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Syntheses and eliminations of some substituted cyclobutanes

Carl Herbert Hendrickson
Iowa State University

SYNTHESES AND ELIMINATIONS OF SOME SUBSTITUTED CYCLOBUTANES

by

Carl Herbert Hendrickson

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Head of Major Department

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Dean of Graduate College

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INTRODUCTION

It is the nature of man to investigate and explain. Through his continued searching he brings to light the fundamental laws which control the universe that surrounds him. Explanations are not easily uncovered but require the thoughts of many minds. Bits of information must be obtained stepwise and recorded as foundations for further investigations. It is this record of the past coupled with his most recent discoveries which man must use to unravel the mysteries confronting him.

The bimolecular elimination reaction is well documented. Studies have been presented which deal with effects realized as due to the nature of the attacking base and of the leaving group. The olefinic composition of elimination products has been attributed to both electronic and steric properties of the reactants. The extensive investigation of this reaction has prompted the division of bimolecular eliminations into three categories; E_1, E_2 and E_{1cB}.

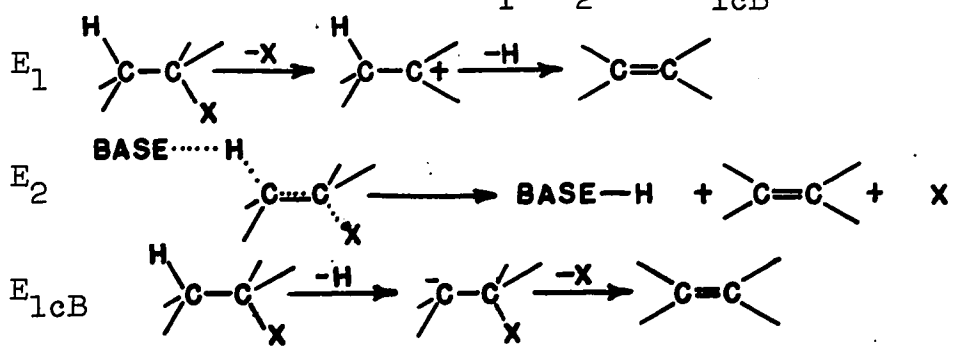

Fig. 1. Elimination reaction

That a trans and co-planar relationship of leaving groups is a necessary prerequisite for E_2 elimination has been a long standing contention. This dissertation substantiates a recent report that a cis and co-planar stereorelationship of leaving groups may also give rise to facile E_2 reactions. Investigations concerning the base-induced elimination from cis- and trans-2-arylcyclobutyl p-toluenesulfonates and the effects of substituent and solvent changes on the mode of reaction are reported. Implications of the data recorded are discussed and the synthetic methods employed are presented.

HISTORICAL

The elimination reaction is recognized as being one of utmost chemical importance, both as a synthetic route and as a philisophical lecturn from which new mechanistic explanations of reaction processes may be advanced. Indicative of the high interest in elimination chemistry, and to a lesser extent to its long period of recognition, are the innumerable investigations dealing with the nature of elimination reactions which have been reported. This dissertation is concerned with one general type of elimination reaction, the bimolecular 1,2- or beta-elimination. Because of the vast amount of material which has been accumulated in this area, and because excellent general reviews are available, a complete literature survey has not been attempted but rather important historical developments and investigations of current significance are summarized.

The beta-elimination involves the removal of two groups from adjacent atoms which are capable of forming multiple bonds. E.G.

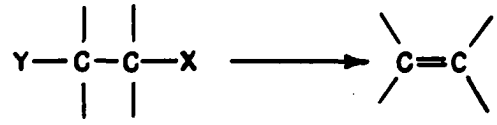

Fig. 2. Beta-elimination

The bulk of the mechanistic studies on beta-eliminations has dealt with molecular involvement in the transition state and/or the timing of bond breaking. Ingold reported the first studies of elimination mechanisms in 1927[1], and later, in 1950, presented three general types of beta-elimination mechanisms with a discussion as to their various roles.[2] Since that time beta-eliminations have been extensively reviewed by Cram[3], Gould[4], Hine[5], Bunnett[6] and Banthrope[7].

Bunnett, in his 1962 review, presented the modern concept of elimination reactions. Many of the arguments developed in this dissertation are presented in much the same manner as used by Bunnett. However, the reader is

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[1]Hanhart, W., and C. K. Ingold, J. Chem. Soc., 997 (1927).

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

[3]Cram, D. J., "Olefin-Forming Elimination Reactions", in M.S. Newman, "Steric Effects in Organic Chemistry", John Wiley and Sons, Inc., New York, N.Y., 1956, Chapter 6.

[4]Gould, E. S., "Mechanism and Structure in Organic Chemistry", Henry Holt and Co., Inc., New York, N.Y., 1959, pp. 472-504.

[5]Hine, J., "Physical Organic Chemistry", 2nd edition, McGraw-Hill Book Co., Inc., New York, N.Y., 1962, pp. 186-222.

[6]Bunnett, J. F., Angew. Chem. Intern. Ed., 1, 225 (1962).

[7]Banthrope, D. V., "Elimination Reactions", in E. D. Hughes, "Mechanisms in Organic Chemistry", Vol. 2, Elsevier, New York, N.Y., 1963.

referred to his article for a more extensive and diversified approach.

Discussions of elimination chemistry by Ingold and Hughes[8,9,10], Hine[11] and Skell[12] have included all but the most recent literature.

The unimolecular beta-elimination, chemically abbreviated as E_1, is envisioned mechanistically as the heterolytic cleavage of the C-X bond in a rate determining step. The resulting carbonium ion then loses a beta-hydrogen to a solvent or base molecule.

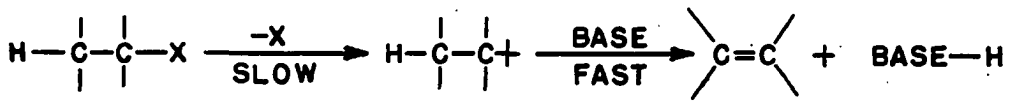

Fig. 3. E_1 elimination

Removal of a beta-hydrogen in a rate determining step by base, forming an intermediate carbanion with subsequent loss of a leaving group to yield olefin is designated as the E_{1CB} or carbanion mechanism.

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[8]Banthrope, D. V., E. D. Hughes and C. K. Ingold, J. Chem. Soc., 4054 (1960).

[9]Hughes, E. D., Quart. Reviews, 5, 261 (1951).

[10]Ingold, C. K., Proc. Chem. Soc., 265 (1962).

[11]Hine, J., and O. B. Ramsay, J. Am. Chem. Soc., 84, 973 (1962).

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

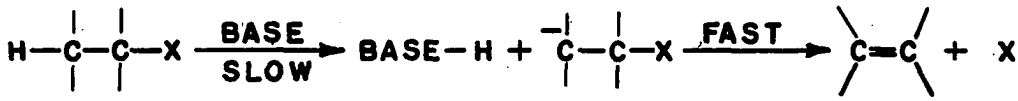

Fig. 4. E_{1CB} elimination

A further implication of the carbanion mechanism is a rapid equilibrium between base and substrate with loss of the leaving group in a slow step.

Fig. 5. E_{1CB} elimination

The bimolecular, E_2, mechanism involves the simultaneous loss of a beta-hydrogen and a leaving group with assistance to base.

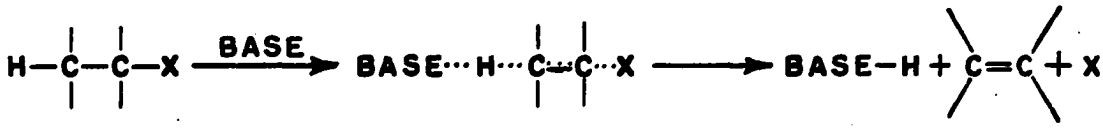

Fig. 6. E_2 elimination

By no means do all beta-eliminations adhere rigorously to the three classifications mentioned above. At present, the scope of the E_2 reaction has been extended to include the nearly "nearly E_1" elimination in which considerable amount of C-X bond breaking has occurred before the simultaneous loss of H and X, as well as the "nearly E_{1CB}"

elimination where the C-H bond is partially broken before the concerted loss of X and H. In the "nearly E_1" elimination, the alpha-carbon may acquire a certain amount of positive charge in the transition state whereas in the "nearly E_{1CB}" mechanism the beta-carbon may develop a partial negative charge.

Remaining is the "central E_2" or that mechanism describing simultaneous loss of H and X with equal amounts of bond breaking of both the C-H and C-X bonds in the transition state.

This extended viewpoint is still not sufficient to cover the multitude of transition states which may be possible. No mention has been made of the amount of double bond formation in the transition state, which may vary from nearly total formation, when both the C-H and the C-X bonds are nearly broken in the transition state, to nearly negligible formation in those cases having very little C-H and/or C-X bond breaking in the transition states. The double bond formation need not parallel the amount of C-H and C-X bond breaking due to the possibility of developing partial charges on the alpha- and beta-carbons. Bunnett[13] has given a detailed discussion of the multiplicity of E_2 transition states in terms of nine basic factors with five

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[13]Bunnett, op. cit., p. 225.

criteria for evaluation of these various factors.

Two general rules have been formulated as aids for predicting the olefinic products from elimination reactions involving unsymmetrical reactants. The Hofmann[14] rule states, in a generalized form, that in the elimination of onium salts ($-NR_3^+$, $-SR_2^+$ and $-PR_3^+$) the olefin bearing the least number of alkyl groups will be the major product. Hughes and Ingold[15] have explained adherence to the Hofmann rule as being due to inductive effects of the alkyl groups which influence the reactivity of the beta-hydrogens. The positive charge of the onium moiety acidifies the beta-hydrogens, an effect which is lessened by an adjacent alkyl group. The loss of the most acidic beta-hydrogen will give rise to the predominate product. The Saytzeff[16] rule states that in the E_2 elimination of secondary and tertiary alkyl halides and alkyl sulfonate esters, as well as all E_1 eliminations, the principal product will be the olefin bearing the greatest number of alkyl groups. Hyperconjugative assistance by the alkyl substituents toward the developing double bond has been postulated to outweigh any directive effect arising from differences in beta-hydrogen acidity and, thus, the more thermodynamically stable isomer

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[14]Hofmann, A. W., Ann., 79, 11 (1851).

[15]Banthrope, op. cit., p. 4054 and papers cited therein.

[16]Saytzeff, A., Ann., 179, 296 (1875).

predominates.

Colter[17] has found that changes in olefin composition produced by electronic effects in the leaving group are in the opposite direction to those predicted by Hughes and Ingold's theory. Brown[18] does not confer with the opinion that inductive effects should govern product formation in Hofmann eliminations. He chooses to explain observed product ratios as being the resultant of steric factors arising from molecular interaction of the base, reactant and leaving group in the transition state. Ledger and McKenna[19] employed Brown's steric explanation to give rationale to their observations concerning the E_1 and E_2 product ratios and rates of eliminations of 7-α-cholestanyl trimethylammonium ion. However, Saunders[20] and DePuy[21] have shown

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[17]Colter, A. K., NASA Doc. N63-14616, 12 pp. (1963). Original not available for examination; abstracted in Sci. Tech. Aerospace Rept., 10, 646 (1963).

[18]Brown, H. C., and I. Moritani, J. Am. Chem. Soc., 78, 2203 (1956), and H. C. Brown, J. Chem. Soc., 1248 (1956) and papers cited therein.

[19]Ledger, R., and J. McKenna, Chem. and Ind., 783 (1963).

[20]Saunders, W. H., Jr., S. R. Fahrenholtz and J. P. Lowe, Tetrahedron Letters, 18, 1 (1960) and Saunders, W. H., Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe and M. Schreiber, J. Am. Chem. Soc., 87, 340 (1965).

[21]DePuy, C. H., and C. A. Bishop, J. Am. Chem. Soc., 82, 2532 (1960) and C. H. DePuy, and C. A. Bishop, J. Am. Chem. Soc., 82, 2535 (1960).

E_2 rates and product ratios to be inversely related to steric size of halogen leaving groups.

One might consider that elimination products are a function of the amount of double bond character of the transition state. The development of the double bond will involve eclipsing of the various groups substituted on the resulting olefin. If these groups are of sufficient size as to cause steric interactions in the transition state this transition state could be energetically unfavorable relative to one involving the same amount of double bond character but not having the forementioned steric interactions. Such may be the case where Saytzeff products would be predicted but Hofmann products are observed.

It is reasonable that inductive effects could play a role in the double bond nature of the transition state. Saunders[22] holds that polar effects play the major role in determining product ratios with steric effects coming into play only in cases involving extreme hindrance. This contention is supported by Banthrope, Hughes and Ingold[23].

Cram[24], Hine[25], Barton[26] and Bunnett[27] have given

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[22]Saunders, op. cit., p. 340.

[23]Banthrope, op. cit., p. 4054.

[24]Cram, op. cit., Chapter 6.

[25]Hine, op. cit., pp. 186-222.

[26]Barton, op. cit., p. 1048.

[27]Bunnett, op. cit., p. 225.

discussions on the greater facility of trans elimination over cis elimination. The preferred geometry is agreed to be a trans co-planar arrangement of the leaving groups. E.g.

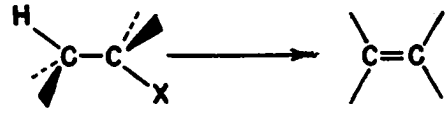

Fig. 7. trans Elimination

The first demonstration of this favored arrangement was recorded by Michael[28], who found that chlorofumaric acid reacted fifty times faster than chloromaleic acid in the base induced elimination of hydrogen chloride to give the same product, acetylene dicarboxylic acid.

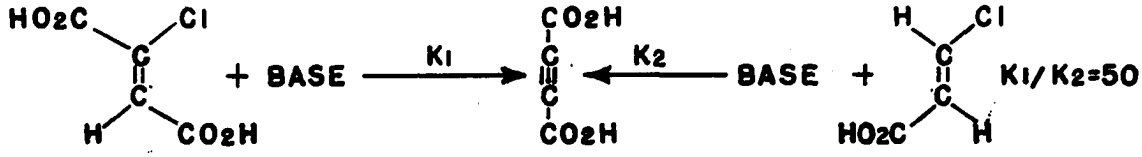

Fig. 8. First cis/trans ratio

Frankland[29] has given a review of studies of the stereochemical course of the E_2 elimination in acyclic systems which have shown the predominate olefinic product to be that which would arise from trans elimination.

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[28]Michael, A., J. prakt. Chem., 52, 308 (1895).

[29]Frankland, P. F., J. Chem. Soc., 654 (1912).

Cristol's[30] work with the bimolecular elimination of the five isomers of hexachlorobenzene has further pointed up the desirability of having a trans arrangement of the leaving groups. Cristol found the rate of elimination of hydrogen chloride from the beta-isomer, the one having all chlorines trans thus requiring cis elimination, to be several thousand times slower than elimination of the same elements from any of the other isomers, each having at least one vicinal trans relationship of H and Cl.

Later work by Cristol[31] has brought to light that a trans arrangement of leaving groups is not always a prerequisite to facile elimination. Examination of the bimolecular elimination of the geometric isomers of 11, 12-dichloro-9,10-dihydro-9,10-ethanoanthracene (Fig. 9) led to the first example of a cis E_2 being faster than the corresponding trans elimination.

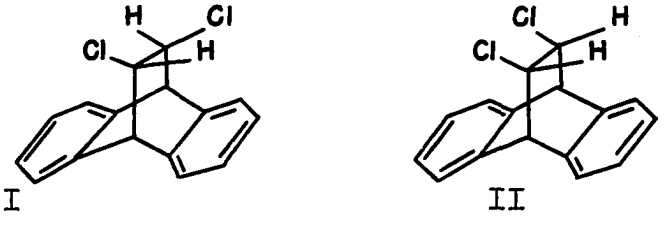

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Fig. 9. 9,10-ethanoanthracenes

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[30]Cristol, S. J., J. Am. Chem. Soc., 69, 338 (1947) and S. J. Cristol, N. L. Hause and J. S. Meek, J. Am. Chem. Soc., 73, 674 (1951).

[31]Cristol, S. J., and N. L. Hause, J. Am. Chem. Soc., 74, 2193 (1952).

Although both isomers were somewhat unreactive, the isomer having the chlorines trans (I) eliminated hydrogen chloride some eight times faster than the corresponding cis isomer (II).

DePuy and co-workers[32] have proposed that the ease of E_2 elimination may be a function of the dihedral angle between H and X. Accordingly, a plot of rate of elimination for a given system versus dihedral angle between the leaving group and beta-hydrogen should exhibit maxima at 0° and 180° and a minimum at 90°. Eliminations in systems which cannot assume a cis or trans co-planar arrangement of H and X will not only be slower but may proceed by a "nearly E_{1CB}" or, in the extreme case, by an E_{1CB} mechanism.

Invoking this approach, Cristol's elimination data from the vicinal dichlorobicyclo (2.2.2) octane derivatives becomes more meaningful. A considerable amount of energy would be involved in getting the leaving groups into a co-planar arrangement for the isomer having the chlorines cis (II) due to the necessity of introducing torsional strain into the rigid bicyclic system. It does not seem unreasonable that trans elimination would be energetically unfavored. However, in the other isomer (I) the leaving

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[32]DePuy, C. H., R. D. Thurn and G. F. Morris, J. Am. Chem. Soc., 84, 1314 (1962).

groups are *cis* and co-planar in the ground state and accordingly, elimination should be fast relative to the *trans* isomer.

Other data has been reported which may be interpretated as showing a relation between the dihedral angle between leaving groups and the rate of elimination. Cristol and Hoegger[33] have reported the loss of hydrogen chloride from endo-*cis*-2,3-dichloronorborane to be 85 times slower than elimination of the same elements from *trans*-2,3-dichloronorborane. LeBel[34] has found *cis* elimination of halogen halide from *trans*-2,3-dihalonorborane to be favored over *trans* elimination of the same elements from the endo- or exo-*cis* analogs, with *cis* elimination being 30-67 times faster than *trans*.

Csapilla[35] has recently suggested that favored *cis* over *trans* elimination can be attributed to the importance of π-orbital overlap between the various participants in the transition state. The π-orbital overlap will be at a maximum when all the involved centers lie in the same plane.

First considerations of the *cis* bimolecular elimination

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[33]Cristol, S. J., and E. F. Hoegger, J. Am. Chem. Soc., 79, 3438 (1957).

[34]LeBel, N. A., P. D. Peirne, E. R. Harger, J. C. Powers and P. M. Subramanian, J. Am. Chem. Soc., 85, 3199 (1963).

[35]Csapilla, J., Chimia, 18, 37 (1964).

were that it proceeds via a carbanion intermediate or an E_{1CB} mechanism. Cristol initiated a considerable amount of investigation when he proposed the beta isomer of hexachlorobenzene eliminated by an E_{1CB} mechanism.[36] Submitted as proof that a carbanion mechanism was operative in his case, was Cristol's observation that deuterium was incorporated in unreacted starting material after one half-life when the elimination was carried out in deuterated solvent. This cannot be held as being conclusive proof of a carbanion intermediate owing to the fact that less than 1 per cent deuterium exchange was recorded. However, deuterium exchange is not a necessary condition for a carbanion intermediate in an elimination reaction since the carbanion may react to give products faster than it can abstract a proton from solvent.

Hine[37] has examined the trichlorobenzene mixture produced when the beta isomer of hexachlorobenzene was eliminated in deuterated methanol. Based on comparison of the rate constant for the dehydrochlorination in methanol with that for the exchange of 1,2,4-trichlorobenzene-3-d Hine concluded that if the dehydrochlorination is carbanion in nature the intermediate carbanions almost always lose

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

[37] Hine, J., R. D. Weimar, Jr., P. B. Langford and O. Bertrand, J. Am. Chem. Soc., 85, 3894 (1963).

chloride ions and reprotonation is a rare fate.

Kwart[38] has recently reported a preferred cis-elimination involving 2-exo-bromo-3-exo-d-norbornane in which the olefinic product isolated resulted from 93% elimination of deuterium bromide. When the kinetic isotope correction is applied the preference for cis-elimination is calculated to be greater than 98%. LeBel[39] contends that the hydrogen halide elimination of trans-dihalonorbornanes employs a concerted mechanism with considerable E_{1cB} character. Supporting evidence is found in the relative rates of dehydrohalogenation of trans-2,3-dihalonorbornanes, trans-exo-2-bromo-3-chloronorbornane (III) eliminates hydrogen bromide seven times faster than trans-endo-2-bromo-3-chloronorbornane (IV) eliminates hydrogen chloride.

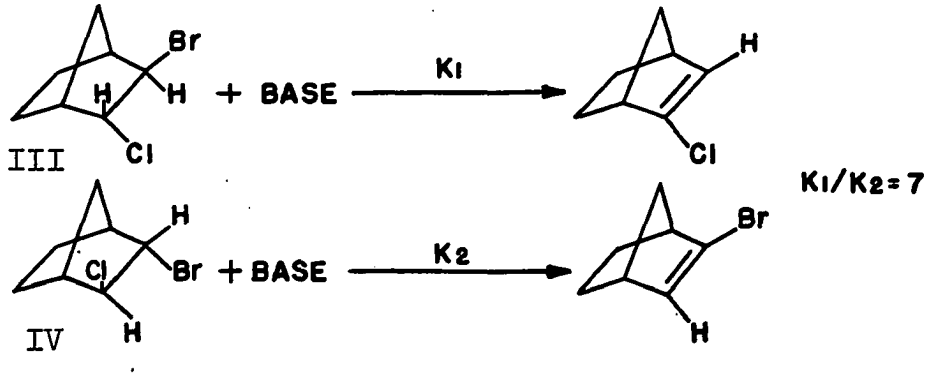

Fig. 10. 2,3-dihalonorbornanes

[38]Kwart, H., T. Takeshita and J. L. Nyce, J. Am. Chem. Soc., 86, 2606 (1964).

[39]LeBel, N. A., P. D. Beirne and P. M. Subramanian, J. Am. Chem. Soc., 86, 4144 (1964).

Since both isomers undergo exo-cis elimination, a concerted mechanism would require III to be faster than IV due to bromine being the better of the two leaving groups in E_2 reactions. However, in view of other pertinent data, if an E_{1CB} mechanism were operative for both isomers the trans-endo-2-bromo isomer (IV) should have the faster rate of dehydrohalogenation. Hine[40] has shown that beta-halogens vary in their ability to stabilize a carbanion in the order of Cl > Br > I and that the stabilizing ability of alpha-halogens vary in the opposite order, I > Br > Cl. Considering the stabilizing role of halogens toward a carbanion, one sees that dehydrochlorination would have been favored if an E_{1CB} mechanism were operative.

Using kinetic and product analysis and specific deuterium labeling as a basis, LeBel has also proposed that exo-cis-elimination should be general for most trans-2,3-dihalo-norbornanes. That his observations are most likely a manifestation of steric factors is pointed up by the preferential elimination of hydrogen chloride over hydrogen bromide from trans-endo-2-bromo-3-chloronorbornane (II).

The elimination of 1,1,1-trifluoro-2,2-dichloroethane with methoxide has been substantiated as proceeding through

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[40]Hine, J., and P. B. Langford, J. Org. Chem., 27, 4149 (1962).

a carbanion intermediate by deuterium exchange. Hine[41] found the rate of exchange to be faster than the rate of elimination. Although several other papers have been published on the E_{1CB} mechanism by Cristol[42], Papathanassiou[43] and Bordwell[44], Hine's is the only case which is verified by deuterium exchange.

Banthrope[45] had previously reported to have evidence of a carbanion intermediate in the beta-phenylethyl trimethyl ammonium system. When the elimination was carried out with methoxide in deuteromethanol Banthrope claimed to observe a large amount of deuterium incorporation in the starting material. This data was in direct conflict with earlier work published by Doering[46]. In fact, the method of recovery of the unreacted starting material has been shown to be responsible for Banthrope's results[47].

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[41]Hine, J., R. Wiesboeck and R. G. Ghirardelli, J. Am. Chem. Soc., 83, 1219 (1961) and J. Hine, R. Wiesboeck and O. B. Ramsay, J. Am. Chem. Soc., 83, 1222 (1961).

[42]Cristol, S. J., and P. Pappas, J. Org. Chem., 28, 2066 (1963) and papers cited therein.

[43]Papathanassiou, P. G., Dissertion Abstr., 22, 3406 (1962).

[44]Bordwell, F. G., E. W. Garbisch, Jr., J. Org. Chem., 28, 1765 (1963) and F. G. Bordwell, R. L. Arnold and J. B. Biranowski, J. Org. Chem., 28, 2496 (1963).

[45]Banthrope, D. V., and J. H. Ridd, Proc. Chem. Soc., 225 (1963).

[46]Doering, W. von E., and H. Meislich, J. Am. Chem. Soc., 74, 2099 (1952).

[47]Banthrope, D. V., and J. H. Ridd, Proc. Chem. Soc., 365 (1964).

Bourns and Smith[48], investigating the same problem but using beta, beta-d_2-beta-phenylethyltrimethylammonium ion (V) and ethoxide in ethanol, observed no loss of deuterium in recovered starting material and found the styrene produced to contain exactly one-half the amount of the heavier isotope that was present in the starting material.

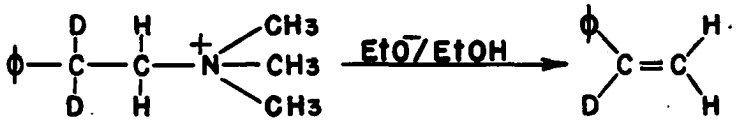

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Fig. 11. beta-phenylethyl system

If the quality of the transition state is "nearly E_{1CB}", introduction of an electronegative beta-substituent should help to stabilize the negative charge which develops on the beta-carbon and therein cause an acceleration of elimination. Bordwell[49] has reported that the elimination of trans-2-p-toluenesulfonyl cyclohexyl p-toluenesulfonate with hydroxide ion gives 1-p-toluenesulfonyl cyclohexene exclusively. In this case, the hydrogen acidity controls the E_2 reaction to such an extent that cis-elimination of an acidic hydrogen is preferred over the trans-elimination of a non-acidic hydrogen.

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[48]Bourns, A. N., and P. J. Smith, Proc. Chem. Soc., 336 (1964).

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

Application of the Hammett sigma-rho treatment[50] is a means of discerning the importance of beta-substituent stabilization. The magnitude of rho for a beta-carbon is interpreted as being directly related to the amount of negative carge on the beta-carbon in the transition state, i.e., rho is a measure of the amount of E_{1CB} character. Although no maximum value for rho has been asserted, it may be approximately five as determined by Szwarc[51] for the "living" polystyrene anionic homo- and co-polymerization. Rho for a given reaction varies inversely as a function of temperature.

DePuy, Thurn and Morris[52] and Smith[53] have found trans-2-phenylcyclopentyl p-toluenesulfonate to give a fast cis-elimination, as compared to the cyclohexyl analog, in the presence of t-butoxide in t-butyl alcohol to yield 1-phenyl-cyclopentene. Comparison of the rho for this reaction to that for the elimination of the same elements for beta-phenylethyl p-toluenesulfonate[54] have led these authors to

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[50]Hammett, L. P., "Physical Organic Chemistry", McGraw-Hill Book Co., Inc. New York, N.Y., 1940, p. 184.

[51]Shima, M., D. N. Bhattacharyya, J. Smid and M. Szwarc, J. Am. Chem. Soc., 85, 1306 (1963).

[52]DePuy, op. cit., p. 1314.

[53]Smith, J. A., "Bimolecular Elimination Reactions of Cyclopentyl Compounds", Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1964.

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

propose that the cis-elimination in the cyclopentyl system is highly concerted. Similar observations have been made by Beckman[55] in the investigation of E_2 eliminations of trans-endo-2-aryl-3-p-toluenesulfonoxy norbornane. A discussion pertaining to the relationship of dihedral angle between leaving groups and the rate of elimination concerning the cyclopentyl, cyclohexyl and norbornyl systems mentioned above and recent data on the analogous cyclobutyl system will be presented in a later section of this dissertation.

Bordwell[56] has reported the rate of cis-elimination of 1-phenyl-1-acetoxy-2-nitrocyclohexane to be four times that of trans-elimination in the base-solvent system of piperidine, chloroform and ethanol. The difference in rates can be explained as being due to steric hindrance of carbanion formation by the attacking base and steric assistance by the nitro group. The Hammett rho-value for the alpha-carbon is +1.45 for both isomers. The deuterium isotope effect is also the same for both isomers as are the thermodynamic activation parameters and salt effects. Bordwell considers this to be the first system in which both cis- and trans-elimination proceed through a carbanion intermediate.

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[55]Beckman, J. A., "Concerted Cis and Trans Bimolecular Eliminations in the Bicyclo(2.2.1.) Heptane System", Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1965.

[56]Bordwell, op. cit., p. 2496.

In general, if a bond to a given element or its heavier isotope is broken in the rate controlling step of a reaction, the rate constant for the reaction involving the lighter isotope exceeds the rate constant for the same reaction of the corresponding heavier isotope compound. Westheimer[57] has presented the modern theory of deuterium isotope effects in a recent review article. The ratio of the rate constant for an elimination involving hydrogen to the rate constant for the same reaction involving deuterium, k_H/k_D, has been employed to gain insight as to the degree of C-H bond breaking in the transition state.

The ratio, k_H/k_D, will be near unity for "nearly E_1" or "nearly E_{1CB}" transition states and will approach a maximum value for an E_2 transition state in which the hydrogen is one-half transferred. This maximum is calculated to be seven at 25° from the consideration of changes in zero point energy in going from reactants to the activated complex. Wiberg[58] has recently observed k_H/k_D to be 12.1 for the chlorination of methane at 0° and suggests this high value (12.1 compared to 7) emphasized the importance of considering the symmetry of the activated complex in discussing the magnitude of an isotope effect.

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[57] Westheimer, F. H., Chem. Revs., 61, 265 (1961).

[58] Wiberg, K. B., and E. L. Motell, Tetrahedron, 19, 2009 (1963).

Shiner and Smith[59] observed the deuterium isotope effect for the elimination of ethyltrimethylammonium bromide to be four at 137° (ca. 5.6-6.5 at 50°) and concluded the reaction occurred by a highly synchronous process.

From the previous discussion, one sees the possibility that a given value of k_H/k_D may arise from one of two conditions, one when the transition state is on the "nearly E_1" side of "central E_2" and the other when the transition state resembles something between "central E_2" and "nearly E_{1CB}". To help resolve this ambiguity, Bunnett[60] has proposed the use of Hammett sigma-rho in concert with deuterium isotope effect. A value of k_H/k_D near unity and a low rho for the beta-carbon should be observed for eliminations having transition states on the "nearly E_1" side of "central E_2". Reactions with transition states lying on the "nearly E_{1CB}" side of "central E_2" should also have values of k_H/k_D near unity but should exhibit high values for rho. The isotope effect for leaving groups is less complicated since the magnitude of the ratio of the rate constant involving the lighter isotope to the rate constant for the some reaction involving the heavier isotope depends only on the extend of C-X bond breaking.

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

[60]Bunnett, op. cit., p. 225.

Bourns[61] has studied the elimination of beta-phenylethyltrimethylammonium bromide with ethoxide and found k_H/k_D equal to 3.0, k_{14_N}/k_{15_N} to be 1.009 and a value of +3.77 for rho (all measurements at 60°). The observed nitrogen isotope effect is approximately one-third the calculated maximum and indicates a small amount of C_{alpha}-N bond breaking in the transition state. The values of rho and k_H/k_D suggest a greater amount of C_{beta}-H bond breaking. The conclusion that this reaction proceeds through a transition state with considerable E_{1CB} character is quite reasonable. Saunders[62] has found k_H/k_D = 5.9, rho = +2.21 and k_{32_S}/k_{34_S} = 1.0015 for the elimination of beta-phenylethyldimethylsulfonium bromide at 30° and assumed the reaction to be "nearly E_{1CB}" in nature. The value of k_{32_S}/k_{34_S} is small when compared to 1.018 for the same ratio in the S_N1 reaction of t-butyldimethylsulfonium ion. This data shows that the breaking of the C-N bond is further advanced in the transition state than the C-S bond. In other words, the elimination of trimethylammonium bromide proceeds by a more concerted mechanism than dimethyl sulfonium bromide.

Bunnett[63] has proposed that the bimolecular elimination

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[61] Ayrey, G., A. N. Bourns and V. A. Vyas, Can. J. Chem., 41, 1759 (1963).

[62] Saunders, W. H., Jr., and D. H. Edison, J. Chem. Soc., 82, 138 (1960) and papers cited therein.

[63] Bunnett, J. F., G. T. Davis and H. Tanida, J. Am. Chem. Soc., 84, 1606 (1962).

of benzyldimethylcarbinyl chloride proceeds via a mechanism on the "nearly E_1" side of "central E_2". His argument is based on a small deuterium isotope effect, $k_H/k_D = 2.6$, and only a slight rate enhancement due to a beta-phenyl substituent.

The roles played by the base and solvent in an E_2 elimination are rather difficult to evaluate. Polar solvents enhance the formation of ions from a neutral reactant and, as a result, may shift the transition state toward "nearly E_1". Also, better solvation of the leaving group will facilitate C-X bond breaking in the transition state. Cram[64] attributed the change in mechanism from "nearly E_1" towards "central E_2" in the 1-X-1,2-diphenyl propane system which accompanied the change in base-solvent system from ethoxide in ethanol to t-butoxide in t-butyl alcohol to be due to the differences in base strength. Bunnett[65] discusses the same data from the stand point of effects due to changing solvent and leaving groups.

In most investigations of E_2 eliminations the conjugate acid of the base is used as the solvent. For this reason there is very little data concerning a given base in a variety of solvents. However, data of this nature might

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[64]Cram, D. J., F. D. Green, and C. H. DePuy, J. Am. Chem. Soc., 78, 790 (1956).

[65]Bunnett, op. cit., p. 225.

be of questionable value since a change in solvent not only alters base strength but solvation properties as well. Froemsdorf has shown that the products obtained from the elimination of 2-butyl p-toluenesulfonate and bromide to be sensitive to solvent effects alone.[66] Schrieseim[67] has reported data from the elimination of aliphatic sulfoxides with t-butoxide in dimethyl sulfoxide which shows the reaction to be E_2 in nature. However, the reactions proceeded with such velocity that reproducible data were not obtained.

Predictions of kinetic efficiency as a function of thermodynamic base strength appear to be impossible in view of the available data. P. B. de la Mare and Vernon[68] reported sodium thiophenoxide to be ten times more effective than sodium phenoxide or ethoxide in prompting the elimination from t-butyl chloride. This in direct contrast to base strengths, phenoxide and ethoxide being stronger bases than thiophenoxide. Bunnett[69] has shown sodium thioethoxide to be seven times more effective than sodium ethoxide in the

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[66] Froemsdorf, D. H., and M. E. McCain, J. Am. Chem. Soc., 87, 3983 (1965) and Froemsdorf, D. H., M. E. McCain, W. W. Wilkison, J. Am. Chem. Soc., 87, 3984 (1965).

[67] Hofmann, J. E., T. J. Wallace and A. Schrieseim, J. Am. Chem. Soc., 86, 1561 (1964).

[68] de la Mare, P. B. D., and C. A. Vernon, J. Chem. Soc., 41 (1956).

[69] Bunnett, op. cit., p. 1606.

elimination of benzyldimethylcarbinyl chloride. His explanation for the observed results concerns thermodynamic and kinetic properties. He suggests that alkoxide or hydroxide has a greater thermodynamic affinity for hydrogen or carbon whereas thiophenoxide has a greater kinetic reactivity than alkoxide ions toward hydrogen or carbon[70]. In E_2 eliminations which are "nearly E_1" thioethoxide is a more effective base than methoxide.

Smith[71] has suggested a relationship between the ratio of rate constants determined with ethoxide and t-butoxide, respectively. The rate of a reaction with a transition state on the E_{1CB} side of "central E_2" should be influenced considerably by the strength of the base. Solvation plays a minor role in reactions having very little C-X bond breaking in the rate determining step. The overall effect of a change in solvent-base system on the rate of an elimination having a "nearly E_1" transition state may be slight. It is possible that rate enhancement due to solvation may be compensated for by the decreased ability of the base to remove the beta-hydrogen when changing from t-butoxide-t-butyl alcohol to ethoxide-ethanol.

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[70]Bunnett, J. F., C. F. Hauser and K. V. Nahahedian, Proc. Chem. Soc., 305 (1961).

[71]Smith, op. cit.

Winstein[72] proposed the merged bimolecular elimination and substitution mechanism to account for the olefinic products in the reactions of trans-4-t-butyl cyclohexyl p-toluenesulfonate with halide ions in acetone. Eliel[73] suggested that such a mechanism may be involved in the eliminations from butyl and cyclohexyl bromides and p-toluenesulfonates with thiophenoxide and hydroxide. Winstein[74], at a later date, submitted that merged eliminations are probably E_2 eliminations induced by the thermodynamically weak bases. However, several authors have considered the merged elimination to be an actuality. Bordwell[75] recently proposed that such a mechanism is operative in the elimination of cis-4-methyl-4-phenylcyclohexyl p-toluenesulfonate with potassium t-butoxide. Csapilla[76] in 1964 advanced a "new mechanistic interpretation of E_2 reactions" which is a further extension of the merged elimination. Bunnett[77] has

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[72]Winstein, S., D. Darwish, and N. J. Holness, J. Am. Chem. Soc., 78, 2915 (1956).

[73]Eliel, E. L., and R. G. Haher, J. Am. Chem. Soc., 81, 1249 (1959) and E. L. Eliel, and R. S. Ro, J. Am. Chem. Soc., 79, 5995 (1957).

[74]Winstein, S., Abstract of the 144th Am. Chem. Soc., Meeting, Los Angeles, California, 1963, 8M.

[75]Bordwell, F. G., and A. Adbun-Nur, J. Am. Chem. Soc., 86, 5695 (1964).

[76]Csapilla, op. cit., p. 37.

[77]Bunnett, op. cit., p. 225.

argued quite convincingly that the data submitted as evidence for a merged elimination can more aptly be explained by invoking an E_2 mechanism.

The influence of the leaving group on the mechanistic pathway of an E_2 elimination has received considerable attention. Saunders[78] and DePuy[79,80] have found cases in which rho for the beta-carbon varies with the leaving group which indicates that the leaving group is a factor in determining the degree of C-H bond breaking in the transition state.

The role of the p-toluenesulfonoxy moiety as a leaving group seems to be somewhat ambiguous. As a rule, the order of facility for S_N2 and S_N1 reactions is OTos > I > Br > Cl while for the elimination of HX from beta-phenylethyl derivatives is I > Br > OTos > Cl. DePuy and Bishop[81] have shown that the above order of ease of elimination of bromide and p-toluenesulfonoxy may be reversed. The ratio of the rate of elimination of beta-phenylethyl bromide to the rate of elimination of the corresponding tosylate to be 3.4. However, $k_{Br}/k_{OTos} = 0.77$ for the secondary butyl system and k_{Br}/k_{Otos}

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[78]Saunders, W. H., Jr., and R. A. Williams, J. Am. Chem. Soc., 79, 3712 (1957).

[79]DePuy, op. cit, p. 2532.

[80]Banthrope, op. cit.

[81]Bishop, C. A., and C. H. DePuy, Chem. and Ind., 297 (1959).

is equal to 0.33 for the n-propyl system. Smith[82] has found the elimination rate ratio of cyclopentyl bromide to tosylate to be 0.49.

Bishop[83] suggests that the facility of the tosylate moiety as a leaving group parallels the amount of C-X bond breaking in the transition state. The partial negative charge which develops on the anionic leaving group can be stabilized by resonance. Smith mentions the possibility of the tosylate group being involved in a cyclic state and actually aid in abstraction of the beta-hydrogen. Such a concept is not unfounded. Curtin[84] has developed the idea of a cyclic transition state involving the leaving group in the E_2 elimination of 1,2-diphenylethyl acetates.

The ratio of k_{Br}/k_{OTos} may serve as an added means of differentiating E_2 transition states. It is proposed that tosylate will be a better leaving group compared to bromide in "nearly E_1" eliminations in which tosylate will exhibit its greater ability to stabilize the forming anion, and in "nearly E_{1CB}" in which the tosylate group will be more effective in stabilizing a partial negative charge in the

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[82] Smith, op. cit.

[83] Bishop, C. A., "Pyrolytic and Base-Catalyzed Elimination Reactions", Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1961.

[84] Curtin, D. Y., and D. B. Kellom, J. Am. Chem. Soc., 75, 6011 (1953).

beta position. In eliminations with a "central E_2" transition state the bromide ion should be a better leaving group. A limitation to this proposal is the fact that transition states on either side of "central E_2" may give rise to the same value for k_{Br}/k_{OTos}. Other criteria such as Hammett sigma-rho or effect of changing the solvent-base system may need to be considered to get a better picture of the transition state.

RESULTS AND DISCUSSION

Early discussions concerning bimolecular eliminations have been based on the premise that trans co-planarity of leaving groups is a necessary condition for a concerted elimination[85,86,87,88]. If an elimination were observed from a system in which this arrangement was physically impossible or highly improbable, some mechanism other than a concerted one was assumed to be operative. The dehydrochlorination of the beta-isomer of hexachlorobenzene in which all hydrogens and chlorines are cis to one another is such an example[89]. The rate of elimination from the beta-isomer was found to be 7,000 to 24,000 times slower than from the various other isomers, each of which have at least one trans relationship between H and Cl. The activation energy for the elimination from the beta isomer is 9-13 kcal. higher than that for elimination from any of the other isomers and suggests that the reactions are mechanistically different. Also, a small amount of deutrium exchange was observed when

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[85] Cram, op. cit., Chapter 6.

[86] Hine, op. cit., pp. 186-222.

[87] Bunnett, op. cit., p. 225.

[88] Banthrope, op. cit., Vol. 2.

[89] Cristol, op. cit., p. 338.

the reaction was carried out in deuterated solvent. Using these data as a basis, Cristol postulated that the dehydrohalogenation of the beta=isomer proceeds via an E_{1CB} mechanism, i.e., by complete removal of a proton followed by loss of halide. Recently, Hine[90] has investigated this problem and concedes that Cristol's earlier conclusions are most likely correct. Bordwell[91] has proposed that both the cis and trans elimination of acetic acid from the isomeric 1-phenyl-1-acetoxy-2-nitrocyclohexanes also proceed through a carbanion intermediate.

Numerous other examples of cis elimination are on record. Cristol[92] found the cis bimolecular elimination of HCl from d,l-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene (I) to be eight times faster than trans elimination from the corresponding meso isomer (II) (Fig. 9). Kwart and co-workers[93] have cited an example of a preferred cis elimination from 2-exo-bromo-3-exo-d-norbornane (VI) in which the product is almost exclusively that resulting from loss of deuterium bromide. This observation may be the resultant of steric

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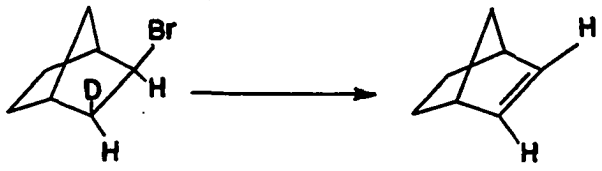
[90]Hine, op. cit., p. 3894.

[91]Bordwell, op. cit., p. 2496.

[92]Cristol, op. cit., p. 2193.

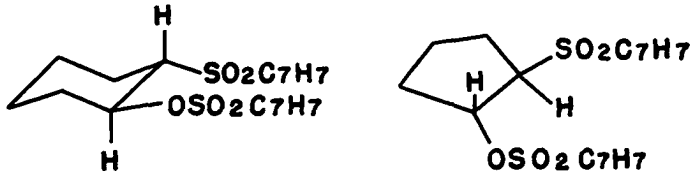
[93]Kwart, op. cit., p. 2606.



VI

Fig. 12. Halonorbornane

factors with preferential attack of the exo-H since LeBel[94] has found hydrogen chloride to be eliminated from trans-endo-2-bromo-3-chloronorbornane (IV) instead of the expected hydrogen bromide. LeBel has presented evidence which indicates that this elimination is concerted. Bordwell[95] and Goering[96] have also observed bimolecular cis eliminations from cyclohexyl (VII) and cyclopentyl (VIII) tosyloxysulfones.



VII VIII

Fig. 13. Cycloalkyl tosyloxysulfones

In most of the examples cited above the seemingly facile cis eliminations have been explained in terms of retardation of trans elimination due to involvement of a rigid ring

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[94]LeBel, op. cit., p. 4144.

[95]Bordwell, op. cit., p. 1141.

[96]Goering, H. L., D. I. Relgea and K. L. Howe, J. Am. Chem. Soc., 79, 2502 (1957).

system or because the hydrogen lost by cis-elimination is more acidic than the hydrogen which would have been lost to give trans-elimination. cis-E_2 eliminations, as a rule, have been found to occur considerably slower and require more forceful conditions as compared to trans eliminations from systems which can easily achieve the requisite stereo-relationships. However, DePuy and co-workers[97] and Smith[98] have recently reported the first example of a rapid concerted cis E_2 elimination from their investigations of the reactions of trans-2-arylcyclopentyl tosylates with potassium t-butoxide in t-butyl alcohol. These workers found elimination to occur smoothly at reasonably low temperatures.

Determination of the rates of elimination from cis- and trans-2-phenylcyclopentyl p-toluenesulfonates established the ratio of $k_{\text{trans } E_2}/k_{\text{cis } E_2}$ to be nine. The small value of this ratio is interesting when compared with data obtained by Cristol and Stermitz[99] who found that while trans E_2 elimination from cis-2-phenylcyclohexyl p-toluenesulfonate with potassium hydroxide was quite rapid, no cis-E_2 elimination could be observed from the corresponding trans isomer. DePuy and co-workers[100] further substantiated

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[97] DePuy, op. cit., p. 1314.

[98] Smith, op. cit.

[99] Cristol, S. J., and F. R. Stermitz, J. Am. Chem. Soc., 82, 4962 (1960).

[100] DePuy, C. H., G. F. Morris, J. S. Smith and R. J. Smat, J. Am. Chem. Soc., 87, 242 (1965).

these results with their observation that cis-2-phenylcyclohexyl p-toluenesulfonate eliminated quite easily with potassium t-butoxide in t-butyl alcohol at 50° but no reaction was observed with trans-2-phenylcyclohexyl p-toluenesulfonate after 22 days. They estimated the ratio of $k_{trans\ E_2}/k_{cis\ E_2}$ to be greater than 10^4. DePuy et al., concluded that cis elimination from the cyclopentyl system involves an E_2 mechanism since one would not expect such a drastic difference between the five- and six-membered ring compounds if a carbanion mechanism was involved. And since the hydrogen being removed in both the cyclopentyl and cyclohexyl cases occupies an "axial" position (Fig. 14) it is unlikely that the observed differences in rates of cis elimination are the resultant of steric interactions.

Fig. 14. Cycloalkyl p-toluenesulfonates

One is then left to consider the differences in stereoelectronic configuration of the leaving groups in the two ring systems. Previous work by Bordwell and Landis[101] and DePuy et al. has lead to the contention that the configuration

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

exhibiting the more facile cis E_2 elimination will be that which allows the leaving groups to be cis and co-planar in the transition state. A further extention of this idea has been presented by DePuy concerning the relationship of the dihedral angle between leaving groups and the rate of elimination. As stated, a plot of the rate of elimination versus dihedral angle would exhibit maxima at 0° and 180° and a minimum at 90°.

To achieve a cis and co-planar relationship between the leaving groups in the case of trans-2-phenylcyclohexyl p-toluenesulfonate one finds it necessary to involve the energetically unfavorable boat form of the cyclohexyl ring (Fig. 15). In the case of the nearly planar five-membered

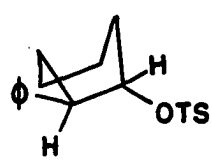

Fig. 15. Cyclohexyl ring in boat form

ring no energy barrier of this magnitude need be overcome to obtain the proposed desirable orientation of leaving groups. This consideration of the energetics of the transition state may explain the observed differences in the ease of cis-elimination from trans-2-phenylcyclopentyl and trans-2-phenylcyclohexyl p-toluenesulfonate. Beckman[102] has

[102]Beckman, op. cit.

reported cis elimination to occur readily from trans-2-aryl-3-p-toluenesulfonoxy norbornane (Fig. 16) with potassium

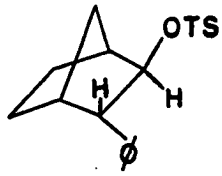

Fig. 16. p-Toluenesulfonoxy norbornane t-butoxide in t-butyl alcohol. In this case the leaving groups are held in a cis and co-planar configuration due to the rigidity of the norbornane ring system.

This dissertation presents an extension of the previous investigations of E_2 eliminations involving cyclic systems which include the beta-phenylethyl moiety. As both the cyclohexyl and cyclopentyl systems have been studied the cyclobutyl system was an obvious problem to consider. Therefore, the rates of elimination from cis- and trans-2-arylcyclobutyl p-toluenesulfonates were examined.

The preparation of the desired trans-2-arylcyclobutyl alcohols was straight forward with only minor difficulties encountered in one step of the synthetic route. Chart 1 gives a schematic of the method employed.

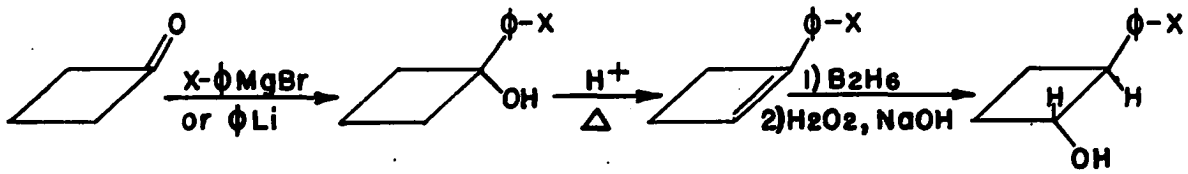

Chart 1. Schematic for trans alcohols

Attempts to dehydrate 1-phenylcyclobutanol in a solvent, methylene chloride, cyclohexane or benzene, with a catalytic amount of p-toluenesulfonic acid present failed to yield the desired cyclic olefin[103]. Dehydration was carried out by heating the pure alcohol with a few milligrams of p-toluenesulfonic acid at reflux under high vacuum for a short period of time and then increasing the heat input to effect distillation of the cyclic olefin. The olefins obtained by this procedure were quite pure as shown by gas phase chromatography and N.M.R. The yields of the trans alcohols prepared by hydroboration of the cyclic olefins were high and the compounds were shown to be isomerically pure by gas phase chromatography.

The preparation of the cis isomers of 2-arylcyclobutanol was somewhat more involved. These isomers could be prepared by oxidizing the corresponding trans alcohol to the ketone with subsequent reduction to the cis alcohol. This route was not chosen due to an insufficient amount of the necessary trans alcohols and also, the reported yield of the ketone from the oxidation reaction is marginal. However, the route chosen which is outlined in Chart 2 was lengthy and time-consuming. Perhaps one factor which lead to the choice of

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[103]The N.M.R. of the olefinic material recovered was identical with that of styrene. This interesting observation was not investigated further.

the latter route over the former was the involvement of the not-too-common cyclization to yield a four-membered ring. Although the cyclization was not original with this author it was felt that further investigation of this interesting reaction would be valuable.[104]

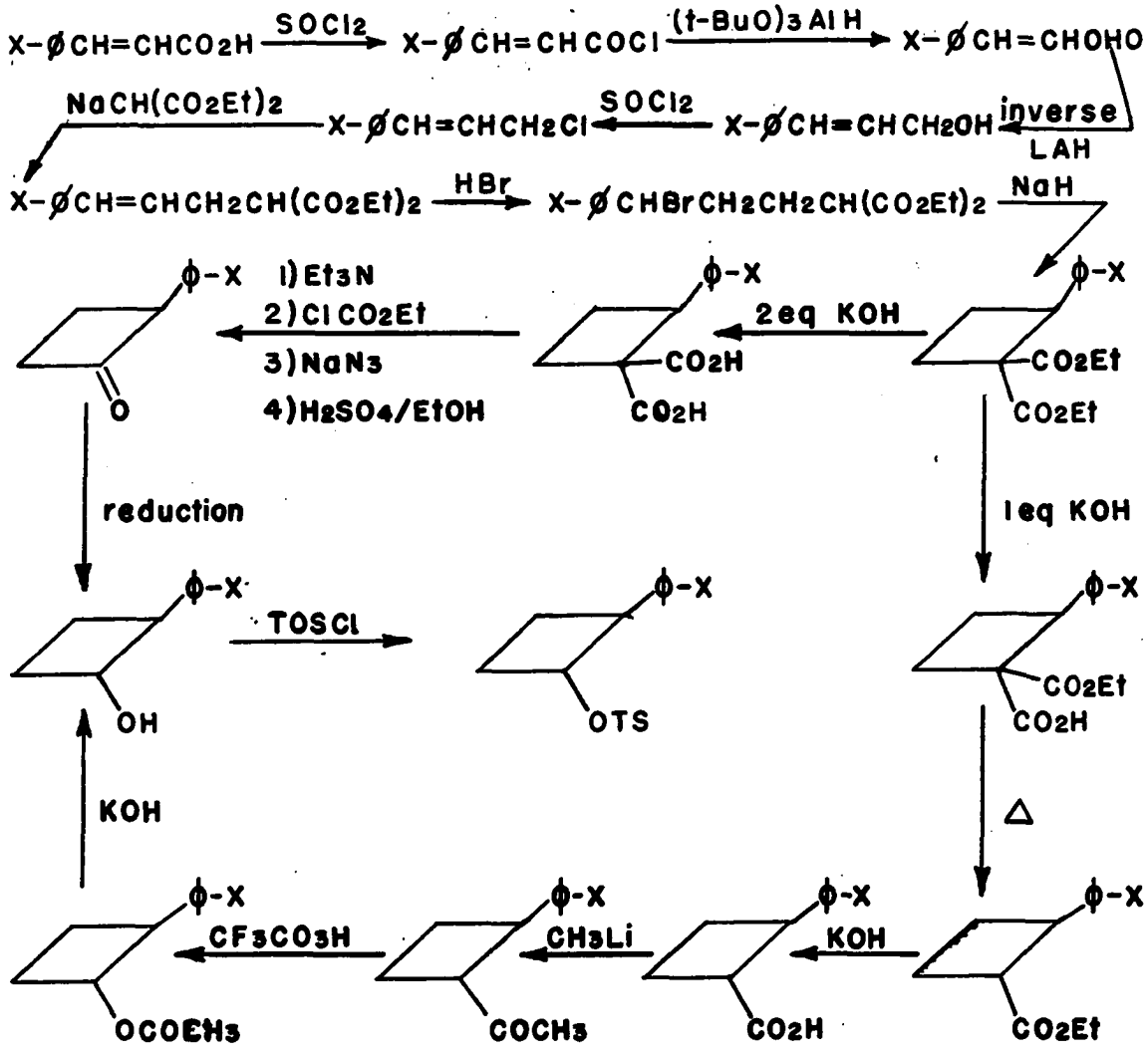

Chart 2. Schematic for cis compounds

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[104]Beard, C., and A. Burger, J. Org. Chem., 26, 2335 (1961).

cis-2-Phenylcyclobutanol was synthesized by the Raney nickel reduction of 2-phenylcyclobutanone. This reaction gave a mixture of 45% cis- and 55% trans-2-phenylcyclobutanol as determined by gas phase chromatography. This result was surprising in view of the fact that reduction of 2-phenylcyclopentanone with the same catalyst gives a 79% cis and 21% trans mixture of alcohols[105]. One finds it difficult to explain the results for the cyclobutyl case by invoking any argument concerning stereochemical control. It may be possible that the cis alcohol is first formed but isomerizes to the thermodynamically more stable trans alcohol while on or near the catalyst surface. Once the trans alcohol is formed it may not be as readily re-absorbed on the catalyst as the cis alcohol which would allow preferential isomerization of the cis alcohol and could explain the greater percentage of trans alcohol which was formed. This author does not feel that the mixture obtained is necessarily the equilibrium composition as the catalyst was removed very soon after the requisite amount of hydrogen had reacted. However, the equilibrium composition was not determined and it seems that this point would be worthy of further investigation.

cis-2-(p-Chlorophenyl)cyclobutanol was prepared by

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[105]Smat, R. J., "Synthesis and Elimination Reaction of Cyclopentanol and its Derivatives", Unpublished M.S. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa, 1962.

the Baeyer-Villiger oxidation of an isomeric mixture of 2-(p-chlorophenyl) cyclobutyl methyl ketone with subsequent saponification of the ester and separation of the resulting isomeric alcohols by spinning band distillation. The cis-m-Cl and p-CH_3 substituted 2-arylcyclobutanols were prepared by hydride reduction of the corresponding ketones which yielded a cis-trans mixture of alcohols. The isomeric alcohols were then separated by spinning band distillation. Assignments of the cis and trans alcohols by gas phase chromatography were based on comparison of retention times with those of known samples of trans alcohols. In all cases the samples of cis alcohol were determined to be greater than 98% isomerically pure by gas phase chromatography. The alcohols were converted to the desired p-toluenesulfonates by Tipson's method[106]. The p-toluenesulfonates were obtained as colorless solids and remained as such at 10° for an indefinite period. Aliquots of a given tosylate-base solution were withdrawn from a constant temperature bath at various time intervals and the progress of the reaction was followed either titrimetrically (second-order) or spectrophotometrically (psuedo-first-order). The data obtained in this manner were applied to the appropriate rate law equation to determine the rate constants.

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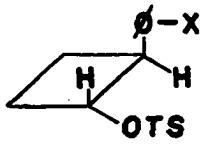
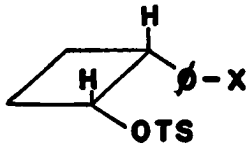
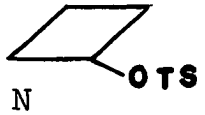
[106]Tipson, R. S., J. Org. Chem., 9, 235 (1944).

cis-Elimination from the *trans*-2-arylcyclobutyl *p*-toluenesulfonates was found to occur smoothly at 50° in potassium *t*-butoxide-*t*-butyl alcohol to give a quantitative yield of the corresponding 1-arylcyclobutene. The reactions of *trans*-2-phenyl- and *trans*-2-(*p*-chlorophenyl)cyclobutyl *p*-toluenesulfonates under the above conditions were found to give good second-order kinetics when followed titrimetrically. The fact that the second-order rate law applies to indicative that one is dealing with a bimolecular reaction.

Once the molecularity of the reaction was established the eliminations of the remaining *trans* *p*-toluenesulfonates were followed spectrophotometrically. All rate constants for the *trans* E_2 reactions were determined from spectrophotometric data with the exception of that of cyclobutyl *p*-toluenesulfonate which was obtained titrimetrically. The rate constants for the reaction of a number of *p*-toluenesulfonates in potassium *t*-butoxide-*t*-butyl alcohol solution are given in Table 1 along with data for 2-phenylethyl *p*-toluenesulfonate for comparison.

There are two reasons for believing that the formation of 1-phenylcyclobutene from *trans*-2-phenylcyclobutyl *p*-toluenesulfonate in basic solution is indeed a *cis* elimination. First, it was necessary to increase the temperature from 50° to 70° to cause the rate of reaction of cyclobutyl *p*-toluenesulfonate to be rapid enough to allow measurement.

Table 1. Rate constants for the eliminations from p-toluenesulfonates in potassium t-butoxide-t-butyl alcohol solution

X	E_2 type	Base conc.	Temp., °C	k_2[a] x 10^4, l. $mole^{-1}$ sec^{-1}
				
p-CH_3	cis	0.1 N	50	2.26 ± 0.05
p-CH_3	cis	0.3 N	50	2.12 ± 0.02
p-H	cis	0.1 N	50	5.10 ± 0.13
p-H	cis	0.1 N	70	33.00 ± 1.00
p-Cl	cis	0.1 N	50	28.30 ± 0.50
m-Cl	cis	0.1 N	50	88.60 ± 1.70
				
p-CH_3	trans	0.1 N	50	4.36 ± 0.09
p-H	trans	0.1 N	30	2.49 ± 0.08
p-H	trans	0.1 N	50	13.00 ± 0.20
p-Cl	trans	0.1 N	50	31.30 ± 0.40
m-Cl	trans	0.1 N	50	75.30 ± 1.00
				
	trans[b]	0.1 N	70	0.89 ± 0.06[c]
		ϕCH_2CH_2OTS		
	trans[b]	0.1 N	50	110.00 ± 4.00[d]

[a]Calculated from pseudo-first-order rates followed spectrophotometrically.

[b]Presumably.

[c]Second-order rate.

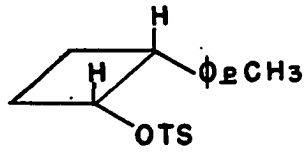
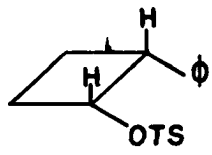
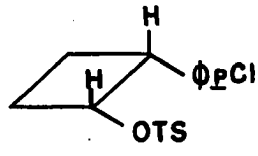
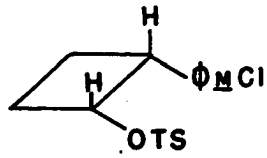
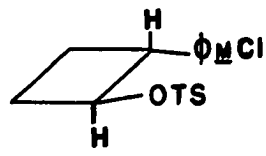
[d]DePuy, C. H., and C. A. Bishop, J. Am. Chem. Soc., 82, 2532 (1960).

If in the trans-2-aryl case the proton were being removed from the 3-position first, followed by rearrangement to the conjugated olefin it would seem unlikely that there would be such a difference in the rates of reaction. Secondly, there was a moderately large substituent effect on the rate of reaction of trans-2-arylcyclobutyl p-toluenesulfonates which indicates elimination occurs directly toward the aromatic ring.

The cis-2-arylcyclobutyl p-toluenesulfonates gave trans E_2 reactions in ethanol-sodium ethoxide solution. The results of this investigation are summarized in Table 2. The cis E_2 elimination from trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate in sodium ethoxide-ethanol was also examined. Since this compound gave the fastest E_2 reaction the E_2/E_1 ratio should be a maximum. There was evidence that solvolysis occurred with the sodium ethoxide-ethanol solution as the yields of olefin were less than 100%. There was no attempt made to determine the amount of olefin formed by solvolysis. However, measures were taken to maximize the E_2/E_1 ratio by carrying out the reactions under pseudo-first-order conditions and increasing the base concentration by a factor of two. When a more highly concentrated base solution was used the originally colorless reaction mixture turned an orange-red color within a short period of time which made spectrophotometric measurements meaningless.

Although cis-2-phenylcyclobutyl p-toluenesulfonate

Table 2. Rate constants for elimination from p-toluenesulfonates in sodium ethoxide-ethanol solution at 50°

Compound	E_2 type	Base conc.	k_2[a] x 10^4 l. mole^{-1} sec^{-1}
	trans	0.2 N	0.98 ± 0.06
	trans	0.2 N	1.16 ± 0.04
	trans	0.2 N	2.57 ± 0.03
	trans	0.2 N	4.54 ± 0.02
	cis	0.2 N	0.56 ± 0.01

[a]Calculated from psuedo-first-order rates followed spectrophotometrically.

Table 2 (Continued)

Compound	E_2 type	Base conc.	$k_2 \times 10^4$ l. mole^{-1} sec^{-1}
ϕCH_2CH_2OTs	trans[b]	0.1 N	3.8[c]
$m\text{-}Cl\phi CH_2CH_2OTs$	trans[b]	0.1 N	26.7[d]

[b]Presumably.

[c]DePuy, C. H., G. F. Morris, J. S. Smith and R. J. Smat, J. Am. Chem. Soc., 87, 242 (1965).

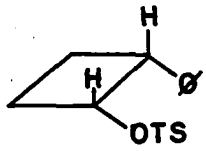
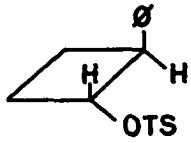
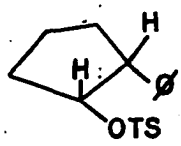
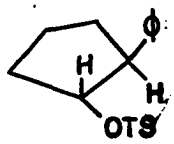
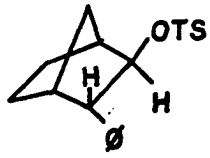
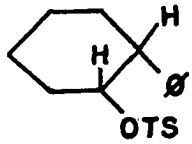
[d]Calculated from DePuy, C. H., G. F. Morris, J. S. Smith and R. J. Smat, J. Am. Chem. Soc., 87, 242 (1965).

reacted more rapidly than trans-2-phenylcyclobutyl p-toluenesulfonate in potassium t-butoxide-t-butyl alcohol solution, the rate ratio was only 2.5. This is another example of a rapid cis E_2 elimination which is nearly as fast as a trans E_2 reaction from the same system. DePuy et al.[107] reported the first example of such a reaction with data from the cyclopentyl system. In their case the ratio of $k_{trans\ E_2}/k_{cis\ E_2}$ was nine (Table 3).

Another interesting aspect of the present work was uncovered with the examination of the reactions of cis- and trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonates.

[107]DePuy, op. cit., p. 1314.

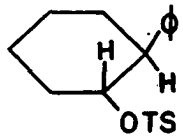
Table 3. Rate ratios and comparison of rate constants with varying base-solvent systems at 50°

	E_2 type	Base/Solvent	$k_2 \times 10^4$ l. mole^{-1} sec^{-1}	k_{trans}/k_{cis}
	trans	EtONa/EtOH	1.16	
	trans	t-BuOK/t-BuOH	13.00	
	cis	t-BuOK/t-BuOH	5.10	2.5
	trans	EtONa/EtOH	24.2[a]	
	trans	t-BuOK/t-BuOH	26.4[a]	
	cis	t-BuOK/t-BuOH	2.9[a]	9.1
	cis	t-BuOK/t-BuOH	13.6[b]	
	trans	t-BuOK/t-BuOH	1.93[a]	

[a]DePuy, C. H., G. F. Morris, J. S. Smith and R. J. Smat, J. Am. Chem. Soc., 87, 242 (1965).

[b]Beckman, J. A., "Concerted Cis and Trans Bimolecular Eliminations in the Bicyclo(2.2.1.) Heptane System", Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1965.

Table 3 (Continued)

	E_2 type	Base/Solvent	$k_2 \times 10^4$ l. mole^{-1} sec^{-1}	k_{trans}/k_{cis}
	cis	t-BuOK/t-BuOH	no reaction after 22 da.	$< 10^4$
ϕCH_2CH_2OTS	trans	t-BuOK/t-BuOH	110.00[c]	
	trans	EtOHa/EtOH	3.8[a]	

[c]DePuy, C. H., and C. A. Bishop, J. Am. Chem. Soc., 82, 2532 (1960).

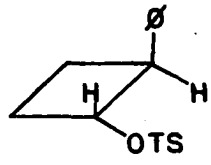
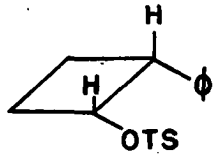
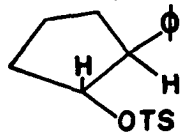
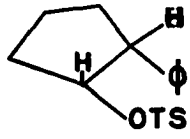
This is an example of a rapid cis E_2 elimination which is faster than the trans E_2 elimination from the same system.

Incorporation of the beta-phenylethyl moiety into the cyclobutyl ring gives a 4-fold reduction in the rate of trans elimination in potassium t-butoxide-t-butyl alcohol solution[108]. A decrease in rate of elimination by a factor of one-half is observed in sodium ethoxide-ethanol solution.

The Hammett rho-value (Table 4) for the trans elimination from the cyclobutyl system is greater in t-butyl alcohol solution (rho = 2.2) than in ethyl alcohol solution (rho = 1.3)

[108]A statistical correction of two must be applied to the beta-phenylethyl system since there are twice as many beta-hydrogens available for removal.

Table 4. Hammett correlation of rates and enthalpies and entropies of activation for the beta-elimination of 2-arylalkyl p-toluenesulfonates

Compound	E_2 type	Base/Solvent	rho[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]
	cis	t-BuOK/t-BuOH[d]	2.90±0.06	19.7	-12.9
	trans	t-BuOK/t-BuOH[d]	2.18±0.04	17.0	-21.3
	trans	EtONa/EtOH[e]	1.26±0.06		
	cis	t-BuOK/t-BuOH[d]	2.77±0.04	17.6	-18.1[f]
	trans	t-BuOK/t-BuOH[d]	1.48±0.09	15.1	-21.7[f]
	trans	EtONa/EtOH[e]	0.99±0.006[f]		
	trans	t-BuOK/t-BuOH[d]	3.39±0.29	14.7	-25.2[g]
ϕCH2CH2OTS	trans	EtONa/EtOH[d]	2.27±0.08	20.4	-11.2[f]

[a] At 50° and calculated by method of least squares.

[b] In kcal. mole^{-1}.

[c] In cal. mole^{-1} deg.$^{-1}$.

[d] 0.1 N base.

[e] 0.2 N base.

[f] DePuy, C. H., G. F. Morris, J. S. Smith and R. J. Smat, J. Am. Chem. Soc., 87, 242 (1965).

[g] DePuy, C. H., and C. A. Bishop, J. Am. Chem. Soc., 82, 2532 (1960).

and both are smaller than the corresponding values for beta-phenylethyl p-toluenesulfonate (rho = 3.4 in t-butyl alcohol and 2.3 in ethanol). Based on these rho-values and the effect of solvent on the rate of reaction one would place the trans E_2 elimination from the arylcyclobutyl system near "central E_2" on the E_2 elimination scale[109]. Smith[110] found the rates of trans elimination for cis-2-phenylcyclopentyl p-toluenesulfonate in potassium t-butoxide-t-butyl alcohol or sodium ethoxide-ethanol at 50° to be nearly equal (Table 3). For this reason he placed a considerable amount of importance on the C-O bond breaking in the transition state as the decrease in base strength of ethoxide was seemingly compensated for by the better solvation power of ethanol. Breaking of the C-O bond in the trans elimination for the cyclobutyl case must not be as significant since a 10-fold decrease in the rate constant was observed in going from t-butyl alcohol solution to ethanol solution. Reactions in t-butyl alcohol solution are shifted toward the E_{1CB} side of the E_2 scale and C-H bond breaking becomes more important. This is reflected in the increase of rho for t-butyl alcohol solution over ethanol solution. trans Eliminations from cis-2-arylcyclobutyl p-toluenesulfonates must have a

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[109] Bunnett, op. cit., p. 225.

[110] Smith, op. cit.

transition state involving more C-H bond breaking than the corresponding five-membered ring system (rho = 2.2 and 1.5 respectively).

A further importance is placed on C-H bond breaking in the cis elimination from trans-2-arylcyclobutyl p-toluenesulfonates as indicated by the larger rho-value (rho = 2.9). The cis E_2 reaction is slower by at least a factor of 100 in ethanol solution than in t-butyl alcohol based on the results involving trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate. The cis E_2 elimination from both trans-2-arylcyclobutyl and trans-2-arylcyclopentyl p-toluenesulfonates closely resembles the elimination from beta-phenylethyl p-toluenesulfonates in that the rho-values are comparable and all three systems are affected similarly by changes in solvent.

Arguments put forward by DePuy[111] defending a cis E_2 reaction from the trans-2-arylcyclopentyl system are applicable to the trans-2-arylcyclobutyl system. The reaction with the four-membered ring does have E_{1CB} character as shown by the Hammett rho-value of 2.9. However, this value does not seem large enough to indicate involvement of a carbanion mechanism in which the beta-proton is completely removed in the rate determining step. Reactions in which

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[111] DePuy, op. cit., p. 242.

benzyl carbanions are assumed to be involved have been examined by Szwarc[112]. He has found the Hammett rho-value to be near five in these cases. Eliminations from the beta-phenylethyl system have been reported with rho-values as high as four. Also, the conditions of the reaction necessary to cause cis-elimination from the trans-2-arylcyclobutyl system are mild and hardly seem forceful enough to produce a benzyl carbanion. A visual representation of the Hammett rho-values for the cyclobutyl system is given in Graph 1. The beta-aryl rho-values of the substituents examined are recorded in Table 5.

One may further conclude that the cis E_2 elimination from trans-2-arylcyclobutyl p-toluenesulfonate is highly concerted. Comparison of rho-values for trans-2-arylcyclobutyl p-toluenesulfonate (rho = 2.9) and beta-arylethyl p-toluenesulfonate (rho = 3.4) indicates the reaction of the cyclic system shares the same degree of concertedness as that of the open chain compound which is capable of assuming a trans co-planar configuration of the leaving groups.

The observation that trans-2-phenylcyclobutyl p-toluenesulfonate gives a rapid cis E_2 reaction lends support to the posutlation that cis co-planar stereo-relationship

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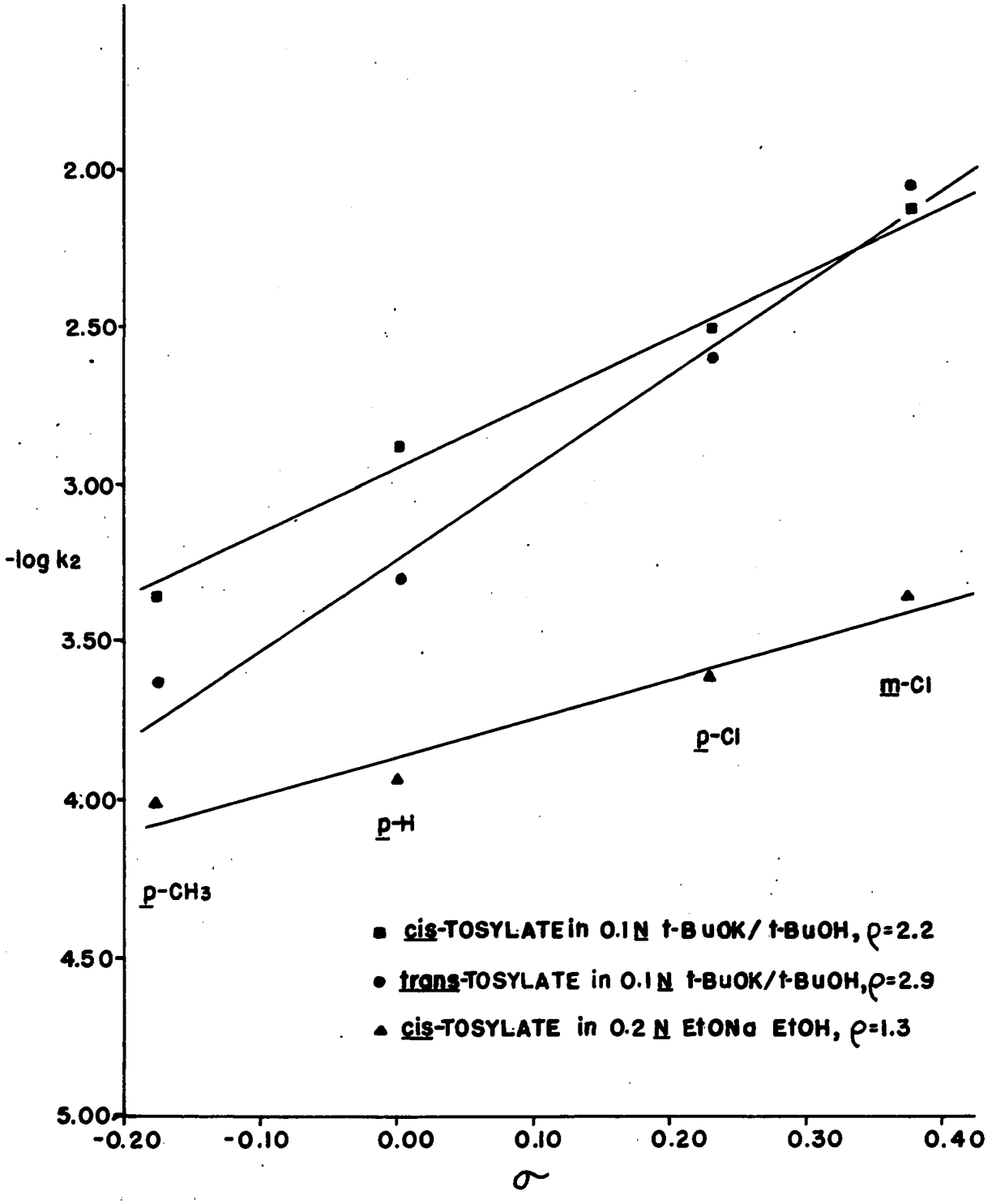
[112]Shima, op. cit., p. 1306.



Graph 1. Plot of - log k_2 vs. sigma for E_2 elimination from 2-arylcyclobutyl p-toluenesulfonates at 50°

Table 5. Hammett beta-aryl sigma values

Substituent	Sigma[a]
p-CH_3	-0.170
p-H	0.000
p-Cl	+0.227
m-Cl	+0.373

[a]Values obtained from Jaffe, H. H., Chem. Revs., 53, 191 (1953).

of leaving groups is also a favorable orientation which leads to elimination. Fast cis E_2 eliminations have been reported previously[113,114,115]. It is interesting to note that for trans-2-aryl-3-p-toluenesulfonoxy norbornane (Fig. 16) where the dihedral angle between leaving groups is rigidly held at 0°, the rate of elimination is more rapid than for either the corresponding cyclobutyl or cyclopentyl system (Table 3).

The dihedral angle between the leaving groups is also 0° in the planar configuration of the cyclobutyl and cyclopentyl ring systems (Fig. 17), however, there is evidence

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[113]DePuy, op. cit., p. 1314.

[114]Beckman, op. cit.

[115]DePuy, op. cit., p. 242.

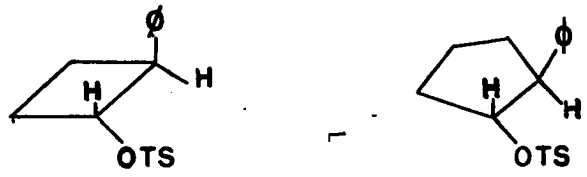

Fig. 17. Cycloalkyl p-toluenesulfonates

that both the four- and five-membered rings are puckered which would cause the dihedral angle between cis-1,2 groups to assume a value other than zero. The difference between the rates of elimination for these two systems may be an indication of the degree of non-planarity of the two rings.

The fact that trans-2-phenylcyclohexyl p-toluenesulfonate gives no elimination in potassium t-butoxide-t-butyl alcohol solution at 50° while the cyclobutyl, cyclopentyl and norbornyl analogs all readily react under these conditions adds further support to a cis E_2 elimination. It seems highly unlikely that the latter three examples would yield carbanions so much more easily than the former. In both cis and trans elimination from the cyclohexyl p-toluenesulfonates (Fig. 18) the hydrogen to be removed is in an

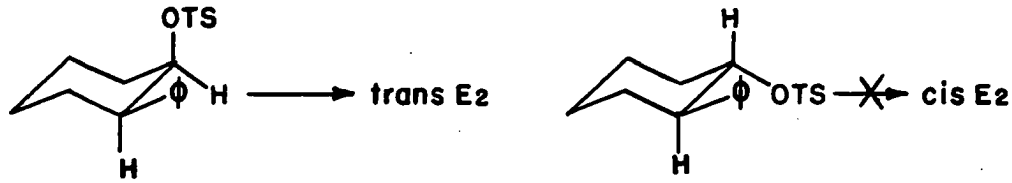

Fig. 18. Cyclohexyl p-toluenesulfonates

axial position which would indicate that steric factors are not the controlling influence.

The present work could be extended to examine further the validity of the conclusion that the trans-2-arylcyclobutyl p-toluenesulfonates do give cis E_2 eliminations. One could substitute the benzylic hydrogen with deuterium and determine if a kinetic isotope effect is observed. Smith[116] performed this experiment with trans-2-phenylcyclopentyl p-toluenesulfonate and found the ratio k_H/k_D to be 5.6 at 50° which is near the theoretical maximum at this temperature[117]. These data were interpreted as being evidence that C-H bond breaking is occurring in the transition state. If a carbanion were involved one would expect a smaller isotope effect, as the increase in energy necessary to break the C-H bond would be offset by the energy gained in forming the C-H bond with alkoxide upon complete proton transfer.

The transition state of the trans elimination from the cis-2-arylcyclobutyl system could be studied with respect to changing the leaving group. If the transition state does lie near "central E_2" on the E_2 scale of elimination the effect on the rate as a result of changing the leaving group should be slight. An enhancement of rate may be realized with

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[116] Smith, op. cit.

[117] Westheimer, op. cit., p. 265.

increased facility of the leaving group if the transition state is near the E_1 side of the E_2 scale.

Finally, the direction of the reaction from trans-2-phenylcyclobutyl p-toluenesulfonate could be investigated further by determining the stability of 3-phenylcyclobutene under the conditions which give rise to elimination. If 3-phenylcyclobutene were found to be unchanged under the conditions employed for elimination one could conclude that the benzylic hydrogen is removed in the transition state to give rise to the observed products.

EXPERIMENTAL

Preparation of Materials

Cyclobutanone

Cyclobutanone was purchased from Aldrich Chemical Company, Inc. and used without further purification.

Cyclobutanol Cyclobutanol was prepared by lithium aluminum hydride reduction of cyclobutanone. Cyclobutanone (5.0 gm., 0.07 mole) in 25 ml. anhydrous ether was added dropwise to a stirred solution of 0.83 gm. (0.021 mole) lithium aluminum hydride in 75 ml. anhydrous ether. After the addition was complete, the reaction was heated at reflux for one hour. Distilled water was added to destroy excess hydride and was followed by sufficient 10% sulfuric acid solution to dissolve solids. The two phases were separated and the aqueous phase was extracted with ether. The combined organic material was washed with water and dried over anhydrous magnesium sulfate. After filtering, the solution was concentrated using a rotary evaporator[118] at room temperature, and the residue was fractionated by distillation using a 10 cm. column packed with glass beads.

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[118] In all cases the rotary evaporator was operated at reduced pressure (water pump).

Cyclobutanol, 3.77 g. (74% yield), b.p. 124° (atmospheric pressure)[119]; lit. b.p. 125°[120].

IR: 2.75, 3.01, 3.37μ in carbon tetrachloride[121].

NMR: 1.87 (broad multiplet, 6 H), 4.11 (pentuplet with further splitting, 1 H), 4.72 (singlet, 1 H)[122].

1-Arylcyclobutanols The 1-arylcyclobutanols were prepared from the appropriate Grignard reagents or aryllithium reagents and cyclobutanone. Lithium wire (2.33 gm., 0.33 mole) was pounded into a thin ribbon, washed with anhydrous ether and added to a 250 ml. three-necked round bottom flask with 40 ml. dry ether. The flask was fitted with a condenser, mechanical stirrer and an addition funnel. The apparatus was equipped to accommodate a positive pressure of nitrogen. Bromobenzene (25.5 gm., 0.16 mole) in 40 ml. anhydrous ether was added, with stirring, at a rate sufficient to maintain gentle reflux. After the addition of the bromobenzene

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[119] All temperatures are in Centigrade degrees. Melting points and boiling points are uncorrected. Pressures are given in millimeters of mercury unless stated otherwise.

[120] Roberts, J. D., and C. W. Sauer, J. Am. Chem. Soc., 71, 3925 (1949).

[121] Infrared will be abbreviated as IR. All IR spectra were recorded on Perkin-Elmer Model 21 or Infra-Cord Spectrometers.

[122] Nuclear magnetic resonance will be abbreviated as NMR. All NMR spectra were recorded from a Varian Associates HR-60 spectrometer and carbon tetrachloride was used exclusively as the solvent with tetramethylsilane as internal standard. Peak positions are given in units of delta.

solution, the reaction mixture was stirred for an additional hour at room temperature. Cyclobutanone (5.0 gm., 0.07 mole) in 12 ml. ether was then added to the phenyllithium solution at such a rate as to maintain gentle reflux. The mixture was stirred an additional two hours at room temperature after the addition was completed. The excess lithium and phenyllithium was destroyed by the addition of distilled water followed by dilute sulfuric acid solution. The two phases were separated and the aqueous phase was extracted with ether. The combined organic material was dried over anhydrous magnesium sulfate, then filtered and concentrated by rotary evaporator and hot water bath. The product was recovered by fractional distillation at reduced pressure and the opaque semi-solid alcohol was then recrystallized from pentane at -15° to yield 7.53 gm. (72% yield) 1-phenylcyclobutanol.

1-phenylcyclobutanol, b.p. 84-5° (0.55 mm), m.p. 38-9°, lit., b.p. 92-8° (1 mm), m.p. 41-2°[123].

IR: 2.77, 2.88, 3.38, 515, 5.33, 5.53, 6.25, 6.70, 6.92, 7.05μ in carbon tetrachloride.

NMR: 2.10 (broad multiplet), 2.94 (broad singlet), 7.27 (multiplet).

1-(m-chlorophenyl)cyclobutanol, b.p. 85-6° (0.5 mm).

IR: 2.98, 3.37, 6.26, 6.36, 6.75, 7.08μ between salt

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[123]Burger, A., and R. Bennett, J. Med. Pharm. Chem., 2, 687 (1960).

plates.

1-(p-chlorophenyl)cyclobutanol, b.p. 96-8° (3.0 mm).

IR: 2.98, 3.37, 5.25, 6.27, 6.69, 7.15μ between salt plates.

1-(p-methylphenyl)cyclobutanol, b.p. 98°(3.0 mm).

IR: 3.00, 3.45, 5.34, 5.63, 6.30, 6.62, 6.90μ between salt plates.

1-Arylcyclobutenes The 1-arylcyclobutenes were prepared by acid-catalyzed dehydration of the corresponding 1-arylcyclobutanols in essentially the same manner as reported by Burger[124]. Three to four grams of the alcohol and p-toluenesulfonic acid (1 mg./gm. alcohol) were placed in a micro-distillation apparatus with a 10 cm. Vigreux column and a full vacuum was applied to the system. The alcohol-acid mixture was then heated at reflux for 10 to 15 minutes. The heat input was then increased to effect distillation. The purity of the alcohol is a crucial factor as attempts to dehydrate the crude alcohol obtained by concentrating the work-up of the alcohol preparation gave poor yields of the desired olefin and an increase in pot residue. The 1-arylcyclobutenes decompose rather rapidly at room temperature when highly concentrated. Yields of the 1-arylcyclobutenes were between 70 and 80%.

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[124] Ibid., p. 687.

1-phenylcyclobutene, b.p. 72-3° (0.7 mm), lit. b.p. 74-5° (3.5 mm)[125].

IR: 3.27, 3.42, 3.52, 5.14, 5.33, 5.55, 5.73, 5.93, 6.20, 6.26, 6.34, 6.71, 6.91, 7.03μ between salt plates.

NMR: 2.46 (multiplet, 2H), 2.73 (multiplet, 2H), 6.14 (triplet, 1H), 7.17 (multiplet, 5H).

UV: λ_{max} 255.6 mμ (ε = 14,000),[126] lit. λ_{max} 255 (ε = 13,800)[127].

1-(m-chlorophenyl)cyclobutene, b.p. 73° (0.2 mm).

IR: 3.28, 3.43, 3.53, 5.16, 5.34, 5.68, 5.94, 6.28, 6.40, 6.80, 7.03μ between salt plates.

NMR: 2.49 (multiplet), 2.70 (multiplet), 5.96 (triplet), 7.14 (multiplet).

UV: λ_{max} 257.2 mμ (ε = 14,400).

1-(p-chlorophenyl)cyclobutene, b.p. 79-81° (0.2 mm).

IR: 3.29, 3.43, 3.54, 5.28, 5.49, 5.66, 6.30, 6.73, 6.84, 7.13μ in carbon tetrachloride.

UV: λ_{max} 261.0 mμ (ε = 18,300).

1-(p-methylphenyl)cyclobutene, b.p. 82-3° (3.0 mm).

IR: 3.30, 3.43, 3.53, 5.27, 5.59, 5.66, 6.22, 6.63, 6.94μ between salt plates.

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[125] Ibid., p. 687.

[126] Ultra-violet will be abbreviated UV. All UV spectra were obtained from a Beckman DK-2A spectrometer using 95% ethanol as the solvent.

[127] Ibid., p. 687.

NMR: 2.07 (singlet, 3H), 2.27 (multiplet, 2H), 2.47 (multiplet, 2H), 6.23 (triplet, 1H), 7.13 (quartet, 4H).

UV: λ_{max} 255.0mμ (ϵ = 13,640).

Substituted cinnamic acids Substituted cinnamic acids (p-Cl, m-Cl and p-CH_3) were purchased from Aldrich Chemical Company, Inc. and used without further purification.

Substituted cinnamoyl chlorides Substituted cinnamoyl chlorides were prepared by the reaction of the corresponding acid with thionyl chloride. p-Chlorocinnamic acid (100.0 gm., 0.55 mole) and thionyl chloride (100.0 gm., 0.84 mole) were added to 500 ml. of benzene and the resulting mixture was heated at reflux for approximately nine hours. The solvent was then removed using a rotary evaporator and a steam bath and the crude residue was recrystallized from hexane. The crystalline material was recovered by suction filtration and pressed dry using a rubber dam to yield 105.7 gm. (0.52 mole, 95% yield) of p-chlorocinnamoyl chloride.

p-chlorocinnamoyl chloride, m.p. 77-8°; lit. m.p. 78-9°[128].

p-methylcinnamoyl chloride, m.p. 71-4°.

m-chlorocinnamoyl chloride, m.p. 19-21°.

Substituted cinnamaldehydes Substituted cinnamaldehydes were prepared by hydride reduction of the corresponding

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[128]Andrews, E. R., M. G. Van Campen and E. L. Schuman, J. Am. Chem. Soc., 75, 4003 (1953).

acid chlorides at low temperature following a procedure reported by Brown[129]. p-Chlorocinnamoyl chloride (24.9 gm., 0.12 mole) in 62 ml. diglyme[130] was added to a 250 ml. 3-necked flask fitted with a mechanical blade stirrer, a pressure compensating addition funnel and a condenser. A thermometer was suspended from the top of the condenser into the diglyme solution. The flask was flushed with nitrogen and cooled to -73° with a dry ice-trichloroethylene bath. A solution of lithium aluminum tri-t-butoxy hydride[131] (31.0 gm., 0.13 mole) in 125 ml. diglyme was added with stirring over a period of one hour at such a rate as to allow maintenance of the temperature below -70°. A positive atmosphere of nitrogen was maintained throughout the addition of the hydride solution. After the addition was completed the reaction mixture was allowed to come to room temperature with stirring. Hydrolysis was carried out by pouring the reaction mixture onto ice in a four-liter beaker. The ice was allowed to melt and the organic layer was taken up in ether. The aqueous layer was extracted twice with ether, the organic material was combined and dried over anhydrous magnesium sulfate. After filtering, the solution was

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[129]Brown, H. C., and S. Rao, J. Am. Chem. Soc., 80, 5377 (1958).

[130]Diglyme is bis-2-methoxy diethyl ether.

[131]Brown, op. cit., p. 5377.

concentrated by stripping off the ether and the aldehyde was recovered by fractional distillation at reduced pressure to yield 9.43 gm. (0.057 mole, 46% yield) of p-chlorocinnamaldehyde[132].

p-chlorocinnamaldehyde, b.p. 100° (0.5 mm), m.p. 55°.

IR: 5.90, 6.14, 6.24, 6.63μ in KBr.

m-chlorocinnamaldehyde, crude[133].

IR: 5.57, 5.80, 5.92, 6.12, 6.76, 6.98μ in carbon tetrachloride.

UV: λ_{max} 279 mμ.

p-methylcinnamaldehyde, crude[134].

IR; 5.60, 5.83, 5.94, 6.14, 6.22, 6.61μ in carbon tetrachloride.

UV: λ_{max} 295 mμ.

Substituted cinnamyl alcohols Substituted cinnamyl alcohols were prepared by lithium aluminum hydride reduction of the corresponding aldehydes at -10° using a procedure

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[132]There was considerable difficulty experienced in performing the distillation as the aldehyde solidified in the delivery tube of the distillation apparatus.

[133]Gas phase chromatography analysis of the crude product from hydride reduction of m-chlorocinnamoyl chloride showed only a minor amount of material other than the desired product to be present. Therefore, the crude material was used in subsequent reactions without further purification.

[134]The crude p-methylcinnamaldehyde was treated in the same manner as the m-chloro analog.

recorded in Organic Reactions[135]. A solution of 9.45 gm. (0.057 mole) of p-chlorocinnamaldehyde in 60 ml. of ether was placed in a 100 ml. 3-necked flask fitted with a blade stirrer, addition funnel and a thermometer. The system was protected from atmospheric moisture. The solution was cooled to -10° with an ice-salt water bath[136]. A solution of lithium aluminum hydride (0.61 gm., 0.016 mole) in 10 ml. ether was added dropwise with stirring over a one hour period. The rate of addition was such that the temperature did not exceed 0°. After an additional 15 minutes, to allow completion of the reaction, water was cautiously added to decompose excess hydride reagent and was followed by 20 ml. of 10% sulfuric acid. The aqueous and organic phases were separated and the aqueous phase was extracted two times with ether. The organic material was combined and washed twice with saturated sodium bicarbonate solution, twice with distilled water and then dried over anhydrous magnesium sulfate. After filtering, the ethereal solution was concentrated by rotary evaporator to leave 8.6 gm. of residue (m.p. 40-50°). Gas phase chromatography analysis (6 mm x 1 M

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[135]Brown, W. G., "Reduction by Lithium Aluminum Hydride", in Roger Adams, "Organic Reactions", Vol. 6, John Wiley and Sons, Inc., New York, N.Y., 1953, p. 490.

[136]At this point some of the aldehyde crystallized from the solution.

column of Ucon LB 550X, 1:9.5 on firebrick, 150°) showed the residue to be > 90% of the desired alcohol and the bulk of the impurities to be unreacted starting material.

p-chlorocinnamyl alcohol, crude[137].

IR: 2.76, 2.97, 3.30, 3.43, 3.49, 5.28, 5.93, 6.14, 6.28, 6.70, 7.11μ in carbon tetrachloride.

p-methylcinnamyl alcohol, b.p. 103° (0.2 mm), m.p. 45-7°.

IR: 2.73, 2.97, 3.29, 3.41, 3.47, 5.26, 5.80, 5.92, 6.04, 6.18, 6.61, 7.25μ in carbon tetrachloride.

UV: λ_{max} 255.5 mμ.

m-chlorocinnamyl alcohol, crude[137].

IR: 3.00, 3.41, 3.49, 5.16, 5.36, 5.98, 6.27, 6.38, 6.77, 7.00μ between salt plates.

UV: λ_{max} 251.5 mμ.

3-Arylpropenyl chlorides The various 3-arylpropenyl chlorides were prepared by the reaction of the corresponding alcohols with thionyl chloride at 0°. Thionyl chloride (144.0 gm., 1.22 mole) was added dropwise with stirring to cinnamyl alcohol (147.0 gm., 1.10 mole) at 0°.[138] The reaction mixture was allowed to stir an additional two hours

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[137]The recovered products were used in subsequent reactions without further purification.

[138]In the event the alcohol was a solid enough ether was added to give solution at 0°. It is felt by this author that the addition of ether increases the amount of side products. This opinion is based on the amount of pot residue after distillation. No attempts were made to characterize the light-yellow colored residue.

after the addition of the thionyl chloride was completed. The gaseous by-products of the reaction, hydrogen chloride and sulfur dioxide, were removed by adding 50 ml. portions of ether and then evacuating on a rotary evaporator at room temperature. This procedure was repeated several times. The product was recovered by fractional distillation at reduced pressure to yield 137.1 gm. (0.9 mole, 90% yield) of cinnamyl chloride.

cinnamyl chloride, b.p. 86° (1.2 mm), lit. b.p. 51-3° (0.1 mm)[139].

IR: 3.29, 5.12, 5.29, 5.52, 6.06, 6.34, 6.67, 6.89, 6.94μ between salt plates.

NMR: 4.10 (doublet, 2H), 6.35 (AB pattern with B portion further split, 2H), 7.24 (singlet, 5H).

p-chlorocinnamyl chloride, b.p. 120-22° (2.5 mm).

IR: 3.33, 5.34, 6.01, 6.34, 6.76, 7.03μ in chloroform.

NMR: 4.08 (doublet, 2H), 6.32 (AB pattern with B portion further split, 2H), 7.21 (multiplet, 4H).

UV: λ_{max} 259 mμ (ε = 20,054).

m-chlorocinnamyl chloride, b.p. 109-11° (2.0 mm).

IR: 3.28, 3.37, 5.14, 5.33, 6.26, 6.77, 7.00μ between salt plates.

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[139]Valkanas, G., E. S. Wright and M. Weinstock, J. Chem. Soc., 4248 (1963).

NMR: 4.11 (doublet), 6.34 (AB pattern with B portion further split), 7.18 (multiplet).

UV: λ_{max} 253.3 mμ.

p-methylcinnamyl chloride, b.p. 99-100° (2.1 mm).

IR: 3.28, 3.40, 5.26, 5.82, 5.86, 6.07, 6.41, 6.61, 6.93μ in carbon tetrachloride.

NMR: 2.28 (singlet, 3H), 4.06 (doublet, 2H), 6.25 (AB pattern with B portion further split, 2H), 7.00 (quartet, 4H).

UV: λ_{max} 259.2 mμ.

Diethyl (3-aryl-2-propenyl) malonates. The diethyl (3-aryl-2-propenyl) malonates were prepared by reaction of the corresponding 3-arylpropenyl chlorides with sodium diethyl malonate. Diethyl malonate (164.0 gm., 0.9 mole) was added during a 30 minute period to a hot solution of 23.14 gm. (1.01 mole) sodium in 750 ml. of absolute ethanol. Cinnamyl chloride (137.1 gm., 0.9 mole) was added with vigorous stirring at a rate sufficient to maintain gentle reflux. After the addition was complete heating was continued until the mixture was neutral to moist litmus (approximately two hours). The solvent was removed by distillation. The oil which separated when the residue was poured into water was fractionated by distillation at reduced pressure to yield 155.8 gm. of diethyl cinnamyl

malonate (0.59 mole, 67% yield)[140].

diethyl cinnamyl malonate, b.p. 137-41° (0.4 mm), lit. b.p. 137-40° (0.1 mm)[141].

IR: 3.37, 5.11, 5.32, 5.77, 6.24, 6.68, 6.90μ between salt plates.

NMR: 1.21 (triplet, 6H), 2.69 (multiplet, 2H), 3.54 (multiplet, 1H), 4.30 (quartet, 4H), 6.24 (AB pattern with B portion further split, 2H), 7.03 (broad singlet, 5H).

diethyl 3-(p-chlorophenyl)-2-propenyl malonate, crude.

NMR: 1.28 (triplet), 2.71 (multiplet), 3.35 (multiplet), 4.12 (quartet), 6.22 (AB pattern with B portion further split), 7.23 (doublet).

UV: λ_{max} 256.5 mμ.

diethyl 3-(m-chlorophenyl)-2-propenyl malonate, crude.

NMR: 1.24 (triplet), 2.73 (multiplet), 3.37 (multiplet), 4.14 (quartet), 6.24 (AB pattern with B portion further split), 7.17 (doublet).

UV: λ_{max} 255.2 mμ.

diethyl 3-(p-methylphenyl)-2-propenyl malonate, crude.

NMR: 1.21 (triplet), 2.31 (singlet), 2.70 (triplet),

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[140]In the preparation of the substituted diethyl (3-aryl-2-propenyl) malonates final traces of solvent and unreacted diethyl malonate were removed by distillation under reduced pressure and the residue was used in subsequent reactions without further purification.

[141]Barnard, D., and L. Bateman, J. Chem. Soc., 926 (1950).

3.40 (quartet), 4.14 (quartet), 6.10 (AB pattern with B portion further split), 7.08 (quartet).

UV:, λ_{max} 255.2 mμ.

Diethyl (3-bormo-3-arylpropyl) malonates The diethyl (3-bromo-3-arylpropyl) malonates were prepared by hydrobromination of the corresponding diethyl (3-aryl-2-propenyl) malonates. Dry hydrogen bromide was passed through diethyl cinnamyl malonate (155.8 gm., 0.6 mole) for two hours. The temperature of the reaction mixture rose to 53° during the early part of the reaction and was maintained at this temperature for approximately one hour by means of a water bath[142]. The water bath was removed and the exothermic reaction maintained a temperature between 40-50°. The product was then treated with ice water and extracted with a mixture of benzene and ether (15:85). The organic material was washed with ice water and ice-cold 2% sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. After filtering, the solvent was removed by rotary evaporator and steam bath. The product so obtained was used in subsequent reaction without further purification.

diethyl [3-bromo-3-(m-chlorophenyl) propyl] malonate, crude.

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[142]For the preparation of the m-chlorophenyl compound it was necessary to dissolve the olefin in glacial acetic acid and to heat the solution at 60° to effect the reaction. The uptake of hydrogen bromide was monitored by UV.

NMR: 1.24 (triplet), 2.00 (multiplet), 3.28 (multiplet), 4.14 (quartet), 4.82 (multiplet), 7.23 (multiplet).

diethyl [3-bromo-3-(p-chlorophenyl) propyl] malonate, crude.

NMR: 1.22 (triplet), 2.03 (multiplet), 3.32 (multiplet), 4.11 (quartet), 4.97 (multiplet), 7.25 (broad singlet).

diethyl [3-bromo-3-(p-methylphenyl) propyl] malonate, crude.

NMR: 1.20 (triplet), 2.02 (multiplet), 2.31 (singlet), 3.23 (multiplet), 4.12 (quartet), 4.85 (multiplet), 7.12 (multiplet).

Diethyl 2-arylcyclobutane-1,1-dicarboxylates The diethyl 2-arylcyclobutane-1,1-dicarboxylates were prepared by the base-induced cyclization of the corresponding diethyl (3-bromo-3-arylpropyl) malonates. Diethyl [3-bromo-3-(p-methylphenyl) propyl] malonate (max. 0.2 mole) in 50 ml. dry tetrahydrofuran[143] was slowly added to a suspension of sodium hydride (8.8 gm., 0.20 mole, 55.1 per cent in mineral oil) in 150 ml. dry tetrahydrofuran with vigorous stirring over a 1.5 hour period. The addition was carried out under a positive atmosphere of nitrogen[144]. The reaction mixture

[143] Freshly distilled from sodium and lithium aluminum hydride.

[144] In carrying out this reaction it is advisable to be certain that hydrogen is being evolved during the early period of addition of the bromo compound. If a considerable amount of the bromo compound is present when the reaction is initiated the rate of hydrogen evolution may become uncontrollable.

was allowed to stand nine hours at room temperature after which time the solvent was removed by distillation until the internal temperature of the distillation flask reached 80°. Ice was then added and the mixture was diluted with distilled water. After separating the organic layer, the aqueous phase was extracted three times with ether and the combined organic material was washed with distilled water. The solvent was removed by rotary evaporator and steam bath. The recovered material was used in subsequent reactions without further purification.

diethyl 2-(p-methylphenyl) cyclobutane-1,1-dicarboxylate, crude.

IR: 3.38, 5.76, 6.61, 6.90, 7.33μ in chloroform.

NMR: 0.72 (triplet), 1.23 (triplet).

diethyl 2-(p-chlorophenyl) cyclobutane-1,1-dicarboxylate, crude.

NMR: 0.78 (triplet), 1.26 (triplet).

diethyl 2-(m-chlorophenyl) cyclobutane-1,1-dicarboxylate, crude.

IR: 3.22, 5.72, 6.24, 6.35, 6.75, 7.31μ between salt plates.

NMR: 0.80 (triplet), 1.24 (triplet).

2-Arylcyclobutane-1,1-dicarboxylic acid The crude product from the preparation of diethyl 2-phenylcyclobutane-1, 1-dicarboxylate was saponified by treatment with boiling

potassium hydroxide solution (100 gm. in 300 ml. of 50% ethanol) for three hours. The bulk of the solvent was removed by rotary evaporator and steam bath and the residue was taken up in water. The aqueous solution was washed twice with ether to remove residual mineral oil and then acidified with 180 ml. of 37% hydrochloric acid solution. The organic acid which separated was isolated by ether extraction and recrystallized from chloroform. The product was recovered by suction filtration to yield 73.3 gm. (0.33 mole, 56% yield based on diethyl cinnamyl malonate) of 2-phenyl-cyclobutane-1,1-dicarboxylic acid.

2-phenylcyclobutane-1,1-dicarboxylic acid, m.p. 171-2°, lit. m.p. 173-4[145].

2-(p-methylphenyl) cyclobutane-1,1-dicarboxylic acid, crude.

IR: 3.26, 3.78, 5.78, 6.55, 7.05μ in chloroform.

2-(m-chlorophenyl) cyclobutane-1,1-dicarboxylic acid, crude.

IR: 3.13, 3.63, 5.76, 6.22, 6.32, 6.74, 7.02μ between salt plates.

cis- and trans-2-Phenylcyclobutane carboxylic acid A solution of 40 gm. of 2-phenylcyclobutane-1,1-dicarboxylic acid in 150 ml. mesitylene was heated at reflux for 1.5 hour,

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[145]Beard, op. cit., p. 2335.

cooled to room temperature and extracted with 70 ml. of ice-cold 15% sodium hydroxide solution. After being washed twice with ether, the alkaline solution was acidified with 10% hydrochloric acid solution below 10° and the oil which separated was taken up in ether. The bulk of the solvent was removed by rotary evaporator and steam bath and final traces were removed under full vacuum at room temperature.

cis- and trans-2-phenylcyclobutane carboxylic acid, crude mixture.

IR: 3.38, 3.79, 5.88, 6.23, 6.67, 7.03μ between salt plates.

1-Carbethoxy-trans-2-(p-chlorophenyl) cyclobutane carboxylic acid 1-Carbethoxy-trans-2-(p-chlorophenyl) cyclobutane carboxylic acid was prepared by the selective saponification of diethyl 2-(p-chlorophenyl) cyclobutane-1, 1-dicarboxylate using one equivalent of base. The diethyl ester (47.5 gm. crude product from cyclization reaction) was dissolved in 250 ml. ethanol and potassium hydroxide (10 gm., one equivalent based on weight of crude diester) was added with enough water to dissolve the hydroxide. The resulting solution was stirred overnight at room temperature and then heated 1.5 hours at 50°. The bulk of the solvent was removed by distillation and the residue was taken up in distilled water. The aqueous solution was then washed with ether to remove residual mineral oil and any unsaponified diester.

The aqueous solution was then acidified with concentrated hydrochloric acid. The oil which resulted was taken up in ether[146]. The solution was dried over anhydrous magnesium sulfate, filtered and the solvent was removed by rotary evaporator and steam bath to yield 34.3 gm. crude product.

1-carbethoxy-trans-2-(p-chlorophenyl) cyclobutane carboxylic acid, red-orange oil.

NMR: 0.82 (triplet, 3H), 2.47 (multiplet, 4H), 3.80 (quartet, 2H), 4.28 (multiplet, 1H), 7.23 (singlet, 4H), 10.28 (singlet, 1H).

cis- and trans-1-Carbethoxy-2-(p-chlorophenyl) cyclobutane

A mixture of cis- and trans-1-carbethoxy-2-(p-chlorophenyl) cyclobutane was obtained from the decarboxylation of 1-carbethoxy-trans-2-(p-chlorophenyl) cyclobutane carboxylic acid in boiling mesitylene. The half-acid ester (34.3 gm., 0.12 mole) was dissolved in 150 ml. of mesitylene and heated at reflux (165°) for approximately four hours. The solvent was then removed by distillation at reduced pressure (water pump). The residue was then fractionated by low pressure distillation to yield 10.2 gm. (0.043 mole, 38% yield) of a mixture of cis- and trans-1-carbethoxy-2-(p-chlorophenyl) cyclobutane.

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[146]Attempts to obtain a crystalline product failed.

cis- and trans-1-carbethoxy-2-(p-chlorophenyl) cyclobutane, mixture[147], b.p. 85-97° (0.1 mm).

NMR: 0.82 (triplet), 1.22 (triplet).

cis- and trans-2-(p-Chlorophenyl) cyclobutane carboxylic acid Saponification of a mixture of cis- and trans-1-carbethoxy-2-(p-chlorophenyl) cyclobutane gave a mixture of cis- and trans-2-(p-chlorophenyl) cyclobutane carboxylic acid. The ester (10.15 gm., 0.043 mole) was dissolved in 48 ml. of 95% ethanol and 23 ml. of distilled water. Potassium hydroxide (4.0 gm., 0.06 mole) was added and the solution was heated at reflux with stirring for approximately four hours. The bulk of the solvent was removed by distillation using a water aspirator. The residue was taken up in distilled water. The resulting solution was cooled to 0° and acidified by dropwise addition of concentrated hydrochloric acid. The orange-colored oil which resulted was taken up in ether and the aqueous phase was extracted twice more with ether. The combined organic material was washed with distilled water and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was stripped off by rotary evaporator and steam bath to yield 9.0 gm. (0.043 mole, 99% yield) of a crude mixture of the mono-acids.

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[147]The ratio of cis to trans products was 60:40 based on integration of the area of the methyl resonance absorption in the NMR spectrum at 0.82 (cis) and 1.22 (trans).

cis- and trans-2-(p-chlorophenyl) cyclobutane carboxylic acid, crude mixture.

IR: 3.37, 3.78, 5.89, 6.69, 7.03μ between salt plates.

cis- and trans-2-Arylcyclobutyl methyl ketones Treatment of a mixture of the corresponding cis- and trans-2-arylcyclobutane carboxylic acid with methyllithium, following a procedure reported by DePuy[148], afforded a cis-trans mixture of the desired methyl ketone. A cis-trans mixture of 2-phenylcyclobutane carboxylic acid was dissolved in 60 ml. of ether and transferred to a 1-liter 3-necked flask fitted with a magnetic stirrer, reflux condenser and pressure-compensating addition funnel[149]. Methyllithium (325 ml. of 0.87 M ethereal solution) was added dropwise with stirring over a 30 minute period[150]. After completion of the addition, the reaction mixture was allowed to stand 15 hours at room temperature and the 290 ml. of a saturated solution of ammonium chloride was added; very slowly at first. The two phase system was stirred until both layers became clear. The two phases were separated and the aqueous phase was extracted two times with ether. The combined organic

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[148]DePuy, C. H., L. R. Mahoney, and K. L. Eliers, J. Org. Chem., 26, 3616 (1961).

[149]The addition funnel was closed to the atmosphere and the reflux condenser was fitted with a drying tube.

[150]About midway through the addition the solution to a white gelatinous mass which was difficult to stir.

material was washed once with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After filtering, the solvent was stripped off by rotary evaporator and steam bath. The residual oil was fractionated by low pressure distillation to yield 19.2 gm. (0.11 mole, 85% yield) of a mixture of cis- and trans-2-phenylcyclobutyl methyl ketone[151].

cis- and trans-2-phenylcyclobutyl methyl ketone, mixture b.p. 80-90° (0.4 mm).

IR: 3.39, 5.87, 6.24, 6.68, 6.90μ between salt plates.

NMR: 1.39 (singlet), 1.69 (singlet).

cis- and trans-2-Arylcyclobutyl acetates Baeyer-Villiger oxidation of a mixture of cis- and trans-2-aryl-cyclobutyl methyl ketone gave a cis-trans mixture of the corresponding acetate[152]. 2-Phenylcyclobutyl ketone (12.0 gm., 0.07 mole) in 190 ml. of methylene chloride and 142 gm. of sodium monohydrogen phosphate were added to a 3-necked

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[151]It was not possible to obtain pure cis ketone but fractions taken near the end of the distillation were essentially pure trans ketone as shown by gas phase chromatography. The fractions which contained cis ketone were combined to give 12.0 gm. of material which was a 35:65 mixture (cis:trans). The composition was based on the integrated areas of the methyl resonance absorption of the NMR spectrum at 1.39 (cis) and 1.69 (trans).

[152]Attempts to obtain a crystalline product failed.

500 ml. flask. Trifluoroperacetic acid[153] in an ice-water cooled addition funnel was added with vigorous stirring to the ketone solution over a two hour period. The reaction mixture was maintained between 0-10° with an ice-water bath. After total addition of the peracid solution the reaction mixture was allowed to come to room temperature overnight. The reaction mixture was filtered and the sodium monohydrogen phosphate was washed twice with methylene chloride. The combined organic material was washed once with a saturated solution of sodium bicarbonate and once with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporator and steam bath. The residue was fractionated by low pressure to yield 9.73 gm. (0.05 mole, 75% yield) of a mixture of cis- and trans-2-phenylcyclobutyl acetate.

cis- and trans-2-phenylcyclobutyl acetate, mixture, b.p. 69-74° (0.27 mm).

IR: 3.35, 5.75, 6.26, 6.70, 6.94μ between salt plates.

cis- and trans-2-(p-chlorophenyl)cyclobutyl acetate, crude mixture.

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[153]Hydrogen peroxide (7.05 ml., 90%) was added dropwise to a solution of trifluoroacetic anhydride (43.5 gm., 0.21 mole) in 80 ml. of methylene chloride in a 3-necked 100 ml. flask fitted with an addition funnel, condenser and thermometer and cooled with an ice-water bath. The reaction mixture was stirred with a magnetic stirrer. The rate of addition of the hydrogen peroxide was such to keep the temperature between 0-10°.

IR: 3.30, 5.70, 6.65, 6.91μ between salt plates.

2-Arylcyclobutanones A modified Curtius degradation of the various 2-arylcyclobutane-1,1-dicarboxylic acids was used to prepare the 2-arylcyclobutanones. The procedure followed was that reported by Burger[154]. A solution of 2-phenylcyclobutane-1,1-dicarboxylic acid (8.80 gm., 0.04 mole) in 16 ml. of acetone and 20 ml. of distilled water was treated at -10-0° with triethylamine (9.6 gm., 0.096 mole) in 80 ml. acetone, added dropwise with stirring, followed by a solution of ethyl chloroformate (10.40 gm., 0.096 mole) in 20 ml. of acetone. After stirring the mixture at -5 to 0° for 30 minutes, following the addition of the ethyl chloroformate, a solution of sodium azide (7.84 gm., 0.12 mole) in 24 ml. of distilled water was added and stirring was continued for another hour. The reaction mixture was poured into 1200 ml. of ice-cold saturated sodium chloride solution and 600 ml. of ice water and the resulting mixture was extracted with 5-180 ml. portions of ether. The combined ether extracts were dried over magnesium sulfate. The ether was removed by distillation and 200 ml. of absolute ethanol was added to the residue. The resulting solution was heated at reflux for two hours and then the solvent was removed by distillation at reduced pressure. Sulfuric acid

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[154]Beard, op. cit., p. 2335.

(200 ml. of 2% solution) was added to the residue and the ketone was recovered by steam distillation. The distillate was extracted with ether and the combined organic material was dried over anhydrous magnesium sulfate. After filtering, the ether was removed by rotary evaporator and the oily residue (2.6 gm.) was fractionated by low pressure distillation to yield 1.9 gm. of 2-phenylcyclobutanone (0.014 mole, 35% yield).

2-phenylcyclobutanone, b.p. 58-62° (0.2 mm), lit. b.p. 116° (7 mm)[155].

IR: 3.37, 5.62, 6.24, 6.68, 6.89, 7.18μ between salt plates.

NMR: 2.56 (multiplet, 4H), 4.27 (triplet, 1H), 6.91 (singlet, 5H).

2-(m-chlorophenyl)cyclobutanone, b.p. 93° (0.5 mm).

IR: 3.36, 5.59, 6.25, 6.74, 7.02μ between salt plates.

NMR: 2.66 (multiplet, 4H), 4.38 (triplet, 1H), 7.14 (singlet, 1H).

2-(p-methylphenyl)cyclobutanone, b.p. 80° (0.5 mm).

IR: 3.38, 5.25, 5.60, 5.95, 6.23, 6.59, 6.87, 7.17μ between salt plates.

NMR: 2.59 (multiplet superimposed on a singlet at 2.28, 7H), 4.34 (triplet, 1H), 7.01 (singlet, 4H).

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[155]Beard, op. cit., p. 2335.

trans-2-Arylcyclobutanols. The trans-2-arylcyclobutanols were prepared by hydroboration of the corresponding olefins followed by basic hydrogen peroxide oxidation using a procedure of Brown's[156]. Five grams of 1-(p-methylphenyl) cyclobutene (0.035 mole) in 11 ml. of tetrahydrofuran was added to a 100 ml. 3-necked flask fitted with an air condenser and gas bubbler. The olefin solution was cooled(0-3°) with an ice-water bath. In another 100 ml. 3-necked flask equipped with a pressure-compensating addition funnel, gas bubbler and an outlet tube connected to the bubbler in the flask containing the olefin solution, was placed 3.64 gm. (0.47 mole) boron trifluoride etherate in 14 ml. diglyme. Sodium borohydride (0.36 gm., 0.018 mole) in 18 ml. diglyme was added dropwise over a one hour period. The generated diborane was carried into the olefin solution with a stream of dry nitrogen. After the addition was completed, the reaction mixture was allowed to stand one hour at room temperature. The reaction mixture was cooled again with an ice-water bath and approximately 10 gm. of ice were added, followed by 9.5 ml. of 3 N sodium hydroxide solution and then after 20 minutes by 5 ml. of 30% hydrogen peroxide solution maintaining the temperature below 10°. After one hour at room temperature, the mixture was diluted with 27 ml. of

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[156]Brown, H. C., and S. Rao, J. Am. Chem. Soc., 81, 6428 (1959).

distilled water and extracted three times with ether. The combined extracts were dried over anhydrous magnesium sulfate. The mixture was filtered and the solution was concentrated by rotary evaporator at room temperature. The alcohol was then purified by fractional distillation at reduced pressure to yield 3.75 gm. of trans-2-(p-methylphenyl)cyclobutanol (0.023 mole, 65% yield).

trans-2-phenylcyclobutanol, b.p. 95° (2.6 mm), lit. b.p. 78-81° (0.3 mm)[157].

IR: 3.05, 3.45, 5.15, 5.35, 6.00, 6.25, 6.70, 6.94μ between salt plates.

NMR: 1.82 (multiplet, 4H), 3.05 (multiplet, 1H), 3.90 (multiplet, 1H), 4.12 (singlet, 1H), 7.08 (singlet, 5H).

trans-2-(p-methylphenyl)cyclobutanol, b.p. 93-5° (0.1 mm).

IR: 2.98, 3.36, 5.25, 5.58, 6.22, 6.58, 6.83, 6.93μ between salt plates.

NMR: 1.60 (multiplet superimposed on a singlet at 2.25, 7H), 3.04 (multiplet, 1H), 4.26 (singlet, 1H), 6.04 (singlet, 4H).

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[157]Beard, op. cit., p. 2335.

trans-2-(m-chlorophenyl)cyclobutanol, b.p. 57° (0.1 mm).

IR: 3.02, 3.36, 6.24, 6.75, 6.99μ between salt plates.

NMR: 1.76 (multiplet, 4H), 3.05 (multiplet, 1H), 3.91 (multiplet, 1H), 4.72 (singlet, 1H), 7.07 (multiplet, 4H).

trans-2-(p-chlorophenyl)cyclobutanol, b.p. 85-7° (0.5 mm).

IR: 3.00, 3.40, 5.27, 6.26, 6.69, 6.85, 7.09μ between salt plates.

NMR: 1.84 (multiplet, 4H), 3.01 (multiplet, 1H), 3.89 (quartet, 1H), 4.28 (singlet, 1H), 7.07 (quartet, 1H).

cis- and trans-2-Phenylcyclobutanols (mixture)

a) Hydrogenation of 3.38 gm. (0.023 mole) of 2-phenylcyclobutanone in 15 ml. of absolute ethanol at a slight positive pressure using Raney nickel W-2 catalyst[158] gave a 45:55 mixture[159] (cis to trans) of 2-phenylcyclobutanol. The reaction time was approximately four hours. The catalyst was removed by filtration and the ethanol was removed by distillation. The alcohols were separated by fractional distillation at reduced pressure using a Nester/Faust 18-inch spinning band column.

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[158]Horning, E. C., "Organic Syntheses", Collective Vol. 3, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 181.

[159]Composition based on peak areas of the gas phase chromatography recorder trace. Analysis was performed using a 6 mm. x 1 meter column of Ucon LB550X 1:9.5 on firebrick at 170°.

b) Reaction of a cis-trans mixture of 2-phenylcyclobutyl acetate with methyllithium gave a mixture of cis- and trans-2-phenylcyclobutanol. 2-Phenylcyclobutyl acetate (9.73 gm., 0.051 mole) was dissolved in 50 ml. of anhydrous ether in a 3-necked flask equipped with a magnetic stirrer, reflux condenser and a pressure-compensating addition funnel. A solution of methyllithium in ether (110 ml., 0.96 M) was added dropwise with stirring over a period of 30 minutes to the acetate solution under a nitrogen atmosphere. The reaction mixture was stirred an additional hour at room temperature. The material was then added rapidly to a stirred saturated aqueous solution of boric acid plus a slight excess of boric acid and then transferred to an addition funnel with enough water to dissolve the remaining boric acid. The organic and aqueous layers were separated and the aqueous layer was extracted two times with ether. The combined organic material was washed twice with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After filtering, the ether was stripped off by rotary evaporator and steam bath to yield 8.09 gm. of residual oil. The residual oil was fractionated by distillation at reduced pressure using an 18-inch Nester/Faust spinning band column to yield 1.18 gm. cis-2-phenylcyclobutanol, which gave only one peak on gas phase chromatography analysis, and 4.53 gm. trans-2-phenylcyclobutanol which was also pure by gas phase

chromatography.

cis-2-phenylcyclobutanol, b.p. 71-3° (0.9 mm).

IR: 2.93, 3.37, 5.16, 5.36, 5.57, 6.28, 6.72, 6.90, 7.17μ between salt plates.

NMR: 1.73 (multiplet superimposed on a singlet at 2.27 which disappeared when the sample was shaken with D_2O, 5H), 3.50 (multiplet, 1H), 4.18 (multiplet, 1H), 7.13 (singlet, 5H).

cis- and trans-2-(p-Chlorophenyl)cyclobutanols (mixture) Saponification of a cis and trans mixture of 2-(p-chlorophenyl)cyclobutyl acetate gave a mixture of cis- and trans-2-(p-chlorophenyl)cyclobutanol. The ester (7.60 gm., crude mixture) was dissolved in 20 ml. of 95% ethanol and 15 ml. of distilled water. Sodium hydroxide (2.0 gm.) was added and the solution was heated at 50° with stirring for approximately three hours. The bulk of the solvent was removed by distillation at reduced pressure. The residual oil was fractionated by low pressure distillation using an 18-inch Nester/Faust spinning band column to yield 0.75 gm. of cis-2-(p-chlorophenyl)cyclobutanol and 3.81 gm. trans-2-(p-chlorophenyl)cyclobutanol.

cis-2-(p-chlorophenyl)cyclobutanol, b.p. 51° (0.2 mm).

IR: 2.93, 3.35, 5.25, 5.58, 5.78, 6.05, 6.25, 6.66, 6.83, 7.07μ between salt plates.

cis- and trans-2-(p-Methylphenyl)cyclobutanol (mixture)

Lithium aluminum hydride reduction of 2-(p-methylphenyl)-cyclobutanone gave a mixture of cis- and trans-1-(p-methyl-phenyl)cyclobutanol. A solution of 2-(p-methylphenyl)cyclo-butanone (1.0 gm. in 5 ml. of ether) was added dropwise with stirring to 30 ml. of a 0.23 M solution of lithium aluminum hydride in ether. The reaction mixture was allowed to stir at room temperature for 30 minutes and the excess hydride was destroyed by the dropwise addition of distilled water at 0°. Sufficient 10% sulfuric acid solution was added to dissolve the solids. The organic material was taken up in ether and the aqueous phase was extracted twice with ether. The combined organic material was dried over anhydrous sodium sulfate and the solution was filtered. The ether was stripped off by rotary evaporator. Gas phase chromatography analysis of the residual oil showed that is was composed of a 30:70 mixture (cis-trans) of 2-(p-methylphenyl)cyclobutanol. The reaction procedure described above was carried out on 3.28 gm. of the ketone and the combined alcoholic residues were fractionated by low pressure distillation using an 18-inch Nester/Faust spinning band column to yield 0.9 gm. of cis-2-(p-methylphenyl)cyclobutanol and 3.81 gm. of trans-2-(p-methylphenyl)cyclobutanol.

cis-2-(p-methylphenyl)cyclobutanol, b.p. 45° (0.8 mm).

IR: 2.94, 3.42, 5.27, 5.59, 5.90, 6.59, 6.85, 6.94, 7.15μ between salt plates.

NMR: 1.56 (singlet, 1H), 2.10 (multiplet superimposed on a singlet at 2.30, 7H), 3.55 (multiplet, 1H), 4.25 (multiplet, 1H), 7.03 (singlet, 4H).

cis- and trans-2-(m-Chlorophenyl)cyclobutanol (mixture)

a) Lithium aluminum hydride reduction of 2-(m-chlorophenyl)-cyclobutanone gave a mixture of cis- and trans-2-(m-chlorophenyl)cyclobutanol. A solution of 2-(m-chlorophenyl)-cyclobutanone (0.5 gm. in 5 ml. of ether) was added dropwise with stirring to 20 ml. of a 0.23 M ethereal solution of lithium aluminum hydride. The reaction mixture was allowed to stir 30 minutes at room temperature and the excess hydride was destroyed by the dropwise addition of water at 0°. Sufficient 10% sulfuric acid solution was added to dissolve the solids and the two phases were separated. The aqueous phase was extracted twice with ether and the combined organic material was dried over anhydrous sodium sulfate. After filtering, the solvent was removed by rotary evaporator. Gas phase chromatography analysis (6 mm. x 1 meter column of Ucon LB550X 1:9.5 on Chromosorb P at 170°) showed the residual oil to contain a 20:80 mixture (cis-trans) of 2-(m-chlorophenyl)cyclobutanol. The reaction procedure was repeated twice more, once on a 0.5 gm. sample and once on a 1.7 gm. sample, as given above except the reaction time was shortened to 10 minutes. Gas phase chromatography analysis on the resultant material showed it to be a 23:77 mixture

(cis-trans) of the desired alcohols.

b) Sodium borohydride reduction of 2-(m-chlorophenyl)-cyclobutanone using a procedure reported by Eliel[160] gave a mixture of cis- and trans-2-(m-chlorophenyl)cyclobutanol. A solution of 2-(m-chlorophenyl)cyclobutanone (0.5 gm., 0.003 mole in 1 ml. of methanol) was added dropwise with stirring to a solution of sodium borohydride (0.1 gm., 0.0026 mole) and sodium (0.11 gm.) in 20 ml. of anhydrous methanol. The reaction mixture was allowed to stir 2.5 hours at room temperature. The excess hydride was destroyed by the dropwise addition of 10% sulfuric acid solution. The organic material was taken up in ether and dried over anhydrous sodium sulfate. After filtering, the solvent was removed by rotary evaporator. Analysis by gas phase chromatography of the residual oil showed it to be a 23:77 mixture (cis-trans) of the isomeric 2-(m-chlorophenyl)cyclobutanols. The combined alcoholic material from a) and b) was fractionated by low pressure distillation using an 18-inch Nester/Faust spinning band column to yield 0.47 gm. of cis-2-(m-chlorophenyl)cyclobutanol and 1.95 gm. of trans-2-(m-chloropheyl)-cyclobutanol.

cis-2-(m-chlorophenyl)cyclobutanol, b.p. 63-4° (0.8 mm).

IR: 2.98, 3.40, 6.27, 6.37, 6.76, 6.84, 7.02μ between

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[160]Haubenstock, H., and E. L. Eliel, J. Am. Chem. Soc., 84, 2368 (1962).

salt plates.

NMR: 2.09 (multiplet superimposed on a singlet at 2.13, 5H), 3.52 (multiplet, 1H), 4.23 (multiplet, 1H), 7.13 (multiplet, 4H).

Cyclobutyl and 2-arylcyclobutyl p-toluenesulfonates

The p-toluenesulfonates were prepared by the reaction of the appropriate alcohol with p-toluenesulfonyl chloride using dry pryidine as a solvent as reported by Tipson[161]. Cyclobutanol (3.77 gm., 0.05 mole) was dissolved in 18 ml. of dry pyridine[162] at 0°. p-Toluenesulfonyl chloride (14.30 gm., 0.075 mole) was added rapidly with swirling while keeping the reaction flask in the ice-water bath. The reaction mixture was allowed to stand for 30 minutes at 0° and then placed in the refrigerator at -20° for 48 hours[163]. The reaction mixture was then poured into an ice-water slurry and a solid separated which was recovered by suction filtration and washed twice with ice-cold 10% hydrochloric acid followed by ice-cold distilled water and finally with ice-cold pentane[164]. The solid material was taken up in

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[161]Tipson, op. cit., p. 235.

[162]Distilled from barium oxide.

[163]In the case of the cis alcohols the reaction mixture was left to stand in the refrigerator for 72 hours.

[164]Pentane was purified by shaking with concentrated sulfuric acid, washing with distilled water and drying over anhydrous magnesium sulfate. The dried solvent was then distilled and only a sharp middle fraction was collected.

ether and dried over anhydrous magnesium sulfate. The solution was filtered and the cyclobutyl p-toluenesulfonate was recovered by recrystallization from ether:pentane to yield 10.33 gm. of material (0.046 mole, 92% yield). The product was recrystallized from ether:pentane until a constant melting point was obtained.

cyclobutyl p-toluenesulfonate, m.p. 23°, lit. m.p. 24-5°[165].

IR: 3.34, 3.38, 7.27, 8.43, 8.49, 9.12, 9.53, 10.74, 11.12, 11.80μ in carbon tetrachloride.

NMR: 1.92 (multiplet, 4H), 2.39 (singlet, 3H), 4.66 (pentuplet, 1H), 7.46 (quartet, 4H).

cis-2-phenylcyclobutyl p-toluenesulfonate, m.p. 64-5°.

IR: 3.38, 6.25, 6.68, 6.87, 7.27, 7.43, 8.43, 8.50μ in carbon tetrachloride.

NMR: 2.24 (multiplet superimposed on a singlet at 2.32, 7H), 3.55 (multiplet, 1H), 5.12 (multiplet, 1H), 7.23 (quartet superimposed on a singlet at 7.13, 9H).

ANALYSIS: calc. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60.

found: C, 67.43; H, 5.77; S, 10.72[166].

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[165] Roberts, J. D., and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951).

[166] Analyses were performed by Drs. G. Weiler and F. B. Strauss, Microanalytical Laboratory, 164, Banbury Road, Oxford, England.

trans-2-phenylcyclobutyl p-toluenesulfonate, m.p. 86-7°.

IR: 3.36, 6.25, 6.67, 7.27, 8.43, 8.50μ in carbon tetrachloride.

NMR: 1.98 (multiplet, 4H), 2.35 (singlet, 3H), 3.47 (multiplet, 1H), 4.70 (multiplet, 1H), 7.07 (multiplet superimposed on a quartet at 7.35, 9H).

ANALYSIS: calc. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00; S, 10.60.

found: 67.20; H, 5.71; S, 10.80.

cis-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate, m.p. 36-8°.

IR: 3.37, 6.25, 6.74, 7.26, 7.41, 8.42, 8.49μ in carbon tetrachloride.

NMR: 2.29 (multiplet superimposed on a singlet at 2.40, 7H), 3.68 (multiplet, 1H), 5.16 (multiplet, 1H), 7.05 (multiplet superimposed on a quartet at 7.29, 8H).

ANALYSIS: calc. for $C_{17}H_{17}ClO_3S$; C, 60.62; H, 5.09; Cl, 10.53; S, 9.52.

found: C, 60.57; H, 5.11; Cl, 10.50; S, 9.41.

trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate, m.p. 33-4°.

IR: 3.37, 6.25, 6.75, 7.27, 8.43, 8.49μ in carbon tetrachloride.

NMR: 1.02 (multiplet superimposed on a singlet at 2.32, 7H), 3.61 (multiplet, 1H), 4.68 (multiplet, 1H), 6.96 (multiplet superimposed on a quartet at 7.37, 8H).

ANALYSIS: calc. for $C_{17}H_{17}ClO_3S$: C, 60.62; H, 5.09; Cl, 10.53; S, 9.52.

found: C, 60.69; H, 5.14; Cl, 10.39; S, 9.55.

cis-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate, m.p. 46-7°.

IR: 3.38, 6.25, 6.68, 7.27, 7.92, 8.43, 8.50μ in carbon tetrachloride.

NMR: 2.25 (multiplet superimposed on a singlet at 2.40, 7H), 3.71 (multiplet, 1H), 5.14 (multiplet, 1H), 7.09 (multiplet superimposed on a quartet at 7.26, 8H).

ANALYSIS: calc. for $C_{17}H_{17}ClO_3S$: C, 60.62; H, 5.09; Cl, 10.53; S, 9.52.

found: C, 60.56; H, 5.20; Cl, 10.71; S, 9.39.

trans-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate, m.p. 87°.

IR: 3.37, 6.25, 6.68, 7.26, 8.42, 8.49μ in carbon tetrachloride.

NMR: 2.02 (multiplet superimposed on a singlet at 2.37, 7H), 3.41 (multiplet, 1H), 4.66 (multiplet, 1H) 6.99 (multiplet superimposed on a quartet at 7.35, 8H).

ANALYSIS: calc. for $C_{17}H_{17}ClO_3S$: C, 60.62; H, 5.09; Cl, 10.53; S, 9.52.

found: C, 60.27; H, 5.14; Cl, 10.70; S, 9.65.

cis-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate, m.p. 56-7°.

IR: 3.37, 6.25, 6.60, 7.27, 7.42, 8.42, 8.49μ in carbon tetrachloride.

NMR: 2.23 (multiplet superimposed on singlets at 2.29 and 2.36, 10H), 3.67 (multiplet, 1H), 5.08 (multiplet, 1H), 6.97 (singlet superimposed on a quartet at 7.24, 8H).

ANALYSIS: calc. for $C_{18}H_{19}O_3S$: C, 68.33; H, 6.37; S, 10.13.

found: C, 68.25; H, 6.34; S, 10.55.

trans-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate, m.p. 70-1°.

IR: 3.37, 6.25, 6.60, 6.68, 6.82, 6.93, 7.27, 8.43, 8.50μ in carbon tetrachloride.

NMR: 1.96 (multiplet superimposed on singlets at 2.26 and 2.37, 10H), 3.43 (multiplet, 1H), 4.68 (multiplet, 1H), 6.88 (singlet superimposed on a quartet at 7.36, 8H).

ANALYSIS: calc. for $C_{18}H_{19}O_3S$: C, 68.33; H, 6.37; S, 10.13.

found: C, 68.01; H, 6.34; S, 10.22.

Sodium ethoxide in ethanol

Anhydrous ethanol was prepared by the method of Manske[167]. The center cut of the distillation of ethanol from diethyl phthalate and sodium was taken. Sodium metal was cut clean of any oxides, washed in anhydrous ethanol and

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[167]Manske, R. H., J Am. Chem. Soc., 53, 1106 (1931).

added to the anhydrous ethanol to be used in kinetic determinations. The resulting basic solution (approximately 0.2 N) was stored under a positive atmosphere of prepurified nitrogen.

Potassium t-butoxide in t-butyl alcohol

Eastman Kodak White Label t-butyl alcohol was distilled four times from clean metallic sodium under anhydrous conditions. Only a sharp center fraction (b.p. 82°, 1 atm.) was collected and used in subsequent distillations. Metallic potassium was cut in small cubes and melted in n-heptane[168]. Any material which floated to the top of the hot solvent was removed by decantation. The potassium was allowed to solidify, washed in pure t-butyl alcohol and then transferred to the t-butyl alcohol which was to be used in kinetic determinations.

Kinetic data

a) Psuedo-1st order rate constants Approximately 5×10^{-3} M solutions of the p-toluenesulfonates in the desired base/solvent system were prepared. The requisite amount of p-toluenesulfonate was weighed and transferred to a 50 ml. volumetric flask and the flask was then placed in the constant temperature bath. The base solution which had been

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[168]Purification steps were taken to minimize problems which have previously been encountered with the t-butoxide/t-butyl alcohol system. See DePuy, op. cit., p. 2421.

equilibrated at the given bath temperature was transferred to the flask containing the p-toluenesulfonate using a 50 ml. pipette. A five ml. aliquot was withdrawn and quenched in 40 ml. of ice-cold 95% ethanol in a 50 ml. volumetric flask after sufficient time has been allowed for dissolution and equilibration of the system. The time at which this aliquot was withdrawn was recorded as "zero time". The material was allowed to come to room temperature and the volumetric flask was filled to the mark with 95% ethanol. A five ml. aliquot of the resulting solution was withdrawn and further diluted by adding to a 50 ml. volumetric flask and filling to the mark with 95% ethanol. An ultra-violet spectrum was obtained of the final solution. Subsequent aliquots were withdrawn at the appropriate times and treated in the same manner. The rate of reaction was followed by observing the absorbance at the appropriate wavelength; λ_{max} of the olefin being produced. The psuedo-1st order rate constant was calculated by applying the integrated 1st order rate equation, Eq. 1.

$$k = \frac{2.303}{t} \log \frac{A_\infty - A_o}{A_\infty - A_t} \qquad (1)$$

t = time in seconds

A_∞ = absorbance after ten half-lives or more[169]

A_o = absorbance at zero time

A_t = absorbance at time t

The 2nd-order rate constant was determined by dividing the psuedo-1st order constant by the base concentration.

b) Second order rate constants Approximately 5×10^{-2} M solutions of the appropriate p-toluenesulfonates were prepared in the same manner as described above for the psuedo-1st order determinations. Five ml. aliquots were withdrawn and quenched by adding to 50 ml. of an ice-water slurry. The consumption of base was determined by titration with standard hydrochloric acid solution to the phenolphthalein end-point. The 2nd order rate constants were determined by applying the integrated 2nd order rate equation, Eq. 2.

$$k = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \qquad (2)$$

t = time in seconds

a = concentration of base in moles/liter at zero time

b = concentration of p-toluenesulfonate in moles/liter at zero time

x = amount of base consumed in moles/liter at time t

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[169] There was relatively poor agreement between the experimentally determined A's and those calculated using the extinction coefficient of the corresponding olefin. This may have been due to materials which were present in the kinetic samples but not in the samples of olefin used in the determination of the extinction coefficients.

Table 6. Second-order rate constant for the elimination of cyclobutyl p-toluenesulfonate with potassium t-butoxide in t-butyl alcohol at 70°

time[a]	a-x[b]	b-x[c]	$\log \frac{b(a-x)}{a(b-x)}$	$k_2 \times 10^5$[d]
zero	4.51	2.40	-------	----
8,123	4.34	2.23	0.01578	9.89
24,118	4.12	2.01	.03782	8.31
85,189	3.45	1.34	.13672	8.55
175,980	2.88	0.77	.29885	8.97
280,980	2.52	.41	.50515	9.76
543,080	2.30	.19	.80956	7.93
704,970	2.18	.07	1.21775	9.22
∞	2.11	----	-------	----
calc. ∞	2.13		k_2(ave.) = 8.95±0.59[e]	

[a] All times are given in seconds.

[b] a = 0.0923.

[c] b = 0.0491.

[d] in liter mole^{-1} sec^{-1}, conc. HCl = 0.1023 M.

[e] Error terms given are average deviations.

Table 7. Second-order rate constant for the elimination of trans-2-phenylcyclobutyl p-toluenesulfonate with potassium t-butoxide in t-butyl alcohol at 50°

time	a-x[a]	b-x[b]	$\log \frac{b(a-x)}{a(b-x)}$	$k_2 \times 10^4$[c]
zero	4.28	2.18	------	----
3,616	3.96	1.86	1.0815	4.62[d]
7,258	3.67	1.57	1.1875	5.19
10,926	3.45	1.35	1.2982	5.22
14,402	3.29	1.19	1.4045	5.17
18,040	3.16	1.06	1.5144	5.03
21,599	3.04	0.94	1.6429	5.03
25,249	2.93	.83	1.7933	5.06
∞	2.10	----	------	----
calc. ∞	2.10		k_2 (ave.) = 5.12±0.07	

[a] a = 0.0929, a-x given in ml. of standard acid.

[b] b = 0.0472, b-x given in ml. of standard acid.

[c] in liter $mole^{-1}$ sec^{-1}, conc. HCl = 0.1001.

[d] not included in average rate constant.

Table 8. Psuedo-1st order rate constant for the elimination of trans-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

Time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.046	-------	----
4,358	.108	0.04292	2.27
9,557	.174	.09380	2.26
14,251	.227	.13946	2.25
19,467	.278	.18846	2.23
27,968	.349	.26744	2.20
33,675	.391	.32196	2.20
41,091	.435	.38753	2.17
∞	.705	-------	----

k_1 (ave.) = 2.23±0.03

$k_2 = 2.19 \times 10^{-4}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.107×10^{-3} M.

[b] base concentration = 0.1019 M.

[c] absorbance at 258 mμ.

[d] average of 2 runs, $k_2 = 2.26 \times 10^{-4}$.

Table 9. Psuedo-1st order rate constant for the elimination of trans-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate[a] with 0.3 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.067	-------	----
1,782	.158	0.04623	5.97
3,224	.229	.08608	6.15
5,675	.333	.14990	6.08
9,152	.456	.24545	6.18
13,067	.565	.34941	6.16
18,500	.674	.48637	6.06
25,346	.778	.67597	6.14
∞	.968	-------	----

k_1 (ave.) = 6.11±0.06

$k_2 = 2.10 \times 10^{-4}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.259×10^{-3} M.

[b] concentration of base = 0.2910 M.

[c] absorbance at 258 mμ.

[d] average of 2 runs, $k_2 = 2.12 \times 10^{-4}$.

Table 10. Psuedo-1st order rate constant for the elimination of trans-2-phenylcyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.068	-------	----
2,729	.165	0.05807	4.90
6,598	.295	.15052	5.23
11,917	.435	.27864	5.38
19,117	.575	.46117	5.56
28,114	.666	.88498	5.24
51,113	.792	1.18173	5.33
∞	.843	-------	----

k_1 (ave.) = 5.27±0.13

$k_2 = 5.17 \times 10^{-4}$ liter $mole^{-1}$ sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.046×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 255 mμ.

[d] average of 3 runs, $k_2 = 5.10 \times 10^{-4}$.

Table 11. Psuedo-1st order rate constant for the elimination of trans-2-phenylcyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 70°.

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.064	-------	----
350	.141	0.04532	2.98[d]
790	.241	.11227	3.27
1,356	.350	.19934	3.39
1,927	.443	.29054	3.47
2,852	.558	.43863	3.54
3,716	.633	.57236	3.55
4,822	.696	.72905	3.48
∞	.841	-------	----

k_1 (ave.) = 3.45±0.08

k_2 = 3.39 x 10-3 liter mole^{-1} sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 5.100 x 10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 255 mμ.

[d] not included in average rate constant.

[e] average of 3 runs, k_2 = 3.31 x 10^{-3}.

Table 12. Psuedo-1st order rate constant for the elimination of trans-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.175	-------	----
412	.285	0.05222	2.92
950	.411	.12093	2.93
1,686	.552	.21343	2.92
2,630	.693	.33112	2.90
3,932	.836	.49586	2.90
5,595	.948	.69055	2.84
7,561	1.010	.85368	2.60[d]
∞	1.146	-------	----

k_1 (ave.) = 2.90±0.02

$k_2 = 2.85 \times 10^{-3}$ liter mole^{-1} sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 5.150×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 255 mμ.

[d] not included in average rate constant.

[e] average of 2 runs, $k_2 = 2.77 \times 10^{-3}$.

Table 13. Second-order rate constant for the elimination of trans-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate with 0.1 N potassium t-butoxide in t-butyl alcohol at 50°

time	a-x[a]	b-x[b]	$\log \frac{b(a-x)}{a(b-x)}$	$k_2 \times 10^4$[c]
zero	6.76	1.84	-------	----
729	6.30	1.38	0.09370	3.01
1,430	6.00	1.08	.17898	2.99
2,237	5.74	0.82	.27935	2.92
3,158	5.54	.62	.38537	2.86
4,293	5.34	.42	.53854	2.93
5,617	5.20	.28	.70309	2.93
7,774	5.10	.18	.88655	2.67[d]
∞	4.92	----	-------	----
calc. ∞	4.96		k_2 (ave.) = 2.94±0.04	

[a] a = 0.1353, a-x given in ml. of standard acid.

[b] b = 0.03678, b-x given in ml. of standard acid.

[c] in liter $mole^{-1}$ sec^{-1}, conc. HCl = 0.1001 N.

[d] not included in average rate constant.

Table 14. Psuedo-1st order rate constant for the elimination of trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.151	-------	----
218	.286	0.08543	9.03
434	.392	.16671	8.85
638	.482	.25013	9.03
848	.566	.34577	9.39
1,029	.612	.40870	9.15
1,236	.665	.49570	9.24
1,429	.703	.56889	9.17
∞	.907	-------	----

k_1 (ave.) = 9.12±0.13

$k_2 = 8.95 \times 10^{-3}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.094×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 257 mμ.

[d] average of 2 runs, $k_2 = 8.86 \times 10^{-3}$.

Table 15. Psuedo-1st order rate constant for the elimination of trans-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.2 N sodium ethoxide[b] in ethanol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^6$ sec^{-1}
zero	0.032	-------	----
2,612	.036	0.01565	1.38
29,609	.072	.18976	1.48
72,271	.100	.39987	1.27
105,445	.113	.54793	1.20
196,312	.137	1.14999	1.35
237,536.	.140	1.35411	1.31
∞	.145	-------	----

k_1 (ave.) = 1.33±0.07

$k_2 = 5.58 \times 10^{-5}$ liter mole^{-1} sec^{-1}

[a] concentration of p-toluenesulfonate = 5.079×10^{-3} M.

[b] concentration of base = 0.2386 N.

[c] absorbance at 257 mμ.

Table 16. Psuedo-1st order rate constants for the elimination of cis-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.082	-------	----
659	.107	0.01272	4.44
1,619	.141	.03065	4.36
3,037	.196	.06130	4.65
5,426	.270	.10629	4.51
9,124	.379	.18241	4.60
15,457	.527	.31324	4.67
23,373	.664	.48420	4.77
∞	.948	-------	----

k_1 (ave.) = 4.57±0.12

$k_2 = 4.49 \times 10^{-4}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.057×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 258 mμ.

[d] average of 2 runs, $k_2 = 4.32 \times 10^{-4}$.

Table 17. Psuedo-1st order rate constant for the elimination of cis-2-(p-methylphenyl)cyclobutyl p-toluenesulfonate[a] with 0.2 N sodium ethoxide[b] in ethanol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k \times 10^5$ sec^{-1}
zero	0.049	-------	----
3,086	.086	0.03852	2.88[d]
8,3177	.128	.08682	2.40
18,634	.214	.20652	2.52
33,367	.305	.38422	2.65
65,674	.389	.65722	2.31
101,308	.440	.98628	2.24
153,057	.468	1.59096	2.39
∞	.485	-------	----

k_1 (ave.) = 2.42±0.11

$k_2 = 1.01 \times 10^{-4}$ liter $mole^{-1}$ sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 5.322×10^{-3} M.

[b] concentration of base 0.2386 N.

[c] absorbance at 258 mμ.

[d] not included in average rate constant.

[e] average of 2 runs, $k_2 = 9.88 \times 10^{-5}$.

Table 18. Psuedo-1st order rate constant for the elimination of cis-2-phenylcyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 30°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.058	-------	----
1,786	.097	0.02036	2.97[d]
5,692	.181	.06819	2.77
12,740	.304	.14922	2.70
18,849	.393	.21906	2.68
28,556	.507	.32858	2.65
36,037	.572	.40620	2.60
46,780	.662	.54357	2.68
∞	.904	-------	----

k_1(ave.) = 2.68±0.04

$k_2 = 2.60 \times 10^{-4}$ liter mole^{-1} sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 5.014×10^{-3} M.

[b] concentration of base = 0.1031 N.

[c] absorbance at 255 mμ.

[d] not included in average rate constant.

[e] average of 3 runs, $k_2 = 2.49 \times 10^{-4}$.

Table 19. Psuedo-1st order rate constant for the elimination of cis-2-phenylcyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.084	-------	----
644	.156	0.03539	1.27
1,666	.256	.08987	1.24
2,824	.360	.15482	1.26
4,206	.468	.23462	1.28
6,231	.585	.34157	1.26
10,235	.746	.55206	1.24
15,070	.854	.78769	1.20
∞	1.004	-------	----

k_1 (ave.) = 1.25±0.02

$k_2 = 1.23 \times 10^{-3}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.244×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 255 mμ.

[d] average of 3 runs, $k_2 = 1.30 \times 10^{-3}$.

Table 20. Psuedo-1st order rate constant for the elimination of cis-2-phenylcyclobutyl p-toluenesulfonate[a] with 0.2 N sodium ethoxide[b] in ethanol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.040	------	----
547	.049	0.0676	2.85
1,206	.058	.01362	2.60
2,534	.081	.03167	2.88
4,227	.102	.04883	2.66
6,251	.130	.07282	2.68
9,820	.184	.12321	2.89
30,262	.371	.36427	2.77
∞	.623	-------	----

k_1 (ave.) = 2.76±0.10

$k_2 = 1.16 \times 10^{-4}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.132×10^{-3} M.

[b] concentration of base = 0.2386 N.

[c] absorbance at 255 mμ.

[d] average of 3 runs, $k_2 = 1.15 \times 10^{-4}$.

Table 21. Psuedo-1st order rate constant for the elimination of cis-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.144	-------	----
315	.239	0.04400	3.22
678	.336	.09406	3.20
1,112	.439	.15440	3.20
1,572	.535	.21936	3.21
2,119	.624	.28973	3.15
2.785	.719	.38004	3.14
3,379	.795	.46884	3.20
∞	1.130	-------	----

k_1 (ave.) = 3.19±0.02

$k_2 = 3.13 \times 10^{-3}$ liter mole^{-1} sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.080×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 261 mμ.

[d] average of 2 runs, $k_2 = 3.12 \times 10^{-3}$.

Table 22. Psuedo-1st order rate constant for the elimination of cis-2-(p-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.2 N sodium ethoxide[b] in ethanol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^5$ sec^{-1}
zero	0.061	-------	-----
1,276	.115	0.03367	6.08
2,303	.156	.06109	6.11
4,693	.243	.12574	6.17
11,056	.417	.29389	6.12
18,480	.549	.48683	6.07
34,609	.696	.91035	6.06
47,541	.746	1.26868	6.15
∞	.785	-------	----

k_1 (ave.) = 6.11±0.03

$k_2 = 2.56 \times 10^{-4}$ liter $mole^{-1}$ sec^{-1}[d]

[a] concentration of p-toluenesulfonate = 5.068×10^{-3} M.

[b] concentration of base = 0.2386 N.

[c] absorbance at 261 mμ.

[d] average of 2 runs, $k_2 = 2.57 \times 10^{-4}$.

Table 23. Psuedo-1st order rate constant for the elimination of cis-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.1 N potassium t-butoxide[b] in t-butyl alcohol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.181	-------	----
199	.270	0.05774	6.65[d]
376	.359	.12434	7.62
546	.426	.18221	7.69
713	.484	.23941	7.73
912	.546	.31024	7.83
1,149	.608	.39492	7.92
1,387	.660	.48140	7.99
∞	.896	-------	----

k_1 (ave.) = 7.80±0.12

$k_2 = 7.65 \times 10^{-3}$ liter mole^{-1} sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 5.044×10^{-3} M.

[b] concentration of base = 0.1019 N.

[c] absorbance at 258 mμ.

[d] not included in average rate constant.

[e] average of 2 runs, $k_2 = 7.53 \times 10^{-3}$.

Table 24. Psuedo-1st order rate constant for the elimination of cis-2-(m-chlorophenyl)cyclobutyl p-toluenesulfonate[a] with 0.2 N sodium ethoxide[b] in ethanol at 50°

time	A_t[c]	$\log \frac{A_\infty - A_o}{A_\infty - A_t}$	$k_1 \times 10^4$ sec^{-1}
zero	0.058	-------	----
631	.103	0.02840	1.04
1,152	.145	.05669	1.13
2,697	.245	.13254	1.13
4,306	.331	.21040	1.13
6,212	.415	.30287	1.12
9,047	.502	.42536	1.08
14,978	.606	.63968	0.98[d]
∞	.769	-------	----

k_1 (ave.) = 1.11±0.03

$k_2 = 4.64 \times 10^{-4}$ liter mole^{-1} sec^{-1}[e]

[a] concentration of p-toluenesulfonate = 4.954×10^{-3} M.

[b] concentration of base = 0.2386 N.

[c] absorbance at 258 mμ.

[d] not included in average rate constant.

[e] average of 2 runs, $k_2 = 4.54 \times 10^{-4}$.

SUMMARY

Data has been presented as a basis for the argument that trans-2-arylcyclobutyl p-toluenesulfonates eliminate by a cis E_2 mechanism in potassium t-butoxide-t-butyl alcohol solution and not by a carbanion mechanism. The cis E_2 elimination from this system closely resembles that from beta-phenylethyl p-toluenesulfonate in solvent and substituent effects.

The Hammett rho-value for the trans elimination from cis-2-arylcyclobutyl p-toluenesulfonates is greater in t-butyl alcohol solution (rho = 2.2) than in ethanol solution (rho = 1.3). The trans elimination is placed near "central E_2" on the E_2 elimination scale with C-H bond breaking playing a more important role in t-butyl alcohol.

Comparison of the rates of cis and trans elimination from the 2-arylcyclobutyl system, $k_{trans}/k_{cis} = 2.5$, shows that the elimination from trans-2-phenylcyclobutyl p-toluenesulfonate is an example of a cis elimination being nearly as rapid as the trans elimination from the corresponding isomeric compound. This data lends further support to the postulate that a cis and co-planar stereo-relationship of leaving groups is conducive to E_2 elimination.

The methods of synthesis of the various cyclobutyl compounds and precursors has been reported along with the pertinent physical data. A short discussion of likely extensions of the present work has also been presented.

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