The Carbanion Mechanism of Olefin-forming Elimination. Part 9.[1] Proton Tunnelling and Isotope Effects in the Dehydrochlorination of 1,1-Diaryl-2,2-dichloroethanes

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Rate constants for the dehydrochlorination of $(p\text{-}ClC_6H_4)_2CH\cdot CHCl_2$ and its deuterio-analogue induced by NaOMe–MeOH have been obtained at five temperatures in the 0—45 °C range. The values of the respective Arrhenius parameters substantiate the earlier view that proton tunnelling is important in this $E2$ reaction. Tunnelling is less significant in the $E2$ reactions of $Ph_2CH\cdot CHCl_2$ and $Ph_2CD\cdot CHCl_2$ and is apparently of no consequence in the dehydrochlorination of $(p\text{-}NO_2\cdot C_6H_4)_2CH\cdot CHCl_2$. The latter substrate reacts at a rate equal to the estimated rate of carbanion formation, and an $E1cB$ mechanism is induced. Isotope effects decrease as dimethyl sulphoxide is added to MeOH for the dehydrochlorination of $Ph_2CH\cdot CHCl_2$.

PART 6 [2] of this series was concerned with the mechanism of dehydrochlorination of 1,1-bis-(p-chlorophenyl)-2,2-dichloroethane (DDD) by NaOMe in MeOH [equation (1)]. The conclusion was that the reaction proceeded

$$Ar_2CH\cdot CHCl_2 + OMe^- \longrightarrow Ar_2C{:}CHCl + MeOH + Cl^- \quad (1)$$

predominantly *via* a concerted $E2$ pathway with a no more than 30% contribution from an $E1cB$ route involving rate-determining carbanion formation. Incidental to this study was the observation that the high isotope effects and relationships amongst the activation parameters in the reactions of DDD and $(p\text{-}ClC_6H_4)_2CD\cdot CHCl_2$([^{2}H]DDD) were indicative of a significant proton tunnelling effect.

These activation parameters were, however, calculated from rate constants obtained at only two temperatures, 30 and 45 °C. In the present work the study of the temperature dependence of k_2 is extended to six temperatures in the 0—45 °C range. Furthermore we have investigated substituent effects on isotope effects and activation parameters in studying the behaviour of $Ph_2CH\cdot CHCl_2$, $(p\text{-}NO_2\cdot C_6H_4)_2CH\cdot CHCl_2$, and their deuterio-analogues, and have also studied solvent effects on the reactions of $Ph_2CH\cdot CHCl_2$ with ^-OMe in MeOH–Me_2SO mixtures. As before [2,3] we accept that any or all the following interdependent observations may be used as criteria for significant tunnelling; abnormally large isotope effects, $(E_a)_D - (E_a)_H$ larger than *ca.* 1.15 kcal mol^{-1}, A_D/A_H greater than 2, and the occurrence of non-linear Arrhenius plots.

RESULTS

Rate constants for the second-order reactions of the substrates $Ar_2CH\cdot CHCl_2$ and $Ar_2CD\cdot CHCl_2$ (Ar = Ph, p-ClC_6H_4, or p-$NO_2C_6H_4$) with NaOMe–MeOH are shown in Table 1. The reactions of the nitro-compounds were too fast to be followed accurately using conventional continuous spectrophotometric monitoring, and so measurements were done using NaOAc–HOAc buffers of varying composition, as has been described for a similar reaction.[1] Arrhenius plots of the data for R = H and R = Cl are strictly linear, with correlation coefficients greater than 0.999. The 45 °C rate constant for DDD from the previous study [2] lies slightly below the line described by the other points, but the remaining earlier values fall accurately on the present plots. The deviation of the 45 °C DDD k_2 value is at the wrong end of the temperature range and in the wrong direction for it to be viewed as a tunnelling-related departure from linearity.[4] However, linearity of Arrhenius plots is not necessarily a negative tunnelling criterion.[5]

TABLE 1

Rate constants and isotope effects for reactions of $(p\text{-}RC_6H_4)_2CH\cdot CHCl_2$ and $(p\text{-}RC_6H_4)_2CD\cdot CHCl_2$ with NaOMe in MeOH

		10^5k_2/l mol^{-1} s^{-1} [b]		
R	T/°C	H-Compound	D-Compound	k_H/k_D
H	0.0	0.646	0.063 7	10.2
H	21.4	14.7	1.71	8.6
H	25.0	21.9	2.84	7.7
H	30.0	39.5	5.63	7.0
H	35.0	72.4	10.9	6.6
H	45.0	214	38.6	5.5
Cl	0.0	12.0	0.692	17.3
Cl	21.4	170	14.6	11.6
Cl	25.0	263	21.6	12.1
Cl [a]	30.0	458	42.3	10.8
Cl	35.0	783	78.5	10.0
Cl [a]	45.0	1 740	243	7.2
NO_2	30.0	48 100	11 300	4.3
NO_2	45.0	200 000	51 000	3.9

[a] From ref. 2. [b] Uncertainties *ca.* ±2% except for p-NO_2-compounds, for which 5% uncertainties are estimated.

Activation parameters, together with the attendant uncertainties based on standard deviations in slope and intercept of the Arrhenius plots, are shown in Table 2. Quasi-thermodynamic activation parameters are also presented.

The reactions of $Ph_2CH\cdot CHCl_2$ and $Ph_2CD\cdot CHCl_2$ in MeOH–Me_2SO mixtures containing NaOMe (0.02M) were also examined. Rate constants and isotope effects are displayed in Table 3.

DISCUSSION

Proton Tunnelling.—Curvature or the lack of it of Arrhenius plots is perhaps the least reliable experimental observation related to the tunnelling phenomenon, in that other factors can cause curvature.[4] We

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[1] Part 8, D. J. McLennan and R. J. Wong, *Austral. J. Chem.*, 1976, **29**, 787.

[2] A. B. N. Gray and D. J. McLennan, *J.C.S. Perkin II*, 1974, 1377.

[3] See references cited in refs. 1 and 2; also M. J. Stern and R. E. Weston, *J. Chem. Phys.*, 1974, **60**, 2803, 2808, 2815.

[4] (*a*) E. F. Caldin, *Chem. Rev.*, 1969, **69**, 135; (*b*) J. R. Hulett, *Quart. Rev.*, 1964, **18**, 227; (*c*) M. J. Stern and R. E. Weston, *J. Chem. Phys.*, 1974, **60**, 2803; (*d*) E. S. Lewis in 'Proton Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, ch. 10; (*e*) R. E. Weston in 'Isotopes and Chemical Principles,' ed. P. A. Rock, American Chemical Society (A.C.S. Symposium No. 11), Washington D.C., 1975, ch. 3.

[5] V. J. Shiner and B. L. Martin, *Pure Appl. Chem.*, 1964, **8**, 371.

are thus not disturbed by its absence, even though other manifestations of proton tunnelling are evident.

Other items of evidence do suggest that tunnelling is important in the reactions of DDD and $Ph_2CH{\cdot}CHCl_2$. Isotope effects, particularly in the former case, are abnormally high. The Arrhenius activation energy differences, $(E_a)_D - (E_a)_H$, are respectively 3.1 ± 0.7 and 2.2 ± 0.4 kcal mol^{-1}, which again are higher than the 'classical' value of *ca.* 1.15 which is based on the difference in zero-point energies of C–H and C–D bonds. Finally, the values of $\log(A_D/A_H)$, 1.3 ± 0.5 ($A_D/A_H = 17.6$) and 0.9 ± 0.3 ($A_D/A_H = 7.9$), respectively, are greater than the 'classical' limit. The previous claim for the demonstration of tunnelling is thus sustained.

TABLE 2

Activation parameters for the reactions of $Ar_2CH{\cdot}CHCl_2$ and $Ar_2CD{\cdot}CHCl_2$ with NaOMe in MeOH

	$Ph_2CH{\cdot}CHCl_2$	$Ph_2CD{\cdot}CHCl_2$	$(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$	$(p\text{-}ClC_6H_4)_2CD{\cdot}CHCl_2$	$(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CHCl_2$	$(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CHCl_2$
E_a/kcal mol^{-1}	22.2 ± 0.3	24.6 ± 0.1	19.4 ± 0.4	22.5 ± 0.3	18.3 ± 0.6	19.3 ± 0.5
$\log(A/\text{l mol}^{-1}\text{ s}^{-1})$	12.6 ± 0.2	13.5 ± 0.1	11.6 ± 0.3	12.9 ± 0.2	12.8 ± 0.5	12.9 ± 0.4
$\Delta H^‡$/kcal mol^{-1}	21.6 ± 0.3	24.0 ± 0.1	18.8 ± 0.4	21.9 ± 0.3	17.7 ± 0.6	18.7 ± 0.5
$\Delta S^‡$/cal K^{-1} mol^{-1}	-4.8 ± 0.7	-0.7 ± 0.5	-7.2 ± 0.8	-3.8 ± 0.7	-3.7 ± 1.7	-3.3 ± 1.4

TABLE 3

Rate constants and isotope effects for the reactions of $Ph_2CH{\cdot}CHCl_2$ and $Ph_2CD{\cdot}CHCl_2$ with NaOMe (*ca.* 0.02M) in MeOH–Me_2SO at 30 °C

Mole % Me_2SO	$[Me_2SO]$/M [a]	10^5k_2/l mol^{-1} s^{-1} $Ph_2CH{\cdot}CHCl_2$	10^5k_2/l mol^{-1} s^{-1} $Ph_2CD{\cdot}CHCl_2$	k_H/k_D
0	0	39.5	5.63	7.0
2.33	0.564	59.4	8.28	7.2
5.96	1.41	105	15.4	6.8
8.46	1.97	151	21.7	6.9
12.45	2.82	261	40.4	6.4
19.56	3.38	766	118	6.5
27.35	5.64	1 850	313	5.9

[a] At room temperature; methanol molarities calculated from densities are, respectively, 24.70, 23.64, 22.26, 21.34, 19.82, 18.91, and 14.98.

Koch and his co-workers have recently reported anomalous Arrhenius parameters in dehydrohalogenations thought to proceed by *E*1cB mechanisms, either in the rate-determining proton transfer or internal return variants.[6] However, their isotope effects, all lower than 4, are governed by entropy effects and A_D/A_H ranges from 0.21 to 0.67. This behaviour, which is opposite to that reported here, is not easily explained.

The magnitude of the experimental errors (two-point Arrhenius plots) obscures the $(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CHCl_2$ reaction as far as the relationship between the activation parameters and tunnelling is concerned. However, the isotope effects are conspicuously lower than the theoretical maximum for proton transfer without tunnelling[7] and we take this to mean that tunnelling is unimportant in this reaction.

If the magnitude of the tunnel correction is judged on the basis of the deviation of Arrhenius parameters from their ideal values, then the *para*-substituents are playing a role, in that the corrections are in the order $NO_2 \leqslant Cl > H$, as are the isotope effects. We are further reminded that no observations consistent with the tunnelling criteria are observed for the *E*1cB reactions of the derivatives $Ar_2CH{\cdot}CCl_3$,[1,8] and this in itself suggests that the *para*-nitro-derivative, the most acidic substrate of the three, undergoes elimination *via* carbanionic intermediates. This suspicion will be confirmed in a later section.

It then seems likely that the *E*2 components of the DDD and $Ph_2CH{\cdot}CHCl_2$ reactions (*ca.* 90%; see a following section) are responsible for tunnelling. No purpose is served, however, in treating the matter quantitatively by calculating barrier widths *etc.*,[4] for the *E*2 potential energy surface is a multidimensional one, whereas the theories consider tunnelling parallel to the reaction co-ordinate through a two-dimensional barrier. Bell and his co-workers have shown theoretically that for simple proton-transfer processes the tunnel correction is greater the closer is the proton to a symmetrical position with respect to the donor acid and the acceptor base in the transition state.[9] Here, k_H/k_D also achieves its maximum value, and decreases as the position of the transition state changes on the reaction co-ordinate. This simple relationship between k_H/k_D and the disposition of the proton is not necessarily obeyed in *E*2 reactions, but, as we show in the following paper, is a good approximation if the partial bond between C_α and the leaving group is hardly severed in the transition state. This is likely to be the case for reactions of $Ar_2CH{\cdot}CHCl_2$, for the electron-withdrawing substituent groups on C_α and C_β are predicted by *E*2 transition state rules[10] to engender carbanion character in the transition state. Further application of the rules allows the prediction that, as a substituent in the series is changed from *p*-Cl to *p*-H, the $C_\beta \cdots H$ partial bond will be lengthened, the $C_\alpha \cdots Cl$ bond will be largely unaltered, and the transition state will become even more carbanionic. That this situation is the same as for simple proton transfer is clear.

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[6] H. F. Koch, D. B. Dahlberg, M. F. McEntee, and C. J. Klecha, *J. Amer. Chem. Soc.*, 1976, **98**, 1060.

[7] *E.g.* (*a*) E. S. Lewis and L. H. Funderburk, *J. Amer. Chem. Soc.*, 1967, **89**, 2322; (*b*) E. S. Lewis and J. K. Robinson, *ibid.*, 1968, **90**, 4337; (*c*) H. Wilson, J. D. Caldwell, and E. S. Lewis, *J. Org. Chem.*, 1973, **38**, 564; (*d*) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, **A294**, 273; (*e*) E. F. Caldin and S. Mateo, *J.C.S. Chem. Comm.*, 1973, 854.

[8] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, (*a*) 526; (*b*) 1373.

[9] R. P. Bell, W. H. Sachs, and R. L. Tranter, *Trans. Faraday Soc.*, 1971, **67**, 1995.

[10] (*a*) R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274; (*b*) R. A. More O'Ferrall, in 'Chemistry of Carbon–Halogen Bonds,' ed. S. Patai, Wiley, New York, 1973, ch. 9; (*c*) D. A. Winey and E. R. Thornton, *J. Amer. Chem. Soc.*, 1975, **97**, 3102.

Thus the decrease in k_H/k_D on going from DDD to $Ph_2CH{\cdot}CHCl_2$ must be a consequence of the proton's being at least half transferred in the former case and even more so in the latter. We do not know if the DDD isotope effect is the maximum one obtainable for the $Ar_2CH{\cdot}CHCl_2$ series, but it is the highest of the three we have measured, so an assumption that the proton is half transferred for DDD cannot be too far from the truth. This type of transition state mapping [10c] depends on our assumption concerning the degree of rupture of the $C_\alpha \cdots Cl$ bond at the transition state, an assumption that will be experimentally and theoretically justified in following papers.

Effect of Dimethyl Sulphoxide.—The addition of dimethyl sulphoxide to the NaOMe–MeOH medium causes a significant increase in the rate of dehydrochlorination of $Ph_2CH{\cdot}CHCl_2$ (Table 3). Similar accelerations have been reported for $E2$ reactions involving $PhCH_2{\cdot}CH_2{\cdot}SMe_2^+$ [11a] and $PhCH_2{\cdot}CH_2{\cdot}NMe_3^+$ [11b] (both with ^-OH–H_2O), $PhCH_2{\cdot}CH_2Br$ (Bu^tOK–Bu^tOH),[12] the $E_{CO}2$ reaction of benzyl nitrate (^-OEt–EtOH),[13] and acetylene-forming eliminations from *cis*-1-aryl-2-halogenoethenes (^-OMe–MeOH).[14] A decrease in initial state solvation of the base, with a resultant increase in basicity is clearly responsible, and we now enquire into the effect of added dimethyl sulphoxide on transition-state character.

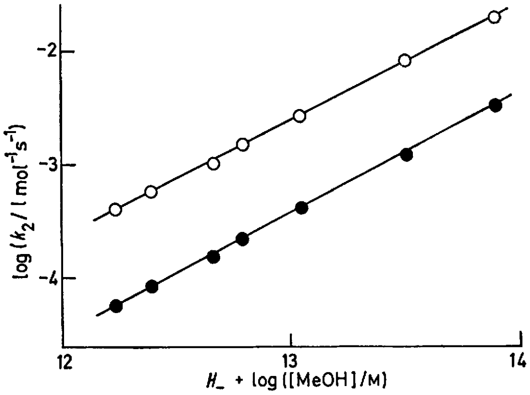

FIGURE 1 Plots of log k_2 for dehydrochlorination of $Ph_2CH{\cdot}CHCl_2$ (open circles) and $Ph_2CD{\cdot}CHCl_2$ (closed circles) by ^-OMe in MeOH–Me_2SO at 30 °C against $H_- + \log[MeOH]$. The values of [MeOH] are normalized; see refs. 10 and 15

The log k_2 values can be correlated with a basicity function for OMe^-–MeOH–Me_2SO [15] that has been successfully employed previously for an $E2$ reaction.[11a] The function, $H_- + \log[MeOH]$, is appropriate for low, constant concentrations of base.[16] The excellent linear plots for $Ph_2CH{\cdot}CHCl_2$ and $Ph_2CD{\cdot}CHCl_2$ shown in Figure 1 have slopes of 1.08 and 1.04, respectively. Little significance can be attached to thse values, however, for two reasons. First, the H_- function used here was generated by nitrogen acid indicators [15] and may not be appropriate for what is almost a carbon acid ionization. Secondly, the slope of the plot for $PhCH_2{\cdot}CH_2{\cdot}SMe_2^+$ is almost the same [11a] despite the fact that the cationic reactant may interact specifically with dimethyl sulphoxide in ways unavailable to the present neutral reactants.

More insight can be gained from cognizance of the fact that k_H/k_D decreases by a small but significant amount as $[Me_2SO]$ increases (Table 3). This can be contrasted with other results.[11,12,14] The $E2$ rules [10] predict that the effect of an increase in basicity on a system whose transition state is already very carbanion-like is to decrease the extent or proton transfer without, however, much affecting the degree of rupture of the $C_\alpha \cdots X$ bond. Since we have already expressed the opinion that the proton is more than half transferred when ^-OMe–MeOH is the medium, k_H/k_D would be expected to increase with increasing $[Me_2SO]$ and perhaps even pass through a maximum. It does not, so either the rules are wrong, or transition-state character is shifting as required, but with other factors controlling trends in k_H/k_D.

We believe that the latter is the case and that a tunnelling effect is the principal component of the ' other factors '. If the tunnelling contribution to k_H/k_D, substantial in ^-OMe–MeOH, is decreased in magnitude by increasing [MeSO], the decrease in k_H/k_D can be understood in the following way. The size of the solvation shell and the strength of the solvational bonds to the methoxide ion should be decreased when $[Me_2SO]$ increases, and so the effective size of the base decreases. In terms of a simple model for proton tunnelling.[7a,b] the concomitant decrease in the magnitude of solvated base–substrate repulsive steric interactions is held to reduce the probability of barrier penetration since the barrier width becomes greater. The proton transfer from ethyl 2-oxocyclopentanecarboxylate to the small but heavily solvated fluoride ion (in D_2O) is accompanied by a greater tunnelling contribution than when the base is the more delocalized and less strongly solvated chloroacetate ion.[17]

Proton tunnelling in solution reactions has another origin according to a more sophisticated theory,[18] the essence of which is that under normal non-tunnelling circumstances the species being transferred has the mass of the proton plus a function of the mass of the solvating molecules that are travelling in concert (or acting as if

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[11] (*a*) A. F. Cockerill, *J. Chem. Soc.* (*B*), 1967, 964; (*b*) W. H. Saunders and K. Brown, quoted by A. F. Cockerill in ' Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, vol. 9, 1973, ch. 3.

[12] A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, *J. Amer. Chem. Soc.*, 1967, **89**, 901.

[13] C. A. Pollock and P. J. Smith, *Canad. J. Chem.*, 1971, **49**, 3856.

[14] G. Marchese, F. Naso, and V. Sgherza, *Gazzetta*, 1971, **101**, 251.

[15] R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, 1962, **18**, 917.

[16] M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, *J. Amer. Chem. Soc.*, 1963, **85**, 2380; R. A. More O'Ferrall, *J.C.S. Perkin II*, 1972, 976.

[17] R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, **A235**, 453; J. R. Jones, *Trans. Faraday Soc.*, 1969, **65**, 2430.

[18] J. L. Kurz and L. C. Kurz, *J. Amer. Chem. Soc.*, 1972, **94**, 4451.

they are) with the proton.[19] If species A and B in the transition state A ⋮ H ⋮ B are inherently bulky close to the reaction site so that solvent is excluded from the cavity between them, the effective mass of the species undergoing transfer is close or equal to that of the proton itself [19] so that tunnelling of a light particle may be permitted.[4a]

While this model is unable to explain the behaviour of the ethyl 2-oxocyclopentanecarboxylate system, it can qualitatively accommodate the present results if a little speculation is permitted. Note that a caveat to the *E*2 transition state rules [20] is not applicable here, in that the basicity increase is not accompanied by an increase in the size of the base.

In principle, examination of trends in Arrhenius parameters could be used to decide the role of tunnelling in changing k_H/k_D. We choose not to do so for the reason that $(E_a)_D - (E_a)_H$ and A_D/A_H values may simply reflect properties of the solvent mixtures themselves, rather than characteristics of the reactions proceeding in those solvents.[21]

Reactions with Bu^tOK–Bu^tOH.—Rate constants for reactions of DDD, $Ph_2CH{\cdot}CHCl_2$, and their deuterio-analogues are presented in Table 4. The isotope effects are not abnormally high and, for $Ph_2CH{\cdot}CHCl_2$, the isotope-induced changes in the Arrhenius parameters are normal. As previously suggested,[2] tunnelling appears to be inconsequential.

TABLE 4

Rate constants, activation parameters, and isotope effects for reactions of $Ar_2CH{\cdot}CHCl_2$ and $Ar_2CD{\cdot}CHCl_2$ with Bu^tOK–Bu^tOH [a]

T/°C	10^5k_2/ l mol^{-1} s^{-1}	E_a/ kcal mol^{-1}	log (A/ l mol^{-1} s^{-1})	k_H/k_D
(a) Ar = Ph; H-compound				
30	86.2			
45	414	20.0 ± 0.4	11.3 ± 0.3	
(b) Ar = Ph; D-compound				
30	14.2			6.1
45	74.7	21.1 ± 0.4	11.4 ± 0.3	5.5
(c) Ar = p-ClC_6H_4; H-compound [b]				
30	1 070			
(d) Ar = p-ClC_6H_4; D-compound [b]				
30	217			4.9

[a] [Bu^tOK] *ca.* 0.06M. [b] From ref. 2.

In contrast to the ^-OMe–MeOH results, introduction of an electron-withdrawing substituent lowers k_H/k_D. Neglecting for the moment the effect of the solvent polarity change on transition state character, it is to be expected that the increase in base strength on going from ^-OMe to Bu^tO^- will occasion a decrease in the extent of proton transfer.[10] The proton appears to be more than half transferred for Ar = Ph when ^-OMe is the base, so an increase in base strength could lead to the proton's becoming half or less transferred. The further introduction of an electron-withdrawing substituent should, if parallel effects dominate,[10] lead to an even less well transferred proton and a lower isotope effect. Such is the case. In turn, the hypothesis presented in both this and the previous section, namely that β-substituent effects are manifested by changing the position of the transition state along the reaction co-ordinate, requires that all transition states be very carbanionic with little $C_\alpha \cdots Cl$ extension.[10,22] Direct evidence on this point is presented in a following paper. For reasons discussed in the two following papers, it is to be expected that a decrease in solvent polarity will hinder extension of the $C_\alpha \cdots Cl$ bond at the transition state (a perpendicular effect). Thus the change of solvent from MeOH to Bu^tOH is expected only to affect the carbanionic charge on C_β, and not primarily the degree of proton transfer.

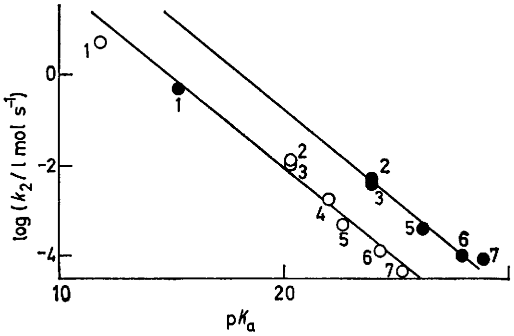

FIGURE 2 Plots of log k_2 for dehydrochlorination of $Ar_2CH{\cdot}CCl_3$ (open circles; data from ref. 7) and $Ar_2CH{\cdot}CHCl_2$ (closed circles; data from ref. 2 and present work) by ^-OMe in MeOH at 30 °C; substituents: 1, p-NO_2; 2, p-Br; 3, p-Cl; 4, p-F; 5, unsubstituted; 6, p-Me; 7, p-MeO

In summary, the β-substituent effect on k_H/k_D for reactions in ^-OMe–MeOH parallels the behaviour found in several reaction systems involving poor leaving groups where the proton might be expected to be more than half transferred,[22,23] whilst the behaviour in Bu^tOK–Bu^tOH parallels that for substituted 9-benzyl-9-trimethylammoniofluorenes with ^-OEt–EtOH where a proton half transferred or less is suggested.[24] The substituent dependence of k_H/k_D in the $ArCHMe{\cdot}NMe_3^+$ series is also in line with this pattern,[25] and since the aryl group is α-bound, k_H/k_D increases with increasing σ in both ^-OEt–EtOH and Bu^tO^-–Bu^tOH.

Mechanisms of Elimination.—In Figure 2 are plotted log k_2 values for carbanion formation from the substrates $Ar_2CH{\cdot}CCl_3$(DDT) (^-OMe–MeOH at 30 °C) against pK_a values referred to dilute aqueous solution as standard state.[8b] A linear plot makes comparison

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[19] (*a*) R. P. Bell, *Chem. Soc. Rev.*, 1974, **3**, 513; (*b*) E. F. Caldin and S. Mateo, *J.C.S. Faraday I*, 1975, 1876.

[20] D. J. McLennan, *J.C.S. Faraday I*, 1975, 1516.

[21] D. W. Earls, J. R. Jones, and T. G. Rumney, *J.C.S. Faraday I*, 1972, 925.

[22] P. J. Smith and A. N. Bourns, *Canad. J. Chem.*, 1974, **52**, 749.

[23] P. J. Smith, C. A. Pollock, and A. N. Bourns, *Canad. J. Chem.*, 1975, **53**, 1319; L. F. Blackwell and J. L. Woodhead, *J.C.S. Perkin II*, 1975, 234; L. F. Blackwell, P. D. Buckley, K. W. Jolly, and A. K. H. MacGibbon, *ibid.*, 1973, 169.

[24] P. J. Smith and S. K. Tsui, *J. Amer. Chem. Soc.*, 1973, **95**, 4760.

[25] P. J. Smith and S. K. Tsui, *Tetrahedron Letters*, 1973, 61.

easier, although a parabola provides a slightly better fit.[1] Also shown is the corresponding Brönsted plot for the reactions of $Ar_2CH{\cdot}CHCl_2$ with ^-OMe–MeOH at 30 °C. Rate constants have been reported[2] and pK_a values are calculated as before,[8] taking $\sigma^*_{CHCl_2} = 1.94$. The correlation coefficients of the two plots are respectively 0.990 and 0.983 (excluding the p-NO_2 point from the $Ar_2CH{\cdot}CHCl_2$ plot for reasons that will be made apparent later). Both have the same slope of 0.364 and the DDD compounds (excluding p-NO_2) are seen to react faster than the DDT compounds, at a given pK_a value, by an average of 1.1 log units (a factor of 13 in rates). This discrepancy is comparatively small * but it can be shown to be significant at the 99.9% confidence level.

Taken at face value, this means that compounds in the DDD series undergo elimination faster than they are calculated to form carbanions. We have claimed that this means they prefer the $E2$ pathway since the leaving chlorine is in a more propitious environment for departure than it is in the DDT series.[2] However, it now seems clear that the tunnel effect is of importance in the DDD series, and it might be thought that, on the basis of the identical slopes of the Brönsted plots, a common E1cB mechanism is in operation, with tunnel-related rate enhancements in the DDD series.

Inferential evidence suggests, however, that this is not so. The isotope effects for the reactions of DDD and $Ph_2CH{\cdot}CCl_3$ (which have roughly the same pK_a value) differ by a factor of only two at 30 °C, and if tunnelling is solely responsible, compounds in the DDD series still react at an enhanced rate. Similarly, it can be shown that deuteron transfers are less subject to tunnelling than are proton transfers and hence accord more closely with classical behaviour.[4a] Plots of log k_D against pK_a are again of equal slope but different intercept for the DDT and DDD series, with the latter reacting faster by an average of 0.5 log units (admittedly not a very reliable figure since the DDD ' plot ' contains only two points).

More direct evidence on this point has been sought in a chlorine isotope effect study reported in a following paper. The conclusion that can be reached for the present results is that the dehydrochlorination of $Ar_2CH{\cdot}CHCl_2$ compounds proceeds by the $E2$ mechanism to the extent of *ca.* 90% and *via* rate-determining carbanion formation in *ca.* 10% of molecular events. The $E2$ transition state must be close to the carbanion extreme for this to be so[10a,b] but this does not necessarily mean that the C_β–H is largely broken, although, as has been discussed in the previous sections, this is likely to be the case. However, the low Brönsted β parameter of 0.364 points to a less than half transferred proton, as is the case with all compounds in the E1cB DDT series.[1] This conclusion must, however, be tempered by the probability that α is a measure of charge delocalization rather than of proton transfer,[8] as a result of the β-carbon centre being substantially pyramidal in the transition state.

We return now to the reaction of $(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CHCl_2$. The log k_2/pK_a point lies on the Brönsted plot for carbanion formation (the DDT series). Furthermore, calculation of log k_T for detritiochlorination by the previously described procedure[8b] shows that this rate is accurately described by the Brönsted equation for carbanion-forming detritioprotonation of fluorene derivatives.[26] The isotope effect is normal, and tunnelling does not seem to be of importance. The value of k_H/k_D is appropriate for a substrate of this pK_a value (15.3) when considered in the context of the DDT series.[1]

These facts lead to the conclusion that introduction of a *para*-nitro-group switches the dehydrochlorination mechanism from predominantly $E2$ to E1cB. A suggestion that systematic changes in substituents will not lead to such a changeover[13] is seen to be unfounded. While the introduction of progressively stronger electron-withdrawing groups on C_β may lead to a less transferred proton in an extremely carbanionic $E2$ transition state[10b,c,22] (in contrast to the earlier predictions of More O'Ferrall,[10a] which are now seen to apply properly only to near-central transition states), it is also predicted that $C_\alpha \cdots X$ bond breaking will decrease, albeit only by a small amount.[10] If that bond is not much broken in the first place, as here, it is not difficult to imagine that the introduction of a substituent as powerful as p-NO_2 could cause the transition state to be reached without any C_α–X rupture. The $Ar_2CH{\cdot}CHCl_2$ system thus appears to represent the first example of a changeover from $E2$ to E1cB elimination induced by a change in substituent on a β-bound aryl ring. For reasons associated with the mechanistic switch, we do not claim that the variable isotope effects in Table 1 represent an observation of an isotope effect maximum.

EXPERIMENTAL

Materials.—Samples of DDD and [^{2}H]DDD were available from the previous study, as was 1,1-dichloro-2,2-diphenylethane.[2] The deuteriated analogue of the latter was prepared in the usual way[2,8] by reduction ($LiAlD_4$) of 1,1-dichloroacetophenone[27] (Aldrich) followed by condensation of the resulting 1,1-dichloro-2-phenyl[2-^{2}H]ethanol with benzene in conc. H_2SO_4. Mass spectrometry indicated 98.6% deuteriation at C-1 in $Ph_2CD{\cdot}CHCl_2$. Rate constants were appropriately corrected. The protio- and deuterio-*para*-nitro-derivatives were prepared by nitrating[28] $Ph_2CH{\cdot}CHCl_2$ and $Ph_2CD{\cdot}CHCl_2$, respectively.

Kinetics.—The usual spectrophotometric procedures were employed for reactions in MeOH.[2,8] Depending on the rate, [NaOMe] was varied between 0.23 and 0.42M, but k_2 is known to be insensitive to base concentration in this range.[2] In all pairs of runs involving a given substrate and

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* The discrepancy becomes larger if the rate constants are adjusted to take into account the number of chlorine atoms potentially available for elimination.

[26] A. Streitwieser, W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

[27] R. Nouri-Bimorghi, *Bull. Soc. chim. France*, 1965, 3178.

[28] D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1972, 279.

its deuterio-analogue, identical base concentrations were employed. Dehydrochlorinations of the *para*-nitro-compounds were examined using methanolic NaOAc–HOAc buffers containing NaOAc (0.100M) and HOAc (0.005 2—0.083M). The data were analysed as before[1] to obtain k_{OMe} and k_{OAc}, the respective rate constants for $^{-}$OMe and $^{-}$OAc attack. The former were subject to a ±2% uncertainty, but errors involved in extrapolating plots of k_{ψ} *vs.* $[\mathrm{HOAc}]^{-1}$ to $[\mathrm{HOAc}]^{-1} = 0$ lead to errors of *ca.* 10% in k_{OAc}. The recorded values of the latter are (in l mol^{-1} s^{-1}): for $(p\text{-}NO_2{\cdot}C_6H_4)_2CH{\cdot}CHCl_2$, $(6.3 \pm 0.6) \times 10^{-6}$ (30 °C) and $(1.43 \pm 0.16) \times 10^{-5}$ (45 °C); for $(p\text{-}NO_2{\cdot}C_6H_4)_2CD{\cdot}CHCl_2$, $(1.65 \pm 0.13) \times 10^{-6}$ (30 C°) and $(4.0 \pm 0.5) \times 10^{-6}$ (45 °C).

Solutions of NaOMe in MeOH–Me_2SO mixtures were made up by pipetting methanolic 0.08M-NaOMe (25 ml) into a weighted volumetric flask (50 ml), reweighing, adding an accurately known weight of purified Me_2SO, and allowing the mixture to come to room temperature before making up to the mark with an accurately known weight of MeOH. Solutions of substrate were made up separately using the same proportions of MeOH and Me_2SO in the solvent. Reactions were initiated by mixing equal volumes of base and substrate solutions, and were followed at 270 nm using a solvent blank of the same MeOH–Me_2SO composition. The small quantity of NaOMe was ignored in calculating methanol molarities for the $H_{-} + \log [\mathrm{MeOH}]$ plot. The product olefin, $Ph_2C{:}CHCl$ underwent slow decomposition in the basic 27.35 mole % dimethyl sulphoxide solution (presumably giving diphenylacetylene), but the amount of decomposition occurring during 10 half-lives of the dehydrochlorination (*ca.* 5 h) was negligible.

No detectable $Ph_2CH{\cdot}CHCl_2$ was produced by hydrogen exchange when a reaction mixture containing $Ph_2CD{\cdot}CHCl_2$ and $^{-}$OMe in 27·35 mole % Me_2SO in MeOH was set aside for about one half-life. A carbon tetrachloride extract examined by n.m.r. under conditions where 3% $Ph_2CH{\cdot}CHCl_2$ would have been visible showed only resonances corresponding to $Ph_2CD{\cdot}CHCl_2$ and $Ph_2C{:}CHCl$.

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