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Base promoted cis eliminations

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BASE PROMOTED CIS ELIMINATIONS

by

Robert Dean Thurn

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1964

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INTRODUCTION

The investigation of the order and rate of elimination reactions has been one of the most versatile tools for the organic chemist in determining what is happening within a molecule he will never see.

In the present work, the base promoted elimination of the elements of *p*-toluenesulfonic acid was studied in a series of phenyl substituted trans-2-phenylcyclopentyl tosylates.

This particular system was chosen because the synthesis of the necessary trans-2-phenylcyclopentanol did not appear difficult, and the five membered ring should not present some of the conformational difficulties found in the analogous cyclohexyl compounds. Also, it was hoped that a concerted base promoted cis elimination could be demonstrated with a mildly acidifying group (the phenyl ring) on the carbon bearing the proton to be eliminated.

As it turned out, the synthesis of these compounds presented few difficulties and the elimination was shown to be bimolecular and concerted; however, more recent investigations¹ have shown that although the conclusions drawn in

¹J. Smith, Ames, Iowa. Base promoted elimination of trans-2-phenylcyclopentyl tosylates. Private communication. 1963.

this thesis are correct, the actual bimolecular rate constants for both cis and trans eliminations can be increased over those reported. The reader should refer to the forthcoming dissertation of J. Smith for details.

REVIEW OF LITERATURE

Most olefin forming reactions fall into two classes, one a bimolecular process and the other a unimolecular and often multistage process. These olefin forming reactions are brought about by the elimination of two substituents from two adjacent carbon atoms, termed the α and β atoms.

Usually in a base promoted bimolecular elimination the substituent eliminated from the β atom is the anion of a strong acid and the substituent eliminated from the α atom is a proton, giving an olefin as the product. The loss of two substituents from vicinal carbon atoms had been termed "beta elimination." The bimolecular reaction has been termed the E2 reaction, and the unimolecular reaction has been termed the E1 reaction. The E2 reaction is pictured as a smooth concerted process where there is some double bond formation in the transition state. The E1 reaction involves an initial ionization to a carbonium ion, the

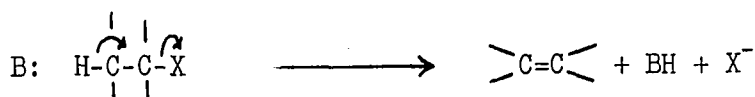


Figure 1. The E2 reaction

rate determining step, and ionization to the olefin. A special case of the E1 reaction is the E1CB² (elimination,

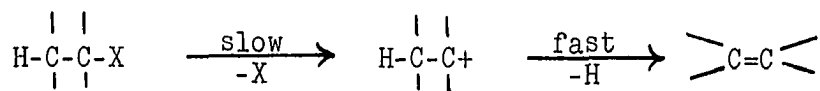


Figure 2. The E1 reaction

unimolecular, conjugate base). In this case there is elimination from a carbanion formed in a prior rate determining equilibrium.

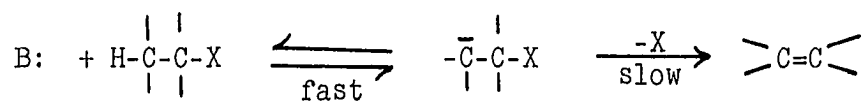


Figure 3. The E1CB elimination

The literature is rich in examples of the bimolecular base promoted eliminations assuming a trans steric course.

²C. K. Ingold, Structure and mechanism in organic chemistry. New York, N.Y., Cornell University Press, 1953.

Michel³ observed that the loss of hydrogen chloride from chlorofumaric acid was fifty times faster than the analogous reaction with chloromaleic acid. Frankland⁴ in 1912 summarized the literature and concludes that trans elimination is favored over cis.

The first significant alicyclic system studied was the β isomer of benzene hexachloride in which the chlorine atoms are all trans to each other and hence there is no proton trans to any one chlorine atom.⁵ It was found that the isomer did not react with base under conditions where

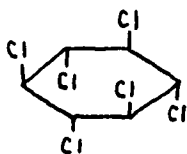


Figure 4. β Isomer of benzene hexachloride

the other isomers smoothly eliminated HCl. Cristol visualized the process of trans elimination as being analogous to a Walden inversion, proceeding smoothly through a transition state in a one-step mechanism. Later it was

³A. Michel, J. Prakt. Chem., 52, 308 (1895).

⁴P. F. Frankland, J. Chem. Soc., 654 (1912).

⁵S. J. Cristol, J. Am. Chem. Soc., 69, 338 (1947).

shown that benzene hexachloride reacted 7,000 to 24,000⁶ times slower than the other isomers which contain at least one trans, vicinal hydrogen-chlorine grouping.

The interesting thing is that there must be a mechanistic pathway other than trans elimination operative here. The reaction was found to be a second order elimination. The energy of activation was found to be 9.6 to 12.5 kcal./mole higher for the cis elimination than the trans. A calculation of the interatomic distances and repulsive forces due to inter-action between the carbon-chlorine dipole and incoming hydroxide showed that the difference in activation energy between cis and trans elimination caused by Coulombic forces was at most 3 kcal./mole. From this the author assumed there must be an appreciable difference in the mechanism of elimination of this isomer as compared to the others.

Cristol proposed a multistage process for the cis elimination occurring in β hexachlorocyclohexane. He suggested that the first and rate determining step was formation of an anion which could either collapse to olefin or protonate to the original compound. When the reaction was carried out in deuterated solvent, there was recovered a

⁶S. J. Cristol and D. D. Fix, J. Am. Chem. Soc., 75, 2647 (1953).

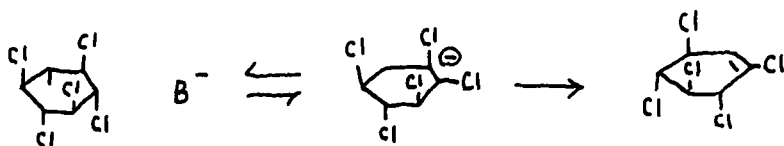


Figure 5. The elimination reaction in β benzene hexachloride

small amount of deuterated starting material after one half life.⁷ Cristol estimates that 150 carbanions go to olefin for every one that returns to starting material, based on the less than 1% deuterated benzene hexachloride recovered at one half life; he considers this further evidence for the two stage reaction. The author cites the work of Skell and Hauser who were unable to detect any deuterium exchange after a half life in the elimination of 1-bromo-2-phenylethane with a deuterated solvent.⁸ If the above reaction path applies, the reaction when carried out in deuterated solvent should produce deuterated trichlorobenzene. Such evidence bearing on this point is not available.

⁷S. J. Cristol, N. L. Hause and J. S. Meek, J. Am. Chem. Soc., 73, 674 (1951).

⁸P. S. Skell and C. R. Hauser, J. Am. Chem. Soc., 67, 1661 (1945).

In the trans eliminations mentioned thus far, the molecule was able to attain a coplanar state without excessive strain to the molecule. A system in which the elements of hydrochloric acid can not become coplanar is found in the diastereomers of 11,12-dichloro-9,10-ethanoanthracene.⁹ It was shown that cis elimination was 8 times faster than trans. However, in the transition state, the leaving groups (for trans elimination) could not become



Figure 6. 11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene

oriented much more than 120° without causing undue strain to the molecule.

Cristol¹⁰ also studied the elimination of endo-cis and trans-1, 2-dichloronorbornane using sodium n-pentoxide in n-pentanol. The trans isomer (i.e. the one undergoing the cis elimination) reacted faster than the cis isomer (the

⁹S. J. Cristol and N. L. Hause, J. Am. Chem. Soc., **74**, 2193 (1952).

¹⁰S. J. Cristol and E. F. Hoegger, J. Am. Chem. Soc., **79**, 3438 (1957).

trans elimination). This marked increase in cis/trans elimination is attributed to factors decreasing trans elimination and not factors increasing cis elimination. The author also says that the cis elimination has a carbanion intermediate as he has argued before.

In a following paper, this was tested with a strongly acidifying group.¹¹ The cis and trans isomers of 11-p-toluenesulfonyl-12-chloro-9,10-ethanoanthracene were prepared. Here trans elimination is favored over cis by a

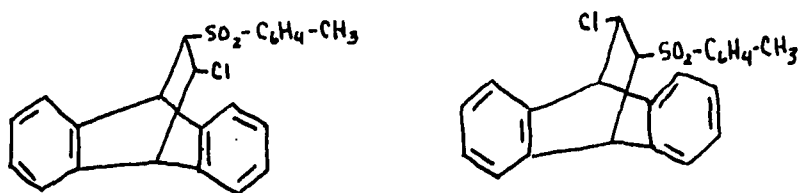


Figure 7. The cis and trans isomers of 11-p-toluenesulfonyl-12-(chloro-9,10-ethanoanthracene)

factor of only three. In the two previous systems studies, the dichlorodihydroethanoanthracenes and the 2,3-chlorobornanes, cis elimination is favored over trans. However, the substitution of a chlorine atom by the

¹¹S. J. Cristol and R. P. Arganbright, J. Am. Chem. Soc., 79, 3441 (1957).

p-toluenesulfonyl group increases the rate by ten powers of ten. The comment was made that there is a striking lack of stereospecificity in these reactions, and that in this system and others previously studied, where the bonds are rigidly held and a trans coplanar transition state is impossible, the multiple stage mechanism is rate controlling. The tremendous increase in reactivity observed when the chlorine atom is replaced by acid strengthening arenesulfonyl group may also be rationalized by the carbanion mechanism for both cis and trans elimination.

In a recent paper, Hine and Ramsey¹² determined the Taft substituent constant (σ^*) for the p-toluensulfonylmethyl group by measurements of the acidity of p-toluenesulfonylacetic acid. They also measured the deuterium exchange for cis-2-methoxycyclohexyl-p-tolyl sulfone and cis-2-fluorocyclohexyl-p-tolyl sulfone. The latter compounds were chosen in order to determine the rate of carbanion formation of a p-tolylcyclohexyl sulfone where the β -substituent was electron withdrawing, but not easily lost as an anion as to make deuterium exchange at the α -carbon unobservable. The author reasoned that an unstable intermediate formed in a rate process should

¹²J. Hine and O. B. Ramsey, J. Am. Chem. Soc., 84, 973 (1962).

resemble the transition state, and therefore, the effect of substituents on the rate constants should be similar to the effect on the equilibrium constant. From the results obtained in this work, it was shown that the rate of cis-elimination for trans-2-p-toluenesulfonylcyclohexyl p-toluenesulfonate is not faster but slower than would be predicted from carbanion formation based on the σ^* values of the groups used. Therefore, the reaction intermediate could easily have involved a carbanion transition state, although the data does not prove that it did.

As another test of the carbanion mechanism, Cristol dehydrobrominated the isomers of bromostyrene and p-nitro-bromostyrene using sodium hydroxide in isopropyl alcohol.¹³ Since the carbanion mechanism involves a concentration of charge, it should be sensitive to charge dispersing agents such as nitro groups. The effect of the p-nitro group was found to be greater in the cis elimination than in the trans elimination. The difference in rates between trans and cis elimination was decreased by a factor of 13 by the addition of the p-nitro group. This certainly indicates some stabilization of a negative charge in the transition state, but how much is difficult to say. Also, it is

¹³S. J. Cristol and W. P. Norris, J. Am. Chem. Soc., 76, 3005 (1954).

difficult to compare elimination from unsaturated carbon as in this case, to eliminations from saturated carbon.

In addition to the work of Cristol is that of Bordwell et al.^{14,15,16,17,18}. He studied the base catalyzed elimination of trans and cis-2-(p-tolylsulfonyl)-cyclohexyl-p-toluenesulfonate and the corresponding cis and trans isomers in the cyclopentane series with triethylamine, trimethylamine and hydroxide ion.



Figure 8. β -Bromostyrene and p-nitro- β -Bromostyrene

¹⁴J. Weinstock, R. G. Pearson and F. G. Bordwell, J. Am. Chem. Soc., 76, 4748 (1954).

¹⁵F. G. Bordwell and R. J. Kern, J. Am. Chem. Soc., 77, 1141 (1955).

¹⁶F. G. Bordwell and M. L. Peterson, J. Am. Chem. Soc., 77, 1145 (1955).

¹⁷J. Weinstock, R. G. Pearson and F. G. Bordwell, J. Am. Chem. Soc., 78, 3468 (1956).

¹⁸J. Weinstock, R. G. Pearson and F. G. Bordwell, J. Am. Chem. Soc., 78, 3473 (1956).

He reported the α,β -sulfone as the sole product in every case, so that cis elimination must occur in the two trans isomers studied. He observed increased rate of elimination with increased concentration of amine even though the concentration of hydroxide remains constant showing that these reactions are general base catalyzed. In the carbanion

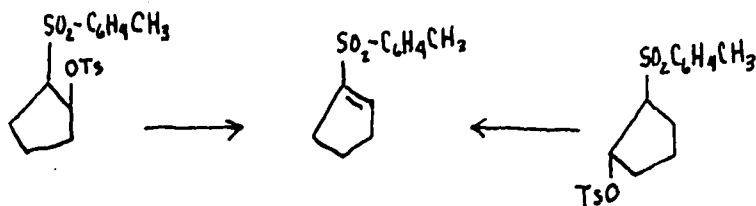


Figure 9. Eliminations involved in the work of Bordwell et al.

mechanism the rate of the reaction will be a function of the carbanion concentration, which concentration will be determined by the ratio of the base and its conjugate acid. In aqueous solutions this is specific hydroxide catalysis. On the other hand, if the reaction proceeds by a concerted path, or a rate controlling ionization followed by rapid reaction of the anion, the reaction rate will be dependent upon the sum of all the bases present (general base

catalysis). The fact that the author observed general base catalysis indicated to him at the time that the carbanion mechanism is not operative here but that the two cis eliminations are concerted. However, it is obvious from later work by the same author, that the mechanism is E1CB and that probably the primary controlling factor here is steric hindrance. The higher activation energies required in cis elimination are explained as necessary to force the reaction against an unfavorable steric arrangement of groups.¹⁹ It was also observed that the rate ratio of triethylamine versus trimethylamine was one fifth slower for the cis eliminations than for the trans eliminations, even though triethylamine is the stronger Brönsted base. This is explained as a steric factor where the proton to be abstracted is somewhat shielded. Again, rates with hydroxide are faster than rates with alkyl amines because of hydroxide's higher basicity, but the ratio $k\text{-OH}/k\text{-Me}_3\text{N}$ for the compounds undergoing cis elimination is one-twentieth of that for the trans elimination. This is explained by electrostatic considerations. The negatively charged hydroxide ion has to come in past polarized sulfur-oxygen bonds. Also, the amine in the transition state will be

¹⁹E. D. Hughes, C. K. Ingold and R. Pasternak, J. Chem. Soc., 3832 (1953).

partially positive when it is near the negatively polarized oxygen of the tosylate group. It was also noted that with the cyclopentane derivatives, the trans elimination is favored over cis by only 6.5 fold with triethylamine, as compared to 20 fold for the hydroxide ion; with trimethylamine the factor is 1.2. These data show that steric and electrostatic effects are reduced to a minimum in trimethylamine and that there is little preference for trans elimination. The authors interpret this as meaning that the planar 4-centered transition state is of very little importance in their system.

Another point of interest is that trans elimination using hydroxide ion is faster in the cyclopentane series than in the cyclohexane series. This is interpreted by use of the general rule that it is easier to introduce a double bond into a five membered ring than into a six membered ring. The 240 fold greater rate of removal of a proton in 2-carbethoxycyclopentanone as compared to the analogous 2-carbethoxycyclohexanone is an example of this rule. The 1.7 kcal. lower heat of hydrogenation of cyclopentene as compared to cyclohexene also illustrates this rule. In going from cyclopentane to cyclopentene, the number of opposed hydrogens is probably reduced. However, if one considers the steric requirements that must be operative for E1CB, it can be argued here that the

cyclopentyl system offers a less sterically hindered proton to the approaching hydroxide ion than does the cyclohexyl system.

In two recent papers Bordwell et al.^{20,21} studied the elimination of the elements of acetic acid from cis and trans 2-nitro-1-phenylcyclohexyl acetate in chloroform-ethanol solution. Their results seem to indicate conclusively that the reaction goes E1CB and that the steric factor is of prime importance. The investigators observed

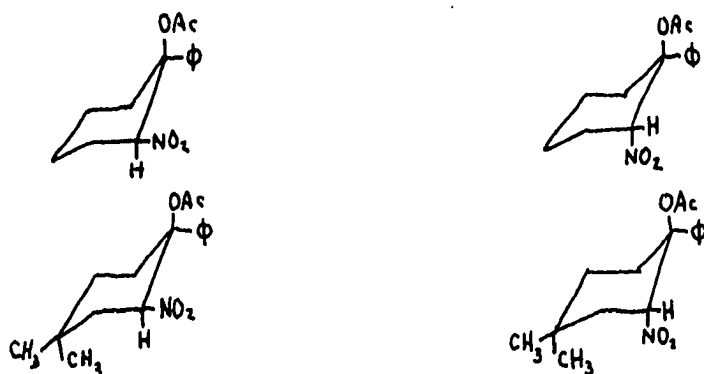


Figure 10. Cis and trans-2-nitro-1-phenylcyclohexyl acetate and their 4,4-dimethyl derivatives

²⁰F. G. Bordwell, R. L. Arnold and J. B. Biranowski, J. Org. Chem., 28, 2496 (1963).

²¹F. G. Bordwell and E. W. Garbisch, Jr., J. Org. Chem., 28, 1765 (1963).

a small temperature effect on the rates, a dependence in the rate on solvent polarity, a deuterium isotope effect of 4.9 and that the addition of 0.1 M. lithium bromide doubled the rate. It was also found that Hammett plots for the rates of elimination of m and p substituted 1-acetoxy-1-phenyl-2-nitrocyclohexanes in each instance gave a ρ of + 1.45. This identical response of both cis and trans to the above m and p substitution show that the elimination must be E1CB in both cases.

The cis elimination of trans-2-nitro-1-phenylcyclohexyl acetate was about 4 times faster than the corresponding trans elimination in the cis isomer. Since the acidifying effect of the nitro group should be approximately equal in either case, the rate determining step must be proton abstraction. The lower reactivity of the cis isomer may then be attributed to the greater steric effect for the approach of base to the axial proton on the carbon possessing the nitro group. This steric effect is even more pronounced in the case of the 4,4-dimethyl derivatives of cis and trans-2-nitro-1-phenylcyclohexyl acetate. The rate of trans elimination falls by almost a factor of 5 when the cis isomer has relatively bulky groups in the 4 position indicating that the steric factor is of prime importance (the effect is not felt with only one methyl group in the 4 position). In the case of the cis elimination,

4,4-disubstitution increases the rate of elimination by a factor of 5 indicating that there is steric assistance to carbanion formation.

It was estimated that if these cis eliminations have any carbanions formed, that their lifetime can be no more than 10^{-8} seconds. A study of base catalyzed deuterium isotope exchange of the proton at the sulfone group of cyclopentyl and cyclohexyl-*p*-tolylsulfone was carried out.²² It was demonstrated that deuterium exchange is 10^{-3} to 10^{-5} times slower than the rate of cis elimination with trans-2-*p*-tolylsulfonylcyclohexyl and cyclopentyl tosylate. It was also shown that the deuterium exchange for the cyclopentyl system proceeds about 1.5 times faster than the cyclohexyl system whereas the rate ratio of the base elimination of the corresponding trans sulfone tosylates is 60. This suggests in view of the work of Bordwell that most of the carbanion formed goes on to product. The cyclopentyl system also would be expected to exchange deuterium faster than cyclohexyl, since carbanion formation has been shown to be sensitive to its steric environment.

Another system similar to those mentioned before was

²²J. Weinstock, J. L. Bernardi and R. G. Pearson, J. Am. Chem. Soc., 80, 4961 (1958).

investigated by Goering *et al.*²³ A study was carried out on the base promoted elimination of cis and trans-2-chlorocyclohexylaryl sulfones and cis and trans-2-chlorocyclopentylaryl sulfones in 80% ethanol. The dehydrochlorination of the four isomers was so rapid that it was difficult to get good kinetics except in the case of the trans-2-chlorocyclohexylaryl sulfones. It was pointed out that this least reactive member of the series is 10^6 times more reactive than cyclohexyl chloride.²⁴ From this it is clear that a cis dehydrohalogenation occurs since only a cis proton to the leaving group is attached to the same carbon atom as the *p*-tolylsulfone group. It was also pointed out that the rate of trans-2-chlorocyclohexyl phenyl sulfone is the same as trans-2-tosyloxycyclohexyl phenyl sulfone. Since tosylates are usually more reactive as leaving groups than chloride (cyclohexyl tosylate reacts 180 times more rapidly than cyclohexyl chloride), the reaction must involve a two step process, whose rate determining step is the formation of a carbanion.

The rates for various *p*-substituted trans-2-chlorocyclohexyl sulfones were also determined. The kinetic

²³H. L. Goering, K. I. Relyea and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).

²⁴E. D. Hughes, C. K. Ingold and J. B. Rose, *J. Am. Chem. Soc.*, **75**, 3839 (1953).

data gave an excellent fit to the Hammett equation having a ρ at 0°C. of $1.42 \pm .01$. The relative amount of carbanionic character can be determined by a Hammett plot.^{25,26} By varying substituents on a phenyl ring attached to the α carbon atom, the effect of these substituents will be reflected in the rate of elimination. This effect is measured by the slope of the line ρ on a Hammett plot. A steeper slope, i.e. a higher value of ρ , indicates the substituents on the phenyl ring have a greater effect on the transition state. Also, a positive value for ρ indicates some degree of carbanion character in the transition state. In the case mentioned above, trans-2-chlorocyclohexylaryl sulfones, it is difficult to compare this value to the others as the aromatic ring is insulated somewhat from the α carbon by the sulfur atom. In the aromatic series a ρ of 1.42 would be considered a low value, but here again it is hard to compare it to aromatics.

In contrast to the work of Bordwell is that of LeBel et al.,²⁷ who studied a system which did not have a

²⁵L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N.Y. (1940) p. 184.

²⁶H. H. Jaffe, Chem. Rev., 53, 191 (1953).

²⁷N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers and P. M. Subramanian, J. Am. Chem. Soc., 85, 3199 (1963).

strongly acidifying group present. They studied the base promoted elimination of the isomers of 2-bromo-3-chloro-norbornanes using sodium pentoxide in n-pentanol. Their results show that the cis elimination is faster than the trans. They interpret this as being due to the fact that cis eliminants can become coplanar and trans eliminants can not.

To test the possibility of an E1CB mechanism, the elimination of HX from endo-cis-2-chloro-3-bromonorbornane and endo-2-chloro-exo-3-bromonorbornane was carried out with t-butoxide. In both cases the predominate produce was

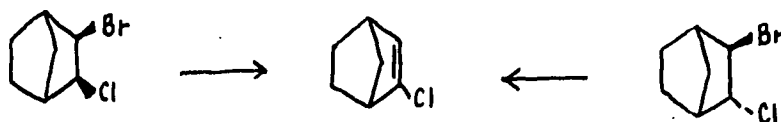


Figure 11. The base promoted elimination of cis and trans-2-chloro-3-bromonorbornane

the 2-chloro-2-norbornene. If an E1CB mechanism had been operative here the more acidic proton (the carbon bearing the bromo group) would have been removed at least one half of the time giving more bromonorbornene than

chloronorbornene in the product mixture. Since the molecule did eliminate HBr the transition state must have been influenced by the nature of the leaving group which is bromide here. Bromide is a better leaving group than chloride so it must follow that the cis elimination was coplanar and concerted and the trans elimination had at least some degree of concert.

The authors could not detect any deuterium exchange with the endo-cis or the trans dibromo derivatives, nor could they detect any isomerization under basic conditions. The absence of deuterium exchange does not preclude an E1CB mechanism but its absence is a prerequisite for demonstrating the presence of a concerted or synchronous elimination.

One of the arguments for the multiple mechanism involving a carbanion intermediate is the great increase in rate when strongly acidifying groups are placed on the α carbon. To determine if acid strengthening influences would change the mechanism from E2 to one involving a carbanion intermediate, the two diastereoisomers of 2-benzenesulfonyl-3-iodobutane were prepared by Skell and McNamara and subjected to basic dehydrohalogenation.²⁸

²⁸P. S. Skell and J. H. McNamara, J. Am. Chem. Soc., 79, 85 (1957).

The results indicated that there were two distinct unsaturated sulfones as products of the reaction. Thus the dehydrohalogenation is a stereospecific reaction, and the loss of hydrogen halide occurs simultaneously in a trans elimination even with a strongly acidifying group present. Had there been a discrete anion of any lifetime ($> 10^{-9}$ sec.), the same mixture of isomers would have been obtained in all cases. Similar results were observed in the elimination of the brosylates of dl-threo and dl-erythro-3-p-tolylsulfonyl-2-butanol with trimethylamine or hydroxide ion in 50% aqueous dioxane. These results were compared to the brosylate of trans-2-p-tolylsulfonylcyclopentanol which underwent cis elimination seven times faster than the above threo form and three times faster than the erythro form. The activation energy of the cis elimination was found to be comparable to the two trans eliminations.²⁹ The data presented show no basis for an energetically unfavorable two stage cis elimination as suggested by Cristol to explain the higher activation energy for the dehydrohalogenation of β -hexachlorobenzene. The author does concede that if sufficiently strong electron withdrawing groups were used in alicyclic systems, that it may be

²⁹F. G. Bordwell and P. S. Landis, J. Am. Chem. Soc., 79, 1593 (1957).

possible to get an E1CB mechanism to occur, which is probably the case here.

If one visualized the E1CB mechanism in which the lifetime of the intermediate carbanion diminished continuously, it is obvious that the mechanism will merge into an E2 mechanism in which the two substituents are lost simultaneously.³⁰ However, as this lifetime becomes shorter, the various means of detecting E1CB will disappear, at different stages. The first to go would be deuterium exchange. At some later stage the mechanism will show trans preference and would correctly be called an E2 mechanism, in which there is some double bond character and some degree of breaking for the carbon-hydrogen and carbon-X bond. This argument implies various degrees of carbanionic character and visualizes different variations in transition state.

An example of this is the investigation of Cram, Greene and DePuy³¹ on the eclipsing effects of the diastereomers of 1,2-diphenyl-1-propyl-X system where X is chlorine, bromine and trimethyl ammonium ion. A comparison was made of kE2 threo/ kE2 erythro. When the ratio was close to one, it indicated that the transition state was

³⁰V. J. Shiner and M. L. Smith, J. Am. Chem. Soc., 80, 4095 (1958).

³¹D. J. Cram, F. D. Greene and C. H. DePuy, J. Am. Chem. Soc., 78, 790 (1956).

close to reactants (i.e. the eclipsing of two phenyl groups in erythro was not important in the transition state). If the transition state were close to products the ratio would be much more than one since the equilibrium ratio of trans to cis olefin is about 50. The possible transition states are shown as structures I, II, and III. The structures I and III are similar to starting materials with little eclipsing and therefore $k\text{-threo}/k\text{-erythro}$ should be close to one. Thus, the greater the value of this ratio, the closer the transition state will be to II. When $X=\text{Br}$, Cl and $-\text{N}(\text{R})_3$, the ratios change from 0.7 to 1.1 to 57 respectively with sodium ethoxide in ethanol. The bromide and chloride must then have structures close to I (the better leaving group giving the smaller ratio), whereas the trimethyl ammonium ion must possess the character of II.

In a poorer solvating medium, t-butyl alcohol and t-butoxide the ratio is 5.4 and 15 for bromide and chloride, respectively, indicating a structure more like II but where the better leaving group (bromide) produces a less eclipsed transition state. With trimethylammonium ion, the ratio $k\text{-threo}/k\text{-erythro}$ falls to 1.1 indicating a transition state like starting material. In view of the acidifying influence of the ammonium ion and the stronger base used, the transition state might look more like III.

Thus, the influence of solvent, leaving group and base all show that the transition state can be varied from one resembling starting material to one resembling products.

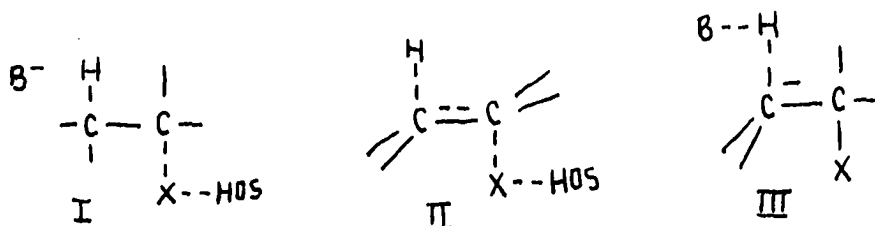


Figure 12. Three possible transition states

A method of measuring the degree of carbanionic character on the α carbon is to measure the ρ value from a Hammett plot (vide infra). Various values have been reported in the literature. Cristol studied a series of 2,2-diaryl-monochloro-, dichloro-, and trichloroethanes in ethanolic sodium hydroxide. In the dichloro and trichloro systems ρ was 2.456 and 2.729, respectively.

For 2-phenylethyl chloride with ethanolic hydroxide the ρ is 1.65.³² A series of *m*- and *p*-substituted β -phenylethyl bromides and chlorides gave a value of 2.1,

³²M. Simonetta and G. Favini, *J. Chem. Soc.*, 1840 (1954).

the sulfonium salts 2.7.^{33,34} The positive ρ value, as in these compounds indicate that there is some carbanion character in the transition state. It was found, though, that the sulfonium salt did not exchange deuterium with the solvent,³⁵ indicating that there was no discrete carbanion intermediate. The sulfonium salt also shows a considerable isotope effect, k_H/k_D being 5.1. This is not the calculated maximum for complete carbon-hydrogen bond breaking in the transition state, but does show considerable carbanionic character. The data indicate some double bond character and the absence of a discrete anion.

Recently, Cristol studied the rates of reaction of 2-phenyl-cyclohexylammonium ion, 2-phenylcyclohexyldimethylsulfonium ion, and 2-phenylhexyl tosylate with hydroxide in ethanol.³⁶ He found that trans elimination was favored over cis in both onium series, the difference in reactivity being 133 for the ammonium compounds and 383 for the sulfonium compounds. The cis cyclohexyltrimethyl

³³C. H. DePuy and D. H. Froemsdorf, J. Am. Chem. Soc., 79, 3710 (1957).

³⁴W. H. Saunders, Jr., and R. A. Williams, J. Am. Chem. Soc., 79, 3710 (1957).

³⁵W. H. Saunders, Jr., and D. H. Edison, J. Am. Chem. Soc., 82, 138 (1960).

³⁶S. J. Cristol and F. R. Stermitz, J. Am. Chem. Soc., 82, 4693 (1960).

ammonium ion was considered as abnormally unreactive when compared to its acyclic analog. This is explained by conformational difficulties.³⁷ It is of interest that 2-phenylcyclohexyl tosylate did not give second order kinetics.

More recently,³⁸ it was found that the elimination of hydrogen bromide from the addition product of deuterium bromide and acenaphthylene (85% cis addition) gave 95 ± 10% deuterium in the 1 position, using tertiary butoxide in t-butyl alcohol. The authors quote Cristol, Stermitz and Ramsey to explain their cis addition. Cristol et al.³⁹ had prepared cis and trans dichloroacenaphthylene. Dehydrochlorination with sodium hydroxide in ethanol gave a rate for trans elimination about 750 times faster than for cis elimination. It was assumed that there was some freedom of rotation and that the molecule can approach a trans coplanar state for the elimination. The cis elimination was thought to go by a carbanion intermediate which is stabilized by the neighboring aromatic system.

³⁷S. Winstein and N. J. Holness, J. Am. Chem. Soc., 77, 5562 (1955).

³⁸M. J. S. Dewar and R. C. Fahey, J. Am. Chem. Soc., 84, 2012 (1962).

³⁹S. J. Cristol, R. F. Stermitz and P. S. Ramsey, J. Am. Chem. Soc., 78, 4939 (1956).

DISCUSSION

In view of the great amount of work done to determine the mechanistic pathway of the base promoted cis elimination, it was thought that a study of the tosylates of 2-phenylcyclopentanols should help to elucidate the problem. In previous work cis eliminations were observed to be E1CB where conformational or steric difficulties prevented a concerted trans elimination and where there were strongly acidifying groups on the α -carbon. Consequently, there has been great interest in the nature of the base promoted elimination in systems with an α carbon bearing only a mildly acidifying group.

With this in mind a series of m and p substituted trans 2-phenylcyclopentyltosylates were prepared. The cyclopentyl system, being more planar than the corresponding

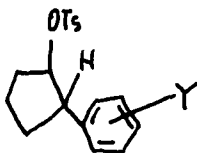


Figure 13. m and p-Substituted trans-2-phenylcyclopentyl tosylates

cyclohexyl compounds should not have some of the conformational difficulties found in the cyclohexyl compounds. trans-2-Phenylcyclopentanol is a known compound.⁴⁰ The addition of phenyl lithium to cyclopentene oxide is assumed to give the trans isomer by analogy with the reaction of cyclohexene oxide.⁴¹ p-Tolylcyclopentanol was prepared by a similar reaction. p-Chlorophenyl lithium was obtained

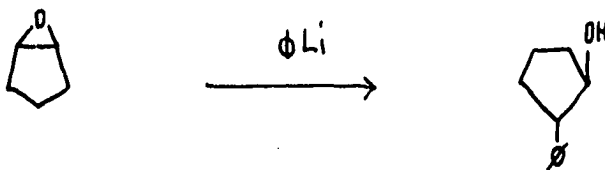


Figure 14. trans-2-Phenylcyclopentyl tosylate from cyclopentene oxide

by halogen metal interchange of n-butyl lithium and p-chlorobromobenzene and gave the corresponding alcohol upon addition to the epoxide, but m-chlorophenyl lithium was not stable for enough time to add to the epoxide and

⁴⁰W. H. Tallent, J. Org. Chem., 21, 862 (1956).

⁴¹J. W. Cook, C. L. Hewett and C. A. Lawrence, J. Chem. Soc., 71 (1936).

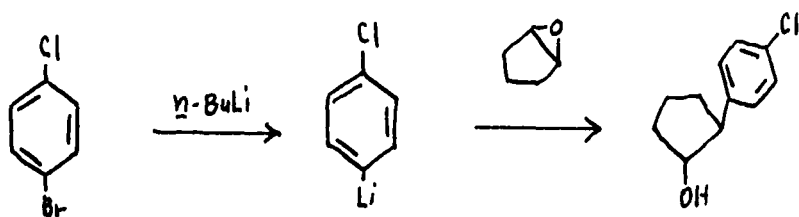


Figure 15. Preparation of trans-2-(p-chlorophenyl)-cyclopentanol

yields were very poor. None of the yields were above 46% for the alcohols mentioned above and a better synthetic scheme was obviously needed.

An alternate route to the desired trans alcohols was available by means of hydroboration⁴² of the 1-arylcyclopentenes. Addition of cyclopentanone to m-chlorophenyl magnesium bromide and dehydration of the tertiary alcohol so obtained, gave 1- (m-chlorophenyl)-cyclopentene. Reaction of this compound with diborane generated in situ and oxidation gave the expected alcohol in excellent yield. Later, several of the other previously prepared alcohols were prepared by this method and gave identical tosylates unequivocally establishing the configuration of these

⁴²H. C. Brown, Chem. Weekblad, 59, 41-55 (1963).

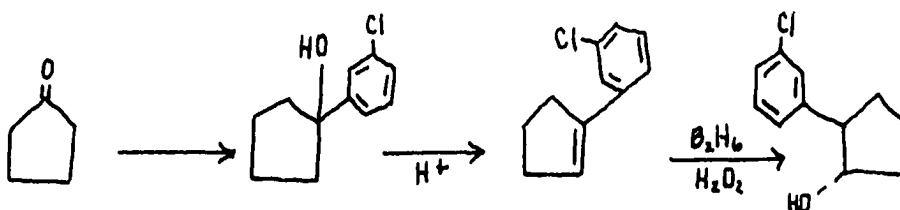


Figure 16. Preparation of t-2-(m-chlorophenyl)-cyclopentanol

alcohols as trans. cis-2-Phenylcyclopentanol was prepared by the Raney nickel reduction of 2-phenylcyclopentanone.

It was found that the tosylates slowly solvolyzed in absolute ethanol, so tertiary butyl alcohol was used as a solvent and t-butoxide as the base. The rate was followed titrimetrically, and rates reported were the average of two or more runs, and average deviations have been calculated. The system also lends itself to ultraviolet analysis in that the conjugated olefin has a distinct peak at 257μ ($\epsilon=15,000$), whereas the unconjugated olefin gives merely benzene absorption. The rates were measured at two different temperatures so that entropies and energies of activation might be calculated. The rates were clearly second order as shown by the constant value of k obtained by using the second order rate expression.

A gas phase chromatogram of the products of the base elimination of 2-phenylcyclopentyl tosylate showed 8% of the 3-phenyl cyclopentene. With trans-2-(m-chlorophenyl)-cyclopentyl tosylate the rate was sufficiently fast that the U.V. and titrimetric method agreed to within 1% of each other. The appropriate corrections were applied to the rate constants for this small amount of trans elimination that occurred.

The cis isomer of 2-phenylcyclopentanol was prepared by Raney nickel reduction of 2-phenylcyclopentanone. The tosylate had a distinctly different melting point (about 20°C. higher) than the trans tosylate prepared via hydroboration or phenyl lithium on the epoxide and reacted ten times faster in t-butoxide. Its rate was determined pseudo first order and infinity points were occasionally checked. The reaction was followed by use of an ultraviolet spectrometer.

In Table 1 are recorded the various Arrhenius

Table 1. The various Arrhenius quantities determined

Isomer	Ea	H	F	S	Type of elimination
<u>Trans</u>	24.5	23.9	24.4	-1.65	<u>Cis</u>
<u>Cis</u>	11.8	11.2	22.1	-36.5	<u>Trans</u>

quantities. The cis elimination has a higher energy of activation than the trans. This has been observed before. Cristol reported 9.6 to 12.5 k-cal. higher activation energy for the β isomer of benzene hexachloride. He comments that this higher activation energy is probably necessary to force the reaction against an unfavorable steric arrangement of groups.⁴³ In the present study with cis and trans-2-phenylcyclopentyl tosylates this also is probably an important factor. When ethoxide ion in t-butyl alcohol is used instead of the bulky t-butoxide ion, the rate doubles even though a weaker base is being used. Another important consideration is that the two bulky 1,2-groups in the cis isomer will tend to twist out of an eclipsed position making the two trans leaving groups more coplanar, thereby increasing the rate of elimination. See Figure 17.



Figure 17. trans-2-Phenylcyclopentyl tosylate and cis-2-Phenylcyclopentyl tosylate

⁴³E. D. Hughes, C. K. Ingold and R. Pasternak, J. Chem. Soc., 3832 (1953).

It is recognized that the cyclopentyl system is not planar, but has a pucker to it. In the Newman projection the structure drawn for cis-2-phenylcyclopentyl tosylate is drawn to indicate that the two cis groups being crowded probably twist away from each other making the transition state closer to coplanarity.

This increase in rate in going from cis to trans elimination in the 2-phenylcyclopentyl system is to be expected. The $k_{\text{trans}}/k_{\text{cis}}$ for 2-(*p*-tolylsulfonyl)-cyclopentyl tosylate was 20 with hydroxide ion in 50% dioxane.

Under the same conditions as used for the trans-2-phenylcyclopentyl tosylates, trans-2-phenylcyclohexyltosylate did not react after 22 days⁴⁴ whereas the cis-2-phenylcyclohexyl tosylate reacted rapidly. Thus, in the cyclohexyl system $k_{\text{trans}}/k_{\text{cis}} > 10^4$, whereas in the cyclopentyl system this is about 13. For cyclohexyl tosylate to achieve a coplanar state the ring has to eclipse all of its groups (i.e. attain the boat form), whereas the cis isomer can easily get the acidic proton and tosylate group trans to each other when phenyl and tosylate are both axial. Coplanarity in this case is apparently very important.

⁴⁴G. M. Morris, Ames, Iowa. Base promoted elimination of trans-2-phenylcyclohexyl tosylate. Private communication. 1959.



Figure 18. trans-2-Phenylcyclohexyl tosylate



Figure 19. cis-2-Phenylcyclohexyl tosylate

p-Tolylsulfonylcyclohexyl tosylate is 60 times slower than the five membered analog in its cis elimination, the 6 membered ring is 30 times slower than the 5 membered ring. A comparison of the rates of endo-cis and trans-2,3-dichloronorborane show that the cis elimination is 8 times faster than the trans. In all of these cases the cis elimination can occur through an almost planar transition state, whereas the trans elimination has difficulty getting

even near one.

However, in the case of cis and trans-11-p-toluene-sulfonyl-12-chloro-9,10-ethanoanthracene the cis compound (trans elimination) reacted about three times faster than the trans isomer.

It must be remembered that trans elimination is much faster than cis all other things being equal (there is no cis elimination observed in freely rotating systems) and that cis elimination is noted when the situation is such that trans elimination is prevented or greatly reduced by the inability of the molecule to approach a state of coplanarity. If the system under study can attain a state near coplanarity, the trans elimination although reduced in rate could still be faster. In a system where trans eliminants and cis eliminants were the same number of degrees away from coplanarity the trans elimination should have the much faster rate.

In view of these results some generalizations can be made. It appears that the rate is determined more by the planarity of departing groups (either cis or trans) in a concerted mechanism. As the dihedral angle varies from 0 or 180° toward 90°, this concertedness should be lost and the mechanism should be more like E1CB and should have higher ρ values. Also, the rate should fall off appreciably. This should apply to either trans or cis

elimination. In the study of cis and trans-2-chlorocyclopentylaryl sulfones where the investigator determined the rate with methyl and chloro radicals in the para position, the difference in rate increased more rapidly for the trans eliminating system than for the cis system. This would indicate that there was more carbanionic character in the transition state for the trans eliminating system than for the cis, or if the author had measured it, ρ would have been greater for the trans elimination as compared to the cis elimination. In this system the trans elimination did go faster but appeared to have more carbanionic character in the transition state. Again, we can say that the coplanarity attained in the trans elimination was slightly less than for the cis elimination.

It has been the view that cis elimination becomes operative because of strongly acidifying groups.⁴⁵ It was shown that the chlorosulfone group would not change the mechanism from E2 to E1CB in a normal, free-to-rotate system. The implication is that the strongly acidifying groups tend to encourage a carbanion mechanism in the cis elimination. This is probably so in cases where cis elimination occurs through a transition state that is far from

⁴⁵S. J. Cristol and R. P. Arganbright, J. Am. Chem. Soc., 79, 3441 (1957).

This lack of isomerization has been observed in other systems. Bordwell and Kern were unable to isomerize 3-p-tolylsulfonylcyclohexene with sodium hydroxide.⁴⁶ Likewise, 3-phenylcyclohexene was only 4.5% isomerized after refluxing in alcoholic hydroxide for a day.⁴⁷

There is also the possibility that the rate measured is simply the formation of a carbanion which rapidly isomerizes to the cis isomer which in turn does a rapid trans elimination. This is extremely unlikely because of the comparatively low ρ value which would be much higher if there were a discrete anion formed in the rate determining step. A value of 2.7 in another system⁴⁸ did not exchange deuterium.

The ρ value for the 2-arylcyclopentyl tosylates is of interest since it is a measure of the degree of carbanionic character. The fact it is positive indicates some concentration of negative charge in the transition state, since electron withdrawing substituents on the aromatic ring would tend to spread this charge out and speed up the

⁴⁶F. G. Bordwell and R. J. Kern, J. Am. Chem. Soc., 77, 1141 (1955).

⁴⁷J. Weinstock and F. G. Bordwell, J. Am. Chem. Soc., 77, 6706 (1955).

⁴⁸W. H. Saunders, Jr. and D. H. Edison, J. Am. Chem. Soc., 82, 138 (1960).

elimination, which is observed in this case. In a non-rigid system, β -arylethyl tosylate, the ρ measured under identical conditions, was 3.39, indicating that the trans elimination here developed more negative character on the α carbon in the transition state than the corresponding cis elimination in a rigid system. Therefore, detosylation of trans-2-arylcyclopentyl tosylate must be a base promoted concerted process and not a multistage elimination as has been suggested for cis eliminations.

Cyclopentyl tosylate was reacted under similar conditions and was found to go approximately twice as fast as the trans-2-phenyltosylate. This is unexpected as the trans compound should then react to give 66% of the 3-phenylcyclopentene instead of the 8% observed. However, for the trans elimination to occur in this latter case, the phenyl will be in a crowded conformation that is not favored.

It is unfortunate that the chemist does not have a large number of molecules at hand that would have frozen configurations, so that he might study the rates of various base promoted eliminations through the entire spectrum of dihedral angle.

EXPERIMENTAL

Purification of materials Dry ethanol was prepared by adding ethyl formate to a sodium ethoxide solution and then distilling. The primary alcohols were removed from t-butanol by distilling three times from potassium.

Kinetic measurements t-Butoxide solutions were prepared by dissolving freshly cut potassium in t-butyl alcohol.

A quantity of the tosylate was weighed into a 50 ml. volumetric flask and t-butoxide solution added to the mark so that the resulting solution was approximately .05M. in tosylate and 0.1 M. in base. The flask contents were equilibrated at the required temperature in a water bath and samples removed with a calibrated 5 ml. pipette at the required intervals. The appropriate corrections were applied for volume expansion. Corrections were also applied for the disappearance of tosylate that occurred while the sample was equilibrating at the required temperature by titration of a blank.

Spectrophotometric determinations of the cis-2-phenylcyclopentyl tosylate were run pseudo-first order. The resulting rate constant was converted to a second order rate constant by dividing K -pseudo first order by the base concentration. Solutions of potassium ethoxide in t-butyl

alcohol were prepared by adding approximately 150% of the required amount of ethanol to t-butoxide solutions.

The samples upon removal from the bath were quenched with ice water and titrated with approximately 0.2 M. hydrochloric acid. The indicator used was phenolphthalein. The acid solution was standardized at the beginning and at the end of the present study. There was virtually no change in its titer. Results of the various determinations are listed in the following tables:

Table 2. trans-2-p-Tolycyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = 0.0474$, $T = 46.9$ C.,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^6$
0	3.40	-
15,250	3.30	1.63
70,680	2.93	2.17
83,840	2.88	2.11
96,780	2.83	2.09
191,280	2.55	2.14
237,600	2.47	2.12
254,300	2.44	2.14
$K_2 = 2.13 \pm .03 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$		
$K_2 = 5.48 \pm .08 \times 10^{-5} \text{ l. sec.}^{-1} \text{ mole}^{-1}$		

Table 3. trans-2-p-Tolycyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0490$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^6$
0	3.41	-
4,230	3.37	2.28
10,000	3.32	2.18
20,000	3.23	2.32
30,000	3.18	2.04
43,750	3.10	1.97
76,848	2.92	2.04
106,500	2.79	2.08

$K_2 = 2.13 \pm .12 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 5.48 \pm 0.34 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 4. trans-2-Phenylcyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $T = 46.9 \text{ C.}$, $N_{\text{Tos}} = 0.0481$,
 $N_{\text{base}} = 0.1085$)

Time (sec.)	ml. acid	$K \times 10^6$
0	2.79	-
5,130	2.71	5.33
13,586	2.58	5.03
26,472	2.41	5.30
36,445	2.31	5.27
50,634	2.23	4.75
79,966	2.03	5.02
105,671	1.95	4.67

$K_2 = 5.05 \pm .26 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 1.30 \pm .08 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 5. trans-2-Phenylcyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{base}} = 0.0677$, $T = 46.9^{\circ}\text{C.}$,
 $N_{\text{Tos}} = .05035$)

Time	ml. acid	$K \times 10^6$
0	1.74	-
6,000	1.62	9.15
13,440	1.59	5.28
21,288	1.54	5.06
32,028	1.46	4.68
66,450	1.27	4.64
107,748	1.08	4.96
289,200	0.89	3.12

$K_2 = 4.92 \pm 0.33 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 1.27 \pm .08 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 6. trans-2-(p-chlorophenyl)-Cyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0466$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^5$
0	2.76	-
4,374	2.52	1.93
7,719	2.40	1.80
12,636	2.26	1.72
16,636	2.15	1.73
20,838	2.08	1.70
29,148	1.97	1.67
34,800	1.91	1.88
47,598	1.79	1.64

$K_2 = 1.76 \pm .09 \times 10^{-5} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 4.53 \pm .23 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 7. trans-2-(p-chlorophenyl)-Cyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0502$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^5$
0	2.24	-
4,476	1.915	1.77
6,720	1.82	2.03
14,820	1.63	1.89
24,030	1.48	1.85
66,068	1.11	2.18
$K_2 = 1.94 \pm .14 \times 10^{-5} \text{ ml.}^{-1} \text{ sec.}^{-1}$		
$K_2 = 4.99 \pm .39 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$		

Table 8. trans-2-(m-chlorophenyl)-Cyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0428$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^5$
0	2.57	-
1,065	2.46	3.92
2,340	2.34	4.09
4,230	2.20	4.09
5,875	2.11	3.99
8,538	2.00	3.82
13,685	1.84	3.75
16,087	1.78	3.81
25,060	1.65	3.71
$K_2 = 3.89 \pm .14 \times 10^{-5} \text{ ml.}^{-1} \text{ sec.}^{-1}$		
$K_2 = 1.00 \pm .035 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$		

Table 9. trans-2-(m-chlorophenyl)-Cyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0462$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^5$
0	2.66	-
1,550	2.49	3.85
3,150	2.32	4.27
4,040	2.24	4.38
6,062	2.11	4.30
7,200	2.05	4.27
8,000	2.03	4.05
10,730	1.94	3.85
14,070	1.81	4.12
$K_2 = 4.14 \pm .19 \times 10^{-5} \text{ ml.}^{-1} \text{ sec.}^{-1}$		
$K_2 = 1.04 \pm .05 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$		

Table 10. trans-2-Phenylcyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0521$, $T = 73.8^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^4$
0	3.19	-
192	3.07	1.56
382	2.97	1.53
615	2.88	1.42
924	2.71	1.64
1,275	2.61	1.56
1,908	2.42	1.64
2,861	2.25	1.63
4,296	2.07	1.73
$K_2 = 1.59 \pm .09 \times 10^{-4} \text{ ml.}^{-1} \text{ sec.}^{-1}$		
Volume correction 80° to 30°		
$K_2 = 4.28 \pm .22 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$		

Table 11. trans-2-phenylcyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0405$, $T = 78.8^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^4$
0	3.21	-
423	3.02	1.54
1,011	2.81	1.61
1,297	2.70	1.78
1,588	2.65	1.69
2,088	2.54	1.83
2,317	2.51	1.73
3,094	2.42	1.70
3,810	2.35	1.74

$K_2 = 1.70 \pm .086 \times 10^{-4} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 Volume correction 80° to 30°
 $K_1 = 4.57 \pm .22 \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 12. trans-2-Phenylcyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0471$, $T = 46.9^{\circ}\text{C.}$,
 potassium ethoxide in t-butoxide)

Time	ml. acid	$K \times 10^6$
0	3.22	-
2,927	3.13	8.30
6,770	3.02	8.60
10,901	2.92	8.56
22,229	2.72	8.18
45,569	2.44	8.22
76,302	2.26	7.98
90,480	2.19	8.36

$K_2 = 8.31 \pm .20 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 2.14 \pm .05 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 13. cis-2-Phenylcyclopentyl tosylate

($N_{\text{Tos}} = 3.95 \times 10^{-3}$, $N_{\text{base}} = 0.1120$, $T = 46.9^\circ\text{C.}$,
 samples withdrawn were diluted 100 times before
 each measurement)

Time	\bar{A}	$K \times 10^4$
0	.095	-
810	.175	1.91
2,640	.310	1.82
3,530	.366	1.86
5,230	.438	1.79
7,020	.513	1.94
9,520	.555	1.77
15,878	.622	1.68
	.662	-

$K_{\text{pseudo}} = 1.82 \pm .08 \times 10^{-4} \text{ sec.}^{-1}$
 $K_2 = 1.62 \pm .07 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 14. cis-2-Phenylcyclopentyl tosylate

($N_{\text{Tos}} = 4.72 \times 10^{-3}$, $N_{\text{base}} = 0.1167$, $T = 25.9^\circ\text{C.}$,
 samples withdrawn were diluted 100 times before
 each measurement)

Time	\bar{A}	$K \times 10^5$
0	.076	-
5,491	.245	5.65
8,118	.295	5.23
10,938	.351	5.21
13,218	.390	5.17
17,329	.441	4.96
21,285	.488	4.94
32,763	.581	4.88
∞	.709	-

$K_{\text{pseudo}} \text{ first order} = 5.06 \pm .14 \times 10^{-5} \text{ sec.}^{-1}$
 $K_2 = 4.34 \pm .12 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Table 15. Cyclopentyl tosylate

($N_{\text{acid}} = 0.1945$, $N_{\text{Tos}} = .0440$, $T = 46.9^{\circ}\text{C.}$,
t-butoxide in t-butyl alcohol)

Time	ml. acid	$K \times 10^6$
0	3.35	-
4,045	3.23	8.46
4,899	3.22	7.58
5,971	3.19	7.80
7,578	3.14	8.36
10,028	3.06	9.28
17,664	2.92	8.71
22,513	2.76	10.89

$K_2 = 8.71 + .10 \times 10^{-6} \text{ ml.}^{-1} \text{ sec.}^{-1}$
 $K_2 = 2.24 \pm .26 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$

Correction applied for trans elimination A sample
(0.05 N.) of trans-2-phenylcyclopentyl tosylate was heated
at 46.9 C. in 0.1 N. t-butoxide-t-butyl alcohol solution
for approximately ten half lives. The resulting solution
was poured into ice water and the mixture extracted with
ether. The ether extract washed with dilute hydrochloric
acid, water and then dried over sodium sulfate. The ether
solution was concentrated and samples were analyzed by gas
phase chromatography. Integration showed 8% of 3-phenyl-
cyclopentene and 92% of 1-phenylcyclopentene. The cor-
rected rate constants are shown in the following table:

Table 16. Rate constant corrections

Substituent	K-observed	K-corrected
p-CH ₃	5.48 x 10 ⁻⁵	4.5 x 10 ⁻⁵
H	1.30 x 10 ⁻⁴	1.2 x 10 ⁻⁴
p-Cl	4.84 x 10 ⁻⁴	4.7 x 10 ⁻⁴
m-Cl	1.03 x 10 ⁻³	1.02 x 10 ⁻³

Cyclopentene oxide The method first used was essentially that of Emmons and Pagano who epoxidized pentene.⁴⁹ To a suspension of 8.2 ml. (0.3 mole) of 90% hydrogen peroxide in 50 ml. methylene chloride cooled in an ice bath was added 50.8 ml. (0.36 mole) of trifluoroacetic anhydride over a period of 10 minutes. The solution of peroxytrifluoroacetic acid so obtained was stirred in the cold 15 minutes and then transferred to a dropping funnel equipped with a pressure equalizing tube. It was then added dropwise to a mixture of 95 g. (0.9 mole) of sodium carbonate, 14 g. (0.2 mole) of cyclopentene and 200 ml. of methylene chloride. After addition was complete,

⁴⁹W. D. Emmons and A. S. Pagano, J. Am. Chem. Soc., 77, 89-92 (1955).

the mixture was stirred 30 minutes. The insoluble salts were filtered and then triturated with 300 ml. of methylene chloride. The combined organic solutions were dried over sodium sulfate. The solvent was removed through a 30 cm. tube packed with 1/4 inch glass helices. The residual material was distilled giving 12 g. (75%) of epoxide b.p. 99-100 (lit. 100-101) that gave a negative Beilstein test.

Although yields were excellent by the above method, the removal of large quantities of solvent was too tedious for the weight of epoxide obtained. The method of Goodman *et al.*⁵⁰ using N-bromosuccinimide in water on cyclopentene followed by treatment with sodium hydroxide was found to be more adaptable to large scale preparations although the yields were of the order of 50%.

Preparation of trans-2-phenylcyclopentanol by use of diborane In a 2 liter, 3 necked, round bottomed flask equipped with a stirrer was placed 11 g. (0.29 mole) of sodium borohydride, 450 ml. of diglyme (bis-(2-methoxyethyl)-ether) and 94 g. (0.65 mole) of 1-phenylcyclopentene. In an addition funnel equipped with a pressure equalizing side arm was placed 55.2 g. (0.39 mole) of boron trifluoride etherate and 75 ml. of diglyme. The whole system was

⁵⁰L. Goodman, A. Benitz and B. R. Baker, J. Am. Chem. Soc., 80, 11680 (1958).

flushed with dried nitrogen and kept under a slight positive pressure of nitrogen. The gas escape from the system was through about one cm. of mineral oil so that there was always a visual indication that the system was air tight. The boron trifluoride etherate was added over a period of 80 minutes and the reaction mixture allowed to stir an additional 2 hours. At this time 20 ml. of water was added (gas evolution), then 40 ml. of 3 N. sodium hydroxide and finally 40 ml. of 30% hydrogen peroxide (exothermic). The reaction mixture was allowed to cool to room temperature and was stirred for one hour. The resulting mixture was treated with ether and ice water, the organic layer separated and washed with ice water numerous times. The organic layer was dried over anhydrous sodium sulfate. The ether was removed and the residue distilled, b.p. 133-135°C. (9-10 mm.) giving 75.3 g. (72%) of product.

The preparation of 2-phenylcyclopentanol from cyclopentene oxide A solution of phenyl lithium was prepared from 2.1 g. lithium and 22.6 g. bromobenzene in 170 ml. of ether. To this was added dropwise 12 g. (0.14 mole) of cyclopentene oxide at a rate to maintain gentle reflux. After addition was complete, the mixture was stirred an additional 3½ hours and then poured into ice water. The aqueous layer was removed, extracted once more with ether and the organic solutions combined. After drying the

ethereal extracts over sodium sulfate the solvent was evaporated and the residue distilled giving 5.38 g. (32%) of alcohol b.p. 115-116/2 mm.

2-(p-Chlorophenyl)-cyclopentanol n-Butyllithium
was prepared by the action of lithium metal on n-butyl bromide in ether at -20°C . This solution so obtained was added dropwise to 19.1 g. (0.1 mole) of p-bromochlorobenzene dissolved in 50 ml. of dry ether all under a blanket of nitrogen. A 10% excess of n-butyl lithium was added. This solution was allowed to stir 10 minutes and 8.4 g. (0.1 mole) of cyclopentene oxide in 20 ml. of dry ether was added dropwise. The reaction mixture was stirred one and a half hours. Acidified ice water was added and the organic layer removed. The aqueous layer was extracted and the ether extracts combined, dried over sodium sulfate and the ether evaporated. The residue was distilled yielding 7.3 g. (32%) of alcohol b.p. 135-145/4 mm.

2-p-Tolylcyclopentanol A solution of p-tolyllithium was prepared by the addition of 49 g. (0.29 mole) of p-bromotoluene in 142 ml. of dry ether to 4.1 g. (0.58 mole) lithium cuttings in 71 ml. of ether. To this reagent was added 12 g. (0.14 mole) of epoxide in 50 ml. of ether at a rate to maintain reflux. After addition was complete, the reaction mixture was stirred two hours. At this time cold, dilute sulfuric acid was added, the layers separated

and the layer extracted again with ether and the combined organic solutions dried over sodium sulfate. The ether was removed giving 11.5 g. (46%) of alcohol b.p. 133-135/4 mm.

This alcohol was also prepared by hydroboration of the corresponding olefin. The method was essentially that used for trans-2-phenylcyclopentanol. The yield was 74% of material b.p. 98-101/0.15 mm.

1-(m-Chloro)-cyclopentene m-Chlorophenyl magnesium bromide (0.16 mole) was prepared by the reaction between magnesium and an ethereal solution of m-chlorobromobenzene. To this solution was added dropwise 55.6 g. (0.68 mole) of cyclopentanone in 100 ml. of ether. The addition rate was adjusted so as to maintain brisk reflux. The reaction mixture was stirred an hour after addition was complete and then poured into cold, dilute sulfuric acid. The ether layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with dilute sodium bicarbonate, water and then dried over sodium sulfate. After evaporation of the solvent, a small amount (0.1 g.) of p-toluenesulfonic acid was added to the pot residue and slow distillation was begun. The resulting olefin was obtained in 63% yield (67 g.) b.p. 97-98/1 mm.

2-(m-Chlorophenyl)-cyclopentanol This was prepared by hydroboration of the olefin by essentially the same procedure as that used for the preparation of trans-2-

phenylcyclopentanol. The yield of alcohol was 58%, b.p. 139-143/4 mm.

Cyclopentanol This was prepared by the lithium aluminum hydride reduction of cyclopentanone. The yield was 45%, b.p. 138-139, of alcohol.

Tosylates The tosylates mentioned in this study were all prepared by the method of Tipson.⁵¹ For every gram of alcohol was used 10 ml. of pyridine and 1.5 equivalents of *p*-toluenesulfonyl chloride. The alcohol was dissolved in the pyridine and cooled in an erlenmeyer flask to -5 to -10°C. The *p*-toluenesulfonyl chloride was added all at once and the resulting solution stirred for one hour. The reaction mixture was then placed in the refrigerator overnight during which time crystals of pyridine hydrochloride separated. The mixture was then poured into about an equal volume of ice water and the sides of the beaker scratched to induce crystallization. The tosylate usually precipitated without any trouble in a few minutes. The solid was then filtered, taken up in ether and the resulting solution dried over sodium sulfate. The ether solution was allowed to stand with de-colorizing charcoal 5 minutes and was then filtered into an erlenmeyer flask. Hexane was then added until the volume was increased by

⁵¹R. S. Tipson, J. Org. Chem., 9, 235-41 (1944).

about one fifth (never to the cloud point) and the erlenmeyer flask was then placed in a Dewar flask containing Dry Ice. It was found that wrapping the erlenmeyer flask in a towel prevented rapid cooling and gave better recrystallization. The tosylates were usually recrystallized three times and then dried in vacuo over paraffin strips. The yields were 60 to 70% after one recrystallization.

trans-2-phenylcyclopentyl tosylate m.p. 66-67°C.

trans-2-(p-Chlorophenyl)-cyclopentyl tosylate m.p. 93-94°C. Calc. for $C_{18}H_{19}ClSO_3$: C, 61.62; H, 5.46; S, 9.14; Cl, 10.11. Analyzed: C, 61.04; H, 5.30; S, 10.58; Cl, 11.92.

trans-2-p-tolylcyclopentyl tosylate m.p. 86-87°C.

Calculated for $C_{19}H_{22}SO_3$: C, 69.06; H, 6.74. Found: C, 68.05; H, 6.28.

trans-2-(m-Chlorophenyl)-cyclopentyl tosylate m.p.

54-55°C. Calc. for $C_{18}H_{19}ClSO_3$: C, 61.62; H, 5.46. Found: C, 61.59; H, 5.21.

cis-2-Phenylcyclopentyl tosylate m.p. 84-85°C. with some decomposition near the melting point. This tosylate will slowly decompose in a closed container over a period of weeks but will keep for months in the refrigerator.

Cyclopentyl tosylate m.p. 26-27°C., lit.⁵² m.p. 27-28°C.

Attempted isomerization of 3-phenylcyclopentene

Into a 100 ml. volumetric flask was weighed 76 mgs. of a mixture of 1- and 3-phenylcyclopentene (94% 3-phenylcyclopentene and 6% 1-phenylcyclopentene by VPC analysis). Then 0.12 M. t-butoxide was added to the mark and the resulting solution heated in a water bath at 50°C. for 48 hours. The solution was then allowed to cool to room temperature and 1 ml. was withdrawn and diluted to 100 ml. with 95% ethanol. The ultraviolet absorbance at $\lambda_{\text{max}} = 258$ was 0.735, which calculated out to the same concentration of 1-phenylcyclopentene as that obtained from a weight calculation at the start of the experiment (4.7×10^{-3} M.).

⁵²W. Huckel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanock, M. Heinzel, A. Hubele, J. Kurz, M. Maier, D. Maucher, G. Naher, R. Neidlein, and R. B. Rashingkar, Ann. 624, 142-255 (1959).

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