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Concerted cis and trans bimolecular eliminations in the bicyclo (2.2.1) heptane system

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CONCERTED CIS AND TRANS BIMOLECULAR ELIMINATIONS IN THE BICYCLO (2.2.1) HEPTANE SYSTEM

by

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INTRODUCTION

The mechanistic picture of β-elimination reactions is by no means a clear one. There appear to be several factors which are capable of influencing the nature of the transition state. Much work has appeared in the literature over the past two decades in which some of these factors were studied in an effort to evaluate and place proper emphasis on the manner in which they influence the transition state. While much of this work has allowed correlations to be made, new ideas have arisen which have often served to complicate the picture.

The commonly accepted concept of a preferred trans coplanar pathway for β-eliminations has been modified by the observation that cis coplanar eliminations in some systems occur readily. These observations have opened a new area of research in the field of β-elimination chemistry.

At the outset it was planned to prepare the four possible stereoisomers of a series of 2-tosyloxy-3-arylnorbornanes. It was felt that kinetic studies of the β-elimination of these compounds would shed some light on the mechanism of cis eliminations. Important conclusions regarding the influence of the dihedral angle between the β-proton

and the leaving group upon the relative rate of elimination in the various isomers could be made. Such conclusions could then be applied to other systems to make predictions about rates in those systems. The substituted norbornanes were very useful because of their rigid geometry and well-defined bond angles.

One major difficulty which could not have been anticipated was encountered. The synthesis of the compounds in which the substituents at both the 2- and the 3- positions of the norbornane ring were exo had not been previously reported. The compounds in which the tosyloxy groups were endo and the aryl groups were either exo or endo had not been previously synthesized. Thus the synthesis of the compounds for kinetic studies presented a major research problem in itself.

It was found that the three series of compounds in the previous paragraph could not be prepared either in sufficient yield or purity to make their kinetic study possible. Although several approaches to the synthetic problem were taken, none proved to give the correct answer.

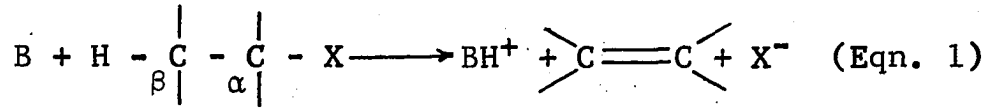
The purpose of this thesis is to report the efforts to synthesize these compounds which were needed to fulfill the

original objective. The results of the kinetic studies on the exo-2-tosyloxy-endo-3-arylnorbornanes, giving rise to a cis elimination, are also reported.

HISTORICAL

Elimination Reactions

In the beta elimination reaction, unsaturation is introduced into an organic molecule by the removal of a substituent from each of two carbon atoms, usually adjacent, in the molecule. Most often a proton is lost from one carbon atom, known as the β-carbon atom; and a nucleophilic group, X, is removed from the adjacent or α-carbon atom. In this situation two σ bonds are broken and a new π bond is formed between the carbon atoms. In the present case, we shall concern ourselves with only those beta eliminations which are promoted by some basic species, as in (Eqn. 1).



(Eqn. 1)

Volumes of work regarding some aspect of the beta elimination reaction have appeared in the literature. It is of interest both from a synthetic standpoint and a theoretical or mechanistic one. Ingold[1] has set down a generalized mechanistic theory based upon kinetic evidence and polar

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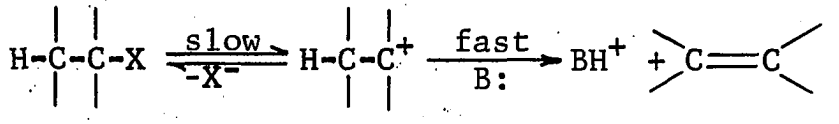
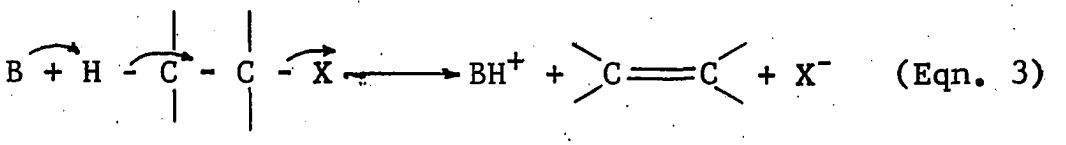
[1]Ingold, C. K., Structure and Mechanism in Organic Chemistry. Ithaca, N. Y., Cornell Univ. Press. 1953.

effects. This theory has been widely accepted and much of the work which appears in the literature is correlated on this basis. Their theory suggests two basic mechanistic pathways for beta eliminations, the unimolecular E1 reaction and a bimolecular E2 reaction. The unimolecular E1 reaction (Eqn. 2) involves ionization to form a carbonium ion in the rate determining step, followed by rapid removal of a proton with formation of a π bond. The E2 or bimolecular elimination (Eqn. 3), the most widely observed type, is characterized by the fact that it exhibits second order kinetics and involves simultaneous removal of the β-proton and the leaving group. The E1cB



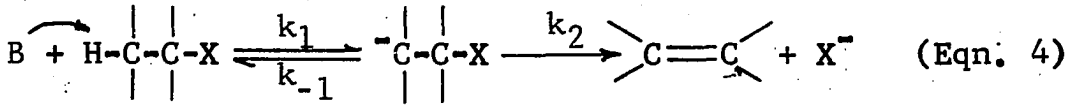
(Eqn. 2)

elimination (Eqn. 4) is a special case of the E2 elimination in which the β-proton is removed to form a carbanion.



(Eqn. 3)

This step may be followed by a rapid ejection of the leaving group with formation of the olefin, or the ejection of the leaving group may be slow and rate determining.



(Eqn. 4)

Prior to the work of Cristol[2, 3, 4] and co-workers on the benzene hexachloride isomers, the need for a trans coplanar relationship between the β-proton and the leaving group in the transition stage of a beta elimination was universally accepted. Cristol was able to show that the β-isomer of benzene hexachloride, in which all the adjacent chlorine atoms in the molecule were trans, and thus only a cis relationship between hydrogen and chlorine was available, did indeed eliminate. The β-isomer eliminated approximately 10^4 times slower than the other isomers in which a trans relationship was available, but the fact that it eliminated at all and exhibited good second order kinetics was surprising.

This discovery opened a new area of study in mechanistic interpretation of elimination reactions. Here was a type of elimination which had not been previously observed. There were two possibilities which could explain Cristol's results, a concerted cis elimination in which hydrogen and chlorine

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[2]Cristol, S. J., J. A. Chem. Soc., 69, 338 (1947).

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

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

were removed simultaneously from adjacent carbon atoms, or an E1cB type elimination involving carbanion intermediate.

In a later paper Cristol[5] concluded that an E1cB mechanism was operating when he carried out the base-catalyzed elimination of β-benzene hexachloride in deuterated solvent and recovered unreacted substrate after one-half-life. Although less than 1% deuterium was incorporated into the unreacted substrate, he concluded that a carbanion intermediate was involved. He pointed out, however, that in order to explain the results, the decomposition of the carbanion to give products would have to be 150 times as fast as the reaction with deuterium to give deuterated substrate. Recently Hine and co-workers[6] have also studied this elimination and have shown that it proceeds by way of a carbanion intermediate.

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[5]Cristol and Fix, op. cit.

[6]Hine, J., Weimar, R. D., Jr., Langford, P. B., and Ramsay, O. B., J. Am. Chem. Soc., 85, 3894 (1964).

In a series of papers by Bordwell and co-workers,[7,8,9,10,11] the rates of *cis* eliminations in the *p*-toluenesulfonylcyclohexyl tosylates and *p*-toluenesulfonylcyclopentyl tosylates were studied. Several factors became evident from these studies. Considerable rate enhancement was observed with the β-*p*-toluenesulfonyl group present in the molecule. Such a fact would seem to favor the carbanion mechanism, as this mechanism would be expected to be facilitated by the presence of an electron attracting group which would facilitate the removal of the β-proton. The marked influence of this effect was more clearly shown by the fact that *trans*-2-*p*-toluenesulfonylcyclohexyl tosylate gave 1-*p*-toluenesulfonylcyclohexene, the *cis* elimination product, rather than the 3-isomer, the product of *trans*

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

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

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

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

[11]Weinstock, Pearson and Bordwell, *op. cit.*, p. 3473.

elimination. It was shown that the 3-isomer did not rearrange to the 1-isomer under the conditions of the reaction.

The elimination of the trans-2-p-toluenesulfonylcyclopentyl tosylates and brosylates proceed in the same manner. In one case, the rate of the above trans compound was compared with the cis isomer using trimethylamine as the base. The rates were nearly the same at 25 C., and the energies of activation for the two eliminations differed by only 0.3 kcal. per mole.

These workers concluded on the basis of the observed general base catalysis that the cis eliminations were not proceeding by way of a stable carbanion intermediate. Hine and co-workers[12] have recently shown in a study of the rate of carbanion formation in cyclohexylsulfone systems that the eliminations were proceeding by an ElcB mechanism. They observed that the rate of cis elimination from trans-2-p-toluenesulfonylcyclohexyl tosylate is slower than would have been predicted by observing the rate of carbanion formation. Further evidence of a carbanion mechanism for elimination in cyclohexyl compounds has recently been presented by Bordwell

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

and co-workers[13]. In a study of eliminations from cis and trans 1-acetoxy-1-phenyl-2-nitrocyclohexanes, several results were obtained which pointed to a carbanion mechanism. Steric assistance to carbanion formation and steric hindrance to carbanion formation were shown to be important in determination of the k-cis/ k-trans ratio in this system. It is not unreasonable to assume that the same factors are important in the cyclohexyl and cyclopentyl sulfone tosylate eliminations.

In other work Cristol[14], et al., showed that when a trans coplanar relationship could not be attained, the preference for trans over cis elimination was greatly reduced. In the case of the isomeric 11, 12-dichloro-9, 10-dihydro-9, 10-ethanoanthracenes, cis elimination (from the trans compound) was shown to be favored over trans elimination (from the cis compound) by a factor of 9. In the trans elimination, the angle between the β-proton and the leaving group is approximately 130°. Cristol explained the results on the basis of highly favorable entropy factor for the cis

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

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

elimination although the activation energy for the trans elimination was lower by 4 kcal. per mole. The ethano bridge in these molecules make them so rigid that it is impossible for them to attain a trans coplanar transition state. This was the first instance in which the bond angles were well-defined in an elimination study.

A very similar situation exists in the 2,3-dichloronorbornanes. Cristol and Hoegger[15] have shown that the cis elimination from the trans-dichloride is favored over trans elimination from the endo-cis-dichloride, even though the energy of activation is virtually the same for both eliminations. Here again the entropy factor favors the cis elimination by about 10 entropy units.

These workers also showed that when an acid strengthening group was incorporated into the molecules, the rate of elimination was greatly enhanced.[16] Substitution of a p-toluenesulfonyl group for one of the chlorine atoms in either the dichloroethanoanthracenes or the dichloronorbornanes gave rise to a rate enhancement of approximately 10^{10} times

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

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

for the elimination of hydrogen chloride. Here again this was interpreted by Cristol to mean that the reactions were proceeding by a carbanion route.

Some of the questions regarding the degree of carbanionic character in an elimination reaction can be answered in a semi-quantitative way in some systems by use of the Hammett equation.[17,18] This equation has been used to

$$\log \frac{k}{k_o} = \rho\sigma$$

correlate the rates of a large number of compounds containing benzene rings with meta or para substituents on the benzene ring. The equation says that the rate for a substituted benzene compound, k, is related to the rate of the unsubstituted benzene compound, k_o, by two constants, ρ and σ. The σ-value, which is different for each substituent, is a measure of that substituent's ability to control electron density at the carbon atom α to the benzene ring. The ρ-value of the reaction is obtained by determining the slope of the straight line resulting from a plot of σ versus log k

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[17]Hammett, L. P., Physical Organic Chemistry. New York, N. Y., McGraw-Hill Book Co. 1940.

[18]Jaffe, H. H., Chem. Rev., 53, 191 (1953).

and is a measure of the sensitivity of the reaction to changes in electron density at the phenyl bearing carbon atom. A large positive value of ρ indicates an increase in electron density at the β-carbon atom in going from the ground state to the transition state. It is not known how large ρ may be, but the β-phenylethyl compounds[19] having values in the range of 2-3.5 for ρ are usually considered to be good models for concerted E2 reactions.

DePuy, Thurn and Morris[20] in 1962 published the first case in which a rapid concerted cis elimination occurred. In their study of cis and trans-2-arylcyclopentyl tosylates, they noted that in the potassium t-butoxide-t-butanol system these compounds showed a value of k-trans/k-cis of only 14 and a ρ-value of 2.34. The analogous cyclohexyl compounds under the same conditions gave a value of k-trans/k-cis of greater than 10^4. The value for k-trans/k-cis in the cyclopentyl compounds has recently been revised to 9.7 and the

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[19]Bishop, C. A. Pyrolytic and Base-Catalyzed Elimination Reactions: Effect of Structure on the Rate of Reaction. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1961.

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

value of ρ has been revised to 2.76,[21] but these changes are not significant. This ρ-value should be compared with the value of 3.39 for the β-phenylethyl tosylate series[22] which is usually considered to be concerted.

These workers stated that this data indicated that a concerted cis elimination had occurred. A theory was advanced which stated that the rate of elimination depends on the dihedral angle between the β-proton and the leaving group. When this angle approaches 0^{o} or 180^{o}, the rates should increase; and when the angle approaches 90^{o}, the rates should fall. The scope of this theory has not been widely tested and will not be known until more data has been gathered. However, if one looks back at some of the previously reported data on β-eliminations in the literature,[23,24,25] it can be seen that these results fit the

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[21]Smith, J. S., Bimolecular Elimination Reactions of Cyclopentyl Compounds. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1964.

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

[23]Cristol and Hause, op. cit.

[24]Cristol and Hoegger, op. cit.

[25]Cristol and Arganbright, op. cit.

theory nicely. More recent data, to be discussed shortly, has substantiated this postulate.

The exact nature of this angular dependence of elimination rates is difficult to understand. The enhanced rate is usually accompanied by a favorable entropy factor rather than a favorable activation energy as this parameter is usually higher for cis eliminations. That the effect is probably tied in with facility for electronic rearrangements is shown by the rate enhancement in these reactions by an electron attracting group in the β-position. The ease of rehybridization of either the α- or β-carbon atom is probably influential in this situation.

In the trans-2-arylcyclopentyl tosylates, Smith[26] has again noted the preference for cis elimination over trans elimination even though both could occur in the system. He observed from 85-100% 1-phenylcyclopentane in the products, the lower value being derived from the p-methylphenyl compound which reacted slower than the other compounds studied. It was also shown that 3-phenylcyclopentene, the product of trans elimination, did not rearrange under the elimination conditions. The driving force for conjugation in the

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[26]Smith, op. cit.

olefinic products probably exerted some influence on the k-trans/k-cis ratio. Here again a favorable entropy factor for the cis elimination was noted.

Some of the most recent data which seemingly fits the DePuy theory is that of LeBel[27] and co-workers. These workers have carried out a detailed kinetic analysis of the elimination of a series of 2,3-dihalonorbornanes. These workers showed that in the 2, 3-dihalonorbornane system the cis elimination is favored over the trans elimination. With the dibromides the ratio was 31, with the bromochlorides 29 and with the dichlorides 67 at 110°C. using sodium pentoxide in n-pentanol as the solvent system. With the stronger base, t-amyloxide, the ratio k-cis/k-trans for elimination of hydrogen bromides from the dibromides was 71 at 50°C. and 15 at 110°C. The entropy and enthalpy of activation terms for these eliminations varied in the same direction and by approximately the same amount whether a cis or trans pathway was being followed. Such variances in the activation parameters are probably not coincidental and indicate that both eliminations are proceeding by the same mechanistic

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

pathway. If the trans elimination had been occurring by a concerted pathway and the cis elimination by a carbanionic pathway, one would not expect the activation parameters to show such marked similarities. The activation enthalpies and entropies for dibromides were quite similar to those for the bromochlorides, and the latter eliminated at a slightly slower rate. The dichlorides were shown to eliminate at a much slower rate than either the dibromides or bromochlorides. This was due to a higher activation enthalpy (5-6 kcal./mole) for the elimination of hydrogen chloride as compared to hydrogen bromide although the entropy factor favored elimination of hydrogen chloride.

High hydrogen-deuterium isotope effect values of 3.4 for the trans and 3.6 for the cis elimination in the dibromides at 110°C. also indicate a concerted path for these eliminations. The similarity of the deuterium isotope values again indicates a similar mechanism for both eliminations. This evidence adds to the facts already discussed, pointing to a concerted cis elimination.

LeBel[28] also showed that both bromochlorides preferentially eliminated hydrogen bromide to give greater than 95%

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[28] Ibid.

of 2-chloro-2-norbornene in the product. The predominance of cis over trans elimination by a factor of 29 indicates a concerted process. In a two-step carbanion process the rate should not be effected by the leaving group, and the probability of elimination of either hydrogen chloride or hydrogen bromide should be nearly equal. This then would be reflected in a greater percentage of the bromo olefin in the product than was observed. The slower rate of elimination of hydrogen bromide from the bromochlorides by a factor of three rather than from the dibromides was explained by the greater stability of 2-bromo-2-norbornene over 2-chloro-2-norbornene. This would be expected in an elimination in which the transition state exhibited some of the characteristics of the products, that is to say, some double bond character.

One further point of importance in eclipsed or sterically hindered eliminations is the availability of the β-proton for removal by the basic species. LeBel[29] has shown that rate of elimination from the endo-cis-dibromonorbornene is about three times as fast as from the exo-cis-isomer. This can be explained in two ways. The exo-protons in this series of compounds bearing no syn-7-substituent

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[29] Ibid.

should be more available than the endo-protons.[30] The endo-protons are made less accessible by the endo-5 and 6 protons across the ring. Another possible explanation for the observed rate enhancement is that the leaving group in the endo-position is assisted in leaving by steric crowding from the 5- and 6- endo-protons. Which of these two effects is predominant could be tested by preparing analogous compounds with bulky syn-7-substituents and kinetically analyzing their eliminations.

In a very recent study, Kwart[31] and co-workers have reported the elimination reactions of 2-exo-p-toluenesulfoxy-3-endo-d-norbornane and 2-exo-bromo-3-exo-d-norbornane. Although they did not carry out a detailed kinetic analysis of these eliminations, some interesting facts arise from their product analyses by deuterium tracer studies.

A very bulky base, 3-methyl-3-pentoxide, was used in order to force preferential abstraction of the exo-proton or deutron in the elimination. In the case of the tosylate, the reaction was carried out in both a polar and a non-polar

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[30]Kaplan, L., Kwart, H. and von R. Schleyer, P., J. Am. Chem. Soc., 82, 2341 (1960).

[31]Kwart, H., Takeshita, T. and Nyce, J. L., J. Am. Chem. Soc., 86, 2607 (1964).

solvent to determine the effect of this factor on the mechanism and hence the product of the reaction. In 3-methyl-3-pentanol the 2-exo-p-toluenesulfoxy-3-endo-d-norbornane gave only 18% of the product of cis elimination, 3-deutero-2-norbornene. However, in a non-polar solvent, p-cymene, 65% of the cis elimination product was observed. With the tert-alcohol solvent, the 2-exo-bromo-3-exo-d-norbornane gave 98% of the cis elimination products.

Several facts are inherent in these observations and some important mechanistic conclusions can be drawn from them. This study is unique in that it is the first case studied in which the rate enhancing influence of an electron attracting substituent in the β-position is absent.

The authors interpret the small amount of cis elimination product from the tosylate in the polar solvent as being attributed to a large amount of an E1 elimination occurring under these conditions. When the same compound is eliminated in the less polar solvent, the reaction becomes almost purely E2 in nature. The bromide exhibits E2 elimination even in the polar alcohol solvent. These results seem to be reasonable in view of the ease of solvolysis of tosylates in polar media.

When appropriate corrections were applied for deuterium

isotope effects, the need for co-planarity and the relative accessibilities of endo versus exo hydrogens in this system, these workers arrived at a predicted value of k-cis/k-trans for the tosylate elimination of approximately 84 under E2 conditions. The observed value of approximately 2.3 may be explained either by steric arguments or by the electronic influence of the leaving group. The magnitude of the steric effect in this system may possibly be tested by carrying out a similar study of the endo-norbornyl tosylate.

The analogous prediction of k-cis/k-trans $\cong$ 49 in the bromide is in much better agreement with the observed value of 15.4. Here, apparently the bulky base is not influenced as much by the leaving group and the rates are more nearly normal. One further factor which gives the steric argument some support in this system is the observance of a small amount of γ-elimination product (3-deuteronortricyclene) in the tosylate elimination. This product is not observed in the bromide elimination, possibly because of the smaller steric demand of the bromine atom. Basic attack on the norbornyl bromide could occur exclusively at the β-position, whereas the tosylate might force some of this attack to occur at the C_6 position.

One can readily see from the foregoing discussion of

elimination reactions that it is indeed a complex subject. No attempt has been made to review the literature on all aspects of the fascinating field. Only those works dealing extensively with eliminations in bicyclic compounds and as a consequence, those dealing with the question of the mechanism of cis eliminations have been presented. There are many good references dealing with general reviews in elimination chemistry. Several additional references dealing with other areas and aspects of the subject have been included in the bibliography. One recent review which deals with a theoretical model for elimination reactions and deserves special mention is that of Bunnett.[32]

Synthetic

In order to study the kinetics of elimination of the 3-aryl-2-toluene-sulfoxybicyclo (2.2.1) heptanes, it is highly desirable that one be able to obtain these compounds in a stereochemically pure form. Upon review of the literature of the synthesis of arylbicyclo (2.2.1) heptyl compounds, it is found that very few have been previously

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[32]Bunnett, J. F., Angew. Chem., Int. Ed., 1, 225 (1962).

reported. The work of Kleinfelter and Schleyer[33,34] in which they reported the syntheses of a series of 2-arylnorbornenes and one 2-arylnorbornanone stands alone as far as compounds immediately pertinent to the present investigation are concerned. Most of the previous workers have not been concerned with the stereochemical purity of those few compounds which have been reported.

Kleinfelter and Schleyer have prepared a series of 2-aryl-2-norbornenes by the action of an aryl Grignard or an aryllithium reagent on norbornanone followed by a dehydration of the tertiary alcohol thus formed. Their olefins were contaminated by appreciable amounts of arylnortricyclenes as evidenced by the comparison of their ultraviolet absorption molar extinction coefficients with those reported in this thesis. In all cases compared, their olefins exhibited appreciably lower absorption values. Upon treatment with the appropriate acid, the 2-aryl-2-endo-nornbornanols and the 2-aryl-2-norbornenes were transformed into 1-aryl-2-exo-norbornyl esters. These esters were saponified to yield

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[33]Kleinfelter, D. C. and von R. Schleyer, P., J. Am. Chem. Soc., 83, 2329 (1961).

[34]Kleinfelter, D. C. and von R. Schleyer, P., J. Org. Chem., 26, 3740 (1961).

1-aryl-2-exo-norbornanols, which in turn were oxidized with chromic acid to 1-aryl-2-norbornanones.

A very important result of the chromic acid oxidation of the alcohols to the ketones was the facility with which the oxidation proceeded beyond the ketone stage. The acidic products of this oxidation were shown to be acids derived from the cleavage of the 1,2-carbon-carbon bond of the norbornane ring. It is found that this cleavage or a similar one is the predominant reaction in attempted syntheses of 3-aryl-2-norbornanones by oxidation of 2-aryl-3-norbornanols. This point will be further elaborated upon in the discussion section of this thesis.

Wildman and Hemminger[35] have reported the synthesis of 3-phenylnorbornanone by a Diels-Alder route from cyclopentadiene and β-nitrostyrene. The Diels-Alder adduct was hydrogenated to remove the 5-double bond, and the Nef reaction was carried out on the saturated nitro compound. This ketone is believed to be predominantly the exo-phenyl isomer; although Kleinfelter and Schleyer,[36] who have also prepared

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[35]Wildman, W. G. and Hemminger, C. H., J. Org. Chem., 17, 1641 (1952).

[36]Kleinfelter and Schleyer, J. Am. Chem. Soc., p. 2329.

it, have stated that it may be a mixture of the exo and endo phenyl isomers.

Kleinfelter and Schleyer have also prepared a 2-phenyl-norbornanone by the pinacol rearrangement of 3-endo-phenylnorbornane-2,3-cis-exo-diol. Again they note that this product may have been a mixture of the endo- and exo-3-phenylnorbornanones, although the 2,4-dinitrophenylhydrazone derivative had a much higher melting point than the same derivative of the Nef ketone after several recrystallizations.

Erman and Flautt[37] have carried out a similar study in the camphor system. p-Anisyl Grignard reagent was added to camphor to yield 2-endo-p-anisyl-2-exo-borneol. Dehydration and hydroboration of the resulting olefin yielded 2-exo-p-anisyl-3-endo-norborneol. These authors also noted that chromic acid oxidation of this alcohol gave rise to ring cleavage products if the theoretical amount of oxidizing agent was exceeded. The 2-exo-p-anisyl-3-bornanone was easily epimerized under either acidic or basic conditions.

Recently Dinwiddie and McManus[38] have reported a study

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[37]Erman, W. F. and Flautt, T. J., J. Org. Chem., 27, 1526 (1962).

[38]Dinwiddie, J. G., Jr. and McManus, S. P., J. Org. Chem., 28, 2416 (1963).

of a series of bicycloheptyl compounds derived from the Diels-Alder reaction of cyclopentadiene with cis- and trans-benzalacetone and with acetylphenylacetylene. These workers have noted the difficulty of purification of bicyclic compounds by the usual physical methods. They were able to obtain pure isomers of these compounds only by cumbersome chemical separations.

The reaction of trans-benzalacetone with cyclopentadiene yielded different mixtures of endo-2-acetyl-exo-3-phenyl-5-norbornene and exo-2-acetyl-endo-3-phenyl-5-norbornene depending upon the temperature at which the reaction was carried out. At higher temperatures a large percentage of the exo-phenyl isomer was found in the products under a situation which would be expected to give the thermodynamically more stable isomer as the predominant product. Oxidation of the mixed acetyl compounds with hypobromite followed by iodolactonization gave poor yields of the pure norbornene carboxylic acids.

The reaction product of acetylphenylacetylene and cyclopentadiene was hydrogenated to remove the double bonds prior to the hypobromite oxidation. Under the oxidation conditions, the saturated compound with both the phenyl and acetyl groups in the endo-position, the compound epimerized at the

position alpha to the carbonyl group to yield endo-3-phenylnorbornane-exo-2-carboxylic acid. This observation is another demonstration of the relative ease with which endo substituents in the norbornane system are transformed to the exo-position.

This brief resumé summarizes the meager list of bicyclic compounds pertinent to the present study which have been reported in the literature. The experimental work which was carried out in an effort to synthesize compounds needed for this kinetic study of eliminations is reported in the discussion section of this thesis.

RESULTS AND DISCUSSION

Synthetic

The endo-3-aryl-exo-norbornanols were easily prepared by conventionally stereoselective reactions. An appropriate aryl Grignard reagent or aryl-lithium reagent was added to norcamphor using ether as the solvent. This addition is known to give the exo-aryl adduct. Dehydration of the alcohols produced 2-aryl-2-norbornenes in relatively pure form. These olefins were hydroborated by the procedure of Brown,[39,40] which is known to be highly stereoselective, to give very pure alcohols. The p-toluenesulfonate esters of these alcohols were white crystalline solids which were easily recrystallized. Upon prolonged standing at ambident temperatures, the tosylates underwent a slow decomposition which could be prevented by refrigeration.

The NMR spectrum of endo-3-phenyl-exo-2-norbornanol consists of a multiplet at 3.72 p.p.m., a broad singlet at 3.43 p.p.m., a triplet centered at 2.74 p.p.m. with spacings

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[39]Brown, H. C. and Subba Rao, B. C., J. Am. Chem. Soc., 81, 6428 (1959).

[40]Brown, H. C. and Zweifel, G., J. Am. Chem. Soc., 81, 247 (1959).

of about 3.6 cycles/sec., and the remainder of the spectrum is a series of broad multiplets above 2.5 p.p.m. The 3.72 p.p.m. multiplet is assigned to the endo-C_2 proton which is coupled to the exo-C_3 proton and is further broadened by coupling to the endo-C_6 proton. The 3.43 p.p.m. singlet is assigned to the hydroxyl proton and can be removed by deuteration. The triplet at 2.74 p.p.m. is assigned to the C_3 benzylic proton coupled to the C_4 bridgehead proton and the endo-C_2 proton. These assignments are consistent with published NMR data on other bicycloheptyl derivatives.[41,42]

Several approaches to the syntheses of the other isomers of the 3-aryl-2-norbornanols were taken. The most logical route from the endo-3-aryl-2-norbornanols seemed to be by way of a 3-phenyl-2-norbornanone derived from the alcohol by an oxidation reaction. This ketone would then be reduced or epimerized and then reduced to prepare the remaining three isomers desired, assuming that reasonable purification procedures could be found.

The initial efforts to oxidize endo-3-phenyl-3-exo-2-

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[41] Anet, F. A. L., Can. J. Chem., 39, 789 (1961).

[42] Flautt, T. J. and Erman, W. F., J. Am. Chem. Soc., 85, 3212 (1963).

norbornanol were made by the method of Jones[43] using chromic acid in acetone solution. Many experiments were carried out in which concentrations, temperatures and reaction times were varied. It was found that in order to oxidize the alcohol completely, an excess of chromic acid was required. Secondary oxidation processes were prevalent in these reactions and greatly reduced the yields of the desired endo-3-phenyl-2-norbornanone and complicated the products with mixtures of other oxidation products. The infra-red spectra showed two carbonyl absorption bands in addition to the 5.73 μ ketone absorption. Some of these materials appeared to be acids but could not be removed by basic washing of an ether solution of the oxidation products. The oxidation products could not be purified by vacuum distillation, elution chromatography or vapor phase chromatography.

When it became apparent that this method of oxidation would not produce an easily purified product, other methods of oxidation of the alcohol were tried. The chromium (VI) oxide-pyridine complex was prepared according to the method

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[43]Bowden, K., Heilbron, I. M., Jones, E. R. H. and Weedon, B. C. L., J. Chem. Soc., 39 (1946).

of Holum[44] in an effort to find a milder oxidizing agent. The actual problem is not one of strength but rather of selectivity. What is needed is a reagent which will affect only the oxidation to the ketone stage and not beyond. The great ease with which the 3-aryl-2-norbornanones are oxidized further is probably due to the ease of enolization of such a ketone. As chromic acid oxidations are usually carried out in acid solution, it seemed reasonable that oxidation under basic conditions should suppress enolization and hence be more selective. Here again a product was obtained in which the infrared spectrum exhibited three carbonyl absorptions as well as a hydroxyl absorption. It was not found possible to find conditions for this reaction which would improve the selectivity of the oxidation.

Another chromic acid oxidation which was utilized was that of Brown[45] who carried out the oxidations of several secondary alcohols in ether solution. This method gave essentially the same results as the two previous oxidations even when carried out at -15°C. The oxidation of the enol

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[44]Holum, J. R., J. Org. Chem., 26, 4814 (1961).

[45]Brown, H. C. and Garg, C. P., J. Am. Chem. Soc., 83, 2952 (1961).

appeared to proceed at a faster rate than the oxidation of the alcohol. The quality of the product was poor even when the oxidizing agent was added rapidly and the reaction was quenched immediately following the addition.

The best results were obtained in a chromic acid oxidation of the organoborane[46] derived from hydroboration of 2-phenyl-2-norbornene. The hydroboration was carried out in ether solution according to the method of Sondheimer.[47] This method always yielded mixtures of alcohol, ketone and other carbonyl bearing species which were unidentified but could not be removed by basic treatment. Attempts to purify the products by distillation or preparative scale vapor phase chromatography were unsuccessful. From the data which could be obtained from analytical vapor phase chromatography, there appeared to be as much as 40% of the desired 3-phenyl-2-norbornanone in the product, but the validity of such a conclusion is questionable since the other products were not identified.

It is quite probable that the 3-phenyl-2-norbornanone

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[46]Brown and Garg, op. cit., p. 2951.

[47]Sondheimer, F. and Nussim, M., J. Org. Chem., 26, 630 (1961).

which was derived from these oxidations was a mixture of the exo and endo phenyl isomers. Kleinfelter[48] has noted the ease of epimerization of these compounds. Particularly in those oxidations conducted under acidic conditions, the acid catalyzed enolizations of the ketone would be expected to give rise to a mixture of isomers.

An Oppenauer oxidation[49] of endo-3-phenyl-exo-2-norbornanol using aluminum isopropoxide and cyclohexanone was attempted. The reaction mixture was refluxed several hours longer than the usual time required for such oxidations. The infra-red spectrum gave no indication of ketone formation. This was attributed to the inaccessibility of the endo-C_2 hydride for transfer to the cyclohexanone. The influence of the endo-C_5 and C_6 protons across the ring greatly hinders approach to the endo-C_2 hydrogen by an external reagent.

Refluxing an isopropanol solution of endo-3-phenyl-exo-2-norbornanol with aluminum isopropoxide in the presence of a trace of acetone for three days brought about no epimerization of the hydroxyl group. The NMR spectrum of the product

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[48]Kleinfelter and Schleyer, J. Am. Chem. Soc., p. 2329.

[49]Sondheimer, F., Danieli, N. and Mazur, Y., J. Org. Chem., 24, 1278 (1959).

showed no change from the spectrum of the starting material. This reaction also depends upon the transfer of the endo-C_2 hydrogen as hydride and, as a consequence, probably does not react for the same steric reasons that the Oppenauer oxidation did not occur.

The search for oxidizing reagents was concluded with an N-bromosuccinimide oxidation following the methods of Fieser.[50] The reaction was carried out using N-bromosuccinimide in aqueous solution. Although a small amount of a carbonyl compound was formed in the reaction, as evidenced by the 5.85 μ absorption in the infra-red spectrum, it was not 3-phenyl-2-norbornanone, which absorbs at 5.73 μ.

Following the many unsuccessful attempts to prepare any of the desired compounds by oxidation, it was decided to use another pathway to synthesize the aryl ketones. Wildman and Hemminger[51] had reported the synthesis of 3-phenyl-2-norbornanone by a Nef reaction on 2-nitro-3-phenylnorbornane which was obtained from the Diels-Alder reaction of β-nitrostyrene and cyclopentadiene. Kleinfelter and

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[50]Fieser, L. F. and Rajagopalan, S., J. Am. Chem. Soc., 71, 3938 (1949).

[51]Wildman and Hemminger, op. cit.

Schleyer[52] have more recently reported the reaction to yield exo-3-phenyl-2-norbornanone. In the present case the product was shown to be a mixture of three components by analytical vapor phase chromatography, but the mixture could not be resolved. This reaction might be expected to yield a mixture of the two epimeric ketones since the work-up involves an acidic solution.

The Diels-Alder reaction of trans-benzalacetone with cyclopentadiene was performed under conditions shown by Dinwiddie and McManus[53] to give the largest percentage of exo-3-phenyl-endo-2-acetylnorbornene in the product. Hydrogenation of this adduct followed by analytical vapor phase chromatography indicated approximately an 80:20 mixture of isomers. Presumably the isomer present in the greater amount was the exo-3-phenyl-endo-2-acetylnorbornane. A Baeyer-Villiger oxidation was carried out on the mixture of acetyl compounds to yield a mixture of 2-acetoxy-3-phenylnorbornanes. Analytical vapor phase chromatography showed the product contained a 67:33 mixture of isomers. It was not possible to

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[52]Kleinfelter and Schleyer, J. Am. Chem. Soc., p. 2329.

[53]Dinwiddie and McManus, op. cit.

separate the two isomers by preparative scale vapor phase chromatography. Since the Baeyer-Villiger oxidation is known to proceed with retention, the endo-acetoxy compound should be present in the greater amount.

Several of the crude product mixtures from the various oxidation reactions were reduced with lithium aluminum hydride. In one case the NMR spectrum of the reduction product showed a quartet at 5.01 p.p.m. which would be expected for the exo-C_2 proton of endo-3-phenyl-endo-3-norbornanol. However, this quartet represented only a fraction of a proton, indicating impurities in the alcohol. A crystalline tosylate could not be made from the impure alcohol.

The successful syntheses of exo-3-aryl-endo-2-norbornanol, exo-3-aryl-exo-2-norbornanol and endo-3-aryl-endo-2-norbornanol await the discovery of a selective oxidizing agent for the transformations described above as well as better purification techniques for these compounds. It is quite reasonable to assume that such conditions and techniques are available at the present time; and if applied in the proper combinations, they would yield the three isomers which were so elusive during the course of the present investigation.

Elimination Reactions

At the outset of this work it was planned to study the kinetics of elimination of p-toluenesulfonic acid from the four isomers of 3-aryl-2-p-toluenesulfoxynorbornane. It was felt that this system with its rigid boat form cyclohexane ring and well-defined angles at the C_2 and C_3 positions would provide a valuable test of the theory of DePuy, Thurn and Morris.[54] A study of base strength and solvent polarity versus the ratio k-*cis*/k-*trans* in this system should give valuable insight into the mechanism of *cis* elimination reactions.

A comparison of the rates of elimination for the *endo*-aryl-*exo*-tosyloxy series is given in Table 1. The base, solvent, temperature and percent olefin in the product are also shown. These data are the only ones currently available on the 3-aryl-2-norbornyl-tosylate system. Several interesting facts can be noted by comparing this data with that from the 2-phenylethyl system[55] and the 2-phenylcyclo-

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[54]DePuy, Thurn and Morris, *op. cit.*

[55]Bishop, *op. cit.*

Table 1. Rates of elimination of endo-3-aryl-exo-2-tosyloxynorbornane

Aryl	Base/Solvent	T. (°C.)	% olefin	$k_{E2} \times 10^4$ (l./mole-sec.)
C_6H_5	t-BuOK/t-BuOH	30	100	2.34 ± 0.05
C_6H_5	t-BuOK/t-BuOH	50	100	13.6 ± 0.4
p-ClC_6H_4	t-BuOK/t-BuOH	30	100	13.8 ± 0.4
p-$CH_3C_6H_4$	t-BuOK/t-BuOH	30	100	.88 ± 0.04
m-ClC_6H_4	t-BuOK/t-BuOH	30	100	41.7 ± 0.8
p-ClC_6H_4	EtONa/EtOH	50	48.5	1.45 ± 0.06
m-ClC_6H_4	EtONa/EtOH	50	74.5	2.37 ± 0.08
m-ClC_6H_4	EtONa/EtOH	30	74.9	.258 ± 0.01

pentyl system[56] shown in Table 2.

The data show that the rate of elimination of endo-3-phenyl-exo-2-tosyloxynorbornane in potassium t-butoxide-t-butanol at 50°C. is slower than 2-phenylethyl tosylate under the same conditions by a factor of only 8.7. The latter compound is usually considered to undergo a concerted E2 elimination under these conditions. This comparison can be further extended to the 2-phenylcyclopentyl tosylates as shown in Table 3. In the case of the norbornyl compound, the dihedral angle between the β-proton and the tosylate group should be

[56]Smith, op. cit.

Table 2. Rates of elimination of 2-phenylethyltosylate and 2-phenylcyclopentyl tosylate

Tosylate	Base/Solvent	T (°C.)	$k_{E2} \times 10^4$ (1./mole-sec.)
2-phenylethyl	t-BuOK/t-BuOH	50	110.0
2-phenylethyl	t-BuOK/t-BuOH	30	20.3
2-phenylethyl	EtONa/EtOH	30	1.2
trans-2-phenylcyclopentyl	t-BuOK/t-BuOH	50	3.0
trans-2-phenylcyclopentyl	t-BuOK/t-BuOH	30.3	.483
cis-2-phenylcyclopentyl	t-BuOK/t-BuOH	50	29.1
cis-2-phenylcyclopentyl	t-BuOK/t-BuOH	30.3	5.95

Table 3. Relative rates of elimination of some tosylates in potassium-t-butoxide-t-butanol at 50°C.

Compound	Relative rate
2-phenylethyl tosylate	1
endo-3-phenyl-exo-2-norbornyl tosylate	.12
cis-2-phenylcyclopentyl tosylate	.26
trans-2-phenylcyclopentyl tosylate	.027

very nearly 0^{o}, and the rate is very fast. The comparable angle in the trans-2-phenylcyclopentyl tosylate deviates somewhat from 0^{o}, and this compound is seen to eliminate slower than the norbornyl compound by a factor of 4.4. cis-2-Phenylcyclopentyl tosylate, which undergoes trans elimination is faster than the norbornyl compound by a factor of 2.2. These comparisons indicate that the dihedral angle between the β-proton and the leaving group is an important factor in determining the rates of eliminations. One can only surmise as to why angles near either 0^{o} or 180^{o} should be markedly better for eliminations. Presumably this is tied in with the ability of the electron pair, which was the beta carbon-hydrogen bond, to move into the position between the α- and β-carbons forming the π bond. Another possibility is that the β-electron pair can best displace the leaving group when it is either exactly cis or exactly trans to the leaving group.

The Hammett equation has been applied to this data and the results are shown in Table 4. A comparison of this data indicates that the cis elimination from the norbornyl compound gives nearly the same build up of negative charge on the β-carbon atom in going to the transition state as does the β-phenylethyl tosylate. This is another exhibition of

Table 4. Hammett correlations of rates of eliminations of endo-3-aryl-exo-2-norbornyl tosylates, 2-phenylethyl tosylates and 2-phenylcyclopentyl tosylates at 30°C.

Compound	Base/Solvent	
endo-3-aryl-exo-2-norbornyl tosylate	t-BuOK/t-BuOH	3.24 ± 0.11
2-phenylethyl tosylate	t-BuOK/t-BuOH	3.39 ± 0.29
cis-2-phenycyclopentyl tosylate	t-BuOK/t-BuOH	1.48 ± 0.09
cis-2-phenylcyclopentyl tosylate	EtONa/EtOH	0.99 ± 0.06
trans-2-phenylcyclopentyl tosylate	t-BuOK/t-BuOH	2.76 ± 0.04
endo-3-aryl-exo-2-norbornyl tosylate	EtONa/EtOH	2.10[a]

[a]Based on points from two compounds only.

the concerted nature of this elimination. A plot of this data is shown in Figure 1.

The paucity of data in this system allows few other conclusions to be drawn regarding the mechanism of the reaction or the nature of the transition state in the reaction. A knowledge of the percent of double bond character in the transition state would be very useful in making predictions about eliminations in similar systems. Furthermore, data on those compounds giving rise to trans eliminations in the aryl

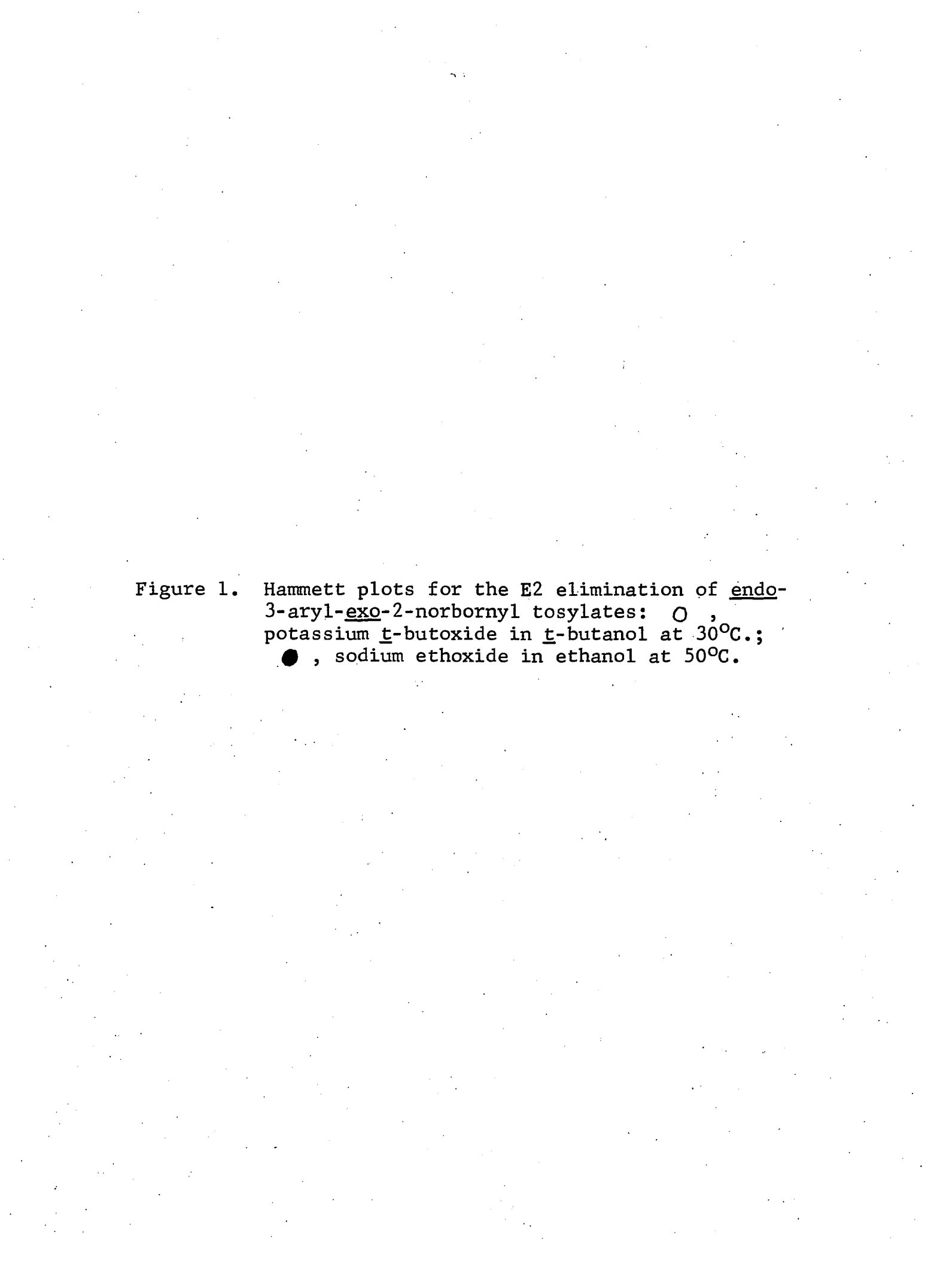
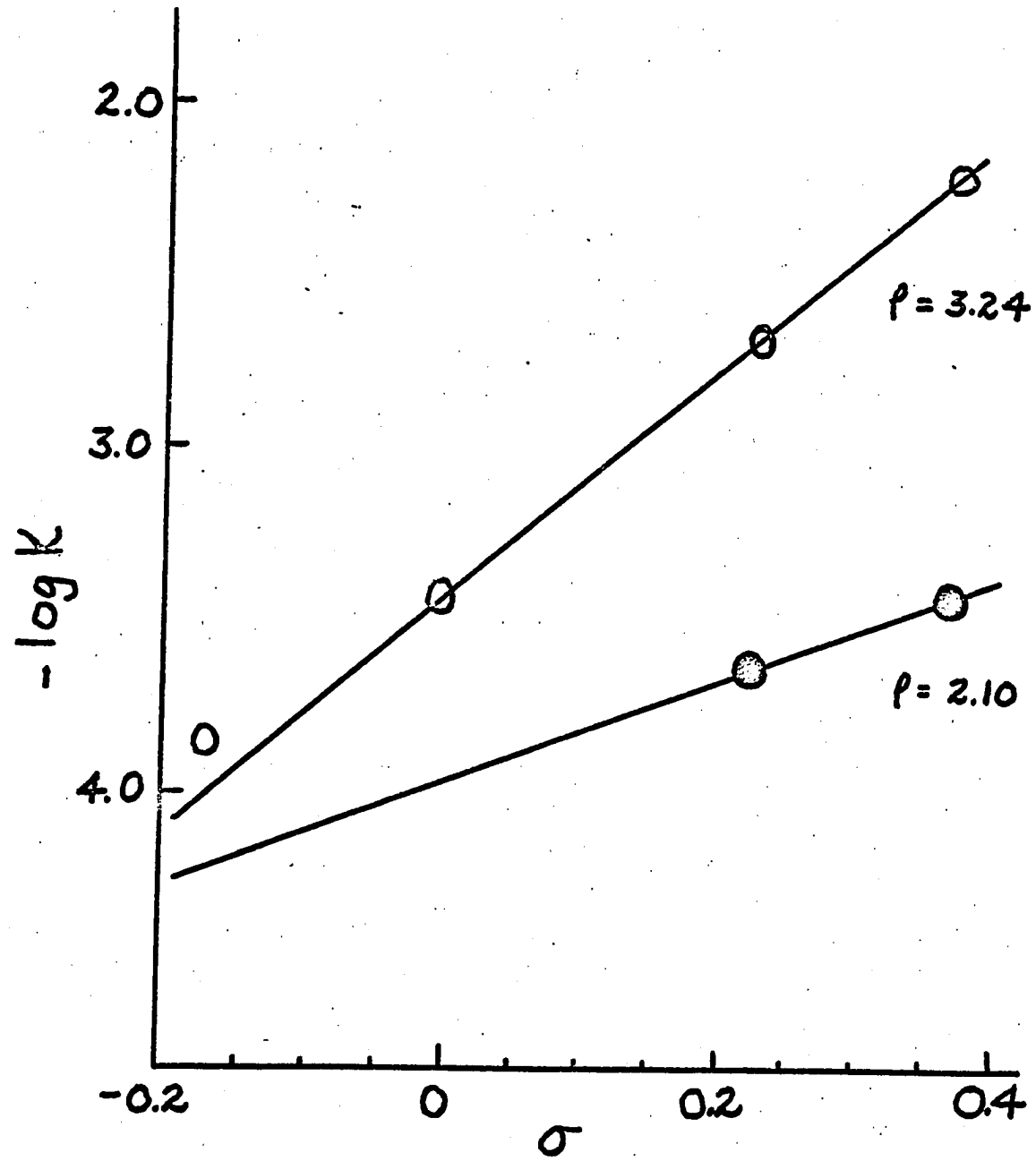


Figure 1. Hammett plots for the E2 elimination of endo-3-aryl-exo-2-norbornyl tosylates: ○ , potassium t-butoxide in t-butanol at 30°C.; ● , sodium ethoxide in ethanol at 50°C.


2.0
3.0
4.0
-log K
ρ = 3.24
ρ = 2.10
-0.2
0
0.2
0.4
σ

norbornyl system would be most desirable to obtain. This data would be a good indicator of the effect of having a dihedral angle radically different from 0^{o} or 180^{o}. ρ-values in these skew eliminations should be higher and should give an indication of a maximum ρ-value which could be observed in any elimination system.

The stronger base, t-butoxide, yields a higher ρ-value for the reaction than does the ethoxide. This variable cannot be completely divorced from the change to a more polar solvent in going from the stronger to the weaker base. The stronger base and less polar solvent would be expected to advance C-H bond breaking over C-O bond breaking in the transition state. The more polar solvent, ethanol, should facilitate the cleavage of the C-O bond and hence, help to remove charge from the β-carbon atom more rapidly. It is difficult to determine which of these factors is more important in determining ρ-values.

An examination of the enthalpies and entropies of activation for the arylnorbornyl system reveals nothing surprising. These values along with those for the 2-phenylethyl system are presented in Table 5. The midpoint of the temperature range, T_m, is shown in each case. The enthalpy of activation, H^{+}, was obtained from the slope of a log k versus 1/T plot

Table 5. Enthalpies and entropies of activation for eliminations from endo-3-aryl-exo-2-norbornyl tosylates and 2-phenylethyl tosylates

Compound	Solvent/Base	T_m (°C.)	H (kcal./mole)	S (cal./deg./mole)
endo-3-phenyl-exo-2-norbornyl tosylate	t-BuOK/t-BuOH	40	16.5	-20.7
endo-3-m-Cl-phenyl-exo-2-norbornyl tosylate	EtONa/EtOH	40	21	-10
2-phenylethyl tosylate	t-BuOK/t-BuOH	40	14.7	-25.2
2-phenylethyl tosylate	EtONa/EtOH	42	20.4	-11.2

and the equation, $H = E_a - RT$. The intercept of the same plot yielded the values of the entropy of activation, S . The values for the 2-phenylethyl tosylates were taken from the literature.[57] The fact that activation parameters for the norbornyl compounds are very similar to and vary in the same manner as those for the 2-phenylethyl compounds indicates a considerable degree of concerted character in this elimination. These observations are consistent with

[57] Bishop, op. cit.

previous observations reported in the literature.[58]

The data which has been presented here leaves little doubt as to the concerted nature of the cis elimination in the endo-3-aryl-exo-2-norbornyl tosylates. This concertedness was reflected in the rates of elimination, the activation parameters and the ρ-values for the reactions. This is another piece of data to add to those already reported supporting the theory of dihedral angle effect upon the rate of elimination reactions as previously discussed.

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[58]LeBel, et al., op. cit.

EXPERIMENTAL

Experimental Conditions

Boiling points

All boiling points are uncorrected and are recorded in degrees Centigrade. Pressures associated with these temperatures were read from a McLeod gauge and are recorded in millimeters of mercury.

Melting points

All melting points are uncorrected and are reported in degrees Centigrade. Melting points were taken on a Fisher-Johns Melting Point Apparatus.

Nuclear magnetic resonance spectra (NMR)

The nuclear magnetic resonance spectra were determined on a Varian Associates HR-60 high resolution spectrometer at 60 megacycles using carbon tetrachloride solutions and tetramethylsilane as an internal standard.

Vapor phase chromatography (VPC)

Vapor phase chromatographic analyses were from either a Perkin-Elmer Vapor Fractometer model 154C or an Aerograph Hy FI model 600 Gas Chromatograph. The columns used were either UCON-LB-550X or SE-30 silicone gum rubber on Chromosorb.

Infrared spectra

All infrared spectra were recorded on a Perkin-Elmer model 21 infrared spectraphotometer as carbon tetrachloride solutions in a 0.5 mm. sodium chloride cell or as neat liquids in sodium chloride capillary cells.

Ultraviolet spectra

The ultraviolet spectra were recorded on a Beckman model CK-2A recording spectrophotometer using 95% ethanol solutions.

Elemental analyses

Elemental analyses were performed by the Weiler and Strauss Analytical Laboratory, Oxford, England.

Preparation and Purification of Materials

Preparation of 2-phenylbicyclo (2.2.1) heptyl compounds

2-Arylbicyclo (2.2.1) hept-2-enes To an ether solution of phenyl lithium prepared from 5.0 g. (0.721 g. atoms) of lithium and 93.0 g. (0.592 moles) of bromobenzene was added an ether solution of 50.0 g. (0.454 moles) of 2-norbornanone (Aldrich Chemical Company) at a rate sufficient to maintain gentle reflux. The solution was allowed to stir for 2 hours and water was added slowly to remove excess phenyl lithium and hydrolyze the salts. The aqueous phase

was separated and extracted three times with portions of fresh ether. The combined ether solutions were dried over magnesium sulfate and most of the ether was removed by atmospheric distillation. Approximately 0.1 g. of p-toluenesulfonic acid was added and the contents of the flask were heated vigorously to promote dehydration. The water formed in the dehydration was removed by azeotropic distillation with benzene and the residue was distilled to yield 56.4 g. (0.331 moles) of olefin, b.p. 79-81°C. (0.7 mm.) (lit.[59] b.p. 124-128°C. (17 mm.)). This represents 73% of theoretical yield. VPC analysis showed the olefin to be at least 98% pure.

The p-methylphenyl compound was made by the same procedure using p-bromotoluene. The m-chlorophenyl and p-chlorophenyl compounds were made by the same procedure using Grignard reagents for the reduction.

2-p-Methylphenylbicyclo (2.2.1) hept-2-ene, b.p. 89-90°C. (0.3 mm.), 73.4% yield.

2-m-Chlorophenylbicyclo (2.2.1) hept-2-ene, b.p. 99-100°C. (0.45 mm.), 78.3% yield.

2-p-Chlorophenylbicyclo (2.2.1) hept-2-ene, b.p. 106-

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[59]Kleinfelter and Schleyer, J. Org. Chem., p. 3740.

110°C. (0.9 mm.), m.p. 55-57°C., 73% yield.

endo-3-Arylbicyclo (2.2.1) heptan-2-ols (exo) 27.0 g. (0.159 moles) of 2-phenylbicyclo (2.2.1) hept-2-ene and 3.2 g. (0.085 moles) of sodium borohydride were dissolved in 150 ml. of diglyme. To this a solution of 13.0 g. (0.092 moles) of boron trifluoride etherate in 40 ml. of diglyme was added over a period of one hour. The solution was chilled in an ice bath and stirred for two additional hours. Twenty ml. of water were added cautiously, followed by 40 ml. of 3 molar sodium hydroxide and 40 ml. of 30% hydrogen peroxide. This mixture was stirred for one hour and was then poured into ice water. The organic material was extracted with ether and the ether solution was dried and distilled to yield 21.8 g. of alcohol, b.p. 111-113°C. (0.7 mm.). This represents 73% yield. NMR analysis indicated that the hydroxyl group was exclusively in the exo position.

endo-3-p-Methylphenylbicyclo (2.2.1) heptan-2-ol (exo), b.p. 130-133°C. (0.7 mm.), m.p. 81.5-82°C., 77% yield.

endo-3-m-Chlorophenylbicyclo (2.2.1) heptan-2-ol (exo), b.p. 153-159°C. (0.9 mm.), m.p. 75.5-76°C., 66% yield.

endo-3-p-Chlorophenylbicyclo (2.2.1) heptan-2-ol (exo), b.p. 124-129°C. (0.5 mm.), 55% yield.

endo-3-Arylbicyclo (2.2.1) heptyl-2-p-toluenesulfonates (exo) The p-toluenesulfonates were prepared according to the method of Tipson[60] and were recrystallized at least three times from ether-pentane solutions. As a typical example, 1.5 equivalents of p-toluenesulfonyl chloride and 1.0 g. of an alcohol were dissolved in 10 ml. of anhydrous pyridine which was chilled in an ice-salt bath to -5°C. The solution was swirled occasionally for one hour at -5°C., and was then placed in the freezer overnight. As the tosylate formed, crystals of pyridine hydrochloride precipitated. The solution was poured into an equal volume of ice-water. Scratching of the vessel walls caused crystallization of the crude tosylate, which was filtered and washed with 10% hydrochloric acid and then several times with water. The recrystallized tosylates were vacuum dried and stored in a refrigerator to prevent decomposition which occurred slowly at room temperature.

endo-3-Phenylbicyclo (2.2.1) heptyl-2-p-toluenesulfonate (exo), m.p. 94-95°C.

Anal. Calcd. for $C_{20}H_{22}O_3S$: C, 70.14; H, 6.48. Found: C, 70.24; H, 6.33.

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

endo-3-p-Methylphenylbicyclo (2.2.1) heptyl-2-p-toluenesulfonate (exo), m.p. 81.5-82°C.

Anal. Calcd. for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 70.39; H, 6.08.

endo-3-m-Chlorophenylbicyclo (2.2.1) heptyl-2-p-toluenesulfonate (exo), m.p. 84-85°C.

Anal. Calcd. for $C_{20}H_{21}ClO_3S$: C, 63.72; H, 5.62. Found: C, 63.84; H, 5.58.

endo-3-p-Chlorophenylbicyclo (2.2.1) heptyl-2-p-toluenesulfonate (exo) m.p. 109.5-110°C.

Anal. Calcd. for $C_{20}H_{21}ClO_3S$: C, 63.72; H, 5.62. Found: C, 63.94; H, 5.50.

2-Nitro-3-phenylbicyclo (2.2.1) hept-5-ene This compound was prepared by the method of Allen, Bell and Gates.[61] 74.5 g. (0.5 moles) of β-nitrostyrene and 66 g. (1.0 moles) of freshly distilled cyclopentadiene were heated at the reflux temperature of the mixture for six hours. Excess cyclopentadiene was removed at reduced pressure and the product was distilled to yield 99 g. (92%) of a yellow oil, b.p. 129-135°C. (0.6-1.0 mm.) (Lit. b.p. 145°C. (1.0 mm.)).

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[61] Allen, C. F. H., Bell, A. and Gates, J. W., Jr., J. Org. Chem., 8, 373 (1943).

2-Nitro-3-phenylbicyclo (2.2.1) heptane 19.8 g. (0.1 moles) of 2-nitro-3-phenylbicyclo (2.2.1) hept-5-ene and 450 mg. of 5% palladium on charcoal catalyst in 125 ml. of glacial acetic acid were hydrogenated at room temperature and atmospheric pressure. The hydrogen was allowed to proceed until 105% of the theoretical hydrogen uptake was observed. The catalyst was removed by filtration, and the filtrate was concentrated at reduced pressure. The residue was dissolved in 200 ml. of ether and washed twice with 10 ml. portions of 2 N hydrochloric acid and twice with water. The ether solution was dried and the ether removed on a rotary evaporator. Distillation of the residue yielded 17.2 g. (86%) of 2-nitro-3-phenylbicyclo (2.2.1) heptane, b.p. 125-134°C. (0.4-0.6 mm.) (lit.[62] b.p. 128-132°C. (0.3 mm.)). Analysis by nuclear magnetic resonance and by gas-phase chromatography indicated the ratio of exo-nitro to endo-nitro compounds to be approximately 1:3.

3-phenylbicyclo (2.2.1) heptan-2-one This compound was prepared by carrying out a Nef reaction according to the method of Wildman.[62] A solution of sodium ethoxide was prepared from 2.08 g. (.09 moles) of sodium and 75 ml. of

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[62] Wildman and Hemminger, op. cit.

anhydrous ethanol. This ethoxide solution was added slowly under a nitrogen atmosphere to a vigorously stirred solution of 9.75 g. (0.045 moles) of 2-nitro-3-phenylbicyclo (2.2.1) heptane in 75 ml. of anhydrous ethanol at 0°C. This solution was allowed to warm to room temperature and stand overnight under a nitrogen atmosphere. The ethanolic solution was slowly added to a stirred solution of 60 ml. of concentrated hydrochloric acid in 1000 ml. of water and 600 ml. of ethanol at 0°C. under a nitrogen atmosphere. The reaction mixture was stirred for one hour at 0°C. and for six hours at room temperature. It was then refluxed for one hour and allowed to stand overnight. The reaction mixture was diluted to 3 l. with water and extracted with ether. Drying and evaporation of the ether extracts yielded 7.3 g. (0.039 moles) of a pale yellow oil. This represents 86% yield of crude 3-phenylbicyclo (2.2.1) heptan-2-one. The infra-red spectrum had a broad carbonyl absorption in the 5.71-5.80 μ region. Gas phase chromatographic analysis indicated a mixture of three compounds, although they could not be resolved.

3-phenylbicyclo (2.2.1) heptan-2-ol A solution of 1.86 g. (0.01 moles) of the crude 3-phenylbicyclo (2.2.1) heptan-2-one in 15 ml. of ether was added to a slurry of 0.38 g. (.011 moles) of lithium aluminum hydride in ether. The

mixture was allowed to stir two hours before the excess hydride was removed by cautious addition of water. 30 ml. of a slurry of sodium sulfate in water was added to coagulate lithium salts. Extraction with ether and evaporation yielded 1.7 g. of a pale yellow oil. Attempts to prepare a crystalline tosylate from this material by usual methods were unsuccessful. The alcohol could not be purified by gas phase chromatography or elution chromatography.

endo-2-acetyl-exo-3-phenylnorbornane and exo-2-acetyl-endo-3-phenyl-norbornane The reaction of trans-benzalacetone with excess dicyclopentadiene was carried out according to the method of Dinwiddie and McManus.[63] The product, a mixture of endo-2-acetyl-exo-3-phenyl-5-norbornene and exo-2-acetyl-endo-3-phenyl-5-norbornene, was isolated by a rapid low pressure distillation. This material was hydrogenated at atmospheric pressure in 95% ethanol using 5% palladium on charcoal catalyst, 105% of the theoretical uptake of hydrogen being observed. Fractional vacuum distillation of the hydrogenated adduct yielded a mixture of endo-2-acetyl-exo-3-phenyl-norbornane and exo-2-acetyl-endo-3-phenylnorbornane, b.p. 97-113°C. (0.5 mm.). Vapor phase

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[63]Dinwiddie and McManus, op. cit.

chromatographic analysis of this mixture indicated 79:21 ratio of endo-acetyl to exo-acetyl compound.

endo-2-acetoxy-exo-3-phenylnorbornane and exo-2-acetoxy-endo-3-phenyl-norbornane A solution of pertrifluoroacetic acid was prepared by adding 7 ml. (0.273 moles) of 90% hydrogen peroxide to a solution of 57.5 g. (0.273 moles) of trifluoroacetic anhydride in 75 ml. of methylene chloride cooled in an ice bath. The peracid solution was then added to a solution of 21.4 g. (0.1 moles) of the methyl ketone mixture over a three hour period. This solution was allowed to stand overnight and was then neutralized with a saturated sodium carbonate solution. The aqueous layer was separated and extracted with three 20 ml. portions of methylene chloride. The combined extracts were dried over anhydrous magnesium sulfate and the solvent was removed on a rotary evaporator. Distillation of the residue yielded 17.5 g. (0.07 moles) of a mixture of endo-2-acetoxy-exo-3-phenylnorbornane and exo-2-acetoxy-endo-3-phenylnorbornane, b.p. 115-120°C. (0.6 mm.). Vapor phase chromatographic analysis indicated the isomers were present in a 67:33 ratio, although attempts to separate the isomers by preparative vapor phase chromatography were unsuccessful. Therefore, it was not possible to rigorously determine the structure of either isomer al-

though it is most likely that the 67% isomer is the endo-acetoxy compound.

Attempted Meerwein-Pondorff equilibration of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol A solution containing 5.5 g. (0.027 moles) of aluminum isopropoxide, 5.0 g. of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol and 5 drops of acetone in 100 ml. of freshly purified (distilled from aluminum isopropoxide) isopropanol was refluxed for seventy-six hours. The solution was neutralized with 2 N hydrochloric acid diluted with water and extracted with three 20 ml. portions of ether. The extracts were dried over anhydrous magnesium sulfate and evaporated to yield a pale yellow oil. The NMR spectrum of the oil was identical with the NMR spectrum of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol.

Attempted Oppenauer oxidation of endo-3-(p-chlorophenyl) bicyclo (2.2.1) heptan-exo-2-ol A solution of 1.0 g. (.0045 moles) of exo-2-hydroxy-endo-3-p-chlorophenylnorbornane and 9.3 ml. of cyclohexanone in 60 ml. of toluene was dried by distilling out a small amount. A solution of 0.416 g. (0.0135 moles) of distilled aluminum isopropoxide in 2 ml. of toluene was added and the mixture was refluxed for twenty-six hours. After removing volatile components by distillation, the residue was extracted with ether. Evaporation of the

ether yielded 0.8 g. of a pale yellow oil. The infrared spectrum of the oil in carbon tetrachloride solution showed no carbonyl absorption.

Oxidation of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol with chromium (VI) oxide-pyridine complex The complex was prepared according to the method of Holum[64] by slow addition of 1.64 g. (1.64×10^{-2} moles) of chromium (VI) oxide to 16 ml. of anhydrous pyridine which was at 0°C. and was vigorously stirred. One g. of the alcohol (5.3×10^{-3} moles) in 10 ml. of pyridine was added at once. The solution was stirred for thirty minutes and then was allowed to stand for twenty-three hours at room temperature. The solution was poured into 100 ml. of water and was extracted with five portions of ether. The extracts were washed three times with 10% hydrochloric acid, with 10% sodium carbonate and with water. The extracts were then dried and evaporated. The residue was a yellow oil which weighed 0.64 g. The infrared spectrum contained a strong hydroxyl absorption, a broad carbonyl absorption at 5.73-5.75 μ and a sharp carbonyl absorption at 5.95 μ. Several modifications of this method were used in an effort to optimize the yield of desired endo-

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[64]Holum, op. cit.

3-phenylnorbornanone. When shorter reaction times or lower temperatures were used, the amount of unoxidized starting alcohol in the product was larger. When longer reaction times or elevated temperatures were used, the amount of acidic products increased. In one experiment the reaction was carried out as above but on a 0.05 mole scale. In this case, almost no absorption was observed at 5.73 μ in the infra-red spectrum.

Oxidation of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol with Jones reagent Jones reagent was prepared by adding 26.72 g. of chromium trioxide to 23 ml. of concentrated sulfuric acid and diluting to 100 ml. with water. One ml. of this solution is equivalent to 0.004 moles of alcohol. 1 g. (5.3×10^{-3} moles) of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol was dissolved in 200 ml. of purified acetone. The solution was cooled to 5°C. and the Jones reagent (1.33 ml., 5.3×10^{-3} moles) was added with vigorous stirring. The oxidation mixture was poured immediately into 500 ml. of 10% sodium bicarbonate solution. The solution was extracted with three 50 ml. portions of ether. The extracts were dried and evaporated to yield 0.91 g. of a yellow oil. The infra-red spectrum exhibited a broad hydroxyl absorption at 2.90 μ and three sharp carbonyl bands at 5.73, 5.80 and 5.95 μ. Several

modifications of this procedure were used, but none could be found which would selectively oxidize alcohol to ketone. In all cases the product contained unoxidized alcohol and an unidentified acidic material.

Oxidation of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol with chromic acid in ether solution. Ethyl ether, 20 ml., and 10 g. (.053 moles) of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol were placed in a 100 ml. flask fitted with stirrer, condenser and an addition funnel. This solution was cooled to -15°C. and a chromic acid solution, prepared from 5.30 g. (.0178 moles) sodium dichromate dihydrate and 3.98 ml. (.071 moles) of concentrated sulfuric acid diluted to 26.5 ml., was added slowly with vigorous stirring. Stirring was continued for fifteen minutes and the ether layer was then separated. The aqueous layer was extracted with ether and the combined extracts were washed with saturated sodium bicarbonate solution and then water. Drying over anhydrous magnesium sulfate and evaporation yielded 7.3 g. of a yellow oil. The infra-red spectrum showed a broad hydroxyl absorption at 2.90 μ and three carbonyl absorptions at 5.73, 5.80 and 5.95 μ. The oil was distilled to yield 6.2 g. of a yellow oil, b.p. 90-125°C. (0.6-1.0 mm.). The infra-red spectrum of the distilled material was identical to that of

the crude material. The oil could not be further purified by vapor phase chromatography. Changes in temperature or reaction time had very little effect upon the quality of the product. This procedure was tried on the substituted phenyl alcohols, but all produced similar results.

Oxidation of the diborane adduct of 2-phenyl-2-norbornene with chromic acid A solution of 31.2 g. (0.22 moles) of boron trifluoride etherate in 300 ml. of ether was added to a solution of 34 g. (0.20 moles) of 2-phenyl-2-norbornene and 7.6 g. (0.20 moles) of lithium aluminum hydride in 300 ml. of ether. After stirring for one hour, the excess hydride was destroyed by cautious addition of water. The solution was then cooled to 0°C. and a solution of chromic acid, prepared from 44.0 g. (0.148 moles) of sodium dichromate dihydrate and 33 ml. (0.59 moles) of concentrated sulfuric acid diluted to 180 ml. of water, was added slowly. The ether layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with saturated sodium bicarbonate solution and water and were dried and evaporated. The residue was a pale yellow oil which weighed 33.1 g. (89%) and had a broad boiling range of 93-113°C. (0.8 mm.). The infra-red spectrum showed a strong hydroxyl absorption and the three carbonyl absorption bands at 5.73,

5.80 and 5.95 μ. Efforts to improve on the yield of ketone from this reaction by changing reaction conditions were unsuccessful. The procedure gave essentially the same results for the substituted phenyl olefins.

Oxidation of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol with N-bromosuccinimide A mixture of 1.0 g. (5.3 x 10^{-3} moles) of endo-3-phenylbicyclo (2.2.1) heptan-exo-2-ol and 1.25 g. (7.0 x 10^{-3} moles) of N-bromosuccinimide were dissolved in 30 ml. of acetone. This solution was warmed on a steam bath for twenty minutes after which time it became slightly yellow. After allowing the solution to stand at room temperature for one additional hour, it was diluted with 100 ml. of water. Extraction with ether yielded 0.6 g. of an oily substance which was a lachrymator. The infra-red spectrum exhibited absorbance in the 2.9 μ region and a carbonyl absorption at 5.85 μ.

Hydride reduction of crude alcohol-ketone mixtures from various oxidation experiments The crude oxidation products from the foregoing oxidation experiments were each reduced by conventional lithium aluminum hydride reduction methods. Although oils which exhibited no carbonyl absorption in the infra-red could be obtained, crystallizable tosylates could not be prepared from them. Attempts to purify the reduction

products by elution chromatography were unsuccessful, also.

Purification of materials

Anhydrous ethanol Residual water was removed from "absolute" ethanol by the method of Manske[65] using sodium and diethyl phthalate followed by distillation.

Anhydrous tert-butanol tert-Butanol was distilled three times from sodium and one time from potassium in an apparatus designed to exclude moisture. By this method the tert-butanol reacted with the potassium to give a solution of potassium tert-butoxide which discolored very slowly. All samples of tert-butanol were stored in Pyrex ware which had been washed with 5% hydrofluoric acid, rinsed and dried.

Purified potassium Lump potassium was melted and dispersed in n-heptane under a nitrogen atmosphere. The potassium was cooled and the impurities decanted. This procedure was repeated if necessary to give a very shiny metallic potassium for the preparation of potassium tert-butoxide solutions.

Potassium tert-butoxide solutions Purified potassium was washed once in pentane and twice in tert-butanol before transferring to the anhydrous tert-butanol in a flask equipped

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

with a drying tube. Rate constants determined with solutions prepared by this method were consistent and reproducible.

n-Pentane The pentane used in recrystallizations of tosylates was washed with portions of concentrated sulfuric acid until the acid remained colorless. This was followed by a water wash, drying over magnesium sulfate and distillation.

Anhydrous pyridine Anhydrous pyridine was prepared by distillation of commercial anhydrous pyridine from barium oxide.

Aluminum isopropoxide Commercial aluminum isopropoxide was vacuum distilled just prior to use.

Acetone Acetone was distilled from excess potassium permanganate to remove oxidizing materials.

Boron trifluoride etherate Boron trifluoride etherate was distilled from calcium hydride before use.

Kinetic Procedures and Data

Kinetic procedures

Accurately weighed tosylate samples were placed in 50 ml. volumetric flasks. A solution of base of the desired concentration was then added; and after equilibration at the reaction temperature in a constant temperature bath, the

flask was filled to the calibration mark with base. The flasks were shaken to insure uniformity, and a 5 ml. sample was pippeted into another 50 ml. volumetric flask containing ice-cold 95% ethanol. This solution was diluted to the calibration mark with 95% ethanol and 5 ml. was again diluted to 50 ml. This solution was then analyzed on the ultra-violet spectrophotometer. Samples were withdrawn at appropriate intervals between 20% and 80% completion and all were treated in the same manner. Infinity points were determined experimentally and checked well with values calculated from the molar extinction coefficients of the olefins.

That the rates closely followed psuedo-first order kinetics was determined by applying the integrated rate equation to the data. The overall rate was obtained by taking an average of the individual rates from each point.

$$kt = 2.303 \log \frac{A_\infty - A_o}{A_\infty - A_t}$$

A_∞ = absorbance at least ten half-lines.

A_o = absorbance at zero time.

A_t = absorbance at time t.

The Hammett equation was applied to the data. ρ, the slope of the line obtained when log k was plotted versus σ,

was obtained by the method of least squares.

$$\log \frac{k}{k_o} = \rho\sigma$$

The tosylates were examined under simulated reaction conditions in order to determine if any of the product olefin was derived from solvolytic elimination. The tosylates were dissolved in a solution of sodium acetate in either t-butyl alcohol or ethanol of approximately the same ionic strength as the base used for eliminations. The solutions were then heated at the elimination temperatures for at least ten half-lives. No olefin could be detected under these conditions.

Molar extinction coefficients of the 2-arylnorbornenes

Solutions of the olefins in 95% ethanol were prepared. These solutions were diluted to approximately 10^{-5} molar and were analyzed on a Beckman DK-2A Spectrophotometer. Table 6 compares the results with the literature values.

Kinetic data

The rates of elimination of the phenylnorbornyl tosylates in potassium-t-butoxide-t-butanol solutions and in sodium ethoxide-ethanol solutions reported in this thesis are the average of two or more kinetic runs. The psuedo-first order rates of reaction and the amount of elimination product for

Table 6. Ultraviolet absorption of 2-arylnorbornenes in 95% ethanol

Ar	τ max. (lit.)[a]	τ max. found	ε (lit.)	ε found
C_6H_5	262.5	262.5	10715	14790
p-$Ch_3C_6H_4$	264.0	264.5	12023	15612
p-ClC_6H_4	267.0	267.5	15490	18788
m-ClC_6H_4	--	265.0	--	14099

[a]Kleinfelter, D. C. and von R. Schleyer, P., J. Org. Chem., 26, 3740 (1961).

typical runs are reported in Tables 7 through 14. The absorbances reported in the second column of each table are taken from the ultra-violet spectra of 5 ml. aliquots of the kinetic samples which were twice diluted one to ten with 95% ethanol. The initial base and substrate concentrations, per cent olefin, average rate constant, average second-order rate constant and the exact temperature are also included. The rate derived from supplying time and absorbance data to a first-order least squares computer program is also included.

Table 7. Rate of psuedo-first order elimination of endo-3-phenylbicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in potassium-t-butoxide-t-butanol solution at 30°C.[a]

Time elapsed (sec.)	Absorbance[b]	$10^5 k$ ($sec.^{-1}$)
0	0.073	--
3007	0.143	2.81
6121	0.208	2.78
10181	0.279	2.68
17183	0.395	2.71
23773	0.480	2.68
27742	0.528	2.70
32456	0.577	2.70
∞	0.937	--
Rate over entire period[c]		2.72 ± .04
Computer rate		2.68 ± .02
Second order rate		2.35 ± .04x10^{-4} l. $mole^{-1}$ $sec.^{-1}$

[a]Exact temperature = 29.92 ± .01°C.

[b]Base conc. = 0.1157 M; Tosylate conc. = 0.0066 M.

[c]Product contained 100% olefin.

Table 8. Rate of psuedo-first order elimination of endo-3-phenylbicyclo (2.2.1) heptyl-exo-2-p-toluene-sulfonate in potassium-t-butoxide-t-butanol solution at 50°C.[a]

Time elapsed (sec.)	Absorbance[b]	10^4k (sec.$^{-1}$)
0	0.160	--
495	0.285	4.02
1089	0.429	4.51
1542	0.504	4.45
2058	0.570	4.35
2647	0.621	4.13
3169	0.675	4.29
∞	0.853	--
Rate over entire period[c]		4.29 ± .15
Computer rate		4.24 ± .23
Second order rate constant		1.34 ± .05x10^{-3} l. mole^{-1} sec.$^{-1}$

[a]Exact temperature = 50.07 ± .01°C.

[b]Base conc. = 0.3192 M; tosylate conc. = 0.0057 M.

[c]Product contained 100% olefin.

Table 9. Rate of psuedo-first order elimination of endo-3-(p-chlorophenyl) bicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in potassium-t-butoxide-t-butanol solution at 30°C.[a]

Time elapsed (sec.)	Absorbance[b]	10^4k ($sec.^{-1}$)
0	0.140	--
647	0.202	1.48
1247	0.267	1.66
1909	0.321	1.62
2632	0.370	1.57
4316	0.474	1.56
5881	0.541	1.51
7469	0.601	1.51
∞	0.821	--
Rate over entire period[c]		1.56 ± .05
Computer rate		1.50 ± .09
Second order rate		1.35 ± .04x10^{-3} 1. $mole^{-1}$ $sec.^{-1}$

[a]Exact temperature = 29.92 ± .01°C.

[b]Base conc. = 0.1157 M; tosylate conc. = .0043 M.

[c]Product contained 100% olefin.

Table 10. Rate of psuedo-first order elimination of endo-3-(m-chlorophenyl) bicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in potassium-t-butoxide-t-butanol solution at 30°C.[a]

Time elapsed (sec.)	Absorbance[b]	$10^4 k$ ($sec.^{-1}$)
0	0.140	--
446	0.232	4.93
856	0.300	4.92
1271	0.356	4.90
1749	0.410	4.95
2200	0.455	5.12
2743	0.488	5.01
3277	0.515	4.99
∞	0.606	--
Rate over entire period[c]		$4.97 \pm .05$
Computer rate		$5.04 \pm .12$
Second order rate		$4.30 \pm .05 \times 10^{-3}$ l. $mole^{-1}$ $sec.^{-1}$

[a]Exact temperature = $29.92 \pm .01$°C.

[b]Base conc. = 0.1157 M; tosylate conc. = 0.0044 M.

[c]Product contained 100% olefin.

Table 11. Rate of psuedo-first order elimination of endo-3-(p-methylphenyl) bicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in potassium-t-butoxide-t-butanol solution at 30°C.[a]

Time elapsed (sec.)	Absorbance[b]	$10^5 k$ ($sec.^{-1}$)
0	0.058	--
9026	0.117	1.07
17962	0.167	1.04
27554	0.213	1.00
38607	0.294	1.20
50360	0.320	1.05
66607	0.375	1.03
88715	0.438	1.00
∞	0.697	--
Rate over entire period[c]		1.06 ± .05
Computer rate		1.01 ± .02
Second order rate		9.13 ± .39x10^{-5} 1. $mole^{-1}$ $sec.^{-1}$

[a]Exact temperature = 29.92 ± .01°C.

[b]Base conc. = 0.1157 M; tosylate conc. = 0.0046 M.

[c]Product contained 100% olefin.

Table 12. Rate of psuedo-first order elimination of endo-3-(m-chlorophenyl) bicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in sodium ethoxide-ethanol solution at 30°C.[a]

Time elapsed (sec.)	Absorbance[b]	$10^5 k$ ($sec.^{-1}$)
0	0.040	--
1655	0.049	1.46
4500	0.068	1.72
7232	0.083	1.76
11171	0.113	1.93
14551	0.132	1.93
18245	0.150	1.90
23644	0.175	1.88
∞	0.416	--
Rate over entire period[c]		$1.86 \pm .06$
Computer rate		$1.95 \pm .06$
Second order rate		$2.48 \pm .09 \times 10^{-5}$ l. $mole^{-1}$ $sec.^{-1}$

[a]Exact temperature = $30.01 \pm .01$°C.

[b]Base conc. = 0.7494 M; tosylate conc. = 0.0039 M.

[c]Product contained 75.4% olefin.

Table 13. Rate of psuedo-first order elimination of endo-3-(m-chlorophenyl) bicyclo (2.2.1) hepty1-exo-2-p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.[a]

Time elapsed (sec.)	Absorbance[b]	10^4k (sec.$^{-1}$)
0	0.033	--
338	0.052	1.85
682	0.067	1.75
1084	0.086	1.78
1446	0.100	1.74
1816	0.119	1.85
2173	0.130	1.78
2561	0.148	1.87
∞	0.335	--
Rate over entire period[c]		1.80 ± .05
Computer rate		1.85 ± .08
Second order rate		2.33 ± .07x10^{-4} l. mole^{-1} sec.$^{-1}$

[a]Exact temperature = 50.07 ± .01°C.

[b]Base conc. = 0.7744 M; tosylate conc. = 0.0032 M.

[c]Product contained 74.2% olefin.

Table 14. Rate of psuedo-first order elimination of endo-3-(p-chlorophenyl) bicyclo (2.2.1) heptyl-exo-2-p-toluenesulfonate in sodium ethoxide-ethanol solution at 50°C.[a]

Time elapsed (sec.)	Absorbance[b]	10^4k (sec.$^{-1}$)
0	0.060	--
1342	0.110	1.19
2989	0.163	1.22
3977	0.180	1.10
4979	0.204	1.12
6262	0.230	1.12
7551	0.248	1.08
8510	0.259	1.05
∞	0.398	--
Rate over entire period[c]		1.12 ± .05
Computer rate		1.02 ± .02
Second order rate		1.45 ± .06x10^{-4} 1. mole^{-1} sec.$^{-1}$

[a]Exact temperature = 50.07 ± .01°C.

[b]Base conc. = 0.7744 M; tosylate conc. = 0.0043 M.

[c]Product contained 49% olefin.

SUMMARY

The synthesis of a series of endo-3-aryl-exo-2-norbornyl tosylates was investigated. It was found that these compounds were easily prepared and purified. The synthesis of the other isomers of 3-aryl-2-norbornyl tosylate were shown to be very difficult to prepare. These compounds or their precursors could be prepared only in very low yield and in a highly impure form. Various reagents were investigated for their ability to oxidize endo-3-phenyl-exo-2-norbornanol to to endo-3-phenyl-2-norbornanone. This transformation was shown to be very difficult to perform in a highly selective manner. Presumably the oxidation of the enol from the ketone proceeded at a faster rate than the oxidation of the alcohol. This enolic oxidation could not be suppressed even with the use of a very mild oxidizing agent.

The base promoted eliminations of a series of endo-3-aryl-exo-2-norbornyl tosylates were investigated in two different solvent and base systems. The rates of elimination were noted to closely parallel the rates of a similar series of 2-phenylethyl tosylates. The ρ-value in t-butoxide-t-butanol was determined to be 3.2 for this cis elimination as compared to the value of 3.4 for the 2-phenylethyl series.

This result was interpreted to mean that the cis eliminations in this system were occurring by a concerted pathway similar to the trans elimination of the 2-phenylethyl tosylates. A determination of the entropies and enthalpies of activation in this system showed that they also closely paralleled the same parameters for the 2-phenyl-ethyl system. These values when taken individually or collectively indicate that base promoted cis eliminations from the arylnorbornyl tosylates occur rapidly and by a concerted pathway.

The results reported herein lend credence to the recent theory of the angular dependence of the rates of elimination reactions. When the dihedral angle between the β-proton and the leaving group approaches either 0^{o} or 180^{o}, other things being equal, elimination reactions approach a maximum rate. Presumably when the dihedral angle deviates greatly from either of those values, the rates fall. Unfortunately in the present work, this idea could not be tested due to unavailability of the compounds needed in the study.

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