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SOLVENT AND STRUCTURAL EFFECTS ON BIMOLECULAR
ELIMINATION REACTIONS

by

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INTRODUCTION

It appears that the main difficulty in characterizing the beta elimination reaction is caused by a fault in human nature: the strong desire to classify information as it is obtained. Although this is a useful tool for learning, it often prevents us from obtaining a clear picture of the whole body of information. Just as it has been useful to classify all elements as metals or non-metals, all chemical bonds as ionic or non-ionic, so it has proved useful to place elimination reactions in three categories: E_1 or cationic, E_2 or concerted, and E_{1cb} or anionic. But at the same time it has made it harder to understand that there is no sharp break between any of the categories. Continuous spectra exist and our tendency to classify tends to obscure this fact of nature.

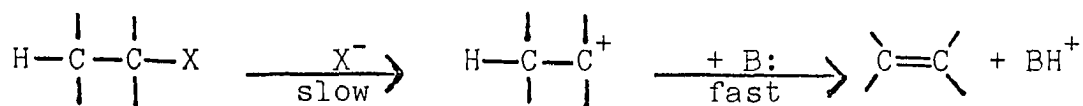
The primary purpose of this thesis is to report an investigation of the beta-elimination reaction in the 1-phenyl-2-propyl system, in which the effects of solvent and structure on the reaction were studied. The conclusions drawn from this research are discussed in light of the information previously obtained in other systems.

HISTORICAL

Beta eliminations are those reactions in which two atoms or groups are removed from adjacent carbon atoms, forming a carbon-carbon double bond. The principal mechanisms of the beta-elimination reaction were recognized by Ingold (1) in 1950. These views have had to be modified in recent years, due to the extensive amount of data that has been collected since that time. The modern theory of beta-elimination reactions has been stated in a recent review by Bunnett (2). All but the most recent literature in this field has been thoroughly reviewed by Ingold, Hughes and co-workers (3, 4, 5), and by Bishop (6), Hine (7), Skell (8), and Smith (9). It is the concern of this thesis to add only the most recent pertinent data in this most interesting area of chemistry.

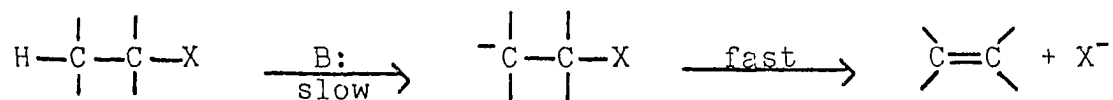
The beta-elimination has in the past been divided into three mechanistic classes:

The E_1 or unimolecular beta-elimination, in which the rate determining step is the formation of a carbonium ion intermediate which in a subsequent, fast step, loses a beta hydrogen atom, giving an olefin as product:

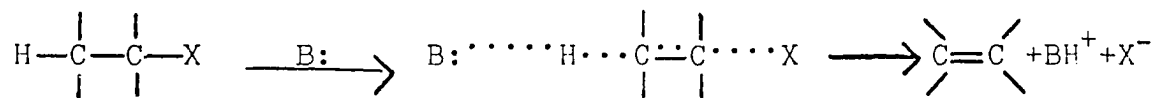


The E_{1cb} or carbanion mechanism, in which the rate determining step is the removal of a beta hydrogen atom by the base forming

a carbanion intermediate which subsequently separates from the leaving group, X:



The E₂ or bimolecular or concerted mechanism, in which the beta hydrogen atom and the leaving group depart simultaneously under the influence of base:



As Smith (9) points out, the E₂ mechanism in its current interpretation is no longer restricted to the concerted transition state but encompasses the range from the nearly E₁ transition state to the other end of the scale, the nearly E_{1cb} transition state, including within its spectrum, transition states with widely differing amounts of carbon-hydrogen and carbon-leaving group bond breaking. As the beta-elimination becomes more thoroughly investigated it becomes increasingly difficult to distinguish the exact point at which the E₁ mechanism gives way to the E₂ elimination, and where it in turn gives way to the E_{1cb} mechanism.

In order to understand the beta-elimination in all its ramifications it is necessary to understand what effects the various factors have on the mechanism and rate of the reaction. Bunnett (2) has discussed nine basic factors which

Table 1. Change in transition state with changes in the substrate and the reaction conditions

Factor	Transition state		
	E_1	E_2	E_{1cb}
alpha-aryl group		←	
alpha-alkyl group		←	
better leaving group		←	
more electronegative leaving group			→
beta-aryl group			→
beta-alkyl group		←	
electronegative beta-substituent			→
more polar solvent		←	
stronger base		?	

affect the beta-elimination reaction. The problem discussed above is further complicated by the fact that the amount of double bond character present in the transition state may vary almost independently of the bond breakage, although it is affected by some of the same factors.

The following is a discussion of the ways in which these changes in the substrate or in the reaction conditions are

thought to affect the elimination transition state and its amount of double bond character.

The introduction of an alpha-aryl substituent favors a transition state with carbonium ion character by its ability to stabilize a positive charge on the alpha carbon atom. In the case of a transition state of the E_2 type, the alpha-aryl substituent allows an increase in double bond character by stabilizing the incipient double bond by conjugation.

The introduction of an alpha-alkyl group has the effect of stabilizing a carbonium ion intermediate by induction and thus shifts the mechanism toward the E_1 transition state. In most cases it seems to have little effect on the amount of double bond character, though in some cases it may cause increased carbon-leaving group bond breaking through steric interference, and thus lead to more double bond character.

The introduction of a better leaving group causes more carbon-leaving group bond breaking and therefore the mechanism is shifted toward the E_1 transition state. Increased bond breaking also means that the transition state has an increased resemblance to the products and therefore has more double bond character.

The introduction of a more electronegative leaving group has the effect of acidifying the beta-hydrogen atoms by its inductive effect and thus favors beta carbanion formation. Since it would also destabilize any positive charge on the

alpha carbon atom it would shift the mechanism toward the E_{1cb} transition state. At the same time this substituent inhibits the spreading of electron density over the alpha and beta carbon atoms, decreasing the amount of double bond character.

The introduction of a beta-aryl substituent would stabilize a carbanion and thus shift the transition state toward the E_{1cb} . Such substitution favors increased double bond character in the same way as an alpha-aryl substituent.

The introduction of a beta-alkyl substituent has the effect of destabilizing carbanion formation by its inductive effect and shifts the mechanism toward the E_1 transition state. It would also stabilize a carbonium ion by its long range inductive effect. The steric and inductive effects of the beta-alkyl substituent tend to decrease the interaction between the base and the beta-hydrogen atoms and therefore decrease the amount of double bond character present in an E_2 type transition state.

The introduction of an electronegative beta substituent would favor the E_{1cb} transition state by stabilizing a carbanion on the beta carbon atom and at the same time destabilizing a carbonium ion on the alpha carbon atom. If the transition state is of the E_2 type, the increase in carbon-hydrogen bond breaking caused by the increase in electron attracting ability of the beta substituent leads to more double bond

character in the transition state.

The introduction of a more polar solvent into the reaction favors the production of ions from neutral molecules, leading to transition states of the E_1 type. A more polar solvent also means better solvation of the leaving group, causing increased carbon-leaving group bond breaking in the transition state. This would also favor increased double bond character. It should be noted that trends in solvent effects are difficult to assess because the change in solvent also effects base strength and other solvation properties. It is generally the case that a transition state with any type of charge is favored over a neutral transition state in more polar solvent systems. It is concluded from this effect and from the decreased aggressiveness of bases due to increased solvation, as reported by Winstein (10), that double bond character is not affected by a more polar solvent.

The effect of the introduction of a stronger base into the reaction has not been decided. Bunnett (2) declines to predict the effect that a stronger base would have on the E_2 transition state because of the variation of base strengths with solvation and mechanism. P. B. D. de la Mare and Vernon (11) discovered that sodium thiophenoxide acted ten times more effectively than did sodium ethoxide or sodium phenoxide in the elimination reaction of tertiary-butyl chloride, even though the latter two are considered to be stronger bases by

a factor of one thousand. It has been pointed out in explanation of this phenomenon that the nucleophilicity of the thiophenoxide ion toward carbon is greater than that of ethoxide by a factor of from one hundred to one thousand. Winstein (12) proposed the "merged substitution-elimination" mechanism to explain the olefinic product in the $\text{S}_{\text{N}}2$ displacement of trans-4-t-butylcyclohexyl tosylate with lithium bromide in acetone solution. The reaction was definitely not E_1 in nature and the leaving group appeared to be in a position to depart with the beta proton. Eliel (13, 14) found thiophenoxide to be ten times more effective than hydroxide under identical reaction conditions in the elimination of bromides and tosylates in the butyl and cyclohexyl systems. He concluded that the reactions were similar to the previously described "merged" eliminations. Similarly, Bunnett (15) found that thioethoxide was more than seven times faster than methoxide in the elimination of 2-chloro-2-methyl-1-phenylpropane. He later stated (16) that the order of thermodynamic affinity for hydrogen or carbon was methoxide or hydroxide greater than thiophenoxide, but the order of kinetic reactivity was thiophenoxide greater than the alkoxide ions. Recently a set of experiments by Bunnett (17) has shown that the thioethoxide ion is more reactive than methoxide ion when the eliminations are "nearly" E_1 in character. Winstein (18) has since stated that the "merged" eliminations were actually E_2

Table 2. A comparison of base effectiveness in an E_2 elimination (15, 17)

X (in decreasing leaving ability)	Cl	S(CH ₃) ₂	SO ₂ CH ₃
$\frac{\text{rate CH}_3\text{CH}_2\text{S}^-}{\text{rate CH}_3\text{O}^-}$	6.5 to 11.4	0.79 to 0.86	0.0 to 0.05
$k_H/k_D = 2.6$, and rho is very small.			

eliminations effected by thermodynamically weak bases such as chloride ion and bromide ion.

The extent of carbon-leaving group bond breaking has been measured by the leaving group isotope effect. When there is such bond breaking in the rate determining step, the compound containing the lighter isotope reacts at a faster rate than the compound containing the heavier isotope and this difference in rate is called the isotope effect. The larger the isotope effect the more carbon-leaving group bond breaking taking place in the transition state. Thus E_1 reactions have the maximum leaving group isotope effect. Nitrogen and sulfur have been the only leaving group isotope effects measured in elimination reactions.

Colter and Johnson (19) have suggested that the extent of carbon-leaving group bond breaking can also be measured by the

Hammett rho value for the elimination of meta and para substituted benzene sulfonates. The rho value becomes more positive as the separation of the leaving group from the carbon atom in the transition state increases.

Attempts have also been made to measure the extent of carbon-hydrogen bond breaking by measuring the decrease in rate when the beta-hydrogens are replaced by deuterium atoms. This rate decrease is thought to be at a maximum when the beta-hydrogen atom is fifty per cent transferred from the carbon atom to the base in the transition state. The maximum kinetic isotope effect decreases with increasing temperature, the maximum rate decrease at room temperature being a factor of about seven or eight.

The Hammett rho value is evaluated from rate measurements on the elimination rates of compounds having meta and para substituted beta-aryl substituents. It gives a measure of the negative charge located on the beta carbon atom in the transition state and increases with increasing charge.

Earlier investigations have shown that the trans-elimination of H and X is favored over cis-elimination and that the favored conformation for the two groups leaving is anti-coplanar. De Puy and co-workers (20) have suggested that the ease of E_2 eliminations may vary with the dihedral angle between H and X, and that a plot of the rate of elimination of a given system versus the dihedral angle between the

hydrogen and the leaving group may show maximums at both 0° (cis-coplanar), and at 180° (trans-anticoplanar), and a minimum at 90° . Reactions in which the leaving atoms cannot assume a coplanar or anti-coplanar configuration are not only much slower but may proceed through the extreme E_{1cb} transition state. It had been conjectured that the cis elimination, because of the inability to attain a trans-coplanar configuration, would be of the E_{1cb} type. That this is not the case has been shown most recently by Le Bel and co-workers (21) in an investigation of the elimination of exo-cis-, endo-cis-, and trans- 2,3-dibromo-, bromochloro-, and dichloro-norbornanes, in which cis elimination of the trans compounds is favored over the trans elimination of the cis compounds. The cis elimination was found to proceed as much as eighty-five times faster than the trans elimination. The relative rates found for the various substrates and the value of the deuterium isotope obtained (3.6) are consistent with a concerted mechanism with a fair amount of double bond character in the transition state. There was no deuterium exchange in the reaction.

In light of the above it appears that although the trans elimination is preferred, when the anti-coplanar configuration required for trans elimination is energetically unfavorable a cis elimination may take place.

This has been found to be true by Smith (9) in the trans-

1-aryl-2-cyclopentyl system. In an investigation of the elimination of cis- and trans-1-aryl-2-cyclopentyl p-toluene-sulfonates in potassium t-butoxide/t-butyl alcohol solution, he found that the major product from the trans-tosylate was 1-phenylcyclopentene, the product of cis-elimination, and that there was only a small amount of 3-phenylcyclopentene, the product of trans-elimination. Smith also showed that 3-phenylcyclopentene did not isomerize under the reaction conditions. The rho value for the cis-elimination was found to be 2.76 while that for the trans-elimination of cis-1-phenyl-2-cyclopentyl tosylate was 1.48, indicating that the cis elimination has more carbanion character than the trans elimination. This rho value, together with an isotope effect, k_H/k_D , of 5.6, suggests a high degree of concerted character for the transition state of the reaction. Indeed, it appears that there is less carbanion character in the cis elimination of trans-1-phenyl-2-cyclopentyl tosylate than there is in the elimination of beta-phenylethyl tosylate for which the rho value is 3.39.

The E_{1cb} mechanism has been the subject of many investigations and much debate since Cristol's (22, 23) early work on beta-hexachloro-benzene, in which trans-elimination is not possible and which was thought to proceed through a carbanion intermediate. It has been considered that deuterium exchange is a sufficient and necessary condition for a carbanion

elimination mechanism. Thus Hine (24, 25) considered that the elimination of 1,1,1-trifluoro-2,2-dichloroethane with methoxide ion proceeds through a carbanion intermediate because the rate of deuterium exchange is faster than the rate of elimination. Breslow (26) has pointed out that deuterium exchange is not proof that a carbanion mechanism is operating, but may be only an "irrelevant side reaction". In his view, deuterium exchange requires reversible carbanion formation; for this to occur it is only necessary that the transition state leading to carbanion formation be of lower energy than the transition states leading to both E_2 elimination and E_{1cb} elimination.

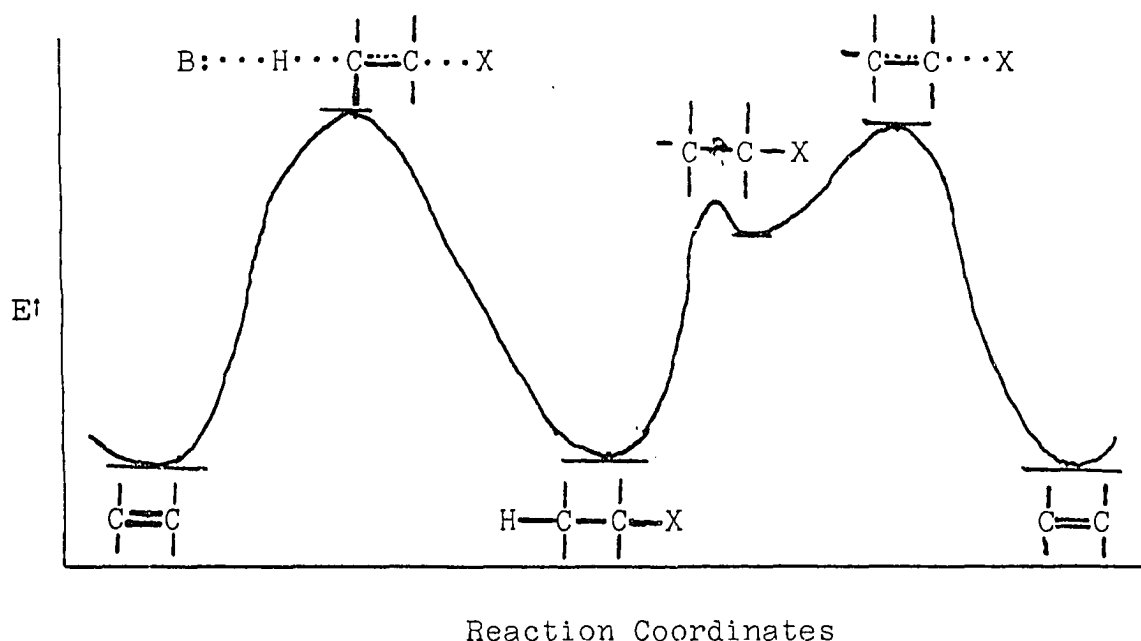


Figure 1. Energy diagram for carbanion formation

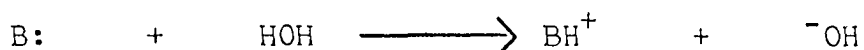
To account for the relative lack of deuterium exchange in many E_{1cb} -like reactions it has been suggested that these carbanions would have extremely short lifetimes, of the order of 10^{-9} seconds, and that elimination from the carbanion is preferred to recombination. On the basis of enthalpy considerations the E_2 transition state should be more stable; it has less negative charge on the carbon atoms and thus resembles the stable hydrocarbon more than the unstable carbanion. This is the case in the beta-phenylethyl system. Cases with more carbanion character localized on the beta carbon atoms react slower, cases with electron withdrawing substituents on the phenyl ring, decreasing the charge density on the beta carbon atom, react faster. This is to be expected since electron withdrawing groups lower the energy of a partially anionic transition state. It would not be expected if the important factor was the ability of the incipient anion to push off the leaving group. Entropy considerations would favor the stepwise carbanion process since the E_2 mechanism ties down the base in the transition state. Breslow has pointed out that the only valid criteria for the operation of a carbanion mechanism are general versus specific base catalysis, and deuterium isotope effects (with complications when exchange occurs, explainable by both mechanisms).

Bordwell (27), investigating the elimination of cis- and trans-p-tolylsulfonylcyclohexyl- and p-tolylsulfonylcyclopentyl

tosylates, found the reactions to be general base catalyzed.

In his view, if an E_{1cb} mechanism were operating here the rate of the reaction would be a function of the anion,

$\begin{array}{c} | \\ -C-C-X \\ | \end{array}$, and the concentration of this anion in turn a function of the base, $B:$, and its conjugate acid, BH^+ .



In aqueous solution the rate would therefore depend only on the hydroxide ion concentration and specific base catalysis would be observed. Since the reaction was found to be general base catalyzed he concludes that the mechanism must be either concerted or a rate controlling ionization followed by a rapid reaction of the anion which, if formed, must have a life time of only 10^{-9} seconds.

It would appear from the foregoing discussion that for most of the reactions in which a carbanion mechanism has been postulated, what has been called the " E_2 , nearly E_{1cb} transition state" may well be operating.

The beta-phenyl ethyl system has been perhaps the most thoroughly investigated of all the beta-elimination reactions known. Bishop (6) studied extensively the effects of leaving group, base and solvent on the reaction. Some of the data that he collected are shown in Tables 3 and 4.

Table 3. The effect of change in leaving group on the beta-phenyl ethyl elimination reaction in sodium ethoxide, ethanol solution at thirty degrees

Leaving group:	F	Cl	OTos	Br	I
Relative rate:	1	70	391	4,300	28,000
Rho:	3.12	2.61	2.27	2.14	2.07

Table 4. Effects of changes in solvent and base on the beta-elimination in the beta-phenylethyl system at thirty degrees

X	Base	Solvent	Relative rate	Rho
OTos	EtO ⁻	EtOH	1	2.27
Br	EtO ⁻	EtOH	11	2.14
I	EtO ⁻	EtOH	68	2.07
OTos	t-BuO ⁻	t-BuOH	52	3.39
Br	t-BuO ⁻	t-BuOH	233	2.08
I	t-BuO ⁻	t-BuOH	1,030	1.88
OTos	EtO ⁻	t-BuOH	11	2.60
Br	EtO ⁻	t-BuOH	61	2.28
I	EtO ⁻	t-BuOH	300	2.07

As seen from the above data, the reaction is greatly affected by the leaving group, the base, and to much smaller extent the solvent. The leaving group affects the transition

state of the reaction by acidifying the beta hydrogen atoms, making their removal easier, and by synchronous bond breaking so that the negative charge is removed from the molecule and resides on the leaving group to a greater or lesser degree.

For bromides and iodides a stronger base was found to give more carbon-hydrogen bond breaking, resulting in more double bond character since these leaving groups can relieve the extra negative charge. For tosylates, on the other hand, the stronger base gives a transition state with more carbanion character since carbon-oxygen bond breaking apparently does not increase as rapidly as carbon-hydrogen bond breaking, as evidenced by the large increase in ρ in changing from ethoxide to *t*-butoxide as the base. This is in contrast to the decrease in the value of ρ for the bromides and iodides for the same change in base.

That the solvent had a small effect upon the transition states is seen by the small effect upon the ρ value upon changing from ethoxide in *t*-butyl alcohol to ethoxide in ethanol. The rate of the reaction was seen to be highly dependent upon the leaving group, increasing in the order: Fluoride, chloride, tosylate, bromide, iodide. This is apparently in the order of effectiveness of leaving ability as seen in the corresponding decrease in ρ , indicating that less negative charge resides upon the beta carbon atom and that correspondingly more carbon-leaving group bond breaking

is occurring.

In contrast to the effect on the transition state, it is seen that the solvent affects the rate of the reaction more than does the base. For beta-phenylethyl tosylate the rate increases by a factor of eleven in changing from ethanol to t-butyl alcohol as the solvent, whereas the rate is increased by only a factor of 4.5 when changing from ethoxide in t-butyl alcohol to t-butoxide in t-butyl alcohol.

Saunders (28) studied the deuterium isotope effect for the beta-phenylethyl system. With ethoxide the value for tosylates was smaller than the value for the bromides (5.66 at 30 degrees vs. 7.11). With the stronger base, potassium t-butoxide, both these values rose, to 8.01 and 7.89, respectively. It would seem that in ethanol the tosylates have less bond breaking than the bromides but yet more negative charge at the beta-carbon atom, as measured by ρ . These facts are interpreted by Bishop (6) to mean that the tosylate group is removing less of the negative charge from the system and that consequently carbon leaving group bond breaking has not progressed as far in the transition state as in the case of the bromide. The increase in base strength causes increased carbon-hydrogen bond breaking; this is compensated for in the case of the bromides by increased carbon-leaving group bond breaking and ρ does not increase much. In the case of the tosylates the net result is additional negative charge

residing on the beta carbon atom, as indicated by the large increase in the rho value.

RESULTS AND DISCUSSION

This thesis presents an investigation of elimination reactions in the 1-aryl-2-propyl system. The purposes of the investigation were to clarify the reaction mechanism by determining the effects of base, solvent and structure on the reaction; to determine what information can be obtained from the bromide/tosylate and t-butoxide/ethoxide rate ratios, which were suggested by Bishop (6) and Smith (9) as possible indicators of the elimination reaction transition state, and to determine what effects the introduction of an alpha-alkyl substituent has on the rate and transition state of the E_2 elimination reaction.

To achieve these aims a series of meta and para substituted 1-aryl-2-propyl-p-toluenesulfonates (tosylates) were prepared and converted to the corresponding bromides by reaction with lithium bromide in acetone solution. The base catalyzed elimination of these compounds was then studied in sodium ethoxide-ethanol and potassium t-butoxide-t-butyl alcohol solutions. The rate constants were determined under psuedo-first order conditions and the reactions were followed by ultraviolet spectroscopy. The rate constants and rho values were calculated by the Iowa State University--IBM 7074 computer, using a computer program prepared by Wiberg (29) and adapted to the 7074 by L. B. Rodewald of Iowa State University. The program for calculating the rate constants is

included in the experimental section.

The results of this investigation are summarized in Tables 5, 6, 7 and 8. The second order rate constants were obtained by dividing the corresponding pseudo-first order rate constants, obtained by the computer, by the base concentration. That the reactions were second order was shown by repeating the reactions at different base concentrations. Good agreement was obtained for the second order rate constants calculated in this manner. Each rate is the average of two or more kinetic runs.

As pointed out by Bishop (6), the transition state of a reaction is often not affected in the same manner as the rate. This is certainly true in the 1-phenyl-2-propyl system. The reaction rates for both the tosylates and the bromides increased in changing the reactions from ethoxide ion in ethanol to t-butoxide ion in t-butyl alcohol solution. In contrast the rho value for the tosylates increased considerably in changing to t-butyl alcohol, while the rho value for the bromides decreased just as considerably.

As seen in Table 9, the t-butoxide/ethoxide rate ratio for 1-phenyl-2-propyl tosylate, 2.7, is considerably less than that for beta-phenylethyl tosylate, 18.4. This was not unexpected. Smith (9) found the t-butoxide/ethoxide rate ratio for cis-1-phenyl-2-cyclopentyl tosylate to be even smaller (1.2). It is generally considered that the

Table 5. Rates of elimination of $Y-C_6H_4CH_2CH(CH_3)-X$ in sodium ethoxide/ethanol solution

Y	X	T, °C	$k_{E_2} \times 10^4$ (liter mole ⁻¹ sec ⁻¹)
H	OTos	30	0.42
Br	OTos	30	1.94
Cl	OTos	30	1.08
MeO	OTos	30	0.28
H	OTos	50	3.42
Br	OTos	50	16.4
Cl	OTos	50	9.85
Me	OTos	50	2.87
MeO	OTos	50	2.32
H	Br	50	19.2
Br	Br	50	155.
Cl	Br	50	85.4
Me	Br	50	17.7
H	Br	30	2.55
Br	Br	30	20.9

introduction of an alpha-alkyl group favors the E_1 type mechanism by its ability to stabilize a positive charge by its inductive effect which at the same time retards carbon-hydrogen bond breakage, as has been mentioned above. Thus the transition state for the elimination of 1-phenyl-2-propyl tosylate must have considerable E_1 character. As seen in Table 10, ρ for this system is much smaller than for the beta-phenylethyl system, for the reaction in ethanol. As in the case of beta-phenylethyl tosylate, ρ increases when the elimination is

Table 6. Rates of elimination of $Y-C_6H_4CH_2CH(CH_3)-X$ in potassium t-butoxide/t-butyl alcohol solution

Y	X	T, °C	$k_{E_2} \times 10^4$ (liter mole ⁻¹ sec ⁻¹)
H	OTos	50	9.32
Br	OTos	50	52.0
Cl	OTos	50	21.8
Me	OTos	50	4.56
MeO	OTos	50	2.74
H	Br	50	94.1
Br	Br	50	274.
Cl	Br	50	177.
Me	Br	50	45.5
H	OTos	30	2.39

Table 7. Enthalpies and entropies of activation for eliminations from $Y-C_6H_4CH_2CH(CH_3)-X$

X	Y	Base	T _m (°C)	H _{kcal}	S _{e.u.}
OTos	H	EtO ⁻	40	19.8	-4.7
OTos	H	t-BuO ⁻	40	12.7	-25.5
OTos	Cl	EtO ⁻	40	19.9	1.8
OTos	Br	EtO ⁻	40	18.9	-2.75
OTos	MeO	EtO ⁻	40	19.8	-5.6
Br	H	EtO ⁻	40	19.1	-4.0
Br	Br	EtO ⁻	40	19.8	2.1

Table 8. Hammett correlations of the rates of elimination of 1-aryl-2-propyl compounds

Compound	Solvent	Temp. (°C)	Rho	Intercept	Root mean square error
OTos	EtOH	30	1.31	-4.267	0.067
OTos	EtOH	50	1.33	-3.335	0.067
OTos	t-BuOH	50	1.88	-3.044	0.026
Br	EtOH	50	1.84	-2.543	0.105
Br	t-BuOH	50	1.37	-2.074	0.032

Table 9. A comparison of t-butoxide/ethoxide and bromide/tosylate rate ratios at 50°C

System	$\frac{k_{t\text{-BuOH}}}{k_{\text{EtOH}}}$	$\frac{k_{\text{Br}}}{k_{\text{OTos}}} (\text{EtOH})$	$\frac{k_{\text{Br}}}{k_{\text{OTos}}} (t\text{-BuOH})$
2-phenethyl tosylate	18.4	5.7	3.4
2-phenethyl bromide	10.8		
1-phenyl-2-propyl tosylate	2.7	5.6	10.0
1-phenyl-2-propyl bromide	4.9		
cis-1-phenyl-2-cyclopentyl tosylate	1.2	--	--
1-phenyl-2-methyl-2-bromopropane	0.14	--	--
cyclopentyl	--	--	0.5

Table 10. Effect of solvent on rate and rho values, at 50 degrees

System	$k_{E_2} \times 10^4$		ρ_{ho}	
	EtOH	t-BuOH	EtOH	t-BuOH
beta-phenylethyl tosylate	5.98	111.0	2.27	3.39
beta-phenylethyl bromide	34.2	369.	2.14	2.08
1-phenyl-2-propyl tosylate	3.42	9.32	1.32	1.88
1-phenyl-2-propyl bromide	19.2	94.1	1.84	1.37
cis-1-phenyl-2-cyclopentyl tosylate	24.2	29.1	0.99	1.48
trans-1-phenyl-2-cyclopentyl tosylate	--	3.0	--	2.76
1-phenyl-2-methyl-2-bromopropane	19.2	2.37	--	--
cyclopentyl tosylate	--	3.86	--	--
cyclopentyl bromide	--	1.94	--	--

carried out in t-butyl alcohol, although the increase is only half as large as in the case of beta-phenylethyl tosylate.

As Smith (9) pointed out, the increase in rho caused by changing from ethoxide/ethanol to t-butoxide/t-butanol is fifty percent for both beta-phenylethyl tosylate and for cis-1-phenyl-2-cyclopentyl tosylate. The same percentage increase is observed here. One wonders about the cause of this coincidence. The considerable variation in the size of the rho

and the differences in reaction rates among the three systems suggest that the phenomenon is not caused by a similarity in reaction systems. That it is not simply a measure of the differences between the two sets of reaction conditions is shown by the lack of a similar trend with other leaving groups. The rho value for beta-phenylethyl bromide decreases slightly in changing from ethanol to t-butyl alcohol solution. Rho for 1-phenyl-2-propyl bromide decreases considerably for the same change. It must then appear that this phenomenon is a peculiarity of the tosylate leaving group and the difficulty that it apparently has in compensating for the increased carbon-hydrogen bond breaking, caused by the stronger base and the concomitant poorer solvating powers of the less polar solvent.

It appears that the t-butoxide/ethoxide rate ratio is a valid measurement of the amount of carbanion character in the transition state of a reaction. The beta-phenylethyl elimination is known to have a fair amount of carbanion character. For the reaction in ethanol solution there is a considerable amount of carbon-hydrogen bond breaking, as measured by the deuterium isotope effect. Rho has a high value, indicating a fair amount of negative charge on the beta-carbon atom in the transition state. This suggests that carbon-hydrogen bond breaking is farther advanced than carbon-leaving group bond breaking in the transition state. In addition, both the rho

value and the value of the deuterium isotope effect increase significantly when the reaction conditions are changed to t-butoxide in t-butyl alcohol. As discussed previously, both the change to a stronger base and the change to a less polar solvent favor an E_{1cb} type transition state. The reaction rate is also increased and therefore the transition state for the reaction must lie on the E_{1cb} side of the central E_2 mechanism.

The rate increase for 1-phenyl-2-propyl tosylate upon changing to t-butyl alcohol is not nearly as large as the increase found in the beta-phenylethyl system. Therefore, the transition for the 1-phenyl-2-propyl system must lie closer to the central E_2 mechanism than does the transition state for the beta-phenylethyl system. This is confirmed by a lower rho value. 1-Phenyl-2-propyl tosylate also reacts slower than beta-phenylethyl tosylate. This is consistent with the above discussion.

The importance of the bromide/tosylate rate ratio is much less clear. As seen in Table 9, the value depends to a large extent on the solvent. It is also quite temperature dependent, since the value for the reaction in ethanol for the beta-phenylethyl system falls from a value of 11 at thirty degrees, to a value of 5.7 at fifty degrees. If we compare the beta-phenylethyl and 1-phenyl-2-propyl systems, the situation is also confusing. Beta-phenylethyl bromide reacts 5.7

times more rapidly than beta-phenylethyl tosylate at fifty degrees in ethanol solution. In t-butyl alcohol solution at the same temperature the difference in rate decreases to 3.4. In the 1-phenyl-2-propyl system the bromide is 5.6 times more reactive than the tosylate in ethanol and the difference increases in going to t-butyl alcohol (to 10.0).

More information is needed before any conclusions can be drawn from the bromide/tosylate rate ratio. It would be helpful to have the values for the cyclopentyl system in t-butyl alcohol at thirty degrees and in ethanol at both thirty and fifty degrees, and also the value for the 1-phenyl-2-propyl system in t-butyl alcohol at thirty degrees, in order to understand better the effects of changes in solvent and temperature on this ratio. There may be an influence of the differences in enthalpy and entropy values, corresponding to the changes in solvent and leaving group, on the magnitude of this bromide/tosylate rate ratio. This is indicated by a study of the thermodynamic values that have been determined, as seen in Table 11. The additional rate data suggested above would also provide more information about these thermodynamic values, thus providing additional information about the factors affecting the bromide/tosylate rate ratio. The answer may lie in the differences in entropy changes for the two systems caused by the change in solvent systems.

A consideration of the elimination of beta-phenylethyl

Table 11. A comparison of enthalpies and entropies in the beta-phenethyl and 1-phenyl-2-propyl systems

Compound	System	H _{Kcal/mole}	S _{e.u.}
2-phenethyl tosylate	ethoxide/ethanol	20.4	-11.2
2-phenethyl bromide	ethoxide/ethanol	20.4	- 6.8
1-phenyl-2-propyl tosylate	ethoxide/ethanol	19.8	- 4.7
1-phenyl-2-propyl bromide	ethoxide/ethanol	19.1	- 4.0
2-phenethyl tosylate	t-butoxide/t-butyl alcohol	14.7	-25.2
2-phenethyl bromide	t-butoxide/t-butyl alcohol	13.0	-25.0
1-phenyl-2-propyl tosylate	t-butoxide/t-butyl alcohol	12.7	-25.5

tosylate and bromide and 1-phenyl-2-propyl tosylate and bromide separately under each solvent system may aid in understanding the data collected thus far, and help to clarify the picture of the E₂ transition state. In ethoxide/ethanol solution, a system of relatively high solvating power and low base strength, beta-phenylethyl tosylate has a rho value of 2.27, indicating that a fair amount of negative charge is localized on the beta-carbon atom in the transition state. This suggests that the

carbon-hydrogen and carbon-leaving group bond breakings are not synchronous. The kinetic isotope effect of 5.66, together with its increase in size to 8.01 when the elimination is conducted in t-butoxide/t-butyl alcohol solution, suggest that there is less than fifty per cent double bond character in the transition state. This must be so because the carbon-hydrogen bond is less than half broken, as indicated by the fact that the kinetic isotope effect increases rather than decreases when the reaction conditions are changed from ethoxide ion in ethanol to t-butoxide ion in t-butyl alcohol.

In t-butoxide/t-butyl alcohol solution the rho value increases to 3.39. This indicates that there is even more carbanion character in the transition state than when the reaction is carried out in ethanol solution. Because the deuterium isotope effect is now 8.01, the carbon-hydrogen bond must be half broken in the transition state, since this value is near the theoretical maximum. This suggests that carbon-leaving group bond breaking has fallen significantly behind carbon-hydrogen bond breaking. There is no sizable increase in the amount of double bond character in the transition state, which resembles the E_{1cb} type.

For beta-phenylethyl bromide in ethanol solution, rho has a value of 2.14, slightly smaller than for the tosylate. k_H/k_D , on the other hand, is higher and has a value of 7.11. This suggests that both carbon-hydrogen and, to a lesser

degree, carbon-leaving group bond breaking are more advanced than in the case of beta-phenylethyl tosylate. There is thus more double bond character and slightly less carbanion character in the transition state. The reaction is more concerted and the transition state resembles the products more than in the case of the tosylates.

In t-butoxide/t-butyl alcohol solution ρ for beta-phenylethyl bromide decreases slightly while k_H/k_D increases to 7.89. This means that while the extent of carbon-hydrogen bond breaking has increased, it has been compensated for by additional carbon-leaving group bond breaking. There is additional double bond character and the transition state bears a greater resemblance to products than does the transition state for the reaction in ethanol. The large t-butoxide/ethoxide rate ratio for the tosylate, compared with the smaller one for the bromide, indicates that there is significantly more carbanion character in the tosylate elimination than in the bromide elimination. In the E_2 spectrum of transition states both fall on the E_{1cb} side of the center, but the bromide transition state is much nearer the center.

For 1-phenyl-2-propyl tosylate, ρ in ethanol solution has a value of 1.32. There is less carbanion character in the transition state than with beta-phenylethyl tosylate. ρ again increases with the change to the t-butoxide/t-butyl alcohol solvent system, indicating a shift toward more E_{1cb}

character in the transition state. Because the t-butoxide/ethoxide rate ratio is very small, 2.7, and because of the relative size of the rho values, it appears that the transition state for the reaction, especially in ethanol, is much nearer the center of the E_2 spectrum of transition states than the transition state of beta-phenylethyl tosylate. It may be on the E_1 side of the center.

For 1-phenyl-2-propyl bromide the reaction in ethanol has a rho value of 1.84, compared with 2.14 for beta-phenylethyl bromide. In changing to t-butoxide in t-butyl alcohol the rho value decreases, as in the case of beta-phenylethyl bromide, but it does so to a greater extent, to 1.37. The t-butoxide/ethoxide rate ratio is 4.9, greater than for the tosylate. It seems that both the tosylate and the bromide have some E_1 character in the transition state, but the transition state for the bromide has more double bond character. Because the transition state for the 1-phenyl-2-propyl system has more E_1 character than the beta-phenylethyl system, the rates are not increased as much in changing to t-butoxide/t-butyl alcohol as they are in the beta-phenylethyl system.

The elimination of alpha, alpha-dimethyl-beta-phenylethyl bromide is particularly interesting. Whereas for the reaction in ethoxide/ethanol the addition of one alpha-methyl group cuts the reaction rate by nearly one half, the addition of a second methyl group has no effect on the rate. In contrast,

the situation for the reaction in t-butyl alcohol is quite different. The reaction rate is lowered by a factor of four by the addition of one alpha methyl group. The addition of a second alpha methyl group causes a tremendous lowering of the rate to 1/120 of the value of beta-phenyl ethyl bromide. It might be argued that steric effects are the principal causes of the reaction rates found in this system. If this were the case some sign of steric influence might have been observed for the reaction in ethanol. On the contrary, there is no decrease in rate upon the addition of the second methyl group. Although the steric requirements of t-butoxide are certainly greater than those of ethoxide, a similar decrease in rate, though smaller, would have been expected for the reaction in ethanol. Also the steric requirements in the cis-1-phenyl-2-cyclopentyl system, which has both an alpha and a beta alkyl substituent, should be at least as great as in this system. In the cis-1-phenyl-2-cyclopentyl system the t-butoxide/ethoxide ratio was 1.2 and therefore this author does not believe that the steric requirements of the t-butoxide ion account for the large decrease in rate.

It appears that the rate of an E_2 elimination is favored by the introduction of some of the factors which give E_{1cb} character to the transition state, such as a less polar solvent, a stronger base, and a beta-aryl substituent. It is also favored by the presence of a better leaving group, which has

the reverse effect on the transition state. These rate increasing factors seem to have their largest effect on the rate when the transition state is on the same side of the center of the E_2 spectrum as the direction which these factors favor. Also, the farther the transition state is from the center, the larger is the increase in the rate caused by the change in the reaction. In the case under discussion, the introduction of the methyl groups shifts the transition state toward the E_1 side of the spectrum. The change from ethoxide in ethanol solution to t-butoxide in t-butyl alcohol solution thus has the opposite effect in the present system that it does in the beta-phenylethyl system. The t-butoxide/ethoxide rate ratio for beta-phenylethyl bromide is 10.8; for 1-phenyl-2-propylbromide it is 4.9; for 1-phenyl-2-methyl-2-propyl bromide it is 0.14. On the other hand the ethoxide/t-butoxide ratio is 8.1. It may well be that the t-butoxide/ethoxide rate ratio is a very useful tool in determining the position of a reaction transition state in the E_2 spectrum of transition states. Considering also the value of 1.2 obtained by Smith (9) in the case of cis-1-phenyl-2-cyclopentyl tosylate, one is tempted to devise a scale such as that given in Figure 2.

It would be extremely interesting to know how well this picture corresponds to all that is known about the E_2 elimination. It certainly agrees with the data for the

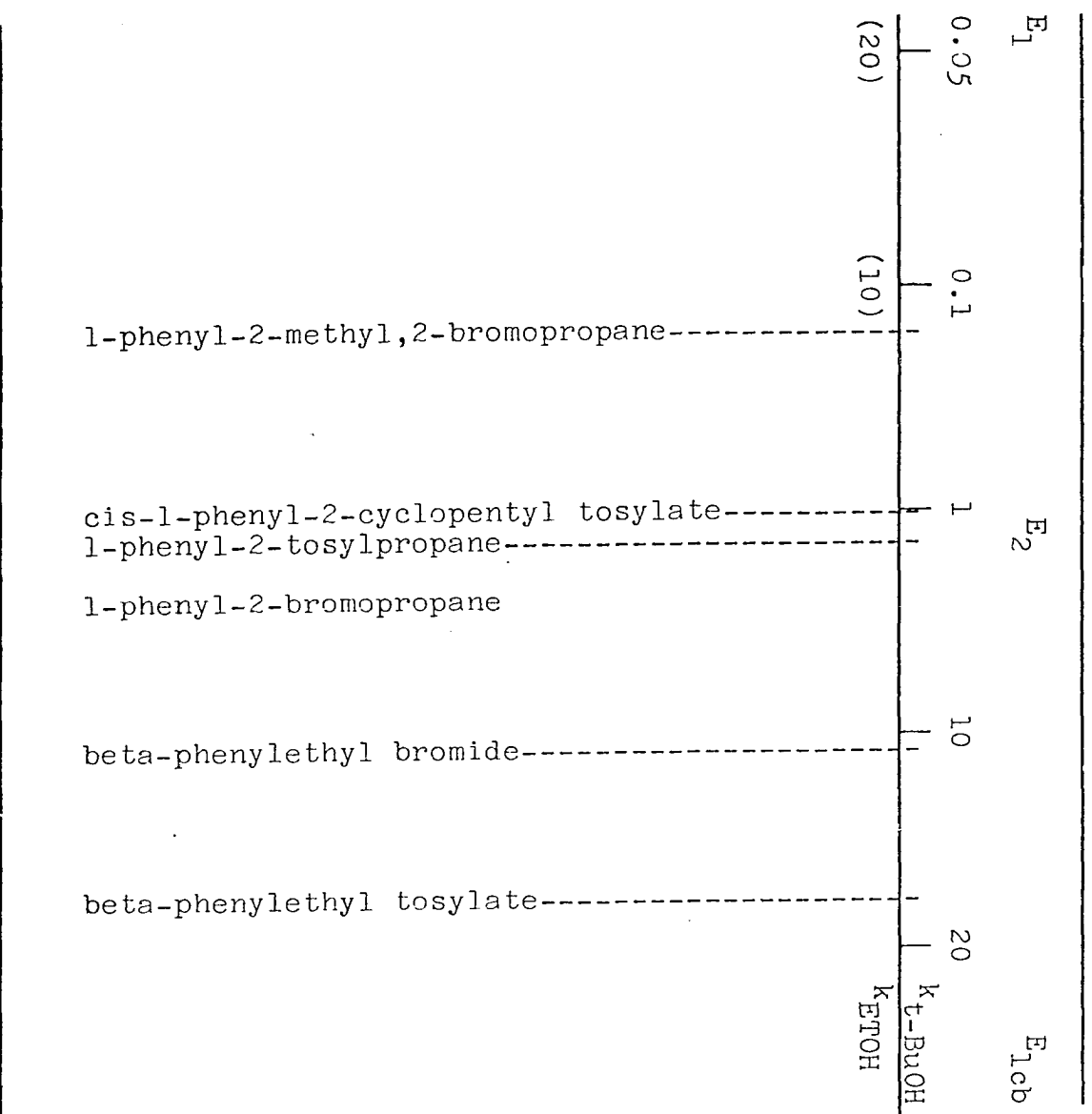


Figure 2. Correlation of transition state with
t-butoxide/ethoxide rate ratio

beta-phenylethyl and 1-phenyl-2-propyl systems; the t-butoxide/ethoxide ratio increases in the same direction as the rho value for the reaction in ethanol solution. The cis-1-phenyl-2-cyclopentyl tosylate rate ratio and rho value both agree on its position on the chart. This author believes that the t-butoxide/ethoxide rate ratio may be as important as the rho value in determining the relative position of the transition state in the E_2 reaction spectrum.

EXPERIMENTAL

Preparation and Purification of Materials

Preparation of aryl-acetic acids

Phenylacetic acid was obtained from Eastman Co., and p-methoxyphenylacetic acid was obtained from Aldrich Co. These were used without prior purification.

p-Chlorophenylacetic acid p-Chlorobenzyl chloride (Eastman Kodak practical grade) was fractionated prior to conversion to p-chlorobenzylmagnesium chloride by reaction with magnesium in anhydrous ether solution. The Grignard reagent thus prepared was carbonated by pouring the ethereal solution over an excess of dry ice and stirring the resultant mass for one hour, at which time evolution of carbon dioxide ceased. An excess of cold dilute hydrochloric acid and ice was then carefully added and the layers were separated. The aqueous layer was extracted with ether, and the combined ether solutions were then extracted with ten per cent sodium hydroxide solution. The aqueous extracts were acidified and the precipitated p-chlorophenylacetic acid was collected by filtration. It was recrystallized from an ether-pentane solution.

m. p. 103-104.5°C. (Lit. m.p. 104-105°C.) (30)

m-Bromoacetophenone This was prepared by the method of Pearson and Pope (31). To a stirred mixture of 339 g. of anhydrous aluminum chloride and 93 g. of acetophenone was added 140 g. of bromine, at room temperature, during ten minutes. The semi-solid mass was stirred for one hour and quenched by carefully pouring the reaction mixture into a slurry of ice and acid. The product was extracted with ether and the ether solution was washed with a saturated sodium bicarbonate solution and with water. After drying over anhydrous magnesium sulfate, the ether was removed and the residue fractionated to give 118.5 g. (74%) of m-bromoacetophenone, b. p. 77-79 °C (0.3 mm.) [Lit. b. p. 94-95°C. (2 mm.)] (31).

m-Bromophenylacetic acid This was prepared by the method of Solmssen and Wenis (32). Sulfur (28 g.) was added to a mixture of 75 g. morpholine and 115 g. m-bromoacetophenone. The mixture was stirred under reflux for eighteen hours, and the resulting thiomorpholide was hydrolyzed by boiling for eighteen hours with 1.5 liters of ten per cent potassium hydroxide solution. The solution was acidified after cooling and the product collected by filtration. Recrystallization from ether solution yielded 99.0 g. (72%) of m-bromophenylacetic acid, m. p. 98-99.5 °C. (Lit. m. p. 100 °C.) (33).

p-Methylphenylacetic acid This was similarly prepared from p-methylacetophenone (Eastman White Label); m. p. 90-91 °C. (Lit. m. p. 91 °C.) (34).

Preparation of arylacetones

These compounds were prepared from the corresponding phenylacetic acids by the method of Tegner (35). For example, 1000 ml. of a 0.9 M solution of methyl lithium in anhydrous ether was added slowly to a stirred solution of 45 g. (0.3 mole) of phenylacetic acid in 250 ml. anhydrous ether, during two hours. The reaction was stirred at room temperature for twelve hours and quenched by the addition of 400 ml. water. The layers were separated and the ether layer washed with water and dried over anhydrous magnesium sulfate. The ether was removed and the residue fractionated to yield 35.4 g. of phenylacetone, b. p. 120-122 °C., (30 mm.) [Lit. b. p. 109-112 °C., (24 mm.)] (36).

p-Chlorophenylacetone, b. p. 163-65 °C. (20 mm.) [Lit. b. p. 80-85 °C. (0.4 mm.)] (37).

m-Bromophenylacetone, b. p. 95-97 °C. (0.2 mm.).

p-Methoxyphenylacetone, b. p. 154-55 °C. (30 mm.) [Lit. b. p. 147-147 °C. (22 mm.)] (38).

p-Methylphenylacetone, b. p. 70-71 °C. (1.0 mm.) [Lit. b. p. 92-94 °C. (3.0 mm.)] (39).

Preparation of 1-aryl-2-propanols

These compounds were prepared by lithium aluminum hydride reduction of the corresponding arylacetones. For example, 12.0 g. of phenylacetone in 100 ml. of anhydrous ether was added dropwise to a stirred solution of 2.1 g. of lithium aluminum hydride in 50 ml. anhydrous ether, at a rate which provided gentle reflux. The reaction was stirred for five hours at room temperature and quenched by the addition of wet ether. The reaction mixture was then poured into 100 ml. cold dilute hydrochloric acid and the ether layer separated. The aqueous layer was extracted with ether and the combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed and the residue fractionated to yield 11.0 g. (93 %) of 1-phenyl-2-propanol, b. p. 127-28 °C. (15 mm.) [Lit. b. p. 92 °C. (2.0 mm.)] (40).

1-(p-chlorophenyl)-2-propanol, b. p. 152-54 °C. (15.0 mm.).

1-(m-bromophenyl)-2-propanol, b. p. 94-5 °C. (0.1 mm.).

1-(p-methoxyphenyl)-2-propanol, b. p. 158-161 °C. (15 mm.)

[Lit. b. p. 121 °C. (3 mm.)] (40).

1-(p-methylphenyl)-2-propanol, b. p. 66-67 °C. (0.4 mm.) [Lit. b. p. 97 °C. (2 mm.)] (40).

Preparation of 1-aryl-2-propyl tosylates

These compounds were prepared from the corresponding alcohols by Tipson's (41) procedure. The alcohol was dissolved in anhydrous pyridine and the solution cooled to -5 C.

p-Toluenesulfonyl chloride was then added in portions with shaking until the solid dissolved. After swirling for one hour by hand the solutions were placed in the freezer for twenty-four hours, then poured into ice water. The precipitated tosylate was filtered, and recrystallized from an ether-pentane solution.

1-Phenyl-2-p-toluenesulfonylpropane m. p. 93.5-95 °C.

Anal. Calcd. for $C_{16}H_{18}O_3S$: C, 66.17; H, 6.25; S, 11.04;
Found: C, 66.14; H, 6.14; S, 10.91.

1-(p-Chlorophenyl)-2-p-toluenesulfonylpropane m. p. 79.5-80.5 °C.

Anal. Calcd. for $C_{16}H_{17}ClO_3S$: C, 59.17; H, 5.28; Cl, 10.92; S, 9.87; Found: C, 59.25; H, 5.31; Cl, 11.00; S, 9.99.

1-(m-Bromophenyl)-2-p-toluenesulfonylpropane m. p. 57-58 °C.

Anal. Calcd. for $C_{16}H_{17}BrO_3S$: C, 52.03; H, 4.64; Br, 21.64; S, 8.68; Found: C, 52.08; H, 4.63; Br, 21.62; S, 8.81.

1-(p-Methoxyphenyl)-2-p-toluenesulfonylpropane m. p. 77-78 °C.

Anal. Calcd. for $C_{17}H_{20}O_4S$: C, 63.74; H, 6.29; S, 10.08; Found: C, 63.76; H, 6.39; S, 10.01.

1-(p-Methylphenyl)-2-p-toluenesulfonylpropane m. p. 49-50 °C.

Anal. Calcd. for $C_{17}H_{20}O_3S$: C, 67.06; H, 6.62; S, 10.53.
Found: C, 67.17; H, 6.69; S, 10.49.

Preparation of 1-aryl-2-bromopropanes

These compounds were prepared by reacting the corresponding tosylate with lithium bromide in acetone solution (42). For example, 5.10 g. of 1-phenyl-2-propyl tosylate was added to 4.2 g. of lithium bromide in 35 ml. anhydrous acetone and the resulting solution stirred for three days at room temperature. The inhomogeneous mixture was then poured into 100 ml. water and extracted with three fifty ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and the ether was removed. The residue was then carefully fractionated to give 2.80 g. (87%) of 1-phenyl-2-propanol, b. p. 46-47 °C. (0.1 mm.) [Lit b. p. 88-89 °C. (4.0 mm.)] (43).

1-(p-Chlorophenyl)-2-bromopropane, b. p. 80-81 °C. (0.5 mm.).

1-(m-Bromophenyl)-2-bromopropane, b. p. 90-91 °C. (0.5 mm.).

1-(p-Methylphenyl)-2-bromopropane, b. p. 63-63.5 °C. (0.25 mm.).

Nuclear magnetic resonance (N.M.R.) spectra were run on each of these compounds to certify their structure and determine their purity. From the integration of the spectra the purity was found to be high.

Preparation of 1-phenyl,2-methyl,2-propanol

This compound was prepared by the addition of an ethereal solution of phenylacetone to an ethereal solution of methylmagnesium iodide. The reaction was stirred for two hours at room temperature and poured into ice and cold dilute sulfuric

acid. The layers were separated and the aqueous layer extracted with ether. The combined ether extracts were washed with water, saturated sodium bicarbonate solution and water. The ether solution was then dried over anhydrous magnesium sulfate and the ether was removed. Careful fractionation of the residue gave 1-phenyl,2-methyl,2-propanol, b. p. 65.0 °C. (1 mm.) [Lit. b. p. 94 °C. (7 mm.)] (44).

Preparation of 1-phenyl,2-methyl,2-bromopropane

1-phenyl,2-methyl,2-propanol was added to an excess of concentrated hydrobromic acid and the mixture was shaken at room temperature for fifteen minutes. The reaction mixture was then poured into an equal volume of water and extracted with ether. The combined ether extracts were washed with water, five per cent sodium bicarbonate solution, and water. The ether solution was then carefully dried over anhydrous magnesium sulfate and the ether removed. The residue was carefully fractionated to give a color-less liquid, b. p. 51.0 °C. (1 mm.) [Lit. b. p. 83-85 °C. (4.5 mm.)] (45). An N.M.R. spectrum was taken to certify the structure and purity of the compound. Integration of the spectrum showed the purity to be very good.

Purification of Materials

Anhydrous ethanol: The last traces of water were removed from commercial absolute ethanol by the method of Manske (46)

using sodium ethoxide and diethyl phthalate.

Anhydrous tertiary butanol: Commercial t-butanol (Eastman White Label) was fractionally distilled, a sharp center fraction boiling 82-82.5 °C. (1 Atm.) being taken. This sample was then distilled twice from sodium.

Potassium: Commercial (Malinkrodt) potassium metal was purified by repeated fusion under heptane. The lighter impurities floated to the surface and were skimmed off.

Measurement of Reaction Rates

A solution approximately 0.01 molar in the desired substrate and 0.1 molar in the base was prepared by adding the base solution, equilibrated at the reaction temperature, to an accurately weighed sample of the substrate in a 50 ml. volumetric flask. The flask was immersed immediately in the constant temperature bath and periodically shaken until the substrate had all dissolved.

Five ml. aliquots were then withdrawn at appropriate intervals and quenched by draining into ice-cold 95% ethanol. These solutions were immediately diluted to the proper concentrations for ultraviolet spectroscopy.

The ultraviolet absorptions were measured with a Beckman DK-2A Ratio-Recording Spectrophotometer, or with a Beckman DU if the Dk-2A was not operational.

All the reactions were done under pseudo-first order

conditions and the rate constants were calculated by the use of the equation:

$$k_1 = \frac{2.303}{t} \log \frac{A_{\infty} - A_0}{A_{\infty} - A_t}$$

Second order rates were obtained by dividing the first order rate constant by the base concentrations.

The rates calculated by average agreed well with those determined by the computer using the method of least squares, as seen in Tables 13-38.

The Hammet equation, $\log \frac{k}{k_0} = \sigma\rho$, was applied to the data and ρ obtained by the method of least squares. The results are given in Table 8.

The extinction coefficients and lambda-max were determined experimentally from completely reacted solutions of the bromides. The wavelengths used for calculating the rate constants and the corresponding log e values are given in the following table.

Table 12. Absorption maxima and extinction coefficients for some meta and para substituted alpha-methyl styrenes in 95% ethanol solution

Compound	λ_{\max} (m μ)	log e
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$	248	4.27
m-BrC ₆ H ₄ CH=CHCH ₃	250	4.22
p-ClC ₆ H ₄ CH=CHCH ₃	255	4.39
p-MeC ₆ H ₄ CH=CHCH ₃	253	4.32
p-MeO-C ₆ H ₄ CH=CHCH ₃	258	4.35
$\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2$	244	4.05

Table 13. Rate of reaction of 1-phenyl-2-tosylpropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.072	--
6.0	.097	2.44
12.5	.121	2.40
26.0	.169	2.54
35.0	.193	2.49
47.0	.230	2.53
61.5	.248	2.44
73.0	.263	2.35
1000.	.369	--

average rate = $2.46 \pm .06$; computed rate = 2.400.

root mean square error = 0.030; intercept = 1.640×10^{-2} .

concentration of base = 0.6960 M; concentration of substrate = 0.0216 M. log e = 4.25.

Table 14. Rate of reaction of 1-(p-chlorophenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.128	--
5.0	.208	7.01
15.0	.322	6.83
25.0	.398	6.82
35.0	.454	7.05
45.0	.478	6.55
55.0	.500	6.46
65.0	.522	6.96
500.	.550	--

average rate = $6.81 \pm .18$; computed rate = 6.72.
 root mean square error = 0.057; intercept = 9.040×10^{-3} .
 concentration of base = 0.6960 M; concentration of substrate = 0.0209 M; log e = 4.38.

Table 15. Rate of reaction of 1-(p-methoxyphenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.056	--
7.3	.083	1.49
15.1	.118	1.72
30.2	.158	1.49
41.5	.189	1.49
56.3	.241	1.67
70.4	.268	1.61
88.3	.292	1.51
1,000	.495	--

average rate = $1.58 \pm .07$; computed rate = 1.544.
 root mean square error = 0.021; intercept = 8.586×10^{-3} .
 concentration of base = 0.6960 M; concentration of substrate = .0205 M. log e = 4.37.

Table 16. Rate of reaction of 1-(m-bromophenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.310	--
4.5	.480	2.06
10.3	.690	2.14
16.2	.900	2.14
24.1	1.190	2.27
32.3	1.410	2.23
43.1	1.650	2.15
54.6	1.950	2.25
650.0	3.450	--

average rate = $2.18 \pm .06$; computed rate = 2.247.
 root mean square error = 0.009; intercept = 6.837×10^{-3} .
 concentration of base = 0.1385 M; concentration of substrate = 0.0189 M. $\log e = 4.26$.

Table 17. Rate of reaction of 1-(m-bromophenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.198	--
18.6	.287	2.74
39.8	.393	2.86
63.1	.487	2.72
84.5	.593	2.84
117.0	.698	2.65
151.7	.836	2.68
201.4	1.004	2.58
3,890.0	3.145	--

average rate = $2.74 \pm .08$; computed rate = 2.615.
 root mean square error = 0.003; intercept = 4.941×10^{-3} .
 concentration of base = 0.1385 M; concentration of substrate = 0.0186 M. $\log e = 4.23$.

Table 18. Rate of reaction of 1-phenyl-2-bromopropane in sodium ethoxide-ethanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.170	--
10.3	.240	3.28
16.3	.290	3.60
25.3	.350	3.50
37.2	.430	3.49
47.7	.500	3.49
59.0	.580	3.55
73.6	.670	3.51
4,200.	3.640	--

average rate = $3.49 \pm .06$; computed rate = .543.

root mean square error = 0.001; intercept = 6.909×10^{-4} .

concentration of base = 0.1385 M; concentration of substrate = 0.0185 M. $\log e = 4.30$.

Table 19. Rate of reaction of 1-phenyl-2-bromopropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.170	--
12.3	.490	1.46
31.9	.980	1.56
48.4	1.330	1.59
65.4	1.590	1.53
81.9	1.830	1.53
100.8	2.000	1.45
950.	3.310	--

average rate = $1.52 \pm .04$; computed rate = 1.459.

root mean square error = 0.017; intercept = 1.883×10^{-2} .

concentration of base = 0.0860 M; concentration of substrate = 0.0199 M. $\log e = 4.22$.

Table 20. Rate of reaction of 1-(p-methoxyphenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.470	--
33.6	.590	1.88
54.0	.650	1.78
73.8	.720	1.83
104.1	.810	1.79
124.8	.880	1.82
151.8	.980	1.87
172.6	1.030	1.85
191.6	1.070	1.80
222.5	1.160	1.79
244.7	1.220	1.82
265.5	1.280	1.83
285.3	1.330	1.83
305.0	1.440	1.97
325.6	1.450	1.87
341.9	1.490	1.86
368.8	1.560	1.88
4,500.	3.680	--

average rate = $1.84 \pm .04$; computed rate = 1.883.

root mean square error = 0.006; intercept = 3.860×10^{-3} .

concentration of base = 0.6960 M; concentration of substrate = 0.0194 M. $\log e = 4.28$.

Table 21. Rate of reaction of 1-(m-bromophenyl)-2-bromopropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^3$ (sec. ⁻¹)
0	.102	--
5.4	.171	1.35
9.4	.207	1.37
15.2	.246	1.47
21.4	.261	1.32
26.1	.272	1.31
31.4	.285	1.48
37.2	.288	1.38
350.0	.297	--

average rate = $1.38 \pm .05$; computed rate = 1.402.
 root mean square error = 0.092; intercept = 1.854×10^{-2} .
 concentration of base = 0.0897 M; concentration of substrate = 0.0187 M. $\log e = 4.19$.

Table 22. Rate of reaction of 1-phenyl-2-tosylpropane in potassium-t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.180	--
6.8	.280	1.03
14.1	.380	1.02
22.7	.500	1.04
32.1	.600	1.99
42.3	.725	1.01
53.7	.855	1.02
66.0	.980	1.01
1,300.	2.600	--

average rate = $1.02 \pm .01$; computed rate = 1.009.
 root mean square error = 0.002; intercept = 7.891×10^{-4} .
 concentration of base = 0.1130 M; concentration of substrate = 0.0143 M. $\log e = 4.26$.

Table 23. Rate of reaction of 1-(p-chlorophenyl)-2-tosyl propane in sodium ethoxide-ethanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.124	--
30	.211	5.44
60	.279	5.05
90	.346	5.04
120	.418	5.26
150	.463	5.00
180	.513	5.00
210	.582	5.20
240	.588	4.97
270	.670	5.32
300	.757	6.32
330	.762	5.83
360	.775	5.55
390	.789	5.34
420	.798	5.10
450	.814	4.99
2,400	1.056	--

average rate = $5.23 \pm .20$; computed rate = 5.072.

root mean square error = 0.083; intercept = 2.696×10^{-2} .

concentration of base = 0.4890 M; concentration of substrate = 0.0410 M. $\log e = 4.31$.

Table 24. Rate of reaction of 1-phenyl-2-tosylpropane in potassium t-butoxide-t-butanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.106	--
22.0	.160	2.65
42.5	.210	2.69
61.9	.250	2.60
85.5	.300	2.58
109.6	.350	2.58
130.6	.395	2.61
2,400.	1.670	--

average rate = $2.62 \pm .03$; computed rate = 2.570.
 root mean square error = 0.001; intercept = 1.621×10^{-3} .
 concentration of base = 0.1130; concentration of substrate = 0.0128. $\log e = 4.22$.

Table 25. Rate of reaction of 1-phenyl-2-tosylpropane in sodium ethoxide-ethanol solution at 30 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.060	--
30	.094	2.02
60	.127	2.03
90	.161	2.08
120	.204	2.27
150	.230	2.19
180	.242	1.97
215	.294	2.19
5000	1.011	--

average rate = $2.11 \pm .09$; computed rate = 2.06.
 root mean square error = 0.009; intercept = 1.311×10^{-2} .
 concentration of base = 0.4890 M; concentration of substrate = 0.0550 M. $\log e = 4.23$.

Table 26. Rate of reaction of 1-(p-chlorophenyl)-2-bromopropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.040	--
3.4	.077	7.31
11.1	.133	7.36
16.0	.165	7.66
21.2	.188	7.54
26.2	.202	7.15
31.7	.225	7.74
370.	.280	--

average rate = $7.46 \pm .191$; computed rate = 7.505.

root mean square error = 0.031; intercept = 2.127×10^{-3} .

concentration of base = 0.0897 M; concentration of substrate = 0.0115 M. $\log e = 4.38$.

Table 27. Rate of reaction of 1-phenyl-2-bromopropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.236	--
7.2	.330	1.31
11.5	.390	1.34
16.5	.470	1.43
22.6	.560	1.48
28.1	.630	1.47
35.6	.720	1.47
920.0	2.050	--

average rate = $1.41 \pm .06$; computed rate = 1.526.

root mean square error = 0.002; intercept = 1.586×10^{-3} .

concentration of base = 0.0897 M; concentration of substrate = 0.0195 M. $\log e = 4.02$.

Table 28. Rate of reaction of 1-phenyl-2-bromopropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.225	--
6.70	.785	8.25
10.35	1.050	8.64
13.90	1.270	8.93
17.50	1.415	8.72
20.90	1.550	8.78
24.40	1.670	8.89
329.0	2.210	--

average rate = $8.79 \pm .09$; computed rate = 9.03.

root mean square error = 0.010; intercept = 2.505×10^{-2} .

concentration of base = 0.1130 M; concentration of substrate = 0.0119 M. $\log e = 4.27$.

Table 29. Rate of reaction of 1-(p-methylphenyl)-2-bromopropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.020	--
7.1	.040	1.74
17.6	.070	1.87
29.3	.100	1.92
41.9	.130	1.99
68.3	.170	1.87
90.0	.201	1.91
110.2	.220	1.90
890.0	.300	--

average rate = $1.89 \pm .05$; computed rate = 1.90.

root mean square error = 0.010; intercept = 7.279×10^{-4} .

concentration of base = 0.1080 M; concentration of substrate = 0.0144 M. $\log e = 4.32$.

Table 30. Rate of reaction of 1-(p-methylphenyl)-2-tosylpropane in sodium ethoxide-ethanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.080	--
9.30	.108	3.18
24.90	.150	3.03
44.90	.205	3.03
64.35	.260	3.11
89.90	.330	3.17
109.00	.380	3.20
143.80	.460	3.17
3,200.	1.670	--

average rate = $3.13 \pm .06$; computed rate = 3.197.

root mean square error = 0.002; intercept = 2.151×10^{-3} .

concentration of base = 0.1080 M; concentration of substrate = 0.0111 M. $\log e = 4.18$.

Table 31. Rate of reaction of 1-phenyl-2-methyl-2-bromopropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.150	--
9.3	.172	2.85
29.9	.220	2.87
49.3	.260	2.79
68.9	.310	2.96
90.1	.350	2.88
111.7	.390	2.83
158.0	.480	2.86
2,960.0	1.540	--

average rate = $2.86 \pm .04$; computed rate = 2.853.

root mean square error = 0.022; intercept = 4.110×10^{-4} .

concentration of base = 0.1046 M; concentration of substrate = 0.0121 M. $\log e = 4.10$.

Table 32. Rate of reaction of 1-(p-chlorophenyl)-2-bromopropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 (x 10^3)$ (sec. ⁻¹)
0	.380	--
6.05	1.350	1.81
10.45	1.750	1.81
13.86	1.975	1.88
17.70	2.110	1.83
21.20	2.210	1.86
24.74	2.260	1.80
190.0	2.400	--

average rate = $1.83 \pm .03$; computed rate = 1.820.

root mean square error = 0.029; intercept = 8.719×10^{-3} .

concentration of base = 0.1046 M; concentration of substrate = 0.0105 M. $\log e = 4.36$.

Table 33. Rate of reaction of 1-(p-methylphenyl)-2-tosylpropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.110	--
9.51	.168	4.52
22.36	.240	4.39
36.06	.322	4.52
49.31	.397	4.56
63.86	.493	4.82
82.86	.581	4.67
106.59	.700	4.70
3,600.0	2.380	--

average rate = $4.60 \pm .11$; computed rate = 4.767.

root mean square error = 0.002; intercept = 3.340×10^{-3} .

concentration of base = 0.1046 M; concentration of substrate = 0.0133 M. $\log e = 4.25$.

Table 34. Rate of reaction of 1-(p-methoxyphenyl)-2-tosylpropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^5$ (sec. ⁻¹)
0	.150	--
22.40	.235	2.76
39.25	.292	2.67
60.75	.378	8.83
83.70	.457	2.81
109.52	.543	2.81
141.20	.638	2.77
4,700.0	2.485	--

average rate = $2.77 \pm .04$; computed rate = 2.795.

root mean square error = 0.002; intercept = 6.301×10^{-4} .

concentration of base = 0.1046 M; concentration of substrate = 0.0122 M. $\log e = 4.26$.

Table 35. Rate of reaction of 1-(m-bromophenyl)-2-bromopropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^3$ (sec. ⁻¹)
0	.298	--
5.38	.679	2.70
8.63	.798	2.75
11.80	.871	2.88
14.98	.906	2.85
17.96	.927	2.87
21.03	.938	2.81
240.0	.957	--

average rate = $2.81 \pm .06$; computed rate = 2.886.

root mean square error = 0.031; intercept = 4.980×10^{-2} .

concentration of base = 0.1020 M; concentration of substrate = 0.0063 M. $\log e = 4.18$.

Table 36. Rate of reaction of 1-(p-methylphenyl)-2-bromopropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.021	--
14.16	.103	4.19
21.50	.138	4.44
36.82	.159	4.47
34.00	.180	4.38
40.37	.194	4.25
52.57	.220	4.28
290.0	.290	--

average rate = $4.34 \pm .09$; computed rate = 4.207.

root mean square error = 0.013; intercept = 2.395×10^{-2} .

concentration of base = 0.1020 M; concentration of substrate = 0.0152 M. $\log e = 4.28$.

Table 37. Rate of reaction of 1-(m-bromophenyl)-2-tosylpropane in potassium t-butoxide-t-butanol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.300	--
8.60	.632	4.82
15.02	.830	4.82
22.70	1.037	4.95
30.30	1.191	4.94
38.70	1.328	4.96
50.40	1.480	5.09
370.0	1.803	--

average rate = $4.93 \pm .07$; computed rate = 5.117.

root mean square error = 0.009; intercept = 2.377×10^{-2} .

concentration of base = 0.1020 M; concentration of substrate = 0.0126 M. $\log e = 4.16$.

Table 38. Rate of reaction of 1-(p-chlorophenyl)-2-tosylpropane in t-butoxide-t-butyl alcohol solution at 50 degrees

Time elapsed (min.)	Absorbance	$k_1 \times 10^4$ (sec. ⁻¹)
0	.152	--
11.23	.498	2.26
16.43	.645	2.28
21.74	.782	2.28
30.10	.985	2.30
37.48	1.148	2.32
50.30	1.371	2.28
1,150.0	2.600	--

average rate = $2.29 \pm .02$; computed rate = 2.303.

root mean square error = 0.003; intercept = 1.487×10^{-3} .

concentration of base = 0.1020 M; concentration of substrate = 0.0126 M. $\log e = 4.31$.

Table 39. Product analysis of the elimination reactions of some $Y-C_6H_4CH=CHXCH_3$ compounds

Y	X	Base	1-olefin	Styrene		Ether
				cis-	trans-	
H	OTos	EtO ⁻	1	3.5	77	18.5
Me	OTos	EtO ⁻	2.8	9	71	17.2
Br	OTos	EtO ⁻	3	7	86	4.0
H	OTos	t-BuO ⁻	2	4	94	0.0
Me	OTos	t-BuO ⁻	1.5	7	91	0.0
Br	OTos	t-BuO ⁻	3	6	91	0.0
Me	Br	EtO ⁻	1	4	95	0.0
Br	Br	EtO ⁻	2.5	14.5	83	0.0
Me	Br	t-BuO ⁻	0	1.5	98.5	0.0
Br	Br	t-BuO ⁻	3	6	91	0.0

Computer Program

```
C  PROGRAM FOR LEAST SQUARES ANALYSIS OF FIRST ORDER RATE
    CONSTANTS
C  JOBNO=JOB NUMBER (999 FOR EXIT)
C  N=NUMBER OF KINETIC POINTS EXCLUSIVE OF INFINITY POINT
    AND INITIAL POINT
C  TNFPT=INFINITY POINT
C  TINIT=INITIAL POINT
C  TITLE CARD IS 80 COLUMNS LONG
C  ABS AND TIME ARE THE KINETIC POINTS AND THEIR RESPECTIVE
    TIMES ONE EACH TO CARD
    DIMENSION ABS(40),TITLE(16),Y(40),V(40),TIME(40),W(40)
1  READ INPUT TAPE 1,3,JOBNO,N,TNFPT,TINIT
    IF(JOBNO-999)7,400,7
400 STOP 88
    7  READ INPUT TAPE 1,2,(TITLE(I),I=1,16)
        DO 9 I=1,N
9  READ INPUT TAPE 1,4, ABS(I),TIME(I)
    X=TNFPT-TINIT
    DO 5 I=1,N
5  Y(I)=LOGF(X/(TNFPT-ABS(I)))
    SLOPE=0.0
    B=0.0
    CALL LEASQ(N,TIME(1),Y(1),SLOPE,B,V(1),W(1))
    WRITE OUTPUT TAPE 2,10,JOBNO,(TITLE(I),I=1,16)
```



```

WRITE OUTPUT TAPE 2,11,SLOPE,B
G=N
RMSE=0.0
Do 100 I=1,N
100 RMSE=RMSE+W(I)**2
RMSE=SQRTF(RMSE/G)
DO 12 J=1,N
12 WRITE OUTPUT TAPE 2,13, Y(J),TIME(J),V(J)
WRITE OUTPUT TAPE 2,14,RMSE
GO TO 1
3 FORMAT(214,2F5.3)
2 FORMAT(16A5)
4 FORMAT(F5.3,F10.2)
10 FORMAT(16H1 PROBLEM NUMBER 14,5X,16A5)
11 FORMAT(16HO RATE CONSTANT=E11.4 / 12HO INTERCEPT=E11.4
/1HO /15HO
1KINETIC DATA / 60HO Y(I) TIME(I)
CALCUL
2ATED ABS(I) /1HO)
13 FORMAT(1H 3F15.3)
14 FORMAT(26HO ROOT MEAN SQUARE ERROR=F5.3)
END

SUBROUTINE LEASQ(N,X,Y,SLOPE,B,CALCY,DIF)
DIMENSION X(40),Y(40), CALCY(40),DIF(40)

```

```
SUMX=0.0
SUMY=0.0
SUMXY=0.0
SUMXX=0.0
DO 10 J=1,N
SUMX=SUMX+X(J)
SUMY=SUMY+Y(J)
SUMXX=SUMXX+X(J)**2.
10 SUMXY=SUMXY+X(J)*Y(J)
G=N
DENOM=SUMX**2.-G*SUMXX
SLOPE=(SUMX*SUMY-G*SUMXY)/DENOM
B=(SUMX*SUMXY-SUMY*SUMXX) /DENOM
DO 11 J=1,N
CALCY(J)=SLOPE*X(J)+B
11 DIF(J)=Y(J)-CALCY(J)
RETURN
END
```

SUMMARY

The base catalyzed elimination reaction of a series of meta and para substituted 1-phenyl-2-propyl tosylates and bromides with ethoxide ion in ethanol, and with t-butoxide ion in t-butyl alcohol was investigated and compared with work in the beta-phenylethyl and cyclopentyl systems. The Hammett rho value was calculated in each case and, for the tosylates, was found to increase from 1.32 in ethoxide/ethanol to 1.88 in t-butoxide/t-butyl alcohol, while the rho value for the bromides decreased from 1.84 to 1.37. The changes in rho were compared with the corresponding changes in the beta-phenylethyl system. The t-butoxide/ethoxide and bromide/tosylate rate ratios were calculated and discussed in view of the corresponding values obtained in the beta-phenylethyl, and cyclopentyl systems. The t-butoxide/ethoxide rate ratio was found to be a meaningful measure of the position of the transition state of an elimination reaction in the E_2 spectrum of transition states. The bromide/tosylate rate ratio was found to be highly dependent upon solvent and temperature. Further work is indicated before the significance of this ratio can be known.

The effect of alpha-methyl groups upon the rates of elimination reactions was investigated. A significant decrease in the rate in t-butyl alcohol solution was observed and interpreted in terms of increased E_1 character.

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