# Chloride-ion Promoted Dehydrochlorination of 1,1-Diaryl-2,2,2-trichloroethanes in Dipolar Aprotic Solvents [1]

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Rate constants are reported for the second-order dehydrochlorination reactions of $Ar_2CH\cdot CCl_3$ compounds promoted by $Bu^n{}_4NCl$ in acetone and by LiCl in dimethylformamide. Rate data for the dehydrochlorination reactions of $Ar(Ph)CH\cdot CCl_3$ compounds in the latter system are also presented. A modified Hammett-equation analysis yields $\rho$ values of 1·31 (acetone) and 0·99 (dimethylformamide). It is considered that these parameters are diagnostic of a significant degree of β-carbanionic character in the *E*2 transition states, and that the system provides the first clear example of a halide-promoted *E*2H reaction. The *E*2C mechanism can be definitely rejected for this particular case.

SECOND-ORDER olefin-forming eliminations of organic halides and sulphonate esters do not necessarily require the agency of a strong base. Weakly basic systems such as halide ions in dipolar aprotic solvents [1-9] and thiolate ions in both protic [10] and dipolar aprotic [3-5,8,9] solvents are often more effective in promoting such eliminations than are conventionally strong bases such as alkoxide ions in alcohol.

A controversy has arisen as to the nature of the transi-

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[1] Preliminary communication, D. J. McLennan and R. J. Wong, *Tetrahedron Letters*, 1970, 881.

[2] S. Winstein, Accad. Nazionale di Lincei (Roma), VIII Corso Estivo di Chimica, Chimica Teorica, 1965, 327.

[3] G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4735.

[4] G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, 1970, **92**, 115.

[5] A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Letters*, 1968, 2113.

[6] D. J. Lloyd and A. J. Parker, *Tetrahedron Letters*, 1968, 5183.

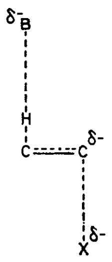
[7] D. J. Lloyd and A. J. Parker, *Tetrahedron Letters*, 1970, 5029.

[8] R. Alexander, E. F. C. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, 1968, **90**, 5049.

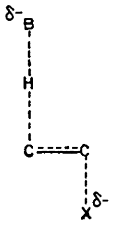
[9] E. F. C. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, 1968, **90**, 6647; A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *ibid.*, 1972, **94**, 2228; G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, 2235; P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *ibid.*, 2240; P. Beltrame, A. Ceccon, and S. Winstein, *ibid.*, p. 2315.

[10] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1956, 41; D. J. McLennan, *J. Chem. Soc. (B)*, 1966, 705, 709; J. F. Bunnett and E. Bachiocci, *J. Org. Chem.*, 1967, **32**, 11.

tion state in eliminations promoted by weak bases. One view [1] is that the transition states belong to the normal [11] $E2$H spectrum of $E2$ transition states (I)—(III)



(I)



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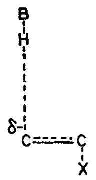
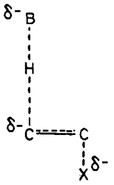
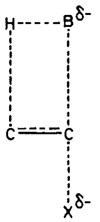


(III)

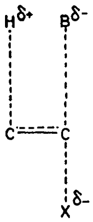
whilst Winstein, Parker, and their co-workers believe that a further dimension must be added to this spectrum.[2-9] Noting that the weak bases in question are also strong carbon nucleophiles, they suggest that bonding interaction between the base and $C_\alpha$ must be invoked in order to compensate for the relative lack of hydrogen basicity, and have suggested an $E2$H—$E2$C spectrum (IV)—(VI) in which the weak bases utilize the $E2$C-like transition states (V) and (VI) with suitable substrates.



(IV)



(V)



(VI)

They characterize $E2$C-like transition states as having well-developed double bonds, with most of the charge residing on B and X and with little if any charge at $C_\alpha$ and $C_\beta$ (' loose ' transition states).

However the picture is incomplete. The substrates that have so far been investigated with respect to halide-promoted eliminations are those (mainly secondary and tertiary alkyl halides and arenesulphonates) which would, under $E2$H conditions (alkoxide ions in alcohol) be predisposed to react *via* paenecarbonium [11] transition states such as (I). We do not imply deliberate omission, for the fact is that the weak bases of interest do not usually promote olefin formation from the more ' acidic ' substrates that would be expected to react through paenecarbanion transition states (III) under $E2$H conditions. For instance, the 2-arylethyl system $Ar{\cdot}CH_2{\cdot}CH_2{\cdot}X$ has been widely employed for $E2$H investigations and transition-state character appears to vary from central (II) to paenecarbanion (III) depending on the choice of base, solvent, and leaving group.[12] However the reaction of 2-phenethyl bromide with benzenethiolate ions in ethanol yields only the product of nucleophilic substitution.[13]

The dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethanes (DDT-type compounds) with strong bases in protic solvents has been held to proceed *via* paenecarbanion $E2$H transition states.[14,15] We have previously found that benzenethiolate ions also promote these reactions, although at a slow rate, as the multiplicity of halogens at $C_\alpha$ retards possible competition by $S_N2$ reactions.[15] With this fact in mind, the late B. D. England and his students investigated the reaction between 1,1,1-trichloro-2,2-bis-*p*-chlorophenylethane (DDT) and chloride ions (from tetra-n-butylammonium chloride) in acetone and found that dehydrochlorination occurred.[16] Kinetics were of the second order when 2,6-lutidine was used to scavenge eliminated HCl. Substitution reactions that may be occurring in competition with the elimination are of course invisible in this system and do not consume the substrate.

We now take up the question of the mechanism of this $E2$ reaction between halide ions and an ' acidic ' substrate. Our recent Hammett $\rho$–$\sigma$ analysis of the reaction between $Ar_2CH{\cdot}CCl_3$ compounds and benzenethiolate ions in ethanol gave results which suggested an $E2$H process, with the transition state having somewhat less carbanionic character than that for ethoxide-promoted elimination.[17] We now apply the same method to the reactions of $Ar_2CH{\cdot}CCl_3$ compounds with chloride ions.

In fact there is now good evidence, arising from comparison of the measured elimination rate constant with an interpolated rate constant for deprotonation, that both the reactions of $OR^-$ in ROH and of $PhS^-$ in EtOH proceed *via* an $E1cB$ mechanism [18] involving the intermediacy of an irreversibly-formed carbanion.[19] Our previous basic conclusion, to the effect that these reactions possessed carbanion-like transition states, is thus unaltered, but comparison of Hammett $\rho$ values for the chloride-promoted and alkoxide-promoted reactions [1] is now invalid.

## RESULTS

The reactions between DDT-type compounds (VII) and $Bu^n{}_4NCl$ in dry acetone displayed the stoicheiometry of equation (1) when excess of 2,4,6-collidine was used as an

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[11] J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; J. F. Bunnett, ' Survey of Progress in Chemistry,' ed. A. E. Scott, Academic Press, New York, vol. 5, 1969, p. 53.

[12] *E.g.*, C. H. De Puy and C. A. Bishop, *J. Amer. Chem. Soc.*, 1960, **82**, 2352; W. H. Saunders and D. H. Edison, *ibid.*, p. 138; R. Baker and M. J. Spillett, *J. Chem. Soc.* (*B*), 1969, 481.

[13] F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1928, 1791.

[14] (*a*) S. J. Cristol, *J. Amer. Chem. Soc.*, 1945, **67**, 1494; (*b*) S. J. Cristol, N. L. Hanse, A. J. Quant, H. W. Miller, K. R. Eiler, and J. S. Meek, *ibid.*, 1952, **74**, 3333.

[15] B. D. England and D. J. McLennan, *J. Chem. Soc.* (*B*), 1966, 696.

[16] B. D. England, P. Ang, and P. R. Fawcet, unpublished results; P. Ang (1968), and P. R. Fawcet (1969), M.Sc. Theses, Victoria University of Wellington.

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

[18] D. J. McLennan, *Quart. Rev.*, 1967, **21**, 490.

[19] D. J. McLennan and R. J. Wong, *Tetrahedron Letters*, 1972, 2887, 2891.

HCl scavenger. The hindered base has no effect on the rate constants[16] but the reaction proceeds to equilibrium

$$\underset{\text{(VII)}}{(p\text{-}RC_6H_4)_2CH{\cdot}CCl_3} + Cl^- \longrightarrow \underset{\text{(VIII)}}{(p\text{-}RC_6H_4)_2C{:}CCl_2} + HCl + Cl^- \quad (1)$$

a; R = OMe
b; R = Me
c; R = H
d; R = F

e; R = Cl
f; R = Br
g; R = $NO_2$

rather than to completion in its absence. All reactions obeyed first-order kinetcs: rate = $k_{obs}[Ar_2CH{\cdot}CCl_3]$, up to about one half-life, consistent with the collidinium chloride existing as tight ion-pairs, so that the concentration of free chloride ion does not change during the reaction.[20] After allowance is made for small and regular salt effects, second-order rate coefficients calculated from $k_2 = k_{obs}/[Cl^-]_0$ are in fact constant. All further runs were carried out at the same initial salt concentration. The requisite olefins (VIII) were isolated in good yield from all runs and their identity established by comparison with authentic samples.[17]

After about one half-life has elapsed for the slower reactions, $k_{obs}$ values begin drifting downwards. This behaviour has been observed in similar systems and has been attributed to acid-catalysed condensation reactions of acetone.[20] Hence the second-order rate constants in Table 1 apply to the first 50% of reaction.

TABLE 1

Rate constants[a] for the reaction of $(p\text{-}RC_6H_4)_2CH{\cdot}CCl_3$ compounds (*ca.* 0·02M) with $Bu^n{}_4NCl$ (*ca.* 0·01M) in acetone[b] at 65 °C

| R | MeO | Me | H | Cl | Br | $NO_2$ |
|---|---|---|---|---|---|---|
| $10^5k_2$/l mol$^{-1}$ s$^{-1}$ | 8·11 | 7·62 | 15·0 | 83·8 | 113 | 1430 |

[a] Mean of two or more concordant runs. [b] 2,4,6-Collidine (*ca.* 0·02M) present.

The above reactions were also studied with lithium chloride as the base in dimethylformamide solvent. At the concentration used, LiCl is about 90% dissociated.[21] The stoicheiometry was as in equation (1). It was not necessary to add an HCl scavenger as dry hydrogen chloride in dimethylformamide did not react with olefin (VIIIe) during a period equivalent to several half-lives of the dehydrochlorination of (VIIe). The dehydrochlorination was expected to be autocatalytic[4] with kinetics given by equations (2) and (3) in which *a* is the initial concentration

$$dx/dt = k_2'(a - x)(a + x) \quad (2)$$

$$k_2' = \frac{1}{2at}\ln\frac{a + x}{a - x} \quad (3)$$

of both substrate and LiCl and *x* is the concentration of olefin at time *t*. However, values of the second-order rate coefficient $k_2'$ so calculated drifted downwards during all runs. Second-order rate coefficients calculated on the assumption of no autocatalysis were also not constant, and it was assumed that the drift was caused by somewhat imperfect autocatalysis.

In correcting the drifting $k_2'$ values from equation (3) we assume that only free chloride ions are catalytically active, and that some equilibrium process consequent to the dehydrochlorination partially deactivates liberated chloride ions. The process could be that in equation (4) in which the $Me_2N{\cdot}CHO,HCl$ complex is presumed to exist as both free ions and a hydrogen-bonded complex or ion-pairs. If the equilibrium constant for reaction (4) is *K*, we can modify the $(a + x)$ term in equation (3) so that it refers to the

$$Me_2N{\cdot}CHO,H^+Cl^- \rightleftharpoons Me_2N{\cdot}CHO,H^+ + Cl^- \quad (4)$$

concentration of free chloride ions rather than to the total chloride concentration. The pertinent rate equation is thus (5) which on integration yields equations (6) or (7). In these equations, $k_2$ is the true second-order rate constant. It can easily be shown that $k_2 > k_2'$ for all *x*, $(a > x)$, so that $k_2'$ should indeed drift downwards. The true $k_2$ values

$$\frac{dx}{dt} = k_2\frac{(a - x)(a + x)K}{K + x} \quad (5)$$

$$k_2 = \frac{1}{2at}\ln\frac{a + x}{a - x} + \frac{1}{Kt}\ln\frac{a}{a^2 - x^2} \quad (6)$$

$$k_2 = k_2' + \frac{1}{Kt}\ln\frac{a}{a^2 - x^2} \quad (7)$$

were therefore calculated from equation (7) by an iterative procedure which employs the drifting $k_2'$ values and calculates the value of *K* necessary for constancy of $k_2$. The *K* needed for convergence should be independent of the substrate and this was found to be the case, within the bounds of the rather large error engendered by the smallness of the drift in $k_2'$. *K* values for convergence ranged between 0·5 and 0·9 mol l$^{-1}$ and a mean value of 0·7 mol l$^{-1}$, calculated from data for 17 substrates, was finally employed in the calculations for all substrates. A specimen run is shown in Table 2.

TABLE 2

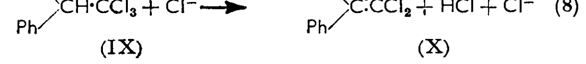
Kinetics of the reaction between $(p\text{-}MeOC_6H_4)_2CH{\cdot}CCl_3$ (0·0200M) and LiCl (0·0200M) in dimethylformamide at 65 °C

| Time/min | Absorbance[a] | $10^5k_2'$[b]/l mol$^{-1}$ s$^{-1}$ | $10^5k_2$[c]/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 0 | 0·154 | | |
| 1200 | 0·262 | 8·51 | 9·40 |
| 2580 | 0·370 | 8·04 | 9·73 |
| 3180 | 0·401 | 7·50 | 9·32 |
| 4110 | 0·450 | 7·04 | 9·10 |
| 5460 | 0·520 | 6·70 | 9·15 |
| 6160 | 0·541 | 6·33 | 8·79 |
| 7320 | 0·608 | 6·44 | 9·41 |
| 8760 | 0·650 | 6·02 | 9·08 |
| 10,140 | 0·673 | 5·52 | (8·48) |
| ∞ | 1·040 | | |

Mean[d] $k_2 = (9{\cdot}25 \pm 0{\cdot}28) \times 10^{-5}$ l mol$^{-1}$ s$^{-1}$.

[a] U.v. absorbance of sample, diluted 250-fold with methanol, at 283 nm. [b] Observed second-order rate constant, calculated from equation (9) (Experimental section). [c] Calculated from equation (7) by use of the appropriate $k_2'$ value and $K = 0{\cdot}7$ mol l$^{-1}$. [d] Uncertainty expressed as standard deviation.

Also investigated were the reactions of substrates having only one *para*-substituted benzene ring [equation (8)].



$$(p\text{-}RC_6H_4)(Ph)CH{\cdot}CCl_3 + Cl^- \longrightarrow (p\text{-}RC_6H_4)(Ph)C{:}CCl_2 + HCl + Cl^- \quad (8)$$

(IX)
a; R = OMe
b; R = Me
c; R = F

(X)
d; R = Cl
e; R = Br

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

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

Unfortunately we were unable to prepare the *para*-nitro-compound by our standard method. The unsymmetrically disubstituted compound 1,1,1-trichloro-2-*p*-chlorophenyl-2-*p*-methoxyphenylethane (XI) was also subjected to dehydrochlorination with LiCl in dimethylformamide. All rate constants for this base–solvent system are shown in Table 3.

TABLE 3

Rate constants [a] for the reaction of $(p\text{-}YC_6H_4)(p\text{-}ZC_6H_4)\text{-}CH{\cdot}CCl_3$ compounds (*ca.* 0·02M) with LiCl (*ca.* 0·02M) in dimethylformamide at 65 °C

| Y | Z | $10^5k_2$/l mol$^{-1}$ s$^{-1}$ | λ [d]/nm |
|---|---|---|---|
| MeO | MeO | 9·66 | 283 |
| Me | Me | 5·29 | 262 |
| H | H | 9·90 [b] | 250 |
| F | F | 25·2 | 248 |
| Cl | Cl | 55·2 [c] | 260 |
| Br | Br | 36·3 | 277 |
| $NO_2$ | $NO_2$ | 406 | 305 |
| H | MeO | 8·64 | 270 |
| H | Me | 7·94 | 255 |
| H | F | 17·6 | 250 |
| H | Cl | 23·0 | 255 |
| H | Br | 24·1 | 255 |
| Cl | MeO | 19·5 | 265 |

[a] Mean of two or more concordant runs. [b] Runs at other temperatures establish $\Delta H^‡ = 21{\cdot}8$ kcal mol$^{-1}$; $\Delta S^‡ = -14{\cdot}7$ cal mol$^{-1}$ K$^{-1}$. [c] Runs at other temperatures establish $\Delta H^‡ = 22{\cdot}5$ kcal mol$^{-1}$; $\Delta S^‡ = -10{\cdot}1$ cal mol$^{-1}$ K$^{-1}$. [d] Wavelength used for spectrophotometric kinetics.

It was found that $(p\text{-}ClC_6H_4)_2CH{\cdot}CHCl_2$ (DDD) was quite unreactive when refluxed in acetone containing $Bu^n{}_4NCl$ and 2,4,6-collidine for 5·5 h. No olefin could be isolated or detected. We therefore estimate that the DDT : DDD rate ratio is at least 70 (per chlorine) at 65 °C.

## DISCUSSION

*Reactions in Acetone.*—A Hammett plot of log $k_2$ against 2σ with use of the results in Table 1 is not satisfactorily linear (Figure 1). The least-squares parameters are: ρ = 1·16; *r* (correlation coefficient) = 0·981; *s* (standard deviation in slope) = 0·19. We have noted almost identical behaviour previously,[17] and following our earlier analysis and one employed by Cockerill and Lamper,[22] we find that optimum linearity is obtained by plotting log $k_2$ against $2\sigma_I + 1{\cdot}45\sigma_R$, whence ρ = 1·31, *r* = 0·998, *s* = 0·03 (Figure 2). The causes of this non-additivity of substituent effects have been discussed.[17,22]

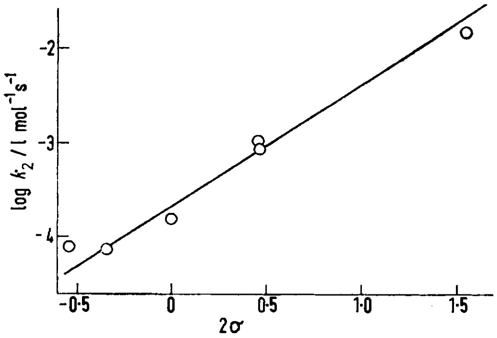

FIGURE 1 Hammett plot for the reaction between $Ar_2CH{\cdot}CCl_3$ compounds and $Bu^n{}_4NCl$ in acetone

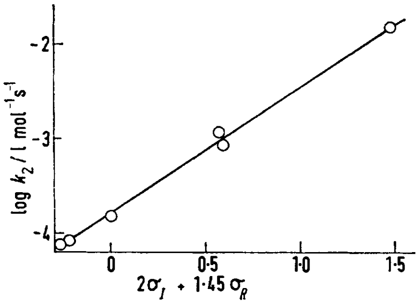

FIGURE 2 Modified Hammett plot for the reaction between $Ar_2CH{\cdot}CCl_3$ compounds and $Bu^n{}_4NCl$ in acetone

We have previously estimated that a Hammett ρ of *ca.* 0·5 would be appropriate for the *E*2C dehydrohalogenation of a β-aryl substituted halide.[1,17] To the examples cited in support of this figure can be added the ρ value of 0·48 for the bromide-promoted dehydrobromination of 1-aryl-2-bromopropanes in acetone.[23] Thus our ρ of 1·31 is significantly different from those for *E*2C-like processes. It is also significantly different from that for the *E*1cB dehydrochlorination [19] of $Ar_2CH{\cdot}CCl_3$ compounds by ethoxide in ethanol (2·34 at 65 °C).[14] The obvious interpretation is that while the transition state for the chloride-promoted reaction is *E*2H-like, and has carbanionic charge at $C_\beta$, it is not as carbanionic as the transition state in the *E*1cB ethoxide-promoted reaction. A consequence of this interpretation is that an increase in basicity might shift the character of *E*2H transition states towards the paenecarbanion extreme, and while current theory is ambiguous on this point,[24] recent results of Yano and Oae [25] indicate that, for the $ArSO_2{\cdot}CH_2{\cdot}CH_2{\cdot}Cl$–amine system at least, this is the case. One conclusion that can be drawn however is that the chloride-promoted reactions are not *E*1cB, as the ρ values seem to be too small to permit consideration of this process.

Can the present results be accommodated within the framework of the *E*2C spectrum? A superficially attractive explanation is available when it is recalled that *E*2C-like transition states are believed to be largely olefinic in character,[2-4] with $C_\alpha$ and $C_\beta$ hybridization being nearly $sp^2$. The dipole–dipole repulsion energy between two identical aryl groups on $C_\beta$ having parallel dipoles should be relieved in an $sp^2$-like transition state relative to an $sp^3$ initial state, and so all of the $Ar_2CH{\cdot}CCl_3$ compounds should be more reactive than the unsubstituted compound. This is not quite the case (Table 1) but the poorness of the unadorned Hammett plot could be a result of the superimposition of such

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[22] A. F. Cockerill and J. E. Lamper, *J. Chem. Soc.* (*B*), 1971, 503.

[23] D. J. Lloyd, Ph.D. Thesis, Australian National University, 1971.

[24] L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 6149; R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274.

[25] Y. Yano and S. Oae, *Tetrahedron*, 1970, **26**, 27.

dipole–dipole effects on the small electronic effect expected for an *E*2C reaction. The question of the *E*2H as opposed to the *E*2C explanation is resolved in the next section.

Similarly the greater reactivity of $\mathrm{Ar_2CH{\cdot}CCl_3}$ than of $\mathrm{Ar_2CH{\cdot}CHCl_2}$ reactivity order may be interpreted qualitatively in terms of both *E*2H and *E*2C mechanisms.[17] However, theoretical calculations involving estimation of steric interactions between non-reacting chlorine atoms and hydrogen atoms in the transition state give results which are not in accord with an *E*2C transition state.

*Reactions in Dimethylformamide.*—In order to resolve the above ambiguity, we have attempted to evaluate the ' true ' electronic effect on the system by carrying out a Hammett equation study of the dehydrochlorination of monosubstituted $\mathrm{Ar(Ph)CH{\cdot}CCl_3}$ compounds using LiCl in dimethylformamide. The dipole–dipole repulsion factor should be much less important in this series. As usual an unmodified Hammett plot of log $k_2$ against $\sigma$ poorly fits the data ($\rho = 0{\cdot}88$, $r = 0{\cdot}938$, $s = 0{\cdot}17$), but an excellent plot of log $k_2$ against $\sigma_I + 0{\cdot}67\sigma_R$ yields the following parameters: $\rho = 1{\cdot}10$, $r = 0{\cdot}997$, $s = 0{\cdot}03$. The $\rho$ value is a little lower than that for the reaction in acetone but it is still larger than that expected to apply to the electronic substituent effect on an *E*2C reaction. In support of our contention that rate changes in the $\mathrm{Ar_2CH{\cdot}CCl_3}$ system represent primarily an electronic effect is the observation that a plot of log $k_2$ against $\Sigma\sigma_I + 0{\cdot}67\Sigma\sigma_R$ for both the $\mathrm{Ar_2CH{\cdot}CCl_3}$ and $\mathrm{Ar(Ph)CH{\cdot}CCl_3}$ systems is clearly linear (Figure 3), whence $\rho = 0{\cdot}99$, $r = 0{\cdot}997$, $s = 0{\cdot}03$. That the rate constants for both monosubstituted and disubstituted derivatives fit the same linear free-energy relationship means that dipole–dipole repulsion effects in the latter series can be of only minor importance. It is also noteworthy that log $k_2$ for the unsymmetrically disubstituted compound (XI) lies on this line. The inductive and resonance effects of the methoxy- and chloro-substituents are clearly governing the reactivity of this compound relative to the unsubstituted compound. If however dipole–dipole repulsions in an *E*2C transition state as opposed to those in the initial state were the most important determinants of reactivity, it could be expected that (XI) would be less reactive than the unsubstituted compound.* This is not so (Table 3) and the $\rho$ values of 1·31 (acetone) and 0·99 ($\mathrm{Me_2N{\cdot}CHO}$) thus primarily represent electronic effects. Our assignment of carbanionic *E*2H transition states to the chloride-promoted eliminations is thus in order.

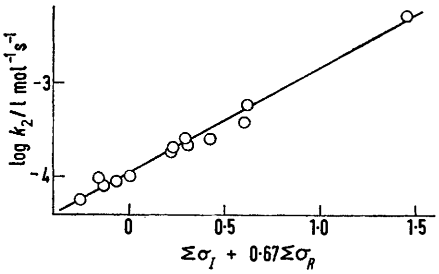

FIGURE 3 Modified Hammett plot for the reactions between ($p$-$\mathrm{YC_6H_4}$)($p$-$\mathrm{ZC_6H_4}$)$\mathrm{CH{\cdot}CCl_3}$ compounds and LiCl in dimethylformamide

It follows that chloride ions in dipolar aprotic solvents are sufficiently strong as bases in the kinetic sense (hydrogen nucleophiles) to promote *E*2H elimination from suitable acidic substrates. This should not be surprising as chloride ion acts as a base (thermodynamically) in dimethylformamide [26] although it is quite weak. It would be surprising however to observe an *E*2H reaction promoted by chloride ions in protic solvents. There is a danger in equating thermodynamic basicity (or the lack of it) with hydrogen nucleophilicity (or the lack of it) in proton transfer reactions,[27,28] and the extension of this warning to *E*2 reactions, where the transfer is coupled to other bond-making and bond-breaking processes, is clear even for *E*2H reactions involving conventionally strong bases in protic solvents.[29] It is thus not sufficient to cite the comparatively low basicity of halide ions as *prima facie* evidence for the non-operation of *E*2H mechanisms in any particular case. Winstein and Parker have clearly pointed out that substrate acidity is also a factor in determining where a transition state should lie on the *E*2H–*E*2C spectrum [3] but of course when acidic substrates such as DDT are involved, halide ions in dipolar aprotic solvents are inferior to alkoxide ions in alcohol as dehydrohalogenating agents.

## EXPERIMENTAL

*Materials.*—Acetone and dimethylformamide were purified and dried by standard methods. Anhydrous LiCl was recrystallized from dry acetone. $\mathrm{Bu^n{}_4NCl}$ was precipitated from a cold dry acetone solution by addition of ether and was recrystallized from dry acetone. Potentiometric titration for chloride ion indicated a purity of 99·1%. All operations involving this salt were performed under nitrogen in a dry-box. Commercial 2,4,6-collidine was distilled from KOH pellets and fractionally distilled. The preparation and properties of substrates (VIIa—g), 1,1-dichloro-2,2-bis-*p*-chlorophenylethane, the olefins (VIIIa—g), and the olefin 2-chloro-1,1-bis-*p*-chlorophenylethene have been described.[17]

2,2,2-Trichloro-1-phenylethanol was prepared by the method of Galun and Kalir.[30] Condensation of bromobenzene and chlorobenzene with this alcohol as described [30] yielded compounds (IXe) and (IXd) respectively. Addition of concentrated sulphuric acid to a mixture of the alcohol and toluene at 0 °C and stirring for 6 h produced the *p*-tolyl

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* This experiment was kindly suggested to us by Dr. A. J. Parker.

[26] B. W. Clare, D. Cook, E. F. C. Ko, Y. 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.

[27] J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271; J. F. Bunnett and L. A. Retallick, *J. Amer. Chem. Soc.*, 1967, **89**, 423.

[28] R. A. Firestone, *J. Org. Chem.*, 1971, **36**, 702.

[29] R. J. Anderson, P. Ang, B. D. England, V. H. McCann, and D. J. McLennan, *Austral. J. Chem.*, 1969, **22**, 1427.

[30] A. B. Galun and A. Kalir, *Org. Synth.*, 1968, **48**, 27.

derivative (IXb), which was recrystallized from ethanol. A similar method was employed for the *p*-fluoro-compound (IXc) by use of fluorobenzene. Chromatographic separation of the crude product on silica gel was followed by recrystallization from ethanol.

The method of Reeve and Fine [31] was used to prepare 2,2,2-trichloro-1-*p*-methoxyphenylethanol from *p*-anisaldehyde, chloroform, and potassium t-butoxide in t-butyl alcohol. The product was recrystallized from benzene and had m.p. 58—60 °C (lit.,[32] m.p. 55—56 °C). A solution of the alcohol (5 g) in benzene (10 ml) was added dropwise to a cooled and stirred mixture of benzene (20 ml) and concentrated $H_2SO_4$ (25 ml) during 1 h. The mixture was stirred for a further 15 min and was then poured on ice. The crude oil obtained after ether extraction and solvent evaporation was chromatographed on a silica gel column with n-hexane for development and elution. After recrystallization from ethanol a yield of 11·5% of compound (IXa) was obtained.

The major product appeared to be a trimeric compound, 1-methoxy-2-(2,2,2-trichloro-1-*p*-methoxyphenylethyl)-4-(2,2,2-trichloro-1-phenylethyl)benzene, m.p. 184—188 °C, δ 3·73 (3H, s, MeO); 3·76 (3H, s, MeO); 5·05 (1H, s, benzylic); 5·67 (1H, s, benzylic); 6·7—7·8 (12H, m, aromatic) (Found: C, 51·7; H, 3·7; Cl, 38·6. Calc. for $C_{24}H_{20}Cl_6O_2$: C, 52·1; H, 3·6; Cl, 38·5%). This compound may be formed by attack of the carbonium ion derived from the alcohol at a ring position *ortho* to the methoxy-group of another alcohol molecule, followed by normal condensation with benzene. The unsymmetrically disubstituted compound (XI) was prepared in exactly the same manner as compound (IXa) except that chlorobenzene was used in place of benzene.

Attempted preparations of 1,1,1-trichloro-2-*p*-nitrophenyl-2-phenylethane by condensation of benzene with 2,2,2-trichloro-1-*p*-nitrophenylethanol [32] were unsuccessful.

Samples of product olefins were obtained by dissolving the diaryltrichloroethanes (0·4 g) in ethanol (50 ml) containing dissolved KOH (0·6 g) and allowing reaction to proceed for 48 h at room temperature. The olefins were isolated after normal work-up and recrystallized from ethanol. Data for the substrates are in Table 4, properties of the olefinic products are shown in Table 5, and Table 6 gives microanalytical results for new compounds. M.p.s are uncorrected.

TABLE 4

M.p.s and n.m.r. spectra of substituted DDT-type compounds

| Compound | M.p./°C | Lit. m.p./°C (ref.) | δ [a] |
|---|---|---|---|
| (IXa) | 50—51·5 | | 5·00 [b] |
| (IXb) | 81—82·5 | 72·5 (*d*) | 5·02 [c] |
| (IXc) | 53—55 | 50—52 (*e*) | 5·02 |
| (IXd) | 78—79 | 77—77·5 (14*a*) | 5·02 |
| (IXe) | 99—100 | 95—96 (30) | 5·00 |
| (XI) | 104—106 | | 4·98 [f] |

[a] Chemical shift of benzylic proton downfield from tetramethylsilane in p.p.m. ($CDCl_3$ solvent). [b] Also methoxy-proton resonance at δ 3·78. [c] Also methyl proton resonance at δ 2·32. [d] F. D. Chattaway and R. J. K. Muir, *J. Chem. Soc.*, 1934, 701. [e] I. E. Balaban and F. K. Sutcliffe, B.P., 597,091, 1948 (*Chem. Abs.*, 1949, **43**, 350i). [f] Also methoxy-proton resonance at δ 3·75.

*Kinetics*.—The reactions between $Ar_2CH{\cdot}CCl_3$ compounds and $Bu^n{}_4NCl$ in acetone were followed by acid–base titration (Radiometer titrigraph) for the liberated acid. The reaction mixture was contained in sealed ampoules which were cooled and opened at various times, and the contents washed into water. Organic material was quantitatively extracted with carbon tetrachloride before titration.

TABLE 5

Dehydrochlorination products of substituted DDT-type compounds

| Olefin | M.p./°C | Lit. m.p./°C (ref.) | $\lambda_{max.}$ [a]/nm | log ε [b] |
|---|---|---|---|---|
| (Xa) | 84—85·5 | | 247 | 4·124 |
| (Xb) | 89—90 | 87·5 (*c*) | 243 | 4·155 |
| (Xc) | 54·5—55·5 | | 245 | 4·120 |
| (Xd) | 109—110 | 110—111 (*d*) | 243 | 4·167 |
| (Xe) | 112—113 | 113 (*c*) | 244 | 4·187 |
| (XII) [e] | 58—60 | | 251 | 4·236 |

[a] U.v. maximum in nm above 220 nm, in EtOH. [b] Molar extinction coefficient. [c] Ref. *d* of Table 4. [d] E. E. Fleck and H. L. Haller, *J. Amer. Chem. Soc.*, 1944, **66**, 2095. [e] 1,1-dichloro-2-*p*-chlorophenyl-2-*p*-methoxyphenylethylene.

TABLE 6

Microanalytical results for new compounds

| | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|
| Compound | C | H | Cl | C | H | Cl |
| (IXa) | 57·2 | 4·3 | | 57·1 | 4·2 | 38·7 |
| (XI) | 51·3 | 3·4 | | 51·5 | 3·4 | 45·1 |
| (Xa) | 64·4 | 4·5 | 25·2 | 64·5 | 4·3 | 25·4 |
| (Xd) | 63·0 | 3·5 | 26·3 | 63·0 | 3·4 | 26·5 |
| (XII) | 57·8 | 3·7 | 33·6 | 57·5 | 3·5 | 33·9 |

The reactions involving LiCl in dimethylformamide were followed spectrophotometrically. The reaction mixture (5 ml samples) was contained in sealed ampoules, which were opened at various times, and 1 ml was pipetted into a 250 ml volumetric flask containing redistilled methanol. The solution was made up to the mark with methanol and the u.v. absorbance of a sample of this solution was measured with a Shimadzu QV50 spectrophotometer. Blank solutions were prepared by dissolving 1 ml of dimethylformamide in methanol and making up to 250 ml. The wavelengths chosen for each compound were close to those of maximum absorption of the corresponding product olefin, but in all cases the substrate had non-negligible absorbance at these wavelengths. If $A_0$, $A_t$, and $A_\infty$ are the respective absorbances at time = 0, *t*, and infinity respectively, equation (3) can be modified [33] to (9). The latter was used in calculating individual values of $k_2'$. Equation (8) was similarly modified to allow calculation of $k_2$ directly from the absorbance

$$\frac{1}{2a}\ln\frac{A_\infty + A_t - 2A_0}{A_\infty - A_t} = k_2{}'t \qquad (9)$$

data. The u.v. spectra of all infinity samples were identical to those of the authentic olefins. In several cases the product was isolated from an ' infinity ' ampoule and its identity confirmed by m.p. and mixed m.p. with an authentic sample. When olefin (VIIIe) (*ca.* 0·02M) and dry hydrogen chloride (*ca.* 0·02M) in dimethylformamide were mixed and left at 65 °C for several days, no change in u.v. absorbance at 245 nm was observed.

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[31] W. Reeve and L. W. Fine, *J. Org. Chem.*, 1964, **29**, 1148.

[32] E. D. Bergmann, D. Ginsberg, and D. Lavie, *J. Amer. Chem. Soc.*, 1950, **72**, 5012.

[33] K. G. van Senden and H. N. Koning, *Rec. Trav. chim.*, 1962, **81**, 49.

1,1-Dichloro-2,2-bis-*p*-chlorophenylethane (0·01 mol) was refluxed for 5·5 h in dry acetone containing $Bu^n_4NCl$ (0·01 mol) and 2,4,6-collidine (0·01 mol). An ether extract of the reaction mixture after normal work-up was examined by g.l.c. and t.l.c. No compound other than the starting material was detected, even though check experiments showed that an amount of the olefin 2-chloro-1,1-bis-*p*-chlorophenylethylene corresponding to a 5% yield was easily detectable. Starting material was recovered from the extract in 96% yield.

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