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# Directive effects and mechanisms of bimolecular elimination reactions

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# DIRECTIVE EFFECTS AND MECHANISMS OF BIMOLECULAR ELIMINATION REACTIONS

by

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# INTRODUCTION

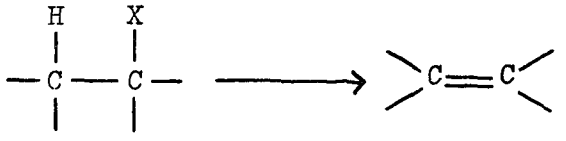
The nature of processes known as base-promoted, beta elimination reactions has been the concern of many organic chemists in recent years. Early investigations of elimination reactions revealed that there are two general mechanistic classes for the processes, unimolecular and bimolecular. The existence of two distinct pathways for the reactions was interpreted as reflecting a clear-cut difference in the timing for the expulsion of the groups on the adjacent carbon atoms. The unimolecular, E1 reactions were envisioned as cationic processes in which the rate is independent of the nature and concentration of the base. The bimolecular reactions were divided into anionic, E1cb, and concerted, E2, eliminations, in which the base plays an important role in deciding both the reaction rates and products obtained. Later work make it apparent that the mechanisms for E2 eliminations are flexible, such that E2 reactions can vary from the nearly cationic extreme to the anionic, and no clear-cut break occurs between the E1cb, E2, and E1 mechanisms. The structure of the substrate and the nature of the base and solvent used for E2 reactions have been shown to determine the position of the eliminations on the spectrum of E2 mechanisms that exists between the E1cb and E1 extremes.

Two conflicting schools of thought have developed concerning the relative influence of steric and electronic factors upon the rates and direction of E2 eliminations. Because of the difficulty involved in varying either the steric or electronic character of the reactants without affecting the other, the controversy has remained largely unsettled.

The objective of this thesis is twofold: to report a continuing investigation of the effects of substrate structure, base and solvent, and leaving group on the rates and mechanisms of E2 elimination reactions and to discuss an attempt to ascertain the role of steric effects in aliphatic E2 eliminations. The first of these objectives involved a kinetic study of the elimination reactions of 2-phenylethyl compounds with beta methyl and beta vinyl substituents and a comparison of their behavior with other 2-phenyl-substituted compounds previously examined. The second was approached by a study of the asymmetric elimination reactions of several aliphatic compounds in an attempt to isolate steric effects.

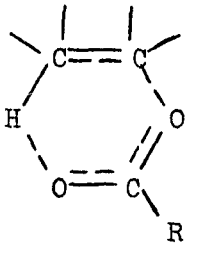
# HISTORICAL

The formation of unsaturation in organic molecules through the loss of two atoms or groups are processes known as elimination reactions. When the groups being removed are on adjacent atoms, the reactions are termed beta eliminations. This thesis discusses olefin-forming, beta elimination reactions, in which one of the groups being expelled is a proton.



(1)

Olefin-forming beta eliminations can be further divided into two basic types, intramolecular and heterolytic. The most extensively studied intramolecular reactions have been the heat-promoted eliminations of esters, xanthates, amine oxides, and halides. These reactions have been shown to occur predominantly through a cis-cyclic transition state I (1).



I

Heterolytic eliminations require the assistance of other molecules to expel the proton and X group. Because a base is generally responsible for carbon-hydrogen bond cleavage, the reactions are termed base-promoted, beta elimination reactions.

In 1851 Hofmann (2) observed that ethyl-substituted quaternary ammonium hydroxides preferentially expel ethylene upon decomposition rather than more substituted olefins.

$$(RCH_2CH_2)_3N^+ - CH_2CH_3 + OH^- \longrightarrow (RCH_2CH_2)_3N + CH_2 = CH_2 \quad (2)$$

Several years later Saytzeff (3) reported that the reactions of secondary and tertiary halides with base generally yield the more highly substituted olefins as the major products.

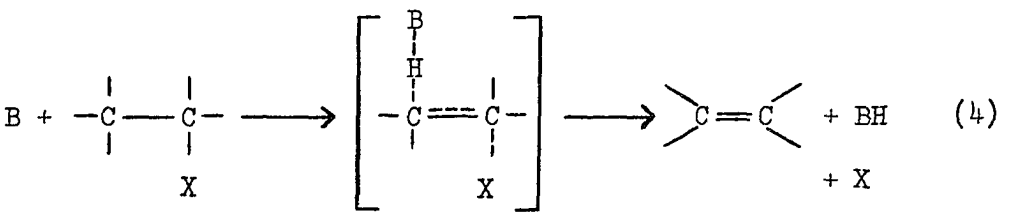
$$RCH_2\underset{X}{\underset{|}{C}} - CH(CH_3)_2 + OH^- \longrightarrow RCH_2C = C(CH_3)_2 \quad (3)$$

These early observations led to two general rules of orientation in elimination chemistry. The Hofmann Rule states that eliminations of 'onium groups ($-NR_3^+$, $-SR_2^+$, and $-PR_3^+$) from a molecule give predominately the olefin having the least number of alkyl substituents on the double bond. The Saytzeff Rule says that compounds having neutral leaving groups such as halides yield, as the chief products, the most highly substituted olefin.

This contrast displayed by two seemingly similar processes was not immediately appreciated. In 1927 Ingold and Hanhart (4) recognized that the eliminations of halides with base and of quaternary ammonium hydroxides belonged to the same mechanism class. Ingold later termed them E2 (elimination, bimolecular) (5) because their rates depended upon the concentration of both the base and the substrate. Hughes and Ingold (6) proposed that the polar effects of the 'onium groups were producing the Hofmann products. The strong electron-withdrawing, inductive effect of these groups enhanced the

acidity of the beta protons so that this was the factor controlling the direction of elimination. The beta carbon which had the least number of electron-donating alkyl groups substituted on it would have the most acidic proton. This proton would then be preferentially removed by base to give the least substituted olefin. When the leaving group was neutral, Hughes and Ingold proposed that activation of the beta protons through induction was not as great, and the stability of the olefinic products determined the product distribution.

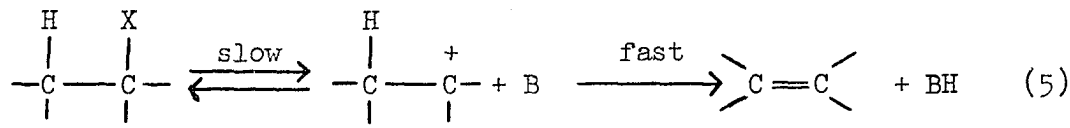
The E2 elimination is now pictured as proceeding through a one-step, concerted pathway in which the beta proton is removed simultaneously with the leaving group, X, in the transition state. The



(4)

C-H and C-X bonds are equally broken in the transition state, and double bond character has developed between the carbon atoms. In the ideal case the C-H and C-X bonds would be fifty percent broken and the double bond fifty percent formed. Bunnett (7) has pointed out that the C-H and C-X bond breaking and double bond formation might be greater or less than one-half completed in the transition state in many cases. Or double bond formation might lag behind the bond breaking of the leaving groups. This would result in partial charges on the alpha and beta carbons rather than their delocalization over the carbon-carbon bond as in the ideal case.

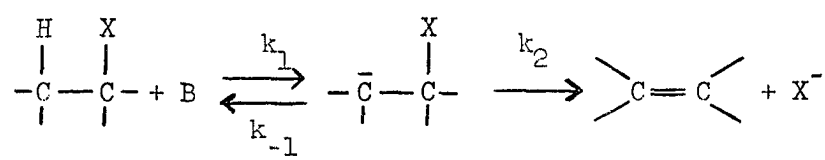
A unimolecular beta elimination was discovered in 1935 by Hughes (8) for the reactions of halides in aqueous alcohol solution. This E1 reaction was observed to be first-order for substrate and insensitive to base. It is a two-step process involving rate-determining formation of a carbonium ion, followed by rapid reaction with base or solvent to remove a proton.




(5)

The E1 reaction is accelerated by branching at the beta carbon, so that formation of Saytzeff product is generally favored. The reaction is characterized by competition from SN1 reaction, independence of olefin composition and $kE_1/kSN1$ on the leaving group, reversibility of the reaction, and rearrangement of products (9).

A third type of beta elimination, the E1cb, was proposed by Ingold, Hughes, and Patel (10). This bimolecular reaction was envisioned as a two-step elimination, in which a beta proton is removed by base to produce an intermediate carbanion. The carbanion then expels the leaving group to yield olefin.




(6)

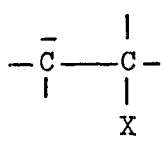
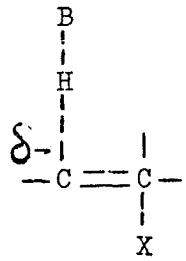
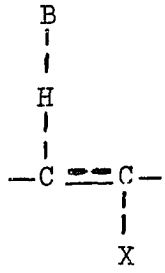
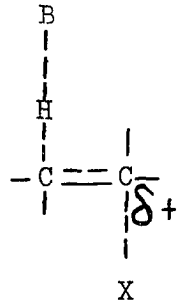
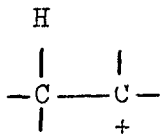
The E1cb mechanism has been proposed for systems which contain electron-withdrawing substituents on the alpha and beta carbons and for which a favored co-planar arrangement of the beta proton and leaving group is hindered (11,12,13,14,15,16,17). The mechanism

could involve either a rapid equilibrium of the reactant with the carbanion ($k_{-1} > k_2$) or slow formation of the carbanion followed by rapid reaction to form olefin ($k_2 > k_1$). The observation of deuterium exchange with solvent has been interpreted as evidence for the carbanion mechanism (11,18). However, it has been argued that the formation of a carbanion, as evidenced by deuterium exchange, could be an irrelevant side reaction (19). If $k_2 \gg k_{-1}$ deuterium exchange would not be anticipated even if the Elcb mechanism were operative. There is no unequivocal evidence yet for the Elcb mechanism.

When they proposed the Elcb mechanism, Hughes, Ingold, and Patel considered the likelihood of a graded range of mechanisms between the Elcb and the E2 reactions. Since then, a modern theory for E2 reactions has evolved, which encompasses the entire range of beta eliminations from the E1 to the Elcb extremes. The accumulated evidence is that the E2 reactions can differ in the relative extents of C-H and C-X bond rupture in their transition states. Between the central E2 mechanism described earlier and the extreme Elcb mechanism lies the "carbanion-like" reactions, involving more C-H bond breaking than C-X. The transition states for these eliminations have a partial negative charge on the beta carbon. The carbanion character increases as C-H bond breaking becomes more advanced relative to that of the C-X bond. When C-X bond breaking in the transition state is greater than that of the C-H bond, the mechanism is between the E1 and central E2 extremes. The reaction is said to be "carbonium ion-like" because the alpha carbon assumes some partial positive charge. E1-like and Elcb-like transition states would generally have less double bond

character than the central E2 transition state. Bunnett (7) has summarized the factors controlling the position of bimolecular beta eliminations on the mechanism spectrum. The relative "quality" of the transition states for alpha and beta-substituted systems can be interpreted on the basis of the substituents' abilities to stabilize or destabilize ionic character in the transition states. For example, an alpha aryl group would, through conjugation, stabilize positive charge on the alpha carbon, shifting the mechanism to the right (Table 1). The same effect would be predicted for an alpha alkyl

Table 1. The effect of structure and reaction conditions on the transition states of bimolecular elimination reactions

| Elcb | Elcb-like | E2 | E1-like | E1 |
|---|---|---|---|---|
|  |  |  |  |  |

alpha aryl group →

alpha alkyl group →

← beta aryl group

beta alkyl group →

← electronegative beta group

better leaving group →

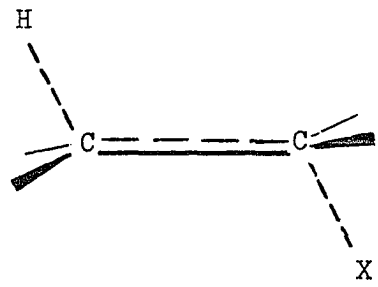
← electronegative leaving group

more polar solvent →

group because of its electron-donating ability. Conversely a beta aryl substituent would encourage negative charge on the beta carbon, facilitating a more Elcb-like mechanism, while a beta alkyl group would inhibit this negative charge. Electron donation by the beta alkyl group might also be felt at the alpha carbon, enhancing carbon-X bond rupture. An Elcb-like mechanism would be anticipated for electronegative beta substituents and leaving groups because of their stabilization of beta negative charge by induction and discouragement of alpha positive charge. A more polar solvent would better solvate the leaving group and, thus, enhance carbon-X bond heterolysis. The more polar solvent would also decrease the strength of the base acting on the beta proton. Also when X is neutral in the reactant and the base is negative, an El-like transition state would be favored in more polar solvent because of the greater separation of charges involved.

Bunnett did not make any prediction of the effect of base strength. The criteria for base strength for elimination reactions is often rather ambiguous. Thermodynamically weaker thiophenoxide and thioalkoxide bases have been observed to be more effective kinetic bases than their corresponding oxygen bases (20,21,22,23,24,25). However, for a given type of base (e.g., the alkoxides), the stronger base shifts the mechanism towards the Elcb region (26,27).

Bimolecular elimination reactions generally proceed most readily when the beta proton and leaving group are in a trans-coplanar conformation in the transition state (13,28,29,30,31,32).




trans-coplanar transition state

II

When a trans-coplanar transition state is energetically unfavored, or impossible, due to the rigidity of the reacting molecule, or when the acidity of the beta proton is enhanced by an electronegative beta substituent, cis eliminations have been observed. These cis eliminations often occur faster than trans elimination when a coplanar conformation is not available for the latter (12,14,16,33,34,35,36,37).

DePuy and coworkers (38) have suggested that the rates of E2 reactions vary steadily with the dihedral angle between the beta proton and the leaving group. The rates are predicted to be maximal when the angle is 0° or 180° and minimal when it is 90°. Eliminations in which a coplanar or anticoplanar arrangement is not possible might be forced closer to the Elcb or El extremes.

Recent studies of eliminations of 1,1,4,4-tetramethyl-7-cyclodecyl compounds have shown that trans and cis eliminations proceed side by side in this system (39,40). This duality of mechanism might exist for other systems as well.

Determination of the nature of transition states of elimination reactions through measurement of the amount of charge concentration, the relative degree of C-H and C-X bond breaking, and the amount of

carbon-carbon double formation in the transition states has been the concern of many investigators. The approaches to such studies have involved an examination of the effects of substituents, leaving groups, and isotopic substitution on reaction rates and product distributions.

A common method of measuring the carbanion character of elimination reactions has been use of the Hammett sigma-rho correlation (41) of beta-aryl substituted systems. The overall effect of the phenyl group is to shift the mechanism into the carbanion-like region of the E2 mechanism spectrum. The amount of negative charge on the carbon in the transition state is reflected by the degree of rate change when different electron-attracting and donating groups are substituted on the beta phenyl ring. The rates follow the relationship:

$$\log \frac{k_o}{k_x} = - \sigma\rho \qquad (7)$$

where $k_o$ and $k_x$ are the rate constants for the unsubstituted and substituted molecules, respectively, and sigma is a constant characteristic of the ring substituent. Sigma is positive for electronegative groups, zero for hydrogen, and negative for electron-donating groups. Rho is a measure of the sensitivity of the reaction to the ring substituents. A large, positive value for rho indicates a large amount of carbanion character in the transition state.

The effect of leaving groups on the rates and rho values for the 2-phenylethyl system is reported in Table 2. Rho is high for electronegative leaving groups indicating a large amount of carbanion character in the transition state. As X becomes a better leaving group and less

Table 2. The relative rates and rho values for bimolecular eliminations of 2-phenylethyl compounds, $C_6H_5CH_2CH_2X$, in sodium ethoxide in ethanol at 30°C

| X | Relative rate | Rho | Reference |
|---|---|---|---|
| $N(CH_3)_3^+$ [a] | | 3.77 | 7 |
| F | 1 | 3.12 | 42 |
| $S(CH_3)_2^+$ | 37,900 | 2.64 | 43 |
| Cl | 68 | 2.61 | 42 |
| oTs[b] | 392 | 2.27 | 26 |
| Br | 4,100 | 2.14 | 44 |
| I | 26,600 | 2.07 | 44 |

[a] 50°C.

[b] *p*-toluenesulfonate.

electronegative, rho decreases, and the rate increases. These data reflect the importance of beta proton acidity rather than product stability in determining the mechanism for 2-phenylethyl compounds. When X is highly electronegative (e.g., $-N(CH_3)_3^+$, $-S(CH_3)_2^+$, -F), the beta proton is rendered acidic by induction, and the reaction assumes more Elcb character. When the leaving group is a very poor one such as fluoride, a greater push by beta negative charge is required to break the strong carbon-X bond. The strength of the carbon-fluorine bond and its electronegativity, thus, result in a high rho value. Rho decreases for the less electronegative leaving groups because of the lower acidity of the beta protons and the increased amount of C-X bond breaking. The latter causes the X group

to assume more of the negative charge, and a greater spread of charge throughout the transition state results.

The lower rate of the p-toluenesulfonate group compared with bromide is surprising. p-Toluenesulfonates are known to react much faster than the corresponding bromides for first-order elimination and substitution reactions (45,46). DePuy and Bishop (26) have proposed that the rates of p-toluenesulfonate eliminations and substitutions are dependent upon the extent of carbon-oxygen bond breaking in the transition state. For first-order reactions this bond breaking is nearly completed in the transition state. In this case, the incipient p-toluenesulfonate anion is stabilized by both the inductive effect of the sulfur atom and by resonance stabilization offered by the other oxygen atoms on sulfur. Carbon-oxygen bond breaking is less advanced for bimolecular reactions, and the only stabilization afforded the incipient anion is induction. The overall prediction is that the rates of p-toluenesulfonate reactions will steadily decrease relative to that of bromides as the amount of C-X heterolysis decreases. It has been proposed that bromide/p-toluenesulfonate rate ratios may be utilized as mechanistic criteria for elimination and substitution reactions (26,27,45,46).

Exploratory investigations have also indicated that tert-butoxide/ethoxide rate ratios reflect the relative position of a compound on the mechanism spectrum (27,47,48). When an elimination is more E1cb, the acidity of the proton is more important in controlling the rate, and the rate becomes more sensitive to base strength.

Deuterium isotope studies of elimination reactions generally involve a comparison of the rates of reaction of compounds with those of their beta-deuterated analogues. When the expulsion of a proton occurs in the transition state of a reaction, the protonated compound reacts faster. High values for the rate ratios, $k_H/k_D$, are believed to indicate a large amount of C-H bond rupture in the transition state. The effect is proposed to be at a maximum when the proton and deuteron are equally bonded to the two reactants (49). The maximum deuterium isotope effect is approximated by:

$$k_H/k_D = e^{(h\nu_H - h\nu_D)/2RT} \qquad (8)$$

where $\nu_H$ and $\nu_D$ are the different stretching frequencies of the C-H and C-D bonds in the reactant. This difference results from their unequal masses. The equation predicts a maximum isotope effect of 6.6 at 30°C for the removal of a proton from a carbon atom. When $k_H/k_D$ is observed to be less than the theoretical maximum, the popular argument is that the proton is more strongly bonded to one of the reacting molecules than to the other (50). It is believed that $k_H/k_D$ varies smoothly with C-H bond breaking. This relation is depicted in Figure 1.

Westheimer has criticized this rationalization for low deuterium isotope effects (51). He stressed the necessity of a detailed vibrational analysis of transition states in order to completely understand the significance of $k_H/k_D$. Wiberg and Motell (52) have presented evidence that the symmetry of the transition state can affect the magnitude of deuterium isotope effects. Another complication

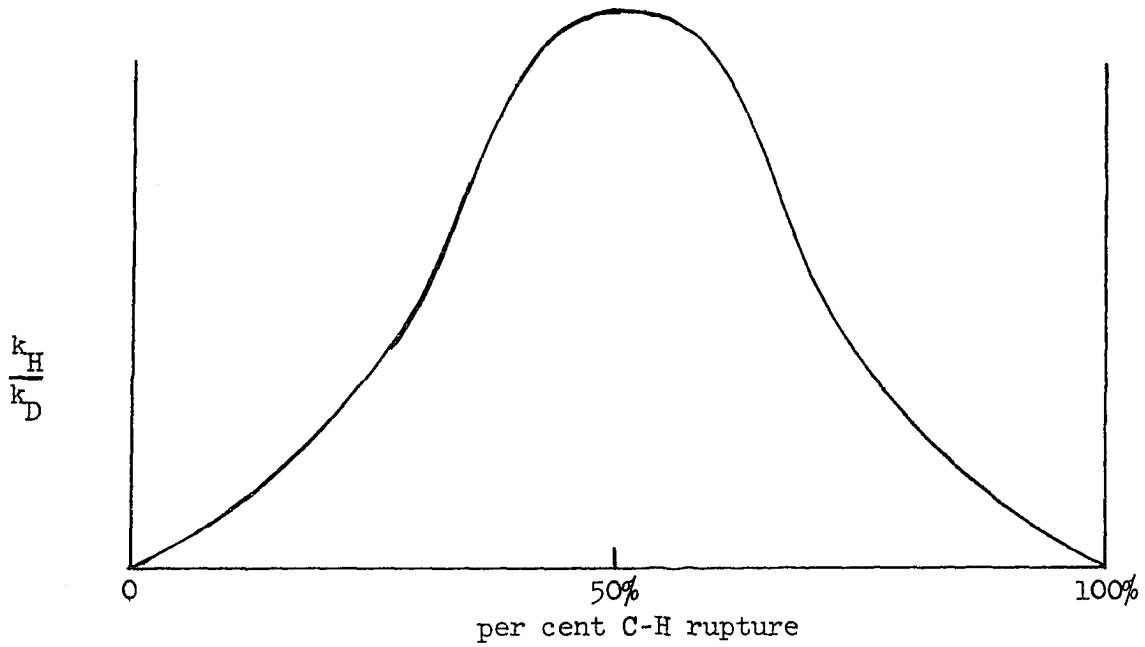
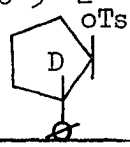



Figure 1. Correlation of $k_H/k_D$ with C-H bond breaking in the transition state.

is the possibility of quantum-mechanical tunneling through the potential energy barrier by the proton. This would also give high isotope effects. Shriner (53) attributed the high values of $k_H/k_D$ that he observed for the elimination of 2-phenyl-1-bromopropane to tunneling.

In Table 3 are listed the deuterium isotope effects for eliminations of various compounds. The calculated values of $k_H/k_D$ were obtained from equation 8 (49). Equation 8 neglects contributions from C-H bending vibrations and the effect of entropy of activation. For this reason, little significance can be attached to small differences observed between some of the experimental $k_H/k_D$ values and those calculated from equation 8. The ambiguities of deuterium isotope effects demand that they be analyzed in conjunction with other mechanistic criteria, such as rho, whenever possible.

Table 3. Deuterium isotope effects in bimolecular elimination reactions

| System | Base | Temp. °C | $\frac{k_H}{k_D}$ obs. | $\frac{k_H}{k_D}$ calc. | Ref. |
|---|---|---|---|---|---|
| $CD_3CH_2N(CH_3)_3^+$ | $OH^-$ | 137 | 4.0 | 4.0 | 54 |
| $(CD_3)_2CHBr$ | $OEt^-$ | 25 | 6.7 | 6.9 | 55 |
| $C_6H_5CD_2CH_2N(CH_3)_3^+$ | $OEt^-$ | 50 | 3.0 | 6.0 | 56 |
| $C_6H_5CD_2CH_2S(CH_3)_2^+$ | $OEt^-$ | 30 | 5.1 | 6.6 | 56 |
| $C_6H_5CD_2CH_2OTs$ | $OEt^-$ | 30 | 5.7 | 6.6 | 56 |
| | $\underline{t}$-$BuO^-$ | 30 | 8.0 | 6.6 | 56 |
| $C_6H_5CD_2CH_2Br$ | $OEt^-$ | 30 | 7.1 | 6.6 | 56 |
| | $OEt^-$ | 50 | 6.0 | 6.0 | 56 |
| | $\underline{t}$-$BuO^-$ | 30 | 7.9 | 6.6 | 56 |
| $C_6H_5CD(CH_3)CH_2Br$ | $OEt^-$ | 25 | 7.5 | 6.9 | 53 |
| $C_6H_5CD_2C(CH_3)_2Cl$ | $OMe^-$ | 75.8 | 2.6 | | 23 |
|   | $\underline{t}$-$BuO^-$ | 50 | 5.6 | 6.0 | 37 |

The high rho values for the 2-phenylethyl dimethylsulfonium and trimethylammonium compounds (Table 2) suggests that C-H bond breaking is quite advanced. Since the $k_H/k_D$ values are less than the calculated maxima, the bonds must be more than one-half broken (see Figure 1). However, it is only about one-half broken for the ethyltrimethylammonium salt, which lacks the activating beta phenyl substituent. The C-H bond for 2-phenylethyl $\underline{p}$-toluenesulfonate in the transition state could be more or less than one-half broken with ethoxide. The

implication is that it is less than one-half broken because $k_H/k_D$ rises with tert-butoxide, with which more C-H heterolysis would be expected. In spite of the lower rho value for the corresponding bromide, the bond breaking is more advanced with ethoxide, according to the deuterium isotope effect. Although no rho is available for 1-phenyl-2-methyl-2-chloropropane, the elimination of this tertiary halide is anticipated to be much less Elcb-like. The low deuterium isotope effect supports this prediction. Rho for trans-2-phenylcyclopentyl p-toluenesulfonate with tert-butoxide at 50° is 2.76 (37), which is larger than that of the 2-phenylethyldimethylsulfonium salt with ethoxide, and $k_H/k_D$ for this cis-elimination is slightly less than the maximum, suggesting that C-H bond breaking is a little more than one-half completed.

Thornton (57) has measured the $k_{CD^-D_2O}/K_{OH^-H_2O}$ solvent isotope effects for 2-phenylethyldimethylsulfonium and trimethylammonium bromides. The ratios were 1.57 and 1.79, respectively. The interpretation of these values is that the beta proton is more tightly bonded to the base in the latter case. The sulfur and nitrogen isotope effects have also been determined for the compounds. For the dimethylsulfonium salt $\frac{k_{S32}}{k_{S34}}$ was 30-40% of the calculated maximum (58), and $\frac{k_{N14}}{k_{N15}}$ was 30% of the maximum for the trimethylammonium salt (59), suggesting that C-X bond heterolysis is less in the latter case. These results complement the rho and $k_H/k_D$ values for the compounds, adding to the evidence that the mechanism for the trimethylammonium compound is more Elcb-like.

The nature of the transition states for eliminations has also been probed from studies of eclipsing effects and product distributions.

When an elimination has more central E2 character, the transition state may assume more double bond character and planarity. Substitutents on the alpha and beta carbons that are destined to be cis in the product come closer together in the transition state, and the more planar it is, the greater will be the degree of eclipsing. The eclipsing will contribute to the energy of the transition state and, therefore, will affect the reaction rate. Cram, Greene, and DePuy (60) related eclipsing effects and reaction mechanism by comparing the rates of elimination of erythro and threo 1,2-diphenyl-1-propyl bromides, iodides, and trimethylammonium salts.

A more common approach is measurement of trans/cis product ratios for eliminations. High values for the ratio are believed to reflect a large amount of eclipsing in the transition state (7). The investigations are usually conducted in conjunction with Hofmann and Saytzeff product determinations. The object of the studies has generally been to clarify the relative influence of polar, conjugative, and steric effects upon the direction of elimination. As described earlier in this section, Hughes and Ingold attributed the greater yields of Hofmann products for 'onium leaving groups to control by the acidities of the beta protons. The predominance of Saytzeff product for uncharged leaving groups was held to be a result of the greater importance of the product stability. The acidity of the beta protons is not as great, and the less electronegative groups are generally better leaving groups. The result is a less Elcb reaction and more double bond character in the transition state. Any substituents on the alpha and beta carbons which can stabilize the incipient double bond of the

transition state will accelerate the reaction. For example, elimination of sec-butyldimethylsulfonium ion, p-toluenesulfonate, and bromide with ethoxide yields 74% (61), 48% (62), and 19% (63) 1-butene respectively. The acidity of the beta methylene protons

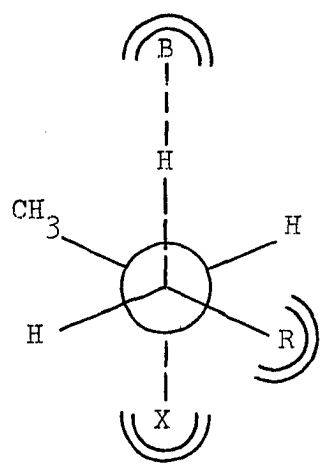
$$CH_3CH_2\underset{\underset{X}{|}}{CH}CH_3 + OEt^- \longrightarrow \underset{\text{1-butene}}{CH_3CH_2CH{=}CH_3} + \underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \qquad (9)$$

is lowered relative to that of the beta methyl protons because the methylene carbon has an electron-donating methyl group substituted on it. Elimination will, thus, go faster in the direction of the methyl group to give more 1-butene for the dimethylsulfonium compound. The transition state giving 2-butene has both an alpha and beta methyl substituent available for stabilization of any double bond character that might develop. The transition state involved in forming 1-butene, however, has only the beta ethyl group. For the bromide, therefore, which has more double bond character in its transition states, elimination will go faster in the direction of the methylene group. The leaving ability of the p-toluenesulfonate group and its electronegativity apparently lie between bromide and dimethylsulfonium ion. This is confirmed from the rho values for their 2-phenylethyl compounds (Table 2). Hughes, Ingold, and coworkers have conducted an extensive study of directive effects in elimination reactions. This work and their arguments are summarized in references (5) and (64).

Studies of the 2-phenylethyl system described earlier show that the electronegativity of the leaving group is important in determining

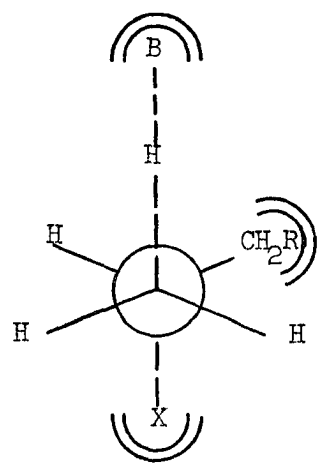
the acidity of the beta protons. The rho values for the various leaving groups change in the same direction as their yields of Hofmann products for the aliphatic systems discussed below. This lends support to the arguments of Hughes and Ingold. The eliminations of the 2-phenylethyl system, however, lie far in the Elcb region. Because of the enhanced acidity of the beta protons, other effects such as steric interactions, which could be significant for the more central E2 reactions of aliphatic systems, might become negligible.

Schramm (65) and Brown (66) have pointed out that steric interactions are probably important in determining the direction of elimination for aliphatic systems. For secondary compounds, the transition states leading to Hofmann and Saytzeff products are depicted by structures III and IV.




Saytzeff

III




Hofmann

IV

The planar character of these transition states may be greater or less than shown, depending upon steric and electronic contributions of the base and solvent, the R substituent, and the leaving group.

Brown agrees that when no serious steric effects are operative (e.g., when the transition states are more planar) transition state III would be the more stable as a result of the added hyperconjugative effect of the extra alkyl group. However, as the transition states become less planar, i.e., slightly more Elcb or El-like, and as the sizes of R, X, and B increase, IV will be energetically favored because of the overall lower number of steric interactions involved in this case.

Brown and coworkers have conducted a detailed study of aliphatic systems in order to elucidate the importance of steric effects for unimolecular (67,68,69,70,71) and bimolecular (72,73,74,75) eliminations. Their results for bimolecular eliminations are summarized in Figures 2, 3, 4, and 5. It is unfortunate that changing the steric nature of a group or molecule generally affects other properties of these moieties as well. For example, when R is varied (Figure 2) from methyl to tert-butyl, the number of protons available for hyperconjugation decreases from three to zero. As the number of branches on the leaving group is increased from zero for bromide, one for p-toluenesulfonate, two for dimethylsulfonium ion, and three for methylsulfone and trimethylammonium ion, Figure 3 shows the amount of Hofmann product to increase. It is reasonable to expect that the steric requirements of the groups will increase with the number of branches. In the examples used, however, the electronegativity increases in the same direction, with the exception of methylsulfone.

In Figures 4 and 5 are shown the effect of base on eliminations of tertiary bromides. The order of increasing steric requirements of

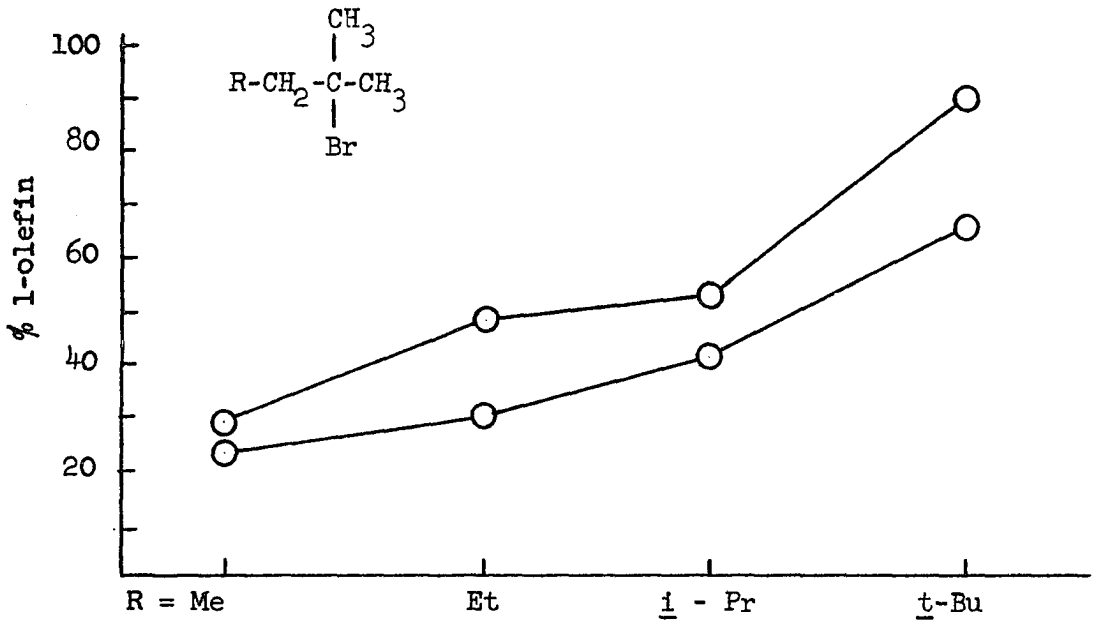



Figure 2. Effect of increasing steric requirements of R in the tertiary bromides, $RCH_2CBr(CH_3)_2$, on the direction of bimolecular elimination.

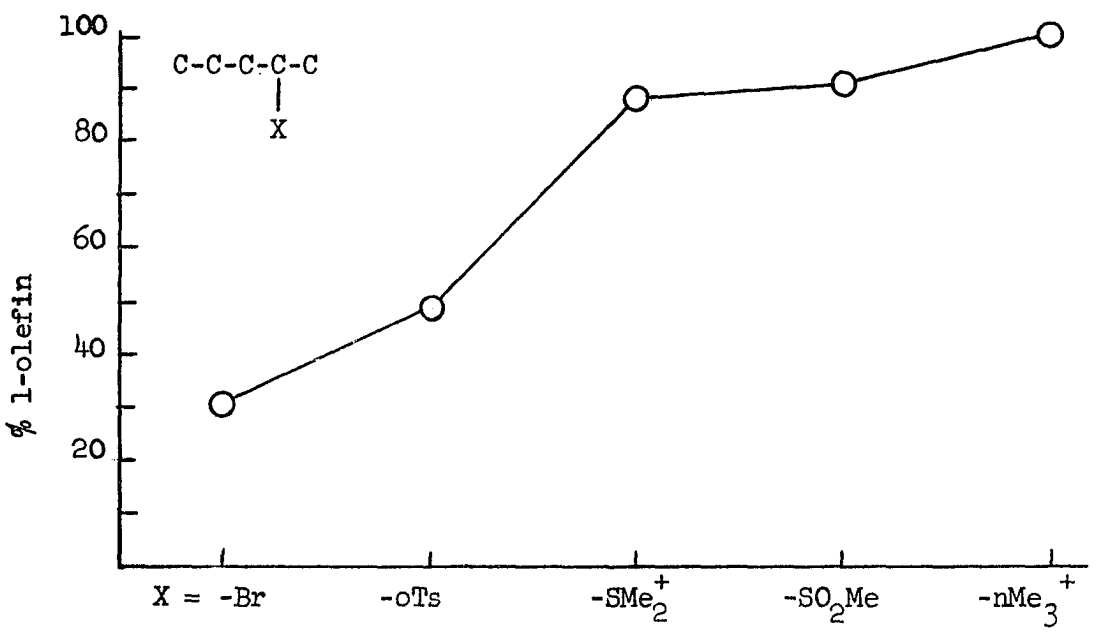



Figure 3. Effect of the steric requirements of the leaving group on the direction of bimolecular elimination.

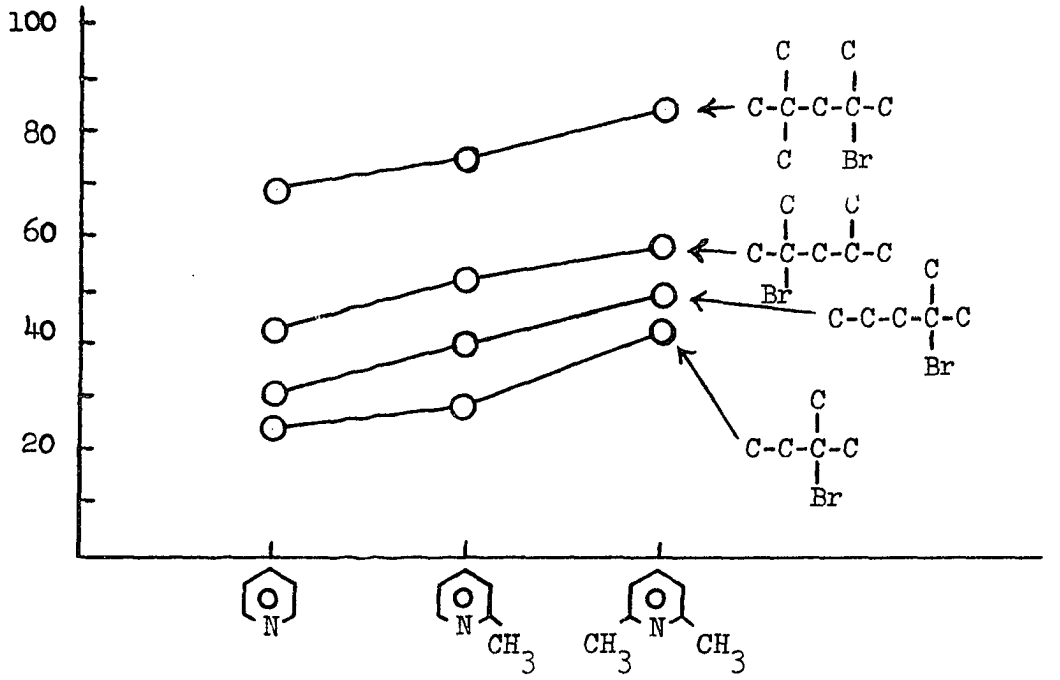



Figure 4. Effect of increasing steric requirements of the pyridine base on the direction of elimination.

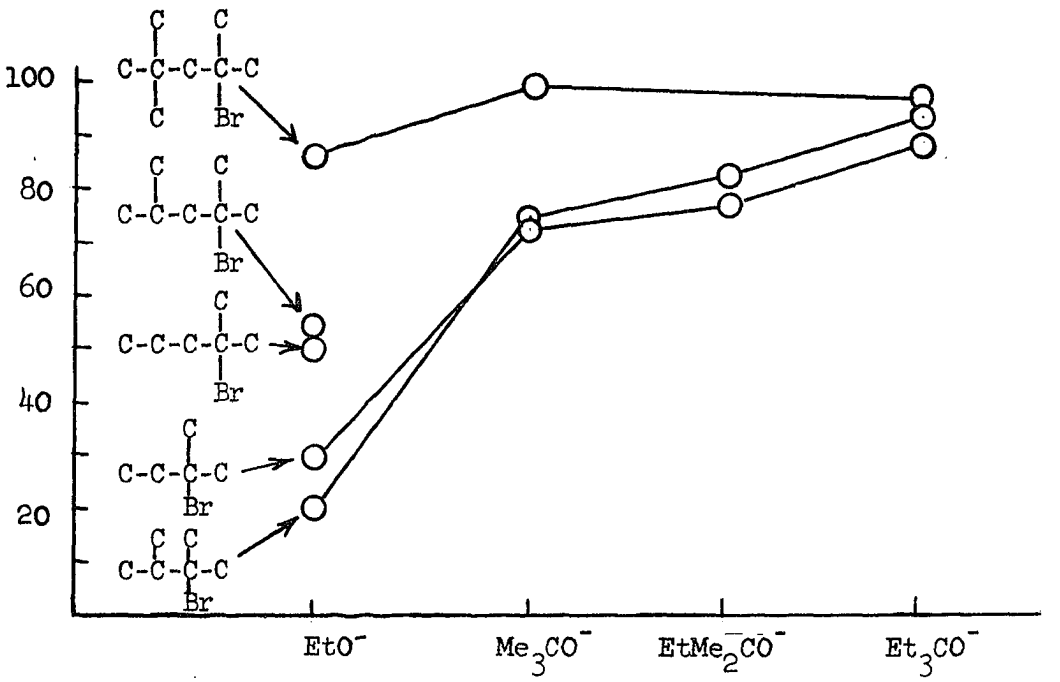



Figure 5. Effect of increasing steric requirements of the alkoxide base on the direction of elimination.

pyridine bases is pyridine < 2-picoline < 2,6-lutidine and pKa is 5.17, 5.97 and 6.75, respectively (74). Reaction of tert-amyl bromide with both pyridine and 4-picoline (pKa 6.02) gave 25% 1-olefin. The steric requirements of the two bases should be nearly identical. The dielectric constants of 4-picoline, pyridine, 2-picoline, and 2,6-lutidine must be similar, e.g., the dielectric constants for pyridine, 2-picoline, and 4-ethylpyridine are 13.23 (76), 10.18 (77), and 10.98 (76), respectively, at 20°C. The evidence is that steric effects, not basicity and polarity of the medium, are controlling the product distributions for the pyridine bases.

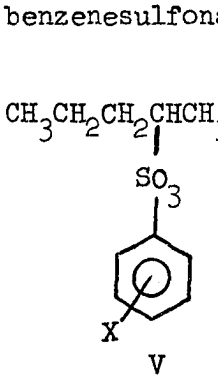
The situation with alkoxide bases is complicated by both large changes in basicities and dielectric constants of the reaction media. The eliminations in Figure 4 were conducted with the corresponding alcohols of the bases as solvents. The conjugate base of ethanol (pKa 18) is weaker than that of tert-butyl alcohol (pKa 19) (78). Those of tert-amyl alcohol and triethylcarbinol are probably stronger than tert-butoxide. The dielectric constants of the alcohols are quite different: ethanol, 25.00 (79); tert-butyl alcohol, 11.23 (76); tert-amyl alcohol, 5.92 (76); and triethylcarbinol, 3.16 (76) at 20°C. The dielectric constants, therefore, probably vary inversely with basicity in the reaction media. The overall effect predicted would be a shift of the mechanism towards the Elcb, Hofmann region as the reaction medium is changed from ethanol, to tert-butyl alcohol, to tert-amyl alcohol, to triethylcarbinol. Whether steric interactions resulting from the loss in planarity or proton acidity are more

important as this happens is extremely difficult to ascertain. Brown argued that the stronger, more reactive bases should be less selective toward the beta protons that are available for removal if proton acidity is controlling the product distributions. Since the selectivity increases (i.e., more of the less stable 1-olefin is produced) with the stronger, bulkier bases, he concluded that the increasing steric requirements ($EtO^- < \underline{t}\text{-}BuO^- < Me_2EtCO^- < Et_3CO^-$) were determining the yield of Hofmann product.

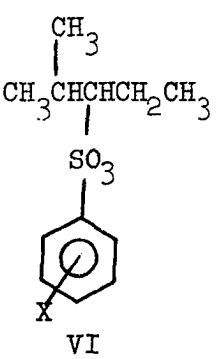
Recent studies of sec-butyl, sec-amyl, and tert-amyl halide eliminations (80,81,82) have shown that the yield of 1-olefin increases in the order of rising electronegativity of the halides (F > Cl > Br > I). Because this trend is in the opposite direction of increasing size of the halides, it suggests the greater importance C-H and C-X bond heterolysis in determining the product distributions. The trans/cis product ratios for the sec-butyl and sec-amyl halides increased in the order I > Br > Cl > F, indicating that the double bond character in the transition state is greater for the less electronegative halides. Brown (82) has proposed that the covalent radii of the halides, which increase with their size, might be compensating for the greater steric bulk. The larger halides, having a larger covalent radius, are further removed from the reaction site, and steric effects are minimized. Recently an investigation of the equatorial-axial equilibrium in halocyclohexanes indicated that the order of steric requirements for the halides is F < I < Br < Cl (83) in this case.

Brown stressed that solvent effects should also be considered for these reactions. It would be anticipated that the degree of solvation of the leaving group will decrease from fluoride to iodide. This solvation might contribute to the steric requirements of the leaving group. Froemsdorf (84) observed that the yield of 1-butene increases and the trans/cis 2-butene ratio decreases as the base/solvent system used to eliminate sec-butyl bromide was changed from ethoxide/ethanol to ethoxide/tert-butyl alcohol to tert-butoxide/tert-butyl alcohol. He attributed this trend to an increasing ratio of C-H to C-X bond-breaking. In reference to this work, Brown suggested that some sort of solvated base ions such as [EtOH·$OEt^-$],[t-BuOH·$OEt^-$], and [t-BuOH·O-t-$Bu^-$] are very probably the actual reacting species. The solvent in this form might reflect a steric control.

Colter (85,86) recently reported an investigation of the effects of ring substitution on the eliminations of 2-pentyl and 2-methyl-3-pentyl benzenesulfonates.



V



VI

X = p-$N(CH_3)_2$, p-$NH_2$, p-$OCH_3$, p-$CH_3$, p-Br, 3,4-di-Cl, p-$NO_2$

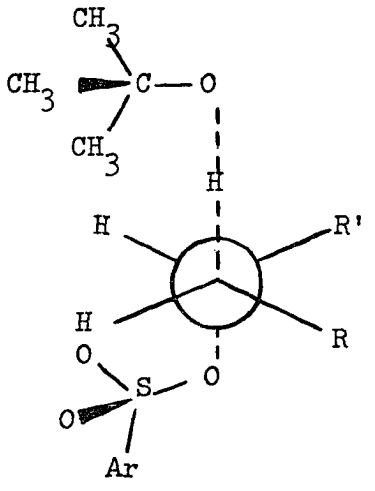
As the ring substituent becomes more electronegative, one of three trends might be observed: 1) the yield of Saytzeff product might increase if C-O bond heterolysis is the predominant factor in

controlling the orientation of elimination. An electronegative ring substituent will stabilize the incipient benzenesulfonate anion in the transition state, giving more C-O bond heterolysis; 2) more Hofmann product might be observed if beta proton acidity is more important because the electronegative ring substituents will increase this acidity through induction; 3) no change in product distribution might be observed if only steric effects are operative.

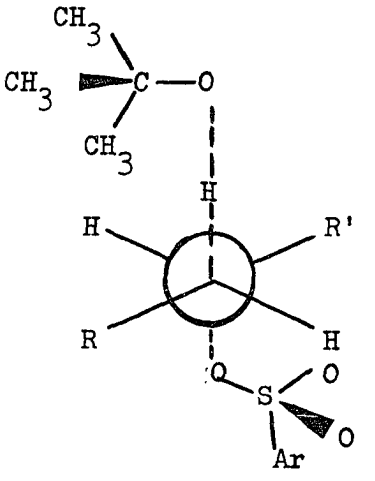
Elimination of the 2-pentylbenzenesulfonates with sodium ethoxide in ethanol and 2-methyl-3-pentylbenzenesulfonates with potassium tert-butoxide in tert-butyl alcohol/dioxane and tert-butyl alcohol/dimethylsulfoxide showed a small but regular increase in the yield of Saytzeff product with increasing electronegativity of the ring substituent. The ratio of trans to cis-2-pentene and 3-methyl-3-pentene and the reaction rate also increased in this direction. The 2-pentyl system has a rho of +1.35, and those for the 3-methyl-2-pentyl compounds in tert-butyl alcohol/dioxane and tert-butyl alcohol/dimethylsulfoxide are +1.51 and +2.40, respectively. This indicates that there is considerable negative charge build-up on the leaving group, and C-X bond heterolysis is well advanced in the transition state. The controlling factor for these systems under the conditions used is, therefore, the amount of C-X bond heterolysis.

Several workers have observed that under certain conditions the yields of cis olefin exceeds that for trans. Brown (87) recently reported that elimination of 2-butyl, 2-pentyl, and 3-pentyl p-toluenesulfonates yields a preponderance of cis 2-olefins with potassium tert-butoxide in tert-butyl alcohol. He pictured the transition states

giving cis and trans olefin as depicted by structures VII and VIII. It was proposed that transition state VII, giving cis-olefin, will be



VII



VIII

favored in these cases because both the bulky base and leaving group can project away from the R groups.

A similar preference for cis olefin has been reported for eliminations of trimethylammonium salts. Cope (88) found that pyrolysis of 2-butyltrimethylammonium hydroxide gives 94.6% 1-butene, 3.2% cis-2-butene, and 2.2% trans-2-butene. Sicher (89) reported that 5-nonyltrimethylammonium ion gives cis/trans product ratios of 2.8 and 4.3 in ethoxide/ethanol and methoxide/methanol, respectively. He attributed this behavior of 'onium compounds to preferred cis elimination, which would offer a more stable transition state to yield cis-product than would trans-elimination.

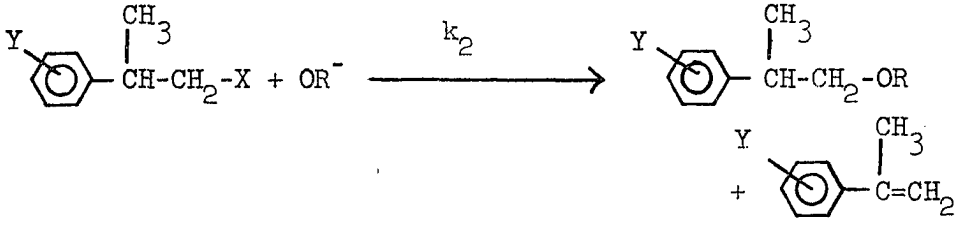
# RESULTS AND DISCUSSION

Mechanistic studies of the eliminations of compounds containing the 2-phenylethyl moiety have been extensive. Bimolecular elimination reactions of 2-phenylethyl compounds, $C_6H_5CH_2CH_2X$, were shown to have considerable carbanion character in their transition states, and the amount of carbanion character is sensitive to the nature of the leaving group. Frey's (27) investigations of the 1-phenyl-2-propyl system indicate that the alpha methyl group shifts the mechanism away from the E1cb region. Studies of cis and trans-2-phenylcyclopentyl (37,38) p-toluenesulfonates reveal that the cis compound, which gives trans elimination, approaches the central E2 region of the mechanism spectrum. The trans compound, however, eliminates through a more carbanion-like transition state because of the required cis elimination. Similarly the cis eliminations of endo-2-phenyl-exo-norbornyl and trans-2-phenylcyclobutyl p-toluenesulfonates were observed respectively by Beckman (90) and Hendrickson (91) to give high rho values.

This thesis reports a continued study of the mechanism of elimination of substituted 2-phenyl tosylates and bromides. The effect of the beta methyl group on the eliminations of the 2-phenyl-1-propyl system is reported and discussed. The eliminations were conducted using potassium tert-butoxide in tert-butyl alcohol and sodium ethoxide in ethanol as base/solvent systems. The scope and limitations of butoxide/ethoxide and bromide/p-toluenesulfonate rate ratios are discussed in view of previous studies and those reported here. Preliminary studies on the effect of beta vinyl substitution on elimination

reactions are presented. Exploratory work aimed at isolating steric effects controlling elimination orientation through the use of optically active reactants and solvents is also reported.

The reaction rates of the 2-phenyl-1-propyl tosylates and bromides were measured titrimetrically by following the consumption of base with standardized acid solution. In many cases, the resulting rate constants observed were the combined rate constants for second-order substitution and elimination ($k_2$ obs. = $k_{SN2} + k_{E2}$). $k_{E2}$ was




(10)

determined by measuring the yields of styrene products spectrophotometrically. The rate constants and yields of olefin for substituted 2-phenyl-1-propyl compounds are reported in Tables 4 and 5. In Table 6 are given the enthalpies and entropies of activation for the eliminations of the para-hydrogen substituted compounds.

The logarithms of the rate constants were plotted against the corresponding sigma values of the ring substituents, and the slopes of the resulting plots represent the rho values. The rho values and the sigma-rho correlations are given in Table 7 and Figure 6. Except for the deviations of the para-methoxy compounds in ethanol, the data fit the correlation very well. Froemsdorf (44) observed the same kind of deviation for 2-(p-methoxyphenyl)ethyl p-toluenesulfonates and bromides in ethanol. He attributed the unexpectedly higher rates of

Table 4. Rates of elimination of 2-phenyl-1-propyl compounds, $Y\text{-}C_6H_4CH(CH_3)CH_2\text{-}X$, in potassium tert-butoxide in tert-butyl alcohol

| Y | X | Temp. °C | $k_2 \times 10^4$ | % yield olefin | $k_{E2} \times 10^4$ |
|---|---|---|---|---|---|
| p-H | oTs | 49.83 | 2.33 ± 0.04 | 92 | 2.14 ± 0.03 |
| | | 29.80 | 0.369 ± 0.011 | 93 | 0.343 ± 0.010 |
| p-Cl | oTs | 49.83 | 7.06 ± 0.10 | 100 | 7.06 ± 0.10 |
| m-Br | oTs | 49.83 | 18.5 ± 0.5 | 96 | 17.8 ± 0.5 |
| p-$CH_3$ | oTs | 49.83 | 1.03 ± 0.01 | 90 | 0.928 ± 0.007 |
| p-$OCH_3$ | oTs | 49.83 | 0.826 ± 0.013 | 80 | 0.661 ± 0.011 |
| p-H | Br | 49.83 | 41.1 ± 1.0 | 100 | 41.1 ± 1.0 |
| | | 29.80 | 8.19 ± 0.18 | 100 | 8.19 ± 0.18 |
| p-Cl | Br | 49.83 | 118 ± 3 | 100 | 118 ± 3 |
| m-Br | Br | 49.83 | 205 ± 4 | 98 | 201 ± 4 |
| p-$CH_3$ | Br | 49.83 | 21.1 ± 0.5 | 100 | 21.1 ± 0.5 |
| p-$OCH_3$ | Br | 49.83 | 15.3 ± 0.7 | 96 | 14.7 ± 0.7 |

these compounds to contributions from product stability. The para-methoxy group lowers the acidity of the beta protons, shifting its elimination away from the Elcb region slightly, and the transition state resembles the styrene product more. Because the p-methoxy-group stabilizes the double bond in the styrene moiety (92), the reaction is accelerated slightly.

Table 5. Rates of elimination of 2-phenyl-1-propyl compounds, $Y\text{-}C_6H_4CH(CH_3)CH_2\text{-}X$, in sodium ethoxide in ethanol

| Y | X | Temp.°C | $k_2 \times 10^4$ | % yield olefin | $k_{E2} \times 10^4$ |
|---|---|---|---|---|---|
| p-H | oTs | 49.83 | 0.869 ± 0.03 | 64 | 0.556 ± 0.02 |
| | | 29.80 | 0.0762 ± 0.0002 | 71 | 0.0541 ± 0.0001 |
| p-Cl | oTs | 49.83 | 2.12 ± 0.02 | 64 | 1.35 ± 0.01 |
| m-Br | oTs | 49.83 | 3.52 ± 0.03 | 75 | 2.64 ± 0.02 |
| p-$CH_3$ | oTs | 49.83 | 0.664 ± 0.000 | 41 | 0.272 ± 0.000 |
| p-$OCH_3$ | oTs | 49.83 | 0.998 ± 0.006 | 28 | 0.279 ± 0.002 |
| p-H | Br | 49.83 | 14.5 ± 0.5 | 100 | 14.5 ± 0.5 |
| | | 29.80 | 1.58 ± 0.02 | 100 | 1.58 ± 0.02 |
| p-Cl | Br | 49.83 | 59.8 ± 0.0 | 97 | 58.0 ± 0.0 |
| m-Br | Br | 49.83 | 112 ± 1 | 100 | 112 ± 1 |
| p-$CH_3$ | Br | 49.83 | 9.34 ± 0.47 | 100 | 9.34 ± 0.47 |
| p-$OCH_3$ | Br | 49.83 | 8.32 ± 0.06 | 100 | 8.32 ± 0.06 |

The data show that the overall effect of adding a beta methyl substituent to the 2-phenylethyl system is a shift of the mechanism away from the carbanion region as indicated by the decrease in rho values. This result agrees with earlier predictions that the acidity of the beta protons will be lowered by a beta alkyl substituent because of its electron-withdrawing ability, and a very Elcb-like mechanism will be less favorable. A secondary, complementing consequence of the inductive electron-withdrawing effect of the beta methyl group might be increased ease in C-X bond heterolysis because of stabilization of

Table 6. Enthalpies, entropies, and free energies of activation for eliminations of 2-phenyl-1-propyl compounds, $C_6H_5CH(CH_3)CH_2$-X

| X | base/solvent | $T_m$ °C | $\Delta H^{\neq}$ kcal/mole | $\Delta S^{\neq}$ cal/mole°C | $\Delta F^{\neq}$ kcal/mole |
|---|---|---|---|---|---|
| oTs | t-BuO$^-$/t-BuOH | 39.82 | 17.19 | -22.27 | 24.16 |
| | EtO$^-$/EtOH | 39.82 | 22.03 | - 9.98 | 25.15 |
| Br | t-BuO$^-$/t-BuOH | 39.82 | 15.05 | -23.05 | 22.27 |
| | EtO$^-$/EtOH | 39.82 | 20.95 | - 6.83 | 23.09 |

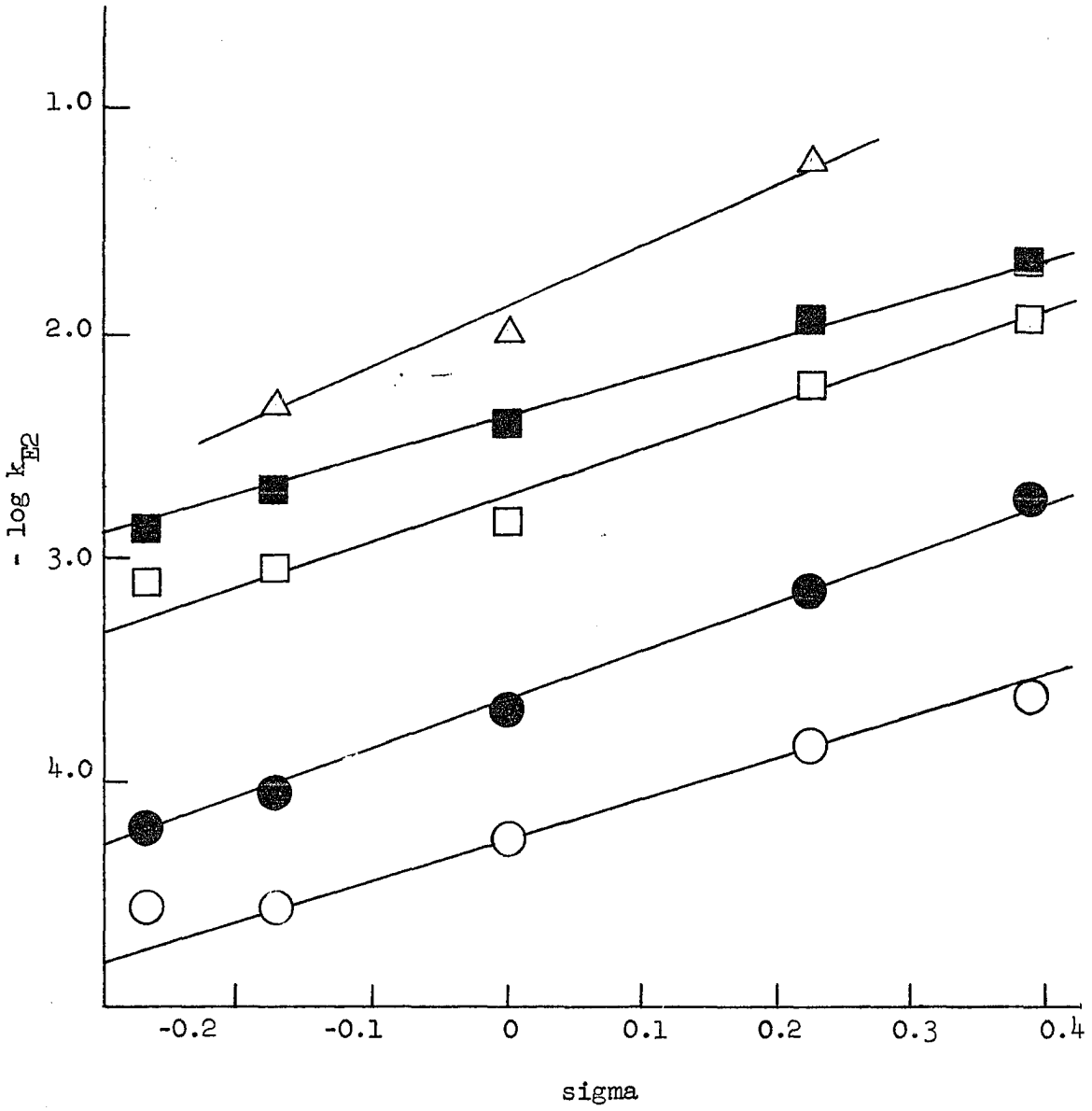
Table 7. Rho values for eliminations of 2-phenyl-1-propyl compounds, $C_6H_5CH(CH_3)CH_2$-X, at 49.83°C

| X | base/solvent | Rho | log $k_o$ |
|---|---|---|---|
| oTs | t-BuO$^-$/t-BuOH | 2.18 ± .03 | -3.632 |
| oTs | EtO$^-$/EtOH | 1.81 ± .02[a] | -4.265 |
| Br | t-BuO$^-$/t-BuOH | 1.75 ± .02 | -2.376 |
| Br | EtO$^-$/EtOH | 2.06 ± .05[a] | -2.728 |

[a]Not including the rates for the p-MeO compounds.

incipient alpha positive charge in the transition state. This must be of minor importance, however, because the rates decrease considerably by addition of the beta methyl group, as much as fifty-two fold for the p-toluenesulfonate in tert-butyl alcohol (Table 8). The studies of 2-phenylethyl compounds discussed in the previous section showed the rate of elimination to increase with the ease of

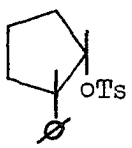
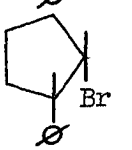
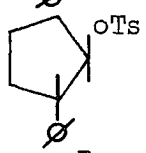
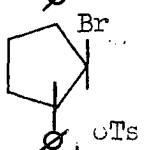
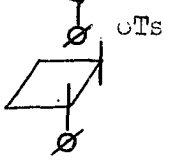
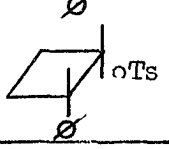
Figure 6. Hammett plots for the bimolecular elimination of 2-phenyl-3-butene-1-ol p-toluenesulfonates in ethoxide/ethanol, △ ; and 2-phenyl-1-propyl compounds: p-toluenesulfonates in ethoxide/ethanol, ○ ; p-toluenesulfonates in tert-butoxide/tert-butyl alcohol, ● ; bromides in ethoxide/ethanol, □ ; and bromides in tert-butoxide/tert-butyl alcohol, ■ .


1.0
2.0
3.0
4.0
- log $k_{E2}$
-0.2
-0.1
0
0.1
0.2
0.3
0.4
sigma

C-X bond breaking. The rate change observed for the 2-phenyl-1-propyl system, therefore, is a consequence of decreased acidity of the beta proton. Within this system, however, the amount of C-X bond heterolysis is important as indicated by the greater rates for the bromides. When the methyl group resides on the alpha carbon as in 1-phenyl-2-propyl system, the shift away from the Elcb region is even more pronounced. Table 8 shows that the rate decrease is not as great, however. In this case, the inductive effect of the methyl group is enhancing the amount of C-X bond breaking. Since the rate decreases in spite of this, the secondary inductive effect of the methyl group must be operative, discouraging removal of the beta-proton.

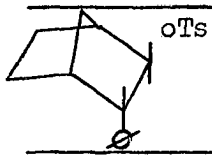
The statistical factor might also be affecting the rates of the systems. On a purely statistical basis, one would predict that the 2-phenylethyl and 1-phenyl-2-propyl systems would react twice as fast as the 2-phenyl-1-propyl system because the latter has only one beta proton available for removal. The 1-phenyl-2-propyl system, however, yielded over 85 per cent <u>trans</u> olefin in nearly every case, whereas statistically a 50-50 mixture of <u>cis</u> and <u>trans</u> olefin would have been anticipated if both protons were equally available. Thus the existence of only one proton for the beta methyl compound and the preference of one over the other for the alpha methyl compound could conceivably contribute statistically to their lower rates. When the rates differ by very much more than a factor of two, however, statistical effects must be minor.

Table 8. Rate constants and rho values for elimination of p-toluenesulfonates and bromides of 2-phenyl compounds at 50°C

| Compound | base/solvent | $k_{E2} \times 10^{-4}$ | Rho | Ref |
|---|---|---|---|---|
| $C_6H_5CH_2CH_2oTs$ | t-BuO⁻/t-BuOH | 111 | 3.39[a] | 26 |
| | EtO⁻/t-BuOH | 22.2 | 2.60[a] | 26 |
| | EtO⁻/EtOH | 5.98 | 2.27[a] | 26 |
| $C_6H_5CH_2CH_2Br$ | t-BuO⁻/t-BuOH | 369 | 2.08[a] | 26 |
| | EtO⁻/t-BuOH | 115 | 2.28[a] | 26 |
| | EtO⁻/EtOH | 34.2 | 2.14[a] | 26 |
| $C_6H_5CH_2(CH_3)CHoTs$ | t-BuO⁻/t-BuOH | 9.32 | 1.88 | 27 |
| | EtO⁻/EtOH | 3.42 | 1.32 | 27 |
| $C_6H_5CH_2(CH_3)CHBr$ | t-BuO⁻/t-BuOH | 94.1 | 1.37 | 27 |
| | EtO⁻/EtOH | 14.6 | 1.84 | 27 |
|  | t-BuO⁻/t-BuOH | 29.1 | 1.48 | 37 |
| | EtO⁻/EtOH | 24.2 | 0.99 | 37 |
|  | t-BuO⁻/t-BuOH | 241 (30°) | | 48 |
|  | t-BuO⁻/tBuOH | 2.9 | 2.76 | (37,38) |
|  | t-BuO⁻/t-BuOH | .285 | | 48 |
|  | t-BuO⁻/t-BuOH | 5.10 | 2.90 | 91 |
|  | t-BuO⁻/t-BuOH | 13.0 | 2.18 | 91 |
| | EtO⁻/EtOH | 1.16 | 1.26 | 91 |

[a]Rho values measured at 30°C.

Table 8 (continued)

| Compound | base/solvent | $k_{E2} \times 10^{-4}$ | Rho | Ref |
|---|---|---|---|---|
|   | | | | |
| | t-BuO⁻/t-BuOH | 13.6 | 3.24 | (90) |
| | EtO⁻/EtOH | 1.1[b] | 2.10 | (90) |

[b]Extrapolated from Hammett correlation for p and m-Cl compounds.

The low rho value for cis-2-phenylcyclopentyl p-toluenesulfonate indicates that the elimination is one of even more central E2 character. Within the set of cyclic systems the dihedral angle of the beta proton and leaving group appears to affect both the rate and mechanism. cis-2-Phenylcyclobutyl and cyclopentyl p-toluenesulfonates have dihedral angles of 140° and 150°, respectively, (93) in the puckered forms. The cyclopentyl compound is able to attain a more trans-coplanar transition state in its elimination, and it reacts faster with a lower rho value. The trans compounds must react via a cis elimination, and the reactions are more Elcb-like. The dihedral angles for endo-3-phenyl-exo-norbornyl, trans-2-phenylcyclobutyl, and trans-2-phenylcyclopentyl p-toluenesulfonates are 0°, 10°, and 20°, respectively (93). Again the rates of elimination decrease as the angle increases or as it becomes more difficult for a coplanar relationship to exist in the transition state. However, the rho values increase with increasing rates for these cis eliminations as contrasted to the more central E2-like trans eliminations.

The factors, therefore, that determine the mechanisms and rates of elimination of these compounds are the relative ease of C-H and C-X bond breaking and the resulting amount of double bond character in the transition states. When the leaving group is a poor one, when cis elimination is required, or when the beta protons are rendered acidic by electron-withdrawing substituents and leaving groups, the mechanism assumes more Elcb character. The degree of stabilization of the beta negative charge has a strong influence on the reaction rate. When electron-donating groups are substituted on the molecule and when the leaving group is less electronegative, beta negative charge is discouraged while C-X bond heterolysis is enhanced. The overall result is a shift in the mechanism towards the center of the mechanism spectrum and more double bond formation in the transition state. Stabilization of the incipient double bond by alpha and beta alkyl substituents and by conjugation with the beta phenyl group increases the rate of reaction as the transition state approaches the central E2 region.

The Hammond postulate (94) states, "If two states, as for example, a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their conversion will involve only a small reorganization of the molecular structures."

Extrapolating this concept to more stable reactants, one might expect that a series of compounds involved in a given reaction, such as elimination, might structurally resemble their transition states

more as their reactivities increase within the series. Because C-H bond heterolysis is more advanced than is C-X bond heterolysis in the transition states for Elcb-like eliminations, variations in the reactivities of 2-phenyl-substituted compounds would be predicted to affect C-H bond heterolysis to a greater extent than that for the C-X bond in the transition state. Therefore, the transition states involved in the elimination reactions of very reactive compounds within this series would have less C-H bond breaking, according to the Hammond postulate, than the transition states derived from the less reactive substances, whereas C-X bond breaking would suffer less change.

If the series of compounds under observation were the various aryl-substituted (i.e., p-H, p-Cl, m-Br, p-Me, p-MeO) compounds of a given 2-phenyl-substituted system, the compounds with the more electronegative ring substituents would be the more reactive because of the enhanced acidity of the beta protons. The Hammond postulate predicts that the amount of C-H bond breaking will be lower in the transition states for the compounds of the system which have more electron-withdrawing ring substituents, and this will be reflected in the magnitudes of the deuterium isotope effects for their elimination reactions. If C-H bond breaking is less than one-half completed in the transition states for the elimination reactions of such a series, one might anticipate that the compounds with the more electron-withdrawing ring substituents will have the lowest values of $k_H/k_D$ of the series (Figure 1, first section). If C-H bond breaking is more than one-half completed, Figure 1 predicts the opposite trend.

This proposal was tested by measuring the deuterium isotope effects for the elimination reactions of para-methyl and meta-bromo-substituted 2-phenyl-1-propyl p-toluenesulfonates and bromides. The results are recorded in Table 9. The more reactive meta-bromo

Table 9. Rates of elimination of 2-phenyl-2-deutero-1-propyl compounds, $Y\text{-}C_6H_4CD(CH_3)CH_2\text{-}X$ at 49.83°C

| Y | X | base/solvent | % yield olefin | $k_{E2} \times 10^4$ | $k_H/k_D$ |
|---|---|---|---|---|---|
| m-Br | oTs | t-BuO⁻/t-BuOH | 90 | 2.83 ± 0.12 | 6.28 ± 0.42 |
| | | EtO⁻/EtOH | 44 | .562 ± 0.035 | 4.69 ± 0.33 |
| m-Br | Br | t-BuO⁻/t-BuOH | 100 | 26.4 ± 0.1 | 7.61 ± 0.18 |
| | | EtO⁻/EtOH | 95 | 15.9 ± 0.0 | 7.01 ± 0.10 |
| p-$CH_3$ | oTs | t-BuO⁻/t-BuOH | 64 | .154 ± 0.002 | 6.04 ± 0.11 |
| | | EtO/EtOH | 15 | .0662 ± .0001 | 4.11 ± 0.01 |
| p-$CH_3$ | Br | t-BuO⁻/t-BuOH | 99 | 3.19 ± 0.01 | 6.60 ± 0.19 |
| | | EtO⁻/EtOH | 94 | 1.47 ± 0.00 | 6.37 ± 0.33 |
| p-H[a] | Tos | t-BuO⁻/t-BuOH | | 0.372 | 6.19 |
| | | EtO⁻/EtOH | | 0.127 | 4.53 |
| p-H[a] | Br | t-BuO⁻/t-BuOH | | 6.05 | 6.95 |
| | | EtO⁻/EtOH | | 3.02 | 6.19 |

[a]Data obtained by extrapolation of deuterated and protonated compounds on Hammett sigma-rho correlations.

compounds have values of $K_H/K_D$ consistently larger than those for their para-methyl analogues. This suggests, on the basis of the Hammond postulate and the correlation in Figure 1, that C-H bond breaking is more than one-half completed in the elimination transition states of the 2-phenyl-1-propyl system.

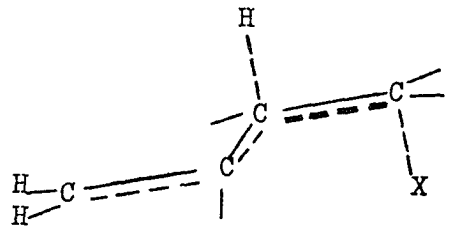
The deuterium isotope effects at 50°C for elimination reactions of the 2-phenyl system are estimated to be (equation 8, first section): 7.1 and 5.0 for the p-toluenesulfonate and 7.0 and 6.3 for the bromide in tert-butyl alcohol and ethanol respectively. The $k_H/k_D$ values for 2-phenylethyl p-toluenesulfonate are higher than those of 2-phenyl-1-propyl p-toluenesulfonate. Thus in view of the discussion in previous paragraphs, C-H bond breaking is lower for the more reactive 2-phenylethyl p-toluenesulfonate. However, the $k_H/k_D$ values are nearly the same for 2-phenylethyl bromide and 2-phenyl-1-propyl bromide in spite of the greater reactivity of the former. The conclusion that C-H bond breaking in the elimination transition states is less for 2-phenylethyl p-toluenesulfonate than for 2-phenyl-1-propyl p-toluenesulfonate is surprising in view of the higher rho values for the former. It is also surprising that the data in Table 9 indicate that, on the basis of the Hammond postulate, C-H bond breaking is more than one-half completed for the 2-phenyl-1-propyl systems. Thus, according to the Hammond postulate, the more reactive and more Elcb-like elimination reactions have less C-H bond breaking in their transition states. This is in direct conflict with conclusions reached earlier in this section. The implication of the anomalies arising in the above discussion is that utilization of the Hammond postulate to predict the relative nature of transition states derived from a series of compounds that differ only slightly in reactivity (by factors of 10-100) is not valid.

This conclusion is supported by the reacting bond rule proposed by Swain and Thornton (95,96). According to this rule, the beta C-H bond in the transition states for E2 reactions should be lengthened when the substrate contains more electronegative substituents. Therefore, C-H bond breaking in the transition state is greater for the 2-(m-bromophenyl)-1-propyl compounds than for their para-methyl analogues. Because the values of $k_H/k_D$ are larger for the meta-bromo compounds, C-H bond breaking is predicted, on the basis of the reacting bond rule, to be less than one-half completed in the elimination transition states of the 2-phenyl-1-propyl system.

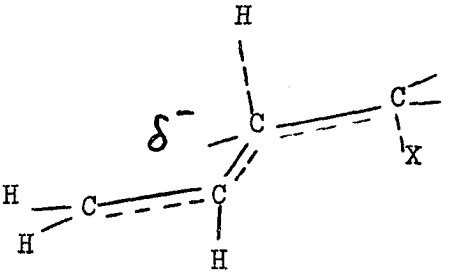
Substitution of a vinyl group on the beta position of a molecule could conceivably affect its elimination mechanism in one of two ways. The additional double bond might enhance double bond character in the transition state through conjugation to give a more central E2 elimination (structure XI). On the other hand, the beta vinyl substituent might act similarly to the beta phenyl group, stabilizing beta negative charge by delocalization (structure X) to give a more Elcb-like reaction.

The rates of reaction for 2-phenyl-3-buten-1-yl and 3-buten-1-yl compounds are given in Tables 10 and 11. The rates were measured titrimetrically, and the reactions were found to give no detectable substitution products by analysis of the product mixtures on the gas phase chromatograph.

The most outstanding effect of beta vinyl substitution is the large increase in reaction rate. Compared with 2-phenylethyl p-toluenesulfonate, the rate of elimination of 2-phenyl-3-buten-1-ol



XI



X

Table 10. Rates of elimination of 2-phenyl-3-buten-1-yl compounds, $YC_6H_4CH(CH{=}CH_2)CH_2Y$, at 49.88°C[a]

| Y | X | Base/Solvent | $k_{E2} \times 10^4$ |
|---|---|---|---|
| p-H | -oTs | t-BuO$^-$/t-BuOH | 1120 ± 50 |
| p-$CH_3$ | -oTs | t-BuO$^-$/t-BuOH | 482 ± 2 |
| p-H | -oTs | EtO$^-$/EtOH | 107 ± 2 |
| p-$CH_3$ | -oTs | EtO$^-$/EtOH | 51.4 ± 0.7 |
| p-Cl | -oTs | EtO$^-$/EtOH | 583 ± 27 |
| p-H | -Br | EtO$^-$/EtOH | 851 ± 42 |

[a]Rho for the p-toluenesulfonate in EtO$^-$/EtOH was 2.68 ± 0.06.

p-toluenesulfonate is ten times greater with tert-butoxide and eighteen times with ethoxide. The elimination of 3-buten-1-ol p-toluenesulfonate proceeds nearly as fast as 2-phenylethyl p-toluenesulfonate with tert-butoxide but two and one-half times faster with ethoxide. The situation is similar for the bromides. The rate of

Table 11. Rates of elimination of 3-buten-1-yl compounds, $CH_2=CHCH_2CH_2X$

| X | Base/Solvent | $k_{E2} \times 10^4$ |
|---|---|---|
| -oTs | t-BuO⁻/t-BuOH | 91.7 ± 0.4 |
| | EtO⁻/EtOH | 14.9 ± 0.7 |
| -Br | t-BuO⁻/t-BuOH | 248 ± 2 |
| | EtO⁻/EtOH | 37.2 ± 0.2 |

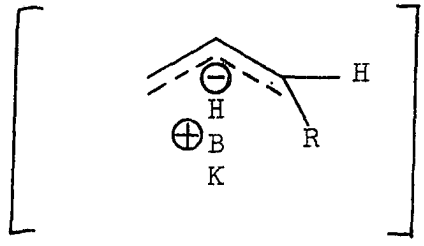
elimination of 2-phenyl-1-bromo-3-butene is one order of magnitude greater than 2-phenylethyl bromide with ethoxide. The rates for 1-bromo-3-butene, however, are similar to those of 2-phenylethyl bromide with both bases. The beta vinyl group affects the rates of bimolecular reactions, therefore, to about the same extent as a beta phenyl substituent. When both moieties are substituted on an ethyl compound, they complement one another, and a very large rate increase is observed. A rho value of +2.68 for 2-phenyl-3-buten-1-ol p-toluenesulfonate with ethoxide compared with 2.27 for 2-phenylethyl p-toluenesulfonate indicates that this rate increase is due, in part at least, to enhanced acidity of the beta proton.

Schriesheim and coworkers reported similar results for the isomerization of olefins in potassium tert-butoxide/dimethylsulfoxide (97). The reaction rate was found to increase by a factor of $10^5$

$$CH_2 = CH\text{-}CH_2\text{-}R \xrightarrow{B} CH_3\text{-}CH = CH\text{-}R \qquad (11)$$

when R is changed from $-CH_3$ to $-CH=CH_2$. Similarly the rate was

$6 \times 10^4$ times faster when $-CH_3$ was replaced with a phenyl group. The mechanism of the rearrangement is believed to involve rate-determining removal of an allylic proton to give an intermediate intimate-ion pair (structure XI) which collapses to starting or rearranged olefin faster than the free carbanion is formed (98).




XI

The previous tables in this section have shown that the rates and mechanisms of elimination reactions can be varied by using different base/solvent systems. Potassium tert-butoxide in tert-butyl alcohol is a more basic, but less polar, reaction medium than sodium ethoxide in ethanol. Because of this, C-H bond breaking is generally more advanced in the former. Bishop's study of 2-phenylethyl p-toluenesulfonate and bromide in tert-butyl alcohol and ethanol using tert-butoxide and ethoxide as bases helped to assess the relative importance of base and solvent in determining rate and mechanism. Rho for the p-toluenesulfonate increased considerably, from 2.27 to 3.39, when the reaction medium was changed from ethoxide/ethanol to tert-butoxide/tert-butyl alcohol. When ethoxide/tert-butyl alcohol was used, rho increased only slightly to 2.60. This indicates that the base is more important than solvent in controlling the mechanism for 2-phenylethyl p-toluenesulfonates. The rho values for the bromide

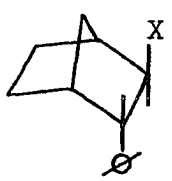
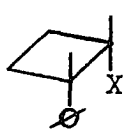
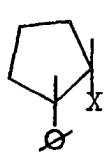
changed very little when the nature of the reaction medium was varied because of the ability of the bromide to relieve beta negative charge by greater C-Br bond breaking as C-H bond breaking increases. The rates for both the p-toluenesulfonate and bromide, on the other hand, varied considerably when either base or solvent was changed. The mechanisms involved in the eliminations of this system must, therefore, be more sensitive to base, whereas both base and solvent affect the rates. This is to be contrasted to the results found by Froemsdorf (84) for 2-bromobutane. The yields of 1-butene were 19%, 38%, and 53% in ethoxide/ethanol, ethoxide/tert-butyl alcohol, and tert-butoxide/ tert-butyl alcohol, respectively. The trans/cis product ratios increased in the opposite direction, 3.35, 2.19, and 1.64 for the respective media. If one assumes that the relative yields of 1 and 2-butene and the trans/cis product ratios reflect the nature of the transition state, the work showed that both solvent and base play an important role in determining the mechanism for this aliphatic system. This might have been predicted for eliminations that proceed through a more nearly central E2 mechanism. As C-X bond breaking increases, the mechanism and rate might be expected to depend more on the polarity of the solvent, which would assist this bond breaking through solvation. The dependence of rate and mechanism on solvent polarity should exceed that of base strength as the mechanism becomes E1-like. Thus E1-like eliminations will occur faster in a more polar solvent such as ethanol than in a less polar one like tert-butyl alcohol, i.e., the tert-butoxide/ethoxide rate ratio is less than one.

As the mechanism becomes more central E2-like, the base strength will become more important, and at some point on the spectrum the tert-butoxide/ethoxide rate ratio will equal one. Beyond this point, the ratio will increase steadily as the mechanism becomes more Elcb.

Table 12 shows the tert-butoxide/ethoxide rate ratios for various p-toluenesulfonates and bromides. In Figure 7 is a plot of the rho values available for 2-phenyl p-toluenesulfonates against the logarithms of their corresponding tert-butoxide/ethoxide rate ratios. In both cases a linear relationship is suggested, but there are two serious deviations with ethoxide/ethanol. It is interesting that the vertical deviations from the lines are nearly identical with ethoxide/ethanol and tert-butoxide/tert-butyl alcohol for cis-2-phenylcyclobutyl p-toluenesulfonate.

One possible use of the tert-butoxide/ethoxide rate ratio is the determination of the relative positions on the mechanism spectrum of the eliminations for aliphatic systems, for which Hammett correlations are not possible. In Table 13 are presented some tert-butoxide/ethoxide rate ratios for aliphatic bromides compiled by Brown (74). These data can be rationalized on the basis of the preceding discussion. Removal of a less acidic, secondary beta proton should involve more E1 character in the transition state than removal of a primary proton for a given compound. The tert-butoxide/ethoxide rate ratios are, thus, less for the former. The eliminations of the tertiary bromides are more E1-like than those of the secondary bromides, and the ratios are lower.

Table 12. tert-Butoxide/ethoxide rate ratios for elimination of p-toluenesulfonates and bromides at 50°

| No. | System | $k_{t\text{-BuO}^-}/k_{\text{EtO}^-}$ Br | oTs |
|---|---|---|---|
| 1 | $C_6H_5CH(CH{=}CH_2)CH_2X$ | | 10.5 |
| 2 | $C_6H_5CH_2CH_2X$ | 10.8 | 18.4 |
| 3 | $CH_2{=}CHCH_2CH_2X$ | 6.66 | 6.15 |
| 4 |  | | 12.4 |
| 5 |  | | 9.50 |
| 6 | $C_6H_5CH(CH_3)CH_2X$ | 2.83 | 3.86 |
| 7 | $C_6H_5CH_2(CH_3)CHX$ | 4.90 | 2.70 |
| 8 |  | | 1.24 |
| 9 | $C_6H_5CHC(CH_3)_2X$[a] | 0.14 | |
| 10 | $CH_3CH(C_6H_5)X$[b] | 0.45 | |

[a] Ref. 27.

[b] This work.

Figure 7. Plot of rho in tert-butoxide/tert-butyl alcohol, ○ , and ethoxide/ethanol, ● , against log ($k_{t\text{-BuO}^-}/k_{\text{EtO}^-}$) for 2-phenyl p-toluenesulfonates.

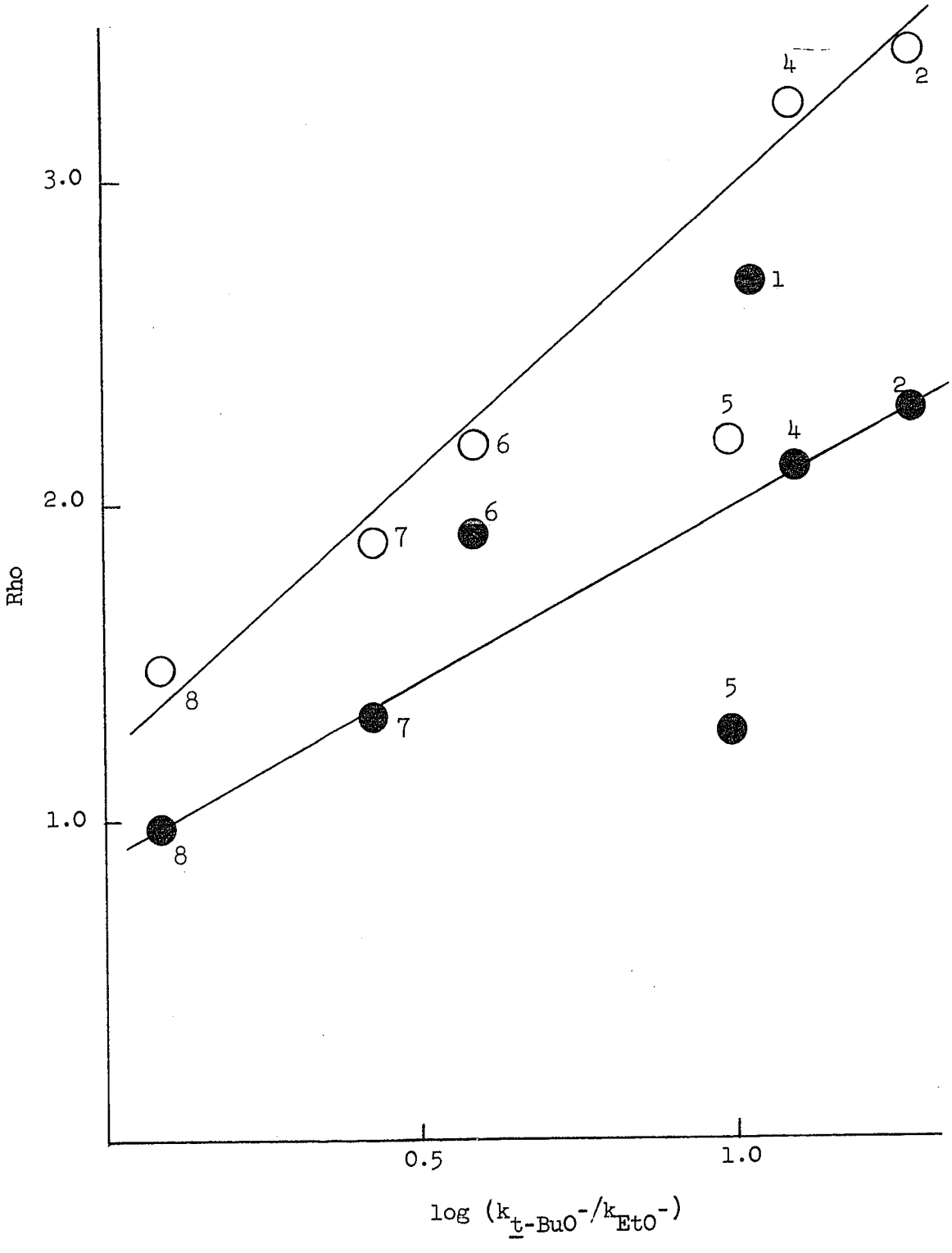

3.0
2.0
1.0
Rho
0.5
1.0
log ($k_{t\text{-BuO}^-}/k_{EtO^-}$)
1
2
4
5
6
7
8

Table 13. Rates and tert-butoxide/ethoxide rate ratios for aliphatic bromides at 25°C.

| Compound | $k_{E2} \times 10^6$ EtO$^-$ [a] prim | sec | $k_{E2} \times 10^6$ t-BuO$^-$ [a] prim | sec | $k_{t\text{-BuO}^-}/k_{\text{EtO}^-}$ prim | sec |
|---|---|---|---|---|---|---|
| $CH_3CHCH_3$ \| Br | 0.395 | | 0.392 | | 0.99 | |
| $CH_3CH_2CHCH_3$ \| Br | 0.217 | 1.41 | 0.247 | 0.329 | 1.14 | 0.234 |
| $CH_3CH_2CH_2CHCH_3$ \| Br | 0.267 | 0.88 | 0.171 | 0.133 | 0.640 | 0.151 |
| $CH_3-C(CH_3)_2-Br$ | 3.33 | | 0.624 | | 0.188 | |
| $CH_3CH_2-C(CH_3)_2-Br$ | 2.83 | 21 | 0.407 | 0.462 | 0.144 | 0.022 |

[a] Rate constants are those per primary or secondary proton.

Brown held that steric factors are also very important for these eliminations. The bulkier tert-butoxide ion would suffer more steric interations upon removal of protons from secondary carbons and from tertiary bromides, and thus, react slower than with ethoxide.

2-Phenyl-1-methyl-1-bromopropane exhibits a tert-butoxide/ethoxide rate ratio of 0.14 at 50°C compared with that of 0.45 for 1-phenylethyl bromide. One might have predicted a lower ratio for the latter bromide because its elimination should be nearly as E1 as that of the tertiary bromide. It would be interesting to determine the tert-butoxide/ethoxide ratios for 2-phenyl-1-methyl-1-bromopropane and 1-phenyl-2-bromopropane at 25°C so that they could be compared with those for tert-butyl and iso-propyl bromides. Addition of beta phenyl groups to these latter compounds should cause an increase in the ratios.

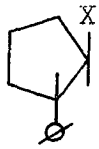
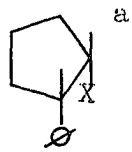
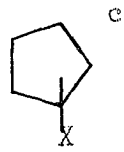
In view of the above discussion, butoxide/ethoxide rate ratios must be interpreted with care. In certain cases, the ratios do appear to reflect the relative nature of the mechanisms for elimination reactions. The correlation of rho and logarithms of the ratios for 2-phenyl substituted p-toluenesulfonates indicates that there is a relation between beta proton acidity and the sensitivity of the elimination reaction to basicity in the E1cb region. There were very serious deviations observed for these compounds, however. For 2-phenyl-3-buten-1-ol p-toluenesulfonate, the sensitivity to base strength as shown by the tert-butoxide/ethoxide rate ratio was much lower than would have been anticipated in view of the high rho value, whereas the opposite kind of deviation was observed for cis-2-phenylcyclobutyl p-toluenesulfonate.

With the present uncertainty of the role of steric factors in aliphatic eliminations, the significance of the tert-butoxide/ethoxide rate ratio in these cases is not at all clear. Also comparison of the

for one type of system with those of another may not be justified as was pointed out with 2-phenyl-1-methyl-1-bromopropane and 1-phenylethylbromide. Like deuterium isotope effects, the tert-butoxide/ethoxide rate ratios must be compared with other mechanistic criteria whenever possible, rho values for aryl-substituted systems and product distributions for aliphatic systems.

In Table 14 are given the bromide/p-toluenesulfonate rate ratios for various systems. As mentioned in the first section, the leaving ability of the p-toluenesulfonate group was proposed to depend on the amount of C-O bond breaking in the transition state. It was suggested by Bishop that the bromide/p-toluenesulfonate rate ratio reflects the relative amounts of C-X bond breaking involved in transition states for elimination reactions. When C-X bond breaking is well advanced, the leaving ability of the p-toluenesulfonate group is accelerated relative to bromide, and the ratio is small. For more carbanion-like eliminations where the demands on the leaving group are less, the p-toluenesulfonate group was believed to react slower than bromide because of its inability to relieve beta negative charge as well. In order to see the relationship of elimination rates for p-toluenesulfonates and their mechanisms, the logarithms of the rates are plotted against the corresponding rho values in Figures 8 and 9 for all of the available data on 2-phenyl-substituted compounds. The most outstanding feature of these correlations is the very obvious rate minima at approximately rho 2.5 in tert-butyl alcohol and rho 1.8 in ethanol. 2-Phenyl-1-propyl p-toluenesulfonate, which displays

Table 14. Rates and bromide/p-toluenesulfonate rate ratios for elimination reactions at 50°C

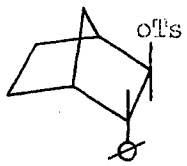
| System | Base/Solvent | $k_2 \times 10^4$ Br | $k_2 \times 10^4$ oTs | $\frac{K_{Br}}{K_{oTs}}$ |
|---|---|---|---|---|
| $C_6H_5CH(CH{=}CH_2)CH_2X$ | $EtO^-/EtOH$ | 851 | 107 | 7.95 |
| $C_6H_5CH_2CH_2X$ | $EtO^-/EtOH$ | 34.2 | 5.98 | 5.72 |
| | $t\text{-}BuO^-/t\text{-}BuOH$ | 369 | 111 | 3.32 |
| $CH_2{=}CHCH_2CH_2X$ | $EtO^-/EtOH$ | 37.2 | 14.9 | 2.50 |
| | $t\text{-}BuO^-/t\text{-}BuOH$ | 248 | 91.7 | 2.70 |
|  | $t\text{-}BuO^-/t\text{-}BuOH$ | 0.285 | 2.90 | 0.10 |
| $C_6H_5CH(CH_3)CH_2X$ | $EtO^-/EtOH$ | 14.5 | 0.556 | 26.1 |
| | $t\text{-}BuO^-/t\text{-}BuOH$ | 41.1 | 2.14 | 19.2 |
| $C_6H_5CH_2(CH_3)CHX$ | $EtO^-/EtOH$ | 19.2 | 3.42 | 5.61 |
| | $t\text{-}BuO^-/t\text{-}BuOH$ | 94.1 | 9.32 | 10.1 |
|  [a] | $t\text{-}BuO^-/t\text{-}BuOH$ | 241 | 5.90 | 40.8 |
| $n\text{-}C_{18}H_{37}X$ [b] | $t\text{-}BuO^-/t\text{-}BuOH$ | 0.0194 | 0.0015 | 12.9 |
|  [c] | $t\text{-}BuO^-/t\text{-}BuOH$ | 1.82 | 3.89 | 0.49 |

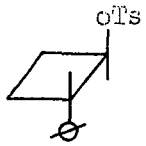
[a] 30°C

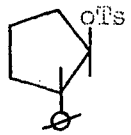
[b] Reference 99.

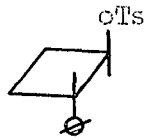
[c] Reference 48.

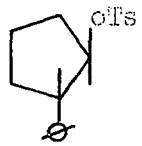
Figure 8. Correlation of log ($k_{E2} \times 10^4$) and rho for eliminations of 2-phenyl-substituted p-toluenesulfonates in tert-butoxide/tert-butyl alcohol.

1. $C_6H_5CH(CH{=}CH_2)CH_2OTs$
2. $C_6H_5CH_2CH_2OTs$
3. 

4. 

5. 

6. $C_6H_5CH(CH_3)CH_2OTs$
7. 

8. $C_6H_5CH_2(CH_3)_2CHOTs$
9. 

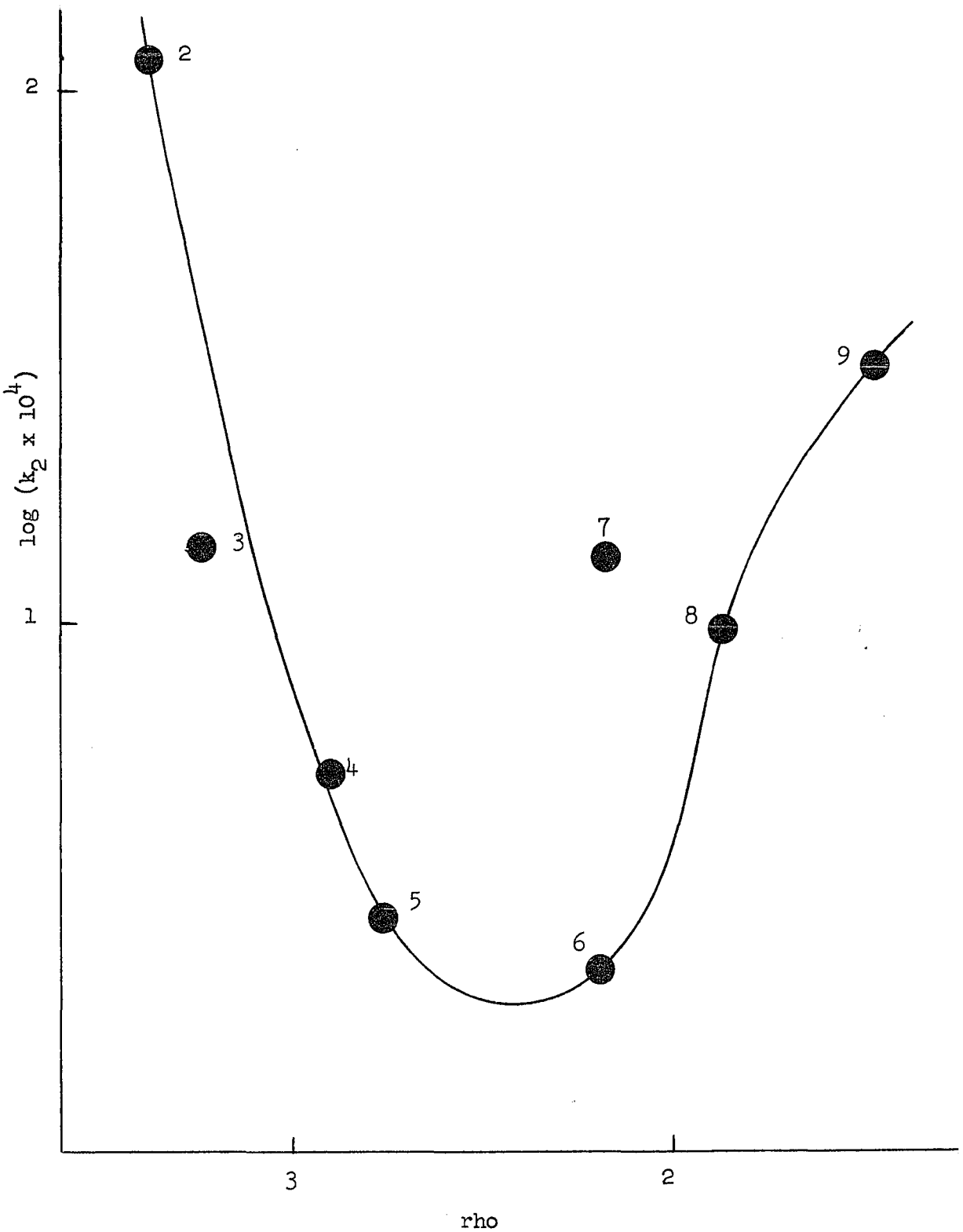
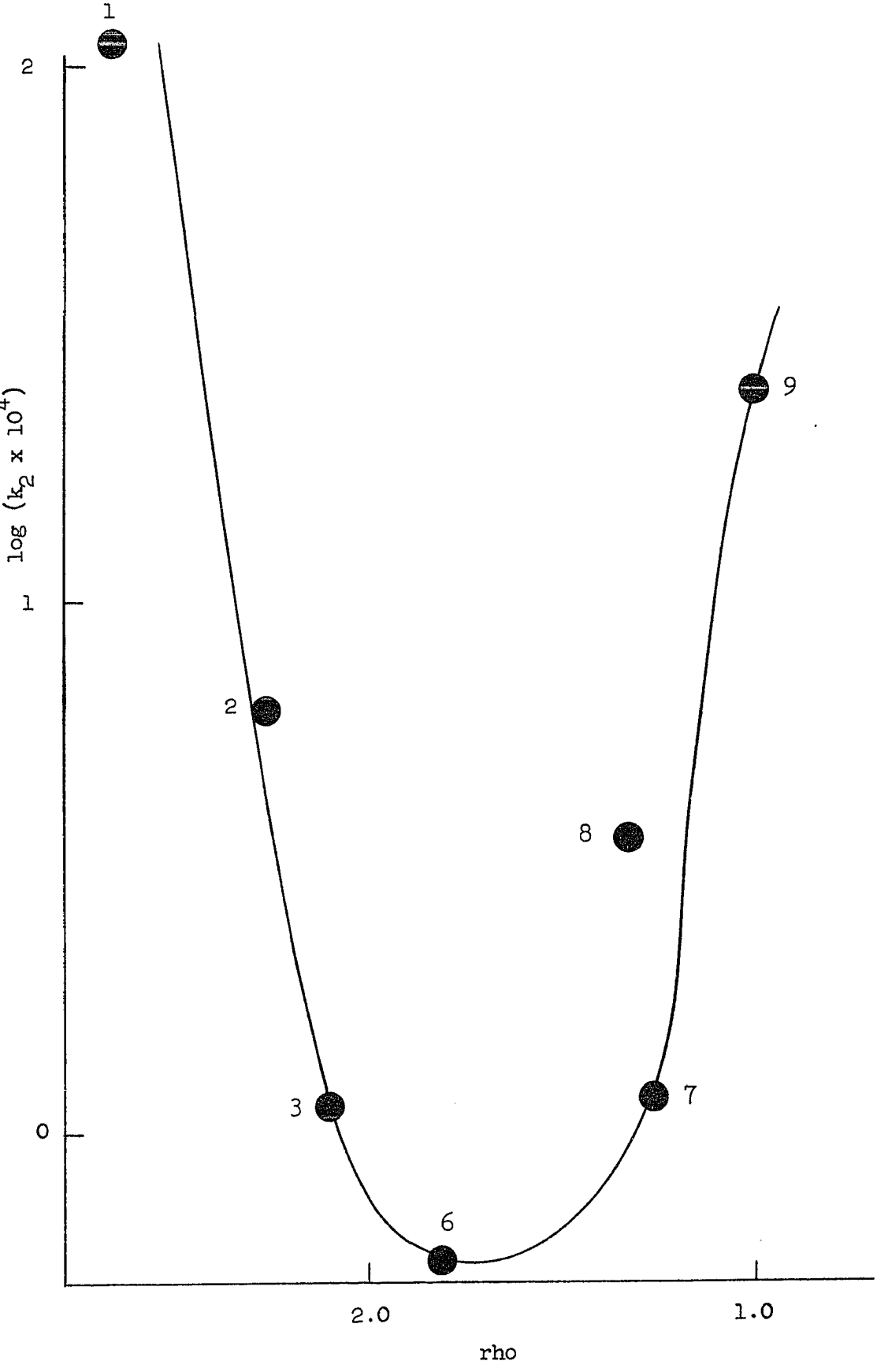

2
1
log ($k_2$ x $10^4$)
2
3
4
5
6
7
8
9
3
2
rho

Figure 9. Correlation of log ($k_{E2} \times 10^4$) and rho for eliminations of 2-phenyl-substituted p-toluenesulfonates in ethoxide/ethanol.


1
2
log ($k_2$ x $10^4$)
1
2
8
9
3
7
0
6
2.0
1.0
rho

one of the highest bromide/p-toluenesulfonate rate ratios, lies very close to the minimum on these plots. The implication is that the rates of p-toluenesulfonates are more important in determining the ratio. It is unfortunate that rho values for more 2-phenyl substituted bromides are not available to see if a trend exists for these compounds. The relative rates of halides change very little from the 2-phenylethyl and cyclopentyl systems (47,48), suggesting that the large variations observed for $k_{Br}/k_{oTs}$ in the various systems are due to the p-toluenesulfonate rates. However, the deviations in the ratio for the cis and trans cyclopentyl systems apparently result from the bromide rates since the p-toluenesulfonates fit the correlations in Figures 8 and 9.

The minima in these correlations indicate that somewhere between the Elcb and E2 mechanisms lies a region that is very unfavorable for p-toluenesulfonate eliminations. Apparently in this region, C-O bond breaking is not advanced enough in the transition state to make possible the conjugative stabilization of the incipient anion by the sulfur oxygens. Also the nature of the systems in this region discourages C-H bond breaking. As the mechanism becomes more Elcb-like, the beta negative charge is stabilized by the electronegativity of the p-toluenesulfonate group. As it moves in the other direction the amount of C-O bond breaking increases, and in both cases, an increase in rate results.

The data in Table 14 and Figures 8 and 9 suggest that the relative rates for bromide and p-toluenesulfonate eliminations vary across the mechanism scale as shown in Figure 10. According to this correlation, a maximum bromide/p-toluenesulfonate rate ratio would exist somewhere

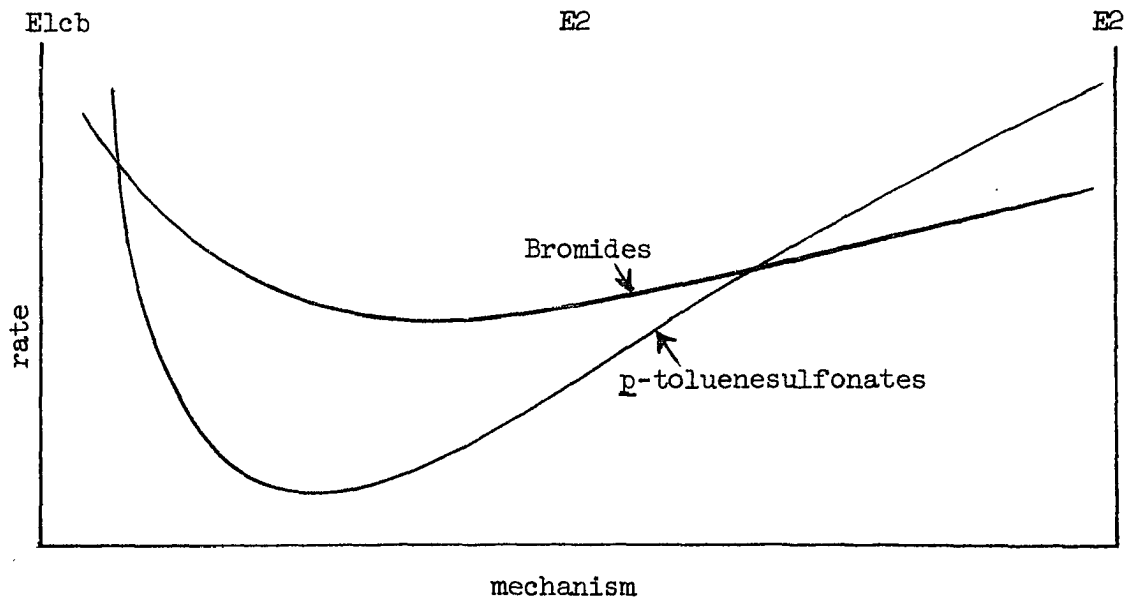



Figure 10. Correlation of mechanism of elimination for bromides and p-toluenesulfonates with reaction rates.

between the Elcb and central E2 extremes. As the mechanism approaches the Elcb extreme, the ratio would be equal to or less than one. As the mechanism moves right, the ratio again decreases until at some point it equals one. The reactions occurring further to the right would give bromide/p-toluenesulfonate rate ratios with values less than one with a minimum value at the E1 extreme. Hoffman (45) observed that the first-order elimination of 1-phenylethyl bromide and p-toluenesulfonate gives a ratio of 0.0023 at 50° in acetonitrile. A very serious complication is immediately obvious for this type

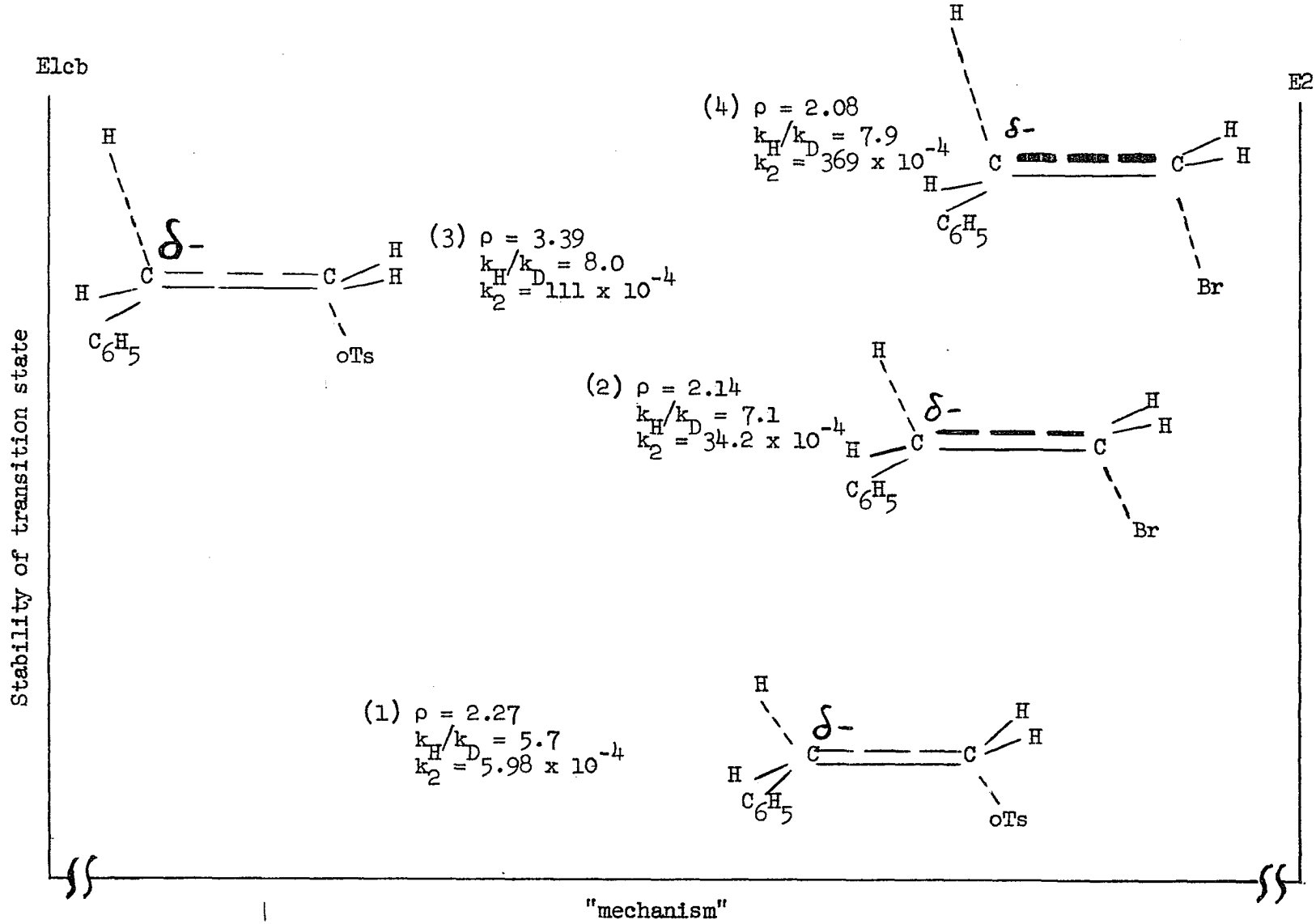
of correlation. Bromides and p-toluenesulfonates seldom eliminate through the same type of transition state. If the difference in their positions on the mechanism scale were large, the rate ratio would be misleading.

Hammett sigma-rho correlations, deuterium isotope studies, and product determinations have shown that the eliminations of bromides are generally more concerted processes than those of the corresponding p-toluenesulfonates. The greater rates for the bromides suggest that a more concerted, central E2 transition state having more double bond character and dispersal of charge is the most favorable when it is allowed. This is obviously not the whole story, however, because a p-toluenesulfonate lying on about the same position of the mechanism spectrum as the bromide, according to similar rho values, still reacts slower, e.g., 2-phenyl-1-propyl bromide (rho 2.06) reacts 26 times faster than the p-toluenesulfonate (rho 1.81) at 50°C in ethanol. Of course, rho does not directly indicate anything about the "concertedness" of a reaction but merely the amount of beta negative charge build-up in the transition state. The deuterium isotope effects for the 2-phenyl-1-propyl and 2-phenylethyl systems reveal that C-H bond breaking for the bromide transition states is equal to or greater than those for the p-toluenesulfonates. For both systems in ethanol, $k_H/k_D$ for the bromides is greater, e.g., for 2-phenylethylbromide $k_H/k_D = 7.1$ and for the p-toluenesulfonate $k_H/k_D = 5.7$. However, the rho values are very close, 2.14 and 2.27, respectively. The bromide reacts 5.7 times faster at 50°C. The greater amount of

beta negative charge that might have been expected from the higher degree of C-H bond breaking for the bromide must be canceled somewhat by more C-Br bond heterolysis and increased double bond character in the transition state. Although both the p-toluenesulfonate and bromide have about equal amounts of carbanion formation in their transition states, the bromide transition state is more stable because of the greater amount of double bond formation and dispersal of charge involved. When $k_H/k_D$ is nearly equal (e.g., the 2-phenylethyl system in tert-butyl alcohol) the p-toluenesulfonate's rho is larger (rho 3.39, $k_H/k_D$ = 8.0) than that for the bromide (rho 2.08, $k_H/k_D$ = 7.9). In this case, the bromide has less carbanion character in the transition state than the p-toluenesulfonate because dispersal of charge is not counteracted by greater C-H bond breaking. The transition states for the reactions discussed above and their approximate relative stabilities are depicted in Figure 11.

The evidence is that the mechanism spectrum is two dimensional rather than one. Just as there is a graded range of transition states horizontally on the spectrum, which represent the degree of beta negative charge or alpha positive charge in the transition state, there is a vertical scale, i.e., for a given rho value there will be a gradient of transition states for which the amount of double bond formation varies. As the scale approaches either the Elcb or El extremes, however, the importance of this vertical spectrum is predicted to diminish.

Figure 11. Transition states and their relative stabilities for the eliminations of the 2-phenylethyl system: (1) p-toluenesulfonate in ethoxide/ethanol; (2) bromide in ethoxide/ethanol; (3) p-toluenesulfonate in tert butoxide/tert-butyl alcohol; (4) bromide in tert-butoxide/tert butyl alcohol.


Elcb
E2
Stability of transition state
"mechanism"
(1) ρ = 2.27
$k_H/k_D$ = 5.7
$k_2$ = 5.98 x $10^{-4}$
(2) ρ = 2.14
$k_H/k_D$ = 7.1
$k_2$ = 34.2 x $10^{-4}$
(3) ρ = 3.39
$k_H/k_D$ = 8.0
$k_2$ = 111 x $10^{-4}$
(4) ρ = 2.08
$k_H/k_D$ = 7.9
$k_2$ = 369 x $10^{-4}$
δ-
oTs
Br
$C_6H_5$

Rausch (93) has pointed out that the relative reactivities of bromides and p-toluenesulfonates might result from different transition states for the two compounds. In view of the above discussion this would appear to be the case for all of the systems reported. Even when the "mechanisms" reflected by rho values are the same, the transition states are not alike. An informative investigation might be a determination of rho and $k_H/k_D$ for a system where $k_{Br}/k_{oTs}$ equals one in order to see if the transition states are similar in such a case.

The sensitivity of p-toluenesulfonate rates to the "mechanism" between the E2 and Elcb extremes is caused by the need of this group for more driving force from C-H or C-O bond breaking. The relatively lower sensitivity of both the rates and mechanism to reaction conditions for bromides reflects the ability of C-Br bond breaking to adapt more to the amount of C-H bond breaking in the transition state.

Rausch has suggested that it might not be possible for the p-toluenesulfonate group to undergo a completely concerted elimination. p-Toluenesulfonates that are forced into the central E2 region (primary leaving group with unactivated beta protons) suffer serious competition from other processes such as $\gamma$ elimination or substitution. Bumgardner (100) observed that reaction of 3-phenyl-1-propyl p-toluenesulfonate with sodium amide in liquid ammonia gave exclusively phenylcyclopropane via $\gamma$ elimination. The corresponding bromide, however, produced only 3-phenyl-1-propene by beta elimination. Arnold (99) found that treatment of n-octadecyl bromides and

p-toluenesulfonates with potassium tert-butoxide/tert-butyl alcohol gave 84% and approximately 1% elimination, respectively; the remainder of the reaction proceeded by substitution.

To see if this behavior was typical of the straight-chain primary compounds, n-octyl bromide and p-toluenesulfonate were treated with tert-butoxide in tert-butyl alcohol. The results are summarized in Table 15 with Arnold's work. Arnold determined the yields of 1-octadecene chemically. The lower sensitivity of the procedure limited the accuracy of the olefin determination in the case of the p-toluenesulfonate reaction. The 1-octene yields were measured with the gas phase chromatograph. As in the n-octadecyl system, n-octyl p-toluenesulfonate gave a very small amount of elimination. The bromide/p-toluenesulfonate elimination rate ratio was 8.1 compared 13 for the eighteen-carbon system. The total second order rate constant for n-octyl bromide is 17 times larger than that of n-octadecyl bromide, and the factor is 15 for the p-toluenesulfonates. It is unlikely that the 10° temperature difference is sufficient to cause this large difference in rates. One possibility is that the very long aliphatic chain of the n-octadecyl system is more coiled in the polar solvent such that it interferes with attack by the bulky tert-butoxide ion, i.e., steric effects are operative. It would be interesting to see if the rate differences of the two systems would become smaller in a less polar solvent such as dimethylsulfoxide using a less bulky base such as ethoxide. The bromide/p-toluenesulfonate elimination rate ratios of 8.0 and 13 for the two systems

Table 15. Rate constants and E2 and SN2 yields from n-octadecyl and n-octyl bromides and p-toluenesulfonates when treated with potassium tert-butoxide/tert-butyl alcohol

| Compound | Temp. | Base Conc. | $k_2 \times 10^4$ | % Elimination | % Substitution |
|---|---|---|---|---|---|
| n-$C_{18}H_{37}Br$[a] | 40° | 0.09M | 0.0232 | 83.7 | 16.3 |
| n-$C_{18}H_{37}$oTs[a] | 40° | 0.09M | 0.1510 | 1 | 99 |
| n-$C_8H_{17}Br$ | 49.83° | 0.103M | .400 ± 0.002 | 53.3 ± 1.4 | 46.7 ± 1.4 |
| n-$C_8H_{17}$oTs | 49.83° | 0.116M | 2.20 ± 0.03 | 1.2 ± 0.3 | 98.8 ± 0.3 |

[a]Reference 99.

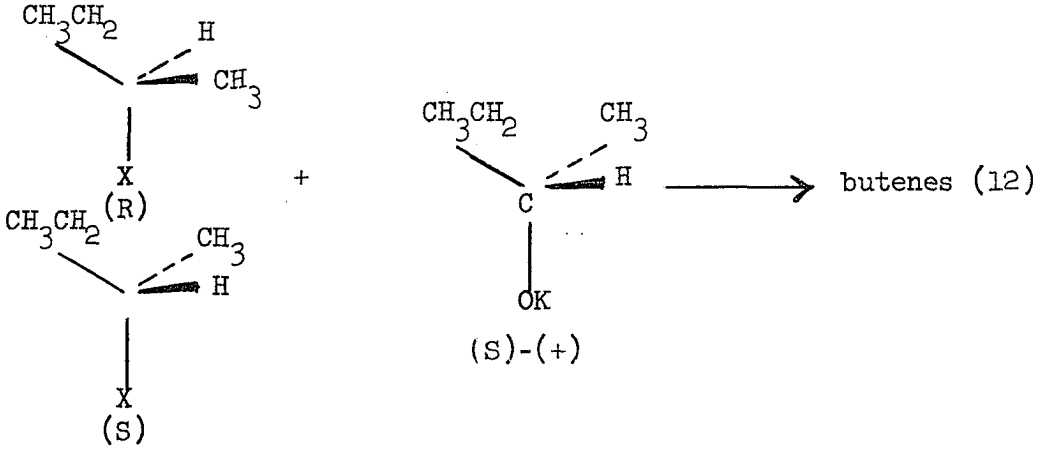
are larger than might have been predicted for a more central E2 elimination based on the trend observed for 2-phenyl-substituted compounds. If the correlation suggested in Figure 10 has any validity, the position of the rate minimum for p-toluenesulfonates on the scale must depend upon the type of systems under consideration. The approximate position of the minimum in Figure 10 was based on the data for 2-phenyl-substituted compounds. For aliphatic systems this minimum might be closer to the central E2 region. A more detailed, systematic study of aliphatic p-toluenesulfonate and bromide elimination reactions in the central E2 and El-like regions is needed before the significance of the bromide/p-toluenesulfonate rate ratio is to be fully understood.

In the first section the difficulties of determining the relative importance of steric and electronic factors in elimination reactions was stressed. When the electronic properties of the

substrate, leaving group, and base are changed, the steric requirements of these moieties are inevitably affected. The studies with halide and benzenesulfonate eliminations suggested that the product distributions depended on the electronegativity of the leaving group rather than its steric bulk in these cases. It was pointed out, however, that the solvent and the covalent radii of the leaving group might be affecting some steric influence.

With the objective of isolating steric factors for these reactions, a study of eliminations with optically active reactants and solvent was conducted. The investigation involved two approaches, a product study of the eliminations of optically active substrates with optically active potassium sec-butoxide/sec-butyl alcohol and attempted asymmetric induction of racemic substrates by elimination with the above optically active base/solvent system.

If (S)-(+)-potassium sec-butoxide/sec-butyl alcohol was reacted separately with the (R) and (S) forms of a sec-butyl substrate, the steric requirements involved in removal of secondary and primary



protons by the base might vary, e.g., the transition states to give 1-butene will actually be diastereoisomers. Since the stabilities of diastereoisomers are different (101), the rates of elimination to give 1-butene might be different enough to show up in the product distributions. The electronic and hyperconjugative properties of the enantiomeric substrates would be identical. Likewise, if one enantiomeric form of substrate was reacted separately with the enantiomers of the base/solvent system, the basicity and polarity of the isomeric reaction media would remain constant. In either case, any variation of product distribution observed when one of the reactants is replaced by its enantiomer would have to be a consequence of steric interactions. Such results, however, could not distinguish the steric effects imposed by base and solvent.

In Table 16 is summarized the results of the studies of the sec-butyl system. The butene products from these eliminations were collected as gases and analyzed in this form on the gas phase chromatograph. Within experimental error the product distributions are identical for a given leaving group. Table 17 reports the data observed for eliminations of racemic and optically active 2-methyl-3-hexanol p-toluenesulfonate. Again the product distributions are identical for the racemic and asymmetric eliminations. The products were collected either by distillation or extraction and analyzed on the gas phase chromatograph. Equilibration of the products to give the identical distributions observed is very unlikely. Equilibration of 1-butene and 2-methyl-2-butene with their isomers is slow even in

Table 16. Relative yields of 1-butene and 2-butenes from elimination of optically active sec-butyl compounds with optically active potassium sec-butoxide/sec-butyl alcohol[a,b]

| X | Substrate enantiomer | Substrate % opt. purity | Base enantiomer | Base % opt. purity | % 1-butene | % 2-butene trans | % 2-butene cis |
|---|---|---|---|---|---|---|---|
| -oTs | (±) | | (±) | | 47.4 ± 0.1 | 28.9 ± 0.9 | 23.7 ± 0.9 |
| -oTs | (+) | 72 | (+) | 78 | 46.9 ± 0.7 | 29.1 ± 0.5 | 24.1 ± 0.2 |
| -oTs | (-) | 46 | (+) | 78 | 47.2 ± 0.4 | 29.0 ± 0.4 | 23.9 ± 0.0 |
| $-N(CH_3)_3I$ | (±) | | (±) | | 91.0 ± 0.2 | 3.2 ± 0.1 | 5.8 ± 0.1 |
| $-N(CH_3)_3I$ | (-) | ≤ 48[c] | (-) | 43 | 91.1 ± 0.4 | 3.3 ± 0.1 | 5.6 ± 0.3 |

[a](+)-potassium sec-butoxide, (+)-2-butanol p-toluenesulfonate, and (+)-2-butanol have the same absolute configurations (102).

[b]conducted at reflux temperature.

[c] $[\alpha]_D^{25}$ - 6.45° in EtOH. This (-)-salt has the (R)-configuration (see synthesis in experimental).

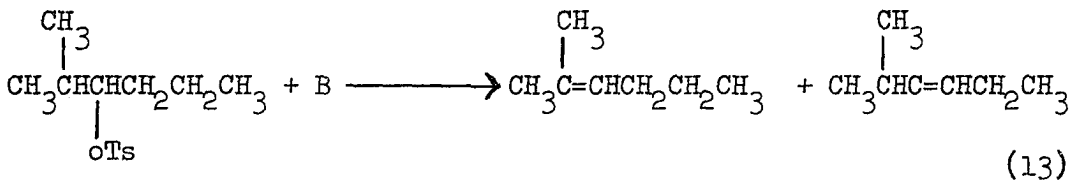
Table 17. Relative yields of 2-methyl-2-hexene and trans-2-methyl-3-hexene from elimination of optically active 2-methyl-3-hexanol p-toluenesulfonate with optically active potassium sec-butoxide/sec-butyl alcohol[a,b]

| p-Toluenesulfonate enantiomer | % opt. purity | Base/Solvent enantiomer | % opt. purity | % 2-ene | % trans-3-ene |
|---|---|---|---|---|---|
| (±) | | (±) | | 79.7 ± 0.2 | 20.3 ± 0.2 |
| (+) | > 90[c] | (+) | 83 | 79.7 ± 0.3 | 20.3 ± 0.3 |
| (+) | > 90[c] | (-) | 89 | 79.7 ± 0.4 | 20.3 ± 0.4 |

[a](+)-2-methyl-3-hexanol p-toluenesulfonate and (+)-2-methyl-3-hexanol have the same absolute configuration.

[b]conducted at 80°C.

[c] $[\alpha]_D^{26}$ + 5.0°.

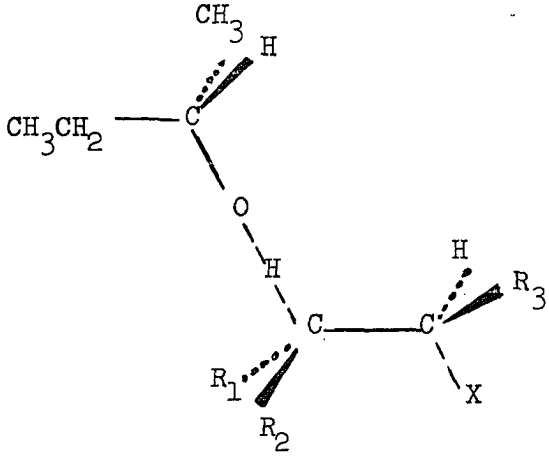


(13)

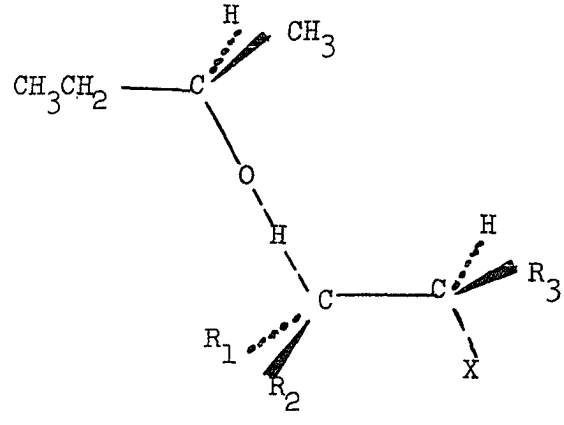
extremely basic media such as potassium tert-butoxide in dimethylsulfoxide (97). The butene products were expelled as gases from the refluxing reaction mixture as fast as they were formed. The reaction time for the 2-methyl-2-hexanol p-toluenesulfonate eliminations never exceeded two hours. Also, similar eliminations discussed in the first section showed no equilibration of products.

The results, thus, neither support nor disprove the participation of steric interactions in controlling product distributions. If

steric factors are important, the most likely reason for the above results is that differences in the steric interactions in the diastereoisomeric transition states are too subtle to seriously affect their relative stabilities. The exact conformations within these transition states are unknown, but it is apparent from structures XII and XIII that the asymmetric centers are some distance apart.



XII



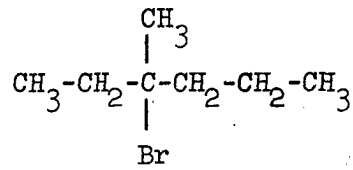
XIII

When $R_1$ and $R_2$ are different, the beta carbon is actually a third asymmetric center, but even in this case, the asymmetric carbon of the base is two atoms removed from the asymmetric beta carbon. Also, the transition states for the p-toluenesulfonates are approaching planarity, and the small interactions that might occur between substituents on the asymmetric centers are diminished even further.

There is another conceivable reason for the unchanging product distributions observed for the asymmetric elimination reactions. For

a given reaction (e.g., with a given enantiomer of each reactant) the stabilities of the transition states giving the various possible olefins might change in the same direction relative to the elimination where one of the reactants is replaced by its enantiomer. That is, the total rate of reaction might be affected as a result of an overall increase or decrease in all of the transition state stabilities because of steric interactions with little or no change in the relative yields of products.

Thus, a series of racemic substrates was treated with a deficiency of optically active base. If the base reacted faster with one of the enantiomers of the mixture, the substrate remaining at the end of the reaction would be rich in the other enantiomer and display optical activity. If this were observed, it would have to be the result of steric interactions. This asymmetric induction was attempted on sec-butyltrimethylammonium iodide, 2-methyl-3-hexyltrimethylammonium iodide, 3-methyl-3-bromohexane, and 2-phenyl-1-propanol p-toluenesulfonate. The latter compound was tested because the asymmetric center is on a beta carbon rather than an alpha carbon. It is therefore closer to the asymmetric center of the base in the transition state. Reaction of these substrates with a deficiency of optically active potassium sec-butoxide/sec-butyl alcohol and recovery and purification of the unreacted compound resulted in optical activity for only 3-methyl-3-bromohexane. When this bromide was partially reacted with 42% optically pure (R)-(-)-base/solvent, the recovered bromide had an optical rotation of $\alpha_D^{26}$ + 0.89 ± 0.06°, a rotation



3-methyl-3-bromohexane

XIV

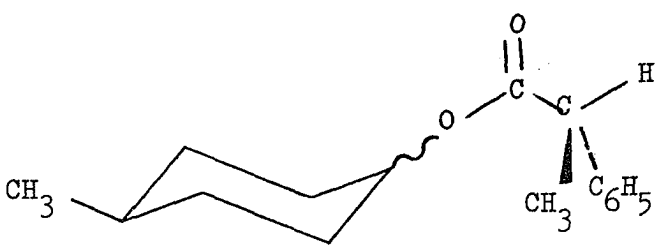
opposite that of the solvent. When it was reacted with more (R)-(-)-base, the rotation rose to $\alpha_D^{26}$ + 1.12 ± 0.08°. Further elimination with (R)-(-)-base resulted in a decrease to $\alpha_D^{26}$ + 1.00 ± 0.07° probably because of dilution by olefin products. The same behavior was observed for the bromide with (S)-(+)-base/solvent, except the optical rotations were levoratotory.

This elimination reaction of 3-methyl-3-bromohexane is probably very E1-like. The ability of the solvent to solvolyze the tertiary bromide in the transition state would be predicted to influence the rate considerably. The steric effect of solvation considered by Brown (82) might be in operation here. Several optically active solvent molecules could be involved in the solvation of the bromide ion, and they would be situated closer to the asymmetric carbon in the substrate molecule than the base would be. Their "combined asymmetry" might, therefore, sterically favor the solvation of bromide from one enantiomer over the other. A study of the corresponding trimethylammonium iodide would be very enlightening. This compound, which would have much less E1 character in the transition state, should display very little, if any, asymmetric induction if only

asymmetric solvation effects are operative. A product study of the eliminations of the optically active forms of these 3-methy-3-hexyl compounds with optically active base/solvent might prove informative.

The other possibility, of course, is that the steric interactions of this bulkly bromide with base are being felt. For this system the alpha proton of the sec-butyl system has been replaced by a n-propyl group.

Goldberg (103,104) reported asymmetric selection for the heat-promoted elimination of the optically active forms of cis and trans-4-methylcyclohexylhydratropate. In these cases, optical activity



XV

was induced into the product, 4-methylcyclohexene. The optical yields, however, were quite low, being a maximum of 0.87%. Much higher optical yields have been reported from the pyrolysis of optically active 4-methylcyclohexyl containing amine oxides (105) and sulfoxides (106), in which the asymmetric center resides on the nitrogen and sulfur and is, thus, more involved in the reaction.

# EXPERIMENTAL

## Preparation and Purification of Materials

The melting points and boiling points reported in this section are all uncorrected. Pressure is given in millimeters of mercury. The melting points were measured on a Fisher-Jones melting point apparatus. The infra-red spectra were measured on either a Beckman IR-5 or Beckman IR-10 instrument. All ultra-violet studies were carried out on a Cary, Model 14 spectrophotometer. The nmr spectra were measured on a Varian A-60 spectrometer. The proton chemical shifts are reported here in ppm downfield from TMS. The multiplicity of the peaks is given by S (singlet), D (doublet), T (triplet), Q (quartet), and M (multiplet). Immediately after this will be given the peak intensity representing the proton ratio. Gas phase chromatography (GPC) analyses were done on the following instruments: Perkin-Elmer 154C, F and M 700, and Aerograph 200. All of the instruments had thermal conductivity detectors. The GPC peak areas were measured with either an Ott planimeter or a Disc chart integrator, Model 204, on a Model SR Sargent recorder. All GPC separations were carried out on the Aerograph 200. Micro-analyses were done by Dr. A. Bernhardt of the Max-Planck Institute. Optical rotations were measured at 24-26°C using the D line of sodium on an O.C. Rudolph polarimeter.

Alcohol Syntheses

The 2-aryl-1-propanols were prepared from the corresponding 2-arylpropenes by hydroboration. The olefins were obtained by dehydrating the 2-aryl-2-propanols.

2-(p-Chlorophenyl)-1-propanol Methylmagnesium iodide was prepared under nitrogen from 6.30 g (0.26 mole) of magnesium metal in 100 ml. of anhydrous ether and 35.5 g. (0.25 mole) of methyl iodide (Eastman, white label) in 100 ml. of anhydrous ether. p-Chloroacetophenone (Eastman, white label), 26.0 g. (0.17 mole), in 100 ml. of ether was added to the Grignard reagent dropwise with stirring during a period of one hour, and the mixture was quenched with saturated ammonium chloride solution. The organic layer was separated, dried with magnesium sulfate, and evaporated under vacuum on a rotary evaporator. The crude alcohol was used without further purification in the following procedure. 2-(p-Chlorophenyl) propene was prepared using the method of Overberger and Saunders (107). A 100 ml. three-necked, round-bottom flask was fitted with a dropping funnel and 10 cm. glass bead distillation column. A powdered mixture of 6 g. of potassium acid sulfate, 0.05 g. of catechol, and 0.05 g. of picric acid was added to the flask. The flask was heated to 220°C with an oil bath, and crude 2-(p-chlorophenyl)-2-propanol was added dropwise. The styrene and water were removed by distillation at 106-115°C at 50 mm. as they were formed. The styrene was dissolved in ether, separated from the water layer, and dried with magnesium sulfate. Upon removal of ether, the residual oil was distilled at 43-45°C/1.5 mm., Lit. 78-80°C/8mm. (108), yield 25.1 g. (97% from p-chloroacetophenone).

nmr 1.86 (Q, 3), 4.88 (M, 1), 5.15 (M, 1), 7.11 (M, 4).

The styrene was hydroborated using a modification of Brown's procedure (109). A 500 ml., three-necked, round bottom flask was fitted with a condenser, stirrer, dropping funnel, and nitrogen inlet. To the flask was added a solution of 25.1 g (0.17 mole) of 2-(p-chlorophenyl)-propene in 75 ml. of bis-(2-ethoxyethyl) ether (Matheson, Coleman, and Bell, b.p. 71-73°/10 mm.), which had been distilled from lithium aluminium hydride. The solution was stirred for 15 min. under nitrogen flow. Sodium borohydride, 5.00 g. (0.13 mole), was added, and the mixture was cooled to 0°C with ice. Boron trifluoride etherate (Matheson, Coleman, and Bell, 47%, practical grade), 24.0 g., was added dropwise with stirring over a period of one hour, followed by an additional hour of stirring at room temperature. Fifty milliliters of 6N sodium hydroxide were added very carefully at 0°C. Hydrogen gas was expelled at this time from the excess diborane. Fifty milliliters of 30% hydrogen peroxide were slowly added to the mixture at 0°C over one hour followed by one hour of stirring at room temperature. The organic layer was extracted with ether. The ether layer was shaken with water four times to remove most of the bis-(2-ethoxyethyl) ether and dried with magnesium sulfate. After distillation of the ether and traces of bis-(2-ethoxyethyl) ether, 2-(p-chlorophenyl)-1-propanol was distilled at 109-112°C/0.3 mm., yield 27.2 g. (98%).

2-(m-Bromophenyl)-1-propanol 2-(m-Bromophenyl)-2-propanol was prepared by treatment of 25 g. (0.12 mole) of methyl 3-bromobenzoate

(Eastman, white label) with 0.30 mole of methylmagnesium iodide in anhydrous ether. The alcohol, upon dehydration, gave 16.1 g. (71% yield from the benzoate) of 2-(m-bromophenyl) propene; b.p. 53.5-56°C/0.8 mm., lit. 68-72°C/2mm. (108). nmr 2.00 (Q, 3), 5.00 (M, 1), 5.20 (M, 1), 7.10 (M, 4).

The styrene, 16.1 g. (0.82 mole), was hydroborated to give 16.0 g. (92%) of 2-(m-bromophenyl)-1-propanol, b.p. 91.5°C/0.44 mm.

2-(p-Methylphenyl)-1-propanol Thirty-three milliliters (0.45 mole) of acetone (Mallinckrodt, Reagent grade) were reacted with 0.42 mole of p-tolylmagnesium bromide (from Matheson, Coleman, and Bell, p-bromotoluene) in anhydrous ether to give 2-(p-methylphenyl)-2-propanol. Dehydration of the crude alcohol yielded 45.1 g. (81%) of 2-(p-methylphenyl)-2-propanol. Dehydration of the crude alcohol yielded 45.1 g. (81%) of 2-(p-methylphenyl)propene; b.p. 48-49°C/3.5 mm., Lit. 76-78°C/19 mm. (110).

nmr 1.87 (Q, 3), 2.05 (S, 3), 4.75 (M, 1), 5.05 (M, 1), 6.91 (Q, 4).

Hydroboration of 45.1 g. (0.34 mole) of the styrene gave 34.0 g. (67%) of 2-(p-methylphenyl)-1-propanol; b.p. 80°C/0.44mm., Lit. 102°C/5 mm. (111).

2-(p-Methoxyphenyl)-1-propanol 2-(p-Methoxyphenyl)-2-propanol was obtained from the reaction of 1.00 mole of methylmagnesium iodide in anhydrous ether with 148 g. (0.99 mole) of p-methoxyacetophenone (Eastman, white label). Dehydration of the alcohol gave 88.9 g. (61%) of 2-(p-methoxyphenyl) propene; b.p. 60.5-62.0°C/1.4 mm., Lit. 63.0-65.5°C/0.5mm. (108).

nmr 1.86 (Q, 3), 3.45 (S,3), 4.70 (M, 1), 5.02 (M, 1), 6.80 (Q, 4).

The styrene, 25.0 g. (0.17 mole), was hydroborated to give 24.2 g. (86%) of 2-(p-methoxyphenyl)-1-propanol; b.p. 95°C/0.5 mm., Lit. 80°/0.15 mm. (112).

2-Phenyl-1-propanol This alcohol was prepared from the hydroboration of 30.0 g. (0.25 mole) of α-methylstyrene (Aldrich, $n_D^{20}$1.5369). The yield of 2-phenyl-1-propanol was 29.0 g. (85%); b.p. 94-96°C/3.5 mm., Lit. 65°C/0.1 mm. (53).

2-(p-Methylphenyl)-2-deutero-1-propanol The alcohol was prepared using a modification of Sondheimer's method (113,114). A 250 ml., three-necked, round bottom flask was fitted with a nitrogen inlet, condenser, stirrer, and addition funnel. To the flask was added 9.20 g. (0.070 mole) of 2-(p-methylphenyl) propene in 50 ml. of anhydrous ether followed by 1.01 g. (0.024 mole) of lithium aluminum deuteride (Alfa Inorganics, Inc.). The mixture was cooled to -15°C with an ice-salt bath and stirred under nitrogen flow for one hour. A solution of 20 g. of 47% boron trifluoride etherate, which was distilled from calcium hydride, in 20 ml. of ether was added dropwise with stirring over a period of two hours. The mixture was stirred for one hour at -15°C and for 36 hours at room temperature. Fifteen milliliters of a saturated solution of sodium sulfate were added carefully at 0°C followed by 75 ml. of tetrahydrofuran. The ether was distilled from the mixture until the equilibrium temperature reached 50°C and 30 ml. of 10% sodium hydroxide were added. Thirty

milliliters of 30% hydrogen peroxide were then carefully dripped into the mixture with stirring at 0°C followed by stirring for one hour at room temperature. After extraction of the organic layer with ether, drying with magnesium sulfate, and removal of ether and tetrahydrofuran, a light-yellow oil was obtained, which upon distillation gave 4.15 g. (40%) of 2-(p -methylphenyl)-2-deutero-1-propanol, b.p. 86-90°C/0.3 mm.

nmr 1.18 (S,3), 2.30 (S,3), 3.49 (S,2), 4.65 (S,1), 7.09 (S,4).

2-(m-bromophenyl)-2-deutero-1-propanol The procedure described above using 14.8 g. (0.075 mole) of 2-(m-bromophenyl)propene gave 6.80 g. (42%) of 2-(m-bromophenyl)-2-deutero-1-propanol, b.p. 103-106°C/0.3 mm.

nmr 1.17 (S,3), 3.45 (S,3), 7.20 (M,4).

2-Phenyl-3-buten-1-ol Phenylmagnesium bromide (from Eastman, white label, phenyl bromide), 0.34 mole, was treated with 20.0 g. (0.29 mole) of butadiene monoxide (Pittsburgh Plate Glass Co.) in anhydrous ether. After addition of the epoxide, the mixture was stirred overnight and then quenched with saturated ammonium chloride solution. The ether layer was separated, dried with magnesium sulfate, and evaporated. The residual liquid was fractionally distilled on the spinning band column (Nester-Faust). The major fraction distilled at 62-63°C/0.6 mm, yield 25.0 g. (58%).

nmr 3.35 (M,4), 4.88 (D,1), 5.10 (S,1), 5.90 (M,1), 7.08 (S,5).

Mass spectrum [m/e (peak height)]17(18), 18(56), 19(18), 51(14), 65(11), 77(10), 91(70), 92(13), 115 (40), 116(14), 117(parent), 118(65), 119(10).

Trichloracetylurethane derivative, nmr 3.73 (T,1), 4.90 (D,2), 4.98 (D,1), 5.11 (S,1), 6.05 (M,1), 7.20 (S,5).

2-(p-Chlorophenyl)-3-buten-1-ol Treatment of 0.33 mole of p-chlorophenylmagnesium bromide (from Eastman, white label p-chlorophenyl bromide) with 20.0 g. (0.29 mole) of butadiene monoxide in anhydrous ether yielded 22.4 g. (42%) of 2-(p-chlorophenyl)-3-buten-1-ol, b.p. 94-95°/0.6 mm.

2-(p-Methylphenyl)-3-buten-1-ol Treatment of 0.33 mole of p-tolylmagnesium bromide (from Matheson, Coleman and Bell p-bromotoluene) with 20.0 g. of butadiene monoxide in anhydrous ether gave 25 g. (53%) of 2-(p-methylphenyl)-3-buten-1-ol, b.p. 79-80°C/0.6 mm.

2-Methyl-3-hexanol Reaction of 2.00 moles of n-propylmagnesium chloride (from Aldrich 1-chloropropane) and 144 g. (2.00 moles) of isobutyraldehyde (Eastman, white label) in anhydrous ether yielded 87.6 g. (38%) of 2-methyl-3-hexanol; b.p. 27-29°C/0.8 mm, Lit. 139-144°C/760 mm. (115).

p-Toluenesulfonates The p-toluenesulfonates were prepared from the corresponding alcohols using Tipson's method (116). A solution of the alcohol in anhydrous pyridine was cooled to 0°C with ice. Recrystallized p-toluenesulfonyl chloride (Eastman, yellow label) was added to the solution. A two to six per cent molar excess of the alcohol was used. The mixture was swirled at 0°C until the

p-toluenesulfonyl chloride was dissolved. The solution was allowed to stand at -20°C for one hour and then at -5°C for 48 hours. Over this period of time, pyridinium hydrochloride crystallized from the solution. Upon pouring the mixture into ice-cold, 6N hydrochloric acid solution, the p-toluenesulfonate precipitated as a yellow oil or solid. It was extracted with ether, and the ether solution was dried with magnesium sulfate and decolorized with activated charcoal. The ester was crystallized two or three times from ether/pentane solution.

2-Phenyl-1-propanol p-toluenesulfonate, m.p. 50.0-50.5°C.

nmr 1.20 (D,3), 2.32 (S,3), 2.97 (M,1), 3.94 (D,2), 7.10 (S,5), 7.35 (Q,4).

Anal. calculated for $C_{16}H_{18}SO_3$: C,66.18; H,6.25; S,11.07. Found: C,66.33; H,6.10; S,11.21.

2-(p-Chlorophenyl)-1-propanol p-toluenesulfonate, m.p. 64.5-65.0°C.

nmr 1.12 (D,3), 2.30 (S,3), 2.89 (M,1), 3.95 (D,2), 7.00-7.67 (two Qs, 8).

Anal. calculated for $C_{16}H_{17}SO_3Cl$: C,59.16; H,5.28; S,9.87. Found: C,59.46; H,5.46; S,10.06.

2-(m-Bromophenyl)-1-propanol p-toluenesulfonate, m.p. 60.5-61.0°C.

nmr 1.25 (D,3), 2.43 (S,3), 3.05 (M,1), 4.03 (D,2), 7.37 (M,8).

Anal. calculated for $C_{16}H_{17}SO_3Br$: C,52.04; H,4.64; S,8.68. Found: C,52.22; H,4.77; S,8.80.

2-(m-Bromophenyl)-2-deutero-1-propanol p-toluenesulfonate, m.p. 62.0-63.0°C.

nmr 1.25 (S,3), 2.43 (S,3), 4.03 (S,2), 7.37 (M,8).

2-(p-Methylphenyl)-1-propanol p-toluenesulfonate, m.p. 42.5-43.0°C.

nmr 1.18 (D,3), 2.22 (S,3), 2.34 (S,3), 2.87 (M,1), 3.87 (D,2), 6.88 (S,4), 7.32 (Q,4).

Anal. calculated for $C_{17}H_{20}SO_3$: C,67.08; H,6.62; S,10.53. Found: C,67.35; H,6.71; S,10.72.

2-(p-Methylphenyl)-2-deutero-1-propanol p-toluenesulfonate, m.p. 39-40°C.

nmr 1.18 (S,3), 2.22 (S,3), 2.34 (S,3), 3.87 (S,2), 6.88 (S,4), 7.32 (Q,4).

2-(p-Methoxyphenyl)-1-propanol p-toluenesulfonate, m.p. 37-39°C, Lit. 34-35°C (112).

nmr 1.10 (D,3), 2.29 (S,3), 2.86 (M,1), 3.60 (S,3), 3.83 (D,2), 6.71 (Q,4), 7.30 (Q,4).

Anal. calculated for $C_{17}H_{20}SO_4$: C,63.73; H,6.29; S,10.01. Found: C,63.55; H,6.23; S,9.93.

2-Phenyl-3-buten-1-ol p-toluenesulfonate, m.p. 63.5-64.0°C.

nmr 2.37 (S,3H), 3.67 (M,1), 4.19 (D,2), 4.94 (D,1), 5.17 (S,1), 5.94 (M,1), 6.83-7.80 (M,9).

Anal. calculated for $C_{17}H_{18}SO_3$: C,67.52; H,6.00; S,10.61. Found: C,67.72; H,5.78; S,10.49.

2-(p-Chlorophenyl)-3-buten-1-ol p-toluenesulfonate, m.p. 49-50°C.

nmr 2.38 (S,3), 3.61 (M,1), 4.14 (D,2), 4.92 (D,1), 5.15 (S,1), 5.90 (M,1), 6.80-7.70, (two Qs,8).

Anal. calculated for $C_{17}H_{17}SO_3Cl$: C,60.62; H,5.09; S,9.52. Found: C,60.60; H,5.13; S,9.44.

2-(p-Methylphenyl)-3-buten-1-ol p-toluenesulfonate, liquid.

nmr 2.29 (S,3), 2.40 (S,3), 3.60 (M,1), 4.11 (M,2), 4.92 (D,1), 5.15 (S,1), 5.88 (M,1), 6.94 (S,4), 7.39 (Q,4).

Anal. calculated for $C_{18}H_{20}SO_3$: C,68.32; H,6.37; S,10.13. Found: C,68.18; H,6.34; S,10.05.

3-Buten-1-ol p-toluenesulfonate, liquid.

nmr 2.10 - 2.70 (M,2), 2.40 (S,3), 4.00 (T,2), 4.90 (M,1), 5.10 (M,1), 5.67 (M,1), 7.50 (Q,4).

This compound was prepared from Aldrich 3-butene-1-ol, $n_D^{20}$ 1.4233.

2-Butanol p-toluenesulfonate, liquid.

nmr 0.78 (T,3), 1.23 (D,3), 1.51 (M,2), 2.41 (S,3), 4.65 (M,1), 7.71 (Q,4).

This compound was prepared from Eastman, white label 2-butanol.

2-Methyl-3-hexanol p-toluenesulfonate, liquid.

nmr 0.73-1.00 (overlapping D and T), 1.00-2.20 (M) total integration from 0.73-2.20 was 14, 2.42 (S,3), 4.47 (M,1), 7.57 (Q,4).

This compound decomposed upon sitting at room temperature for several days.

1-Octanol p-toluenesulfonate, liquid.

nmr 0.87 (T,3), 1.24 (S) and 1.40-2.00 (M) tolal integration from 1.24 to 2.00 was 13, 2.42 (S,3), 3.94 (T,2).

This compound was prepared from Eastman, white label n-octyl alcohol.

Bromide syntheses

1-Phenyl-1-bromoethane A mixture of 47.0 g. (0.45 mole) of styrene (Matheson, Coleman, and Bell, b.p. 40-42°C/15 mm) and 240 g. of 48% hydrogen bromide was stirred at 75° for 14 hours. The yellow organic layer was separated from the mixture, dried with magnesium sulfate, and decolorized with activated charcoal. Fractional distillation yielded 10 g. (12%) of 1-phenyl-1-bromoethane; b.p. 37-38°C/1.1 mm., Lit. 76°/7 mm. (74).

nmr 1.96 (D), 5.07 (Q), 7.25 (M).

3-Methyl-3-bromohexane This bromide was prepared from 3-methyl-3-hexanol. The alcohol was obtained by treating 36.0 g. (0.50 mole) of 2-butanone (Eastman, white label) with 0.50 mole of n-propylmagnesium bromide (from Aldrich 1-bromopropane); yield of 3-methyl-3-hexanol 37.6 g. (65%), b.p. 61-63°/20 mm., Lit. 137-139/760 mm. (117). The alcohol, 10.5 g. (0.09 mole), was dripped slowly into 9.68 g. of phosphorous tribromide (Eastman, yellow label) with stirring and cooling with tap water. The mixture was stirred at room temperature for one hour and fractionally distilled to yield 11.0 g. (68%) of 3-methyl-3-bromohexane, b.p. 70°C/20 mm. The bromide was shaken with 5% sodium bicarbonate solution to remove hydrogen bromide followed

by drying with magnesium sulfate.

IR ($cm^{-1}$) 2960, 2870, 1460, 1380, 1140, 1090, 875 (Neat).

1-Bromooctane This compound was purchased from Halogen Chemicals, Inc.

2-(p-Chlorophenyl)-1-bromopropane The remaining bromides were prepared from the corresponding p-toluenesulfonates. 2-(p-Chlorophenyl)-1-propanol p-toluenesulfonate, 6.64 g (0.02 mole), was dissolved in 40 ml. of acetone (Mallinckrodt, analytical reagent grade). Five grams (0.06 mole) of lithium bromide (Matheson, Coleman, and Bell, anhydrous, reagent powder) were added and dissolved. The solution was stirred for four days at room temperature. Fifty milliliters of water were added to the mixture, and the product was extracted with ether. After drying with magnesium sulfate, decolorization with activated charcoal and removal of ether, the residual oil distilled at 72-74°C (0.3 mm.) to give 4.40 g. (94%) of 2-(p-chlorophenyl)-1-bromopropane.

nmr 1.36 (D,3), 3.15 (M,3), 7.33 (Q,4).

2-Phenyl-1-bromopropane, b.p. 50-54°C/0.2 mm., Lit. 61°C/0.1 mm (53).

nmr 1.32 (D,3), 3.15 (M,3), 7.06 (S,5).

2-(m-Bromophenyl)-1-bromopropane, b.p. 85-85.5°C/0.3 mm.

nmr 1.40 (D,3), 3.25 (M,3), 7.18 (M,4).

2-(m-Bromophenyl)-2-deutero-1-bromopropane , b.p. 90.5-91/0.8 mm.

nmr 1.40 (S,3), 3.42 (S,2), 7.18 (M,4).

2-(p-Methylphenyl)-1-bromopropane, b.p. 55-57°C/0.2 mm., Lit. 88°/6 mm. (111).

nmr 1.39 (D,3), 2.33 (S,3), 3.23 (M,3), 7.11 (S,4).

2-(p-Methylphenyl)-2-deutero-1-bromopropane , b.p. 69.5-70°C/0.5 mm.

nmr 1.39 (S,3), 2.33 (S,3), 3.40 (D,2), 7.09 (S,4).

2-(p-Methoxyphenyl)-1-bromopropane, b.p. 81.5-83.0°C/0.3 mm.

nmr 1.37 (D,3), 3.20 (M,3), 3.75 (S,3), 6.97 (Q,4).

2-Phenyl-1-bromo-3-butene, b.p. 55-56°C/0.9 mm.

nmr 3.54 (M,3), 4.80-5.22 (M,2), 5.62-6.30 (M,1), 7.15 (M,5).

1-Bromo-3-butene, b.p. 89-90°C/624 mm., Lit. 91-92°C/610 mm. (118).

nmr 2.54 (M,2), 3.32 (T,2), 4.92 (M,1), 5.15 (M,1), 5.75 (M,1).

Racemic 2-butyltrimethylammonium iodide 2-(N,N-dimethylamino)-butane was prepared from the reaction of 208 g. (1.51 moles) of 2-bromobutane and 135 ml. (2.04 moles) of dimethylamine (Eastman, white label) in 200 ml. of ether at 120°C for 35 hours in a Fisher high pressure reactor. The reaction produced a large mass of dimethylammonium bromide as side product. The liquid was decanted from the solid and distilled to yield 61.1 g. (60%) of 2-(N,N-dimethylamino)-butane, b.p. 91-93°C, Lit. 93-93.5°C (86). An ether solution of 5.00 g. (0.05 moles) of the amine was added slowly with stirring to a solution of 4.4 ml. (0.07 moles) of methyl iodide in ether in a 100 ml., three-necked flask fitted with a condenser. As the amine was added refluxing was accompanied with precipitation of 2-butyl-

trimethylammonium iodide. The mixture was stirred for three hours followed by rapid filtration of the product. The product was rinsed with ether and crystallized from iso-propyl alcohol/ether solution. It was very hydroscopic; yield 10.5 g. (87%) of the quaternary ammonium salt, m.p. 271-273°C, Lit. 258-259°C (88).

nmr 1.50 (T), 1.86 (D), 2.42 (M), 3.82 (S), 3.97 (M).

Levorotatory 2-butyltrimethylammonium iodide A solution of 4.47 g. (0.02 moles) of (-)-2-butanol p-toluenesulfonate ($[\alpha]_D^{26}$-7.66° Neat, Lit. $[\alpha]_D^{20}$ 11.10°for 100% optically pure (102)) and 2.74 g. (0.06 mole) of dimethylamine in acetone was allowed to stand for four days at room temperature in a tightly stoppered flask. The resulting yellow solution was extracted with pentane. After removal of pentane and dimethylamine by distillation, 2 ml. of liquid boiling at 60-80°C/624 mm. were collected using toluene as a chaser. The liquid was redissolved in pentane in a 25 ml. pear-shaped flask fitted with a condenser and dropping funnel. One milliliter of methyl iodide was slowly dripped in. When refluxing and precipitation ceased, the product was rapidly filtered and rinsed with pentane. Crystallization from iso-propyl alcohol/ether solution gave 1.54 g. (32% yield from p-toluenesulfonate) of (-)-2-butyltrimethylammonium iodide; $[\alpha]_D^{26}$ -6.45° in 95% ethanol, m.p. 267-272 °C.

2-Methyl-3-hexyltrimethylammonium iodide A solution of 5.00 g. (0.02 mole) of 2-methyl-3-hexanol p-toluenesulfonate and 5.0 ml. (0.07 mole) of dimethylamine was heated in a sealed tube at 50°C in an oil bath for four days. During this period of time, a bottom

liquid layer formed. The tube was cooled and opened, and the contents were poured into ether. Upon swirling dimethylammonium p-toluene-sulfonate crystallized. The salt was filtered from the ether solution, and the solution was distilled to remove ether and dimethyl-amine. To the light yellow residue was added 2.0 ml. of methyl iodide, 6.0 ml. of ether, and 7 ml. of iso-propyl alcohol. The resulting solution was refluxed for three hours. The product crystal-lized from the reaction mixture upon cooling. The white crystals were filtered, rinsed with ether, and dried; yield 2.04 g. (40% yield from p-toluenesulfonate), m.p. 214.5-215.5 d°C.

nmr 0.68-1.25 (M,9), 1.38-1.78 (M,4), 1.98-2.68 (M,1), 2.78-3.88 (M) and 3.31 (S), total integration from 2.78 to 3.88, 9.

2-Methyl-2-hexene 2-Methyl-3-hexanol, 9.25 g. (0.08 mole), was heated with 10 ml. of 85% phosphoric acid, and olefin and water were distilled off as they were formed. The organic layer of the distillate was separated and dried with sodium metal and fractionally distilled to give 5.98 g. (76%) of 2-methyl-2-hexene; b.p. 88-89°C/625 mm., Lit. 94.4-94.6°C/760 mm. (119). GPC analysis (20 ft., 20% dioctylphthalate, 100°C) showed it to be pure.

IR ($cm^{-1}$) 2965, 2930, 2870, 1675, 1650, 1455, 1380, 1115, 1075, 885, 860 (Neat).

nmr 0.9 (T,3), 1.00-1.47 (M,2), 1.58 (S,3), 1.68 (D,3), 1.99 (M,3), 5.08 (M,1).

trans-2-Methyl-3-hexene This olefin was prepared by pyrolyzing 2-methyl-3-hexylacetate. The acetate was prepared from 6.08 g. (0.05 mole) of 2-methyl-3-hexanol and 14.1 g. (0.14 mole) of acetic

anhydride in 25 ml. of pyridine. After sitting overnight, the solution was poured into 200 ml. of 6N hydrochloric acid solution and ice. The organic layer was extracted with ether, shaken with aqueous sodium bicarbonate, and dried with magnesium sulfate. Evaporation of the solution on the rotary evaporator under vacuum gave 8.06 g. (97%) of the acetate. Without further purification 2-methyl-2-hexylacetate was slowly dripped into a flask that was heated strongly with an IR lamp, and olefin and acetic acid distilled off as they formed. The distillate was shaken with 5% aqueous sodium bicarbonate solution to remove acetic acid and dried with magnesium sulfate. Fractional distillation gave one fraction boiling at 60°C/625 mm., Lit. 85-86°C/760 mm. (119) for 2-methyl-3-hexene. GPC analysis (20 ft., 20% dioctylphthalate, 100°C) showed two components in a ratio of 3:1, the latter having a retention time identical to that of 2-methyl-2-hexene. A trace of third component was also observed. This might have been cis-2-methyl-3-hexene. The major component was isolated on the GPC (10 ft., 20% silver nitrate, 40°C). The nmr and IR spectra confirmed the structure as trans-2-methyl-3-hexene.

IR ($cm^{-1}$) 3030, 2960, 2930, 2870, 1380, 1360, 1120, 1100, 965 ($CS_2$).

nmr 1.70-1.00 (overlapping D and T, 9), 1.50-2.50 (M,3), 5.34 (M,2).

1-Octene This compound was prepared from n-amyl Grignard reagent and allyl bromide (120). n-Amylmagnesium bromide was prepared from 20.0 g. (0.13 mole) of n-amyl bromide (Halogen Chemicals, Inc.)

and 3.70 g. (0.15 mole) of magnesium in anhydrous ether. The Grignard reagent was transferred to a second reaction flask with a 200 ml. pipette to remove it from unreacted magnesium. An ether solution of 12.1 g. (0.10 mole) of allyl bromide (Matheson, Coleman, and Bell, b.p. 69-71°C) was slowly added, with stirring, at room temperature to the Grignard reagent. No reaction appeared to take place immediately. After stirring at room temperature for three hours, a dark brown lower layer had formed. The reaction mixture was quenched with saturated ammonium chloride solution. The ether layer was removed, dried with magnesium sulfate, and decolorized with activated charcoal. The solution was evaporated on the rotary evaporator, and the residue was fractionally distilled on the spinning band fractionating column to give 5.78 g. (52%) of 1-octene; b.p. 105-106°C/625 mm., Lit. 121.5-122.5/760 mm. (120).

IR ($cm^{-1}$) 3090, 2970, 2930, 2870, 1645, 1465, 1380, 1055, 990, 910, 720 (Neat).

nmr 0.93 (T,3), 1.33 (D,9), 1.60-2.30 (M,2), 4.70-5.18 (M,2), 5.45-6.15 (M,1).

tert-Butyl-n-octyl ether 1-Octanol p-toluenesulfonate, 64.0 g. (0.23 mole), was dissolved in a solution of 43.0 g. (0.39 mole) of potassium tert-butoxide (MSA Research Corp.) in 490 ml. of tert-butyl alcohol. The solution was heated at 50-55°C for five days and poured into one liter of water. The organic layer was separated. The aqueous layer was shaken three times with 100 ml. portions of Skellysolve-B, and the extracts were combined with the original organic

layer. The resulting solution was dried with magnesium sulfate, decolorized with activated charcoal, and evaporated on the rotary evaporator. The residue was distilled on the spinning band fractionating column to give 30 g. (72%) of tert-butyl-n-octyl ether; b.p. 43-45°C/0.66 mm., Lit. 83-85°C/9mm. (121).

nmr 1.6-1.7 (M), 1.14 (S), 1.31 (broad S), total integration from 1.6-1.7, 24; 3.22 (M,2).

Resolution of 2-butanol 2-Butanol was resolved by fractional crystallization of the l-brucine salt of sec-butylhydrogenphthalate (122).

sec-Butylhydrogenphthalate To a one liter, three-necked flask fitted with a condenser, stirrer, and thermometer was added 453 g. (3.06 moles) of phthalic anhydride and 281 ml. (3.06 moles) of 2-butanol. The mixture was stirred at 95°C for 17 hours and then cooled and poured carefully into two liters of 5% sodium carbonate with stirring. After stirring for two hours the aqueous solution was extracted twice with ether to remove diester and unreacted anhydride. The solution was neutralized with hydrochloric acid to precipitate sec-butylhydrogenphthalate as a yellow oil. The ester was extracted with two liters of chloroform. The chloroform solution was dried with magnesium sulfate and evaporated on the rotary evaporator. The residual oil solidified upon standing. Recrystallization in Skellysolve-B gave four crops of sec-butylhydrogenphthalate; yield 540 g. (80%), m.p. 57-59°C, Lit. 56-59° (122).

Brucine-sec-butylhydrogenphthalate A solution of 465 g. (2.09 moles) of sec-butylhydrogenphthalate was prepared in nine liters of distilled acetone and warmed to 45°C. To the solution was added 835 g. (2.09 moles) of anhydrous l-brucine, and the mixture was stirred at 45°C until the brucine dissolved. The dark yellow solution was heated at 45° for 1 1/2 hours longer and then set aside at room temperature to cool. After a period of 24 hours, crystallization of the brucine salt had stopped. The liquid was siphoned from the light yellow crystals. The crystals were washed with two 500 ml. portions of cold acetone, collected, and dried; m.p. 145-155°C, Lit. 154-155°C for the salt of pure d-sec-butylhydrogenphthalate (122). The crystals were redissolved in eight liters of hot acetone. The solution was boiled down to six liters and set aside to cool overnight at room temperature. The resulting crystals were again rinsed with cold acetone, collected, and dried, yield 314 g. This brucine salt of d-rich sec-butylhydrogenphthalate melted at 150-155°C.

Recovery of (+)-2-butanol The brucine sec-butylhydrogenphthalate, 304 g. (0.49 mole), obtained from the second crystallization was dissolved in one liter of hot water. A solution of 125 g. of potassium hydroxide in one liter of water was added. A precipitate of brucine immediately formed. (+)-2-Butanol was steam-distilled from the mixture. The alcohol was salted out of the aqueous distillate with potassium carbonate and extracted with ether. The ether solution was dried with magnesium sulfate and distilled; yield of (+)-2-butanol 21.0 g. (58% from salt), b.p. 94-99°C/760 mm., $[\alpha]_D^{24}$ + 11.95° (Neat);

Lit. 99°C/760 mm., $[\alpha]_D^{20}$+13.87°(Neat) for optically pure alcohol (122).

Recovery of (-)-2-butanol This alcohol was obtained from the first mother liquor of the above crystallizations. After collection of several more crops of salt from the original mother liquor, it was boiled down to a volume 1500 ml. The dark brown solution was shaken with 10% hydrochloric acid solution to decompose the remaining l-rich salt. The freed ester was extracted with ether. This ether solution of l-rich sec-butylhydrogenphthalate was dried with magnesium sulfate and evaporated to give 93.0 g. of ester as a yellow oil, which was boiled with 20% potassium hydroxide solution to free and steam-distil off (-)-2-butanol. After salting the alcohol from the aqueous distillate, extraction with ether, and distillation 28.6 g. (92% from ester) of (-)-2-butanol were obtained; b.p. 94°/626 mm., $[\alpha]_D^{25}$ - 5.84° (Neat). Levarotatory 2-butanol was also obtained from two different methods of stereospecific synthesis of the alcohol. The first method involved the use of (+)-diisopinocamphenylborane which adds stereospecifically to 2-butene to yield predominately (-)-2-butanol upon decomposition with sodium hydroxide and hydrogen peroxide (123). (+)-Diisopinocamphenylborane was prepared in the following manner. A solution of 127 g. (0.81 mole) (+)-2-pinene (K and K, $[\alpha]_D^{25}$+ 22.00°, optically pure $[\alpha]_D^{20}$+ 47.6° (123)) was prepared in 150 ml. of diglyme (bis-(2-methoxyethyl) ether) which had been distilled from lithium aluminum hydride. The solution was added to 300 ml. of a 1M solution of sodium borohydride in diglyme in a

500 ml., round-bottom flask fitted with a thermometer, dropping funnel, stirrer, and nitrogen inlet. Fifty-one milliliters of 47% borontrifluoride etherate in 50 ml. of diglyme were added dropwise at 0°C under nitrogen flow and with stirring. After sitting for six hours at 0°C, a heavy white precipitate of (+)-diisopinocamphenylborane had formed. cis-2-Butene, 49 ml. (0.55 mole), was added to the mixture at 0°C with stirring. The mixture was stirred at 0°C until the solid borane dissolved (4 hours). One hundred twenty milliliters of 3M sodium hydroxide was carefully added to the mixture followed by the dropwise addition of 120 ml. of 30% hydrogen peroxide, keeping the temperature below 45°C by cooling. The reaction mixture was extracted several times with ether, and the extracts were combined, dried with magnesium sulfate, and distilled to yield 11.0 g. (27%) of (-)-2-butanol; b.p. 97-99°/760 mm., $[\alpha]_D^{25}$ - 6.32° (Neat) (45.7% optically pure).

The other method of preparing (-)-2-butanol was the stereospecific conversion of D-(-)-2,3-butanediol to the alcohol (124). A solution of 180 g. (2.00 moles) of D-(-)-2,3-butanediol (National Research Council, Ottawa, Canada, b.p. 65-70°/10 mm., $[\alpha]_D^{26}$ - 12.08°; reported for optically pure b.p. 77.5-78°/10 mm., $[\alpha]_D^{26}$ - 12.92° (116)) and 450 g. (4.41 moles) of acetic anhydride in 815 ml. of pyridine was prepared. The solution became hot and remained so for about 1/2 hour. It was allowed to stand at room temperature overnight. The solution was fractionally distilled to give 309 g. (88.4%) of D-(+)-2,3-diacetoxybutane; b.p. 54°C/1.0 mm., $\alpha_D^{26}$ + 13.42°; reported 82°C/10 mm.,

$\alpha_D^{26}$+ 13.87°. The diacetate, 309 g. (1.78 moles), was dissolved in 460 g. of 12M hydrochloric acid. The solution was cooled to -10°C with an ice/salt bath and saturated with hydrogen chloride until 320 g. of the gas were dissolved. The solution was then sealed in two 500 ml. pyrex flasks and allowed to sit at room temperature for three weeks. The flasks were then opened and poured onto two pounds of solid sodium bicarbonate. The inorganic solids were filtered off by suction and washed with ether. The ether washings were combined with the filtrate, and the organic layer of the resulting mixture was separated. It was carefully shaken with aqueous sodium bicarbonate. The ether solution was then dried with magnesium sulfate and distilled to yield 85.0 g. (44.5%) of L-(+)-erythro-3-chloro-2-butanol; b.p. 65-70°C/15 mm., $\alpha_D^{26}$+ 10.06°; reported 56-62°C/10 mm., $\alpha_D^{25}$+ 9.77°. The chlorohydrin, 40.0 g. (0.37 mole), was dripped slowly into a solution of 250 g. of potassium hydroxide in 125 ml. of water at 90-95°C. As the chlorohydrin was added, an inorganic precipitate formed, and D-(+)-2,3-epoxybutane distilled off and was collected. The epoxide was redistilled to give 19.0 g. (71.3%) of pure compound; b.p. 46-48°C/625 mm., $\alpha_D^{26}$+ 37.76°; reported 53.5°/745 mm., $\alpha_D^{26}$+ 46.75°. The epoxide was dripped into a solution of 3 g. (0.08 moles) of lithium aluminum hydride in 100 ml. of anhydrous ether with stirring. The resulting mixture was refluxed one hour followed by the careful addition of 35 ml. of water. The mixture was then shaken with 50 ml. of 10% potassium hydroxide solution, and the ether layer was separated. The aqueous layer

was shaken three times with portions of ether. The ether layers were combined, dried with magnesium sulfate, and fractionally distilled to yield 11.7 g. (60.8%) of L-(-)-2-butanol; b.p. 92-94°C/625 mm., $[\alpha]_D^{26}$ - 12.3° (Neat); reported 97.5-98.0°/745 mm., $[\alpha]_D^{25}$ - 13.51°.

Resolution of 2-methyl-3-hexanol This alcohol was resolved by fractional crystallization of strychnine 2-methyl-3-hexylhydrogenphthalate (115). The ester was prepared from 75.5 g. (0.51 moles) of phthalic anhydride and 65.5 g (0.56 mole) of 2-methyl-3-hexanol using the procedure described previously for 2-butanol to give 101 g. (78.0%) of 2-methyl-3-hexylhydrogenphthalate, m.p. 56.5-58.0°C, reported 59-60°C. The ester, 101 g. (0.39 mole), was dissolved in 200 ml. of chloroform. The solution was poured into a solution of 131 g. (0.39 mole) of strychnine in one liter of chloroform. The chloroform was then removed from the solution with the rotary evaporator to yield the solid strychnine salt. The salt was redissolved in 2700 ml. of warm, absolute ethanol, and the solution was filtered and set aside to cool at room temperature. Crystallization began immediately. After the solution had cooled to room temperature it was placed in the refrigerator (-5°C) overnight. The resulting crystals were collected and dried; yield 166 g., m.p. 200-211.5°C. This crop was crystallized seven more times from absolute ethanol, to finally yield 66.0 g. of the strychnine salt of the d-rich 2-methyl-3-hexylhydrogenphthalate; m.p. 216-219°C, reported for optically pure salt 212°C. The salt was shaken with 600 ml. of 6N hydrochloric acid and 200 ml. of ether. The ether layer was

separated, dried with magnesium sulfate, and evaporated to yield 29.0 g. (98% from the salt) of (+)-2-methyl-3-hexylhydrogenphthalate; m.p. 76.5-79.5°C, $[\alpha]_D^{26}$ + 7.12° in $CCl_3H$; reported for optically pure ester, m.p. 79-80-, $[\alpha]_D$ + 7.91° in $CCl_3H$ . The ester was boiled with 20 g. of potassium hydroxide in 100 ml. of water and the alcohol was steam distilled off as it formed. It was then extracted from the distillate with ether; the ether solution was dried with magnesium sulfate and evaporated to give 11.7 g. (88.6%) of (+)-2-methyl-3-hexanol; $\alpha_D^{26}$ + 20.0°, reported $\alpha_D$ + 17.49°.

Purification of materials

Ethanol Absolute ethanol was refluxed with sodium and diethylphthalate and distilled according to the method of Mansk (125) to remove residual water.

tert-Butyl alcohol tert-Butyl alcohol (Baker, analyzed reagent) was distilled three times under nitrogen from potassium metal (approximately 3g./liter of alcohol).

2-Butanol Commercial, racemic 2-butanol (Eastman, white label) and the optically active forms were distilled two or three times from sodium metal prior to use.

Potassium Lump potassium was fused in n-heptane and stirred. The impurities were skimmed from the top of the n-heptane. The procedure was repeated three times. It was then rinsed with ether and cut into rods and packed into a 1 x 32 cm. pyrex glass tube and sealed. The metal, in this form, was further purified on a Fisher zone refiner for one week.

Potassium tert-butoxide The solution of potassium tert-butoxide in tert-butyl alcohol was prepared by melting the purified potassium metal directly from the zone-refining tube into a flask containing approximately four liters of the alcohol with a positive flow of nitrogen coming from the flask. The solution was stored under nitrogen.

Sodium ethoxide Freshly cut sodium was rinsed with anhydrous ethanol and then dissolved in the purified, anhydrous ethanol. The solution was stored under nitrogen.

Potassium sec-butoxide Freshly cut and fused potassium was dissolved in cold, purified 2-butanol under nitrogen. The solutions were stored under nitrogen.

Pentane The pentane used for the p-toluenesulfonate crystallizations was purified by shaking three liter batches of commercial pentane with 100 ml. portions of concentrated sulfuric acid until the acid layer was colorless (ten to fifteen times). The pentane was then washed with water, dried with magnesium sulfate, and distilled from sodium.

## Procedures and Data for Product Analyses

Elimination of n-octyl compounds After standing for eight to twelve days at 50°C, the last ampules from the kinetic runs of n-octyl bromide and p-toluenesulfonate with tert-butoxide were opened and the contents were injected directly into the F and M 700 G.P.C. using a 10 ft., 20%, β,β'-oxypropionitrile column at 68°C. The products,

1-octene and tert-butyl-n-octyl ether, were identified by comparing retention times with authentic samples. They had retention times of 1.35 min. and 12.0 min., respectively. Calibration of the detector under these conditions using standard solutions prepared from authentic samples of the products showed the peak area ratios to represent directly the mass ratios of the compounds with a negligible error. The data for the analyses are given in Tables 18 and 19.

Table 18. Product analysis of the elimination of 1-octanol p-toluenesulfonate with 0.1160 M potassium tert-butoxide in tert-butyl alcohol at 49.83°C

| | 1-octene | | tert-butyl-n-octyl ether | |
|---|---|---|---|---|
| Injection | Peak Area | % | Peak Area | % |
| 1 | 1.3 | 0.58 | 223 | 99.42 |
| 2 | 1.5 | 0.94 | 115 | 99.06 |
| 3 | 1.0 | 1.00 | 99 | 99.00 |
| 4 | 1.0 | 0.80 | 124 | 99.20 |
| 5 | 2.0 | 0.58 | 264 | 99.42 |
| 6 | 2.8 | 0.44 | 226 | 99.56 |
| Aver. per cent[a,b] | | 0.72 ± 0.18 | | 99.28 ± 0.18 |

[a]Conc. of p-toluenesulfonate, 0.0419 M.

[b]Aver. molar per cent yields, 1.2 ± 0.3% 1-octene; 98.9 ± 0.3% tert-butyl-n-octylether.

Elimination of sec-butyl compounds 2-Butanol p-toluenesulfonate or 2-butyltrimethylammonium iodide was dissolved in a solution of 2-butanol containing an equivalent amount of potassium sec-butoxide in a 10 ml. flask. The flask was fitted with a condenser and glass tube which led to a collection vessel which was fitted with a rubber

Table 19. Product analysis of the elimination of 1-bromooctane with 0.1028M potassium tert-butoxide in tert-butyl alcohol at 49.83°C

| Injection | 1-octene Peak Area | 1-octene % | tert-butyl-n-octylether Peak Area | tert-butyl-n-octylether % |
|---|---|---|---|---|
| 1 | 18.5 | 39.4 | 39.4 | 61.6 |
| 2 | 49.5 | 39.1 | 39.1 | 61.9 |
| 3 | 30.5 | 42.6 | 42.6 | 57.4 |
| 4 | 32.5 | 40.6 | 40.6 | 59.4 |
| 5 | 32.5 | 42.5 | 42.5 | 57.5 |
| 6 | 31.0 | 43.0 | 43.0 | 57.0 |
| Aver. per cent[a,b] | | 40.7 ± 1.1 | | 59.3 ± 1.1 |

[a]Conc. of bromide, 0.0338 M.

[b]Aver. molar per cent yields, 53.3 ± 1.4% 1-octene; 46.7 ± 1.4% tert-butyl-n-octylether.

septum with a hypodermic syringe and injection into the GPC containing a 15 ft., 20% dimethylsulfolane or a 20 ft., 20% dioctylphthalate column at 20°C. The components of the mixture were identified by comparison of their retention times with commercial samples of the three butenes. Their retention times were: 1-butene, 8.5 min.; trans-2-butene, 10.5 min.; cis-2-butene, 12.0 min. (dimethylsulfolane).

Elimination of 2-methyl-3-hexanol p-toluenesulfonate A solution of 0.66-0.81 mole of the p-toluenesulfonate was prepared in 4.0 ml. of 0.8-0.4 M potassium sec-butoxide in sec-butyl alcohol in a 10 ml. flask. The solution was heated at 80°C for one or two hours, after which the liquid was distilled from the reaction mixture or extracted with three or four milliliters of ether. Analysis of the distillates or ether extracts on a 10 ft., 20% dimethylsulfolane column at 45°C

showed two olefinic products which were identified as trans-2-methyl-3-hexene and 2-methyl-2-hexene by comparison of their retention times (10.0 min. and 16.2 min., respectively) with the authentic samples.

Table 20. Product analysis of the elimination of (±)-2-butanol p-toluenesulfonate with (±)-potassium sec butoxide/sec-butyl alcohol[a,b]

| | 1-butene | | trans-2-butene | | cis-2-butene | |
|---|---|---|---|---|---|---|
| Injection | Peak Area | % | Peak Area | % | Peak Area | % |
| 1 | 371 | 47.4 | 219 | 28.0 | 193 | 24.6 |
| 2 | 311 | 47.3 | 186 | 28.3 | 161 | 24.4 |
| 3 | 417 | 47.3 | 249 | 28.3 | 215 | 24.4 |
| Aver. per cent | | 47.3 ± 0.0 | | 28.2 ± 0.1 | | 24.5 ± 0.1 |

[a]A solution of 25.2 g. (0.11 mole) of p-toluenesulfonate, 100 ml. of 1.1 M base; analyzed on dioctylphthalate column at 20°C.

[b]Duplicate reaction gave 47.5 ± 0.2% 1-butene, 29.7 ± 0.3% trans-2-butene, 22.8 ± 0.3% cis-2-butene; analyzed on the dimethylsulfolane column at 40°C.

Table 21. Product analysis of the elimination of (+)-2-butanol p-toluenesulfonate with (+)-potassium sec-butoxide/sec-butyl alcohol[a,b]

| Injection | 1-butene Peak Area | 1-butene % | trans-2-butene Peak Area | trans-2-butene % | cis-2-butene Peak Area | cis-2-butene % |
|---|---|---|---|---|---|---|
| 1 | 154 | 46.0 | 100 | 29.9 | 81 | 24.1 |
| 2 | 112 | 46.6 | 70 | 29.2 | 58 | 24.2 |
| 3 | 148 | 47.4 | 95 | 29.5 | 79 | 24.5 |
| Aver. per cent | | 46.2 ± 0.4 | | 29.5 ± 0.2 | | 24.3 ± 0.3 |

[a]A solution of 0.23 g. (1.00 mmole) of (+)-p-toluenesulfonate (72% optically pure), 1.00 ml. of 1.0 M (+)-base (78% optically pure); analyzed on dimethylsulfolane column at 40°C.

[b]Duplicate reaction gave 47.5 ± 0.00% 1-butene, 28.6 ± 0.3% trans-2-butene, 23.9 ± 0.2% cis-2-butene; analyzed on dimethylsulfolane column at 40°C.

Table 22. Product analysis of the elimination of (-)-2-butanol p-toluenesulfonate with (+)-potassium sec-butoxide/sec butyl alcohol[a,b]

| Injection | 1-butene Peak Area | 1-butene % | trans-2-butene Peak Area | trans-2-butene % | cis-2-butene Peak Area | cis-2-butene % |
|---|---|---|---|---|---|---|
| 1 | 160 | 46.9 | 100 | 29.3 | 81 | 23.8 |
| 2 | 179 | 46.5 | 113 | 29.4 | 93 | 24.1 |
| 3 | 164 | 47.1 | 102 | 29.3 | 82 | 23.6 |
| Aver. per cent | | 46.8 ± 0.8 | | 29.3 ± 0.3 | | 23.9 ± 0.2 |

[a]A solution of 0.23 g. (1.00 mmole) of (-)-p-toluenesulfonate (46% optically pure), 1.00 ml. of 1.0 M (+)-base (78% optically pure); analyzed on dimethylsulfolane column at 40°C.

[b]Duplicate reaction gave 47.5 ± 0.03% 1-butene; 28.6 ± 0.01% trans-2-butene, 23.9 ± 0.01% cis-2-butene; analyzed on dimethylsulfolane column at 40°C.

Table 23. Product analysis of the elimination of (±)-2-butyltrimethylammonium iodide with (±)-potassium sec-butoxide/sec-butyl alcohol[a,b]

| Injection | 1-butene Peak Area | 1-butene % | 2-butene Peak Area | 2-butene % |
|---|---|---|---|---|
| 1 | 303 | 91.5 | 28.0 | 8.5 |
| 2 | 338 | 90.8 | 34.0 | 9.2 |
| 3 | 340 | 91.4 | 31.0 | 8.3 |
| 4 | 281 | 90.4 | 30.0 | 9.6 |
| Aver. per cent | | 91.1 ± 0.5 | | 8.9 ± 0.5 |
| | trans-2-butene | | cis-2-butene | |
| 5 | 123 | 34.1 | 238 | 65.9 |
| 6 | 86.0 | 36.2 | 152 | 63.8 |
| 7 | 68.5 | 36.8 | 116 | 63.2 |
| Aver. per cent | | 35.7 ± 1.0 | | 64.3 ± 1.0 |

[a]A solution of 0.25 g. (1.03 mmole) quaternary ammonium salt, 3.00 ml. of 0.44 M base; analyzed on dioctylphthalate column at 20°C.

[b]Duplicate reaction gave 90.8 ± 0.2% 1-butene, 3.3 ± 0.1% trans-2-butene, 5.9 ± 0.1% cis-2-butene; analyzed on dioctylphthalate column.

Table 24. Product analysis of the elimination of (-)-2-butyltrimethylammonium iodide with (-)-potassium sec-butoxide/sec-butyl alcohol[a]

| Injection | 1-butene Peak Area | 1-butene % | 2-butene Peak Area | 2-butene % |
|---|---|---|---|---|
| 1 | 337 | 91.0 | 34 | 9.0 |
| 2 | 348 | 91.1 | 34 | 8.9 |
| 3 | 337 | 92.0 | 29 | 8.0 |
| 4 | 360 | 90.4 | 38 | 9.6 |
| Aver. per cent | | 91.1 ± 0.4 | | 8.9 ± 0.4 |
| | trans-2-butene | | cis-2-butene | |
| 5 | 41 | 38.3 | 66 | 61.7 |
| 6 | 68 | 37.9 | 110 | 62.1 |
| 7 | 50 | 36.2 | 88 | 63.8 |
| 8 | 44 | 35.5 | 80 | 64.5 |
| Aver. per cent | | 37.0 ± 1.1 | | 63.0 ± 1.1 |

[a]0.20 g. (0.82 mmole) (-)-quaternary ammonium salt, ($[\alpha]_D^{25}$ - 6.45° in ethanol), 2.00 ml. of (-)- 0.44 M base (43% optically pure ); analyzed on dioctylphthalate column.

Table 25. Product analysis of the elimination of (+)-2-methyl-3-hexanol p-toluenesulfonate with (+)-potassium sec-butoxide/sec-butyl alcohol[a,b,c]

| Injection | 2-methyl-2-hexene Peak Area | % | trans-2-methyl-3-hexene Peak Area | % |
|---|---|---|---|---|
| 1 | 142 | 78.5 | 38 | 21.5 |
| 2 | 131 | 80.5 | 31 | 19.5 |
| 3 | 346 | 80.2 | 85 | 19.8 |
| 4 | 327 | 79.4 | 85 | 20.6 |
| Aver. per cent | | 79.8 ± 0.7 | | 20.2 ± 0.7 |

[a]0.66 g. (2.46 mmole) p-toluenesulfonate, 2.00 ml. of 2.0 M base.

[b]Products collected by extraction with ether.

[c]Duplication reaction gave 79.5 ± 0.3% 2-methyl-2-hexene and 20.5 ± 0.3% 2-methyl-3-hexene; products collected by distillation of reaction mixture.

Table 26. Product analysis of the elimination of (+)-2-methyl-3-hexanol p-toluenesulfonate with (+)-potassium sec-butoxide/sec-butyl alcohol[a,b]

| Injection | 2-methyl-2-hexene Peak Area | % | trans-2-methyl-3-hexene Peak Area | % |
|---|---|---|---|---|
| 1 | 181 | 79.4 | 47 | 20.6 |
| 2 | 146 | 80.2 | 36 | 19.8 |
| 3 | 132 | 79.5 | 34 | 20.5 |
| Aver. per cent | | 79.7 ± 0.3 | | 20.3 ± 0.3 |

[a]0.81 g. (3.01 mmoles) (+)-p-toluenesulfonate (90-100% optically pure), 4.00 ml. of 1.0 M (+)-base (83% optically pure).

[b]Products collected by extraction with ether.

Table 27. Product composition from the elimination of (+)-2-methyl-3-hexanol p-toluenesulfonate with (-)-potassium sec-butoxide/sec-butyl alcohol[a,b]

| Injection | 2-methyl-2-hexene Peak Area | % | trans 2-methyl-3-hexene Peak Area | % |
|---|---|---|---|---|
| 1 | 195 | 80.6 | 47 | 19.4 |
| 2 | 200 | 79.4 | 52 | 20.6 |
| 3 | 164 | 80.0 | 41 | 20.0 |
| 4 | 174 | 78.8 | 47 | 21.2 |
| Aver. per cent | | 79.7 ± 0.4 | | 20.3 ± 0.4 |

[a]0.79 g. (2.94 mmoles) p-toluenesulfonate (90-100% optically pure), 4.00 ml. of 1.0 M (-)-base (89% optically pure).

[b]Products collected by extraction with ether.

## Procedures for Asymmetric Induction Reactions

2-Butyltrimethylammonium iodide A solution of 2.05 g. (8.44 mmoles) of the salt was prepared in 4 ml. of (-)-2-butanol (46% optically pure), and 4 ml. of 1.1 M (-)-potassium sec-butoxide/sec-butyl alcohol (46% optically pure) was pipetted into the solution. The reaction mixture was refluxed for 30 min. During this time, potassium iodide and trimethylamine were produced. Most of the solvent was then distilled from the reaction mixture. The residue was rinsed with ether, and unreacted quaternary ammonium salt was dissolved in hot iso-propyl alcohol and crystallized from iso-propyl alcohol/ether; weight recovered 1.13 g., m.p. 271.5-272.5°C, $\alpha_D^{26} = 0$ (0.39 g. in 4 ml. 95% ethanol).

2-Methyl-3-hexyltrimethylammonium iodide

The salt, 6.30 g. (2.20 mmole), was added to 1.0 ml. of 1.0 M (-)-potassium sec-butoxide/sec butyl alcohol (89% optically pure). The heterogeneous mixture was refluxed for 20 min. Five milliliters of ether were added and the solid salts were filtered. The quaternary ammonium salt was extracted from the solid with hot chloroform. The chloroform solution was filtered, and the salt was precipitated by adding ether. It was filtered, rinsed with ether, and dried; yield 0.40 g., $\alpha_D^{26} = 0$ (0.40 g. in 4 ml. 95% ethanol).

3-Methyl-3-bromohexane

Elimination with (-) base A solution of 5.58 g. (31.0 mmoles) of the bromide was prepared in 9.4 mol. of 1.1 M (-)-potassium sec-butoxide/ sec-butyl alcohol (42% optically pure). The reaction occurred very rapidly at reflux temperature with the precipitation of potassium bromide; refluxing was continued for 30 min. The mixture was distilled to collect 2 ml. of a liquid boiling at 74-78°/626 mm. G.P.C. analysis (5 ft., 20% SE-30 column at 100°) showed the distillate to contain volatile olefins, sec-butyl alcohol, and unreacted bromide). The distillate was shaken twice with water to remove sec-butyl alcohol, and the optical rotation was measured on the neat liquid, $\alpha_D^{26}$ + 0.89 ± 0.06°. Approximately 0.1 g. of sodium was added to the remaining reaction mixture followed by refluxing for a few minutes and distillation of 2 ml. of the mixture, which was worked up as before, $\alpha_D^{26}$ + 1.12 ± 0.08°. Another 0.1 g. of sodium was added to the reaction mixture followed again by refluxing, distillation, and workup, $\alpha_D^{26}$ + 1.00 ± 0.07°.

Elimination with (+)-base 3-Methyl-3-bromohexane, 10.8 g. (66.0 mmole), was reacted with 10 ml. of 3.7 M (+)-potassium sec-butoxide/sec-butyl alcohol (81.4% optical purity) and worked up as before to isolate bromide (and olefins), $\alpha_D^{26}$ - .77 ± 0.10°. $\alpha_D^{26}$ - 1.29 ± 0.10° and $\alpha_D^{26}$ - 0.29 ± 0.11° after further reaction.

2-Phenyl-1-propanol p-toluenesulfonate

A solution of 3.00 g. (10.4 mmole) of the p-toluenesulfonate and 2 ml. of 2.5 M (-)-potassium sec-butoxide/sec-butyl alcohol (88% optically pure) was prepared in a one centimeter-diameter pyrex tube, which was then sealed and placed in a 50°C heat bath for 21 hours. The tube was cooled, opened, and the reaction mixture poured into ether. The insoluble potassium p-toluenesulfonate was filtered from the solution, weight 0.92 g. (88% from base). Skellysolve-B was added to the ether solution, followed by cooling to crystallize unreacted p-toluenesulfonate; weight recovered 0.94 g., m.p. 46-47°C, $\alpha_D^{26}$ 0 (0.824 g. in 4 ml. 95% ethanol).

## Procedures and Data for Kinetic Measurements

### Procedures

The elimination reactions conducted for kinetic analyses were carried out in 20 ml. glass ampules prepared from 18 x 150 mm. pyrex test tubes or in 100 ml. volumetric flasks.

Eliminations in ampules The p-toluenesulfonate or bromide was weighed accurately into a 100 ml. volumetric flask. The compound

was dissolved in 25 ml. to 75 ml. of anhydrous ethanol or tert-butyl alcohol at room temperature (26-27°C). The solution was diluted to 100 ml. with sodium ethoxide/ethanol or potassium tert-butoxide/tert-butyl alcohol solution and shaken thoroughly. Nine 10 ml. aliquots were immediately pipetted into ampules. The ampules were immersed in ice water and sealed when the contents were cold. They were then placed in the constant termperature bath. Upon equilibration to bath temperature an ampule was removed, broken, and the contents run into ice-cold ethanol. The timer was turned on as the ampule drained. The ampule was thoroughly rinsed with ethanol into the cold ethanol solution which was then titrated with standard hydrochloric acid solution to determine the zero point concentration of base. The solutions were titrated to yellow using an ethanol solution of phenophthalein, bromphenol blue, and methyl orange as indicator. This indicator exhibited a sharper and more accurate endpoint than phenophthalein in ethanol. To follow the rate of the reaction, ampules were opened and the contents were titrated at various intervals of time during the reaction. One was opened after several hours or days, depending on the rate of the reaction, to determine the base concentration (infinity point concentration) at the end of the reaction.

Eliminations in flasks Eliminations whose rate constants were greater than $10^{-2}$ were conducted in the 100 ml. volumetric flasks in which the reaction solutions were prepared. This was done to minimize consumption of the reactants before the zero point base concentration was measured. The substrate was dissolved in the desired

amount of solvent at room temperature as before. The solution was equilibrated to reaction temperature, followed by dilution to 100 ml. with base solution that had also been equilibrated to reaction temperature. After thorough mixing and re-equilibration, 10 ml. aliquots were withdrawn from the flask during the reaction with a warmed pipette, quenched in ice-cold ethanol, and titrated. The eliminations of 1-phenyl-1-bromoethane were run in the flasks but the formation of styrene was followed with the ultraviolet spectrophotometer rather than the consumption base titrimetrically. In this case 5 ml. aliquots were removed from the reaction solution during the reaction, diluted to 100 ml. with 95% ethanol, and the absorptions of the resulting solutions were measured. A 10 ml. aliquot was also removed during the reaction and titrated to determine base concentration.

Calculation of rate constants The rate constants were calculated from the second-order rate expression:

$$k_2 = \frac{2.303}{t(a-b)} \log \frac{b}{a} \left(\frac{a-x}{b-x}\right) \qquad (14)$$

where $k_2$ = rate constant (liter·mole$^{-1}$·sec$^{-1}$)

t = time elapsed (sec.)

a = zero point base concentration (moles·liter$^{-1}$)

b = zero point substrate concentration (moles·liter$^{-1}$)

x = base and substration concentration at t (moles·liter$^{-1}$)

The rates were also calculated using the method of least squares with an IBM 7044 computer. The eliminations of 1-phenyl-1-bromoethane were conducted using a very large excess of base; thus, the pseudo

first order rate constant was calculated from the expression:

$$k_1 = \frac{2.303}{t} \log \frac{A_\infty - A_o}{A_\infty - A_t} \qquad (15)$$

where $k_1$ = pseudo first order rate constant ($sec^{-1}$)

$t$ = time elapsed (sec.)

$A_o$ = UV absorbance of reaction at zero time

$A_t$ = UV absorbance of reaction at t

$A_\infty$ = UV absorbance of reaction at infinity point

Second order rate constants were determined by dividing the pseudo first order rate by the base concentration.

Corrections The observed infinity point volumes of hydrochloric acid delivered for the slower reactions ($k_2 = 10^{-6} - 10^{-3}$) agreed well with the calculated values (0.5 - 4.0% deviation). When $k_2 > 10^{-3}$, however, the deviations were generally larger (2.8 - 40%). This was attributed to the consumption of reactants before equilibration of the solutions to reaction temperature. For deviations greater than about 1% the concentration of substrate was calculated from the zero point and infinity point volumes:

$$\text{corrected conc. of substrate} = \frac{(V_{o\,HCl} - V_{\infty HCl})(N_{HCl})}{\text{vol. of aliquot}} \qquad (16)$$

The corrected concentrations generally resulted in more precise rate constants.

The yields of olefin for eliminations of the 2-phenyl-1-propyl system and 1-phenyl-1-bromoethane were determined by diluting the last aliquot 1000 fold (20 fold for the latter system) with 95%

ethanol and measuring the absorbance on the UV spectrophotometer in 1 cm. cells. The extinction coefficients used to calculate the concentrations of the styrene products are listed in Table 28.

Table 28. Ultraviolet absorption data for products of elimination reactions in 95% ethanol

| Compound | $\lambda_{max}$ (mμ) | ε |
|---|---|---|
| 2-phenylpropene | 243 | 11,400 |
| 2-(p-chlorophenyl)propene | 248 | 15,700 |
| 2-(m-bromophenyl)propene | 245 | 10,700 |
| 2-(p-methylphenyl)propene | 248 | 13,700 |
| 2-(p-methoxyphenyl)propene | 257 | 16,200 |
| styrene[a] | 248 | 13,800 |

[a]Reference 43.

The products from eliminations of 2-phenyl-3-buten-1-yl compounds were analyzed by injecting samples of the reaction mixtures at the end of the reactions on the GPC using a 10 ft., 28% β,β'-oxypropionitrile column at 90°C. Only one product was observed for these eliminations for a given compound. The retention time of the product was the same for eliminations with ethoxide and tert-butoxide, eliminating the possibility of it being a substitution product. The 2-phenyl-3-buten-1-ol p-toluenesulfonates were eliminated on a large scale, and the products were isolated. All three compounds (p-H, p-Cl, and p-$CH_3$) showed strong absorptions in their IR spectra at

910 $cm^{-1}$ and 990 $cm^{-1}$, indicating terminal vinyl groups, $RCH=CH_2$, and at 890 $cm^{-1}$, indicating terminal methylene groups, $R_2C=CH_2$. This confirmed that the compounds were the 2-phenyl-1,3-butadiene products, $CH_2=C(Y\text{-}C_6H_5)\text{-}CH=CH_2$. The eliminations of the 3-buten-1-yl bromide and p-toluenesulfonate with ethoxide showed a trace of product other than 1,3-butadiene upon analysis on the β,β'-oxypropionitrile column. This might have been substitution product.

For the eliminations run in ampules at 50°C, a temperature correction was necessary because the solutions were prepared at room temperature (26-27°C) but run at 50°C. The resulting expansion of the solutions decreased the concentration of the reactants. Simple calculations show that, if the volume increased by a factor of "α," the actual rate constant would be $\alpha \cdot k_2 obs$. The value of α was determined by filling a 100 ml. volumetric flask to volume with solvent, equilibrating to 50°C, and marking the new volume. The flask was emptied, dried, and filled with water at room temperature to the 100 ml. mark, followed by addition of water from a burette to the marked level to determine ΔV. ΔV (26°-50°) was +2.34 ± 0.11 ml. for 95% ethanol, +2.38 ± 0.05 ml. for 0.28M ethoxide/ethanol, +3.12 ± 0.07 ml. for tert-butyl alcohol, and +2.86 ± 0.08 ml. for 0.2M tert-butoxide tert-butyl alcohol. Including correction for thermal expansion of the flask, α is then:

$$\alpha = (1.001)\left(\frac{100 \text{ ml.} + \Delta V}{100 \text{ ml.}}\right) \qquad (17)$$

For all of the titrimetric rate measurements the same 10 ml. pipette was used. This pipette was calibrated by delivering samples of absolute ethanol and tert-butyl alcohol at 26°C into vials in the same manner used during the runs. The samples were accurately weighed, and from the densities of the alcohols the volumes delivered were calculated. They were 10.16 ml. for tert-butyl alcohol and 10.20 ml. for ethanol.

Data

The kinetic data are reported in Tables 29-77. The second order rate constants in liter·mole$^{-1}$·sec$^{-1}$ are given for each point of the runs. Also included in the tables are the averages of these constants and the values corrected for volume expansion and pipette errors. At the bottom of the tables are given the substrate concentrations, the corrected computer rates, the observed and calculated infinity points in milliliters, the corrected rates of duplicate runs, and the yields of olefin.

Table 29. 2-Phenylpropan-1-ol p-toluenesulfonate, 49.83°C, 0.1009 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 10.20 | | |
| 3462 | 10.00 | 0.0204 | 1.926 |
| 12192 | 9.57 | 0.0715 | 1.925 |
| 30426 | 8.80 | 0.1978 | 2.130 |
| 66840 | 8.02 | 0.4264 | 2.089 |
| 85140 | 7.76 | 0.5586 | 2.149 |
| 100200 | 7.60 | 0.6719 | 2.296 |
| Aver. rate[a,b,c] | | | 2.07 ± 0.10 |
| Corrected rate | | | 2.17 ± 0.10 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0306 M, computer rate = 2.29 ± 0.02, infinity point: observed 7.11, calculated 7.05.

[b] Duplicate run gave $k_2$ = 2.36 ± 0.03, computer rate = 2.36 ± 0.02.

[c] Average yield of olefin 92%.

Table 30. 2-Phenylpropan-1-ol p-toluenesulfonate, 49.83°C, 0.1420 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 14.35 | | |
| 10740 | 14.00 | 0.0394 | 7.661 |
| 24924 | 13.58 | 0.0955 | 8.000 |
| 44214 | 13.16 | 0.1644 | 7.761 |
| 84840 | 12.49 | 0.1379 | 7.820 |
| 167340 | 11.73 | 0.6541 | 8.157 |
| Aver. rate[a,b,c] | | | 7.88 ± 0.16 |
| Corrected rate | | | 8.24 ± 0.17 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0317 M, computer rate = 8.95 ± 0.11, infinity point: observed 11.20, calculated 11.15.

[b] Duplicate run gave $k_2$ = 8.20 ± 0.13, computer rate = 8.42 ± 0.02.

[c] Average yield of olefin 64%.

Table 31. 2-(p-Chlorophenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.0940 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 9.50 | | |
| 1854 | 9.15 | 0.0334 | 6.687 |
| 4800 | 8.70 | 0.0857 | 6.621 |
| 9684 | 8.10 | 0.1778 | 6.813 |
| 17328 | 7.50 | 0.3172 | 6.772 |
| 33864 | 6.85 | 0.6050 | 6.631 |
| 71040 | 6.40 | 1.233 | 6.440 |
| Aver. rate[a,b,c] | | | 6.66 ± 0.10 |
| Corrected rate | | | 6.92 ± 0.10 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0319 M, computer rate = 7.26 ± 0.03, infinity point: observed 6.30, calculated 6.28.

[b] Duplicate run gave $k_2$ = 7.18 ± 0.17, computer rate = 7.70 ± 0.11.

[c] Average yield of olefin 100%.

Table 32. 2-(p-Chlorophenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.1401 M sodium ethoxide/ethanol.

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 14.16 | | |
| 2480 | 13.95 | 0.0237 | 2.018 |
| 7236 | 13.57 | 0.0715 | 2.091 |
| 14850 | 13.08 | 0.1474 | 2.101 |
| 25686 | 12.57 | 0.2524 | 2.079 |
| 56238 | 11.74 | 0.5493 | 2.067 |
| 91620 | 11.33 | 0.8851 | 2.044 |
| Aver. rate[a,b,c] | | | 2.07 ± 0.02 |
| Corrected rate | | | 2.16 ± 0.03 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0313 M, computer rate = 2.14 ± 0.01, infinity point: observed 11.00, calculated 11.11.

[b] Duplicate run gave $k_2$ = 2.21 ± 0.07, computer rate = 2.10 ± 0.01.

[c] Average yield of olefin 64%.

Table 33. 2-(m-Bromophenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.0953 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 9.40 | | |
| 1445 | 8.74 | 0.0686 | 1.739 |
| 2908 | 8.20 | 0.1449 | 1.826 |
| 5137 | 7.61 | 0.2641 | 1.879 |
| 7392 | 7.28 | 0.3608 | 1.788 |
| 11004 | 6.90 | 0.5257 | 1.750 |
| 18114 | 6.49 | 0.8818 | 1.784 |
| Aver. rate[a,b,c] | | | 1.80 ± 0.04 |
| Corrected rate | | | 1.88 ± 0.04 |

[a] $N_{HCl}$ = 0.1014, conc. of p-toluenesulfonate = 0.0325 M, computer rate = 1.90 ± 0.01, infinity point: observed 6.20, calculated 5.96.

[b] Duplicate run gave $k_2$ = 1.79 ± 0.02, computer rate = 1.80 ± 0.02.

[c] Average yield of olefin 96%.

Table 34. 2-(m-Bromophenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.1430 M sodium ethoxide/ethanol

| | | | |
|---|---|---|---|
| 0 | 14.45 | | |
| 1018 | 14.30 | 0.0145 | 3.030 |
| 4104 | 13.87 | 0.0611 | 3.160 |
| 7962 | 13.40 | 0.1225 | 3.267 |
| 14100 | 12.80 | 0.2253 | 3.393 |
| 21924 | 12.32 | 0.3401 | 3.294 |
| Aver. rate[a,b,c] | | | 3.23 ± 0.11 |
| Corrected rate | | | 3.38 ± 0.11 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0325 M, computer rate = 3.49 ± 0.03, infinity point: observed 10.96, calculated 10.91.

[b] Duplicate run gave $k_2$ = 3.45 ± 0.05, computer rate = 3.54 ± 0.01.

[c] Average yield of olefin 75%.

Table 35. 2-(m-Bromophenyl)-2-deuteropropane-1-ol toluenesulfonate, 49.83°C, 0.0803 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 8.11 | | |
| 6732 | 7.75 | 0.0449 | 2.819 |
| 14934 | 7.37 | 0.1038 | 2.936 |
| 26262 | 7.00 | 0.1784 | 2.869 |
| 32814 | 6.85 | 0.2146 | 2.762 |
| 65580 | 6.23 | 0.4434 | 2.856 |
| 75300 | 6.06 | 0.5481 | 3.074 |
| Aver. rate[a,b,c] | | | 2.89 ± 0.08 |
| Corrected rate | | | 3.02 ± 0.08 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0257 M, computer rate = 3.16 ± 0.06, infinity point: observed 5.51, calculated 5.48.

[b] Duplicate run gave $k_2$ = 3.26 ± 0.05, computer rate = 3.74 ± 0.07.

[c] Average yield of olefin 90%.

Table 36. 2-(m-Bromophenyl)-2-deuteropropane-1-ol p-toluenesulfonate, 49.83°C, 0.1451 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 14.66 | | |
| 6582 | 13.38 | 0.0366 | 1.105 |
| 15774 | 14.00 | 0.0903 | 1.136 |
| 28812 | 13.60 | 0.1617 | 1.114 |
| 55908 | 12.95 | 0.3245 | 1.152 |
| 87540 | 12.50 | 0.5073 | 1.151 |
| 103920 | 12.35 | 0.5948 | 1.137 |
| Aver. rate[a,b,c] | | | 1.13 ± 0.02 |
| Corrected rate | | | 1.19 ± 0.02 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0291 M, computer rate = 1.20 ± 0.01, infinity point: observed 11.72, calculated 11.89.

[b] Duplicate run gave $k_2$ = 1.35 ± 0.04, computer rate = 1.36 ± 0.01.

[c] Average yield of olefin 44%.

Table 37. 2-(p-Methylphenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.1538 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 15.54 | | |
| 9576 | 14.60 | 0.0350 | 10.043 |
| 21540 | 13.67 | 0.0777 | 9.903 |
| 37902 | 12.68 | 0.1370 | 9.922 |
| 77760 | 11.12 | 0.2817 | 9.944 |
| 107520 | 10.45 | 0.3817 | 9.745 |
| 165360 | 9.60 | 0.5898 | 9.791 |
| Aver. rate[a,b,c] | | | 9.89 ± 0.10 |
| Corrected rate | | | 10.4 ± 0.10 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0699 M, computer rate = 10.2 ± 0.03, infinity point: observed 8.44, calculated 8.48.

[b] Duplicate run gave $k_2$ = 10.7 ± 0.3, computer rate = 10.4 ± 0.02.

[c] Average yield of olefin 90%.

Table 38. 2-(p-Methylphenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.2382 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | | | |
| 8538 | 23.24 | 0.0410 | 6.482 |
| 18396 | 22.50 | 0.0842 | 6.178 |
| 33270 | 21.51 | 0.1550 | 6.287 |
| 69120 | 19.96 | 0.3185 | 6.217 |
| 111300 | 18.84 | 0.5244 | 6.356 |
| Aver. rate[a,b,c] | | | 6.30 ± 0.09 |
| Corrected rate | | | 6.59 ± 0.10 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0676 M, computer rate = 6.65 ± 0.04, infinity point: observed 17.10, calculated 17.25

[b] Duplicate run gave $k_2$ = 6.32 ± 0.17, computer rate = 6.64 ± 0.04.

[c] Average yield of olefin 41%.

Table 39. 2-(p-Methylphenyl)-2-deuteropropane-1-ol p-toluenesulfonate, 49.83°C, 0.1105 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 11.72 | | |
| 40320 | 10.89 | 0.0128 | 2.152 |
| 81600 | 10.63 | 0.0302 | 2.204 |
| 172320 | 10.11 | 0.0626 | 2.344 |
| 247680 | 9.80 | 0.1405 | 2.318 |
| 344040 | 9.50 | 0.2705 | 2.260 |
| Aver. rate[a,b,c] | | | 2.26 ± 0.06 |
| Corrected rate | | | 2.36 ± 0.07 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0304 M, computer rate = 2.40 ± 0.02, infinity point: observed 8.40, calculated 8.10.

[b] No duplicate run.

[c] Yield of olefin 64%.

Table 40. 2-(p-Methylphenyl)-2-deuteropropane-1-ol p-toluenesulfonate, 49.83°C, 0.2100 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 21.22 | | |
| 44196 | 20.24 | 0.1440 | 4.188 |
| 80520 | 19.68 | 0.2641 | 4.215 |
| 99840 | 19.46 | 0.3251 | 4.184 |
| 130860 | 19.16 | 0.4277 | 4.200 |
| 166980 | 18.89 | 0.5506 | 4.238 |
| 169980 | 18.88 | 0.5594 | 4.230 |
| Aver. rate[a,b,c] | | | 4.21 ± 0.02 |
| Corrected rate | | | 4.40 ± 0.02 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0308 M, computer rate = 4.42 ± 0.01, infinity point: observed 18.00, calculated 18.11.

[b] No duplicate run.

[c] Yield of olefin 15%.

Table 41. 2-(p-Methoxyphenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.1545 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 15.61 | | |
| 8148 | 15.11 | 0.0253 | 7.416 |
| 26730 | 14.10 | 0.0853 | 7.618 |
| 46710 | 13.31 | 0.1471 | 7.518 |
| 72360 | 12.50 | 0.2320 | 7.654 |
| 114960 | 11.60 | 0.3713 | 7.712 |
| 169500 | 10.85 | 0.5677 | 8.000 |
| Aver. rate[a,b,c] | | | 7.65 ± 0.14 |
| Corrected rate | | | 8.01 ± 0.14 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0580 M, computer rate = 8.39 ± 0.07, infinity point: observed 9.70, calculated 9.75.

[b] Duplicate run gave $k_2$ = 7.96 ± 0.12, computer rate = 8.13 ± 0.005.

[c] Average yield of olefin 80%.

Table 42. 2-(p-Methoxyphenyl)propan-1-ol p-toluenesulfonate, 49.83°C, 0.1832 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 18.51 | | |
| 20358 | 17.48 | 0.1096 | 8.543 |
| 36678 | 16.84 | 0.2240 | 9.692 |
| 73380 | 15.95 | 0.4108 | 8.886 |
| 87720 | 15.72 | 0.4900 | 8.864 |
| 106020 | 15.47 | 0.6000 | 8.982 |
| 124260 | 15.30 | 0.6984 | 8.919 |
| Aver. rate[a,b,c] | | | 8.98 ± 0.24 |
| Corrected rate | | | 9.39 ± 0.25 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0381 M, computer rate = 9.92 ± 0.04, infinity point: observed 14.65, calculated 14.73.

[b] Duplicate run gave $k_2$ = 9.54 ± 0.38, computer rate = 10.0 ± 0.1.

[c] Average yield of olefin 28%.

Table 43. 2-Phenyl-1-bromopropane, 49.83°C, 0.0624 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 6.30 | | |
| 654 | 5.84 | 0.0370 | 4.118 |
| 1558 | 5.35 | 0.0878 | 4.097 |
| 3327 | 4.70 | 0.1881 | 4.112 |
| 4940 | 4.32 | 0.2783 | 4.097 |
| 8178 | 3.91 | 0.4328 | 3.849 |
| 11142 | 3.66 | 0.5930 | 3.871 |
| Aver. rate[a,b,c] | | | 4.02 ± 0.11 |
| Corrected rate | | | 4.21 ± 0.11 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0307 M, computer rate = 4.00 ± 0.04, infinity point: observed 3.20, calculated 3.02.

[b] Duplicate run gave $k_2$ = 4.39 ± 0.13, computer rate = 4.21 ± 0.02.

[c] Average yield of olefin 100%.

Table 44. 2-Phenyl-1-bromopropane, 49.83°C, 0.0675 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 6.82 | | |
| 1538 | 6.41 | 0.0342 | 1.404 |
| 4952 | 5.70 | 0.1143 | 1.455 |
| 8508 | 5.20 | 0.1987 | 1.473 |
| 15468 | 4.63 | 0.3539 | 1.443 |
| 22362 | 4.30 | 0.5097 | 1.437 |
| 26994 | 4.15 | 0.6165 | 1.440 |
| Aver. rate[a,b,c] | | | 1.44 ± 0.12 |
| Corrected rate | | | 1.51 ± 0.16 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0310 M, computer rate = 1.50 ± 0.00, infinity point: observed 3.69, calculated 3.68.

[b] Duplicate run gave $k_2$ = 1.45 ± 0.02, computer rate = 1.40 ± 0.01.

[c] Average yield of olefin 100%.

Table 45. 2-(p-Chlorophenyl)-1-bromopropane, 49.83°C, 0.0752 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 7.60 | | |
| 409 | 6.91 | 0.0874 | 1.013 |
| 728 | 6.50 | 0.1608 | 1.048 |
| 1207 | 6.07 | 0.2679 | 1.052 |
| 1860 | 5.70 | 0.4072 | 1.038 |
| 2960 | 5.30 | 0.6822 | 1.093 |
| 5285 | 5.01 | 1.249 | 1.120 |
| Aver. rate[a,b,c] | | | 1.06 ± 0.03 |
| Corrected rate | | | 1.08 ± 0.03 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0266 M, computer rate = 1.15 ± 0.01, infinity point: observed 4.91, calculated 4.71.

[b] Duplicate run gave $k_2$ = 1.13 ± 0.04, computer rate = 1.20 ± 0.01.

[c] Average yield of olefin 100%.

Table 46. 2-(p-Chlorophenyl)-1-bromopropane, 49.83°C, 0.0646 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 6.53 | | |
| 601 | 5.94 | 0.0515 | 5.788 |
| 1381 | 5.37 | 0.1202 | 5.877 |
| 2341 | 4.90 | 0.2025 | 5.838 |
| 4057 | 4.37 | 0.3506 | 5.834 |
| 6474 | 3.98 | 0.5496 | 5.732 |
| Aver. rate[a,b,c] | | | 5.81 ± 0.03 |
| Corrected rate | | | 6.09 ± 0.03 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0305 M, computer rate = 5.98 ± 0.03, infinity point: observed 3.45, calculated 3.16.

[b] Duplicate run gave $k_2$ = 6.21 ± 0.07, computer rate = 5.97 ± 0.04.

[c] Average yield of olefin 97%.

Table 47. 2-(m-Bromophenyl)-1-bromopropane, 49.83°C, 0.0594 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 6.00 | | |
| 518 | 5.00 | 0.1393 | 1.805 |
| 772 | 4.70 | 0.2074 | 1.803 |
| 1062 | 4.41 | 0.2965 | 1.873 |
| 1633 | 4.05 | 0.4691 | 1.928 |
| 2939 | 3.69 | 0.8491 | 1.939 |
| Aver. rate[a,b,c] | | | 1.87 ± 0.05 |
| Corrected rate | | | 1.90 ± 0.05 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0250 M, computer rate = 2.01 ± 0.01, infinity point: observed 3.47, calculated 3.14.

[b] Duplicate run gave $k_2$ = 2.01 ± 0.06, computer rate = 2.09 ± 0.01.

[c] Average yield of olefin 98%.

Table 48. 2-(m-Bromophenyl)-1-bromopropane, 49.83°C, 0.0896 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 9.05 | | |
| 336 | 8.34 | 0.0788 | 0.906 |
| 693 | 7.78 | 0.1661 | 0.927 |
| 1104 | 7.27 | 0.2815 | 0.986 |
| 1766 | 6.74 | 0.4784 | 1.047 |
| 2432 | 6.48 | 0.6431 | 1.022 |
| 3065 | 6.29 | 0.8375 | 1.056 |
| Aver. rate[a,b,c] | | | 0.991 ± 0.051 |
| Corrected rate | | | 1.01 ± 0.05 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0304 M, computer rate = 1.10 ± 0.01, infinity point: observed 5.98, calculated 5.71.

[b] Duplicate run gave $k_2$ = 1.07 ± 0.03, computer rate = 1.13 ± 0.01.

[c] Average yield of olefin 100%.

Table 49. 2-(m-Bromophenyl)-2-deutero-1-bromopropane, 49.83°C, 0.0560 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 5.66 | | |
| 964 | 5.23 | 0.0249 | 2.625 |
| 2252 | 4.80 | 0.0561 | 2.532 |
| 4535 | 4.24 | 0.1119 | 2.611 |
| 6882 | 3.80 | 0.1758 | 2.595 |
| 9852 | 3.46 | 0.2458 | 2.534 |
| 14064 | 3.12 | 0.3501 | 2.529 |
| Aver. rate[a,b,c] | | | 2.57 ± 0.04 |
| Corrected rate | | | 2.69 ± 0.04 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0334 M, computer rate = 2.64 ± 0.01, infinity point: observed 2.29, calculated 2.21.

[b] No duplicate run.

[c] Yield of olefin 100%.

Table 50. 2-(m-Bromophenyl)-2-deutero-1-bromopropane, 49.83°C, 0.0931 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 9.41 | | |
| 1621 | 8.86 | 0.0745 | 1.583 |
| 3615 | 8.38 | 0.1629 | 1.553 |
| 5591 | 8.01 | 0.2553 | 1.573 |
| 7242 | 7.79 | 0.3268 | 1.555 |
| 8088 | 7.70 | 0.3612 | 1.539 |
| 9912 | 7.51 | 0.4478 | 1.557 |
| Aver. rate[a,b,c] | | | 1.56 ± 0.01 |
| Corrected rate | | | 1.63 ± 0.01 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0263 M, computer rate = 1.61 ± 0.00, infinity point: observed 6.75, calculated 6.75.

[b] No duplicate run.

[c] Yield of olefin 99%.

Table 51. 2-(p-Methylphenyl)-1-bromopropane, 49.83°C, 0.0470 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 4.75 | | |
| 1192 | 4.48 | 0.0233 | 2.063 |
| 2965 | 4.17 | 0.0554 | 1.976 |
| 6018 | 3.90 | 0.0906 | 1.593 |
| 10398 | 3.36 | 0.1917 | 1.950 |
| 15570 | 3.01 | 0.3099 | 2.106 |
| 20400 | 2.86 | 0.3662 | 1.899 |
| Aver. rate[a,b,c] | | | 2.00 ± 0.05 |
| Corrected rate | | | 2.09 ± 0.05 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0252 M, computer rate = 2.05 ± 0.05, infinity point: observed 2.20, calculated 2.16.

[b] Duplicate run gave $k_2$ = 2.25 ± 0.06, computer rate = 2.16 ± 0.01.

[c] Average yield of olefin 100%.

Table 52. 2-(p-Methylphenyl)-1-bromopropane, 49.83°C, 0.1397 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 14.12 | | |
| 2167 | 13.50 | 0.0881 | 8.387 |
| 5610 | 12.81 | 0.2276 | 8.364 |
| 7506 | 12.51 | 0.3128 | 8.593 |
| 10134 | 12.22 | 0.4205 | 8.553 |
| 14514 | 11.88 | 0.6060 | 8.605 |
| 21492 | 11.60 | 0.8749 | 8.392 |
| Aver. rate[a,b,c] | | | 8.48 ± 0.10 |
| Corrected rate | | | 8.87 ± 0.11 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0280 M, computer rate = 8.81 ± 0.05, infinity point: observed 11.29, calculated 11.21.

[b] Duplicate run gave $k_2$ = 9.81 ± 0.18, computer rate = 10.2 ± 0.1.

[c] Average yield of olefin 100%.

Table 53. 2-(p-Methylphenyl)-2-deutero-1-bromopropane, 49.83°C, 0.0846 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 8.55 | | |
| 11508 | 7.90 | 0.0920 | 3.113 |
| 24918 | 7.40 | 0.1945 | 3.040 |
| 43590 | 6.92 | 0.3442 | 3.074 |
| 81600 | 6.41 | 0.6492 | 3.097 |
| 105000 | 6.26 | 0.8234 | 3.053 |
| Aver. rate[a,b,c] | | | 3.08 ± 0.02 |
| Corrected rate | | | 3.22 ± 0.03 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0255 M, computer rate = 3.22 ± 0.01, infinity point: observed 5.95, calculated 5.98.

[b] No duplicate run.

[c] Yield of olefin 99%.

Table 54. 2-(p-Methylphenyl)-2-deutero-1-bromopropane, 49.83°C, 0.0951 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 9.61 | | |
| 13644 | 9.12 | 0.0599 | 1.508 |
| 37890 | 8.46 | 0.1711 | 1.550 |
| 86220 | 7.73 | 0.3795 | 1.511 |
| 111480 | 7.51 | 0.4812 | 1.482 |
| 166020 | 7.18 | 0.7229 | 1.495 |
| 217980 | 7.01 | 0.9523 | 1.500 |
| Aver. rate[a,b,c] | | | 1.51 ± 0.02 |
| Corrected rate | | | 1.58 ± 0.02 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0280 M, computer rate = 1.56 ± 0.00, infinity point: observed 6.78, calculated 5.54.

[b] No duplicate run.

[c] Yield of olefin 94%.

Table 55. 2-(p-Methoxyphenyl)-1-bromopropane, 49.83°C, 0.0486 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 4.91 | | |
| 5182 | 4.19 | 0.0853 | 1.533 |
| 10566 | 3.73 | 0.1626 | 1.433 |
| 18540 | 3.33 | 0.2945 | 1.479 |
| 29550 | 3.02 | 0.4595 | 1.432 |
| 40950 | 2.80 | 0.6608 | 1.503 |
| Aver. rate[a,b,c] | | | 1.48 ± 0.04 |
| Corrected rate | | | 1.55 ± 0.04 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0239 M, computer rate = 1.60 ± 0.02, infinity point: observed 2.52, calculated 2.44.

[b] Duplicate run gave $k_2$ = 1.54 ± 0.06, computer rate = 1.46 ± 0.02.

[c] Average yield of 96%.

Table 56. 2-(p-Methoxyphenyl)-1-bromopropane, 49.83°C, 0.0829 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 8.38 | | |
| 3017 | 7.98 | 0.0622 | 7.882 |
| 7440 | 7.54 | 0.1526 | 7.832 |
| 13278 | 7.10 | 0.2835 | 8.159 |
| 20400 | 6.80 | 0.4181 | 7.831 |
| 32280 | 6.48 | 0.6572 | 7.781 |
| 47454 | 6.26 | 1.004 | 8.085 |
| Aver. rate[a,b,c] | | | 7.93 ± 0.13 |
| Corrected rate | | | 8.29 ± 0.13 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0227 M, computer rate = 8.37 ± 0.07, infinity point: observed 6.09, calculated 6.09.

[b] Duplicate run gave $k_2$ = 8.28 ± 0.20, computer rate = 8.26 ± 0.06.

[c] Average yield of olefin 100%.

Table 57. 2-Phenylpropan-1-ol p-toluenesulfonate, 29.80°C, 0.1689 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 17.07 | | |
| 21312 | 16.51 | 0.0418 | 3.664 |
| 46194 | 16.00 | 0.0864 | 3.493 |
| 77460 | 15.41 | 0.1492 | 3.599 |
| 114960 | 14.88 | 0.2199 | 3.573 |
| 161760 | 14.39 | 0.3034 | 3.504 |
| 252660 | 13.70 | 0.4739 | 3.504 |
| Aver. rate[a,b,c] | | | 3.56 ± 0.06 |
| Corrected rate | | | 3.61 ± 0.06 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0457 M, computer rate = 3.58 ± 0.01, infinity point: observed 12.48, calculated 12.48.

[b] Duplicate run gave $k_2$ = 3.66 ± 0.03, computer rate = 3.79 ± 0.01.

[c] Average yield of olefin 93%.

Table 58. 2-Phenyl propan-1-ol p-toluenesulfonate, 29.80°C, 0.1434 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^6$ |
|---|---|---|---|
| 0 | 14.49 | | |
| 33288 | 14.32 | 0.0103 | 7.558 |
| 86460 | 14.05 | 0.0269 | 7.611 |
| 201060 | 13.55 | 0.0622 | 7.559 |
| 261780 | 13.32 | 0.0803 | 7.490 |
| 357720 | 12.98 | 0.1096 | 7.484 |
| 434160 | 12.73 | 0.1339 | 7.533 |
| 542100 | 12.44 | 0.1652 | 7.444 |
| Aver. rate[a,b,c] | | | 7.53 ± 0.04 |
| Corrected rate | | | 7.68 ± 0.04 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0491 M, computer rate = 7.62 ± 0.02, infinity point: not measured, calculated 9.53.

[b] No duplicate run.

[c] Yield of olefin 71%.

Table 59. 2-Phenyl-1-bromopropane, 29.8°C, 0.1557 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 15.73 | | |
| 3330 | 14.32 | 0.1287 | 7.910 |
| 4771 | 13.90 | 0.1827 | 7.836 |
| 5966 | 13.55 | 0.2363 | 8.105 |
| 9078 | 12.96 | 0.3539 | 7.977 |
| 13878 | 12.37 | 0.5352 | 7.894 |
| Aver. rate[a,b,c] | | | 7.94 ± 0.06 |
| Corrected rate | | | 8.07 ± 0.06 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0432 M, computer rate = 8.01 ± 0.04, infinity point: observed 11.37, calculated 10.99.

[b] Duplicate run gave $k_2$ = 7.96 ± 0.28, computer rate = 8.37 ± 0.03.

[c] Average yield of olefin 100%.

Table 60. 2-Phenyl-1-bromopropane, 29.80°C, 0.1326 M sodium ethoxide ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 13.40 | | |
| 10890 | 12.24 | 0.0535 | 1.551 |
| 44922 | 10.11 | 0.2199 | 1.547 |
| 81180 | 9.00 | 0.3943 | 1.535 |
| 101820 | 8.60 | 0.4964 | 1.540 |
| 166440 | 7.90 | 0.8232 | 1.562 |
| Aver. rate[a,b,c] | | | 1.55 ± 0.01 |
| Corrected rate | | | 1.58 ± 0.01 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0597 M, computer rate = 1.60 ± 0.01, infinity point: observed 7.35, calculated 6.37.

[b] Duplicate run gave $k_2$ = 1.56 ± 0.01, computer rate = 1.56 ± 0.01.

[c] Average yield of olefin 100%.

Table 61. Octan-1-ol p-toluenesulfonate, 49.88°C, 0.1160 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 11.72 | | |
| 10656 | 10.60 | 0.0899 | 2.624 |
| 23406 | 9.65 | 0.2044 | 2.714 |
| 29940 | 9.27 | 0.2635 | 2.735 |
| 38520 | 8.92 | 0.3514 | 2.837 |
| 44862 | 8.72 | 0.4069 | 2.820 |
| 74460 | 8.06 | 0.7048 | 2.943 |
| 84300 | 7.95 | 0.7910 | 2.917 |
| Aver. rate[a,b] | | | 2.80 ± 0.09 |
| Corrected rate | | | 2.93 ± 0.10 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0419 M, computer rate = 2.20 ± 0.03, infinity point: not measured, calculated 7.05.

[b] No duplicate run.

Table 62. 1-Bromooctane, 49.88°C, 0.1028 M potassium t-butoxide/ t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^5$ |
|---|---|---|---|
| 0 | 10.39 | | |
| 37386 | 9.93 | 0.0430 | 3.835 |
| 75480 | 9.56 | 0.0846 | 3.739 |
| 165720 | 8.85 | 0.1906 | 3.837 |
| 253320 | 8.38 | 0.2920 | 3.846 |
| 337020 | 8.08 | 0.3804 | 3.766 |
| 426660 | 7.81 | 0.4870 | 3.808 |
| Aver. rate[a,b] | | | 3.81 ± 0.03 |
| Corrected rate | | | 3.98 ± 0.04 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0338 M, computer rate = 4.00 ± 0.02, infinity point: not measured, calculated 6.98.

[b] No duplicate run.

Table 63. 3-Buten-1-ol p-toluenesulfonate, 49.88°C, 0.07630 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 7.71 | | |
| 526 | 6.91 | 0.1045 | 9.253 |
| 792 | 6.60 | 0.1614 | 9.485 |
| 1123 | 6.35 | 0.2183 | 9.046 |
| 1559 | 6.05 | 0.3064 | 9.149 |
| 2106 | 5.80 | 0.4060 | 8.973 |
| 3256 | 5.17 | 0.6203 | 8.870 |
| Aver. rate[a,b] | | | 9.13 ± 0.17 |
| Corrected rate | | | 9.56 ± 0.18 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0268 M, computer rate = 9.17 ± 0.04, infinity point: observed 5.00, calculated 4.15.

[b] No duplicate run.

Table 64. 3-Buten-1-ol p-toluenesulfonate, 49.88°C, 0.1035 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 10.46 | | |
| 2028 | 9.74 | 0.0849 | 1.321 |
| 4766 | 9.04 | 0.2052 | 1.358 |
| 7482 | 8.60 | 0.3174 | 1.338 |
| 9708 | 8.31 | 0.4203 | 1.365 |
| 12780 | 8.05 | 0.5490 | 1.355 |
| 15924 | 7.87 | 0.6749 | 1.336 |
| 21102 | 7.66 | 0.9062 | 1.354 |
| Aver. rate[a,b,c] | | | 1.35 ± 0.01 |
| Corrected rate | | | 1.41 ± 0.01 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0305 M, computer rate = 1.41 ± 0.00, infinity point: observed 7.38, calculated 7.34.

[b] Duplicate run (in volumetric flask) gave $k_2$ = 1.48 ± 0.05, computer rate 1.56 ± 0.03.

Table 65. 1-Bromo-3-butene, 49.88°C, 0.0449 M potassium t-butoxide/ t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 4.54 | | |
| 188 | 4.00 | 0.0334 | 2.564 |
| 409 | 3.55 | 0.0734 | 2.604 |
| 593 | 3.27 | 0.1042 | 2.540 |
| 886 | 2.92 | 0.1578 | 2.575 |
| 1311 | 2.61 | 0.2263 | 2.494 |
| 1679 | 2.42 | 0.2849 | 2.453 |
| Aver. rate[a,b] | | | 2.54 ± 0.04 |
| Corrected rate | | | 2.58 ± 0.04 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0290 M, computer rate = 2.48 ± 0.02, infinity point: observed 1.61, calculated 1.34.

[b] No duplicate run.

Table 66. 1-Bromo-3-butene, 49.88°C, 0.0691 M, sodium ethoxide/ ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 6.98 | | |
| 371 | 6.65 | 0.0162 | 3.470 |
| 940 | 6.16 | 0.0442 | 3.730 |
| 1960 | 5.55 | 0.0896 | 3.269 |
| 3061 | 5.04 | 0.1418 | 3.680 |
| 5038 | 4.42 | 0.2358 | 3.719 |
| 7134 | 4.04 | 0.3245 | 3.615 |
| Aver. rate[a,b] | | | 3.64 ± 0.07 |
| Corrected rate | | | 3.71 ± 0.07 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0401 M, computer rate = 3.72 ± 0.02, infinity point: observed 2.93, calculated 2.81.

[b] No duplicate run.

Table 67. 2-Phenyl-3-buten-1-ol p-toluenesulfonate, 49.88°C, 0.0445 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 4.50 | | |
| 142 | 3.61 | 0.1364 | 9.46 |
| 231 | 3.26 | 0.2333 | 9.98 |
| 360 | 2.95 | 0.3707 | 10.20 |
| 447 | 2.80 | 0.4726 | 10.47 |
| 531 | 2.70 | 0.5659 | 10.56 |
| 604 | 2.65 | 0.6252 | 10.24 |
| Aver. rate[a,b] | | | 10.2 ± 0.3 |
| Corrected rate | | | 10.3 ± 0.3 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0213 M, computer rate = 10.8 ± 0.1, infinity point: observed 2.35, calculated 1.25.

[b] Duplicate run gave $k_2$ = 10.2 ± 10.6, computer rate = 11.6 ± 0.1.

Table 68. 2-Phenyl-3-buten-1-ol p-toluenesulfonate, 49.88°C, 0.05830 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 5.89 | | |
| 554 | 5.09 | 0.0592 | 9.42 |
| 1118 | 4.48 | 0.1281 | 10.10 |
| 1707 | 4.06 | 0.1981 | 10.23 |
| 2239 | 3.80 | 0.2570 | 10.12 |
| 2844 | 3.57 | 0.3261 | 10.11 |
| 3799 | 3.30 | 0.4404 | 10.23 |
| Aver. rate[a,b] | | | 10.0 ± 0.2 |
| Corrected rate | | | 10.2 ± 0.2 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0322 M, computer rate = 10.5 ± 0.03, infinity point: observed 2.64, calculated 2.59.

[b] Duplicate run gave $k_2$ = 10.6 ± 0.6, computer rate = 11.8 ± 0.0.

Table 69. 2-(p-Chlorophenyl)-3-buten-1-ol p-toluenesulfonate, 49.88°C, 0.0576M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 5.82 | | |
| 294 | 4.45 | 0.2049 | 5.067 |
| 491 | 4.00 | 0.3522 | 5.220 |
| 656 | 3.76 | 0.4806 | 5.330 |
| 887 | 3.56 | 0.6478 | 5.312 |
| 1085 | 3.44 | 0.8088 | 5.451 |
| 1277 | 3.38 | 0.9274 | 5.282 |
| Aver. rate[a,b] | | | 5.28 ± 0.07 |
| Corrected rate | | | 5.38 ± 0.08 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0259 M, computer rate = 5.51 ± 0.3, infinity point: observed 3.20, calculated 2.43.

[b] Duplicate run gave $k_2$ = 5.42 ± 0.22, computer rate = 5.74 ± 0.03.

Table 70. 2-(p-Methylphenyl)-3-buten-1-ol p-toluenesulfonate, 49.88°C, 0.0594 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 6.00 | | |
| 137 | 5.01 | 0.0766 | 4.831 |
| 229 | 4.55 | 0.1310 | 4.928 |
| 348 | 4.15 | 0.1970 | 4.882 |
| 468 | 3.85 | 0.2651 | 4.883 |
| 658 | 3.53 | 0.3688 | 4.831 |
| 821 | 3.35 | 0.4521 | 4.747 |
| Aver. rate [a,b] | | | 4.85 ± 0.05 |
| Corrected rate | | | 4.93 ± 0.05 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0327 M, computer rate = 4.82 ± 0.02, infinity point: observed 2.70, calculated 1.47.

[b] No duplicate run.

Table 71. 2-(p-Methylphenyl)-3-buten-1-ol p-toluenesulfonate, 49.88°C, 0.0594 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^3$ |
|---|---|---|---|
| 0 | 6.00 | | |
| 924 | 5.18 | 0.0542 | 5.356 |
| 1510 | 4.82 | 0.0867 | 5.242 |
| 2519 | 4.35 | 0.1430 | 5.181 |
| 3413 | 4.03 | 0.1948 | 5.209 |
| 4406 | 3.77 | 0.2497 | 5.171 |
| 5363 | 3.59 | 0.2978 | 5.069 |
| Aver. rate[a,b] | | | 5.21 ± 0.06 |
| Corrected rate | | | 5.31 ± 0.07 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate = 0.0341 M, computer rate = 5.15 ± 0.02, infinity point: observed 2.55, calculated 2.35.

[b] Duplicate run gave $k_2$ = 5.35 ± 0.10, computer rate = 5.13 ± 0.01.

Table 72. 2-Phenyl-1-bromo-3-butene, 49.88°C, 0.0462 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 4.67 | | |
| 218 | 3.50 | 0.1934 | 8.523 |
| 448 | 2.97 | 0.4148 | 8.906 |
| 617 | 2.80 | 0.5508 | 8.587 |
| 797 | 2.65 | 0.7437 | 8.976 |
| 1069 | 2.55 | 0.9743 | 8.770 |
| Aver. rate[a,b] | | | 8.75 ± 0.14 |
| Corrected rate | | | 8.93 ± 0.14 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide = 0.0223 M, computer rate = 9.04 ± 0.08, infinity point: observed 2.42, calculated 1.68.

[b] Duplicate run gave $k_2$ = 8.09 ± 0.15, computer rate = 7.79 ± 0.07.

Table 73. 2-Phenylethanol p-toluenesulfonate, 49.83°C, 0.0373 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^2$ |
|---|---|---|---|
| 0 | 3.68 | | |
| 326 | 3.42 | 0.0257 | 1.12 |
| 752 | 3.20 | 0.0535 | 1.01 |
| 1458 | 2.90 | 0.1004 | 0.99 |
| 3342 | 2.42 | 0.2227 | 0.95 |
| 6942 | 2.00 | 0.4473 | 0.92 |
| Aver. rate[a,b,c] | | | 1.00 ± 0.06 |
| Corrected rate | | | 1.02 ± 0.06 |

[a] $N_{HCl}$ = 0.1014, conc. of p-toluenesulfonate 0.0211 M, infinity point: observed 1.60, calculated 1.60.

[b] Duplicate run gave $k_2 = 1.11 \pm 0.13 \times 10^{-2}$.

[c] Reported rate $k_2 = 1.10 \times 10^{-2}$ (47).

Table 74. 2-Phenylethanol p-toluenesulfonate, 49.83°C, 0.1388 M sodium ethoxide/ethanol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{b-x})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 13.88 | | |
| 1090 | 13.31 | 0.0461 | 9.98 |
| 2947 | 12.60 | 0.1186 | 9.49 |
| 5740 | 11.79 | 0.2338 | 9.60 |
| 8694 | 11.16 | 0.3685 | 9.99 |
| 12156 | 10.75 | 0.4989 | 9.67 |
| 18042 | 10.30 | 0.7382 | 9.57 |
| Aver. rate[a,b] | | | 9.72 ± 0.18 |
| Corrected rate | | | 9.91 ± 0.18 |

[a] $N_{HCl}$ = 0.0990, conc. of p-toluenesulfonate 0.0411 M, infinity point; observed 9.74, calculated 9.72.

[b] Duplicate run (2 1/2 months later with same ethoxide/ethanol) gave $k_2 = 10.2 \pm 0.32 \times 10^{-4}$.

Table 75. 1-Phenyl-1-bromoethane, 49.83°C, 0.2031 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (sec.) | Vol. of Titrant (ml.) | log b/a $(\frac{a-x}{box})$ | $k_2 \times 10^4$ |
|---|---|---|---|
| 0 | 20.52 | | |
| 1868 | 19.82 | 0.1261 | 8.74 |
| 4293 | 19.20 | 0.2931 | 8.84 |
| 7152 | 18.74 | 0.4930 | 8.92 |
| 9846 | 18.50 | 0.6573 | 8.64 |
| 13992 | 18.25 | 0.9540 | 8.83 |
| Aver. rate[a,b,c] | | | 8.80 ± 0.08 |
| Corrected rate | | | 9.21 ± 0.08 |

[a] $N_{HCl}$ = 0.0990, conc. of bromide 0.0249 M, computer rate = 9.17 ± 0.06, infinity point: observed 18.00, calculated 17.71.

[b] Duplicate run gave $k_2$ = 9.67 ± 0.37, computer rate = 9.60 ± 0.15.

[c] Average $k_2 = 9.39 \pm 0.22 \times 10^{-4}$.

Table 76. 1-Phenyl-1-bromoethane, 49.83°C, 0.1031 M potassium t-butoxide/t-butyl alcohol

| Time Elapsed (min.) | Absorbance | $\log \frac{A_\infty - A_o}{A_\infty - A_t}$ | $k_1 \times 10^5$ ($sec.^{-1}$) |
|---|---|---|---|
| 0 | 0.036 | | |
| 26.47 | 0.146 | 0.067 | 9.73 |
| 56.56 | 0.245 | 0.138 | 9.39 |
| 97.42 | 0.371 | 0.250 | 9.84 |
| 145.9 | 0.472 | 0.366 | 9.62 |
| 206.1 | 0.572 | 0.522 | 9.73 |
| 278.4 | 0.633 | 0.656 | 9.05 |
| 364.2 | 0.715 | 0.945 | 9.96 |
| 425.2 | 0.740 | 1.090 | 9.84 |
| Aver. rate[a,b,c] | | | 9.73 ± 0.13 |

[a] Conc. of bromide = $1.17 \times 10^{-4}$ M, $k_2 = 9.45 \pm 0.13 \times 10^{-4}$, infinity point: observed 0.802, calculated 0.808, yield of olefin 100%.

[b] Duplicate run with base conc. = 0.1936 M gave $k_1$ = 1.88 ± 0.12, $k_2 = 9.72 \pm 0.62 \times 10^{-4}$, yield of olefin 100%.

[c] Average second order elimination rate = $9.59 \pm 0.14 \times 10^{-4}$.

Table 77. 1-Phenyl-1-bromoethane, 49.83°C, 0.1265 M sodium ethoxide/ethanol

| Time Elapsed (min.) | Absorbance | $\log \frac{A_\infty - A_o}{A_\infty - A_t}$ | $k_1 \times 10^4$ ($sec.^{-1}$) |
|---|---|---|---|
| 0 | 0.140 | | |
| 6.42 | 0.188 | 0.114 | 3.83 |
| 15.03 | 0.240 | 0.121 | 3.08 |
| 25.30 | 0.300 | 0.212 | 3.22 |
| 35.33 | 0.343 | 0.295 | 3.29 |
| 50.63 | 0.390 | 0.405 | 3.07 |
| 60.39 | 0.417 | 0.484 | 3.08 |
| 71.78 | 0.445 | 0.586 | 3.14 |
| 79.90 | 0.465 | 0.675 | 3.25 |
| Aver. rate[a,b,c] | | | $3.35 \pm 0.19$ |

[a]Conc. of bromide = $3.58 \times 10^{-3}$ M, $k_2 = 2.64 \pm 0.16 \times 10^{-3}$, infinity point: observed 0.552, calculated 2.47, yield of styrene = 22%.

[b]Duplicate run with base conc. = 0.2652 M gave $k_1 = 4.33 \pm 0.01$ (two points only), $k_2 = 1.63 \pm .04$, yield of olefin = 29%.

[c]Average second order elimination rate = $2.14 \pm 0.51 \times 10^{-3}$.

## SUMMARY

The kinetics and deuterium isotope effects of the base-promoted elimination reactions of some aryl-substituted 2-phenyl-1-propyl bromides and p-toluenesulfonates in potassium tert-butoxide in tert-butyl alcohol and sodium ethoxide in ethanol were studied. The rho values for the 2-phenyl-1-propyl compounds showed that the beta methyl substituent shifts the mechanism of elimination away from the Elcb region of the mechanism spectrum and lowers the reaction rate as a result of the lower acidity imposed on the beta proton by the methyl substituent.

The rates of elimination of 2-phenyl-3-buten-1-yl and 3-buten-1-yl bromides and p-toluenesulfonates were found to be very large in tert-butoxide/tert-butyl alcohol and ethoxide/ethanol. The beta vinyl group in these compounds was observed to affect the rates of elimination to about the same extent as a beta phenyl substituent. The high rho value for 2-phenyl-3-buten-1-ol p-toluenesulfonate in ethoxide/ethanol implies that the high rates for the beta vinyl-substituted compounds is a result of enhanced acidity of the beta proton.

The value of the tert-butoxide/ethoxide and bromide/p-toluenesulfonate rate ratios as mechanistic criteria for elimination reactions was discussed in view of the data presented here and by previous workers. A linear relationship between rho and the tert-butoxide/ethoxide rate ratios for 2-phenyl-substituted p-toluene-

sulfonates was noted, but deviations from the relationship were observed. A correlation of rate and mechanism of E2 eliminations was proposed to rationalize the bromide/p-toluenesulfonate rate ratios observed.

A product study of the base-promoted elimination reactions of optically active 2-butyl-trimethylammonium iodide, 2-butyl p-toluenesulfonate, and 2-methy-3-hexyl p-toluenesulfonate with optically active potassium sec-butoxide/sec-butyl alcohol showed no steric effect control on the direction of elimination in these cases. This was attributed to the lack of any serious differences in the steric requirements of the enantiomeric forms of the reactants. However, asymmetric induction of racemic 3-methyl-3-bromohexane with optically active potassium sec-butoxide/sec-butyl alcohol was observed, indicating that steric interactions can affect the rates of elimination in some cases.

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