Organic and Biological Chemistry

Elimination Mechanisms. Position of Proton and Substituent Effects upon Geometry in E2 Transition States[1-3]

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Abstract: The isotope effects for DO^- in D_2O *vs.* HO^- in H_2O as attacking bases in the E2, bimolecular elimination, reactions of β-phenylethyl derivatives have been determined; at 80.45°, $k_{DO^-}/k_{HO^-} = 1.79 \pm 0.04, 1.57 \pm 0.04, 1.62 \pm 0.04, 1.73 \pm 0.05$ for β-phenylethyltrimethylammonium, β-phenylethyldimethylsulfonium, β-phenylethylphenyldimethylammonium, and β-(*p*-chlorophenyl)ethyltrimethylammonium ions, respectively. The strong effects observed indicate extensive proton transfer to the base. These and other substituent effects are discussed in terms of hypotheses for predicting substituent effects on transition-state structure. Isotope effects for β-phenylethyl bromide in 40% dioxane–H_2O and –D_2O, and for β-phenylethyltrimethylammonium ion in 50% H_2O–D_2O, have also been determined.

In the base-promoted E2, bimolecular elimination, reactions of ring-substituted β-phenylethyl compounds, *e.g.*

$$C_6H_5CH_2CH_2X + HO^- \longrightarrow C_6H_5CH{=}CH_2 + H_2O + X^-$$

the high, positive ρ values observed suggest that a considerable degree of carbanion character resides on the carbon atom adjacent to the ring.[5] The transition state in such reactions is thought to resemble the diagram in Figure 1. For elimination reactions, however, an uncertainty exists as to the significance of ρ, since it could conceivably be affected by other factors, *e.g.*, the incipient double bond conjugated with the ring in the transition state. The primary hydrogen isotope effects observed in eliminations from β-phenylethyl derivatives indicate appreciable C–H bond breakage in these transition states,[6] although these effects alone do not indicate the extent of proton transfer.

Data will now be presented which are consistent with high carbanion character of these transition states in that the proton is shown to be extensively transferred to the attacking lyoxide (LO^-) ion (L = H or D).

Results

We have made kinetic measurements at 80.45° on the E2 reactions of various β-phenylethyl compounds, using DO^- in D_2O and HO^- in H_2O as attacking bases. The E2 reaction of β-phenylethyltrimethylammonium bromide in 50% H_2O–D_2O with lyoxide ion as attacking base has also been investigated (Table I).

Table I. Rate Constants for Elimination from Y–$C_6H_4CH_2CH_2X$ at 80.45°

Y	X	Solvent[a]	$k_2 \times 10^5$, l. mole^{-1} sec^{-1} [b]
H	S^+Me_2[c]	H_2O	130 ± 2[d]
H	S^+Me_2	D_2O	204 ± 4
H	N^+Me_3	H_2O	5.63 ± 0.12
H	N^+Me_3	D_2O	10.06 ± 0.06
p-Cl	N^+Me_3	H_2O	21.9 ± 0.5
p-Cl	N^+Me_3	D_2O	37.8 ± 0.5
H	N^+Me_2Ph	H_2O	28.5 ± 0.1
H	N^+Me_2Ph	D_2O	46.3 ± 1.0
H	N^+Me_3	50% H_2O–D_2O (v/v)	7.55 ± 0.17
H	Br	40% dioxane–60% H_2O (v/v)	1440 ± 7[e]
H	Br	40% dioxane–60% D_2O (v/v)	2260 ± 8[e]

[a] Base was the conjugate base of the solvent. Initial concentrations *ca.* 0.1 *M* base and 0.05 *M* substrate. [b] Each value is the average of two or more runs with standard deviations. [c] Me = CH_3; Ph = C_6H_5. [d] Lit.[6] $k = 122 \pm 2 \times 10^{-5}$ l. mole^{-1} sec^{-1} at 80.00°. [e] *Ca.* 0.016–0.02 *M* base and 0.01 *M* alkyl bromide.

The preparation of the starting materials is described in the Experimental Section. Reaction rates were followed by titration of the reactant base with standard hydrochloric acid. All reactions followed second-order kinetics. The β-phenylethyldimethylsulfonium bromide is the only compound of the series for which rate data had been determined in aqueous solution.[5b,6]

The reaction of the sulfonium salt in D_2O is complicated by the rapid exchange of D for H at the carbon atoms adjacent to the sulfur atom.[7] However, should there be any substantial olefinic character in the C_α–C_β bond at the transition state of this reaction, the pres-

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[1] Supported in part by the U. S. Atomic Energy Commission, to which royalty-free right of reproduction is hereby granted. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] Preliminary communication: L. J. Steffa and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 2680 (1963).

[3] For further details, *cf.* L. J. Steffa, Ph.D. Dissertation in Chemistry, University of Pennsylvania, 1965; *Dissertation Abstr.*, **26**, 3048 (1965); University Microfilms, No. 65-13,394.

[4] National Institutes of Health Predoctoral Fellow, 1963–1964.

[5] (a) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957); (b) W. H. Saunders, Jr., C. B. Gibbons, and R. A. Williams, *ibid.*, **80**, 4099 (1958); (c) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957); (d) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532, 2535 (1960); (e) W. H. Saunders, Jr., and D. G. Bushman, unpublished results; (f) A. F. Cockerill, S. Rottschaeffer, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **89**, 901 (1967).

[6] W. H. Saunders, Jr., and D. H. Edison, *ibid.*, **82**, 138 (1960).

[7] S. Ašperger, N. Ilakovac, and D. Pavlović, *Croat. Chem. Acta*, **34**, 7 (1962); S. Ašperger, D. Pavlović, L. Klasinc, D. Stefanović, and I. Murati, *ibid.*, **36**, 209 (1964).

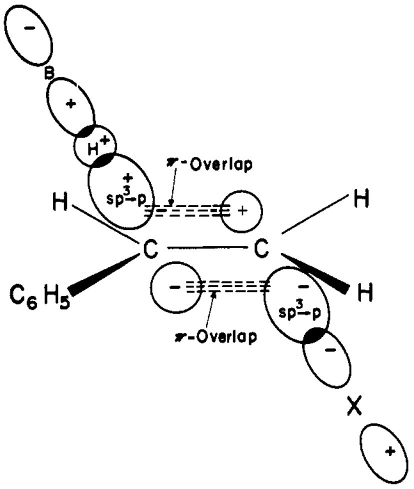

Figure 1. Atomic orbital diagram of an E2 transition state, showing only the orbitals associated with reacting bonds, and representing other bonds by lines.

ence of deuterium on the α-carbon atom would decrease the rate,[7,8] so that the hypothetical rate in D_2O (for an unexchanged salt) would be, if anything, greater than the value recorded in Table I, yielding a correspondingly higher isotope effect (see Table II).

The kinetic determinations upon the trimethylammonium compounds presented some difficulties. The production of the basic trimethylamine precluded direct titration of the alkali. The amine, however, is quite volatile and was removed under reduced pressure. In the case where the weakly basic dimethylaniline was formed, it did not interfere with the alkali titrations.

The extensive reaction time required for the ammonium compounds (up to 125 hr at 80.45°) was a more serious problem in the kinetic determinations. The relative rates for the 'onium leaving groups in H_2O at 80.45° are SMe_2:NMe_2Ph:NMe_3 = 23:5:1. After about 10-hr reaction time at this elevated temperature, the effect of the alkali on glass becomes apparent. Because the glass dissolves, titers begin to increase, accompanied by fading and indistinct end points. To circumvent this difficulty, alkali-resistant glass (Corning No. 7280) was employed, giving good results.

Under the conditions for the reactions of the ammonium compounds there is very probably no appreciable deuterium exchange into the positions α to the nitrogen atom.[9]

By far the greatest difficulty encountered in this research was in the kinetic determinations in aqueous dioxane solutions. The insolubility of β-phenylethyl bromide in water necessitated the use of a mixed solvent which proved to be unsatisfactory for hydroxide-promoted reactions. Foster and Hammett had found solutions of sodium hydroxide in 60.72% dioxane–39.28% H_2O to be very reactive with Pyrex and soft glassware at 60 and 80°.[10] In an attempt to avoid any similar problems and to ensure a high mole fraction of water, we felt that 40% dioxane–60% water (v/v) should be satisfactory. The low solubility of the alkyl halide, even in this medium, necessitated low concentrations of reactants (*ca.* 0.02 *M* HO^- and *ca.* 0.01 *M* alkyl bromide). Blank runs (base only) between 70 and 100°, using Pyrex and alkali-resistant glass, did not yield reliable alkali determinations, especially at longer times and higher temperatures.[3] Similar results were obtained with 40% aqueous diglyme. It was found (using 40% aqueous dioxane (v/v) at 80.45°) that the rate constants for β-phenylethyl bromide varied with the concentration of base and alkyl bromide. With 0.016–0.02 *M* sodium hydroxide and 0.01 *M* alkyl bromide, an average rate constant was obtained which was about 12% higher than that obtained when the base concentration was greater than 0.02 *M* or when the concentration of alkyl bromide was below 0.01 *M*. Rate data were therefore obtained in 40% dioxane–60% D_2O (v/v)[11] using the former concentrations of reactants under exactly the same conditions as in the H_2O runs (Table I). The anomalous results observed in aqueous dioxane possibly introduce considerable uncertainty into the rate data, and consequently further experiments with this system were abandoned.

For the 'onium compounds, olefin yields of 100 ± 3% were obtained spectrophotometrically. Styrene determinations were not carried out for β-phenylethyl bromide, though a 100% styrene yield is reported for this substrate with ethoxide ion in ethanol.[6]

The ratio of the rate constants in D_2O and H_2O provides the secondary isotope effects, k_{DO^-}/k_{HO^-}, as shown in Table II. For the reaction of β-phenylethyltrimethylammonium bromide in 50% H_2O–D_2O (v/v) *vs.* pure H_2O, an isotope effect k_α/k_H = 1.34 ± 0.04 at 80.45° is obtained (k_α referring to a mixed solvent of atom fraction deuterium α).

Table II. Secondary Isotope Effects in the Elimination Reactions of β-Phenylethyl Derivatives at 80.45° for DO^- in D_2O *vs.* HO^- in H_2O

Compound	k_{DO^-}/k_{HO^-} [a]	Relative rate in H_2O
$C_6H_5CH_2CH_2Br$ [b]	1.57 ± 0.01[c]	. .
$C_6H_5CH_2CH_2S^+Me_2Br^-$	1.57 ± 0.04	23
$C_6H_5CH_2CH_2N^+Me_3Br^-$	1.79 ± 0.04	1
p-$ClC_6H_4CH_2CH_2N^+Me_3Br^-$	1.73 ± 0.05	4
$C_6H_5CH_2CH_2N^+Me_2PhBr^-$	1.62 ± 0.04	5

[a] Isotope effects with standard deviation. [b] Solvent was 40% dioxane–60% L_2O (v/v). [c] This value is not reliable (see text).

Discussion

Isotope Effects. The strong secondary isotope effects for DO^- *vs.* HO^- observed in these E2 reactions persuasively indicate a high degree of bond formation between base and proton in the transition states. DO^- is a stronger base than HO^- by a factor of *ca.* 1.88 at 80.45°,[12] and therefore an effect of this magnitude

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(8) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(9) S. Ašperger, L. Klasinc, and D. Pavlović, *Croat. Chem. Acta*, **36**, 159 (1964).

(10) F. C. Foster and L. P. Hammett, *J. Am. Chem. Soc.*, **68**, 1736 (1946).

(11) The molar volumes of H_2O and D_2O are almost exactly equal.

(12) This value is the square root of the equilibrium constant K_B for the reaction $2DO^- + H_2O = 2HO^- + D_2O$, which can be calculated from the isotope effect on the self-ionization of water[13,14] and L,[15] the equilibrium constant for the reaction $2D_3O^+ + 3H_2O = 2H_3O^+ + 3D_2O$. $K_B^{0.5}$ = *ca.* 2.12[13] at 25°. Assuming the temperature dependence of $K_B^{0.5}$ to be inversely exponential (valid if the isotope effect results almost entirely from zero-point energy differences; shown to be

would be expected for complete proton transfer to the base LO^- in the transition state. For a transition state where the proton is half-transferred between substrate and base, the isotope effect should be *ca.* $1.88^{0.5} = 1.37$ (at 80.45°). This application of isotope effects can be thought of as a Brønsted base correlation which should have the greatest possible precision because, unlike usual changes from one base to another, the isotopic bases must give precisely the same reactant and transition-state equilibrium geometries.

In the 'onium series, the relative values of the secondary isotope effects indicate that the extent of proton transfer increases in the order $C_6H_5CH_2CH_2S^+Me_2$ < $C_6H_5CH_2CH_2N^+(C_6H_5)Me_2$ < p-$ClC_6H_4CH_2CH_2N^+Me_3$ < $C_6H_5CH_2CH_2N^+Me_3$. Since our experiments really define only the extent of proton transfer to the base, they do not necessarily give the "degree of carbanion character,"[5] though they are obviously closely related to it. The experimental values of k_{DO^-}/k_{HO^-} include a *solvent* isotope effect, caused by the fact that the DO^- reaction is carried out in D_2O, while the HO^- reaction is carried out in H_2O. The solvent isotope effect should be weak and also should be similar for the 'onium compounds because in each case a positively charged organic ion reacts with base. Even after allowance for a substantial solvent isotope effect (say, 10%), the experimental isotope effect for the sulfonium ion indicates a transition state where the proton is about half-transferred between substrate and base; the proton is therefore more than half-transferred for the other compounds (*cf.* Table III). The primary isotope effect for $C_6H_5CH_2CH_2S^+Me_2$ *vs.* $C_6H_5CD_2CH_2S^+Me_2$ in H_2O, $k_H/k_D = 5.93$ at 30°,[6] also indicates that the proton is rather symmetrically placed in the transition state (*cf.* Table III), probably closer to the base, since the primary effect for $C_6H_5CH_2CH_2Br$ *vs.* $C_6H_5CD_2CH_2Br$ is even larger, 7.11 at 30° in ethanol, but the ρ constant is greater for the sulfonium ion than for the bromide.[6]

Table III. Secondary and Primary Isotope Effects in Proton Transfer LO---L---C

Proton transfer, %	Approx k_{DO^-}/k_{HO^-} (secondary)	Approx k_H/k_D (primary)
0	1.0	1.0
50	1.4	7 or more
100	2.0	1.0

Coupled with primary isotope effects for eliminations under similar conditions, our results provide even stronger evidence of the extent of proton transfer. Primary effects for the sulfonium ion are[6] 4.14 in H_2O at 80°, 5.05 in H_2O at 50°, 5.93 in H_2O at 30°, and 5.07 in ethanol at 30°. Primary effects for $C_6H_5CH_2CH_2N^+Me_3$ *vs.* $C_6H_5CD_2CH_2N^+Me_3$ are 2.98 in ethanol at 50° and 3.02 in 50% ethanol–water at 50°. The latter relatively small primary isotope effects indicate that the respective transition states have either a considerably larger O---L than L---C stretching force constant or a considerably larger L---C than O---L stretching force constant (*cf.* Table III), since a maximum isotope effect is expected when these two force constants are equal.[17] Reference to Table III shows that the only way the ammonium ion can have a smaller k_H/k_D, yet a larger k_{DO^-}/k_{HO^-}, than the sulfonium ion is if, at least for the ammonium compound, the proton is more than 50% transferred to the base in the transition state. This evidence is based only on the relative magnitudes of the secondary and primary isotope effects and is therefore completely separate from the evidence based on the large magnitudes (greater than 1.4) of the secondary isotope effects.

The data for β-phenylethyl bromide are not considered to be reliable, and the use of a different solvent system also makes comparison with the 'onium compounds unreliable. However, it might be expected that the secondary isotope effect for the bromide would be close to that for the sulfonium ion, since the primary isotope effects for the two (in ethanol) are similar.

Our results are consistent with the high positive ρ values for these reactions, which appear to indicate considerable carbanion character in the transition states. For the trimethylammonium compound, we calculate $\rho = 2.6$ at 80.45° (using only two substituents), higher than the ρ value for the sulfonium compound in H_2O, where $\rho = 2.21$ at 30° and 2.03 at 60.55°.[5b]

Substituent Effects on Transition-State Geometry. It is interesting to see how the above and other evidence on changes in transition-state geometry with changes in substituents fits in with the predictions of a recently proposed, simple theory of such changes.[21] Experimental evidence can be divided into two categories: (1) relating to changes in the geometry of one bond (*e.g.*, most isotope effects, Brønsted coefficients); and (2) relating to relative changes in geometry of more than one bond (*e.g.*, ρ values, primary hydrogen isotope effects). Predictions about one bond are reasonably straightforward; predictions about relative changes in more than one bond require a knowledge of the exact normal coordinate motion corresponding to the reaction coordinate of the transition state.[21]

Taking the simpler category first, it is predicted[21] that for leaving groups which are more basic, the transition state will be more product like. The sulfur and nitrogen isotope effects for β-phenylethyldimethylsulfonium ion[22] and β-phenylethyltrimethylammonium

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valid for approximate theoretical calculations of this effect[16]), *ca.* 1.88 is expected at 80.45°.

(13) See L. Pentz and E. R. Thornton, *J. Am. Chem. Soc.*, in press, for experimental data and discussion of K_B.

(14) P. Salomaa, L. L. Schaleger, and F. A. Long, *ibid.*, **86**, 1 (1964); V. Gold and B. M. Lowe, *Proc. Chem. Soc.*, 140 (1963).

(15) V. Gold, *ibid.*, 141 (1963); A. J. Kresge and A. L. Allred, *J. Am. Chem. Soc.*, **85**, 1541 (1963); F. Heinziger and R. E. Weston, Jr., *J. Phys. Chem.*, **68**, 744 (1964).

(16) R. F. W. Bader, Ph.D. Thesis in Organic Chemistry, Massachusetts Institute of Technology, 1957.

(17) This argument is rigorous only if effects due to changes in bending motions of O---L---C are small relative to those due to stretching vibrations and/or are nearly constant for transition states with different degrees of proton transfer.[18] There is theoretical evidence that this maximum should be very broad, giving small isotope effects only for very reactant-like or product-like transition states;[19] however, it appears that such maxima can be realized experimentally.[20]

(18) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(19) A. V. Willi and M. Wolfsberg, *Chem. Ind.* (London), 2097 (1964); R. P. Bell, *Discussions Faraday Soc.*, **39**, 16 (1965); W. H. Saunders, Jr., *Chem. Ind.* (London), 663 (1966).

(20) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* (London), **A294**, 273 (1966).

(21) E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967). The basic predictions for the E2 reaction are discussed in this reference and will not be repeated here.

(22) W. H. Saunders, Jr., A. F. Cockerill, S. Ašperger, L. Klasinc, and D. Stefanović, *ibid.*, **88**, 848 (1966).

ion,[23] respectively, indicate similar amounts of C---S and C---N bond breaking, and it is not possible to decide as yet which bond is more fully broken. On the other hand, the k_{DO^-}/k_{HO^-} effects described above indicate a transition state more product like for NMe_3 than for $NMe_2C_6H_5$ than for SMe_2 as leaving groups. Also, the Brønsted β for E2 elimination from *t*-butyldimethylsulfonium ion (0.46) is greater than for E2 elimination from *t*-butyl chloride (0.17),[24] indicating the former has a more product-like transition state. E2 elimination from 2-butyl bromide gives a volume of activation $\Delta V^{\ddagger}$ indicating a relatively reactant-like transition state, while for 2-methyl-2-butyltrimethylammonium ion $\Delta V^{\ddagger}$ indicates a relatively product-like (or carbanion-like) transition state (both in ethanol–ethoxide).[25] For substituents at the β-carbon atom, it is predicted[21] that for a more electron-withdrawing substituent, the transition state will be more reactant like. The nitrogen isotope effect for p-$ClC_6H_4CH_2CH_2N^+Me_3$ (1.011 ± 0.001) is less than that for $C_6H_5CH_2CH_2N^+Me_3$ (1.015 ± 0.001)[23] (both in ethanol–ethoxide), as expected. The isotope effects k_{DO^-}/k_{HO^-} described above for these same two ammonium ions indicate the former is also more reactant like with respect to the O---H bond. Brønsted correlations for $C_6H_5CH_2CH_2Br$ ($\beta = 0.54$) and p-$NO_2C_6H_4CH_2CH_2Br$ ($\beta = 0.67$), with substituted phenoxide bases, indicate the latter is more product like;[26] we believe this apparent anomaly may result from an important contribution from a "perpendicular effect,"[21] superimposed on the "parallel effect" which is expected to make the *p*-nitro compound more reactant like, but have no evidence that this is the case. For substituents at the α-carbon atom, it is predicted[21] that for a more electron-withdrawing substituent, the transition state will be more product like. Brønsted correlations for E2 elimination from 1-bromocyclohexane ($\beta = 0.36$) *vs.* 1,1-dibromocyclohexane ($\beta = 0.51$) and 1-chlorocyclohexane ($\beta = 0.39$) *vs.* 1,1-dichlorocyclohexane ($\beta = 0.58$), with substituted thiophenoxide bases,[27] indicate the extra 1-bromo or 1-chloro substituent produces a more product-like transition state, as predicted.

The second category, relating to relative changes in more than one bond, is at once more difficult to make predictions about and more difficult to obtain unambiguous experimental evidence about. A great deal of the qualitative experimental evidence on such changes has been discussed in recent reviews,[28-30] the major conclusion of which is that, in addition to being reactant like or product like, the transition states for E2 eliminations may also vary from "E1cB-like" (high ratio of C---H to C---X bond breaking) through synchronous to "E1 like" (low ratio of C---H to C---X bond breaking). Some of the stronger pieces of experimental evidence include: the ρ values for β-phenylethyl compounds are large and positive, and are larger for more basic leaving groups,[5] indicating more carbanion character at the β-carbon atom for more basic leaving groups. On the other hand, the secondary α-deuterium isotope effect is considerably larger for $C_6H_5CH_2CD_2Br$ (1.09 per D atom)[7] than for $C_6H_5CH_2CD_2N^+Me_3$ (*ca.* 1.01–1.02 per D atom),[9] which seems to indicate more double-bond or sp[2] character at the α-carbon atom for the former. However, these results are difficult to interpret quantitatively because the change in nature and charge type of the leaving groups may have large, unpredictable effects on the α-deuterium isotope effect, *e.g.*, steric or solvation effects. Also, it is found that for substituted benzenesulfonate leaving groups, electron-withdrawing substituents give increasing yields of more highly substituted olefin from 2-methyl-3-pentyl benzenesulfonates,[31] which seems to indicate more double-bond character for more electron-withdrawing substituents, in spite of the prediction[21] that the transition state should be more reactant like. We rationalize this observation by assuming that the more highly substituted olefin would probably be always favored unless there were some other factor, such as carbanion character, favoring the less highly substituted olefin. If the more product-like transition state also has more relative carbanion character, and if the carbanion character is a more important determinant of orientation than the double-bond character, these experiments are consistent with predictions. For changes in the strength of the base, there are some indications that increased base strength gives increased carbanion character,[5d,32,33] whereas it is predicted[21] that a stronger base should give a more reactant-like transition state. We believe that these experiments, namely, observation of a higher per cent of 1-butene relative to 2-butene from 2-butyl *p*-toluenesulfonate with stronger bases, are not explained by increased C–H stretching in the transition state for stronger bases.[32] Rather, we predict that the transition states are *more reactant like with stronger bases*, and that the inherent preference for the more highly substituted olefin expected for a fairly reactant-like transition state (*e.g.*, with *p*-toluenesulfonate as leaving group) is observed with the weaker bases used,[32] but that with very strong bases, the transition state becomes so reactant like that essentially no selectivity is observed. It is observed that with the stronger base, *t*-butoxide, 61% 1-butene is formed,[32] and 60% is expected statistically, because there are three 1-protons but only two 3-protons in the reactant. Finally, various types of qualitative evidence[28-30] indicate that substitution of groups on the β-carbon atom which tend to stabilize carbanions leads to more carbanion character in the transition state, and that substitution of groups on the α-carbon atom which tend to stabilize carbonium ions leads to more carbonium ion character in the transition state. These effects can be explained as "perpendicular effects";[21] in contrast to effects associated with the reaction coordinate motion, perpendicular effects are

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(23) A. N. Bourns and P. J. Smith, *Proc. Chem. Soc.*, 366 (1964).

(24) D. J. McLennan, *J. Chem. Soc., B*, 709 (1966).

(25) K. R. Brower and J. S. Chen, *J. Am. Chem. Soc.*, **87**, 3396 (1965).

(26) R F. Hudson and G. Klopman, *J. Chem. Soc.*, 5 (1964).

(27) D. J. McLennan, *ibid., B*, 705 (1966).

(28) W. H Saunders, Jr., in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers Division of John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter 2.

(29) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, 1, 225 (1962).

(30) D. V. Banthorpe in "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 3.

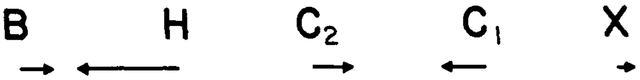
(31) A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965).

(32) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *J. Am. Chem. Soc.*, **87**, 3984 (1965); D. H. Froemsdorf and M. D. Robbins, *ibid.*, **89**, 1737 (1967).

(33) *Cf.* also K. T. Finley and W. H. Saunders, Jr., *ibid.*, **89**, 898 (1967).

predicted[21] to produce just the effects mentioned in the last sentence.

With the reservations mentioned above and the reservation that perpendicular effects may play an important role in some cases, most of the data on E2 eliminations can be explained by a reaction coordinate motion approximately as follows.



By making the H move much more relative to C_1, and C_2 much more relative to X, it turns out that making the transition state more product like (moving along the reaction coordinate as shown by the arrows above) produces *relatively* more carbanion character at C_2 and less carbonium ion character at C_1. On the other hand, of course, making the transition state more reactant like (moving along the reaction coordinate in precisely the opposite way from that shown by the arrows above) produces *relatively* less carbanion character at C_2 and more carbonium ion character at C_1. This hypothetical reaction coordinate differs from most previous suggestions in that, for example, when X is strongly basic the transition state is predicted to have more carbanion character but also more double-bond character. Also, when X is weakly basic the transition state is predicted to have more carbonium ion character but also less double-bond character. The Hofmann and Saytzeff patterns of orientation in eliminations are explained by this hypothesis as arising from an inherent preference for formation of the more highly substituted double bond in the case of all leaving groups X, but with a superimposed preference for forming the less highly substituted double bond in cases where the transition state has considerable carbanion character. The 'onium compounds are supposed to have sufficient carbanion character in the transition state that the less substituted olefin is formed, while the halides are supposed to have sufficiently less carbanion character in the transition state that the inherent preference for formation of the more substituted olefin prevails. The experimental evidence appears to favor relatively large substituent effects on the C---H bond geometry (*cf.* Isotope Effects section above) but relatively small substituent effects on the C---X bond geometry,[22,23] and the proposed reaction coordinate explains these observations very well.

We hope to carry out model calculations of the normal coordinates for E2 transition states, in the hope of predicting more clearly the reaction coordinate motion as well as the other normal coordinate motions which are responsible for perpendicular effects.[21] In addition to the present ambiguity with respect to the exact normal coordinates, it will be noted that no mention has been made of steric effects, and all predictions have been made on the basis of electronic effects.[34] While we do not feel that steric effects are unimportant, we feel they are less important than electronic effects in determining the above mechanistic properties for which evidence is available. Predictions of steric effects can readily be made,[21] however.

Isotope Effect in Mixed H_2O and D_2O. The problem of separating the *solvent* isotope effect from the secondary isotope effect due to DO^- *vs.* HO^- as bases can in principle be solved by studying reactions in mixtures of light and heavy water. This subject has been discussed extensively,[35] but has not been applied to reactions of the E2 type, though some equations for similar reaction mechanisms have been derived.[36] Equations can be derived for two extreme types of transition state: reactant like and product like, and the following is a more rigorous derivation of these equations than previous derivations[36] of similar equations.[37]

For a LO^- promoted E2 reaction in a H_2O–D_2O mixture, there are two possible transition states

$$HO^- + HSX \underset{}{\overset{k_H}{\rightleftarrows}} [HOHSX^-]^{\ddagger}$$

$$DO^- + HSX \underset{}{\overset{k_D}{\rightleftarrows}} [DOHSX^-]^{\ddagger}$$

The observed rate constants in pure solvents are

$$(k_H)_{obsd} = \frac{k_H(\gamma_{HSX})_H(\gamma_{HO^-})_H}{(\gamma_H{}^{\ddagger})_H}$$

$$(k_D)_{obsd} = \frac{k_D(\gamma_{HSX})_D(\gamma_{DO^-})_D}{(\gamma_D{}^{\ddagger})_D}$$

where the γ's are activity coefficients defined relative to the perfect gas at 1-atm pressure (and are therefore not unity even at infinite dilution). If α is the atom fraction of deuterium in a mixture of H_2O and D_2O, the rate in the mixture is

$$\text{rate}_\alpha = \frac{k_H[HSX]_\alpha[HO^-]_\alpha(\gamma_{HSX})_\alpha(\gamma_{HO^-})_\alpha}{(\gamma_H{}^{\ddagger})_\alpha} + \frac{k_D[HSX]_\alpha[DO^-]_\alpha(\gamma_{HSX})_\alpha(\gamma_{DO^-})_\alpha}{(\gamma_D{}^{\ddagger})_\alpha} = (k_\alpha)_{obsd}[HSX]_\alpha[LO^-]_\alpha$$

Hence

$$(k_\alpha)_{obsd} = k_H\frac{[HO^-]_\alpha}{[LO^-]_\alpha}\frac{(\gamma_{HSX})_\alpha(\gamma_{HO^-})_\alpha}{(\gamma_H{}^{\ddagger})_\alpha} + k_D\frac{[DO^-]_\alpha}{[LO^-]_\alpha}\frac{(\gamma_{HSX})_\alpha(\gamma_{DO^-})_\alpha}{(\gamma_D{}^{\ddagger})_\alpha}$$

and

$$\frac{(k_\alpha)_{obsd}}{(k_H)_{obsd}} = \frac{[HO^-]_\alpha}{[LO^-]_\alpha}\frac{(\gamma_{HSX})_\alpha(\gamma_{HO^-})_\alpha(\gamma_H{}^{\ddagger})_H}{(\gamma_{HSX})_H(\gamma_{HO^-})_H(\gamma_H{}^{\ddagger})_\alpha} + \frac{k_D[DO^-]_\alpha}{k_H[LO^-]_\alpha}\frac{(\gamma_{HSX})_\alpha(\gamma_{DO^-})_\alpha(\gamma_H{}^{\ddagger})_H}{(\gamma_{HSX})_H(\gamma_{HO^-})_H(\gamma_D{}^{\ddagger})_\alpha} \quad (1)$$

Since HO^- and DO^- leave the structure of water unchanged,[16,38] $(\gamma_{HO^-})_\alpha = (\gamma_{HO^-})_H = (\gamma_{DO^-})_\alpha = (\gamma_{DO^-})_D$, and these activity coefficients cancel from eq 1.

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[34] For discussion of the relative importance of steric and electronic effects, see ref 28–30 and: H. C. Brown and R. L. Klimisch, *J. Am. Chem. Soc.*, **88**, 1425, 1430 (1966); W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *ibid.*, **87**, 3401 (1965); D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966).

[35] See, for example, (a) C. G. Swain, R. F. W. Bader, and E. R. Thornton, *Tetrahedron*, **10**, 200 (1960); (b) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 2347 (1959); A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964); V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960); E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964, pp 212–226.

[36] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 3884, 3890 (1961).

[37] L. Pentz, Ph.D. Dissertation in Chemistry, University of Pennsylvania, 1965, derives the equation rigorously for specific acid catalyzed reactions.

[38] C. G. Swain and R. F. W. Bader, *Tetrahedron*, 10, 182 (1960).

Considering first a reactant-like transition state, $k_D/k_H = 1.0$, because these rate constants include no solvent effect but only the relative basicity of HO^- *vs.* DO^-; yet, if the transition state is reactant like, none of this relative basicity will be observed because the LO^- is not appreciably neutralized in the transition state. Then, since $[LO^-]_\alpha = [HO^-]_\alpha + [DO^-]_\alpha$, and since molecules differing only by isotopic substitution must have essentially identical activity coefficients $[(\gamma_D{}^\ddagger)_\alpha = (\gamma_H{}^\ddagger)_\alpha]$

$$\frac{(k_\alpha)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}} = \frac{(\gamma_{HSX})_\alpha/(\gamma_H{}^\ddagger)_\alpha}{(\gamma_{HSX})_H/(\gamma_H{}^\ddagger)_H} = y$$

This equation represents only a solvent isotope effect. Since such "solvation" isotope effects are relatively nonspecific, it is reasonable to assume that a linear free energy relationship holds,[39] *i.e.*, that

$$\log y = m\alpha + b$$

When $\alpha = 0$, $(k_\alpha)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}} = 1.0$, so $b = 0$; when $\alpha = 1.0$, $(k_\alpha)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}} = (k_D)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}}$, so $m = \log [(k_D)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}}]$. Then

$$\frac{(k_\alpha)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}} = \left[\frac{(k_D)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}}\right]^\alpha \tag{2}$$

On the other hand, for a product-like transition state, the *entire* relative basicity of HO^- and DO^- must be felt, so $k_D/k_H = K_n' \equiv K_B{}^{0.5}$ (see above). Then, according to eq 1

$$\frac{(k_\alpha)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}} = y\left(\frac{[HO^-]_\alpha + K_n'[DO^-]_\alpha}{[LO^-]_\alpha}\right) \tag{3}$$

Since

$$K_n' = \frac{[HO^-][D_2O]^{0.5}}{[DO^-][H_2O]^{0.5}}$$

eq 3 gives, on substitution for $[DO^-]$

$$\frac{(k_\alpha)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}} = y\left\{\frac{1 + ([D_2O]^{0.5}/[H_2O]^{0.5})}{1 + ([D_2O]^{0.5}/K_n'[H_2O]^{0.5})}\right\} \tag{4}$$

$$= yK_n'\left(\frac{[H_2O]^{0.5} + [D_2O]^{0.5}}{K_n'[H_2O]^{0.5} + [D_2O]^{0.5}}\right) \tag{5}$$

Referring to eq 5, when $\alpha = 0$, $(k_\alpha)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}} = 1.0$, and $b = 0$; when $\alpha = 1.0$, $(k_\alpha)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}} = (k_D)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}}$, so

$$\log [(k_D)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}}] = m + \log K_n'$$

$$m = \log [(k_D)_{\mathrm{obsd}}/K_n'(k_H)_{\mathrm{obsd}}]$$

and eq 4 becomes

$$\frac{(k_\alpha)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}} = \left[\frac{(k_D)_{\mathrm{obsd}}}{(k_H)_{\mathrm{obsd}}K_n'}\right]^\alpha \left\{\frac{1 + ([D_2O]^{0.5}/[H_2O]^{0.5})}{1 + ([D_2O]^{0.5}/K_n'[H_2O]^{0.5})}\right\} \tag{6}$$

The ratio $[D_2O]^{0.5}/[H_2O]^{0.5}$ is related to α by a rather complex expression,[13] since it has recently been discovered[40] that the equilibrium constant for the reaction $H_2O + D_2O = 2HDO$ is not equal to the statistical value 4.0, being *ca.* 3.8 at 75°.

We have carried out experiments at $\alpha = 0.5$ (where $[D_2O]^{0.5}/[H_2O]^{0.5} = 1.0$), since the maximum difference between the predictions of eq 2 and 6 usually occurs at about this atom fraction. Equation 2 predicts $(k_\alpha)_{\mathrm{obsd}}/(k_H)_{\mathrm{obsd}} = 1.34$ for a reactant-like transition state, while eq 6 predicts 1.27 for $K_n' = 1.88$. The observed isotope effect for $C_6H_5CH_2CH_2N^+Me_3$ (Table I) is 1.34 ± 0.04. The data do not allow a decision as to the extent of reactant-like or product-like character, and in fact indicate, if anything, that the transition state is more reactant like, which is inconsistent with all other indications. However, we consider it to be highly satisfactory that the experimental isotope effect falls within the range predicted by eq 2 and 6. Further, more precise studies of such isotope effects in mixed solvents would be essential for detection of such small differences.

Experimental Section

All melting points are corrected. Boiling points are uncorrected.

Reagents. Dioxane (Eastman) was purified according to the method of Fieser,[41] bp 100.0–100.5° (753 mm).

Diglyme (Matheson Coleman and Bell) was first distilled from calcium hydride to dry the reagent, bp 161.5–162° (765 mm) (lit.[42] bp 160–162° (740 mm)). The distillate was redistilled from a small amount of lithium aluminum hydride, bp 79.0–79.5° (36 mm) (lit.[42] bp 75° (35 mm)).

β-Phenylethyl bromide was redistilled commercial material (Matheson Coleman and Bell reagent), bp 88.0–88.5° (9 mm), n^{20}_{D} 1.5572 (lit.[5a] bp 66° (2 mm), n^{26}_{D} 1.5542). This material was shown to be greater than 99.5% pure by gas chromatography.

Styrene was redistilled commercial material (Eastman, White Label), bp 38–39° (15 mm), n^{25}_{D} 1.5432 (lit.[5a] bp 38° (15 mm), n^{25}_{D} 1.5433).

Protium oxide was laboratory distilled water which had been redistilled from alkaline potassium permanganate.

Deuterium oxide (>99.5%) was obtained from Liquid Carbonic Co.

Before their use, prepurified nitrogen was bubbled through the waters to remove traces of carbon dioxide which may have been present.

All procedures for the preparation of protium oxide solutions were carried out under a stream of nitrogen or in a nitrogen-filled drybox. It was found that both methods gave identical results within experimental error.

All deuterium oxide solutions were prepared in a nitrogen-filled drybox. All glassware used for deuterium oxide solutions was dried for at least 5 hr at 200° before use. Upon removal from the oven, the glassware was kept in a desiccator or placed in the drybox while hot. Where it was not possible to dry the glassware, it was rinsed adequately with deuterium oxide before use.

Preparation of Standard Sodium Hydroxide Solutions. Solutions were generally prepared by adding small amounts of freshly cut sodium (Baker prepurified) to water at room temperature in a nitrogen atmosphere. The resulting solution was standardized by titration with 0.02000 *M* hydrochloric acid (brom thymol blue indicator).

Preparation of Standard Sodium Deuterioxide Solutions. Procedures were the same as in the preparation of hydroxide solutions except that all operations were carried out in a nitrogen-filled drybox. A sample of sodium deuterioxide solution thus prepared was analyzed for its deuterium content and found to contain 99.45 atom % excess deuterium.[43]

Preparation of Methyl 2-Phenylethyl Sulfide.[5a,44] β-Phenylethyl bromide (Matheson Coleman and Bell, 30 g, 0.16 mole) was added dropwise to a solution of methanethiol (Eastman, 25 g, 0.32 mole) and sodium hydroxide (6.4 g, 0.16 mole) in hot ethanol to enable gentle refluxing. After the addition was complete, the solution

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[39] This is nearly true even for strongly solvated halide ions.[35a]

[40] L. Friedman and V. J. Shiner, Jr., *J. Chem. Phys.*, **44**, 4639 (1966); J. W. Pyper, R. S. Newbury, and G. W. Barton, Jr., *ibid.*, **46**, 2253 (1967).

[41] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 284.

[42] H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

[43] Analysis performed by Josef Nemeth, Urbana, Ill.

[44] E. H. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 92 (1949).

was refluxed for 0.5 hr longer. The solvent was distilled off and the residue extracted with ether, washed with water, and dried over magnesium sulfate. After the ether was removed, the residue was fractionated under reduced pressure yielding 21.3 g (86%) of colorless liquid, bp 102–103° (11 mm) (lit.[5a] bp 70–71° (11 mm); lit.[45] bp 111° (12 mm)).

Preparation of β-Phenylethyldimethylsulfonium Bromide. Methyl 2-phenylethyl sulfide (21.3 g, 0.140 mole) and methyl bromide (Matheson Co. cylinder, 27 g, 0.28 mole) were dissolved in 350 ml of nitromethane and the solution allowed to stand at room temperature for 44 days. At the end of this time, removal of the solvent with a rotary evaporator at room temperature afforded a 94% yield of crude white crystals which were recrystallized from ethanol–ether to constant mp 137–138° dec (lit.[5a] mp 135.0–135.5° dec (cor)).

Preparation of β-Phenylethyltrimethylammonium Bromide. β-Phenylethyl bromide (Matheson Coleman and Bell, 30 g, 0.16 mole) and trimethylamine (Eastman, 25% in methanol, 19 g, 0.32 mole) were mixed and allowed to stand for 3 days at room temperature. The methanol was then removed on the rotary evaporator affording a quantitative yield of white crystals which were recrystallized from ethanol–ether to constant mp 238.5–239.0° (lit. mp 238–239°,[6] 237.5–238.0° [46]).

Preparation of β-(*p*-Chlorophenyl)ethyl Alcohol. To magnesium (36 g, 1.5 g-atoms, 50% excess) in 25 ml of anhydrous ether was slowly added, with stirring, a solution of *p*-bromochlorobenzene (192 g, 1.0 mole) in 400 ml of anhydrous ether. After standing overnight the resulting solution was filtered and cooled in an ice–salt bath. A cold (0°) solution of ethylene oxide (Eastman, 44 g, 1.3 moles) in 100 ml of anhydrous ether was added slowly to the Grignard solution with cooling and stirring according to the method of Huston and Agett.[47] The ether layer afforded the alcohol in 48% yield at bp 90.5–91.0° (0.7 mm), n^{25}_{D} 1.5484 (lit.[5a] bp 77–78° (0.3 mm), n^{25}_{D} 1.5482).

Preparation of β-(*p*-Chlorophenyl)ethyl Bromide. β-(*p*-Chlorophenyl)ethyl alcohol (71 g, 0.45 mole) was added slowly to phosphorus tribromide (62 g, 0.23 mole, 50% excess) at room temperature, according to the method of Rupe.[48] The alkyl bromide was obtained in 76% yield, bp 81–82° (0.9 mm), n^{25}_{D} 1.5695 (lit.[5a] bp 86.5° (1.6 mm), n^{25}_{D} 1.5697).

β-(*p*-Chlorophenyl)ethyltrimethylammonium Bromide. β-(*p*-Chlorophenyl)ethyl bromide (35 g, 0.16 mole) and trimethylamine (Eastman, 25% in methanol, 19 g, 0.32 mole) were mixed and allowed to stand at room temperature for 3 days. The quantitative yield of salt was precipitated from the solution by adding a large excess of ether and then recrystallized from ethanol–ether to constant mp 240.5–241.0°.

Anal. Calcd for $C_{11}H_{17}NBrCl$: C, 47.42; H, 6.15. Found: C, 47.73; H, 6.17.

***p*-Chlorostyrene.** A solution of β-(*p*-chlorophenyl)ethyltrimethylammonium bromide (11 g, 0.04 mole) in 100 ml of 1.25 *M* sodium hydroxide solution was allowed to react under nitrogen for 18 hr at 80.45°. The solution was extracted with ether, the ether layer dried over sodium sulfate, and the crude product distilled from a small amount of *p*-*t*-butylpyrocatechol. The pure material was collected at bp 47–48° (3 mm), n^{22}_{D} 1.5645 (lit.[5a] bp 38° (2.2 mm), n^{20}_{D} 1.5650).

Preparation of Phenyl-2-phenylethylmethylamine.[49] To magnesium (14 g, 0.58 g-atom) in 100 ml of anhydrous ether was slowly added, with stirring, a solution of isopropyl bromide (Matheson Coleman and Bell, 68 g, 0.55 mole) in 200 ml of anhydrous ether. The solution was allowed to stand overnight and N-methylaniline (Matheson Coleman and Bell, 59 g, 0.55 mole) was added slowly, with stirring, to the solution at room temperature. The ether was distilled off and replaced by 500 ml of benzene (Baker, reagent grade, used without further drying) in which the residue was completely soluble. β-Phenylethyl bromide (Matheson Coleman and Bell, 102 g, 0.55 mole) was added and the resulting solution was refluxed for 70 hr. The benzene layer was decanted from the insoluble residue ($MgBr_2$) which was extracted with fresh benzene. The total benzene solution was washed three times with water. Removal of the benzene by distillation and fractionation of the residue yielded 63.3g (55%) of amine, bp 124–125° (0.5 mm) (lit.[49] bp 124–128° (0.3 mm)), which solidified on cooling.

Phenyl-2-phenylethyldimethylammonium Bromide. Phenyl-2-phenylethylmethylamine (19 g, 0.09 mole) and methyl bromide (Matheson Co. cylinder, 40 g, 0.4 mole) were dissolved in 300 ml of nitrobenzene and allowed to stand at room temperature for 8 days. At the end of this time crystals had appeared in the solution. The crude salt (67%) was precipitated from the solution by adding a large excess of anhydrous ether. Purification was effected by dissolving the salt in warm ethanol and precipitating with ether until a compound of constant melting point, 169–170° dec, was obtained.

Anal. Calcd for $C_{16}H_{20}BrN$: C, 62.75; H, 6.58. Found: C, 62.96; H, 6.75.

Kinetic Procedure. All reactions were carried out in a well-stirred thermostated bath held at 80.45 ± 0.02°.[50] Reaction rates were followed by titration of the reactant base with standard hydrochloric acid (brom thymol blue indicator). For each run the hydrochloric acid solution used for titrations was restandardized to assure reproducibility of the data. Titrations were carried out with a 5-ml (tolerance ±0.01 ml) gravity-filling buret.

Rate constants were determined from the slope of a plot of log $(a - x)/(b - x)$ *vs.* t, derived from the integrated second-order rate expression. All runs consisted of six to ten experimental points and were taken to at least 75% completion; a minimum of one run in each series was taken to 80% or more reaction. A straight line was drawn through the experimental points by inspection with minimum deviation of the data. There were no serious drifts from linearity in the rate plots.

In all cases, runs in deuterium oxide were carried out under the same conditions as those in protium oxide. For the 'onium salt runs, salt concentrations were approximately 0.05 *M* and hydroxide concentrations approximately 0.1 *M*. For the runs of β-phenylethyl bromide, the concentrations of base and alkyl bromide were varied to check the reproducibility of the rate constants.

Reactions of the sulfonium salt were carried out in a 25-ml volumetric flask onto which a rubber serum stopper had been wired. Solutions of the sulfonium salt and base were separately allowed to come to thermal equilibrium. The base was then added to the salt solution. After thermal equilibrium was reached the solution was shaken. At $t = 0$ one or more 1-ml aliquots were withdrawn with a calibrated hypodermic syringe, cooled in ice to quench the reaction, and titrated with standard hydrochloric acid. Additional aliquots were withdrawn periodically during the run and treated similarly. No correction was made in the titers or in the rate constants for the slight temperature decrease experienced by the solution upon being drawn into the syringe. After approximately 80% reaction, it was brought to completion by heating on the steam bath. One or more infinity aliquots were taken. It was shown that, during the run and during the period of completion of the reaction, neither evaporation of the solution nor the effect of the alkali on the glassware was appreciable.

For the quaternary ammonium salt runs, the reaction solutions were prepared at room temperature in a 25-ml volumetric flask. Ampoules of alkali-resistant glassware had been prepared by sealing off one end of a tube and drawing out the other end to form a narrow neck through which a syringe needle could be inserted. Approximately 1.3 ml of the reaction solution was introduced into each ampoule which was then sealed. The ampoules were placed in the kinetic bath and after thermal equilibrium was attained, one or more were removed for the zero point and cooled in cold water. The ampoule was then allowed to come to room temperature and broken open at one end and a 1-ml aliquot withdrawn with a calibrated hypodermic syringe. In the reactions where trimethylamine was produced, the sample was transferred to a 25-ml ground-glass erlenmeyer flask which was placed on a rotary evaporator for at least 30 min at 30–40° to remove the amine. The remaining solution was then titrated with standard hydrochloric acid solution. Additional aliquots were withdrawn periodically and treated accordingly. In the reactions where dimethylaniline was formed, the aliquots were titrated directly after attaining room temperature, since this amine is not basic enough to interfere with the titration of the alkali. Infinity points consisted usually of two or more ampoules which had undergone reaction to completion on the steam bath. Since all aliquots were calibrated with the hypodermic syringe at room temperature (*ca.* 25°), the rate constants were cor-

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(45) J. von Braun, W. Teuffert, and K. Weissbach, *Ann.*, **472**, 121 (1929).

(46) W. E. Truce and J. A. Simms, *J. Org. Chem.*, **22**, 762 (1957).

(47) R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

(48) H. Rupe, *Ann.*, **395**, 114 (1913).

(49) M. S. Kharasch, G. H. Williams, and W Nudenberg, *J. Org. Chem.*, **20**, 937 (1955).

(50) Measured with a National Bureau of Standards Certified calibrated thermometer and rechecked periodically to assure constancy of bath temperature.

rected for thermal expansion of the solutions to obtain the corresponding values at 80.45°.

For the reaction of β-phenylethyltrimethylammonium bromide in a 50% H_2O–D_2O (v/v) mixture, the reaction solutions were prepared by mixing equal volumes (pipet) of H_2O and D_2O solutions.

In the reaction of β-phenylethyl bromide with sodium hydroxide in 40% aqueous dioxane, infinity determinations were not possible because of the inaccuracy of alkali determinations over a long period of time or at high temperatures (see Discussion). For this reason, and because the reaction was fairly fast, rapid mixing without a drop in temperature was necessary to ensure accurate determinations of the initial concentrations. Consequently, in almost all runs a Pyrex glass reaction vessel was used which had two chambers, both easily accessible from the mouth of the vessel. The general procedure was to weigh the alkyl bromide accurately into a semimicro weighing flask which was placed into one chamber of the vessel. The remaining procedures were carried out in a nitrogen atmosphere. By pipet, 10 ml of dioxane was added to this chamber. Into the other chamber was introduced 15 ml of standard sodium hydroxide solution, also by pipet. A rubber serum stopper was wired into the mouth of the vessel which was then placed into the constant-temperature bath. When thermal equilibrium was attained, the solutions in the two chambers were rapidly mixed by shaking the vessel from side to side and the zero time noted. The zero titer ($=a$) was determined by one of two methods: (1) the above procedure was carried out in the absence of the alkyl bromide and, after thermal equilibrium had been reached, the zero titer of the solution was determined by withdrawing a 2-ml aliquot with a calibrated hypodermic syringe, cooling in ice and titrating, under nitrogen, with 0.00990 *M* hydrochloric acid to pH 7, using a Beckman Model H-2 pH meter; or (2) the normality of the stock solution of sodium hydroxide was determined at room temperature and adjusted to the volume of the final solution (4% volume increase in 40% aqueous dioxane solution in going from 25 to 80°). Agreement between the two methods was excellent. The concentration of the alkyl bromide ($=b$) was determined by dividing the number of moles of alkyl bromide weighed into the flask by the final volume of the solution at 80°. Succeeding 2-ml aliquots were withdrawn, quenched in ice, and titrated under nitrogen to pH 7.

Olefin Determinations. Olefin yields were determined spectrophotometrically. Most ultraviolet absorption spectra were determined in 95% ethanol on a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer. This instrument was calibrated against a standard solution of alkaline potassium chromate[51] and found to give accurate optical densities. The extinction coefficient of olefin was also checked on a Cary Model 14 recording spectrophotometer and found to agree well with the value obtained on the Perkin-Elmer instrument. The spectra of the freshly distilled styrenes were determined under the same conditions and at the same time as were the product olefins. Beer's law was obeyed over the concentration ranges used (*ca.* 5×10^{-5} *M*). Molar extinction coefficients are: styrene, λ_{max} 248 mμ (ϵ 1.52×10^4);[52,53] *p*-chlorostyrene, λ_{max} 253 mμ (ϵ 2.06×10^4).[54]

It was established that sodium hydroxide, β-phenylethyldimethylsulfonium bromide, β-phenylethyltrimethylammonium bromide, methyl sulfide, and trimethylamine had no effect on the ultraviolet absorption of the styrenes. Dimethylaniline, formed in the reaction of phenyl-2-phenylethyldimethylammonium bromide with sodium lyoxide, absorbed strongly in the same region as styrene and these determinations were carried out in 70% ethanol, 3.24 *M* in HCl. In this strongly acidic solution, the absorption of the amine virtually disappeared, while that of the styrene remained unchanged except for a shift of the wavelength maximum to 249 mμ. It was necessary to apply a small correction (*ca.* 3%) to account for the absorption of the protonated dimethylaniline and of the unreacted phenyl-2-phenylethyldimethylammonium bromide.

For the sulfonium salt runs, determinations were made on ampoules of reaction solution which had proceeded to completion. In the slower quaternary ammonium salt runs the determinations were made after about 50% reaction. In some of the runs partial polymerization of the styrene occurred so that the results represent maximum yields obtained from at least two separate determinations. Olefin yields were 100 ± 3%. Maximum estimated error for the determinations is 2–3%.

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(51) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(52) Lit.[5a] λ_{max} 248 mμ (ϵ 1.38×10^4).

(53) Lit. λ_{max} 249 mμ (ϵ 1.55×10^4): O. H. Wheeler and C. B. Covarrubias, *Can. J. Chem.*, 40, 1224 (1962).

(54) Lit.[5a] λ_{max} 253 mμ (ϵ 1.97×10^4).

Geometrical Requirements for the Loss of Aldehyde Molecules in the Mass Spectra of Ferrocenyl Esters

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Abstract: The mass spectra of the methyl ω-ferrocenylalkanoates are compared with reference to the loss of CH_2O from the ester function. When $n = 0$, 2, or 3 in $Fc(CH_2)_nCOOCH_3$, the loss of the elements of formaldehyde occurs as a secondary process after loss of C_5H_5; when $n = 1$, 4, or 5, it does not. Another mechanism for loss of formaldehyde during decomposition of these compounds, possibly involving prior transfer of the methoxy group to the cyclopentadienyliron unit, occurs in some cases. Other routes for decomposition apparently lead to C_6H_6 and C_7H_7 units as ligands.

Recently we described an unusual *ortho* effect in the mass spectra of some ferrocenylbenzenes in which a methyl ester function on the benzene ring lost the elements of formaldehyde during a secondary decomposition.[2] We suggested that the structural features of ferrocene esters should be explored in order to determine the generality of the rearrangement. This paper examines the occurrence of this reaction in a series of esters in which the number of methylene units between the ferrocene ring and the ester function is increased from zero to five.

General Aspects of the Spectra. The significant peaks in the mass spectra of six methyl ω-ferrocenyl-

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[1] Du Pont Teaching Fellow, 1966–1967; Enka Summer Fellow, 1966.

[2] D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Am. Chem. Soc.*, **89**, 4917 (1967).