# Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part 15.[1] Non-additivity of Chloro-substituent Effects: Mechanism of the Elimination

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Rates of gas-phase elimination of acetic acid from polychloro-substituted 1-arylethyl acetates, measured between 642.0 and 692.6 K, show that the effects of the chloro-substituents are not additive in this reaction. The reactivities of the esters are greater than calculated on the basis of additivity of the substituent effects, the deviation being greater the less reactive the ester. This result, which parallels that observed with the polymethyl-substituted esters, is attributed to variation in the transition state polarity such that the latter decreases with decreasing ester reactivity. Compounds with buttressed *ortho*-chloro-substituents show particularly enhanced reactivity probably due to enhanced direct *p*-orbital overlap between the *ortho*-chlorine atom and the incipient side-chain α-carbocation. As in nitration pentachloro-substitution produces less deactivation than the 2,3,5,6-tetrachloro-substitution, and the increased buttressing in the former may be reponsible; in nitration the effect would appear as increased co-ordination to the electrophile facilitating substitution. Reduced C–Cl σ-bond overlap (and hence a reduced $-I$ effect) produced by steric crowding cannot at present be ruled out as an alternative explanation.

In the preceding paper we showed that the effect of polymethyl-substitution in the pyrolysis of 1-arylethyl acetates (1) was greater than calculated on the basis of additivity. This we have attributed to increased
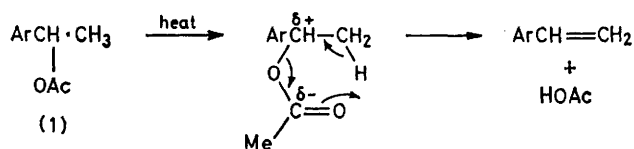
polarity of the transition state with increasing electron supply (to the side-chain α-carbon atom) leading to a greater overall substituent effect. This being so one would expect that electron-withdrawing substituents would produce a *decrease* in the polarity of the transition state and hence a decreased overall substituent

effect, *i.e.* the compounds should be more reactive than calculated. We therefore decided to measure the rates of pyrolysis of a range of polychloro-substituted 1-arylethyl acetates. A second reason for studying these compounds was that in nitration, polychloro-aromatic compounds were more reactive than predicted; in particular, pentachlorobenzene was more reactive than 1,2,4,5-tetrachlorobenzene;[2] no unambiguous explanation of this phenomenon was available. It seemed appropriate therefore to examine the reactivities of the ester derivatives of these compounds in the gas-phase where solvation at least would not be a contributing factor.

[1] Part 14, E. Glyde and R. Taylor, preceding paper.
[2] R. G. Coombes, D. H. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc. (B)*, 1970, 347.

RESULTS AND DISCUSSION

Rate coefficients for pyrolysis of the chloro-substituted esters are given in the Table along with the associated Arrhenius data; the quality of the data is evident from the correlation coefficients. The observed unambiguous. The Figure shows the curve previously obtained for the polymethyl substituents;[1] the deviation obtained with these is of a similar magnitude to that obtained with the deactivating substituents and argues for a similar cause for each. The deviation

Pyrolysis of 1-arylethyl acetate [ArCH(OAc)Me]

Ar	T/°C	$10^3k/s^{-1}$				$\log A / s^{-1}$	E kcal mol⁻¹	$\Delta S\dagger$ cal mol⁻¹ K⁻¹	$\log k/k_0$ (at 625 K)	Corr. coeff.
		419.4	410.3	390.1	368.8					
Ph		100	64.5	24.6	8.74	12.8	42.7	−1.4	0	0.999 8
2,3-Cl₂C₆H₃		43.6	27.9	10.0	3.39	12.7	44.9	−1.8	−0.428	0.999 8
2,5-Cl₂C₆H₃		36.6	23.7	8.56	2.81	12.7	45.1	−1.8	−0.511	0.999 9
2,4-Cl₂C₆H₃		50.2	32.5	11.8	4.05	12.6	44.3	−2.3	−0.356	0.999 9
3,4-Cl₂C₆H₃		58.3	38.2	14.8	4.84	12.5	43.8	−2.7	−0.278	0.999 9
2,3,4-Cl₃C₆H₂		41.0	26.3	9.61	3.29	12.5	44.3	−2.7	−0.45	0.999 9
2,3,6-Cl₃C₆H₂		27.4	17.9	6.54	2.23	12.3	44.1	−3.65	−0.639	0.999 9
2,4,6-Cl₃C₆H₂		33.4	21.6	7.56	2.57	12.7	45.1	−1.8	−0.561	0.999 8
2,4,5-Cl₃C₆H₂		37.3	23.0	8.21	2.71	12.9	45.8	−0.9	−0.472	0.999 8
2,3,5,6-Cl₄C₆H		24.5	15.6	5.50	1.81	12.8	45.8	−1.4	−0.717	0.999 9
2,3,4,5,6-Cl₅C₆		25.1	16.3	5.71	1.88	12.7	45.7	−1.8	−0.70	0.999 9

log $k_{rel.}$ values are plotted against those calculated on the basis of additivity in the Figure. The additive
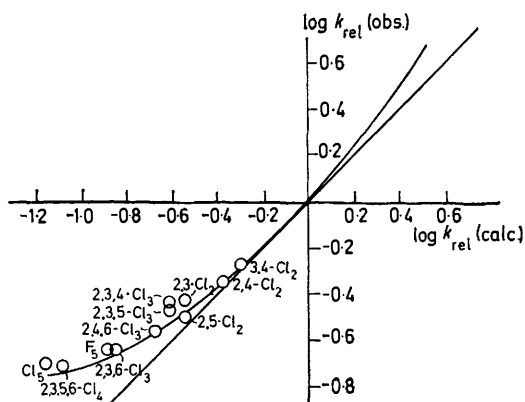
Plot of log $k_{rel.}$ (calc.) vs. log $k_{rel.}$ (obs.) for pyrolysis of polychloro-substituted 1-arylethyl acetates at 625 K

values were calculated using the log $k_{rel.}$ values of −0.312, −0.235, and −0.067 for the ortho-, meta-, and para-chloro-substituents at 625 K; these were calculated by using the $\rho T = \rho'T'$ relationship from the observed values obtained[3,4] at 600 K and since they agree to within better than ±4% with the values calculated similarly from data obtained independently at 647.3 K,[5] we may use these values with confidence.

The main features of the results are as follows. (i) All the esters are more reactive than calculated and this parallels the principal observation in nitration of polychlorobenzene. We may assume that solvation effects do not produce this result.

(ii) The Figure shows that the correlation between observed and calculated reactivity follows a curve instead of the straight line (shown) expected on the basis of additivity. For the more highly substituted esters more than one factor may contribute to this result, but the results for the 3,4-, 2,4-, and 2,5-dichloro-esters are

between observed and calculated reactivities increases with decreasing reactivity (or in general with departure in reactivity from that of the unsubstituted ester). We believe that we are observing the consequence of a change in the polarity of the transition state with a change in ester reactivity, thereby confirming the conclusions reached in the preceding[1] and earlier[6] papers. Thus the transition state becomes more E_i- and less $E1$-like in going to the less reactive esters, so that there is less carbocationic character at the side-chain α-carbon atom and hence a smaller substituent effect which, in the case of a compound containing electron-withdrawing substituents, appears as an increased reactivity.

The situation is therefore the converse of that which should apply in electrophilic aromatic substitution where the transition state is approached through a bond-making rather than a bond-breaking process. For aromatic substitution, greater electron withdrawal should cause a shift in the transition state towards products and thus an increased substituent effect.[7] This may be difficult to observe with compounds containing $+M$ substituents because the $+E$ effect will become particularly significant as the reactivity of the compound decreases. The results for nitration of polychlorobenzenes[2] do however demonstrate both factors nicely, the moderately deactivated compounds being less reactive than predicted, whereas the more deactivated compounds (in which the $+E$ effect is brought more into operation) are more reactive.

It follows that since in aromatic substitution the factors which cause departure from additivity act in opposition whereas in elimination they act together, the deviations should be greater for the latter, and this is certainly so. For example, log f(calc.) − log f(obs.)/ log f(calc.) for the pentachloro compound is much greater (0.396) in the elimination than in nitration (0.283).

[3] R. Taylor, G. G. Smith, and W. H. Wetzel, J. Amer. Chem. Soc., 1962, 81, 4817.

[4] R. Taylor, J. Chem. Soc. (B), 1971, 622.

[5] G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, J. Org. Chem., 1969, 34, 2090.

[6] R. Taylor, J.C.S. Perkin II, 1975, 1025.

[7] R. Taylor, Chem. Soc. Specialist Periodical Report: 'Aromatic and Heteroaromatic Chemistry,' 1973, vol. 1, p. 188.

(iii) The 2,3-dichloro-ester is considerably more reactive than the 2,5-dichloro-ester though each contains an *ortho*- and a *meta*-chloro-substituent. The Figure suggests that the 2,3-dichloro-ester is abnormally reactive, and in this compound the two chlorine atoms and the side chain are buttressed. The reduced electron withdrawal can arise from either (a) reduction in the $-I$ effect through poorer σ-bond overlap or (b) enhanced direct overlap of the chlorine p orbital with the adjacent incipient carbocation, *i.e.* a factor analogous to that which produces diminished overall electron withdrawal in the *ortho*-CF_3 ester.[4] Similar reasoning accounts for the greater reactivity of the 2,3,4- relative to the 2,4,5-trichloro-ester.

The abnormally high reactivity of the 2,3-dichloro-ester relative to the 2-chloro-ester is given by the log (reactivity) difference of -0.116 (*cf.* -0.235 expected for the effect of a *meta*-chloro-substituent). Consistent with this is the difference in reactivity between the 2,3,6-trichloro- and 2,3,5,6-tetrachloro-esters (-0.078) and the same buttressing effect is believed to be responsible.

(iv) The 2,4,6- and 2,3,6-trichloro-esters both differ from the corresponding 2,4- and 2,3-dichloro-esters in having an additional *ortho*-chloro-substituent, and the extra deactivation produced is the same in each case. This suggests that when the side chain is flanked by two chlorine substituents, no significant additional factors are introduced. This view is supported by the fact that the point for the pentafluoro-ester [8] (in which such flanking effects would be considerably less) fits well to the curve for the chloro-compounds.

(v) As in nitration, the pentachloro-compound is more reactive than the 2,3,5,6-tetrachloro-compound. Coombes *et al.*[2] suggested that puckering of the aromatic ring might be an important factor, and this could lead for example to diminished $-I$ electron withdrawal due to the poorer σ-bond overlap. On the other hand the pentafluoro-compound appears to exhibit the same kind of deviation between observed and calculated reactivities and ring puckering would be much less significant here. A more important factor may be the extra buttressing in the pentachloro- relative to the tetrachloro-compound, leading to increased p-orbital overlap as described in (iii). In the case of electrophilic substitution the p-orbital interaction would facilitate attachment of the nitronium ion to the reaction site. It can be argued that there would be less buttressing in the pentafluoro-compound, which nevertheless behaves similarly to the pentachloro-compound. However, the resultant p-orbital interaction would be much stronger for fluorine than for chlorine so that the net effect may well be similar.

(vi) In our previous description of the high reactivity of the pentafluoro-compound [8] we ascribed this to enhanced $+E$ and diminished $-I$ effects. The addi-

tional factor now to be taken into account is the change in the transition state structure.

The esters described were each indicated to be $>98\%$ pure by g.l.c. analysis, and the nature of each was confirmed by n.m.r. and i.r. spectroscopy.

1-Phenylethyl acetate was available from previous studies in this series.

1-(2,3-*Dichlorophenyl*)*ethyl Acetate*.—Treatment of the Grignard reagent from 1,2-dichloro-3-iodobenzene (20 g, 0.073 mol) with an excess of acetaldehyde gave, after normal work-up involving fractional distillation, 1-(2,3-*di-chlorophenyl*)*ethyl alcohol* (7.0 g, 51%), b.p. 111° at 2.2 mmHg (Found: C, 49.9; H, 4.0. $C_8H_8OCl_2$ requires C, 50.2; H, 4.2%). Acetylation of this alcohol with pyridine and acetic anhydride gave, after normal work-up and fractional distillation, 1-(2,3-*dichlorophenyl*)*ethyl acetate* (6.8 g, 79%), b.p. 114° at 2.4 mmHg, m.p. 48° (Found: C, 51.3; H, 4.3. $C_{10}H_{10}Cl_2O_2$ requires C, 51.5; H, 4.3%), τ (CCl_4) 2.17 (3 H, m, ArH), 3.90 (q, J 6.5 Hz, CH), 7.95 (s, $COCH_3$), and 8.50 (d, J 6.5 Hz, CH_3).

1-(3,4-*Dichlorophenyl*)*ethyl Acetate*.—Reduction of 3',4'-dichloroacetophenone (15 g, 0.079 mol) with sodium borohydride gave crude 1-(3,4-dichlorophenyl)ethyl alcohol, which was acetylated as above to give 1-(3,4-*dichloro-phenyl*)*ethyl acetate* (14.5 g, 79% overall), b.p. 107° at 1.2 mmHg, n_D^{20} 1.527 6 (Found: C, 51.7; H, 4.8%), τ (CCl_4) 2.67 (3 H, m, ArH), 4.22 (q, J 6.5 Hz, CH), 7.94 (s, $COCH_3$), and 8.52 (d, J 6.5 Hz, CH_3).

1-(2,4-*Dichlorophenyl*)*ethyl Acetate*.—Reduction of 2',4'-dichloroacetophenone (10 g, 0.053 mol) as above gave crude 1-(2,4-dichlorophenyl)ethyl alcohol, which was acetylated as above to give 1-(2,4-*dichlorophenyl*)*ethyl acetate* (10.1 g, 85% overall), b.p. 100° at 0.9 mmHg, m.p. 25° (Found: C, 52.2; H, 4.4%), τ (CCl_4) 2.67 (3 H, m, ArH), 3.91 (q, J 6.5 Hz, CH), 7.97 (s, $COCH_3$), and 8.53 (d, J 6.5 Hz, CH_3).

1-(2,5-*Dichlorophenyl*)*ethyl Acetate*.—Reduction of 2',5'-dichloroacetophenone (15 g, 0.079 mol) as above gave crude 1-(2,4-dichlorophenyl)ethyl alcohol, which was acetylated as above to give 1-(2,4-*dichlorophenyl*)*ethyl acetate* (10.1 g, 85% overall), b.p. 100° at 0.9 mmHg, m.p. 25° (Found: C, 52.2; H, 4.4%), τ (CCl_4) 2.67 (3 H, m, ArH), 3.91 (q, J 6.5 Hz, CH), 7.97 (s, $COCH_3$), and 8.53 (d, J 6.5 Hz, CH_3).

1-(2,5-*Dichlorophenyl*)*ethyl Acetate*.—Reduction of 2',5'-dichloroacetophenone (15 g, 0.079 mol) as above gave crude 1-(2,5-dichlorophenyl)ethyl alcohol, which was acetylated as above to give 1-(2,5-*dichlorophenyl*)*ethyl acetate* (13.8 g, 76% overall), b.p. 119° at 2.0 mmHg, m.p. 30° (Found: C, 51.6; H, 4.5%), τ (CCl_4) 2.82 (3 H, m, ArH), 3.94 (q, J 6.5 Hz, CH), 7.95 (s, $COCH_3$), and 8.55 (d, J 6.5 Hz, CH_3).

1-(2,3,4-*Trichlorophenyl*)*ethyl Acetate*.—A mixture of 1,2,3-trichlorobenzene (90.8 g, 0.5 mol) and finely ground anhydrous aluminium trichloride (91 g, 0.68 mol) was warmed until molten, and freshly distilled acetyl chloride (39.5 g, 0.51 mol) was added during 20 min to the rapidly stirred mixture. The temperature was raised to and maintained at 80 °C during 1 h and then maintained at 110 °C during a further 8 h. The mixture was allowed to cool overnight, hydrolysed, and extracted with chlorobenzene. Work-up gave 2',3',4'-trichloroacetophenone (50 g, 44%), b.p. 135° at 0.4 mmHg, m.p. 61—63° (lit.,[9] 65.5—66°). G.l.c. analysis indicated a single product, as

[8] R. Taylor, *J. Chem. Soc.* (B), 1971, 255.
[9] C. Fitzmaurice and G. H. Lord, B.P. 1,046,248 (*Chem. Abs.*, 1967, **66**, 37,927).

did the ^{1}H n.m.r. spectrum [τ (CCl$_4$) 2.67 (2 H, m, ArH) and 7.39 (s, COCH$_3$)] and the ^{13}C n.m.r. spectrum [δ (CCl$_4$) -127.7 (d, J 46.4 Hz, ArC) and -30.6 (s, CH$_3$)].

Reduction of this ketone (13.7 g, 0.061 mol) as above gave crude 1-(2,3,4-trichlorophenyl)ethyl alcohol, which was acetylated as above to give 1-(2,3,4-*trichlorophenyl*)-*ethyl acetate* (13.5 g, 83% based on ketone), b.p. 114° at 0.2 mmHg, m.p. 44—46° (Found: C, 44.7; H, 3.4. C$_{10}$H$_9$Cl$_3$O$_2$ requires C, 44.9; H, 3.4%), τ (CCl$_4$) 2.57 (2 H, m, ArH), 3.81 (q, J 6.5 Hz, CH), 7.93 (s, COCH$_3$), and 8.51 (d, J 6.5 Hz, CH$_3$).

1-(2,4,5-*Trichlorophenyl*)*ethyl* *Acetate*.—Acetylation of 1,2,4-trichlorobenzene as above gave 2′,4′,5′-trichloro-acetophenone (56.9 g, 51%), b.p. 108—110° at 0.7 mmHg, m.p. 40—42° (lit.,[10] 114—116° at 2.0 mmHg, m.p. 45.5—46°). Reduction of this ketone as above gave 1-(2,4,5-tri-chlorophenyl)ethyl alcohol, m.p. 80—82° (lit.,[10] 85.5°), and acetylation of this alcohol as above gave 1-(2,4,5-*trichloro-phenyl*)*ethyl acetate* (10.9 g, 85% based on ketone), m.p. 78.5—80° (Found: C, 45.0; H, 3.5%), τ (CCl$_4$) 2.53 (2 H, m, ArH), 3.95 (q, J 6.5 Hz, CH), 7.94 (s, COCH$_3$), and 8.53 (d, J 6.5 Hz, CH$_3$).

1-(2,3,6-*Trichlorophenyl*)*ethyl Acetate*.—In an attempt to prepare 1-(2,3,4,5-tetrachlorophenyl)ethyl acetate, 1,2,3,4-tetrachlorobenzene was treated with n-butyl-lithium followed by an excess of acetaldehyde to give a crude alcohol, subsequently discovered to be 1-(2,3,6-trichlorophenyl)-ethyl alcohol. This was acetylated as above to give 1-(2,3,6-*trichlorophenyl*)*ethyl acetate* (8.9 g, 13% overall), b.p. 102° at 0.2 mmHg (Found: C, 45.1; H, 3.5%). The analytical data showed that a trichloro-ester had been formed instead of the hoped for tetrachloro-ester, and the structure was assigned from the n.m.r. spectrum [τ (CCl$_4$) 2.65 (2 H, m, ArH), 3.51 (q, J 6.5 Hz), 7.93 (s, COCH$_3$), and 8.44 (d, J 6.5 Hz, CH$_3$)].

1-(2,4,6-*Trichlorophenyl*)*ethyl* *Acetate*.—2,4,6-Trichloro-aniline (15 g, 0.076 mol) was diazotised by the method of Hodgson [11] and the product added to freshly prepared copper(I) bromide (15 g) in hydrobromic acid (48%; 75 ml). When nitrogen evolution ceased the mixture was heated to boiling, diluted, and filtered to give a solid which, after washing with dilute hydrobromic acid and water and recrystallisation from ethanol gave 1-bromo-2,4,6-tri-chlorobenzene (10.5 g, 53%), m.p. 66—67° (lit.,[12] 64—65°), mixed m.p. with 1,3,5-trichlorobenzene (m.p. 65—66°) 34—36°.

1-Bromo-2,4,6-trichlorobenzene (10 g, 0.038 mol) was treated with magnesium in ether under nitrogen during

36 h with entrainment with 1,2-dibromoethane. (The disappearance of the starting material was monitored by g.l.c.) Addition of acetaldehyde, hydrolysis, and work-up gave the impure alcohol (6.7 g), b.p. 125° at 15 mmHg. Column chromatography on neutral alumina (98 : 2 benzene–ethanol), gave, after recrystallisation from industrial methylated spirits (i.m.s.), 1-(2,4,6-*trichlorophenyl*)*ethyl alcohol* (1.85 g, 21%), m.p. 72—74° (Found: C, 42.4; H, 3.5. C$_8$H$_7$Cl$_3$O requires C, 42.6; H, 3.1%), τ (CCl$_4$) 2.73 (2 H, s, ArH), 5.43 (q, J 6.5 Hz, CH), and 7.46 (d, J 6.5 Hz, CH$_3$). Acetylation as above gave, after recrystallisation from i.m.s. at $-70°$, 1-(2,4,6-*trichlorophenyl*)*ethyl acetate* (1.77 g, 81%), m.p. 70.5—72° (Found: C, 45.1; H, 3.4%).

1-(2,3,5,6-*Tetrachlorophenyl*)*ethyl Acetate*.—A solution of 1,2,4,5-tetrachlorobenzene (54 g, 0.25 mol) was treated with n-butyl-lithium according to the method of Tamborski et al.[13] followed by an excess of acetaldehyde. The crude alcohol could not be separated from the starting material so acetylation was not attempted as above. However addition to pyridine showed that the alcohol, but not the starting material, was soluble; the latter was therefore filtered off before addition of acetic anhydride. Work-up and re-crystallisation from i.m.s. gave 1-(2,3,5,6-*tetrachlorophenyl*)-*ethyl acetate* (27.3 g, 36% overall), m.p. 137—139° (Found: C, 40.0; H, 2.9. C$_{10}$H$_8$Cl$_4$O$_2$ requires C, 39.8; H, 2.7%), τ (CCl$_4$) 2.41 (H, s, ArH), 3.53 (q, J 6.5 Hz, CH), 7.96 (s, COCH$_3$), and 8.33 (d, J 6.5 Hz, CH$_3$).

1-*Pentachlorophenylethyl Acetate*.—The Grignard reagent formed from hexachlorobenzene (142 g, 0.5 mol) by the method of Pearson and Cowen [14] was treated with an excess of acetaldehyde. Hydrolysis and work-up gave 1-(*penta-chlorophenyl*)*ethyl alcohol* (76 g, 52%), m.p. 127—129° (Found: C, 32.4; H, 1.7. C$_8$H$_5$Cl$_5$O requires C, 32.6; H, 1.7%). Acetylation of the alcohol (15.1 g, 0.051 mol) as above gave, after work-up and recrystallisation from i.m.s. at -70 °C, 1-(*pentachlorophenyl*)*ethyl acetate* (15.2 g, 89%), m.p. 103—104° (Found: C, 36.0; H, 2.3. C$_{10}$H$_2$-Cl$_5$O$_2$ requires C, 35.7; H, 2.1%), τ (CCl$_4$) 3.56 (H, q, J 6.5 Hz CH), 7.96 (s, COCH$_3$), and 8.37 (d, J 6.5 Hz, CH$_3$).

Kinetic Studies.—These were carried out in the manner previously described.[15] All the compounds gave excellent first-order kinetic plots which were linear to beyond 95% of reaction and rate coefficients at any one temperature could be duplicated to within $\pm 1\%$.

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[11] H. Hodgson, *Chem. Rev.*, 1947, **40**, 251.

[12] A. Jackson and T. H. Gazolo, *J. Amer. Chem. Soc.*, 1899, **21**, 55.

[13] C. Tamborski, E. J. Soloski, and C. E. Dillis, *Chem. and Ind.*, 1965, 2067.

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[15] R. Taylor, *J. Chem. Soc. (B)*, 1968, 1397.