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THE E2C MECHANISM. CHARGE DISTRIBUTION AT C_α IN E2C, S_N2 AND SOLVOLYSIS TRANSITION STATES

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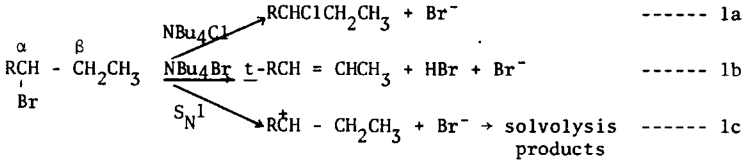
The effects of *para* substituents on the 1-aryl-1-bromopropanes on the rates of their S_N2 reactions (1a) with 0.04M NBu_4Cl in DMF at 25°, of their E2C-like dehydrobrominations (1b) with 0.10M NBu_4Br in acetone containing 0.05M 2,6-lutidine at 75°, and of their S_N1 and E1 solvolyses (1c) in 90% acetone-water at 75°, are shown in the Table. The rates are compared with those of the corresponding reactions of 1-bromopropane and of the S_N2 reactions (1d) of NBu_4Cl with substituted benzyl bromides and methyl bromide in acetone at 0°.



R = H, C_6H_5, $4\text{-}CH_3OC_6H_4$, $4\text{-}CH_3C_6H_4$, $4\text{-}NO_2C_6H_4$

Bunnett[1] has implied that many of those β-eliminations which are induced by weak hydrogen but strong carbon bases like halide ions and mercaptides, proceed through carbonium ion-like (paene-carbonium) E2 transition states, i.e. with positive charge at C_α and very little charge at C_β or H_β. On the other hand we would classify such eliminations as E2C-like reactions which proceed through olefin-like transition states, i.e. with C_α and C_β both possessing much sp^2 character, there being a well developed double bond between them,[2,3] and very loose bonds to base. If E2 transition states were preceded by formation of an intermediate ion pair, as envisaged by Sneen and Robbins[4] for S_N2 and E2 reactions, then a carbonium ion-like E2 transition state might be anticipated.

A carbonium ion-like E2 transition state is readily distinguished from an olefin-like E2 transition state by the effect on rate of changing substituents at C_α from electron withdrawing to electron donating. It is important that changes in the steric effects and the ability of R in (1b) to conjugate with a developing double bond should be minimal.[2] This has been achieved in the E2C-like reactions of the 1-aryl-1-bromopropanes.

The S_N2 reactions (1d) of the substituted benzyl bromides and of methyl bromide with NBu_4Cl in acetone, exhibit the usual[5,6] activation by both electron withdrawing para-nitro and electron donating para-methoxyl groups, relative to para-hydrogen. This results in shallow "U-shaped" Hammett plots of log k versus σ or σ^+.[7] Despite their bulk, α-aryl substituents are almost as effective as α-hydrogen. The behaviour of the benzyl halides has been attributed to movement through a spectrum of transition states; from "tight", with electron withdrawing substituents, to "loose", with electron donating substituents, at C_α.[5] There is some positive charge at C_α in a loose S_N2 transition state, but very little, if any, in a tight S_N2 transition state.[5] The S_N2 reactions (1a) of the 1-aryl-1-bromopropanes and of 1-bromopropane, although slower, show much the same features as the S_N2 reactions (1d) of the benzyl bromides and methyl bromide. Both a para-nitro and a para-methyl substituent accelerate reaction, relative to para-hydrogen, but the overall effect is small.

The rates of the E2C-like dehydrobrominations (1b) of the 1-aryl-1-bromopropanes, like the S_N2 reactions (1a), are extremely insensitive to the nature of the 1-aryl substituent. Unlike the S_N2 reactions (1a), there is a substantial rate enhancement of the E2C reaction from an α-hydrogen to an α-aryl substituent. This is expected for E2C transition states if they are much looser than S_N2 transition states, and is attributed to release of strain in the change from sp^3 to sp^2 hybridisation at C_α.[2] There is also a little conjugation of the aryl group with the developing double bond in the E2C transition state, but this is not as great as might be expected.[2] The weak conjugation of substituents with the developing double bond remains a puzzling feature of E2C reactions.

There is absolutely no correlation between substituent effects in the S_N1 reactions (1c) and the E2C reactions (1b) of the 1-aryl-1-bromopropanes and of 1-bromopropane. Not surprisingly, the S_N1 solvolyses are strongly accelerated by para-tolyl and para-anisyl α-substituents, but are greatly slowed by para-nitrophenyl and hydrogen substituents relative to phenyl. A range of $>10^7$ in rate for reaction (1c) is shown in the Table. The S_N1 reactions have a carbonium ion-like transition state, as confirmed by the excellent correlation with Brown's σ^+ values and a ρ of -5.30.[7] They are thus excellent models for substituent effects if Bunnett's putative "paene-carbonium E2 transition state"[1] is utilised in the E2 dehydrobromination of these same substrates. However, as noted, the E2C-like reactions (1b) show no correlation with the S_N1 reactions (1c) of the same substrates. A Hammett plot versus σ^+ is very poor, but ρ could be no more than -0.6 for the E2C-like reactions. This is very much less than -5.30 observed for S_N1 reactions. We conclude that there is virtually no positive or negative charge at C_α in these E2C-like transition states and suggest that the concept[1] of a spectrum of E2 transition states bounded at one extreme by a paene-carbonium E2 transition state, for elimination induced by weak hydrogen bases, can be discarded.

The substituent effects reported here are in accord with an olefin-like E2C transition state. We have noted previously[2,8] that electron-withdrawing (Br, CO_2Me) and electron donating (CH_3) substituents at C_β have much the same effect on the rate of E2C-like reactions. Thus similar effects at both C_β and C_α agree with the concept of little charge at C_β and C_α in the E2C-like transition state.[2] The large rate-enhancing effects of all substituents studied,[2] relative to a hydrogen substituent, show that the E2C transition state is not reactant-like, there are substantial changes in the hybridisation at C_α and C_β. The similarity in the small response of rates of S_N2 and E2C-like reactions to changes in α-aryl substituents is not because of identical S_N2 and E2C transition states,[3] but it should be noted that S_N2 and E2C-like reactions of the same substrates, respond in virtually the same way to change of solvent,[5] to change of base,[9] to change of leaving group,[10] and now to change of α-aryl substituent. Possibly related things are happening at C_α in the S_N2 and E2C-like transition states. This could be achieved by different interactions of base with C_α in both transition states.

TABLE

Rates of S_N2, E2C and Solvolysis (S_N1 and E1) Reactions (1a - 1d)[a]

log k[b]

R[a]	S_N2(1d)[a] at 0°	S_N2(1a)[a] at 25°	E2C(1b)[a] at 75°	S_N1 + E1(1c)[a] at 75°	S_N1 + E1(1c)'[a,e] at 75°
H	-0.8	-2.0	-5.943	(-8.1)[d]	-5.255
4-$NO_2C_6H_4$	-0.96	-1.75[h]	-3.585	(-7.3)[d]	-4.380
C_6H_5	-1.81	-2.18[g]	-3.364	-4.041	-1.160
4-$CH_3C_6H_4$	-	-1.76[h]	-2.910	-2.475	-
4-$CH_3OC_6H_4$	-1.41	-	<-1.4[c]	+0.1[f]	-

[a] Numbers in parenthesis refer to reactions described in the text. The first column (S_N2(1d)) is for reactions of RCH_2Br, the remaining four columns are for reactions of $RCHBrCH_2CH_3$. [b] k is a second order rate constant in M^{-1} $sec.^{-1}$ for the S_N2 and E2C-like reactions, but is a first order rate constant in $sec.^{-1}$ for solvolysis (1c). [c] Actual value is more negative. 1-p-anisyl-1-bromopropane could not be prepared in a pure state, its dehydrobromination by bromide ion in acetone at 75° can be no faster than this generous maximum value recorded, because the corresponding chloro derivative is solvolysed in dry acetone containing 0.04M NBu_4ClO_4 and 0.05M 2,6-lutidine at 75°, with $k_1 = 6.14 \times 10^{-5}$ $sec.^{-1}$. The rate of acid production in the presence of 0.08M NBu_4Cl + 0.05M lutidine is only a little faster, $k_1 = 6.72 \times 10^{-5}$ $sec.^{-1}$, and in the presence of 0.04M NBuCl is 4.64×10^{-5} $sec.^{-1}$. Salt effects on the solvolysis rate are unknown. We allocate no more than 50% of the acid production to a chloride ion induced E2C reaction and assume that chlorine is replaced not more than 100 times more rapidly than bromine in E2C reactions. We thus estimate this maximum value. [d] These values are estimates of solvolysis rates in 90% acetone-water at 75° from the rates of solvolysis in 50% acetone-water at 75° which are recorded in the adjacent column (1c)[1]. [e] See footnote [d]. [f] This value estimated from the rate of solvolysis of 1-p-anisyl-1-chloropropane ($k_1 = 6.1 \times 10^{-2}$ $sec.^{-1}$) and of 1-phenyl-1-chloropropane ($k_1 = 5.0 \times 10^{-6}$ $sec.^{-1}$) in 90% acetone-water at 75° by assuming that the substituent effect on solvolysis of the bromides is similar to that for the chlorides. [g] The S_N2 reaction was accompanied by 0.86% chloride induced dehydrobromination. [h] Dehydrobromination was <0.2% of the bromide ion produced.

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