# Eliminations promoted by Thiolate Ions. Part IV.[1] A Hammett Equation Study of the Reactions of 1,1-Diaryl-2,2,2-trichloro- and 1,1-Diaryl-2,2-dichloro-ethane with Benzenethiolate Ions in Ethanol

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The Hammett ρ value for the benzenethiolate-promoted dehydrochlorination of 1,1-diaryl-2,2,2-trichloroethane (DDT-type) compounds in ethanol is 2·11 at 65 °C. For $S_N2$ substitution of benzenethiolate for chloride in the 1,1-diaryl-2,2-dichloroethane (DDD) series, $\rho = 0{\cdot}41$. Comparison of the former value with that for the conventional *E*2 reaction promoted by ethoxide in ethanol (2·34) suggests that the transition state for the benzenethiolate-promoted reaction is of the normal *E*2H variety, and is not an *E*2C-like transition state. The DDD $S_N2$ reaction series has been chosen as a model for possible *E*2C dehydrochlorination of DDT, and the disparity between the two ρ values indicates that the DDT transition state has considerably more β-carbanionic character than does the DDD transition state.

The fact that DDT is dehydrochlorinated by weak bases such as benzenethiolate and chloride ions more readily than is DDD is also taken as evidence in favour of the *E*2H mechanism. Potential-energy calculations, based on the assumption that both DDT and DDD eliminate *via* *E*2C transition states, give theoretical DDT : DDD rate ratios close to unity, which are widely different from the experimental values.

The assumption of additivity of substituent constants in diarylmethyl Hammett series is questioned and a novel method of obtaining linear plots is described.

In Part I [2] it was shown that the bimolecular dehydrochlorination of the DDT (Ie) in ethanol [equation (1)] was some 8000 times slower at 65 °C when benzenethiolate ($pK_b = 9{\cdot}8$ in ethanol) [2] was used as base than

$$\underset{\text{(I)}}{(p\text{-}RC_6H_4)_2CH{\cdot}CCl_3} + B^- \longrightarrow \underset{\text{(II)}}{(p\text{-}RC_6H_4)_2C{:}CCl_2} + BH + Cl^- \quad (1)$$

(a) R = OMe
(b) R = Me
(c) R = H
(d) R = F
(e) R = Cl
(f) R = Br
(g) R = $NO_2$

with the strong base ethoxide. This is hardly surprising in view of the difference in basicity of the two species in question, but it is apparently anomalous when it is recalled that thiolate bases are *more* reactive than alkoxides in promoting elimination from such substrates as t-butyl chloride,[1,3] cyclohexyl toluene-*p*-sulphonate,[4] and 2-chloro-2-methyl-1-phenylpropane.[5] If it is assumed that the eliminations proceed *via* a normal *E*2 transition state (now termed *E*2H),[6] an explanation of the varying thiolate : alkoxide rate ratios is readily available.[1,2,4,7] According to the explanation, high thiolate : alkoxide ratios are expected for paenecarbonium [8] transition states (III) and the ratio is expected to decrease as the character of the transition state changes through central (IV) to one of paenecarbanion [8]

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[1] Part III, D. J. McLennan, *J. Chem. Soc.* (*B*), 1966, 709.

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

[3] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 1956, 41.

[4] D. J. McLennan, *J. Chem. Soc.* (*B*), 1966, 705.

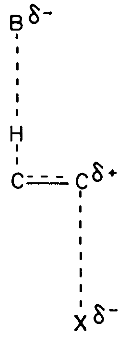
[5] J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Amer. Chem. Soc.*, 1962, **84**, 1606.

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

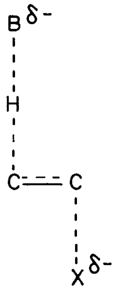
[7] J. F. Bunnett and E. Bachiocci, *J. Org. Chem.*, 1967, **32**, 11; *cf.* G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

[8] (*a*) J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; (*b*) J. F. Bunnett, 'Survey of Progress in Chemistry,' Academic Press, New York, vol. 5, 1969, p. 53.

character (V), to which class DDT-type compounds properly belong.[2]



(III)



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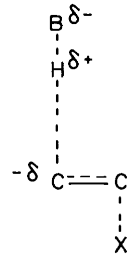
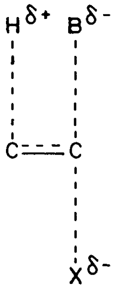


(V)

However, other possible explanations are provided by recent studies by Parker, Winstein, and their coworkers.[6,9-13] They have suggested another dimension to the $E2$ transition-state spectrum (VI—VIII) to be utilized by weak bases which are also strong carbon nucleophiles,[14] such as halide ions in dipolar aprotic solvents and thiolate ions. Such species are held to react *via* $E2$C-like transition states (VI) or (VII) whilst strong bases utilize conventional $E2$H transition states such as (VIII). The similarity of $E2$C to $S_N2$ transition states, as far as the bonding situation at $C_\alpha$ is concerned, is clear. Substrates such as DDT, which have the leaving group in a poor environment for departure, would obviously not react readily in $E2$C thiolate-promoted eliminations as the 'tighter' transition state[12,13] is not the ideal type for such reactions.



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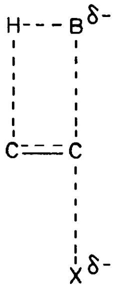

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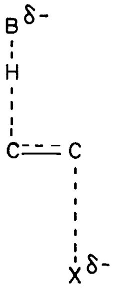

(VIII)

We have argued[15] that most of the experimental evidence presented in favour of the $E2$C mechanism for halide-promoted elimination from 'loose' substrates such as t-butyl chloride and cyclohexyl toluene-*p*-sulphonate can equally well be interpreted in terms of paenecarbonium $E2$H transition states such as (III). Lloyd and Parker however have recently found that the rates of such reactions are fairly insensitive to the electronic effects of *para*-substituents on α-bound aryl groups,[16] and this result is incompatible with electron deficiency at $C_\alpha$ in the transition state. If this is the case, the $E2$C mechanism seems to have been adequately demonstrated for halide-promoted elimination, and by analogy for thiolate-promoted elimination, from 'looser' substrates.

It thus becomes necessary to reopen the question of the mechanism of the benzenethiolate-promoted dehydrochlorination of DDT since the low β-deuterium isotope effect (3·1 at 45 °C) and the low $RS^- : RO^-$ rate ratio are also compatible with a 'tight' four-centre $E2$C transition state.[14,17,18] Such tightness could also account for the high Brønsted β value (0·77) which could be diagnostic of a situation in which the nucleophile is strongly bound to both $C_\alpha$ and $H_\beta$ in an $E2$C transition state as well as to an $E2$H paenecarbanion transition state.

## RESULTS

The solvent throughout was magnesium-dried ethanol. Temperatures in the kinetic runs were controlled to within 0·1 °C. All rate constants have units of l mol⁻¹ s⁻¹. Table 1 shows rate constants for the second-order reactions of *p*-substituted DDT-type compounds with sodium benzenethiolate. All reactions proceeded by the stoicheiometry of equation (1).

TABLE 1

Rate constants[a] for the reaction of $(p\text{-}RC_6H_4)_2CH{\cdot}CCl_3$ compounds (*ca.* 0·01M) with sodium benzenethiolate (*ca.* 0·03M)[b] in ethanol at 65·0 °C

| R | MeO | Me | H | F | Cl | Br | NO₂ |
|---|---|---|---|---|---|---|---|
| $10^5k_2$ | 0·55 | 0·40 | 1·45 | 10·7 | 26·4[c] | 29·8 | 1680 |

[a] Mean of two or more concordant runs. [b] [PhSH] *ca.* 0·001M. [c] Ref. 2.

The $S_N2$ reactions[19] of other 1,1-diaryl-2,2-dichloroethanes with sodium benzenethiolate were also examined.

Except for the *p*-nitro-compound (IXf), the stoicheiometry of the reactions of these derivatives with benzenethiolate in ethanol was as shown in equation (2). The sole organic products of all such reactions (X) were identical to the products of the reactions of $(p\text{-}RC_6H_4)_2C{:}CHHal$ with

$$\underset{\text{(IX)}}{(p\text{-}RC_6H_4)_2CH{\cdot}CHCl_2} + 2PhS^- \longrightarrow \underset{\text{(X)}}{(p\text{-}RC_6H_4)_2C{:}CHSPh} + 2Cl^- + PhSH \quad (2)$$

(a) R = OMe
(b) R = Me
(c) R = H
(d) R = Cl
(e) R = Br
(f) R = $NO_2$

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

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

[11] D. Cook, A. J. Parker, and M. Ruane, *Tetrahedron Letters*, 1968, 5715.

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

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

[14] J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271.

[15] D. J. McLennan and R. J. Wong, *Tetrahedron Letters*, 1970, 881.

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

[17] R. A. More O'Ferrall, *J. Chem. Soc. (B)*, 1970, 785; A. J. Parker, personal communication.

[18] R. F. Hudson, *Chimia (Switz.)*, 1962, **16**, 173.

[19] D. J. McLennan, *Austral. J. Chem.*, 1969, **22**, 1905.

$PhS^-$ in dimethylformamide[20] or to have properties similar to those of the products of the reactions of $(p\text{-}RC_6H_4)_2C{:}CHHal$ with $p\text{-}MeC_6H_4{\cdot}S^-$ in dimethylformamide.[21] The reaction kinetics were strictly of the second-order, first-order in both substrate and benzenethiolate. In all cases the rate of production of PhSH lagged behind the rate of destruction of substrate indicating that, as is the case for compound (Id),[19] the actual product is $(p\text{-}RC_6H_4)_2CH{\cdot}CH(SPh)_2$, which slowly eliminates thiophenol. G.l.c. failed to detect any olefin of the type $(p\text{-}RC_6H_4)_2C{:}CHCl$ (XI) under conditions where 0·5% would have been observed. It is known however that the chloro-olefin (XI; R = Cl) is unstable in the presence of both $PhS^-$ and PhSH and forms (Xd).[19] But at an early stage of the reaction between $PhS^-$ and (IXd), when the benzenethiol concentration was low and where a control experiment showed that the chloro-olefin was largely stable, no such product was actually observed under conditions where an amount corresponding to an overall yield of 0·5% would have been detectable. The anomalous reactions of the *p*-nitro-compound (IXf) are described in the Experimental section. Table 2 shows the second-order rate constants for the $S_N2$ reactions of the DDD-type compounds with benzenethiolate.

TABLE 2

Rate constants [a] for the reactions of $(p\text{-}RC_6H_4)_2CH{\cdot}CHCl_2$ compounds (*ca.* 0·01M) with sodium benzenethiolate (*ca.* 0·03M) [b] in ethanol at 65·0 °C

| R | MeO | Me | H | Cl | Br |
|---|---|---|---|---|---|
| $10^5k_2$ | 50·1 | 66·0 | 81·3 | 122 [c] | 135 |

[a] Mean of two or more concordant runs. [b] [PhSH] *ca.* 0·001M. [c] Extrapolation of rate constants in ref. 19 to 65 °C gives a rate constant of 127 × $10^{-5}$ l $mol^{-1}$ $s^{-1}$.

DISCUSSION

*The DDT Reactions.*—The Hammett plot of log $k_2$ for the reactions of the $Ar_2CH{\cdot}CCl_3$ compounds against $2\sigma$ ($\sigma$ values from Leffler and Grunwald [22]) is shown in Figure 1. The least-squares line gives a $\rho$ value of 1·79 with standard deviation (*s*) of 0·14 and correlation coefficient (*r*) of 0·980. The fit of the data to the least-squares line is not particularly good and, most seriously, the *p*-methoxy-compound ($\sigma = -0{\cdot}27$) is more reactive than the *p*-tolyl derivative ($\sigma = -0{\cdot}17$). The rate constants for three other compounds also deviate significantly. Similar irregular behaviour can be found in other work involving multiple substitution in both rings of $Ar_2C$– systems.[23-25] The assumption that $2\sigma$ adequately represents the total substituent effect, *i.e.*, that substituents affect the rate independently and additively, must therefore be questioned.[23]

In improving the Hammett plot and in finding an adequate substituent parameter,[26] we note that generally the greatest deviations occur with those substituents having the strongest resonance interactions with the reaction centre. If it is assumed that the inductive (field) effects of the substituents are not dependent on the relative orientation of the two benzene rings in the initial and transition states, the relevant total inductive parameter will be $2\sigma_I$ where $\sigma_I$ is the inductive component of the Hammett *para*-substituent constant.[27] On the other hand, if one benzene ring is orientated so that the full resonance effect of its substituent can be felt at the reaction centre, *i.e.* with its plane perpendicular to the lobes of the developing *p*-orbital on $C_\beta$, the other ring cannot adopt such an orientation for steric reasons, and the full resonance effect of the substituent on the latter ring can therefore not be felt at the reaction centre.* The relevant total resonance parameter is thus not $2\sigma_R$ (where $\sigma_R$ is the resonance component of the Hammett *para*-substituent constant [27]) but rather $(1 + \alpha)\sigma_R$ where $\alpha$ is a parameter, with possible values between zero and unity, which is a measure of the inability of both substituents to exert their full resonance electron-donating or -withdrawing powers on the reaction centre because of the inability of the rings to achieve coplanarity. It has recently been shown that the benzene rings in both DDT and its dehydrochlorination product (IIe) in solution are far from being coplanar.[28]

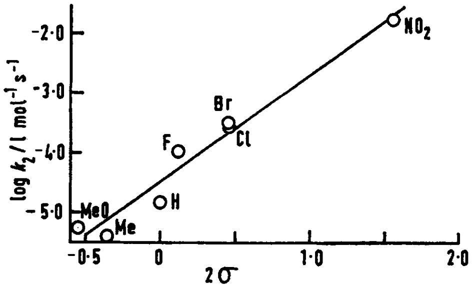

FIGURE 1 Hammett plot of log $k_2$ against $2\sigma$ for the reaction of $Ar_2CH{\cdot}CCl_3$ with $PhS^-$

Consequently, $2\sigma_I + (1 + \alpha)\sigma_R$ should best represent the total substituent effect, and we have computed plots of log $k_2$ against this quantity for various values of $\alpha$. The best plot (Figure 2), as judged by a clear minimum in the standard deviation of the slope, is found for $\alpha = 0{\cdot}37$. The $\rho$ value arising from this much-improved Hammett plot is 2·11, with $s = 0{\cdot}02$, and $r = 0{\cdot}999$.

Cockerill and Lamper [29] have recently and independently used this method to correlate the acidities

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* The real stereochemical situation will obviously not be as suggested here, but it will be equivalent to our model as we are principally concerned with the orientation of one benzene ring relative to the other.

[20] P. Beltrame, D. Pitea, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 1108.

[21] (*a*) P. Beltrame, P. L. Beltrame, and L. Bellotti, *J. Chem. Soc.* (*B*), 1969, 932; (*b*) P. Beltrame, P. L. Beltrame, M. Cereda, and G. Lazzerini, *ibid.*, p. 1100.

[22] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' John Wiley and Sons, New York, 1963, p. 173.

[23] (*a*) E. D. Bergmann, A. F. Hegarty, and J. E. Dubois, *Chem. Comm.*, 1968, 1616; (*b*) A. F. Hegarty and J. E. Dubois, *Tetrahedron Letters*, 1968, 4839.

[24] S. Nishida, *J. Org. Chem.*, 1967, **32**, 2692, 2695, 2697.

[25] E. Berliner and M. Q. Malter, *J. Org. Chem.*, 1968, **33**, 2595.

[26] R. J. Wong, M.Sc. Thesis, University of Auckland, 1970.

[27] P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, New York, 1968, p. 17.

[28] M. L. Kemp and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 7094.

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

of 9-arylfluorenes. Their procedure for calculating the angle between the rings in a non-coplanar aromatic system as applied to the present results enables us to estimate that the angle between the planes of the rings in the DDT–PhS$^-$ transition state is 50°. This is nicely in between the measured angle [28] in the reactant molecule (40°) and in the product (55°). Unpublished results [30] on the $Ar_2CH{\cdot}CCl_3$–$Bu^n{}_4NCl$ reaction in acetone and the $Ar_2CH{\cdot}CCl_3$–LiCl reaction in dimethylformamide reveals the necessity for the modified Hammett treatment. We note that although the assumption is made that direct resonance interaction between the reaction centre and the substituents occurs, use of a $\sigma_R$ value based on $\sigma^-$ for *p*-nitro results in a poorer correlation in all cases.

Cristol *et al.*[31] obtained only a fair Hammett plot of log *k* against 2σ for the $Ar_2CH{\cdot}CCl_3$–$OEt^-$ dehydrochlorination in EtOH: $\rho = 2{\cdot}34 \pm 0{\cdot}24$; $r = 0{\cdot}968$ at 65 °C. The *p*-methoxy-point exhibited a positive deviation from the least-squares line.

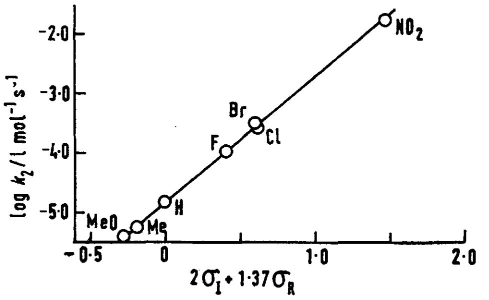

FIGURE 2 Modified Hammett plot of log $k_2$ against ($2\sigma_I + 1{\cdot}37\sigma_R$) for the reaction of $Ar_2CH{\cdot}CCl_3$ with PhS$^-$

It is noteworthy that in one reaction series, involving vinylic nucleophilic substitution in compounds of the type $Ar_2C{:}CHHal$, plots of log *k* against 2σ are clearly linear.[20,21,32] In such a system the hybridization at $C_\beta$ remains $sp^2$ on going from the initial to the transition state and hence the relative orientation of the two rings need not change, whereas in our system and in other badly behaved reactions [24,25] the hybridization of the carbon atom to which both rings are bonded changes from $sp^3$ in the initial state to partial $sp^2$ in the transition state. This factor appears to be a condition for the success of our treatment, which is somewhat equivalent to one in which a different ρ value is associated with each ring.[23a] An advantage of the present method is that a single reaction parameter can be used to describe the overall sensitivity of the reaction to substituent effects.

The ρ value for DDT dehydrochlorination by benzenethiolate (2·11) is comparable with that (2·34 at 65 °C) obtained when the base is ethoxide in 95% ethanol.[31] The latter reaction, involving a strong base reacting with an ' acidic ' substrate which has the leaving group in poor environment for departure, almost certainly proceeds through a paenecarbanion *E*2H transition state, and the relatively large ρ value supports this view. Similarly, the comparable ρ value for the benzenethiolate-promoted elimination seems to be diagnostic of a large amount of negative charge at $C_\beta$ in the transition state. On the other hand, *E*2C-like transition states as visualized by Winstein and Parker [6,9–13,16] have little negative charge residing on $C_\beta$ and little positive charge at $C_\alpha$. They are characterized instead by a large degree of double-bond development.

On this basis it appears that the DDT–PhS$^-$ reaction does indeed pass through a paenecarbanion *E*2H transition state as previously supposed.[2] The large Brønsted β and low deuterium isotope effect thus point to a linear three-centre proton transfer process with the proton closer to the base than to $C_\beta$ instead of to a four-centre *E*2C transition state having a well-formed $S \cdots C_\alpha$ partial bond. The ring substituents appear to have a small but significant influence on the character of this *E*2H transition state. Values of $k_2(PhS^-)/(k_2(OEt^-)$ at 65 °C, with the ethoxide rate constants having been extrapolated from data pertaining to 95% ethanol as solvent at lower temperatures,[31] are, for R = MeO, $4{\cdot}15 \times 10^{-4}$; for R = H, $3{\cdot}0 \times 10^{-4}$; and for R = Br, $1{\cdot}35 \times 10^{-4}$. Such a decrease is consistent [1,2,4,7] with the transition state's becoming more paenecarbanionic as the substituents are made more electron-demanding. This interpretation is in agreement with the observation that the Brønsted coefficient for the $E_2$ reaction series of $p$-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Br$ with $ArO^-$ is greater than that for the $PhCH_2{\cdot}CH_2Br$–$ArO^-$ series,[33] and both these results can be reconciled with More O'Ferrall's [34] theory on the effect of substituents on transition-state geometry.

It is also noteworthy that as the base strength is increased along the series Cl$^-$, PhS$^-$, OEt$^-$ the Hammett ρ value increases for the dehydrochlorination of $Ar_2CH{\cdot}CCl_3$ compounds. This is in accord with Bunnett's prediction [8b] and with the recent results of Yano and Oae.[35]

*The DDD Reactions.*—What should be the magnitude of ρ in *E*2C elimination of HX from compounds having the skeleton Ar–CH–CX? Chloride-promoted dehydrobromination of 2-benzyl-2-bromoindan-1-ones in acetonitrile has a ρ value of 0·44, whilst ρ = 0·17 is obtained for the bromide-induced reaction.[36] These low values are comparable with those found for $S_N2$ displacement of X from compounds having the above skeleton.[15] The analogy between $S_N2$ and *E*2C-like transition states for competitive substitution and elimination from a given substrate has been demonstrated.[6,10] This type of analysis cannot be used for DDT since no substitution can be detected. However the dichloro-analogue of DDT, namely DDD, reacts with benzenethiolate by an

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[30] D. J. McLennan, S. A. Short, and R. J. Wong, unpublished results.

[31] S. J. Cristol, N. L. Hause, A. J. Quant, H. W. Miller, K. R. Eiler, and J. S. Meek, *J. Amer. Chem. Soc.*, 1952, **74**, 3333; S. J. Cristol, *ibid.*, 1945, **67**, 1494.

[32] P. Beltrame, P. L. Beltrame, O. Sighinolfi, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 1103.

[33] R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1964, 5.

[34] R. A. More O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 274.

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

[36] D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1966, **88**, 4489.

$S_N2$ mechanism.[19] The structural similarity of the two compounds makes the $Ar_2CH{\cdot}CHCl_2$–$PhS^-$ series an attractive model for the possible $E$2C reaction of DDT.

A plot of log $k_2$ (Table 2) against $2\sigma$ is accurately linear, with $\rho = 0{\cdot}41$, $r = 0{\cdot}988$, $s = 0{\cdot}03$. The fit of the points is not improved by using the treatment employed for the DDT series (*i.e.*, $\alpha = 1{\cdot}00$).

Several important implications arise from this result. First, since the Hammett $\rho$ is very much different from that found for $E$2H dehydrochlorination of $Ar_2CH{\cdot}CHCl_2$ compounds (2·19 at 65 °C with $OEt^-$ in EtOH),[31] the rate-determining step of the benzenethiolate-promoted reaction is not dehydrochlorination, in accordance with other evidence.[19] This suggestion is substantiated by the non-observation of dehydrochlorination products. Secondly, the Hammett plot is linear, indicating that the balance between bond-making and bond-breaking in the $S_N2$ transition states is largely unaffected by the substituents. This is not always the case.[16,36-38]

Most importantly from the point of view of the DDT–$PhS^-$ reactions, the $\rho$ value for the $S_N2$ reactions of a closely related series is about five times smaller than that for the elimination. A plot of log $k_2$ for the DDT reactions against log $k_2$ for the corresponding DDD compounds is a scatter diagram. The conclusions are that the $S_N2$ and $E$2 transition states are quite dissimilar and that the latter have no significant $E$2C character. A similar conclusion is reached when the $\rho$ value for the fluoride-induced dehydrochlorination of 2-arylethyl chlorides (2·03) is compared with that for the $S_N2$ chloride exchange (0·57) in acetonitrile.[39]

*The DDT : DDD* E2 *Rate Ratio*.—From the observation that the DDD–$PhS^-$ reaction produces <0·5% dehydrochlorination product and from the rate constants [2,19] for the DDD–$PhS^-$ and DDT–$PhS^-$ reactions at 45 °C, it can be deduced that the DDT : DDD dehydrochlorination rate ratio is at least 23 per chlorine ($\Delta G^{\ddagger} = 2{\cdot}40$ kcal mol$^{-1}$ in favour of DDT) when $PhS^-$ is the hydrogen nucleophile. It can also be calculated, albeit roughly, on the basis that DDD is not visibly dehydrochlorinated by $Bu^n_4NCl$ after 5·5 h under reflux in acetone containing 2,4,6-collidine,[15] that the DDT : DDD $E$2 rate ratio with $Cl^-$ is at least 70 per chlorine at 65 °C ($\Delta G^{\ddagger} = 3{\cdot}1$ kcal mol$^{-1}$ in favour of DDT). The DDT : DDD $E$2H rate ratio (ethoxide in ethanol) [2,19] is 3·6 at 45 °C. On the other hand, rates of $S_N2$ reactions are known to be retarded by α-halogen substituents,[40] and this is confirmed by the DDD : DDT $S_N2$ rate ratio for reaction with $PhS^-$, which is at least $1{\cdot}5 \times 10^5$. These rate ratios suggest that the DDT–$PhS^-$ and DDT–$Cl^-$ reactions do not proceed through $S_N2$-like transition states (such as $E$2C), but through $E$2H transition states as does the DDT–$OEt^-$ elimination.

Parker and his co-workers however have reported that large α- and β-bound groups accelerate $E$2C-like reactions [11] and have suggested that non-bonded repulsions between such groups are relieved as the initial state $sp^3$ hybridization changes to near-$sp^2$ in the $E$2C transition state. This consideration applied to DDT and DDD leads to the conclusion that the former should be more reactive than the latter in $E$2C reactions. Thus the observed rate ratio is apparently also qualitatively consistent with the $E$2C mechanism.

In an attempt to resolve this ambiguity we have carried out potential-energy calculations. We have calculated the potential-energy changes ($\Delta W$) caused by interaction of non-bonded and non-reacting atoms for the processes in equations (3) and (4) which are taken as models for

$$CCl_2\ (sp^3) \longrightarrow CCl_2\ (sp^2) \qquad (3)$$

$$CHCl\ (sp^3) \longrightarrow CHCl\ (sp^2) \qquad (4)$$

the situation at $C_\alpha$ in $E$2C reactions of DDT and DDD respectively. The potential function chosen was that so successfully employed by Hughes, Ingold, and their co-workers for calculation of steric contributions to $S_N2$ rates,[41] except that we have replaced their ion–dipole interaction term with a dipole–dipole interaction.[42] The calculations were performed, in the case of the system represented by equation (3), by computing $W$ with $r$, the distance between the two chlorines, being calculated from $sp^3$ C–Cl bond lengths and the appropriate bond angle. A value of $r$ and hence of $W$ was then computed for the $^-CCl_2$ ($sp^2$) system by use of $sp^2$ bond lengths and an angle of 120°, and $\Delta W$ was taken as the difference between the latter and former energy values. The same procedure was followed for the system represented by equation (4).

If $r$ values are calculated by adding the appropriate covalent radii,[43] it is found that $\Delta W = 0{\cdot}641$ kcal mol$^{-1}$ for the $CCl_2$ system and is 0·272 kcal mol$^{-1}$ for the CHCl system. Values of $r$ have also been calculated from measured bond lengths and angles in suitable model compounds [44] and lead to $\Delta W$ values of 0·031 and 0·132 kcal mol$^{-1}$ respectively. Intermediate values of $r$ produce intermediate energy changes.

If all other things in the hypothetical DDT and DDD $E$2C transition states are equal, these potential energy changes can be equated to contributions from non-bonded interactions at $C_\alpha$ to the free energy of activation. From the first pair of energies mentioned above we calculate, *via* the $\Delta G^{\ddagger}$ value, that as far as the situation at $C_\alpha$ is concerned, DDD should be 1·13 times *more* reactive than DDT. Use of the second pair of energies gives the result that DDT should be only 1·16 times more reactive than DDD. Intermediate values of $r$ produce

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[37] Ref. 22, p. 191.

[38] G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1935, 1819.

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[43] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' G. Bell and Sons, London, 2nd edn., 1969, p. 144.

[44] ' Tables of Interatomic Distances and Configuration in Molecules and Ions,' *Chem. Soc. Special Publ.*, 1958, No. 11.

intermediate values of the rate ratio. Thus non-bonded interactions at $C_\alpha$ appear to have a negligible effect on the DDT : DDD *E*2C rate ratio. The not obvious reasons for this are that London forces almost balance the effects of dipole–dipole and van der Waals interactions as the hybridization at $C_\alpha$ is changed from $sp^3$ to $sp^2$, and that the increase in the bond angle from 109° 28′ to 120° is accompanied by a decrease in C–Cl and C–H bond lengths, so that the overall change in *r* is small. It should be noted that we have neglected phenyl–chlorine, phenyl–hydrogen, nucleophile–chlorine, and nucleophile–hydrogen interactions in our calculations. These are longer-range forces than those already mentioned, and rough calculations based on estimated distances show that the DDT : DDD rate ratio is increased by only *ca.* 20% by their inclusion.

The calculated and experimental rate ratios do not agree. The conclusion is that the DDT and DDD transition states do not have near-$sp^2$ hybridization at $C_\alpha$ and are therefore not *E*2C-like. This conclusion is based on the assumptions that (i) the potential function is a good one and (ii) the hypothetical DDT and DDD *E*2C transition states are identical in all respects except at $C_\alpha$. Concerning (i), the suitability of this type of potential function has been amply demonstrated for systems more complex than used here,[41,45] even though the dipole term is more appropriate for long-range interactions.[42] Assumption (ii) is reasonable for *E*2C-like transition states with a well developed double bond, since little negative charge is permitted at $C_\beta$ and hence the inductive effect of the extra α-chlorine in DDT should be of little consequence. It is probably the primary cause of DDT being more reactive than DDD under *E*2H conditions, but even with these paenecarbanion transition states the acceleration is small (3·6-fold) [2,19] and not enough to account for the present discrepancy.

*Conclusion.*—Our conclusion that the reaction of DDT with $PhS^-$ is *E*2H rests on firm experimental grounds. Thus the decrease in $RS^- : RO^-$ *E*2 rate ratios as substrates are changed from the t-butyl chloride type to the DDT type seems, on the basis of evidence available, to be caused by the $RS^-$ transition states shifting from the *E*2C- to the *E*2H-type.

The potential-energy calculations indicate that the DDT : $PhS^-$ and DDT : $Cl^-$ *E*2 transition states are not *E*2C-like.

## EXPERIMENTAL

N.m.r. spectra were run on a Varian Associates T-60 instrument with $CDCl_3$ as solvent. Analytical g.l.c. was performed on a Varian Aerograph Model 1400 instrument with a column of SE-30 on Varaport 30 at 200 °C. U.v. absorption spectra of solutes in 95% ethanol were obtained on a Unicam SP800 instrument.

*Materials.*—DDT (Ie) (Aldrich) was recrystallized repeatedly from ethanol. Compounds (Ia) and (Ib) were prepared by dissolving 1 equiv. of 2,2,2-trichloroethanediol in a 1 : 1 $HOAc–H_2SO_4$ mixture and adding 2 equivs. of anisole and toluene respectively, dropwise at 0 °C. Compound (Ia) was recrystallized from n-hexane and (Ib) from methanol. Compounds (Ic) and (Id), the latter prepared by Mr S. A. Short, were obtained by condensing 1 equiv. of 2,2,2-trichloroethanediol with 2 equivs. of benzene and fluorobenzene respectively, in concentrated $H_2SO_4$ at 0 °C. Compound (Ic) was recrystallized from ethanol and (Id) from chloroform–benzene. The latter melted over a wider range than usual, but t.l.c. and the n.m.r. spectrum revealed no impurity. Compound (If) was prepared in the same way as were (Ic) and (Id) except that portions of oleum were added to the mixture during the addition of bromobenzene. It was recrystallized from ethanol. Compound (Ig) resulted from the nitration of (Ic) with fuming nitric acid according to Haskelberg and Lavie.[46] It was recrystallized from glacial acetic acid. M.p. and n.m.r. data for all compounds are in Table 3.

TABLE 3

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

| Compound | M.p. (°C) | Lit. m.p. (°C) (ref.) | N.m.r. $\delta$ [a] | Lit. n.m.r. $\delta$ [a,b] |
|---|---|---|---|---|
| (Ia) | 89—90 | 87—88 (31) | 4·96 | 4·93 |
| (Ib) | 90—91 | 92 (49) | 4·99 | |
| (Ic) | 64·5—65·5 | 65 (49) | 5·06 | 5·05 |
| (Id) | 38·5—43 | 42—45 (31) | 5·00 | 5·03 |
| (Ie) | 109—109·5 | 108—109 (31) | 5·02 | 5·02 |
| (If) | 142·5—143·5 | 142·9—143·6 (31) | 4·98 | 4·97 |
| (Ig) | 168—169 | 169 (46) | 5·36 | 5·35 |

[a] Chemical shift of benzylic proton downfield from tetramethylsilane in p.p.m. [b] Ref. 47.

Dichloroacetal (1,1-dichloro-2,2-diethoxyethane) was prepared by the method of van Dorp and his co-workers.[48] DDD (IXd) (Aldrich) was recrystallized repeatedly from ethanol. Compounds (IXa), (IXb), (IXc), and (IXe) were prepared from dichloroacetal and anisole, toluene, benzene, and bromobenzene respectively, by use of a method similar to that employed for their trichloro-analogues. Yields and ease of product isolation were improved by adding acid to a stirred mixture of dichloroacetal and the appropriate arene at 0 °C. Nitration of (IXc) according to the method of Delaby and Baronnet [49] afforded compound (IXf). All compounds were recrystallized from ethanol except for (IXf), for which glacial acetic acid was employed. M.p. and n.m.r. data for all the above compounds are in Table 4. Satisfactory microanalytical results for several of the compounds in Tables 3 and 4 were obtained.

The above DDT and DDD compounds, with the exception of (IXf), were dehydrochlorinated by a previously described method.[2] Compound (IXf) was dehydrochlorinated at 0 °C instead of under reflux. Properties of the resulting olefins, most of which were recrystallised from methanol or

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[46] L. Haskelberg and D. Lavie, *J. Amer. Chem. Soc.*, 1947, **69**, 2267.

[47] N. E. Sharpless and R. B. Bradley, *Appl. Spectroscopy*, 1965, **19**, 150.

[48] D. A. van Dorp, J. F. Arens, and O. Stephenson *Rec., Trav. chim.*, 1951, **70**, 289.

[49] R. Delaby and R. Baronnet, *Bull. Soc. chim. France*, 1951, 148.

ethanol, are shown in Table 5.[50–53] Satisfactory microanalyses were obtained for several of these olefins.

TABLE 4

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

| Compound | M.p. (°C) | Lit. m.p. (°C) (ref.) | N.m.r. $\delta$ [a] | N.m.r. $J$[b]/Hz |
|---|---|---|---|---|
| (IXa) | 114—115 | 114·5—115 (31) | 4·48 | 8·0 |
| (IXb) | 78·5—79·5 | 78·5—79 (31) | 4·47 | 8·5 |
| (IXc) | 76—77·5 | 77·5—78 (31) | 4·56 | 8·5 |
| (IXd) | 109—110 | 109·5—110·5 (19) | 4·50 [c] | 8·0 [c] |
| (IXe) | 134—135 | 134—135 (31) | 4·46 | 8·5 |
| (IXf) | 177—178 | 178·5 (48) | 4·83 | 8·0 |

[a] Chemical shift of benzylic proton downfield from tetramethylsilane in p.p.m. [b] Aliphatic AB coupling constant. [c] Ref. 47 reports 4·53, $J$ 8·3 Hz.

TABLE 5

Dehydrochlorination products of substituted DDT- and DDT-type compounds

| Olefin | M.p. (°C) | Lit. m.p. (°C) | $\lambda_{max.}$ [a] | log ε [b] | N.m.r. $\delta$ [c] |
|---|---|---|---|---|---|
| (IIa) | 109—110·5 | 109 (49) | 253 | 4·133 | |
| (IIb) | 85·5—87 | 87 (49) | 246 | 4·352 | |
| (IIc) | 78—79 | 80 (49) | 247 | 4·243 | |
| (IId) | 37—39·5 | 34·5 (31) | 248 | 4·016 | |
| (IIe) | 89—90·5 | 87·5—88 (2) | 245 | 4·243 | |
| (IIf) | 121—121·5 | 121 (49) | 249 | 4·235 | |
| (IIg) | 172—173 | 172—173 (51) | 290 | 4·290 | |
| (XI, R = OMe) | 80·5—81 | 80—81 (31) | 250 | 4·352 [d] | 6·48 [e] |
| (XI, R = Me) | 66—67 | 67 (52) | 240 | 4·294 [f] | 6·56 [g] |
| (XI, R = H) | 42·5—43 | 42 (52) | 254 | 4·125 [h] | 6·68 [i] |
| (XI, R = Cl) | 65—65·5 | 65—65·5 (19) | 244 | 4·271 | 6·53 [j] |
| (XI, R = Br) | 106—107 | 107—108 (53) | 247 | 4·336 | 6·53 |
| (XI, R = $NO_2$) | 145—146 | 146—147 (54) | 300 | 4·292 [k] | 6·92 [l] |

[a] U.v. maximum in nm above 220 nm. [b] Molar extinction coefficient. [c] Chemical shift of vinylic proton downfield from tetramethylsilane in p.p.m. [d] Ref. 51 reports $\lambda_{max.}$ 250 nm, log ε 4·350. [e] Ref. 20 reports $\delta$ 6·49. [f] Ref. 51 reports $\lambda_{max.}$ 240 nm, log ε 4·295. [g] Ref. 20 reports $\delta$ 6·56. [h] Ref. 51 reports $\lambda_{max.}$ 255 nm, log ε 4·124. [i] Ref. 20 reports $\delta$ 6·66. [j] Ref. 21(*b*) reports $\delta$ 6·54. [k] Ref. 32 reports $\lambda_{max.}$ 300 nm, log ε 4·294. [l] Ref. 32 reports $\delta$ 6·94.

Ethanol was dried with magnesium turnings and sodium benzenethiolate solutions were prepared as before.[2] Benzenethiol was purified as before.[2]

*Products*.—The substituted DDT compounds were heated under reflux with sodium benzenethiolate in ethanol under nitrogen and products were recovered as before.[2] M.p., mixed m.p., and u.v. spectral observations showed that the products, recovered in >80% yield, were identical to the appropriate $Ar_2C{:}CCl_2$ olefins. T.l.c. revealed small amounts of diphenyl disulphide, probably arising from slight oxidation of benzenethiolate, as the only contaminant of the crude products. Control experiments showed that the starting materials were not dehydrochlorinated during work-up.

With the exception of (IXf), the substituted DDD compounds were heated under reflux with sodium benzenethiolate in ethanol under nitrogen as before.[19] After work-up, samples of the resulting oils were examined by g.l.c. No $Ar_2C{:}CHCl$ compound was observed, under conditions where 0·5% would have been clearly detectable. The oils were chromatographed on silica gel with 9 : 1 n-hexane–benzene as eluant. All compounds were then recrystallized from ethanol, except for compound (Xa), which remained as an oil. Spectra and comparison with published data for known compounds showed that all products were compounds of the $Ar_2C{:}CH\cdot SPh$ type (see Table 6). Control experiments with use of t.l.c. for detection showed that the starting materials were stable during work-up.

TABLE 6

Products of the reaction of DDD-type compounds with benzenethiolate in ethanol

| Compound | M.p. (°C) | Lit. m.p. (°C) (ref.) | $\lambda_{max.}$ [a] (log ε) [b] | N.m.r. $\delta$ [c] |
|---|---|---|---|---|
| (Xa) | Oil [d] | Oil (20) | 256 (4·292);<br>307 (4·310) [e] | 6·68 |
| (Xb) | 68—69 | 69 (20) | 235 (4·207);<br>310 (4·270) [g] | 6·78 [h] |
| (Xc) | 72·5—73·5 | 72—73 (20) | 268 (4·033);<br>311 (4·269) [i] | 6·89 [f] |
| (Xd) | 70—71 | 70—71 (19) | 238 (4·230);<br>314 (4·300) [k] | 6·78 [l] |
| (Xe) | 99·5—101 | | 245 (4·358);<br>317 (3·982) | 6·80 |

[a] U.v. maxima in nm above 220 nm. [b] Molar extinction coefficient. [c] Chemical shift of vinylic proton downfield from tetramethylsilane in p.p.m. [d] $n_D^{25} = 1·6640$; ref. 20 reports $n_D^{25} = 1·6644$. [e] Ref. 20 reports $\lambda_{max.}$ 256 and 306 nm; log ε 4·29 and 4·30 respectively. [f] Ref. 20 reports $\delta$ 6·69 for *p*-$MeC_6H_4S$ compound. [g] Ref. 20 reports $\lambda_{max.}$ 235 and 310 nm; log ε 4·21 and 4·27 respectively. [h] Ref. 20 reports $\delta$ 6·78 for *p*-$MeC_6H_4S$ compound. [i] Ref. 20 reports $\lambda_{max.}$ 268 and 310 nm; log ε 4·03 and 4·27 respectively. [j] Ref. 20 reports $\delta$ 6·91. [k] From ref. 19. [l] Ref. 21(*a*) reports $\delta$ 6·78 for *p*-$MeC_6H_4S$ compound.

Compound (IXf) was heated under reflux with 2 equivs. of NaSPh and 1 equiv. of PhSH in ethanol for 48 h. Normal work-up produced a dark red gum which was chromatographed on silica gel using a graded series of n-hexane–ether mixtures for elution. Products obtained were: diphenyl disulphide (86%), m.p. 60—61 °C (lit.,[54] 61 °C); the olefin (XI; R = $NO_2$) (6%), m.p. and mixed m.p. with an authentic sample, 145—146 °C (lit.,[51] 146—147 °C); di-(*p*-nitrophenyl)acetylene (10%), m.p. and mixed m.p. with an authentic sample[49] 212—214 °C (lit.,[49] 214 °C); and an intractable dark red tar which resisted elution and which failed to yield crystals from a variety of solvents. The combined aqueous extracts from work-up, which contained a water-soluble compound exhibiting the properties of an acid–base indicator, were acidified with dilute nitric acid, volumetrically diluted, and a sample was titrated with a silver nitrate solution. The amount of chloride ion corresponded to 1·91 equivs. per equiv. of starting material.

*Kinetics*.—The reactions of $Ar_2CH\cdot CCl_3$ with $PhS^-$ and of $Ar_2CH\cdot CHCl_2$ with $PhS^-$ were followed as before.[2,19] In all runs of the latter set, iodometric analysis for ($PhS^-$ + PhSH) was performed on a sample taken at *ca.* 50% reaction (as indicated by chloride-ion analysis). In all cases the production of benzenethiol lagged behind that of chloride ion.

A sample of mixture, taken from the reaction of compound (IXd) with $PhS^-$ at a time when 10% of the substrate

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[52] K. Brand and D. Krucke-Amelung, *Ber.*, 1939, **72**, *B*, 1029.

[53] W. Lorenz, *Chem. Ber.*, 1948, **81**, 422.

[54] 'Dictionary of Organic Compounds,' 4th edn., vol. 3, Eyre and Spottiswoode, London, 1965, p. 1279.

had been consumed as indicated by chloride-ion analysis and when 2% of the theoretical amount of benzenethiol had been produced as indicated by iodometric titration, was subjected to normal product work-up and g.l.c. analysis.. No olefin (XI; R = Cl) was observed where an amount corresponding to a yield of 0·05% would have been detectable. Results of a parallel run involving the reaction of a small quantity of the chloro-olefin with $PhS^-$ and PhSH, both at similar concentrations to those in the previous run, showed that the chloro-olefin was stable and detectable at this stage of the reaction. The conclusion is that it is formed to the overall extent of 0·5% or less.

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