Eliminations promoted by Weak Bases. Part VI.[1,2] Isotope, Basicity, and Substituent Effects on the Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes in Dimethylformamide

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Primary hydrogen isotope effects on the rates of the dehydrochlorination reactions of $Ar_2CH{\cdot}CCl_3$ with the bases Cl^-, Br^-, p-$NO_2C_6H_4S^-$, and 2,4-$(NO_2)_2C_6H_3O^-$ in dimethylformamide are reported. The values of k_H/k_D are in the range 5·1—5·6 and are largely independent of ring substituents in the substrate and of the base employed. It is considered that they are too high to admit the possibility of an E2C mechanism, and an E2H explanation is favoured. Brønsted correlations of log k_2 *vs.* pK_a are not linear. The effect of ring substituents on the equilibrium constants for the reversible dehydrochlorinations promoted by $Bu^n{}_4NCl$ in acetone is negligible, which indicates that the transition states are not olefin-like, but rather have an excess of negative charge on C_β.

In Part V[1] we reported that the Hammett ρ constants pertaining to the reactions in equation (1) have the

$$Ar_2CH{\cdot}CCl_3 + Cl^- \longrightarrow Ar_2C{:}CCl_2 + HCl + Cl^- \quad (1)$$

values 0·99 (solvent dimethylformamide) and 1·31 (solvent acetone) at 65°. Comparison of these with ρ values for halide-induced eliminations from substrates having unactivated β-hydrogens and good leaving groups departing from secondary or tertiary α-carbons, which are generally *ca.* 0·5,[1,2] led to the conclusion that the transition states for $Ar_2CH{\cdot}CCl_3$ dehydrochlorination involve a well broken C_β–H bond and a poorly broken C_α–Cl bond, and hence have little olefinic character. They can thus be represented as paenecarbanion E2H

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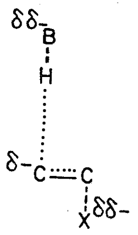
[1] Part V, O. R. Jackson, D. J. McLennan, S. A. Short, and R. J. Wong, *J.C.S. Perkin II*, 1972, 2308.

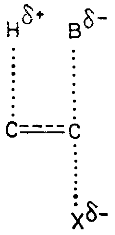
[2] Part IV, D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1972, 279 (note the generalization of the title for the series).

transition states [3] (I). We now present further evidence, based primarily on isotope effects, that supports this contention.

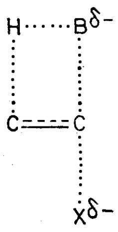


(I)

Previous studies of isotope effects in halide-induced eliminations are few [4-8] in comparison with those for reactions promoted by conventionally strong bases,[9] but distinct patterns of results can be discerned.[7] With some exceptions, hydrogen isotope effects are low and are far from the theoretical maximum of *ca.* 7 at room temperature for proton transfers *via* transition states having a linear $B \cdots H \cdots C_\alpha$ arrangement.[10] Substrates whose reactions fall into this class have unactivated β-hydrogens and good leaving groups departing from secondary or tertiary C_α, *i.e.* the most favoured environment for heterolytic C_α–X cleavage. They are thus structurally suitable for elimination through the proposed *E*2C or *E*2C-like transition states (II) and (III).[4,11] We shall henceforth refer to such substrates as being 'loose,' although it is to be understood that transition states such as (II) or (III) arising from the substrates are the loose species.



(II)



(III)

Theoretical calculations of hydrogen isotope effects for eliminations utilizing such transition states have been performed,[12] and low isotope effects, in the range 2·7—4·2, depending on the identity of B, are predicted. On the other hand, isotope effects pertaining to substrates having either or both an activated β-hydrogen and a leaving group departing from a less than favoured environment (primary C_α), display higher isotope effects and the conclusion is that the transition states are more *E*2H-like, *e.g.* (I).

It is therefore of interest to examine the reactions of $Ar_2CH\cdot CCl_3$ in this regard. These are even tighter substrates than any that have so far been examined and are constitutionally unlikely to eliminate *via* transition states (II) or (III) even when a weak base, which is also a strong carbon nucleophile, is employed.

RESULTS

All reactions subjected to kinetic study were carried out in dimethylformamide at 65°. The reactions induced by LiCl were followed as before and raw rate constants were corrected for imperfect autocatalysis.[1] The reactions promoted by Bu^n_4NOAr (Ar = 2,4-dinitrophenyl) and Bu^n_4NSAr' (Ar′ = *p*-nitrophenyl) were followed spectrophotometrically under first-order conditions: $[Ar_2CH\cdot CCl_3]_0 \gg [\text{base}]_0$, at the absorption maximum of the base. Second-order rate constants (k_2) were calculated from equation (2), in which k_ψ is the observed first-order rate constant. Values of k_2 were insensitive to changes in substrate concentration.

$$k_2 = k_\psi/[\text{substrate}]_0 \qquad (2)$$

The situation presented by the LiBr-induced reactions is that of two competitive consecutive second-order reactions, one of which is autocatalysed. This is not amenable to exact kinetic analysis. An attempt to use the graphical integration method of Saville,[13] with $[LiBr]_0 = [Ar_2CH\cdot CCl_3]_0$ was not marked by precise results because of relative lack of precision in the simultaneous estimation of Br^- and Cl^- by potentiometric titration with $AgNO_3$ after separation of the anions by ion exchange. Therefore first-order conditions were employed with $[LiBr]_0$ being greater than $[Ar_2CH\cdot CCl_3]_0$ by a factor of at least 10^3. Values of k_ψ over the course of a given run were effectively constant, indicating that catalysis by released chloride ion is insignificant. The quotient of k_ψ and $[LiBr]_0$ (equal to k_2) was constant over a base range 0·10—0·15M. These values of k_2 were reasonably close to the approximate values obtained by the Saville method. The salts LiCl and LiBr are more than 90% dissociated in dimethylformamide at the concentrations used.[14] No substitution products of the type $Ar_2CH\cdot CCl_2Br$, *etc.* were observed, suggesting that the bromide-promoted reaction is 100% elimination. It is most unlikely that S_N2 attack on a carbon bearing three chlorines, followed by rapid dehydrobromination, would occur.[1,2]

Reactions of the deuteriated (>99%) $Ar_2CD\cdot CCl_3$ compounds exhibited no unusual phenomena. In particular induction periods were absent, indicating that no competing hydrogen–deuterium exchange was occurring. All rate constants for hydrogen compounds are shown in Table 1.

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[3] J. F. Bunnett, 'Survey of Progress in Chemistry,' ed. A. E. Scott, Academic Press, New York, 1969, vol. 5, p. 53.

[4] G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, 1972, **94**, 2235.

[5] (*a*) D. N. Kevill, G. N. Coppens, and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1964, **86**, 1553; (*b*) D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *ibid.*, 1966, **88**, 4489.

[6] D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, 1969, **34**, 1985.

[7] D. Cook, R. E. J. Hutchinson, J. K. McLeod, and A. J. Parker, *J. Org. Chem.*, 1974, **39**, 534.

[8] J. Hayami, N. Ono, and A. Kaji, *Bull. Chem. Soc. Japan*, 1971, **44**, 1628.

[9] A. Fry, *Chem. Soc. Rev.*, 1972, **1**, 163.

[10] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.* (*B*), 1967, 985.

[11] (*a*) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, 1970, **92**, 115; (*b*) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, 1971, **93**, 4735; (*c*) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, 1972, **94**, 2240; (*d*) A. J. Parker, M. Ruane, D. C. Palmer, and S. Winstein, *ibid.*, p. 2228; (*e*) A. J. Parker, *Chem. Tech.*, 1971, **1**, 297.

[12] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 785.

[13] B. Saville, *J. Phys. Chem.*, 1971, **75**, 2215.

[14] W. M. Weaver and J. D. Hutchinson, *J. Amer. Chem. Soc.*, 1964, **86**, 261.

In the presence of a base such as 2,6-lutidine or 2,4,6-collidine, the reactions of $Ar_2CH{\cdot}CCl_3$ compounds with Bu^n_4NCl in acetone proceed to completion.[1] In the absence of such an HCl scavenger they attain equilibrium [equation (3)], and equilibrium constants for Ar = *p*-ClC_6H_4, *p*-BrC_6H_4, and *p*-$NO_2C_6H_4$ have been measured.

$$Ar_2CH{\cdot}CCl_3 + Bu^n_4NCl \rightleftharpoons Ar_2C{:}CCl_2 + Bu^n_4NHCl_2 \quad (3)$$

Attainment of equilibrium when less powerful electron-withdrawing groups are present on the rings is slower, and the longer exposure of the solvent to acid resulted in more extensive solvent decomposition *via* acid-catalysed condensation reactions,[1, 15, 16] rendering equilibrium ' constants ' meaningless. $Bu^n_4NClO_4$ (0·4M) was present as a supporting electrolyte in excess in all cases. This ensures that the position of equilibrium is not controlled to any extent by a secondary salt effect on the presumably differing degrees of dissociation of Bu^n_4NCl and $Bu^n_4NHCl_2$ in acetone, since the degrees of dissociation of these salts will be invariant with concentration under these conditions.[17] Equilibrium constants are presented in Table 2.

TABLE 1

Rate constants for the reactions of $Ar_2CH{\cdot}CCl_3$ with bases in dimethylformamide at 65°

Substrate	Base	10^5k_2/l mol^{-1} s^{-1}
$(p\text{-}MeOC_6H_4)_2CH{\cdot}CCl_3$	LiCl	9·23 [a]
$Ph_2CH{\cdot}CCl_3$	LiCl	9·54 [b]
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	LiCl	54·6 [c]
$(p\text{-}NO_2C_6H_4)_2CH{\cdot}CCl_3$	LiCl	408 [d]
$Ph_2CH{\cdot}CCl_3$	LiBr	0·288
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	LiBr	1·56 [e]
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	LiBr	1·59 [f]
$Ph_2CH{\cdot}CCl_3$	Bu^n_4NOAr	8·09
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NOAr	44·4 [h]
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NOAr	45·1 [i]
$(p\text{-}MeOC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr' [j]	54·2
$(p\text{-}MeC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	48·9
$Ph_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	106
$(p\text{-}FC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	319
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	570 [k]
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	574 [l]
$(p\text{-}BrC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	590

[a] Ref. 1 reports 10^5k_2 = 9·66 l mol^{-1} s^{-1}. [b] Ref. 1 reports 10^5k_2 = 9·90 l mol^{-1} s^{-1}. [c] Ref. 1 reports 10^5k_2 = 55·2 l mol^{-1} s^{-1}. [d] Ref. 1 reports 10^5k_2 = 406 l mol^{-1} s^{-1}. Runs at other temperatures establish $\Delta H^‡ = 23{\cdot}4$ kcal mol^{-1}; $\Delta S^‡ = -2{\cdot}7$ cal K^{-1} mol^{-1}. [e] [base] = 0·100M. [f] [base] = 0·149M. [g] Ar = 2·4-Dinitrophenyl. [h] [substrate] = 0·0440M. [i] [substrate] = 0·0800M. [j] Ar′ = 4-Nitrophenyl. [k] [substrate] = 0·00922M. [l] [substrate] = 0·0184M.

TABLE 2

Equilibrium constants [a] for the reactions of $Ar_2CH{\cdot}CCl_3$ with Bu^n_4NCl in acetone at 65°

Substrate	$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	$(p\text{-}BrC_6H_4)_2CH{\cdot}CCl_3$	$(p\text{-}NO_2C_6H_4)_2CH{\cdot}CCl_3$
K	27·9	35·5	27·1

[a] $[Substrate]_0 = [Bu^n_4NCl]_0$ = 0·02M, in presence of 0·4M-Bu^nNClO_4.

DISCUSSION

Isotope Effects.—These are gathered in Table 3 and an important fact at once emerges. The value of k_H/k_D for reaction of a given base with a set of substrates differing only in *para*-substituent, or for a given substrate with the series of bases is constant within experimental error. As has been previously pointed out,[18] this means that $\rho_H \approx \rho_D$ (substrate variation) or $\beta_H \approx \beta_D$ (base variation). Thus although transition-state character may change in a subtle fashion on varying the reactants, this is not reflected by the isotope effects. An increase in base strength for instance may cause an increase in the amount of C_β–H bond extension in the presumed *E*2H transition state, but a consequence may be a lessening of coupling between C_β–H stretching and π-bond formation since the incipient double bond should be less extensively formed the more paenecarbanionic is the transition state. The two effects are predicted to act in such a way as to cancel each other out as far as changes in isotope effects are concerned, and the isotope effects tell us practically nothing about the character of the *E*2H transition states. A similar conclusion has been arrived at by others,[19] and the fact that isotope effects in *E*2 reactions are functions of coupling of atomic motions [20] as well as of degrees of proton transfer makes the assignment of transition-state character on these grounds alone a less than certain exercise.[21]

TABLE 3

Hydrogen–deuterium isotope effects for reactions of $Ar_2CH{\cdot}CCl_3$ with various bases in dimethylformamide at 65°

Substrate	Base	k_H/k_D [a]	*p*K_a [b]
$(p\text{-}MeOC_6H_4)_2CH{\cdot}CCl_3$	LiCl	5·21 ± 0·5	3·4
$Ph_2CH{\cdot}CCl_3$	LiCl	4·30 ± 0·4	
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	LiCl	5·60 ± 0·6	
$(p\text{-}NO_2C_6H_4)_2CH{\cdot}CCl_3$	LiCl	5·25 ± 0·5	
$Ph_2CH{\cdot}CCl_3$	LiBr	5·01 ± 0·3	1·8
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	LiBr	5·18 ± 0·3	
$Ph_2CH{\cdot}CCl_3$	Bu^n_4NOAr [c]	5·46 ± 0·3	6·0
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NOAr	5·14 ± 0·3	
$Ph_2CH{\cdot}CCl_3$	Bu^n_4NSAr' [d]	5·14 ± 0·3	6·3
$(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$	Bu^n_4NSAr'	5·20 ± 0·3	

[a] Rate constants for $Ar_2CD{\cdot}CCl_3$ may be derived from this data and results in Table 1. [b] pK_a Of conjugate acid of indicated base in dimethylformamide, from ref. 25. [c] Ar = 2,4-dinitrophenyl. [d] Ar′ = 4-nitrophenyl.

We can state with a reasonable degree of certainty that we are dealing with *E*2H reactions however. The mean isotope effect of 5·3 (corresponding to k_H/k_D 6·3 at 25°) is considerably larger than those calculated for non-linear *E*2C transition states.[12] This important item of evidence supports our earlier conclusion.[1] The theoretical calculations of More O'Ferrall [12] do show that isotope effects should be insensitive to changes in transition state symmetry for non-linear transition states, and this prediction has been confirmed

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[15] S. Winstein, S. G. Smith, and D. Darwish, *Tetrahedron Letters*, 1959, No. 16, 24.

[16] J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, 1970, **35**, 76.

[17] A. Fava, A. Iliceto, and A. Fava, *Tetrahedron Letters*, 1963, 785.

[18] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 526.

[19] L. F. Blackwell, P. D. Buckley, K. W. Jolly, and A. K. H. MacGibbon, *J.C.S. Perkin II*, 1973, 169.

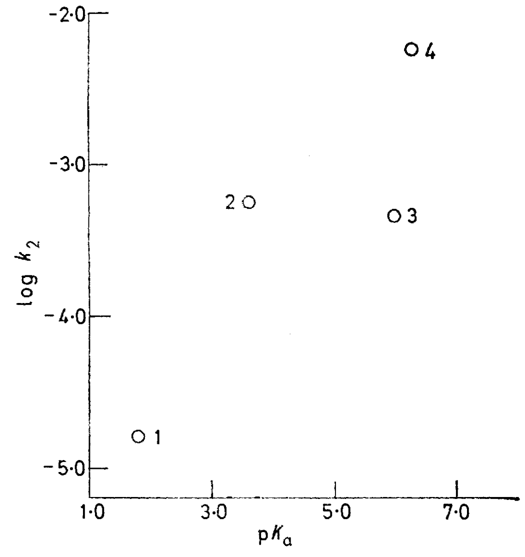
[20] A. M. Katz and W. H. Saunders, *J. Amer. Chem. Soc.*, 1969, **91**, 4469.

[21] P. J. Smith and S. K. Tsui, *J. Amer. Chem. Soc.*, 1973, **95**, 4706; *Tetrahedron Letters*, 1972, 917; 1973, 61.

experimentally.[7] Such is not the case for simple proton-transfer reactions involving a linear arrangement,[10,18] but the lack of change of our isotope effects as base strength is varied over 4·5 pK units and substrate acidity over 13·5 pK units [22] may not be taken as a result favouring E2C transition states (II) or (III) for the reason that activation comprises more than mere proton transfer.

Linear Free Energy Relationships.—A Hammett plot may be constructed for the $Ar_2CH{\cdot}CCl_3$–$Ar'S^-$ reaction series. The optimum plot [1,2,22] of log k_2 against $2\sigma_I + 1{\cdot}44\sigma_R$ yields ρ 1·25 ± 0·06 (r 0·993). The magnitude of ρ is consistent with the involvement of a paenecarbanionic E2H transition state. More importantly, it is significantly larger than ρ for the LiCl-induced reaction (0·99 ± 0·03 at 65°).[1] This further substantiates the view that the proton will be more extensively transferred to stronger bases in E2H transition states.[2,3,22,23]

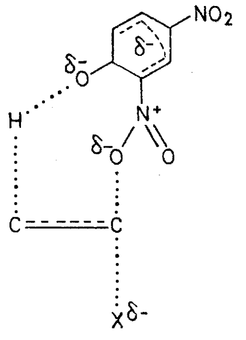
There is no evidence to suggest that the stronger phenoxide and thiolate bases promote E1cB reactions.[24] Hammett ρ values for E1cB dehydrochlorinations in the $Ar_2CH{\cdot}CCl_3$ series in protic solvents with bases varying in strength from PhS^- to Bu^tO^- lie between [22] 2·1 and 3·0. The rate ratio of $(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$ to $Ph_2CH{\cdot}CCl_3$ in these reactions varies between 18 and 85, whereas in all cases considered here the rate ratio lies between 5·0 and 6·5. The latter values are symptomatic of a lesser amount of carbanionic charge at C_β, which in turn is indicative of E2 rather than E1cB reaction.[22,24,25]



Brønsted plot for the reactions of $(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$ with LiBr (1), LiCl (2), $Bu^n{}_4NOAr$ (3), and $Bu^n{}_4NSAr'$ (4) in dimethylformamide

Brønsted plots for the reactions of $Ph_2CH{\cdot}CCl_3$, $(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$, and their deuteriated analogues may also be constructed. One of these is shown in the Figure; the others are similar in appearance.

Linearity is conspicuously absent. In particular, chloride is a more effective base kinetically than is 2,4-dinitrophenoxide despite the fact that the latter is more basic (thermodynamically) by 2·6 pK units.[25] The presence of the *ortho*-substituent may depress the rate of attack of 2,4-dinitrophenoxide. Bifunctional catalysis *via* an E2C-like transition state (IV) is specifically excluded by the lower than expected rate. Thus the Brønsted plot composed of the reactivities of a series of structurally unrelated bases and their basicities is mechanistically uninformative.



(IV)

More instructive is an analysis of the relative reactivity of chloride and bromide ions, which is 35 towards $(p\text{-}ClC_6H_4)_2CH{\cdot}CCl_3$, and 33 towards $Ph_2CH{\cdot}CCl_3$. These values indicate that the bases have a large degree of control over the proton in the transition state, since the ratio of acidity constants in dimethylformamide is [25] 40. In contrast to this, $Cl^- : Br^-$ elimination rate ratios towards 'loose' substrates are typically low and in the range 6—12.[11,16] Cyclohexyl bromide (ratio 17·4) [11c] and the 2-benzyl-2-halogeno-indanones and -tetralones (ratios ranging from 16 to 53) [5] are exceptions. The latter substrates may be special cases, for not only are the β-hydrogens rendered labile by the acidifying aryl groups, a factor which leads to higher $Cl^- : Br^-$ ratios and low k_H/k_D values,[5] but also the departure of the leaving group is assisted by the carbonyl group, thus giving a very product-like transition state as far as the bond changes at C_α and C_β are concerned. The resulting high degree of double bond character means that there will be little carbanionic charge on C_β although the proton is well transferred, and the low Hammett ρ values [5] are testimony to this. Late, paeneolefinic E2H transition states for halide-induced eliminations were first proposed by Bunnett and Baciocchi.[16]

The quality of Brønsted plots, generated by the use of unrelated bases, has been suggested as a probe to examine whether a given transition state is E2C-like (poor correlation expected) or E2H-like (good correlation expected), and some evidence supporting this

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[22] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 1373.

[23] W. P. Jencks, *Chem. Rev.*, 1972, **72**, 720; S. Alunni and E. Baciocchi, *Tetrahedron Letters*, 1973, 4665.

[24] D. J. McLennan, *Quart. Rev.*, 1957, **21**, 490.

[25] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, 1966, **88**, 1911; I. M. Kolthoff, M. K. Chantooni, and H. Smagowski, *Analyt. Chem.*, 1970, **42**, 1622.

view has been presented.[11c,d] However, in the present work we have what is clearly an E2H process yielding a bad correlation. It may be recalled that a non-linear Brønsted plot is also observed for the E1cB reactions of $(p\text{-ClC}_6\text{H}_4)_2\text{CH}\cdot\text{CCl}_3$ with thiolate, phenoxide, and alkoxide bases in ethanol.[18] These are E2H reactions *par excellence* in that the rate-determining step involves nothing other than proton transfer, and the transition states cannot in any way be regarded as E2C-like. Thus we do not consider that the success or failure of Brønsted correlations gives mechanistically significant information in all cases. Caution must be exercised in such interpretations.[26]

We have studied the effects of ring substituents on the position of the equilibrium in equation (3) in order to ascertain whether or not a well developed π-bond is present in the transition states of the $\text{Ar}_2\text{CH}\cdot\text{CCl}_3\text{–Cl}^-$ reactions. It is evident from Table 2 that there is virtually no substituent effect on the equilibrium constants. The substituents have no more effect on the stability of the olefin than they have on that of the substrate. Lack of differential interaction between benzene ring substituents and conjugated exocyclic double bonds has been noted in other studies.[27]

On the other hand, a change in *para*-substituent from Cl or Br to NO_2 causes a 13-fold increase in the rate of the $\text{Ar}_2\text{CH}\cdot\text{CCl}_3\text{–Bu}^{\text{n}}{}_4\text{NCl}$ reaction in acetone,[1] and the most reasonable explanation of the much larger substituent effect on rates than on equilibria is that the transition state does not resemble the products and is therefore not olefin-like. It must have a structure such that strong interactions between substituents and reaction centre are permitted,[28] and the obvious structure in the present case is one in which C_β bears an excess of negative charge, *i.e.* the paenecarbanionic E2H transition state (I).

Microscopic reversibility requires that the reverse reaction in equation (3) must be a concerted, termolecular, presumably [11] *trans*-addition of HCl to the olefin. Such a process has been identified as contributing to the hydrochlorination of cyclohexene by HCl and Cl^- in acetic acid,[29] as well as in other such additions.[30]

EXPERIMENTAL

Materials.—The solvent was dried and purified as before.[1] All substrates were available from previous studies.[1,18] Tetra-n-butylammonium 2,4-dinitrophenoxide was prepared by the method given for the 4-nitrophenoxide [11d] and after recrystallization from 2 : 1 ethyl acetate–ether had m.p. 108—109° (lit.,[31] 108·5—109°). Tetra-n-butylammonium perchlorate, m.p. 211—212·5° (lit.,[11d] 213°), and tetra-n-butylammonium 4-nitrobenzenethiolate, m.p. 109—110° (lit.,[11d] 110°), were prepared as described, the latter from 4-nitrobenzenethiol which was obtained by the method of Price and Stacey.[32]

Kinetics.—The method for the LiCl-induced reactions has been described.[1] In the LiBr-induced reactions, ampoules containing $[\text{LiBr}]_0$ *ca.* 0·01M and $[\text{substrate}]_0$ *ca.* 5×10^{84}M were opened at various times and the contents were quantitatively diluted with methanol. . The u.v. absorbance at quoted wavelengths [1] was then measured. The reactions with the phenoxide and thiolate bases were carried out with $[\text{substrate}]_0$ *ca.* 0·01—0·08M, depending on the rate, and $[\text{base}]_0$ *ca.* 5×10^{-4}M. Ampoules were cooled at various times, the contents were quantitatively diluted with methanol, and absorbances at 360 (phenoxide) [31] and 424 nm (thiolate) [33] were measured. The thiolate and phenoxide bases were stable in dimethylformamide at 65° for periods longer than 10 half-lives of the slowest reactions studied, as long as thiolate solutions were deoxygenated and protected from light. The visible spectra of 'infinity' samples in the thiolate-induced reactions were identical with those of the theoretical amounts of 4-nitrobenzenethiol, indicating that the reactions were 100% elimination. No reaction between the thiol and $(p\text{-ClC}_6\text{H}_4)_2\text{C{:}CCl}_2$ [2] in dimethylformamide at 65° could be detected over one week. The method given by Vogel [34] was used for analysis of mixtures of Cl^- and Br^-.

Equilibrium Studies.—Ampoules containing $\text{Ar}_2\text{CH}\cdot\text{CCl}_3$ and $\text{Bu}^{\text{n}}{}_4\text{NCl}$ (both 0·02M) and $\text{Bu}^{\text{n}}{}_4\text{NClO}_4$ (0·4M) in acetone were placed in a thermostatted bath and removed at various times for analysis. Their contents were transferred to ethanol–water and potentiometric titration with AgNO_3 solution was carried out. Equilibrium constants were reckoned from the titre after it had attained a constant value. Even for those substrates recorded in Table 3 the solutions were coloured when equilibrium was reached, but with the slower reacting substrates, *e.g.* $(p\text{-MeOC}_6\text{H}_4)_2\text{CH}\cdot\text{CCl}_3$ and $\text{Ph}_2\text{CH}\cdot\text{CCl}_3$, the reaction mixture was dark well before the attainment of equilibrium. Furthermore the reaction of chloride ion with the tetra-n-butylammonium cation [11c] becomes significant as longer reaction times are required.

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