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THE NATURE OF THE TRANSITION STATE FOR THE E2 REACTION OF 1-ARYLETHYLAMMONIUM IONS WITH SODIUM ETHOXIDE IN ETHANOL[1]

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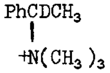
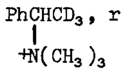
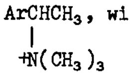
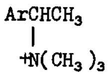
It is generally considered[2,3] that the nature of the transition state for a concerted E2 reaction is variable and that the possibility exists for a spectrum of transition states ranging from an E1cb-like (carbanion) transition state all the way to an E1-like (carbonium ion) transition state. Indeed, two recent theoretical treatments[4,5] have been involved in the prediction of the nature of transition states in E2 processes; i.e. the relative timing of the carbon-hydrogen and carbon-leaving group bond weakening processes. Accordingly, we have determined both the primary and secondary hydrogen-deuterium isotope effects for reaction of several *para*-substituted 1-phenylethyltrimethylammonium salts with ethoxide ion and these values together with the Hammett *rho* value for the reaction are discussed in the light of a variation in the nature of the transition state arising from a structural change in the reactant.

The mechanism of the reaction of 1-arylethyltrimethylammonium ions with sodium ethoxide in ethanol at 70°C was investigated using deuterium tracer techniques[6]. For all the compounds studied no styrene was formed when the substrates were heated in solvent in the absence of base. The reaction of these salts with base as well as several specifically deuterated substrates were second order and the various styrene products were produced in all cases in yields of 100 ± 2 per cent. A deuterium analysis of the styrene products showed that exchange with solvent does not occur at either the α- or β- carbons of the quaternary salts. Furthermore, the position and numbers of deuterium atoms in the styrenes formed from the α-d_1 and β-d_3 ions,  $\underset{+N(CH_3)_3}{PhCDCH_3}$ and  $\underset{+N(CH_3)_3}{PhCHCD_3}$, respectively, is consistent only with an E2 mechanism.

In order to gain an insight into the effect of an α-phenyl substituent on the nature of the transition state for a concerted E2 process both the primary and secondary hydrogen-deuterium isotope effects were determined for the reaction of 1-arylethyltrimethylammonium bromide,  $\mathrm{Ar}\underset{\substack{| \\ {}^{+}\mathrm{N(CH_3)_3}}}{\mathrm{C}}\mathrm{HCH_3}$, with ethoxide. These results, together with the Hammett rho value, are compared and discussed in the light of the isotope effect measurements[7,8] obtained from a study of the reaction of ethyltrimethylammonium ion with base.

p-substituent in  $\mathrm{Ar}\underset{\substack{| \\ {}^{+}\mathrm{N(CH_3)_3}}}{\mathrm{C}}\mathrm{HCH_3}$	relative rates	primary β-deuterium isotope effects at 70°	secondary α-deuterium isotope effects at 70°
MeO	1.0	4.35	1.04
H	1.2	4.45	1.02
CF_3	4.4	4.86	1.07

The magnitude of the primary hydrogen-deuterium isotope effects found for the 1-arylethyl system; i.e., 4.35, 4.45, and 4.86 for the para MeO, H, and CF_3 substituents, respectively, is considerably greater than the primary effect found for reaction of the ethyl substrate at 60°, $k^H/k^D = 2.1$.[9] An interpretation of the magnitude of these effects in terms of the degree of carbon-hydrogen bond rupture at the transition state, however, is made difficult since hydrogen is involved in a three-centre displacement process. As a consequence a small H/D effect can result when the proton is either more than or less than one-half transferred to base with the maximum effect expected for a symmetrical transition state.[11]

The transition state for the reaction of the ethyl compound, however, is assumed to be product-like with the hydrogen more than one-half transferred to base. This is consistent with the low hydrogen-deuterium isotope effect and a large nitrogen isotope effect of 1.86 per cent[7] indicating extensive C-$\overset{+}{\mathrm{N}}$ bond rupture as well at the transition state. This is in accord with experiment[7] and as well the theoretical views of Thornton[5] who predicts that extensive C-H bond rupture should be accompanied by a large degree of carbon-leaving group bond weakening. Furthermore, Thornton[12] has established that for the reaction of the 2-phenylethyltrimethylammonium salt, a reaction which is expected[5] to have less carbon-hydrogen bond weakening at the transition state due to the electron-withdrawing effect of the β-phenyl substituent than for the reaction of the ethyl compound, the proton is more than one-half transferred to base using secondary k^{OD^-}/k^{OH^-} measurements.

The increased magnitude of the H/D effects found in the 1-arylethyl system compared with the value obtained for reaction of the ethyl salt must be interpreted to mean that there is less C-H bond rupture at the transition state for the former substrates. This is as expected[5] if one considers that the α-phenyl substituent facilitates the elimination reaction; i.e., via an inductive effect. Furthermore the trend in the magnitude of the H/D effect with _para_-substituent; i.e., increase in k^H/k^D with an electron-withdrawing substituent, indicates that also for this reaction series the proton is more than one-half transferred to base at the transition state since the relative rates of the three compounds shown in the Table are in accord with the trend in k^H/k^D. The most reactive compound, _p_-CF_3, is expected to have the most reactant-like transition state[5,13] with the least amount of C-H bond rupture and the largest value for the isotope effect only if the proton is more than one-half transferred.

The small secondary α-deuterium isotope effects determined for the reaction of the 1-arylethyl-1-_d_ salts, see Table, are of interest. It is expected that for a transition state which has considerable double-bond or sp^2 character at the α-carbon atom; i.e., a central transition state as represented by Bunnett[2], that a large secondary deuterium effect would result. It is of interest to note that the secondary effect determined by Simon[14] for the reaction of trimethyl-propyl-[α-T]-ammonium salt, which is expected to have a transition state similar to that of the ethyl salt (product-like), also has a low value for the secondary effect, k^H/k^T = 1.10 at 50°.

It is concluded that the reaction of the 1-arylethyl compounds with ethoxide is an E2 process and that in the transition state there is considerable carbon-hydrogen bond rupture. This receives further support from the _rho_ value of + 0.95 obtained from the rate constant data for the _p_-MeO, _p_-Me, H, _p_-Cl, and _p_-CF_3 substrates. It should be noted that for an E1-like transition state the _rho_ value is expected to have a negative value. The conclusion that the transition state has extensive C-H bond rupture (carbanionic) is consistent with the results of Bordwell[15] who found a _rho_ value of + 1.45 for the reaction of the stereoisomeric 1-acetoxy-2-nitro-1-arylcyclohexanes with piperidine and for this system an E1cb mechanism was proposed.

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