The residue was washed thoroughly with water; after drying the m.p. was 59–60°. One crystallization from hexane gave 0.4 g. of material, m.p. and m.m.p. 62–63°.

p-Tolylsulfonylcyclohexane.—One gram of IV in 20 cc. of ethanol with 0.5 g. of 5% palladium-on-charcoal catalyst was subjected to 25 atm. of hydrogen at 50° for one hour in a rotary Ipatieff-type bomb. After removal of the catalyst and solvent the residue was taken up in hexane and treated with silica gel. On cooling the filtrate 0.5 g. of material, m.p. 86–87°, was obtained.

Anal. Calcd. for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.62; H, 7.47.

A comparable experiment with III gave the same product, m.p. and m.m.p. 86–87°.

Reaction of IV with Sodium Methoxide.—The reaction of either III or IV with sodium methoxide in methanol for periods as long as 24 hours appeared to give mixtures of products. From one such experiment with IV a small sample of III, m.p. and m.m.p. 80–81°, was obtained. Attempted reactions of III or IV with piperidine in ethanol were unsuccessful, starting material being recovered in each instance.

trans-2-Hydroxycyclopentyl *p*-Tolyl Sulfide.—Cyclopentene oxide was prepared by the slow addition of cyclopentene to a solution of perbenzoic acid in methylene chloride.[19] The reaction cyclopentene oxide (b.p. 99–100° (745 mm.), $n^{20}D$ 1.4356) and *p*-thiocresol was carried out in a manner comparable to that described above for cyclohexene oxide. A 0.06 mole run gave 10 g. of product, b.p. 162–163° (4 mm.), $n^{20}D$ 1.5778. Three additional distillations were used to obtain an analytical sample, b.p. 135° (1 mm.).

Anal. Calcd. for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.12; H, 7.65.

trans-2-Hydroxycyclopentyl *p*-Tolyl Sulfone.—Twenty grams (0.096 mole) of *trans*-2-hydroxycyclopentyl *p*-tolyl sulfide was oxidized with hydrogen peroxide in the usual way, and the product crystallized from hexane giving 18.5 g. (80%) of material, m.p. 75–76°.

Anal. Calcd. for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 60.45; H, 6.81.

trans-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-Toluenesulfonate (V).—A solution containing 8.2 g. (0.34 mole) of *trans*-2-hydroxycyclopentyl *p*-tolyl sulfone and 13 g. (0.068 mole) of pure *p*-toluenesulfonyl chloride in 30 cc. of dry pyridine was kept at 12° for 2 days.[20] The resulting mixture was poured into 300 cc. of ice-water to which 23 cc. of concd. hydrochloric acid had been added. This mixture was extracted three times with cold chloroform, and the chloroform extract washed with cold dilute hydrochloric acid and finally with water. After drying, the chloroform was removed at steam-bath temperature. The residue was taken up in benzene and the solution refluxed in the presence of silica gel and filtered. Hexane was added to the filtrate to the saturation point, and the solution allowed to cool slowly. On standing at 5° overnight, 8 g. (60%) of product, m.p. 92–93°, was obtained.

Anal. Calcd. for $C_{19}H_{22}O_5S_2$: C, 57.84; H, 5.62. Found: C, 57.86; H, 5.64.

1-*p*-Tolylsulfonyl-1-cyclopentene (VI).—A 4.9-g. sample of V was dissolved in 15 cc. of dry pyridine and refluxed for 4 hours. The mixture was poured into 75 cc. of water and

(15) Microanalyses were by Miss Joyce Sorenson. Melting points are uncorrected.

(16) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 185.

(17) C. C. J. Culvenor, W. Davies and N. S. Heath, *J. Chem. Soc.*, 278 (1949).

(18) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

(19) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

(20) Low temperature appears to be a critical factor for a successful preparation, since the product obtained in a reaction carried out at room temperature was very difficult to purify (the impurity is presumably VI).

15 cc. of concd. hydrochloric acid. The solid product was collected, dissolved in hexane and the solution decolorized with charcoal. On cooling 2.2 g. (80%) of colorless platelets, m.p. 115–116°, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35. Found: C, 64.85; H, 6.37.

An 80% yield of 1-*p*-tolylsulfonyl-1-cyclopentene, m.p. 110–115°, was obtained by heating a solution of V in aqueous alkaline dioxane for one-half hour. A m.m.p. with the above sample was also 110–115°. Recrystallization raised the m.p. to 114–115°.

3-(*p*-Tolylthio)-1-cyclopentene.—A mixture of 20 g. (0.112 mole) of N-bromosuccinimide and 35 cc. (0.35 mole) of cyclopentene in 65 cc. of dry carbon tetrachloride was refluxed for 100 minutes. The mixture was cooled, the succinimide removed, and the filtrate distilled under vacuum. Six grams (0.04 mole, 36%) of a clear liquid, b.p. 56° (55 mm.), was obtained. This material was added immediately to a solution of 5 g. (0.04 mole) of *p*-thiocresol and 1.6 g. (0.04 mole) of sodium hydroxide in 45 cc. of 90% ethanol. After standing 15 hours this mixture was poured into water and the resulting product extracted with chloroform. The chloroform extract was washed twice with 0.5 *N* sodium hydroxide and once with water, and then dried over anhydrous sodium sulfate. Distillation gave 4.3 g. (55%) of product, b.p. 100° (1 mm.), $n^{20}D$ 1.5765.

Anal. Calcd. for $C_{12}H_{14}S$: C, 75.74; H, 7.41. Found: C, 76.01; H, 7.66.

In one experiment a satisfactory product was obtained by adding the original carbon tetrachloride filtrate to the alcoholic solution of sodium *p*-methyl-(thiophenoxide) without trying to isolate the unstable 3-bromocyclopentene.

3-(*p*-Tolylsulfonyl)-1-cyclopentene.—Oxidation of 4.3 g. of 3-*p*-tolylthio-1-cyclopentene with 30% hydrogen peroxide in glacial acetic acid gave the corresponding sulfone. After several crystallizations from hexane and aqueous methanol 2 g. (40%) of sulfone melting at 90–91° was obtained.

Anal. Calcd. for $C_{18}H_{18}O_3S$: C, 64.83; H, 6.35. Found: C, 65.26; H, 6.11.

2-Piperidino-1-*p*-tolylsulfonylcyclopentane.—A solution of 1.1 g. (0.005 mole) of 1-*p*-tolylsulfonyl-1-cyclopentene (VI) and 1 cc. (0.012 mole) of piperidine in 15 cc. of ethanol was refluxed for 3 hours and allowed to stand at room temperature for 19 hours. The solvent was removed by evaporation, and the residue taken up in hexane and decolorized with silica gel. The crystals formed on cooling were collected and dissolved in 10 cc. of 0.5 *N* hydrochloric acid. The solution was filtered and the product reprecipitated by adding 0.5 *N* sodium hydroxide. After drying the solid was recrystallized from hexane giving 0.9 g. (60%) of material melting at 85–86° (discolors slightly on standing).

Anal. Calcd. for $C_{17}H_{25}O_2NS$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.71; H, 8.43; N, 4.43.

The isomeric 3-*p*-tolylsulfonyl-1-cyclopentene failed to add piperidine under these conditions, and also when the solution was refluxed for 32 hours and allowed to stand at room temperature for 50 hours.

Kinetic Experiments.—Dioxane was purified by the method described by Fieser.[21] Aqueous alkaline solutions of dioxane may be stored without change in titer only if light and air are excluded. A 0.0085 *N* solution of sodium hydroxide in 60% dioxane maintained this titer when stored for 96 hours in the dark over nitrogen, but when the open flask was irradiated with a Hanovia type SH ultraviolet lamp the titer had dropped to 0.0065 *N* after one hour (presumably because of hydroperoxide formation).

The solvent compositions are volume per cent.: thus 70% dioxane is a mixture of 70 cc. of dioxane and 30 cc. of water.

(21) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p. 368.

The samples of II and V used in these experiments were purified by four recrystallizations from mixtures of benzene and hexane. The sample was then allowed to react with hydroxide ion in aqueous dioxane for at least ten half-lives and the titration values used to calculate the amount of II or V in the starting sample. These values indicated a purity better than 95%.

The total volume of solvent to be used was decided upon and the volumes of dioxane and water to be used were computed ignoring changes in volume on mixing. Volume measurements were made by buret. Aqueous dioxane solutions of the tosylate to be used (II or V) and sodium hydroxide were prepared and brought to temperature separately. The solutions were mixed at zero time, and 25-ml. samples were removed by pipet at appropriate intervals and quenched in excess standard hydrochloric acid solution. The solutions were then titrated with standard sodium hydroxide using methyl red–brom cresol green mixed indicator. Pipets were cooled to 0° for runs made at 0°, and were heated in a 60° oven for runs made at 40°. Rate constants were calculated using the usual equations for second order reactions. The results are summarized in Tables II and III. In each instance the reaction was followed to 50–75% completeness. The average deviation in the rate constants for an individual run was generally less than 5%.

TABLE II

RATES OF ELIMINATION OF II WITH HYDROXIDE ION IN DIOXANE–WATER MIXTURES AT VARIOUS TEMPERATURES

T, °C.	Dioxane, % (by vol.)	Concn. OH^-, *M*	Concn. II, *M*	No. runs	Av. k_2, l. mole^{-1} sec.$^{-1}$
20	55	0.0085	0.0085	2	0.0224
30	55	.0085	.0085	1	.0577
40	55	.0085	.0085	1	.151
11.8	60	.0085	.0085	1	.0107
20	60	.0085	.0085	2	.0256
30	60	.0085	.0085	1	.0670
40	60	.0085	.0085	1	.178
0.2	70	.0085	.0085	1	.00425
10	70	.0085	.0085	2	.0134
20	70	.0085	.0085	3	.0381
20	70	.0170	.0085	1	.0408
30	70	.0170	.0170	2	.0994
40	70	.0085	.0085	1	.261
10	77.5	.0160	.0160	1	.0242
10	77.5	.0180	.0180	1	.0252
20	77.5	.0331	.0168	1	.0683
20	77.5	.0180	.0180	1	.0728
30	77.5	.0085	.0085	2	.189
40	77.5	.0085	.0085	2	.478
11.8	85	.0065	.0065	1	.0566
20	85	.0075	.0075	1	.144
20	85	.0085	.0085	1	.143
30	85	.0085	.0085	1	.422
30	85	.0065	.0065	1	.420

TABLE III

RATE OF ELIMINATION OF V WITH HYDROXIDE ION

T, °C.	Dioxane, % (by vol.)	$[OH^-]$	[V]	Reacn. %	No. detns. per run	Av. dev.	k_2, l. mole^{-1} sec.$^{-1}$
0.2	70	0.0085	0.0085	57	4	0.0011	0.59
.2	70	.0085	.0085	64	5	.0042	.52
.2	70	.0085	.0085	59	5	.0010	.55

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