Isotope Effect Studies on Elimination Reactions. XI. The Nature of the Transition State for the E2 Reaction of 2-Phenylethyldimethylanilinium Salts Containing Substituents in the Aniline Ring with Sodium Ethoxide in Ethanol¹

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PETER SCHMID and ARTHUR NEWCOMBE BOURNS. Can. J. Chem. 53, 3513 (1975).

Kinetic isotope effects have been determined for the E2 reactions of a series of 2-phenylethyldimethylanilinium salts containing substituents in the aniline ring with sodium ethoxide in ethanol at 40 °C. The nitrogen isotope effect, $(k^{14}/k^{15} - 1)100$, is not very sensitive to substituent changes but appears to increase slightly with increasing electron-withdrawing ability of the substituents, *i.e.*, 1.19 ± 0.07 , 1.13 ± 0.06 , 1.12 ± 0.08 , 1.30 ± 0.07 , and 1.32 ± 0.06 for p-OCH₃, p-CH₃, p-H, p-Cl, and, m-CF₃, respectively. The hydrogen-deuterium isotope effects pass through a minimum in the region of the unsubstituted compound and increase both with increasing electron-donating as well as with electron-withdrawing power of the substituents, *i.e.* $k^{\rm H}/k^{\rm D} = 4.70 \pm 0.06$, 4.61 ± 0.04 , 4.51 ± 0.04 , 4.53 ± 0.09 , 5.00 ± 0.07 , and 5.39 ± 0.07 for p-OCH₃, p-CH₃, p-H, p-Cl, m-CF₃, and p-CF₃, respectively. The results are discussed in terms of recent theoretical treatments of the effect of structural variations in the reactants on the nature of the transition state of E2 elimination reactions. The conclusion is reached that the transition states in the present reaction series can be characterized as 'central with slight carbanion character' and that the effect of a change in the ability of the leaving group on the structure of the transition state manifests itself mainly in the direction perpendicular to the reaction coordinate. A simple novel hypothesis is formulated which emphasizes the importance of the location of the transition state in a More O'Ferrall-type potential energy diagram in determining its sensitivity to structural changes in the reactants.

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On a déterminé les effets isotopiques cinétique de réactions E2 d'une série de sels de phényl-2 éthyl diméthylanilinium (substitués sur le noyau de l'aniline) avec l'éthylate de sodium dans l'éthanol à 40 °C. L'effet isotopique de l'azote $(k^{14}/k^{15} - 1)100$ n'est pas très sensible aux changements de substituant mais il semble qu'il augmente légèrement avec la facilité qu'ont les substituants d'attirer les électrons soit respectivement 1.19 ± 0.07 , 1.13 ± 0.06 , 1.12 ± 0.08 , 1.30 ± 0.07 et 1.32 ± 0.06 pour p-OCH₃, p-CH₃, p-H, p-Cl et m-CF₃. Les effets isotopiques de l'hydrogène passent par un minimum dans la région du composé non-substitué et augmentent avec une augmentation des effets électroaffinitaires et électrodonneurs des substituants soit respectivement $k^{\rm H}/k^{\rm D} = 4.70 \pm 0.06$, 4.61 ± 0.04 , 4.51 ± 0.04 , 4.53 ± 0.09 , 5.00 ± 0.07 et 5.39 ± 0.07 pour p-OCH₃, p-CH₃, p-H, p-Cl, m-CF₃ et p-CF₃. On discute de ces résultats en termes de traitements théoriques récents de l'effet de variations structuralles dans les réactifs sur la nature de l'état de transition des réactions d'élimination E2. On arrive à la conclusion que les états de transition de la série de réactions actuelles peuvent être caractérisés comme étant 'centrés avec un faible caractère carbanionique' et que l'effet d'un changement dans la capacité du nucléofuge sur la structure de l'état de transition se manifeste principalement dans la direction perpendiculaire des coordonnées de la réaction. On formule une nouvelle hypothèse simple qui met en relief l'importance de la position de l'état de transition dans un diagramme d'énergie potentielle du type More O'Ferrall pour déterminer sa sensibilité vis-à-vis des changements structuraux dans les réactifs.

[Traduit par le journal]

Introduction

A large body of evidence suggests that the nature of the transition state in an E2 elimination reaction is variable, *i.e.* that the reacting bonds can be broken or formed in varying degrees (for recent reviews see refs. 3 and 4). A number of

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sometimes conflicting theories concerning the effect of structural changes in the reactants on the nature (*i.e.* the structure and energy) of the transition state have been put forward (5-9).

Bunnett's theory (4, 5), which was developed mainly on an intuitive basis, suggests that a structural change which makes the cleavage of the C_{β} —H bond easier will lead to more exten-

¹For part X see ref. 1.

sive breaking of this bond in the transition state while the C_{α} -X bond (where X is the leaving group) will be correspondingly less broken. In Thornton's treatment (6) substituent effects are considered as linear perturbations of the vibrational potentials for the normal coordinate motions both parallel to and perpendicular to the reaction coordinate. The effects on the parallel motion are expected to dominate in many, but not all, cases. This leads to the prediction that a structural change which makes the breaking of the C_{β} —H bond easier will cause this bond to be broken less in the transition state. The other bond (in our example the C_{α} —X bond) will then follow along in the direction of the coordinate motion set by the former one, and be shorter as well. Recently Thornton and co-worker (7) have expanded the theory to explain more recent data which indicate that in some cases the influence of a substituent change on the perpendicular motion outweighs the effect on the parallel one. A system where this is the case would appear to behave according to Bunnett's theory. A third approach has been developed by More O'Ferrall (8). In his model, reactants, products, and transition state are represented on a common potential energy surface, along with carbonium ion and carbanion intermediates of stepwise reaction paths.² He concludes that structural changes which mainly influence the stability of products and/or reactants are transmitted along the reaction coordinate, resulting in a more or less product-like or reactant-like transition state. This is in agreement with Thornton's theory (6) and the Hammond postulate (11). Structural changes affecting mainly the stability of the carbonium ion and/or the carbanion, however, are expected to exert their effect in the direction perpendicular to the reaction coordinate. Their effect, then, would correspond to what is expected on the basis of Bunnett's theory (4, 5). Jencks (12), in a recent paper, has arrived at essentially the same predictions for structure-reactivity relationships. A somewhat related model has been presented by Critchlow (9). It allows the prediction of the configuration and energy of the transition state of a concerted reaction from the energies required to form the intermediates of the hypothetical stepwise processes. Substitution in the attacking or leaving portion of a concerted

²Diagrams of this type have originally been proposed by Albery (10).

reaction system should manifest itself only in changes in the more remote bond. Interestingly, this model suggests that the energetically less demanding part of the overall process has made greater progress at the transition state. This is in accordance with the principles stated in Bunnett's theory (4, 5), but contrary to the Hammond postulate (11).

In a recent report from this laboratory (2) it was suggested that the apparent contradiction between the theories of Bunnett (4, 5) and Thornton (6) might have its origin in a different sensitivity of the transition state to structural changes, depending on its position in More O'Ferrall's potential energy diagram (8). It was pointed out that in the studies of Bartsch and Bunnett (13) and Bartsch (14) which lend support to Bunnett's theory, the leaving group is always a 'good' one, namely a halogen. In systems which behave according to Thornton's theory, on the other hand, the leaving group is always a 'poor' one, e.g. trimethylamine. We may assume as a working hypothesis that compounds with relatively good leaving groups undergo elimination with strong bases by way of a central transition state in which the extent of C_{β} —H and C_{α} —X bond breaking is approximately equal. For elimination reactions with most quaternary ammonium salt substrates studied so far the transition states appear quite clearly to be strongly carbanion-like (considerably more C_{β} —H than C_{α} —X bond rupture). Reference to More O'Ferrall's potential energy diagram (Fig. 2) shows that a structural change influencing mainly the energy of the carbanion will exert its effect essentially through the perpendicular vibrational mode for a central transition state. For a transition state with considerable carbanion character, however, a similar effect may manifest itself to a greater extent in a direction along the reaction coordinate than perpendicular to it. In the latter case the curvature of the potential energy surface may well be considerably greater in the perpendicular than in the parallel direction whereas in the case of a central transition state the opposite may be true.

Even though there is no question that the leaving group is a very important factor in determining the structure of the transition state in an E2 reaction (ref. 15, p. 499; ref. 4, pp. 72, 73) there have been few systematic studies carried out in this area. In this paper we wish to report the results of such an investigation. We have

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		$k imes 10^{2}$ (1	$k \times 10^2 (1 \mathrm{mol}^{-1} \mathrm{s}^{-1})$				
x	Y	$[EtO^{-}] = 0.0142 \text{ mol/l}$	$[EtO^{-}] = 0.0121 \text{ mol/l}$	k ^H /k ^{D b}	σ ^{- c}		
р-ОМе	H D	$\frac{1.22 \pm 0.01^{a}}{0.259 \pm 0.002}$	$\frac{1.31 \pm 0.01^{a}}{0.279 \pm 0.002}$	4.70±0.06	-0.27		
p-Me	H D	$\begin{array}{c} 1.34 \pm 0.01 \\ 0.291 \pm 0.002 \end{array}$		4.61 ± 0.04	-0.17		
н	H D	1.89 ± 0.01 0.421 ± 0.003	2.18 ± 0.01 0.483 ± 0.004	4.50 ± 0.04	0		
<i>p</i> -Cł	H D	4.26 ± 0.05 0.931 ± 0.019	4.57 ± 0.04 1.01 ± 0.02	4.53 ± 0.09	0.24		
m-CF₃	H D	8.81 ± 0.05 1.74 ± 0.02		5.00 ± 0.07	0.49 ^d		
p-CF₃	H D	$9.32 \pm 0.10 \\ 1.73 \pm 0.01$	$10.05 \pm 0.10 \\ 1.86 \pm 0.02$	5.39±0.07	0.65 ^d		

TABLE 1.	Rate constants and	primary β-hydrog	gen isotope effects	in elimination	reactions of
C ₆	H ₅ CY ₂ CH ₂ N(CH ₃)	₂ C ₆ H₄X ions with	sodium ethoxide	in ethanol at 4	0°C

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^oStandard deviations. ^bRatio of specific rates of elimination; deviation $(\pm k^{H}/k^{D})[(r^{H}/k^{H})^{2} + (r^{D}/k^{D})^{2}]^{1/2}$, where r is the standard deviation in k. ^cSee ref. 19, p. 356. ^cSee ref. 20.

studied the reactions of a series of 2-phenylethyldimethylanilinium salts containing substituents in the aniline ring with ethoxide ion in ethanol. These substrates were chosen for a number of reasons. They are closely related to 2-phenylethylammonium ions which have been studied earlier in these laboratories (2, 16, 17). On the other hand, they contain a much better leaving group and may therefore allow us to test our hypothesis concerning the apparent discrepancies between the theories of Bunnett and Thornton. Furthermore, they contain substituents in the aromatic ring of the leaving group. This feature makes the compounds suitable for a systematic study of the influence of the leaving group by a method combining isotope and substituent effects.3

Results

Hydrogen-Deuterium Isotope Effects

Rate constants have been determined for the elimination reactions of a series of 2-phenylethyldimethylanilinium bromides containing substituents in the aniline ring and their 2,2-dideuterated analogs with sodium ethoxide in ethanol at 40 °C. All the reactions studied were found to be of second order overall, first order with respect to each reactant. The spectrophotometric procedure used to determine the kinetics is described

³For a discussion of the merits of this technique see ref. 18.

in the experimental section. The measured rate constants are shown in Table 1.

The Hammett plots of log k/k_0 vs. σ^- which were obtained for the undeuterated and the deuterated series are reasonably linear. However, a small but apparently systematic deviation from linearity is noticeable in both plots. The slope, ρ , for the undeuterated series is $+1.07 \pm 0.08$, with a correlation coefficient, r, of 0.988. For the 2,2dideuterated series ρ is +1.01 ± 0.08, with a correlation coefficient of 0.985. The errors given are standard deviations.

The primary hydrogen-deuterium kinetic isotope effects calculated from the rate data and the σ^{-} substituent constants are a so presented in Table 1.

It is interesting to note that the rates of the elimination reactions are subject to a strong salt effect while the kinetic isotope effects are independent of the ionic strength, at least in the narrow range studied.

Nitrogen Isotope Effects

The results of the nitrogen isotope effect study of the reaction of 2-phenylethyldimethylanilinium bromides with sodium ethoxide in ethanol at 40 °C are shown in Table 2. The nitrogen isotope effects were determined by comparing the ¹⁴N/¹⁵N ratio of the starting material of natural isotopic abundance with that of the dimethylaniline formed in the reaction carried to some

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TABLE 2. Nitrogen isotope effects for the E2 reaction of $C_6H_5CH_2CH_2\dot{N}(CH_3)_2C_6H_4X$ ions with sodium ethoxide in ethanol at 40 °C

Substituent X	Number of determinations	$(k^{14}/k^{15} - 1)100^a$
p-OCH ₃	10	1.19±0.07
p-CH ₃	9	1.13 ± 0.06
H	8	1.12 ± 0.08
p-Cl	7	1.30 ± 0.07
m-CF ₃	8	1.32 ± 0.06

"The limits shown are the standard deviations.

known extent of completion. The experimental procedure is outlined in the experimental section.

Discussion

Inspection of the isotope effect data in Tables 1 and 2 shows that the reactions of 2-phenylethyldimethylanilinium salts with ethoxide ion in ethanol exhibit β -hydrogen and leaving group isotope effects of significant magnitude. The conclusion seems warranted that both effects are primary ones, *i.e.* that both bonds are being broken in the rate determining step of the reaction (ref. 21, p. 215). This then implies that the reactions occur by a genuine synchronous E2 mechanism, in analogy with the corresponding reactions of 2-phenylethyltrimethylammonium salts (2, 16, 17).

Interestingly, the variation in the nitrogen isotope effect is rather small, while the hydrogen isotope effect changes over a comparably larger range. Clearly, a substituent change in the leaving group has a considerable influence on the breaking of the more distant C_{β} —H bond. This indicates that there must be rather extensive coupling between the C_{α} —X and C_{β} —H bond breaking processes, an observation which has also been made by Willi (22) in his investigation of elimination reactions in 2,2-diphenylethylarenesulfonate systems. Intuitively, one might have expected the substituent change to manifest itself more strongly in the closer bond (ref. 6, p. 2919).

Of special interest is the striking similarity in the shape of the plots of the two isotope effects vs. the σ^- constants (Fig. 1). Both are clearly not linear but rather seem to level out in the direction of stronger electron-donating substituents, *i.e.* upon going to more basic ('poorer') leaving groups. The hydrogen isotope effect even appears to pass through a minimum. The slight increase



FIG. 1. Plot of log $(k^{\rm H}/k^{\rm D})$ and log $(k^{14}/k^{15} - 1)100$ vs. σ^{-} for the reaction of 2-phenylethyldimethylanilinium salts containing substituents in the aniline ring with sodium ethoxide in ethanol at 40 °C.

in the direction of decreasing σ^- values seems to be just outside the experimental error limits. The possible significance of this point will be discussed below.

Leaving Group Isotope Effects

Since the magnitude of the nitrogen isotope effect depends on the extent to which the composite force constant of the C_{α} —N⁺ bond is decreased in going from the initial to the transition state, the effect will increase regularly in a reaction series with the extent of bond weakening in the transition state. The experimental results, therefore, indicate that the extent of carbonnitrogen bond rupture in the transition state is greater the more electron-withdrawing the substituent, *i.e.* the 'better' the leaving group.

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The numerical values of the nitrogen isotope effects are substantial, amounting to between 25 and 40% of the theoretical maximum value.⁴ This implies that there is a fairly sizeable amount of C_{α} —N⁺ bond stretching in the transition state of, perhaps, 25-50%. We shall not attempt to specify more accurately the extent of bond weakening at this point. Theoretical calculations by Saunders and co-workers (refs. 24 and 3a, pp. 76, 77) demonstrate that a general relationship between the value of the leaving group isotope effect and the absolute extent of bond stretching in the transition state is hardly a straightforward matter and depends greatly on the models on which the calculations are based. Further complications can occur when there is extensive coupling between the various atomic motions in the transition state, as seems to be the case in our system. In addition, the present treatment of isotope effects does not take into account solvation effects which, in the case of charged substrates, might be of considerable importance. In spite of these complications we feel that within our reaction series the qualitative interpretation of isotope effects in terms of bond rupture is justified, since the structural changes made in the reactants are only relatively minor and the solvent is the same in all cases.

β-Hydrogen Isotope Effects

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The correlation of the magnitude of the hydrogen isotope effect with the degree of bond stretching in the transition state is somewhat more complicated because the reacting hydrogen is involved in a three-center reaction. In this situation the value of $k^{\rm H}/k^{\rm D}$ is expected to reach a maximum when the force constants of the bonds being formed and broken are equal, *i.e.* the proton is half transferred, as has been pointed out by Melander (25), Westheimer (26) and others (27-29). The unambiguous interpretation of a measured isotope effect, which is smaller than the theoretical maximum, therefore, requires a knowledge of whether the proton is more or less than half transferred in the transition state. This can be obtained from the calculations and experimental results of Steffa and Thornton (30) on the secondary isotope effect k^{OD^-}/k^{OH^-} for proton abstraction by OD^- in D_2O and OH^-

in H_2O . The theoretical value of this isotope effect for a reaction with complete proton transfer at the transition state is 1.88 at 80 °C. For half transfer the effect is the square root of this maximum value, namely 1.37.

The results of Steffa and Thornton's study are presented in Table 3, along with primary hydrogen isotope effect data. One notes that all the secondary isotope effects are greater than 1.37 and, furthermore, that the decrease in k^{OD^-}/k^{OH^-} as one proceeds down the table is paralleled by an increase in primary isotope effect. The combination of these two findings establishes rather convincingly that the proton must be more than half transferred in all the cases listed (compare refs. 2 and 21, p. 272).

After taking into account the possibility of a fairly substantial solvent isotope effect Steffa and Thornton conclude that the reaction of the sulfonium ion represents a case where the proton is approximately half transferred in the transition state. The large value of the primary isotope effect is consistent with this view. Since the isotope effects for the dimethylanilinium salt are rather similar it is reasonable to conclude that in this case the proton is slightly more than half transferred in the transition state.

The Hammett ρ values listed in Table 4 lend further support to this conclusion. The ρ value for the dimethylanilinium leaving group is similar to that for chlorine and dimethylsulfonium leaving group.

On the basis of these findings it is possible to indicate the position of the transition state of the reaction of unsubstituted 2-phenylethyldimethylanilinium ion with ethoxide ion in ethanol in More O'Ferrall's potential energy diagram (Fig. 2). It appears to be located in the quadrant adjoining the carbanion intermediate, close to the center of the diagram. In other words, the transition state is a very central one with slight carbanion character. This is in contrast to what has been found for reactions of 2-phenylethyltrimethylammonium ions where the leaving group is much worse and the transition state is strongly carbanion-like in character (i.e. the C_{β} -H bond is much more stretched than the C_{α} —X bond) (2).

Furthermore, we can relate the trend in the magnitudes of $k^{\rm H}/k^{\rm D}$ and k^{14}/k^{15} with relative amounts of bond rupture. On the side of positive σ^{-} values (*i.e.* upon going to better leaving groups) both $k^{\rm H}/k^{\rm D}$ and k^{14}/k^{15} increase. This

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⁴Biegeleisen and Wolfsberg (23) have calculated a theoretical maximum for the kinetic nitrogen isotope effect of 1.032. Saunders and Cockerill (ref. 3a, p. 89) mention a value of 1.040–1.045.

Substrate	$k^{\text{OD}-}/k^{\text{OH}-a}$	$k^{ m H}/k^{ m D}$
$\overline{C_6H_5-CH_2-CH_2-N(CH_3)_3}$	1.79	3.23
C_6H_5 CH ₂ CH ₂ N(CH ₃) ₂ C ₆ H ₅	1.62	4.50
C_6H_5 — CH_2 — CH_2 — $\dot{S}(CH_3)_2$	1.57	5.05°

TABLE 3. Secondary and primary isotope effects in reactions of 2-phenylethyl derivatives

^aSecondary isotope effect for reaction with OD⁻ in D₂O and OH⁻ in H₂O, T = 80^bC, (see ref. 30). ^bPrimary isotope effect for reaction with EtO⁻ in EtOH. ^cSmith and Bourns (2), T = 40 °C. ^aThis work, T = 40 °C. ^cSaunders and Edison (31), T = 30 °C.



Fig. 2. Schematic potential energy diagram for concerted β -elimination reaction H—C—C—X + B \rightarrow C = C + HX + B.

means that an increase in $C_{\alpha} {\longrightarrow} X$ bond length is coupled with a decrease in $C_{\beta} {\longrightarrow} H$ bond length and indicates that the main effect of changing a substituent in the leaving group is felt in the direction perpendicular to the reaction coordinate. This finding is in contrast with what has been usually found in reactions with quaternary ammonium salts (2, 36, 37). Only recently one case has been found,⁵ namely the E2 reaction of 9-(4-substituted-benzyl)-fluorene-9-trimethylammonium ions with ethoxide in ethanol, where substituents show their effect primarily in the direction perpendicular to the reaction coordinate, rather than parallel to it.

On the side of negative σ^- values (*i.e.* on going to 'poorer' leaving groups) there is relatively little change in the isotope effects and thus the

⁵P. J. Smith, private communication.

bond lengths. The nitrogen isotope effect levels out (within experimental error), whereas $k^{\rm H}/k^{\rm D}$ increases very slightly, indicating a decrease in C_{β} —H bond length.

A few cases reported in the literature represent interesting parallels to this situation: Banger et al. (15) investigated the reaction of substituted 2phenylethylarenesulfonates with potassium-tertbutoxide in tert-butyl alcohol and found that substitution in the 2-phenyl ring has an effect on the Hammett ρ constant and thus the structure of the transition state which is uniform and linear over the entire range studied. This is in complete analogy with observations in 2-phenylethyl systems with trimethylammonium (2) and dimethylanilinium⁶ leaving groups. The effect of substitution in the leaving group, on the other hand, only becomes notable for the stronger electron-withdrawing substituents (*i.e.* the better leaving groups), as is the case in our system. This is taken as an indication of a shift to transition states with less carbanion character. Similarly, Willi (22) observed in his study of elimination reactions of 2,2-diphenylethylarenesulfonates that a para-nitro substituent in the arenesulfonate leaving group gave rise to an unexpectedly large increase in the β -hydrogen isotope effect. Winey and Thornton (7), finally, also found in their study of secondary isotope effects in reactions of 2-(p-trimethylammoniophenyl)-ethyl derivatives with lyoxide ions in water and deuterium oxide, respectively, that the isotope effects become an increasingly more sensitive function of the leaving group as the leaving group ability increases. They, too, conclude that the transition state of the reaction becomes less carbanion-like (or more central) the 'better' the leaving group.

⁶A. N. Bourns and P. B. Barrett, unpublished results.

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Leaving group	Hammett p ^a	k^{H}/k^{Da}	
I	2.07 (32)		
Br	2.14 (32)	7.1 (31)	
OTs	2.27 (33)	5.7 (31)	
Cl	2.61 (33)		
N(CH ₃) ₂ C ₆ H ₅	2.69°		
$\dot{S}(CH_3)_2$	2.75 (34)	5.1 (31)	
F	3.12 (35)		
Å(CH₃)₃	$3.66(2)^{b}$	$3.2(2)^{b}$	

ABLE 4.	Hammett reaction constants and kinetic p-hydrogen
isotope	effects for the reaction of 2-phenylethyl derivatives
	with sodium ethoxide in ethanol at 30 °C

^oReference in parentheses. ^bT = 40 ^oC. ^cA. N. Bourns and P. B. Barrett, unpublished results.

The results of our study, then, can be summarized as follows: (i) the transition state of the reaction of unsubstituted 2-phenylethyldimethylanilinium ion with ethoxide ion in ethanol is a fairly 'central' one; (ii) a substituent change in the leaving group manifests itself mainly in a direction perpendicular to the reaction coordinate; (iii) going to stronger electron-donating substituents, i.e. 'poorer' leaving groups, shifts the structure of the transition state towards the El_{cb} -like extreme; (iv) with increasing El_{cb} character the transition state geometry becomes less sensitive to further changes in the leaving group.

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A Comment on Theoretical Predictions of the Effect of Structural Variations on Transition State Geometry

Table 5 summarizes the effects of structural variations in the reactants on the geometry of the transition state as predicted by the several theories to which reference was made in the Introduction. The following discussion will be limited to the effect of changes in the leaving group.

Interestingly, all the theories agree in their predictions of the influence of a change in the leaving group on the (more distant) C_{β} —H bond. The better the leaving group, the less stretched is the C_6 —H bond in the transition state, *i.e.* the less carbanion character is developed. A large body of evidence, including the kinetic isotope effects and the Hammett reaction constants listed in Table 4 and our own data, lends support to this view. Thornton's updated theory (7) suggests in addition that the C₆—H bond is less sensitive to changes in the leaving group in carbanion-like transition states than in central ones. This is precisely the behavior displayed by our reaction system as well as the ones studied by Banger et al. (15), Willi (22), and Winey and Thornton (7).

There is no agreement between the predictions of the various theories for the effect of a change in the leaving group on the C_{α} -X bond. Bunnett (4) and Thornton (6) come to exactly opposite conclusions. Clearly, Bunnett's and Thornton's views represent two extremes, one considering the effect on the perpendicular, the other one on the parallel motion only. If both effects are taken into account (as in More O'Ferrall's (8) and Critchlow's (9) models and in Thornton's updated theory (7)) an unambiguous prediction is no longer possible. The result of the present as well as various other studies (e.g. Bartsch and Bunnett (13), Bartsch (14), Banger et al. (15)) suggest that in general the effect on the perpendicular motion may be more important. However, the present data also indicate that the sensitivity of the C_{α} -X bond to further changes in the leaving group may be smaller when the leaving group is already a poor one and the transition state shows an appreciable degree of carbanion character.

One point emerges more and more clearly. The hope to find a unique general correlation between the effect of a substituent change on the C—H and C—X bonds in the transition state of an E2 reaction (such as 'any increase in C-H bond length is necessarily coupled with an increase in C-X bond length') is no longer realistic. A theory relating the effect of structural

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					1	Theoretical	prediction	15				
					v	viney and '	Thornton	(7)				
	Bunn	ett (4)	Thorn	ton (6)	Centra	al tr.s. ^b	El _{cb} -lil	ke tr. s.»	More ()'Ferrall 8)	Critch	ılow (9)
Structural variation	СαХ	C_{β} —H	C _a —X	C _β H	С _а —Х	C _β —H	Cα	Сβ—Н	C _α —X	С _β —Н	C _α —X	СβН
Better leaving group	↑	\downarrow	\downarrow	\downarrow	±	\downarrow	\downarrow	±	±	Ļ	±	Ļ
Stronger base	↓	↑	↓	↓	Ļ	±	±	↓	↓	±	Ļ	±
Electron-withdrawing substituent at C_{α}	Ļ	ſ	Ť	↑	↓	Ť	Ļ	±	\downarrow	↑	Ļ	1
Electron-withdrawing substituent at Cβ	Ļ	Ť	Ļ	\downarrow	Ļ	1	Ļ	Ļ	↓	ſ	Ļ	1

TABLE 5.	Effect of structural variations in the reactants on the extent of C_{α} —X and C_{β} —H bond stretching in the
	transition state of E2 reactions as predicted by various theories ^a

^aSymbols indicate the following: \uparrow extent of bond stretching increased, \downarrow extent of bond stretching decreased, \pm no unambiguous prediction possible. ^bTransition state, tr. s.

changes with transition state geometry must take into account both parallel and perpendicular effects if it is to explain all the experimental data available. The single most important factor determining whether the parallel or perpendicular effect will dominate in a particular case appears to be the position of the transition state in the potential energy diagram. However, Thornton's updated theory (7) is the only one which incorporates to some extent the concept of differential sensitivity of the transition state geometry towards structural changes, depending on the character of the transition state. We would therefore like to propose a simple new working hypothesis which, while relying essentially on Thornton's original ideas (6), emphasizes the importance of the location of the transition state in a potential energy diagram as it was developed by More O'Ferrall (8) for elimination reactions (see Fig. 2). It may be stated as follows.

1. The closer the transition state of a concerted reaction is located to a corner of the potential energy diagram, the larger will be the slope of the potential energy surface in the direction to the corner. This will be true as long as there is a considerable energy difference between the corner itself and the transition state. A larger slope very likely corresponds to a large curvature of the energy surface along the line defined by the transition state and the adjacent corner.

2. If the transition state is very reactant- or product-like, the curvature of the energy surface in the parallel direction, *i.e.* along the reaction coordinate, will be large. If, on the other hand, it is very carbanion- or carbonium ion-like the

curvature will be large in the perpendicular direction. Implicit in these statements is the assumption that the curvature in the corresponding other direction will be smaller.

3. In accordance with Thornton's theory (6) a perturbation caused by a substituent change will produce a greater shift in bond lengths, the smaller the curvature of the unperturbed curve. For a reactant- or product-like transition state the effect of a structural change should therefore manifest itself more strongly in the perpendicular than in the parallel direction. Conversely, for a carbanion- or carbonium ion-like transition state the effect in the parallel direction should dominate.

4. For very central transition states it is not possible to predict *a priori* which of the two effects will outweigh the other.

Support for this hypothesis comes mainly from the studies of Smith and Bourns (1) and Smith $(38)^5$ in which the effect of structural variations on the C-H and C-N⁺ bond was simultaneously studied. The transition state of the E2 reaction of 2-arylethyltrimethylammonium ions with ethoxide in ethanol has considerable El_{cb} character (2). In this system any structural change which causes one bond (C-H) to be weakened more in the transition state has a corresponding effect on the other bond $(C-N^+)$. This is the result expected when the effect on the parallel motion dominates. The transition state of the E2 reaction of 9-(4-substituted-benzyl)fluorene-9-trimethylammonium ions with ethoxide in ethanol appears to be reactant-like (38). In this case a trend towards more C-H bond rup-

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ture is associated with a trend towards less C-N⁺ bond rupture.⁵ This combination is consistent with the assumption that the perpendicular motion is more important.⁷ The reaction of 2-phenylethyldimethylanilinium ions with ethoxide in ethanol (this work) occurs via a fairly central transition state: the same probably holds true for reactions of 2-phenylethylarenesulfonates with potassium tert-butoxide in tertbutyl alcohol (15). In both these systems the perpendicular effect is predominant. However, as structural changes shift the transition state structure towards the Elcb extreme, the transition state geometry becomes less sensitive to or almost independent of further structural variations. It appears that in this region parallel and perpendicular effects more or less balance. Presumably the curvature of the potential energy surface in the two directions is of comparable magnitude. It is not unreasonable to assume that in this area we may encounter small changes in bond lengths which are not a priori predictable but reflect subtleties of the energy surface. The small increase in C-H bond weakening upon going from a dimethylanilinium to a dimethyl-panisidinium leaving group, which we observed in this work, may be interpreted on this basis.

Since our working hypothesis has been derived on purely geometrical grounds, which are not peculiar to carbon elimination reactions, the respective conclusions should be equally valid for any reaction which can be represented in a threedimensional More O'Ferrall-type potential energy diagram.

Experimental

Materials

2-Phenylethyldimethylanilinium Bromide

A threefold excess of methyl bromide (15 g, 0.15 mol), cooled in an acetone – Dry Ice bath, was added to a similarly cooled solution of 11.1 g (0.05 mol) N,N-2-phenylethylmethylaniline in 50 ml of acetonitrile. The flask was sealed and the solution was allowed to stand for 60 h in the dark at room temperature. The quaternary

⁷Smith's data $(38)^5$ represent a problem, however, and cannot be considered as final proof of the present hypothesis. Although they seem to indicate that a trend towards the shortening of one bond is associated with a trend towards the lengthening of the other one, they do not appear to represent an effect on the perpendicularmotion as interpreted in Thornton's (6, 7) theory, since the sense of the variation is exactly opposite to the one predicted on the basis of this theory. We are currently trying to establish the causes and implications of Smith's results. salt was precipitated by addition of ether and recrystallized four times from ethanol-ether; yield 14.9 g (92%); m.p. 169-170 °C lit. (30) 169-170 °C).

N, N-2-Phenylethylmethylaniline

This compound was prepared using the method of Oki and Mutai (39): 27.75 g. 2-Bromoethylbenzene (0.15 mol) (Eastman) and 16.05 g (0.15 mol) *N*-methylaniline (Eastman) were treated with 45 ml of 20% aqueous sodium hydroxide for 30 min. Most of the unreacted halide and amine were removed by steam distillation. The residue was extracted with ether. The ethereal solution was dried over potassium carbonate. Removal of the solvent and distillation produced 11.1 g (35%) of the pure product; b.p. 98 °C/0.04 Torr (lit. (40) 124–128 °C/0.3 Torr, (41) 131–134 °C/0.75 Torr). Recrystallization from ethanol yielded a white solid, m.p. 42–43 °C (lit. (41) 42–43 °C, (42) 44 °C).

2-Phenylethyldimethyl-p-anisidinium Bromide

This compound was prepared from N,N-2-phenylethylmethyl-*p*-anisidine and methyl bromide by the same procedure as the unsubstituted compound; m.p. 181– 182 °C.

Anal. Calcd. for $C_{17}H_{22}$ NOBr: C, 60.72; H, 6.59; N, 4.17. Found: C, 60.74; H, 6.60; N, 3.98.⁸

N,N-2-Phenylethylmethyl-p-anisidine

This compound was prepared by means of the Eschweiler-Clarke (43) procedure. To 17 g (0.075 mol) of N-2-phenylethýl-p-anisidine were added 10 g (0.195 mol) of 90% formic acid and 7.5 g (0.085 mol) of 35% formalde-hyde and the mixture heated on the steam bath for 10 h. After cooling and addition of 40 ml 4 N hydrochloric acid, the excess of formaldehyde and formic acid was removed by distillation under reduced pressure. The residue was rendered alkaline with 40% aqueous sodium hydroxide and extracted with ether. After drying over potassium carbonate and removal of the solvent 17.4 g (100%) of the crude product were recovered. Vacuum distillation produced 10 g (59%) of the pure wax-like yellowish white product; b.p. 118 °C/0.03 Torr.

N-2-Phenylethyl-p-anisidine

This compound was prepared by the same method as N,N-2-phenylethylmethylaniline. From 18.5 g (0.1 mol) 2-bromoethylbenzene and 12.3 g (0.1 mol) *p*-anisidine, 11 g (48%) of pure product were obtained; b.p. 140–142 °C/0.5 Torr.

2-Phenylethyldimethyl-p-toluidinium Bromide

This material was prepared from N,N-2-phenylethylmethyl-*p*-toluidine and methyl bromide by the procedure described for the unsubstituted compound; m.p. 177 °C.

Anal. Calcd. for $C_{17}H_{22}NBr$: C, 63.75; H, 6.92; N, 4.37. Found: C, 63.76; H, 6.75; N, 4.27.⁸

N,N-2-Phenylethylmethyl-p-toluidine

N-2-Phenylethyl-p-anisidine (12.3 g, 0.058 mol) was converted into 10.3 g (80%) of this compound by means of the Eschweiler–Clarke procedure described for the corresponding p-anisidine derivative. The material was quaternized without further purification.

N-2-Phenylethyl-p-toluidine

4'-Methyl-phenylacetanilide (12.3 g, 0.054 mol) was

⁸Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

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placed in the thimble of a Soxleth extraction apparatus, the flask of which contained 5.2 g (0.135 mol) lithium aluminum hydride (BDH Chemicals) and 350 ml ether. The extraction and reduction was allowed to proceed for 24 h. After cooling, water was carefully added dropwise until the reaction mixture appeared white. The precipitated aluminum hydroxide was then filtered and washed with ether. Removal of the solvent yielded 11.5 g (100%) of the product, a white, wax-like solid. It was used for the next step without further purification.

4'-Methyl-phenylacetanilide

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A solution of 27 g (0.25 mol) *p*-toluidine (Eastman) and 50 g triethylamine in 50 ml benzene was added slowly whilst stirring to a solution of 38.7 g (0.25 mol) of phenylacetylchloride in 100 ml benzene. After allowing the reaction mixture to stand for 1 h the triethylamine hydrochloride formed was removed by filtration. The benzene solution was concentrated on the rotary evaporator. The precipitated anilide was filtered and thrice recrystallized from ethanol; yield 12.3 g (22%), m.p. 130 °C. Additional crude product was obtained on concentration of the mother liquors.

2-Phenylethyldimethyl-4-chloroanilinium Bromide

This material was prepared from N,N-2-phenylethylmethyl-4-chloroaniline and methyl bromide by the procedure described for the unsubstituted compound; m.p. 170–171 °C.

Anal. Calcd. for C₁₆H₁₉NClBr: C, 56.40; H, 5.62; N, 4.11. Found: C, 56.22; H, 5.66; N, 4.04.⁸

N,N-2-Phenylethylmethyl-4-chloroaniline

N-2-Phenylethyl-4-chloroaniline was methylated by the Eschweiler–Clarke procedure described for the corresponding *p*-anisidine derivative with nearly quantitative yield. The product was purified by dissolving it in petroleum ether and filtering through aluminum oxide, followed by recrystallization from ethanol; m.p. 61-62 °C.

N-2-Phenylethyl-4-chloroaniline

This compound was prepared by reduction of 4'chloro-phenylacetanilide with lithium aluminum hydride as described for the corresponding *p*-toluidine derivative. It was purified by vacuum distillation; b.p. 126– 128 °C/0.15 Torr.

4'-Chloro-phenylacetanilide

This compound was prepared by the procedure described for 4'-methyl-phenylacetanilide; m.p. 163 $^{\circ}$ C (lit, (44) 163–164 $^{\circ}$ C).

2-Phenylethyldimethyl-3-trifluoromethylanilinium Bromide

This compound was prepared by quaternization of N,N-2-phenylethylmethyl-4-trifluoromethylaniline with methyl bromide, as described for the unsubstituted compound; m.p. 160–161 °C.

Anal. Calcd. for C₁₇H₁₉NF₃Br: C, 54.55; H, 5.12; N, 3.74. Found: C, 54.35; H, 5.10; N, 3.66.⁸

N,N-2-Phenylethylmethyl-4-trifluoromethylaniline

N-2-Phenylethyl-4-trifluoromethylaniline was methylated by the Eschweiler–Clarke procedure described for the corresponding p-anisidine derivative. The product was quaternized without further purification.

N-2-Phenylethyl-4-trifluoromethylaniline

This compound was prepared by heating 16.1 g (0.1 mol) 4-trifluoromethylaniline with 13 g (0.13 mol)

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triethylamine and 18.5 g (0.1 mol) 2-bromoethylbenzene in a sealed flask for 48 h. After addition of 100 ml water, the mixture was extracted with ether. After drying over potassium carbonate, removal of the solvent and distillation, 2.7 g (11%) of the pure product were obtained; b.p. 114 °C/0.03 Torr.

2-Phenylethyldimethylanilinium-2,2-d₂ Bromide

This material was prepared from N,N-2-phenylethylmethylaniline- $2,2-d_2$ and methyl bromide as described for the undeuterated compound and purified by recrystallization from isopropanol-ether; m.p. 168 °C.

tion from isopropanol-ether; m.p. 168 °C. Anal. Calcd. for $C_{16}H_{18}D_2NBr$: C, 62.34; H + D, 7.19; N, 4.54. Found: C, 62.30; H + D, 7.01; N, 4.60.⁸ Deuterium content: 1.96 atoms D per molecule.⁹

N, N-2-Phenylethylmethylaniline-2,2- d_2

2-Bromoethylbenzene- $1, 1-d_2$ (4.6 g, 0.025 mol) and 5.4 g (0.05 mol) *N*-methylaniline were heated in a sealed flask for 24 h on the steambath. The reaction product was extracted with ether. After drying of the ethereal solution over potassium carbonate, removal of the solvent and vacuum distillation 2.6 g (50%) of the pure product were obtained; b.p. 102 °C/0.02 Torr.

2-Bromoethylbenzene-1,1-d₂

2-Phenylethanol-2,2- d_2 (6.2 g, 0.05 mol) and 31 g (0.18 mol) 48% hydrobromic acid were heated to reflux for two hours. Extraction of the cool solution with ether, drying of the organic phase over sodium sulfate and removal of the solvent yielded 8.3 g (88%) of the desired bromide.

2-Phenylethanol-2,2-d2

Phenylacetic acid- α , α - d_2 (8.2 g, 0.061 mol) dissolved in 50 ml ether was added dropwise to a solution of 2.64 g (0.07 mol) lithium aluminum hydride in 75 ml ether. After heating the resulting solution to reflux for 2 h, just enough water was added to transform all the lithium aluminum hydride into aluminum hydroxide, which was then filtered off and washed with anhydrous ether. After removal of the solvent 6.6 g (87%) of product were obtained.

Phenylacetic Acid- α , α - d_2

A solution of 93 g (0.39 mol) diethylphenylmalonate (Eastman) in 390 ml dry petroleum ether (30-60 °C) was filtered through a column of alumina (80-200 mesh, Brockman activity 1) and then added to a well-stirred mixture of 170 ml petroleum ether and 18.6 g (0.39 mol) of a 50% dispersion of sodium hydride in mineral oil (Metal Hydrides Inc).

The resulting white solid was removed by filtration and washed repeatedly with petroleum ether. The solvent was removed from the solid by pumping overnight in a vacuum desiccator. The dried sodium salt, 66 g (0.26 mol), was added to 70 ml deuterium oxide. The resulting solution was heated to reflux for 8 h in.a dry nitrogen atmosphere. After cooling, the solution was acidified by adding thionyl chloride and heated again to reflux for 2 h to bring about decarboxylation. After extraction with ether, drying over sodium sulfate and removal of the solvent, 31 g of the crude product were obtained. Recrystallization from petroleum ether yielded 22 g (41%) of pure phenylacetic acid- α , α - d_2 .

⁹Deuterium analyses were performed by Mr. J. Nemeth, 303 W. Washington Street, Urbana, Illinois.

2-Phenylethyldimethyl-p-anisidinium-2,2-d₂ Bromide This salt was prepared from N,N-2-phenylethylmethylanisidine-2 2-d, and methyl bromide as described for

p-anisidine-2,2- d_2 and methyl bromide as described for the corresponding undeuterated unsubstituted material; m.p. 180 °C.

Anal. Calcd. for $C_{17}H_{20}D_2NOBr$: C, 60.36; H + D, 7.15; N, 4.14. Found: C, 60.28; H + D, 6.93; N, 4.13.⁸ Deuterium content: 1.96 atoms D per molecule.⁹

N-2-Phenylethylmethyl-p-anisidine-2,2- d_2

N-2-Phenylethyl-*p*-anisidine-2, $2-d_2$ (1.65 g, 0.0073 mol) was transformed into 1.5 g (85%) of the corresponding *N*-methyl compound by the Eschweiler-Clarke procedure described for the undeuterated compound. The product was quaternized without further purification.

N-2-Phenylethyl-p-anisidine-2,2-d2

4'-Methoxy-phenylacetanilide- $\alpha, \alpha - d_2$ (2.5 g, 0.024 mol) was reduced with lithium aluminum hydride to yield 2.1 g (89%) of the desired amine, using the procedure described for the corresponding undeuterated *p*-toluidine derivative.

4'-Methoxy-phenylacetanilide-2,2-d2

A solution of 5 g (0.033 mol) phenylacetylchloride- α, α d₂ in 10 ml dry benzene was added dropwise to a stirred solution of 4 g (0.033 mol) *p*-anisidine (Eastman) and 3.4 g (0.033 mol) triethylamine in 50 ml benzene. The mixture was allowed to stand for 1 h, after which time the white product was removed by filtration, washed with deuterium oxide and recrystallized from benzene; yield 4.5 g (57%); m.p. 122 °C.

Phenylacetyl Chloride- α , α - d_2

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A mixture of 11 g (0.079 mol) phenylacetic acid- $\alpha, \alpha - d_2$ and 9.4 g (0.079 mol) thionyl chloride (BDH) was provided with a few boiling chips and allowed to stand at room temperature for 24 h. The reaction was quantitative and the product was used without further purification.

2-Phenylethyldimethyl-p-toluidinium-2,2-d2 Bromide

This material was available from an earlier study.¹⁰ It was recrystallized four times from ethanol-ether; m.p. 178 °C.

Anal. Calcd. for $C_{17}H_{20}D_2NBr$: C, 63.35; H + D, 7.50; N, 4.35. Found: C, 63.31; H + D, 7.06; N, 4.34.⁸ Deuterium content: 1.94 atoms D per molecule.⁹

2-Phenylethyldimethyl-4-chloroanilinium-2,2-d2 Bromide

This compound was prepared from N,N-2-phenylethylmethyl-4-chloroaniline-2,2- d_2 and methyl bromide as described for the unsubstituted, undeuterated material; m.p. 170 °C.

Anal. Calcd. for $C_{16}H_{17}D_2NClBr$: C, 56.07; H + D, 6.17; N, 4.09. Found: C, 56.15; H + D, 5.95; N, 3.95.⁸ Deuterium content: 1.89 atoms D per molecule.⁹

N, N-2-Phenylethylmethyl-4-chloroaniline-2,2-d₂

N-2-Phenylethyl-4-chloroaniline- $2,2-d_2$ (2.6 g, 0.0113 mol) was transformed into the corresponding *N*-methylaniline by the Eschweiler-Clarke procedure described for the corresponding undeuterated *p*-methoxy compound; yield 2.46 g (88%). The product was quaternized without further purification.

N-2-Phenylethyl-4-chloroaniline-2,2-d2

Phenylacetyl-4-chloroanilide- $\alpha, \alpha-d_2$ (3.7 g, 0.0151 mol) was reduced with lithium aluminum hydride to the desired

¹⁰A. N. Bourns and B. Wang, unpublished work.

amine, as described for the corresponding undeuterated *p*-toluidine derivative.

Phenylacetyl-4-chloroanilide- α , α - d_2

A solution of 5 g (0.033 mol) phenylacetylchloride- α, α d₂ in 10 ml dry benzene was added dropwise to a stirred solution of 4.15 g (0.033 mol) 4-chloroaniline-N, N-d₂ and 3.4 g (0.033 mol) triethylamine (Eastman) in 50 ml benzene. The mixture was allowed to stand for 1 h, after which time the white product was removed by filtration, washed with deuterium oxide, and recrystallized from chloroform-ether; yield 3.8 g (47%); m.p. 163 °C.

4-Chloroaniline-N,N-d2

A mixture of 10 g (0.079 mol) 4-chloroaniline (Eastman), 20 ml deuterium oxide and enough pyridine to bring all the aniline into solution was allowed to stand overnight at room temperature. Most of the solvent was then removed on the rotation evaporator. This treatment was repeated once. The product was then recrystallized from petroleum ether; m.p. 70 °C. Nuclear magnetic resonance analysis indicated a deuterium content of 1.92 atoms D per molecule.

2-Phenylethyldimethyl-3-trifluoromethylanilinium Bromide-2,2-d₂

This compound was available from an earlier study.¹⁰ It was recrystallized three times from ethanol-ether; m.p. 125 °C.

Anal. Calcd. for $C_{17}H_{17}D_2NF_3Br$: C, 54.26; H + D, 5.62; N, 3.72. Found: C, 54.18; H + D, 5.52; N, 3.66.⁸ Deuterium content: 1.89 atoms D per molecule.⁹

2-Phenylethyldimethyl-4-trifluoromethylanilinium Bromide-2,2-d₂

This material was available from an earlier investigation.¹⁰ It was recrystallized twice from ethanol-ether; m.p. 159 °C. Nuclear magnetic resonance analysis indicated more than 90% deuteration in the benzyl position.

Absolute Ethanol

This solvent was dried by the method of Lund and Bjerrum (45) and stored under anhydrous conditions.

Sodium Ethoxide

Stock solutions of this base were prepared by dissolving clean sodium metal in ethanol under strictly anhydrous conditions in a nitrogen atmosphere.

Product Analyses

The appropriate undeuterated quaternary ammonium salt (300 to 500 mg) was dissolved in 25 ml of a 1.48 N solution of sodium ethoxide in ethanol and the solution allowed to stand for 18-24 h in a thermostatted bath at 40 °C. The solution was then diluted with 25 ml water and extracted three times with 50 ml portions of petroleum ether. After removal of the solvent under reduced pressure the mixture was analyzed by g.l.c., using a column packed with 15% silicon rubber SE30 on Chromosorb W. This procedure was applied to the p-Me, p-H, p-Cl, and m-CF₃ substrates. In all cases three peaks could be distinguished. The two large ones corresponded to the two products of the elimination reaction (styrene and a substituted N.N-dimethylaniline) the third very small one corresponded to the product of a competing substitution reaction, namely a substituted N,N-2-phenylethylmethylaniline. The various peaks were identified by comparing them with the peaks corresponding to authentic samples. A rough comparison of the peak areas indicated the

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Compound	$\lambda_{max}(nm)$	$\epsilon(\lambda_{max}) \times 10^4$	ε(248 nm) × 10 ⁴
N,N-Dimethyl-p-anisidine	249	1.12	1.11
N.N-Dimethyl-p-toluidine	252	1.22	1.12
N.N-Dimethylaniline	248	1.25	1.25
N.N-Dimethyl-p-chloroaniline	260	1.80	1.00
N.N-Dimethyl- <i>m</i> -trifluoromethylaniline	258	1.62	1.00
Styrene	248	1.40	1.40

Fable 6.	Ultraviolet absorption of substituted N,N-dimethylanilines and sty	yrene
	in absolute ethanol, reference 95% ethanol	

following maximal amounts of substitution preducts: p-Me, 0.18%; p-H, 0.16%; p-Cl, 0.23%; m-CF₃, 0.85%. It appears that the percentage of substitution reaction is larger for stronger electron-withdrawing substituents in the leaving group, a trend which has also been observed by Willi (22).

A visual comparison of the u.v. spectra of the actual reaction solutions at infinite time gave no indication of any appreciable amounts of competing substitution reaction. Deuterated and undeuterated starting materials produced solutions with virtually identical spectra. Furthermore, the spectra of the reaction solutions at infinite time appeared identical to the spectra of solutions prepared from authentic samples. This, together with the fact that the infinity value of the optical density in the kinetic runs was within $\pm 1\%$ of the expected value, was taken as evidence that competition by substitution reactions was not important under the experimental conditions.

Kinetic Measurements

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The rate of reaction of undeuterated and deuterated 2phenylethyldimethylanilinium salts with sodium ethoxide in ethanol was determined by spectrophotometrically monitoring the increase in the amount of reaction product (*i.e.* styrene and N,N-dimethylaniline) as a function of time. All the reactions were carried out directly in the spectrophotometer cell and followed to a minimum of 75% completion. Standard wavelength for all the measurements was 248 mm, the wavelength of the absorption maxima of styrene and unsubstituted dimethylaniline. At this wavelength absorption caused by the reactants was negligible. A compilation of the absorption maxima and molar extinction coefficients of the various reaction products as measured under the reaction conditions is given in Table 6.

A Hitachi–Perkin-Elmer model 139 spectrophotometer fitted with a thermostatted cell compartment was used throughout for the kinetic measurements. The temperature in the cell compartment was kept constant at 40 ± 0.05 °C. Ultraviolet–visible spectra were recorded on a Cary 14 spectrophotometer.

The reaction solutions were prepared by mixing appropriate amounts of thermostatted stock solutions of the quaternary anilinium salts and the base in 50 ml volumetric flasks. All reactions were measured under pseudo first-order conditions with the base in large excess (ca. 400 fold) over the quaternary salt. The same sodium ethoxide solution was used for a complete set of experiments. This ensured a constant ionic strength. The

substrate concentration was chosen such that a convenient value of the optical density of the reaction solutions at infinite time would be obtained, *i.e.* $3-4 \times 10^{-5}$ mol/l. Reactions with undeuterated and deuterated substrates were always carried out simultaneously. Excellent firstorder plots were obtained in all cases.

Solutions of the quaternary anilinium salts were entirely stable. Elimination was caused only by ethoxide ion, not by ethanol. No deuterium exchange was detected in solutions of the deuterated salts.

The pseudo first-order rate constants, k', were calculated as -2.3 times the slope of the first-order plots (46). This slope was determined either by visually drawing a straight line or by least-squares treatment, both methods giving the same result. The second-order rate constants, $k_{\rm E}$, were then obtained by division of k' by the ethoxide ion concentration, *i.e.* $k_{\rm E} = k'/[{\rm EtO^-}]$. The rate constants given in Table 1 represent the average of 3 to 6 kinetic runs.

Nitrogen Isotope Effects

The nitrogen isotope effects were determined by comparing the nitrogen isotopic abundance of the dimethylaniline formed in reactions carried out to some known fractional extent (partial reactions) with the isotopic abundance in the starting material or in the product after complete reaction.

The desired extent of reaction was achieved by adding the appropriate amount of base to the quaternary salt solution and allowing the reaction to proceed for more than ten half lives. Runs were set up so that 0.2 mmol of dimethylaniline would be formed, a convenient quantity for the subsequent mass spectrometric analysis. The faster reactions were carried out in 50 ml volumetric flasks, the slower ones in evacuated ampoules. The concentrations were small enough to ensure that practically no reaction occurred during mixing of the reactants. The reaction vessels were kept in a thermostatted bath at 40 ± 0.02 °C.

After the reaction had proceeded for ten or more half lives, water (twice the amount of the alcoholic reaction solution) was added to the reaction mixture. The aqueous solution was extracted three times with 50 ml portions of petroleum ether (30–60); 2.5 ml of concentrated sulfuric acid were then added to the organic phase and the solvent removed on the rotary evaporator. The acid residue was washed with water into a Kjeldahl flask. After the water had been removed by gentle heating, 2 g potassium sulfate and 0.10 g mercuric oxide were added. This mixture was digested in the usual manner for 2.5–3 h. Ammonia was

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then liberated by addition of sodium hydroxide and transferred into excess standard sulfuric acid by steam distillation. The overall yield was always over 90%, usually between 95 and 100%.

This extraction technique was used for partial and complete reactions. For the preparation of nitrogen samples from the quaternary salts it was necessary to remove the halogen by oxidation with hydrogen peroxide prior to digestion, as described by Ayrey *et al.* (47).

The ammonium sulfate solution resulting from the Kjeldahl digestion was concentrated and oxidized with sodium hypobromite to nitrogen gas, which was purified and then analyzed by mass spectrometry. Details of the procedure are given by Ayrey *et al.* (47).

The kinetic isotope effects were calculated as described previously (47).

Financial support for this work was provided by the National Research Council of Canada and McMaster University. We wish to thank Professors E. R. Thornton and W. H. Saunders, Jr. for discussions.

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