J. Am. Chem. Soc. 1983, 105, 3967–3975

Heavy Atom Isotope Effect Studies of Elimination Reaction Mechanisms. 1. A Kinetic and Carbon-14 Kinetic Isotope Effect Study of the Base-Promoted Dehydrochlorination of Substituted 1-Phenylethyl-*2*-^{14}C Chlorides[1]

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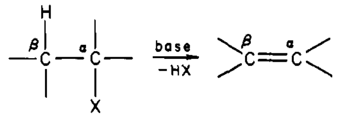
Abstract: Upon treatment with the solvent conjugate base, the primary reaction of substituted 1-phenylethyl chlorides is elimination to substituted styrenes in *t*-BuOH–10% v/v Me_2SO at 60 °C and in bis(2-hydroxyethyl) ether–10% v/v Me_2SO at 45 °C. Kinetic studies using eight substituted chlorides show that these reactions are strongly accelerated by both electron-donating and electron-withdrawing substituents, probably indicating a fairly reactant-like E2 transition state with the mechanism changing from E1-like E2 to ElcB-like E2 as the substituents change from EDG to EWG. In this first carbon isotope effect study of an elimination reaction of an alkyl chloride, carbon-14 kinetic isotope effects have been measured in the alkoxide/bis(2-hydroxyethyl) ether–Me_2SO system for 1-(4-methylphenyl)ethyl-*2*-^{14}C chloride, $k/^{\beta}k$ = 1.038, 1-phenylethyl-*2*-^{14}C chloride, $k/^{\beta}k$ = 1.058, and 1-(4-chlorophenyl)ethyl-*2*-^{14}C chloride, $k/^{\beta}k$ = 1.068. Clearly none of these compounds reacts by an irreversible E1 mechanism, for which no β-carbon isotope effect should be observed. The trend in the results is what would be expected from increased C_β–H bond rupture as the E2 transition state shifts from E1-like to E1cB-like. Theoretical calculations involving E1-like E2 transition-state models show that in this region only for a reaction coordinate motion that strongly couples C_β–H bond rupture, C_α–C_β double bond formation, and C_α–Cl bond rupture does the calculated value for $k/^{\beta}k$ come into the experimentally observed range, and then only for reactant-like models.

For base-promoted β-elimination reactions, distinction among the irreversible E1, the E2, and the irreversible ElcB mechanisms[2–4] can be made by carbon kinetic isotope effect measurements[5] using the successive labeling technique.[6] In particular, for the irreversible E1 mechanism there should be a $^{\alpha}$C but no $^{\beta}$C primary isotope effect, for the E2 mechanism there should be both $^{\alpha}$C and $^{\beta}$C primary isotope effects, and for the irreversible ElcB mechanism there should be a $^{\beta}$C but no $^{\alpha}$C primary isotope effect.[5] There are no examples in the literature[7] where either of these irreversible E1 or ElcB carbon isotope effect predictions have been realized.



For the reversible versions of E1 and ElcB mechanisms, analysis of the isotope effect consequences (see later) are somewhat more complex, but still relatively straightforward. Distinction between reversible and irreversible mechanisms is generally made be various exchange or trapping experiments.

The few reports[8–11] of carbon isotope effect measurements in elimination reactions are all for ElcB-like E2 reactions of quaternary ammonium salts or dimethylsulfonium salts. Considerable attention has also been given to calculations[12–14] of carbon isotope effects to be expected in reactions following various elimination reaction mechanisms.

For the most part, elimination reactions are now discussed in terms of a spectrum[15] of E2 mechanisms bounded on one side by the irreversible E1 mechanism (rate-determing C_α–X bond rupture with no C_β–H bonding changes) and extending through E1-like E2, central E2, and ElcB-like E2 to the irreversible ElcB boundary (rate-determining C_β–H bond rupture with no C_α–X bonding changes). There is not necessarily a smooth merging of the various mechanisms at the boundaries; for example, if the activated complexes have nearly equal energies, Elcb and ElcB-like E2 mechanisms may both operate simultaneously for systems near the boundary. The spectrum of mechanisms can probably best be discussed in terms of our[5] mechanistic diagram (see Figures 1 and 2) representing the reactants and products at the lower left and upper right corners of a square and the carbanion and carbenium ion at the lower right and upper left corners. The abscissa and ordinate are appropriate functions of the C_α–X and C_β–H bonding. These diagrams represent plane projections of the infinite variety of potential surfaces[16] for elimination reactions as set forth so ably by More O'Ferrall.

The present research is the first in a series of experimental heavy atom isotope effect studies of elimination reactions in which we attempt to span the mechanistic spectrum mentioned above.

Very few "clean" (free or nearly free from substitution reaction complications) E1 reactions are known.[17,18] The 1-phenylethyl

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[1] This work was supported by the National Science Foundation and was presented in part at the 179th National American Chemical Society meeting, Houston, TX, March 26, 1980.

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[7] $^{\alpha}$C isotope effect measurements have been made in solvolysis reactions of 1-phenylethyl chloride (Bron, J.; Strothers, J. B. *Can. J. Chem.* **1969**, *47*, 2506–2509, and earlier papers in the series cited there), but less than 1% elimination products were formed. However the solvolysis and elimination reactions may have the same rate-determining ionization step, so the measured isotope effect may also "apply" to the elimination reaction. Carbon isotope effects have also been measured in the solvolysis reactions of *tert*-butyl chloride (Bender, M. L.; Buist, G. J. *J. Am. Chem. Soc.* **1958**, *80*, 4304–4307). For extensive isotope effect calculations for this system see: Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, A. *Ibid.* **1977**, *99*, 3371–3379.

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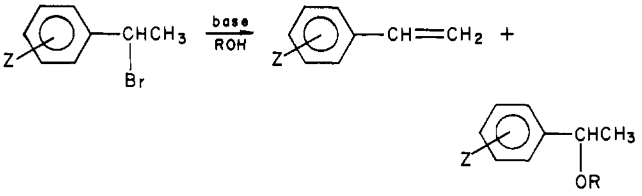
system was thought to be a likely candidate for reaction by the E1-like E2 mechanism, if conditions could be found to avoid or minimize the formation of substitution products. It turned out to be possible to minimize the substitution reaction, but in this work, only at the expense of moving well away from the E1 mechanistic border. Solvolytic reactions of the 1-phenylethyl system have been much studied,[19] and there seems to be general agreement that these are of the S_N1-type involving free carbenium ions or ion pairs of varying degrees of intimacy (interaction with each other and with solvent).

For strong-base-promoted elimination reactions of 1-phenylethyl systems,[20-24] the substitution reactions can be suppressed (but, of course, the reactions then lose much, perhaps all, of their E1 character). Hughes, Ingold, Masterman, and McNulty[21] interpreted their results on the reaction of 1-phenylethyl bromide with sodium ethoxide in ethanol in terms of competing E1, E2, S_N1, and S_N2 reactions (only 34% elimination in the most concentrated base used). Sneen and Robbins[22] proposed a unified S_N2–E2 ion-pair intermediate scheme for the reactions of 1-phenylethyl bromide with sodium ethoxide in ethanol. In a more extensive study using the same reagents, McLennan[23] concluded that the Sneen–Robbins mechanistic scheme gave a less satisfactory account of the results than the original competing E1, E2, S_N1, and S_N2 processes.

Yoshida, Yano, and Oae[24] carried out a study of the base-promoted elimination reactions of a series of 1-phenylethyl bromides in various base–solvent systems and proposed what they considered to be "the first example to show that the transition state of an E2 reaction changes from carbanionic to carbonium ion character by the change of solvents and bases". Reactions of substituted 1-phenylethyl bromides were carried out in t-BuOK/t-BuOH, t-BuOK/t-BuOH–Me_2SO, and EtONa/EtOH.



Z = p-CH_3, H, p-Cl, p-Br, m-NO_2

In the first two solvent/base systems the elimination products were formed in high yields (mostly 85–95%), while in EtONa/EtOH the substituted styrenes were formed only to the extent of ~30%. The Hammett plots were nonlinear, with positive ρ values in all cases except for the p-CH_3 compound (negative ρ for curve tangent) in t-BuOH–Me_2SO. The ρ values were most positive in the t-BuOH–Me_2SO system and least in EtOH. For 1-phenylethyl bromide itself, the β-deuterium kinetic isotope effects,[24] $^{\mathrm{H_3}}k/^{\mathrm{D_3}}k$, were 3.5 in t-BuOH–Me_2SO, 5.0 in t-BuOH, and 3.4 in EtOH as compared[25] to 6.9 and 6.0 for $^{\mathrm{H_2}}k/^{\mathrm{D_2}}k$, in t-BuOH and EtOH, respectively, for the corresponding reactions of 2-phenylethyl bromide. These 1-phenylethyl bromide results were interpreted[24] in terms of a change in the nature of the transition state from E1cB-like E2 (β-proton more than half transferred to base) to E1-like E2 (β-proton less than half transferred to base) as the base/solvent system changed from t-BuOK/t-BuOH–Me_2SO to t-BuOK/t-BuOH to EtONa/EtOH.

There are no reports in the literature of an elimination reaction study of the 1-phenylethyl chloride system in solution. Bridge, Davies, Maccoll, Ross, Stephenson, and Banjoko[26] have examined the gas-phase eliminations at 308 °C of a series of substituted 1-phenylethyl chlorides. A Hammett plot, using σ^+, gave a negative ρ value (-1.36, $r = 0.998$), and an E1 transition state was suggested for this pyrolytic elimination.

Because our eventual aim was to include isotope effect measurements for the compounds successively labeled[6] at $^{\alpha}$C, $^{\beta}$C, and the chlorine leaving group, we chose to work with a series of substituted 1-phenylethyl chlorides rather than bromides. Kinetic and $^{\beta}$C carbon-14 isotope effect results on this system are reported in this paper: For kinetics in t-BuOK/t-BuOH–10% v/v Me_2SO and alkoxide/bis(2-hydroxyethyl) ether–10% v/v Me_2SO, Z = p-CH_3O, p-CH_3, H, m-CH_3O, p-Cl, p-CF_3, m-NO_2, p-NO_2. For $^{\beta}$C carbon-14 isotope effect measurements in alkoxide/bis(2-hydroxyethyl) ether–10% v/v Me_2SO, Z = p-CH_3, H, and p-Cl.

Procedure and Results

The 1-phenylethyl chlorides were prepared from the corresponding alcohols, which had been prepared by reduction of the substituted acetophenones. The ketones were commercially available or were prepared by Friedel–Crafts acylations. The carbon-14 β-labeled 1-phenylethyl chlorides were prepared by the same procedures using acetyl-2-^{14}C chlorides as the acylating agent.

The kinetic study in the t-BuOK/t-BuOH–10% Me_2SO system was carried out at 60 ± 0.1 °C using pseudo-first-order conditions, with concentrations of substrate 0.026–0.029 M and of base 0.26–0.36 M. In the alkoxide/bis(2-hydroxyethyl) ether–10% Me_2SO system the temperature was 45 ± 0.05 °C, and the concentrations of substrate were 0.032–0.038 M and of base 0.34–0.44 M. In this solvent system the alkoxide, $HOCH_2CH_2OCH_2CH_2OK$, was prepared in situ by adding the requisite (small) amount of the stronger base, t-BuOK, to the solvent mixture. It was convenient to make the conjugate base of the solvent this way since we had readily available highly purified t-BuOK. The reactions were conducted under an atmosphere of dry nitrogen, and all reagent transfers were carried out in a drybox in an atmosphere of dry nitrogen. Aliquots were removed periodically by syringe through the septum seal of the reaction flask and quenched over an ice–ether mixture (ice–dichloromethane for the m-nitro compound). The ethereal extract was dried, concentrated, and analyzed by gas chromatography. Appropriate blank and control experiments showed that solvolysis [$ArCH(OH)CH_3$ formation] during workup amounted to less than 1% in all cases and that other potential problems were minimal (see Experimental Section).

For most cases the gas chromatographic analyses showed only residual starting material and the corresponding styrene. In all cases, despite careful gas chromatographic searches, no traces of the solvolytic product ethers [$ArCH(OR)CH_3$] could be found. However in three cases (Z = p-CH_3 and H in t-BuOH–Me_2SO and Z = p-Cl in bis(2-hydroxyethyl) ether–Me_2SO) small amounts (up to 7% and usually much less) of alcohol [$ArCH(OH)CH_3$] were found. For Z = p-CH_3 in the bis(2-hydroxyethyl) ether–Me_2SO system the amounts of alcohol formed were large, ranging up to 50%. Blank and control experiments showed that these large amounts of alcohol could not come from either p-methylstyrene or 1-(4-methylphenyl)ethyl chloride during workup or analysis

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(17) For instance, one of the most studied E1 or (E1-like E2) reactions involves the benzyldimethylcarbinyl system. Large amounts of substitution products are usually present, making heavy atom isotope effect studies difficult at best. For leading references see: Bunnett, J. F.; Sridharan, S.; Cavin, W. P. *J. Org. Chem.* **1979**, *44*, 1463–1471. Bunnett, J. F.; Sridharan, S. *J. Org. Chem.* **1979**, *44*, 1458–1463.

(18) The 1-aryl-1-halopropane system may show clean E1 characteristics under some circumstances (Ford, W. T.; Pietsek, D. J. J. *J. Am. Chem. Soc.* **1975**, *97*, 2194–2198).

(19) For a leading reference to this work, see: Shiner, V. J., Jr.; Hartshorn, S. R.; Vogel, P. C. *J. Org. Chem.* **1973**, *38*, 3604–3610.

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(21) Hughes, E. D.; Ingold, C. K.; Masterman, S.; McNulty, B. J. *J. Chem. Soc.* **1940**, 899–912.

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Table I. Kinetics of the Elimination Reactions of Substituted 1-Phenylethyl Chlorides, $ZC_6H_4CHClCH_3$, Promoted by Potassium *tert*-Butoxide[a] and Potassium Alkoxide[c]

Z	RX concn, M	base concn, M	$10^4 k_2$, $M^{-1} s^{-1}$ ± SD
p-CH_3O	0.019	0.183	high[a,b]
p-CH_3	0.028	0.300	2.81 ± 0.123[a]
H	0.029	0.310	0.219 ± 0.014[a]
p-Cl	0.026	0.262	0.115 ± 0.010[a]
p-CF_3	0.026	0.360	3.11 ± 0.130[a]
p-NO_2	0.013	0.132	high[a,b]
p-CH_3	0.037	0.437	1.83 ± 0.242[c]
H	0.037	0.370	0.239 ± 0.004[c]
m-CH_3O	0.031	0.336	0.175 ± 0.014[c]
p-Cl	0.038	0.383	0.173 ± 0.006[c]
p-CF_3	0.037	0.341	0.083 ± 0.003[c]
m-NO_2	0.032	0.336	0.881 ± 0.220[c]
p-NO_2	0.031	0.300	high[b,c]

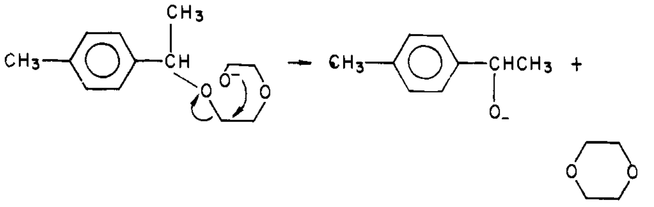
[a] Solvent, *t*-BuOH–10% v/v Me_2SO; at 60 ± 0.1 °C. [b] Reaction too fast to measure accurately. [c] Solvent, bis(2-hydroxyethyl) ether–10% v/v Me_2SO; at 45 ± 0.05 °C.

Table II. Carbon-14 β-Carbon Kinetic Isotope Effects in the Elimination Reactions of Substituted 1-Phenylethyl Chlorides, $ZC_6H_4CHCl^{14}CH_3$, Promoted by Potassium Alkoxide[a]

Z = p-CH_3		Z = H		Z = p-Cl	
f	$k/^{\beta}k$	*f*	$k/^{\beta}k$	*f*	$k/^{\beta}k$
0.167	1.036[b]	0.271	1.058	0.259	1.065
0.333	1.032	0.447	1.060	0.352	1.075
0.438	1.037	0.566	1.051[b]	0.490	1.069[b]
0.577	1.043	0.752	1.062	0.802	1.063[b]
0.695	1.041				
av	1.038		1.058		1.068
SD	±0.004		±0.005		±0.005

[a] Solvent, bis(2-hydroxyethyl) ether–10% v/v Me_2SO; at 45 ± 0.05 °C. [b] Average of values calculated by using all four equations,[29] see text.

or from *p*-methylstyrene during the reaction period. Repeated extraordinary attempts were made to ensure that the reagents and solvents were scrupulously dry. We think it is highly unlikely that the amount of water necessary to account for these results could have been present. We can only speculate that the nature of the solvent is somehow responsible for the formation of the alcohol, perhaps through elimination of 1,4-dioxane from the first formed substitution product:



A careful search for 1,4-dioxane was not made.

Attempts were made to determine the kinetics of the reactions of 1-(4-methoxyphenyl)ethyl chloride in the *t*-BuOH–Me_2SO system and of 1-(4-nitrophenyl)ethyl chloride in both solvent systems, but in all three attempts the rate of disappearance of the chloride was too fast to measure by using our procedures. The major product for the *p*-CH_3O compound was *p*-methoxystyrene. Many products were formed from the *p*-nitro compound, with *p*-nitrostyrene being the highest yield one (but only up to 19%). This compound may react by a radical anion[27] or carbene[28] mechanism, but the reaction was not investigated further.

In all cases first-order plots of time vs. ln (A_0/A), where A_0 and A are the initial and residual concentrations of the substrate chloride, were linear with acceptable point scatter. Pseudo-first-order rate constants were calculated from the plots by the least-squares method, and second-order rate constants were obtained by dividing by the (at least 10-fold excess) base concentrations. These second-order rate constants and the concentration data pertinent to them are given in Table I. Duplicate (preliminary) runs gave rate constant values within a few percent of those reported.

Our original plan had been to measure $^{\beta}C$ carbon-14 isotope effects for several of the substituted 1-phenylethyl chlorides in the *t*-BuOK/*t*-BuOH–Me_2SO system, but despite attempts by many procedures it turned out to be impossible for us to separate the products and recovered reactants from residual *tert*-butyl alcohol in the state of high purity required for the isotope effect measurements. This was not a serious-problem in the alkoxide/bis(2-hydroxyethyl) ether–10% v/v Me_2SO system and, accordingly, the isotope effect measurements and a kinetic study were carried out in this medium.

The isotope effect measurements were carried out in the same manner as the kinetics experiments, except that the required amount of starting material was purified by preparative gas chromatography in a special all-glass system (see Experimental Section) just prior to each run. This was necessary in order to obtain reliable values for the initial activity, R_0, as the organic halides tended to decompose slowly on standing, even at 5 °C. The isotope effect measurements for each compound were carried out for at least four different fractions of reaction, *f*, ranging from 17 to 80% so as to reveal any trends in the measured isotope effect values. Such trends would be expected to show up if the starting material contained either chemical or radioactive impurities. No such trends were noted (see Table II), giving us confidence in the chemical and radiochemical purities of our starting materials.

The workup of the isotope effect reaction mixtures followed the kinetics procedures, except that the final purifications were carried out by preparative gas chromatography in the special all-glass apparatus mentioned above. As was the case in the kinetics runs, small amounts of the alcohols *p*-$ClC_6H_4CH(OH)CH_3$ (up to 5% at 80% reaction) and $C_6H_5CH(OH)CH_3$ (up to 11% at high fractions of reaction) were formed. For the *p*-CH_3 case, the amounts of alcohol formed were large, from 10% at 17% reaction ranging upward to 41% at 70% reaction.

The radioactivity measurements were carried out on a Beckman DPM-100 liquid scintillation counter using the external standard ratio method and a toluene-base cocktail-fluor solution. All counts were carried out to a statistical error of 2σ % (confidence level of 95%). Whenever possible the activities of both the product styrene, R_p, and the recovered 1-phenylethyl chloride, R_r, were determined so as to calculate the isotope effect from both the product and recovered reactant sides. This gives an extremely sensitive check on radiochemical purities and internal consistency of the data. Actually, the isotope effects (the ratio of rate constants, $k/^{\beta}k$) can be calculated in four ways for each point, by using any three of the four available measured quantities, R_0, R_p, R_r, and *f*, and the equations of Tong and Yankwich.[29] Unfortunately, the styrene products partially polymerized in most cases. There appears to be (as expected) a normal isotope effect in these polymerization reactions since the residual monomeric styrenes had activities higher than R_0. This made it impossible to use all four of the $k/^{\beta}k$ equations in most cases, and the results reported in Table II come mostly from the equation[29] relating $k/^{\beta}k$ to R_0, R_r, and *f*. For the four cases (one each for the Z = *p*-CH_3 and H substrates, and two for the Z = *p*-Cl substrate) where there was no detectable polymerization there was good agreement among the $k/^{\beta}k$ values calculated in the four different ways (see Experimental Section).

Discussion

Kinetics. One of the most important ways of gaining useful information about the intimate details of mechanisms of chemical

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(27) For a leading reference see: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734–745.

(28) For a leading reference see: Tewfik, R.; Foruad, M. F.; Farrel, P. G. *J. Chem. Soc., Perkin Trans. 2* **1974**, 31–35.

(29) Tong, J. Y.; Yankwich, P. E. *J. Phys. Chem.* **1957**, *61*, 540–543.

Table III. Relative Rate Data for the Elimination Reactions of Substituted 1-Phenylethyl Bromides[24] and Chlorides, $ZC_6H_4CHXCH_3$,[b] and of the Chlorides[d]

	relative rates		
Z	X = Br[a,b]	X = Cl[b,c]	X = Cl[d]
p-CH_3O		high[e]	
p-CH_3	1.07	12.83	7.66
H	1.00	1.00	1.00
m-CH_3O			0.73
p-Cl	1.85	0.53	0.72
p-Br	1.99		
p-CF_3		14.20	0.35
m-NO_2	4.87		3.69
p-NO_2		high[e]	high[e]

[a] Reference 24; $T = 50$ °C; for Z = H, $k_2 = 1.30 \times 10^{-2}$ M^{-1} s^{-1}. [b] In *t*-BuOK/*t*-BuOH–10% v/v Me_2SO. [c] $T = 60$ °C. [d] In potassium alkoxide/bis(2-hydroxyethyl) ether–10% v/v Me_2SO; $T = 45$ °C. [e] Rate too fast to measure by using present procedures.

reactions is to see what effect an electron-donating group (EDG) or electron-withdrawing group (EWG) will have on the rate of the reaction. In the elimination reactions of substituted 1-phenylethyl chlorides studied here, the rates are strongly accelerated by both EDG and EWG (see Table I). Hammett σp plots of these data have obvious, pronounced minima; relative rate data are given in Table III where they are compared with the data of Yoshida, Yano, and Oae[24] for the corresponding substituted 1-phenylethyl bromides in the same reaction medium as one of those used in this work.

Curved Hammett plots, especially those with minima, are generally taken[30,31] to be indicative of mechanisms changing with substituents. It is easy to see that an EDG would stabilize the developing positive charge on the α-carbon in an E1 or E1-like E2 mechanism and thus shift the mechanism in that direction. It is less easy to see why an (insulated by the CHCl group) EWG should cause such a large increase in rate as is osberved, but it is clear that such a group would destabilize a developing positive charge and thus shift the mechanism away from E1. In fact an EWG should stabilize, by induction, a developing negative charge on the β-carbon in an ElcB or ElcB-like E2 mechanism and thus shift the mechanism in that direction. Both EDG and EWG would be expected to stabilize the developing double bond, causing faster reactions and, in accordance with the Hammond postulate,[32] shifting the mechanism so that the transition state is more reactant-like. For these fairly central E2 reaction coordinates the mechanistic shifts toward or away from the E1 or ElcB mechanisms mentioned above correspond to the "perpendicular effects" in Thornton's analyses,[33] while those stabilizing reactants or products correspond to Thornton's "parallel effects" (or Hammond postulate effects). The More O'Ferrall "potential surface modification" approach[16] amounts to the same thing and is simpler to visualize for many people. In this approach[16] (as in Thornton's) a reference potential surface is established, and changes in system factors that will stabilize or destabilize the reactants or products or potential reaction intermediate carbanions or carbenium ions are considered to pull down (for stabilizing factors) or push up (for destabilizing factors) the corresponding corners of the potential surface. These perturbations in the potential surfaces are transmitted to the transition state and shift it toward (stabilizing) or away from (destabilizing) the intermediate ions (perpendicular effects) or away from (stabilizing) or toward (destabilizing) the products or reactants (parallel effects). These perturbations are easily visualized on our[5] plane projections of such potential surfaces, e.g., Figures 1 and 2.

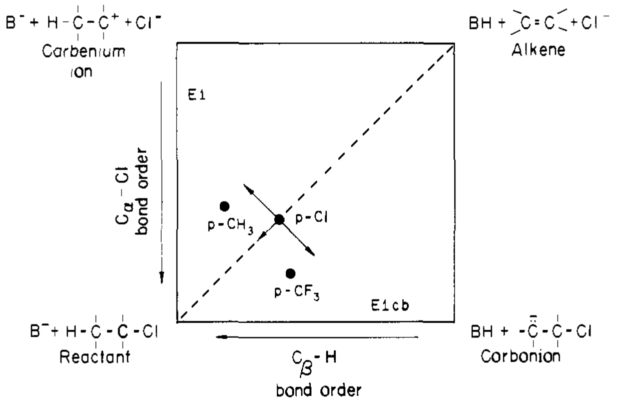

Figure 1. E2 Mechanistic spectrum[5] and transition-state trends diagram for different substituents in the elimination reactions of $ZC_6H_4CHClCH_3$ in *t*-BuOK/*t*-BuOH–10% Me_2SO.

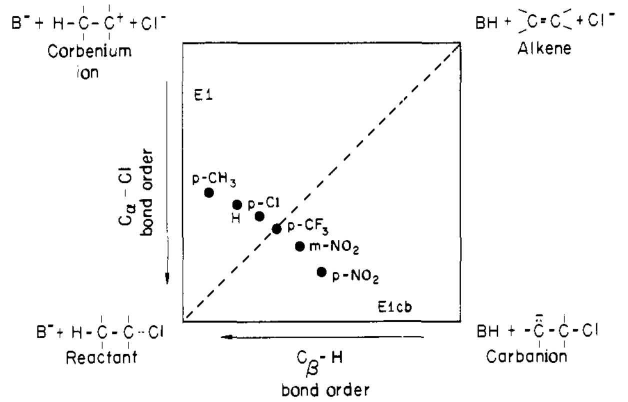

Figure 2. E2 Mechanistic spectrum[5] and transition-state trends diagram for different substituents in the elimination reactions of $ZC_6H_4CHClCH_3$ in ROK/bis(2-hydroxyethyl) ether–10% Me_2SO.

If, as is probably true for the elimination reaction of 1-(4-chlorophenyl)ethyl chloride in the *t*-BuOK/*t*-BuOH–Me_2SO system being studied here, the mechanism is near central E2 with a somewhat reactant-like transition state, substitution of a 4-methylphenyl group for the 4-chlorophenyl group would stabilize the potential carbenium ion, lowering its energy and "pulling down" the (blocking) potential energy maximum between the transition state and the carbenium ion and shifting the transition state sideways (perpendicular to the reaction coordinate) toward the carbenium ion. Such as substitution should also stabilize the product alkene somewhat, and since that perturbation is felt *directly along* (parallel effect) the reaction coordinate, the transition-state energy will be lowered (faster reaction) and pushed back toward the reactants. These changes are illustrated in Figure 1, the net result being a change to a more reactant-like more E1-like E2 mechanism. On the EWG side, e.g., Z = *p*-CF_3, the transition state would be shifted toward the reactants (faster reaction) and carbanion, as shown in Figure 1.

When the elimination reactions are shifted from the more basic less highly ionizing (dielectric constant[34] = 19.1) *t*-BuOK/*t*-BuOH–Me_2SO medium to the less basic more highly ionizing (dielectric constant[34] = 33.6) alkoxide/bis(2-hydroxyethyl) ether–Me_2SO medium, the rates (except for the *p*-CF_3 compound) become somewhat faster (when extrapolated to the same temperature) and slightly less sensitive to the nature of the substituent, and the Hammett plot minimum shifts toward a more EWG (see Tables I and III). A weaker base would destabilize the carbanion, shifting the transition state in the E1 direction. A better ionizing medium would stabilize the resulting more ionic E1-like E2 transition state, again shifting the transition state in the E1 direction. These shifts nicely account for the shift in the Hammett

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(31) Hill, J. W.; Fry, A. *J. Am. Chem. Soc.* **1962**, *84*, 2763–2769.

(32) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.

(33) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915–2927. For specific applications to elimination reactions see: Winey, D. A.; Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102–3108.

(34) Scheflan, L.; Morris, J. B. "The Handbook of Solvents"; Van Nostrand: New York, 1953.

plot minimum toward the EWG side as shown in Figure 2 (compare to Figure 1). (It would take a stronger EWG to shift from the E1 to the E1cB side of the spectrum in this weaker base/solvent system.) If this analysis is correct, the slowness of the reaction of the *p*-CF_3 compound becomes logical, since its transition state is not so E1cB-like in the less basic medium.

When our substituted 1-phenylethyl chloride results are compared to the results for the corresponding substituted 1-phenylethyl bromides[24] (see Table III), the most obvious difference is that the chlorides react more slowly by 2 or 3 powers of 10. The poorer leaving group (chlorine) stabilizes the reactant, causing an already reactant-like transition state to move in the product-like direction (but to a higher energy because of the greater difficulty of breaking the stronger carbon–chlorine bond). For the bromides, the position of the Hammett plot minimum (if there is one—the rate acceleration for the *p*-CH_3 compound is very small) appears to be shifted in the EDG direction. This appears to be in conflict with Thornton's prediction[33] that a better leaving group will shift the transition state in the E1 direction (the bromide transition states appear to be less E1-like than those for the chlorides).

Isotope Effects. There are large $^{\beta}$C carbon-14 kinetic isotope effects for all three compounds investigated in this elimination reaction of HCl from $ZC_6H_4CHCl^{\beta}CH_3$ in alkoxide/bis(2-hydroxyethyl) ether–10% v/v Me_2SO at 45 °C: Z, $k/^{\beta}k$; *p*-CH_3, 1.038; H, 1.058; *p*-Cl, 1.068. The most obvious conclusion from these results is that none of these reactions proceeds by an irreversible E1 mechanism, for which no $^{\beta}$C primary isotope effect would be expected. The trend in these results, low for EDG to high for EWG, is what would be expected from increased $^{\beta}$C–H bond rupture as the E2 transition state becomes less E1-like, the trend proposed from the kinetics discussion above (see Figure 2). The kinetics discussion also suggested that the double-bond character (product-like nature) of the transition states should increase somewhat in going from the *p*-CH_3 to H to *p*-Cl compounds in this base–solvent system. This factor (more bond formation at the β-carbon) should lead to decreased $^{\beta}$C isotope effects; since the isotope effects increase, it can be concluded that changes in the reactant-like product-like nature of the transition state are not the dominant factor (as intimated by the lengths of the arrows in Figure 1) in establishing isotope effect trends in these systems. It should be noted that the amount of double-bond formation is limited by the lesser amount of $^{\alpha}$C–Cl and $^{\beta}$C–H bond ruptures, and it may be that control of this factor shifts from C_{β}–H for EDG to $^{\alpha}$C–X for EWG.

It would be instructive to see if the downward trend in $^{\alpha}$C isotope effects as substitutents become more electron withdrawing predicted from Figure 2 is followed.[35]

It would also be useful to have β-deuterium isotope effect data for these reactions. The prediction from Figure 2 is for increasing $^{\beta}$C–H bond rupture as the substituents become more electron withdrawing. This would lead to increasing β-deuterium isotope effects for stronger EWG, assuming a less than half transferred to base β-hydrogen. This seems likely from the reactant-like nature of all these transition states, but the rather large values of the $^{\beta}$C isotope effects speak against this.[36] The only pertinent data available are those from the work of Yoshida, Yano, and Oae[24] who found β-D_3 isotope effects for unsubstituted 1-phenylethyl bromide of 3.5, 5.0, and 3.4 in the base/solvent systems *t*-BuOK/*t*-BuOH–10% Me_2SO, *t*-BuOK/*t*-BuOH, and EtONa/EtOH. (The fact that there are large β-deuterium isotope effects rules out the reversible E1cB mechanism for these reactions, since such a mechanism would "wash out" the β-deuteriums by exchange.) Yoshida, Yano, and Oae[24] interpreted these results in terms of the proton being more than half transferred[36] to base in the strongest base system, *t*-BuOK/*t*-BuOH–Me_2SO, nearly half transferred in the intermediate base strength system, *t*-BuOK/*t*-BuOH, and less than half transferred in the weakest base system, EtONa/EtOH.[37] This is the trend predicted by Thornton's rules[33] for E1-like E2 reactions, but is opposite to the trend predicted for E1cB-like E2 reactions. Since we are proposing a changeover from E1-like to E1cB-like mechanisms as the substituent becomes more electron withdrawing, it is conceivable that the proton could be less than half transferred in both the stronger base and weaker base systems (i.e., $PhCHBrCH_3$ might have an E1-like E2 mechanism in EtONa/EtOH and an E1cB-like E2 mechanism in *t*-BuOK/*t*-BuOH–Me_2SO, with the proton less than half transferred in both cases). A study of β-deuterium isotope effects as a function of substituent in the different base/solvent systems should resolve these questions.

None of the results of the present study speak directly to the question of whether the mechanism might be reversible E1. Solvolytic reactions (nearly exclusive substitution) of the 1-phenylethyl system[19] seem to be best interpreted in terms of to some extent reversible formation of ions and/or ion pairs of various degrees of intimacy. If an ion pair is formed reversibly in the 1-phenylethyl system, elimination of the β-hydrogen becomes the rate-determining step, and, as far as $^{\beta}$C and primary β-deuterium isotope effects are concerned, the predicted results are qualitatively similar to those for an E2 mechanism. On the other hand, for a rapidly reversible E1 mechanism the $^{\alpha}$C and leaving group chlorine isotope effects should be those (smaller) characteristic of the equilibrium:

$$\mathrm{Ph^{\alpha}CClH^{\beta}CD_3 \underset{fast}{\overset{-Cl^-}{\rightleftharpoons}} Ph^{\alpha}C^{+}H^{\beta}CD_3 \xrightarrow[RD]{B^-,\ -BD} Ph^{\alpha}CH{=}^{\beta}CD_2}$$

For cases of an intermediate nature, where the rate of internal return and of loss of β-hydrogen are comparable, the expected isotope effects fall between the extremes. The usual leaving group exchange and racemization of "unreacted" substrate tests have not been applied to these systems under these conditions. However the fact that, generally, only minor amounts of substitution products (carbenium ion trapping products) are formed in these reactions speaks against rapid reversibility. For the *p*-CH_3 compound, where the substitution product $CH_3C_6H_4CH(OH)CH_3$ makes up a major fraction of the isolated product, the reversible E1 mechanism may be a viable alternative. Even in that case, however, the competition could as well be E1-like E2 vs. S_N2.

Theoretical Calculations

Procedures for calculations of the isotope effects to be expected in elimination reactions under various mechanistic assumptions have been well developed by our group[13,14,38] and by that of Saunders.[12,39] These procedures follow the pioneering work of Bigeleisen and Mayer[40] on methods of isotope effect calculations and use the notation and the cutoff procedures of Wolfsberg and Stern.[41] No previous calculations have extended into the E1-like region of the E2 mechanistic spectrum, and we present here some of the results[42] of our investigation of the variation of isotope effects in this region, with special emphasis on variations with reaction coordinate motions.

The reactant and transition-state models chosen were those for the conventional anti-elimination mechanism, using standard geometries and cutting through the aromatic ring to include only

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(35) It should be remembered that the magnitudes of $^{\alpha}$C isotope effects are also dependent on the amount of double-bond character, the degree of hyperconjugative stabilization, and the degree of solvation (bond formation to $^{\alpha}$C) of the developing carbenium ion.

(36) If the β-hydrogen is more than half transferred, a downward trend in the β-deuterium isotope effect for stronger EWG is predicted, or, if the degree of transfer changes from less than half to more than half for stronger EWG, a Westheimer maximum[37] in the β-deuterium isotope effect would be predicted.

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(40) Bigeleisen, J. *J. Chem. Phys.* **1949**, 17, 675–678. Bigeleisen, J.; Mayer, M. G. *Ibid.* **1947**, *15*, 261–267.

(41) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 325–338. Stern, M. J.; Wolfsberg, M. *J. Chem. Phys.* **1966**, *45*, 4105–4124.

(42) For full details of the experimetnal procedures and calculations see: Hasan, T. Ph.D. Dissertation, University of Arkansas, 1980.

the carbon joined to the aliphatic α-carbon and the two ortho carbons.[43] In these E1-like E2 calculations, C_α–Cl bond rupture was allowed to run ahead of C_β–H bond rupture, resulting in a positive charge buildup at C_α; allowance was made for delocalization of 30% of this charge into the aromatic ring (increasing the C_α–C_{Ar} bond order). Changes in the fraction of charge delocalized due to ring substituent effects were not investigated in these first calculations; likewise in these calculations no account was taken of the solvation of the developing charges on C_α and chlorine (which would be expected to lower the $^\alpha$C and chlorine isotope effects).

The geometry of the transition state was changed progressively from that of the reactant to that of the product alkene in proportion to the bond order changes of the reacting bonds.[43] Constant total bonding was maintained at the β-carbon and the departing β-hydrogen; that is, the amounts by which the base–H_β and the C_α–C_β bond orders (n_{B-H} and $n_{C_\alpha-C_\beta}$) were increased were both the same as the amount by which the C_β–H bond order ($n_{C_\beta-H}$) was decreased.

The reaction coordinate was chosen to correspond to an asymmetric stretching motion of the O–H–C_β–C_α–Cl system, leading to fragmentation of the transition state to products. The reaction coordinate was generated by the use of three off-diagonal (interaction) force constants, each of the form

$$f_{ik} = a_{ik}(F_{ij}F_{jk})^{1/2}$$

representing asymmetric (for $a_{ik} > 0$) stretching motion of adjacent bonds i-j and j-k with stretching force constants F_{ij} and F_{jk}, respectively. The proportionality constants a_{ik} are usually denoted[39] by A (the C_β–H, H–O interaction), B (the C_β–H, C_α–C_β interaction), and C (the C_α–C_β, C_α–Cl interaction). For A, B, and C all positive, the reaction coordinate motion corresponds roughly to the overall asymmetric stretching motion described above.

The condition that the reaction coordinate motion correspond to an imaginary frequency is that the determinant of the force constant matrix for the transition state be negative, $|\mathbf{F}^\ddagger| < 0$, which, when expanded, leads to the following relationship between the proportionality constants:

$$1 - A^2 - B^2 - C^2 + A^2C^2 = D < 0$$

D represents the barrier curvature parameter,[39] and was maintained constant at -0.200[12,39] in this work. Calculations were carried out for transition states located throughout the entire E1-like E2 region (upper left half of Figures 1 and 2). Some of the results are presented in Table IV.[42]

Three different reaction coordinate motions were investigated: (1) a conventional El-like motion, dominated by C_α–Cl bond rupture, $A = B = 0.347976$, $C = 1.043927$; (2) a conventional E1-like E2 motion where C_α–Cl and C_β–H bond ruptures are of comparable importance, $A = B = C = 0.689424$; and (3) an E1-like E2 motion dominated by C_β–H bond rupture, $A = 1.043927$, $B = C = 0.347976$.

The low values calculated for $(^{12}k/^{14}k)_\beta$ for reaction coordinate motion 1 are those expected for a strongly E1-like E2 mechanism–no bonding changes at C_β, so no isotope effect. The small values of $(^{12}k/^{14}k)_\beta$ for reaction coordinate motion 3 result from the constant total bonding imposed on C_β and from the slight motion of heavy atom C_β compared to light atom H_β. Note that $(^{H_3}k/^{D_3}k)_\beta$ goes through a "Westheimer maximum",[37] as expected, in this case and also in case 2. Only by strongly coupling all bonding changes, reaction coordinate motion 2, does the calculated value of $(^{12}k/^{14}k)_\beta$ come into the range of the isotope effects measured in this research, and then only for reactant-like transition states. These conclusions agree with the kinetic and qualitative isotope effect arguments presented in the discussion above.

In all three cases the chlorine isotope effect increases with increased C_α–Cl bond rupture, as expected. The magnitude of this increase is expected to be less when more sophisticated calculations take solvation of the developing chloride ion into consideration.[7,14] The high values of $(^{12}k/^{14}k)_\alpha$ are probably unrealistic for the same reason. For a given value of $n_{C_\alpha-C_\beta}$ the $(^{H}k/^{D}k)_\alpha$ values always increase with increasing C_α–Cl bond rupture due to the decrease in the H–C_α–Cl bending force constant.

Table IV. Calculated Kinetic Isotope Effects for E1-Like E2 Base-Promoted Elimination Reactions of Successively Labeled 1-Phenylethyl Chloride Emphasizing Different Reaction Coordinate Motions[42]

$n_{C_\alpha-C_\beta}$	$n_{C_\alpha-Cl}$	$(^{H_3}k/^{D_3}k)_\beta$	$(^{H}k/^{D}k)_\alpha$	$(^{12}k/^{14}k)_\alpha$	$(^{12}k/^{14}k)_\beta$	$^{35}k/^{37}k$
Reaction Coordinate Motion Dominated by C_α–Cl Bond Rupture						
1.1	0.7	1.0160	1.0422	1.0630	1.0120	1.0149
	0.5	1.0146	1.0779	1.0626	1.0099	1.0178
1.3	0.7	0.9064	1.0234	1.0525	0.9985	1.0165
	0.5	0.9062	1.0587	1.0512	0.9867	1.0193
1.0	0.5	0.8310	1.0399	1.0408	0.9918	1.0203
C_α–Cl and C_β–H Bond Ruptures of Comparable Importance						
1.1	0.9	1.5882	1.0154	1.0657	1.0405	1.0040
	0.7	1.5856	1.0420	1.0687	1.0392	1.0059
	0.5	1.5815	1.0794	1.0738	1.0378	1.0080
	0.3	1.5748	1.1372	1.0804	1.0363	1.0103
1.3	0.7	1.8412	1.0250	1.0614	1.0326	1.0066
	0.5	1.8365	1.0619	1.0649	1.0314	1.0087
	0.3	1.8271	1.1190	1.0707	1.0300	1.0112
1.5	0.5	1.6756	1.0417	1.0423	1.0252	1.0104
	0.3	1.6702	1.0973	1.0478	1.0240	1.0130
1.7	0.3	1.3905	1.0738	1.0250	1.0154	1.0152
Reaction Coordinate Motion Dominated by C_β–H Bond Rupture						
1.1	0.7	2.4123	1.0297	1.0249	1.0085	1.0027
	0.5	2.4196	1.0672	1.0331	1.0092	1.0042
	0.3	2.4274	1.1251	1.0440	1.0103	1.0058
1.3	0.7	6.5879	1.0091	1.0226	0.9973	1.0023
	0.5	6.6070	1.0495	1.0298	0.9975	1.0039
	0.3	6.6254	1.1068	1.0395	0.9981	1.0057
1.5	0.5	6.6331	1.0320	1.0160	1.0176	1.0039
	0.3	6.6581	1.0885	1.0256	1.0188	1.0057
1.7	0.3	3.1621	1.0694	1.0103	1.0308	1.0060

Experimental Section

General Remarks. All melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Hydrogen-1 nuclear magnetic resonance spectra were measured on a Varian Model A-60 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Gas chromatographic analyses were performed on a flame ionization detector Varian 2840 instrument; quantitative analyses were based on peak areas determined with a Disc Integrator Model 204. Preparative gas chromatographic separations were achieved with a Varian Aerograph Autoprep Model 700-A used in a nonautomatic mode. A variety of columns, flow rates, and temperatures was used.[42] Molar response ratios were determined for most of the compounds used in the quantitative work and appropriate corrections made; for a few of the unstable compounds estimated values had to be used.

Preparation of Substituted 1-Phenylethyl Chlorides and 1-Phenylethyl-*2*-^{14}*C* Chlorides. General.[42] The three carbon-14-labeled and the eight unlabeled 1-phenylethyl chlorides (see Tables I and II) were prepared from the corresponding 1-phenylethyl alcohols using thionyl chloride, which had been purified[44] by distillation from quinoline and then from linseed oil in a system kept under nitrogen and protected from moisture. Preliminary experiments using the alcohols and hydrogen chloride[45] gave much poorer yields in our hands. The procedure of Weiss and Snyder[46] using triphenylphosphine and a mixture of chloroform and carbon tetrachloride was tried in a few cases and gave yields, purities, and workup convenience similar to those of the thionyl chloride method.

Except for the unlabeled *p*-(trifluoromethyl)phenyl compound (see below) the carbon-14 labeled and the unlabeled 1-phenylethyl alcohols

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[43] Sims, L. B.; Fry, A.; Netherton, L. T.; Wilson, J. C.; Reppond, K. D.; Crook, S. W. *J. Am. Chem. Soc.* **1972**, *95*, 1364–1365. Netherton, L. T. Ph.D. Dissertation, University of Arkansas, 1977.

[44] Riddick, J. A.; Bunger, W. B. in "Techniques of Organic Chemistry"; Weissberger, A., Ed.; Wiley: New York, 1970; Vol. 2.

[45] Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418–426.

[46] Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1971**, *36*, 403–406.

were prepared by lithium aluminum hydride or sodium borohydride (*m*- and *p*-nitro compounds) reduction of the corresponding acetophenones.

The acetophenones were commercially available (*p*-nitro, *m*-nitro, and *m*-methoxy) or were prepared by Friedel–Crafts acylation[47] of the corresponding aryl compounds with acetyl chloride [*p*-methoxy and both unlabeled (cold runs) and carbon-14-labeled *p*-methyl, unsubstituted, and *p*-chloro]. The acetyl-*2*-^{14}C used was prepared by an exchange reaction with commercial sodium acetate-*2*-^{14}C (see below).

No particular attempts were made to maximize yields in the above reactions, but in all cases except for the conversions of 1-(4-methoxyphenyl)ethyl alcohol and 1-(4-nitrophenyl)ethyl alcohol to the corresponding chlorides (the two most reactive compounds—see synthetic details below) the yields were above 70% (mostly above 80%).[42]

The purities of all the acetophenones prepared, as determined by analytical gas chromatography, were >99.5%. The purities of the initially prepared 1-phenylethyl alcohols and 1-phenylethyl chlorides ranged from >99.5% down to 94%; in every case the only impurity of consequence detected was the corresponding substituted styrene. In several cases final purification to a level acceptable for the isotope effect experiments proved to be very difficult, and eventually an all-glass preparative gas chromatography system was utilized for all the compounds used in the isotope effect experiments (see below). Decomposition of the chlorides to the styrenes is very facile in many cases, even at deep-freeze temperatures.

In all cases the measured physical property and spectral data agree within acceptable limits with values from the literature or with those expected for the compounds prepared.[42] Representative preparative procedures, including all those for new compounds or compounds not well characterized in the literature, are described below.[42]

4-Methoxyacetophenone. Methoxybenzene, 40 mL, and AlCl$_3$, 19 g (0.14 mol), were placed in a three-necked 250-mL flask equipped with a Friedrich condenser and a pressure-equalizing dropping funnel. Dry nitrogen gas was bubbled into the system by means of an inlet tube placed at the head of the condenser. Acetyl chloride, 10.53 g (0.13 mol), in 15 mL of methoxybenzene was added dropwise with constant stirring at room temperature. The reaction mixture was then allowed to reflux for 2 h and was cooled in an ice bath, and the aluminum salts were hydrolyzed with 20% hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether twice. The combined ethereal extract was dried (MgSO$_4$), concentrated, and distilled, giving 15.5 g (80%) of the 4-methoxyacetophenone: bp 115 (5 mm) [lit.[48] bp 82–84 °C (1 mm)]; ^{1}H NMR (CCl$_4$) δ 7.68 (d, 2, $J = 9$ Hz), 6.69 (d, 2, $J = 9$ Hz), 3.76 (s, 3), and 2.4 (s, 3). The ketone thus obtained was >99.5% pure as determined by flame ionization GC.

1-(4-Methoxyphenyl)ethyl Alcohol. 4-Methoxyyacetophenone, 13.5 g (0.09 mol) in 150 mL of anhydrous ether, was added dropwise with stirring to 2 g (0.05 mol) of lithium aluminum hydride in 200 mL of anhydrous ether. The reaction mixture was kept under an atmosphere of dry nitrogen and was allowed to reflux for 16 h. It was then cooled and the excess hydride destroyed by the addition of 2 mL of water, 2 mL of 10% sodium hydroxide solution, and 6 mL of water (*n*, *n*, 3*n* where *n* = number of grams of lithium aluminum hydride used). The organic layer was extracted and the combined ethereal extract was dried (MgSO$_4$), concentrated, and distilled, giving 11.7 g (85%) of 1-(4-methoxyphenyl)ethyl alcohol: bp 96–98 °C (2 mm) [lit.[45] bp 139 °C (15 mm)]; ^{1}H NMR (CCl$_4$) δ 6.95, (d, 2, $J = 9$ Hz), 6.55 (d, 2, $J = 9$ Hz), 4.5 (q, 1, $J = 6$ Hz), 3.7 (s, 1), 3.59 (s, 3), and 1.28 (d, 3, $J = 6$ Hz). The material thus obtained was further purified by distillation on a Nestor/Faust 8 mm × 24 in. Teflon spinning band column at a reflux ratio of 10, bp 112 °C (5 mm). The alcohol was found to give a single peak by GC analysis, representing >99.5% purity.

1-(4-Methoxyphenyl)ethyl Chloride. Thionyl chloride, 1 mL (0.014 mol), was added dropwise, with constant stirring, to 1.63 g (0.011 mol) of 1-(4-methoxyphenyl)ethyl alochol while the reaction mixture was kept at a temperature of 5 °C. After 90 min the excess thionyl chloride was removed by rotary evaporation, and the residue was vacuum distilled to give 0.55 g (31%) of 1-(4-methoxyphenyl)ethyl chloride: bp 70–72 °C (1 mm); ^{1}H NMR (CDCl$_3$) δ 7.2 (m, 2, $J = 8.5$ Hz), 6.75 (m, 2, $J = 8.5$ Hz), 4.98 (q, 1, $J = 6.5$ Hz), 3.69 (s, 3), and 1.78 (d, 3, $J = 6.5$ Hz). This was the only case in which the yield of the chloride was low. The obvious reasons for the poor yield in this case was the accumulation of a pink polymeric material in the distillation flask. Other attempts to prepare the chloride from the alcohol gave no better results. The distilled material was 95–98% pure as determined by flame ionization GC. The only major impurity was 4-methoxystyrene.

1-(4-Nitrophenyl)ethyl Alcohol.[45] A solution of 15.05 g (0.09 mol) of recrystallized commercial 4-nitroacetophenone in 200 mL of methyl alcohol was made basic to litmus with sodium hydroxide, and 1.06 g (0.028 mol) of sodium borohydride was added in portions. After standing overnight under a blanket of dry nitrogen the solution was diluted with 400 mL of water and made acidic to litmus with dilute hydrochloric acid, and the methanol was removed by distillation. The organic layer was separated, dried (Na$_2$SO$_4$), and distilled to yield 9 g (60%) of 1-(4-nitrophenyl)ethyl alcohol: bp 115 °C (1 mm) [lit.[49] bp 137–138 °C (2 mm)]; ^{1}H NMR (CDCl$_3$) δ 7.95 (d, 2, $J = 9$ Hz), 7.38 (d, 2, $J = 9$ Hz), 4.9 (q, 1, $J = 7$ Hz), 3.68 (br s, 1), and 1.44 (d, 3, $J = 7$ Hz). Further purification was carried out on a 6 mm × 8 in. platinum spinning band column, bp 120 °C (1 mm) [lit.[45] bp 118–119 °C (0.8 mm)], at a reflux ratio of 12. The alcohol thus obtained was 94% pure as determined by GC. The major impurity present was 4-nitrostyrene.

1-(4-Nitrophenyl)ethyl Chloride. 1-(4-Nitrophenyl)ethyl chloride was prepared from 1-(4-nitrophenyl)ethyl alcohol and thionyl chloride by the procedure described above for the synthesis of 1-(4-methoxyphenyl)ethyl chloride. Vacuum distillation gave the desired chloride in 60% yield: bp 104 °C (1 mm) [lit.[50] bp 136 °C (8 mm)]; ^{1}H NMR (CDCl$_3$) δ 8.09 (d, 2, $J = 9$ Hz), 7.5 (d, 2, $J = 9$ Hz), 5.09 (q, 1, $J = 7$ Hz), and 1.87 (d, 3, $J = 7$ Hz). The material so obtained was 94% pure as determined by GC analysis. The only major impurity present was 4-nitrostyrene.

1-(4-(Trifluoromethyl)phenyl)ethyl Alcohol. 1-Bromo-4-(trifluoromethyl)benzene, 5.02 (0.02 mol) was added dropwise with stirring to a suspension of 0.72 g (0.03 mol) of Mg turnings in absolutely dry ether. The reaction had to be initiated with a few drops of methyl iodide. Once it was started, a cautious rate of addition of the bromide kept the reaction going smoothly. After this reaction had subsided, 1.2 g (0.03 mol) of acetaldehyde was added and the mixture was allowed to reflux for 15 min. It was then hydrolyzed with 20% hydrochloric acid, the organic layer extracted, and the combined ethereal extract dried (Na$_2$SO$_4$), concentrated, and distilled, giving 2.7 g (71%) of 1-(4-(trifluoromethyl)phenyl)ethyl alcohol: bp 63–65 °C (1 mm); ^{1}H NMR (CDCl$_3$) δ 7.35 (m, 4), 4.78 (q, 1, $J = 7$ Hz), 3.19 (br s, 1), and 1.4 (d, 3, $J = 7$ Hz).

1-(4-(Trifluoromethyl)phenyl)ethyl Chloride. The procedure described above for the preparation of 1-(4-methoxyphenyl)ethyl chloride was followed for the conversion of 1-(4-(trifluoromethyl)phenyl)ethyl alcohol by thionyl chloride to the corresponding chloride. Vacuum distillation gave the desired product, (60%): bp 39 °C (1 mm); ^{1}H NMR (CDCl$_3$) δ 7.39 (s, 4), 4.92 (q, 1, $J = 7$ Hz), and 1.75 (d, 3, $J = 7$ Hz). This product gave a single peak on gas chromatographic analysis, representing a >99.5% purity.

1-(3-Nitrophenyl)ethyl Chloride. A solution of 4.25 g (0.025 mol) of 1-(3-nitrophenyl)ethyl alcohol and 8.85 g (0.034 mol) of Ph$_3$P in 25 mL of CCl$_4$ and 15 mL of CHCl$_3$ was allowed to stir at ambient temperature for 90 h in the dark.[46] The chilled (0.5 °C) solution was diluted with 20 mL of pentane and filtered. The solid was washed with 1:1 pentane–CCl$_4$; the solution was refiltered and washed again with the pentane–CCl$_4$ mixture. This process was repeated until no more Ph$_3$PO precipitate formation occurred upon addition of pentane to the filtrate. Carbon tetrachloride, chloroform, and pentane were removed by distillation at atmospheric pressure. Vacuum distillation of the residue gave the desired chloride in 92% yield: bp 100–103 °C (6 mm); ^{1}H NMR (CDCl$_3$) δ 7.6 (m, 4), 5.0 (q, 1, $J = 7$ Hz), and 1.80 (d, 3, $J = 7$ Hz).

Acetyl-*2*-^{14}C Chloride. Acetyl-*2*-^{14}C chloride was prepared by an exchange reaction between 11.05 g (0.14 mol) of unlabeled acetyl chloride and 4.67 mg (5.7×10^{-5} mol) of commercial sodium acetate-*2*-^{14}C, activity 7.4 Ci/mol. The mixture was allowed to reflux gently for 2 h in a dry nitrogen atmosphere. The acetyl-*2*-^{14}C chloride–inactive sodium acetate (~5 mg) reaction mixture was used without purification for the Friedel–Crafts syntheses of the appropriate acetophenones (see above).

Kinetic Procedures.[42] The reagent grade solvents used were stored under nitrogen over calcium hydride (*tert*-butyl alcohol) or molecular sieves, grade 514, type 4A, [dimethyl sulfoxide, bis(2-hydroxyethyl) ether], distilled, and stored over fresh drying agent.[44] The amounts needed for the experiments were then redistilled under nitrogen directly from the drying agents just before use. All solvent and reagent transfers were carried out in a nitrogen flushed drybox. Commercial potassium *tert*-butoxide, >99% pure, was further purified by sublimation at reduced pressure prior to use. Solutions of the base in the two solvent systems were standardized with hydrochloric acid by using bromothymol blue indicator.

The general procedures for the kinetic runs are outlined under Pro-

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Table V. Fractions of Reaction, Molar Activities, and Carbon-14 Kinetic Isotope Effects for the Potassium Alkoxide Promoted Elimination Reaction of 1-(4-Chlorophenyl)ethyl-*2*-^{14}C Chloride[a]

				$k/{}^{\beta}k$ from			
f	R_0[b]	R_r[b]	R_p[b]	R_0, R_r, R_p	f, R_0, R_r	f, R_0, R_p	f, R_r, R_p
0.259	4289 ± 8	4368 ± 2			1.064		
0.352	4292 ± 5	4424 ± 18			1.075		
0.490	4463 ± 7	4688 ± 4	4264 ± 2	1.068	1.072	1.066	1.069
0.802	4190 ± 4	4646 ± 4	4098 ± 3	1.061	1.068	1.056	1.065
				av 1.065	1.070	1.061	1.067
				±SD 0.005	0.005	0.008	0.002

[a] In bis(2-hydroxyethyl) ether–10% v/v dimethyl sulfoxide. [b] Activity in mCi/mol × 10^4 ± SD.

cedures and Results. Separate, accurately measured solutions of the organic chlorides and the base (equal volumes) were prepared in the nitrogen-flushed drybox and poured together as rapidly as possible in the reaction flask. The reaction flask was sealed with a septum and transferred to the constant temperature bath. The zero time for the kinetic runs was taken as the time of mixing. Control experiments[42] showed that, except for the *p*-nitro and *p*-methoxy compounds (which reacted rapidly even at room temperature), the time required for temperature equilibration was small compared to the time of sampling for kinetic data (<1% change in rate constant for the worst case sample).

Aliquots were withdrawn periodically by bubbling dry nitrogen into the reaction vessel so that a slight positive pressure forced the reaction mixture into a syringe inserted through the septum. For each aliquot, the reaction was quenched by pouring the mixture over ice and diethyl ether. The ether solutions were washed with cold water until the washings were base free as indicated by testing with bromothymol blue. The ethereal extract was dried (Na_2SO_4), concentrated, and analyzed by GC, by using previously determined or estimated molar response ratios.[42] Six to twelve aliquots were taken for every reaction, and for each aliquot, at least three injections were made on the GC. The average value for the relative peak areas was then calculated and used in the determination of the fraction of reaction and the rate constant. Typical sample kinetic data,[42] which give a good pseudo-first-order plot,[42] for the reaction of 0.037 M 1-phenylethyl chloride with 0.370 M potassium alkoxide in bis(2-hydroxyethyl) ether/10% v/v dimethyl sulfoxide at 45.0 °C are as follows (time × 10^{-4} s, % reaction): 0.179, 3.4; 0.369, 8.0; 0.719, 9.5; 1.086, 12.2; 1.791, 17.4; 4.936, 37.7; 7.637, 50.4; 9.342, 56.9. Least-squares analysis of these pseudo-first-order data gives a pseudo-first-order rate constant of 8.80 ± 0.015 × 10^{-6} s^{-1}, which, divided by the base concentration, gives the second-order-rate constant 0.239 ± 0.004 × 10^{-4} M^{-1} s^{-1} reported in Table I, where all the kinetics results are summarized.

Control experiments showed that if the reaction mixtures were quenched with water at room temperature, the starting chlorides reverted rather readily to the corresponding alcohols. However, if ice and ice-cold water were used the hydrolysis was reduced to well below a percent as indicated by GC analysis. In other control experiments, mixtures of known composition of the organic chlorides and the corresponding alcohols and styrenes were prepared and subjected to the workup procedures. In all cases the composition of the recovered mixture was identical with that of the starting mixture, as shown by GC analysis. Finally, for the 1-(4-methylphenyl)ethyl chloride case where large amounts of 1-(4-methylphenyl)ethyl alcohol were found in the bis(2-hydroxyethyl) ether–10% dimethyl sulfoxide system, the product 4-methylstyrene was subjected to the base–solvent kinetic conditions for 24 h (compared to the 5.6 h needed for 85% reaction of the corresponding chloride). The usual workup and analysis showed only 10% of 1-(4-methylphenyl)ethyl alcohol (compared to the 50% alcohol found in the 5.6-h experiment with the chloride).

The reactions of 1-(4-methoxyphenyl)ethyl chloride in the *tert*-butyl alcohol–dimethyl sulfoxide solvent system and of 1-(4-nitrophenyl)ethyl chloride in both solvent systems were carried out as described above, but in these three cases the reactions were "complete" (no organic chloride could be detected by GC analysis) within a few minutes of mixing. In the GC traces many peaks were evident, the major one in each case being the substituted styrene. No attempt was made to study the details of these reactions, but it is evident that elimination is a significant path and that the reactions are very fast.

Carbon-14 Isotope Effect Measurement Procedures. The general procedures for the isotope efect experiments are outlined under Procedures and Results. The size of the organic chloride sample taken for each isotope effect point was such that a minimum of 300 mg each of the recovered reactant and the product would be available after preliminary workup for further purification and radioactivity assay. The fractions of reaction were determined as in the kinetic experiments. Because of the requirement for very high purity for precise carbon-14 isotope effect measurements and the propensity of the organic chlorides to decompose on standing, even at 5 °C, the reactant organic chlorides were purified by preparative GC just prior to use, by use of an all-glass system (see below). The same system was used for the final separation and purification of the recovered reactants and product styrenes. In the preliminary workup it was found that reduction of the volume of solvent-recovered reactant–product mixture to less than about 10 mL by rotary evaporation or evaporation under a stream of dry nitrogen resulted in considerable loss of the product styrene. When attempts were made to separate the mixture in the usual way by preparative GC, serious decomposition of the organic chlorides took place, almost certainly on the heated metal parts of the system. Furthermore, even when GC separations appear to be good, there can sometimes be serious problems with cross-contamination at the tracer level of a compound with a long retention time by one with a shorter retention time (and/or from one injection to the next).

We have found that combination of the use of an all-glass system and a flushing technique can solve both of these problems, giving excellent separations with no decomposition and no cross-contamination.

All-Glass Preparative GC System. The reactant 1-phenylethyl chlorides and the recovered reactant-product mixtures were separated and purified by preparative GC on a 10 ft × $^3/_8$ in. glass column packed with 7% OV-7 and 3% DEGS-PS on Chromosorb W-H.P. A Varian Aerograph Model 700-A instrument was used in this work. A glass insert was used to line the injection port; this was of such a length that it projected well inside the glass column, which was sealed on to the injection port of a Teflon ferrule. The detector was bypassed by using 3-mm glass tubing attached at one end to the column by heat-shrinkable Teflon tubing and pulled out to a smaller diameter at the other end so as to act as a collection tip. This collection end of the bypass tubing was brought to the outsiide of the chromatograph through the coolant gas port and bent at a 90° angle in order to make the attachment and removal of the collection vessels convenient. Optimum recovery and purity were obtained when the collection vessels were cooled in ice water (5 °C). Cooling of the collection vessels to temperatures lower than this caused the compounds collected off the preparative GC to absorb moisture from the atmosphere. Since the detector was bypassed, a visual method was used to determine retention times, and the various fractions collected were analyzed and shown to be pure on a flame-ionization-detector GC. When the optimum conditions for the separations were determined,[42] the reactants and workup mixtures were purified.

Throughout the preparative GC operations, it was necessary to heat the outlet tube with a heat gun to rather high temperature (~350 °C) between collection of various fractions and to use a flushing procedure (see below) in order to prevent cross-contamination. The stability of the compounds to these chromatographic conditions was confirmed by showing that the activities of the radioactive compounds were unchanged after successive passages through the columns under the conditions for separation: After the first and second passes the activities (mCi/mol × 10^4) for 1-(4-methylphenyl)ethyl-*2*-^{14}C chloride, 1-phenylethyl-*2*-^{14}C chloride, and styrene-*β*-^{14}C were 6051 ± 28 and 6057 ± 10, 1651 ± 21 and 1650 ± 3, and 2242 ± 9 and 2240 ± 8, respectively. After the second pass and an acetone flush (next paragraph) an inactive sample of the compound was passed through the column, giving material of background activity.

In order to ensure that all traces of each component were flushed out of the column and collection system, 2–2.5 mL of acetone in 300-μL portions was injected on the column between collection of various fractions. Each portion of the acetone flashed through the column nearly instantaneously and condensed to a liquid in the collection tube without altering the retention times of compounds remaining on the column. The acetone probably vaporizes immediately upon injection, is carried rapidly in the vapor phase by the carrier gas through the length of the column, and condenses upon cooling in the outlet tube, which is at room temperature. It probably accomplishes its flushing action by simple repeated rinsing of the outlet collection tube.

In a control experiment, a mixture consisting of carbon-14-labeled styrene (0.3 mCi/mol) and unlabeled organic chloride was injected on the glass column, and the styrene was collected. Immediately following this, 2–2.5 mL of acetone was injected in about 300-μL portions and the effluent acetone for each injection was collected and counted. The second acetone fraction gave about 20 000 cpm, the fourth 500 cpm, and the sixth and the seventh only background activities. At its normal retention time the unlabeled chloride was then collected and shown to have only background activity.

Radioactivity Determinations and Isotope Effect Calculations. As outlined under Procedures and Results, the radioactivity determinations were performed on a Beckman Model DPM-100 liquid Scintillation counter by using a cocktail solution prepared from 5 g of 2,5-diphenyloxazole, 0.2 g of DMPOP (1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene), and 1 L of toluene, by using the external standard ratio method. Activities were arranged so that a sample size of 10–20 mg gave a suitable count rate. Because of the problem wiht polymerization of the styrenes, the product activities, R_p, could not be determined in many cases and the isotope effects could then only be determined from one of the four equations of Tong and Yankwich[29] relating the fraction of reaction, f, to the reactant, R_0, and recovered reactant, R_r; otherwise all four equations[29] were used. Typical sample data[42] are presented in Table V, and the results of all the isotope effect experiments are summarized in Table II. The good agreement of the $k/^{\beta}k$ values calculated by the four different equations is to be noted, as is the good agrement of the values calculated at the different fractions of reaction. These kinds of agreement give us confidence that our starting materials are chemically and radiochemically pure and that our isotope effect kinetic and workup procedures are satisfactory.

Registry No. p-$CH_3OC_6H_4CHClCH_3$, 1538-89-2; p-$CH_3C_6H_4CHClCH_3$, 2362-36-9; $C_6H_5CHClCH_3$, 672-65-1; p-$ClC_6H_4CHClCH_3$, 20001-65-4; p-$CF_3C_6H_4CHClCH_3$, 85289-90-3; p-$NO_2C_6H_4CHClCH_3$, 19935-75-2; m-$CH_3OC_6H_4CHClCH_3$, 58114-05-9; m-$NO_2C_6H_4CHClCH_3$, 34586-27-1; Ph_3P, 603-35-0; ^{14}C, 14762-75-5; methoxybenzene, 100-66-3; acetyl chloride, 75-36-5; 4-methoxyacetophenone, 100-06-1; 1-(4-methoxyphenyl)ethyl alcohol, 3319-15-1; 4-nitroacetophenone, 100-19-6; 1-(4-nitrophenyl)ethyl alcohol, 6531-13-1; 1-bromo-4-(trifluoromethyl)benzene, 402-43-7; acetaldehyde, 75-07-0; 1-(-(trifluoromethyl)phenyl)ethyl alcohol, 1737-26-4; 1-(3-nitrophenyl)ethyl alcohol, 5400-78-2.

Priority of Aromatic Delocalization: Electron Distributions, Chemical Stability, and σ-Framework in Conjugated Polycycles

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Abstract: NMR studies and theoretical calculations were performed on nonalternant pericondensed polycyclic systems such as aceheptylene, acenaphthylene, and their charged derivatives. The results point toward a significant tendency of the systems to sustain aromaticity or, if impossible, to avoid antiaromaticity and to become nonaromatic. These goals are achieved by sustaining diamagnetic modes of electron distributions over the π-framework. A comprehensive discussion of the various possible delocalization modes enables a better understanding of the role of aromaticity as well as a critical treatment of its definitions.

One of the most striking phenomena related to aromaticity is the unusual tendency of aromatic systems to remain so.[2] This tendency is demonstrated by a large variety of chemical and physical patterns. The predisposition to electrophilic substitutions vs. low proclivity toward additions and the existence of significant dipole moments due to uneven electron distribution over different moieties of the molecule (e.g., azulene and unsymmetrical fulvalenes[3]) are two known examples of the mentioned phenomenon. Nonaromatic species reveal a pronounced tendency to acquire aromaticity via the release of a positive or negative group or via oxidation and reduction processes (e.g., cyclopentadiene, cycloheptatriene,[2c] and cyclooctatetraene[4]). The substantial driving force involved with the aromatic character reflects the low-energy content of aromatic species caused by a stabilizing cyclic electron delocalization.

The most elegant demonstration of the tendency of systems to sustain aromatic character is probably revealed in nonalternant, conjugated, pericondensed polycycles. These compounds can accommodate, in principle, more than one mode of delocalization of electrons over the π-framework. The π-electrons may be evenly distributed over the entire carbon skeleton—including the inner atoms (e.g., C_{13} and C_{11} in **1** and **4**, respectively). Yet, other modes may exist and result in the establishment of a variety of plausible paths of conjugation. For example, π-electrons may be delocalized in the system's periphery and cause, therefore, a peripheral, annulenic-type path of conjugation in which the inner carbons do not participate. On the other hand, conjugated paths may be established over a part of the periphery only (e.g., the naphthalene moiety in **4**). At first sight there is no reason to assume or expect a larger contribution of one conjugation path over the others. Yet, the present study points unequivocally toward the dominance of one particular path of electron distribution in the polycyclic system,

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