Measurement of Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part VI.[1] Further Evidence for the Direct Field Effect, and the Invalidity of σ_o^+ Values

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The relative rates of pyrolysis of 1-arylethyl acetates $XC_6H_4CHMe{\cdot}OAc$ (measured over a 50° range for each compound) are as follows at 600 °K: (X =) H, 1·00; 2-PhS, 0·89; 3-PhS, 0·805; 4-PhS, 1·32; 2-PhO, 1·20; 4-PhO, 2·14; 2-MeS, 1·02; 4-MeS, 1·48; 2-$PhCH_2$, 1·51; 4-$PhCH_2$, 1·51. The abnormally low activation by *ortho*- relative to *para*-oxygen- and -sulphur-containing substituents is shown to be general for reactions involving formation of carbonium ions at the side-chain α-positions. The results parallel those found for *ortho*-halogeno-substituents and show that the rules required to describe the effect of *ortho*-substituents in these reactions are different from those required for electrophilic substitutions; the difference is ascribed to the particular effectiveness of the direct field effect operating between the *ortho*- and the side-chain α-positions, and any attempt to determine σ^+ values from these reactions for application to electrophilic substitutions is invalid. The abnormally high activation by the *ortho*-benzyl substituent is attributed to interaction between the substituent π-electrons and the incipient carbonium ion.

Values of σ_o^+ have been evaluated as −0·27(4-$PhCH_2$), −0·53(4-PhO), and +0·145(3-PhS), but for the sulphur-containing *para*-substituents, correlation with electrophilic substitution data is poor, indicating substantial d_π–p_π conjugation in the gas-phase reaction, and this may arise from the absence of solvent.

Lithiation of diphenyl sulphide and coupling of the intermediate with acetaldehyde produces *ca.* 40% of *meta*-product in contrast to other coupling reactions. Caution is therefore recommended in using lithiation reactions for the preparation of specific isomers.

THE pyrolysis of 1-arylethyl acetates is a useful model reaction for predicting the effects of *meta*- and *para*-substituents in electrophilic aromatic substitutions; the effects of a wide range of substituents have now been measured and shown to correlate with σ^+ values.[1,2] The reaction has also been used to determine electrophilic reactivities of heterocycles and other aromatic compounds which cannot be obtained by traditional methods.[3] Recently it has been proposed, on the basis of good correlations of *ortho*-substituent effects in the pyrolysis of 1-arylethyl acetates, carbonates, and benzoates (I; R = Me, OMe, or Ph), that *ortho*-substituent constants can be obtained from this reaction.[4] We have shown, however, that, relative to electrophilic substitutions,

$$ArCHMe{\cdot}O{\cdot}COR$$

(I)

the reactivities of *ortho*-substituents are abnormal in this reaction, some being abnormally activating and others (the halogens) abnormally deactivating.[1] Analysis of the effects of the latter substituents in a range of reactions showed that in every case where the full or partial carbonium ion is generated at the side-chain α-position, abnormal deactivation occurs. We have attributed this to the direct field effect, which is particularly favoured for reaction at this position since no bonds intervene between the reaction site and the substituent dipole. In the gas phase the direct field effect can be expected to be particularly important.

Abnormally high reactivity was observed for compounds with substituents (trifluoromethyl and phenyl) which have *p*-orbital electrons that are in a sterically favourable position for overlap with the empty *p*-orbitals of the incipient carbonium ion, *i.e.* a direct conjugative effect operates for these substituents.

The present study was undertaken to extend the range of substituents to include those for which little data is available from other reactions, and to include some additional *ortho*-substituents.

RESULTS AND DISCUSSION

Rate coefficients showed linear first-order behaviour for at least 95% of reaction and were reproducible to

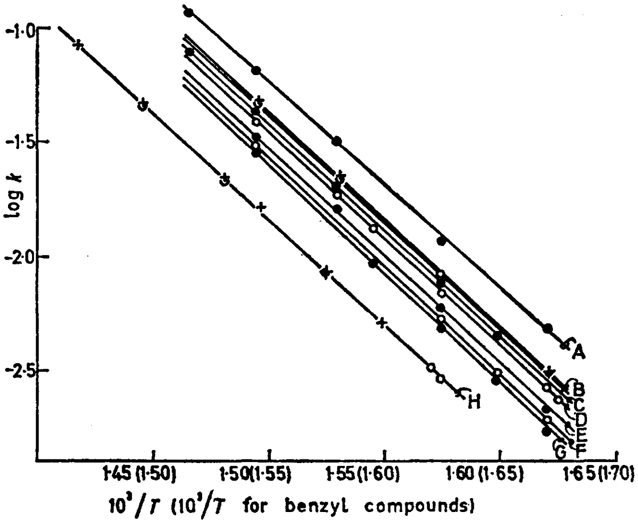

FIGURE 1 Arrhenius plot for 1-arylethyl acetates: A, 4-PhO; B, 2-Me (—+—) and 4-MeS (—○—); C, 4-PhS; D, 2-PhO; E, 2-MeS; F, 2-PhS; G, 3-PhS; H, 2-$PbCH_2$ (—○—) and 4-$PhCH_2$ (—+—)

±2%. The kinetic data are set out in the Table; the $k_{rel.}$ values were obtained from the Arrhenius plots (Figure 1) (the results for the phenyl compound have

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been given previously [5]); in this Figure the data for the benzyl compounds have been offset in the interests of clarity. Changes in reactivity are paralleled by changes in activation energy as is usual in this reaction. The $k_{rel.}$ values are set out in Figure 2 along with those obtained for methyl and methoxy-substituents from previous studies. Smith and his co-workers [4] recently reported that log $k_{rel.}$ for the *ortho*-methyl substituents was 0·17 (at 647 °K) in contrast to the value of 0·215 (at 600°K) originally reported.[2] Since this discrepancy is large and is important for part of our analysis, we repeated the measurements with the sample used in the original work, and obtained a value of 0·175 (at 600°K) in excellent agreement with that of Smith. We cannot account for the original discrepancy but point out that the original data were obtained with a less sophisticated version of the apparatus currently employed.

Pyrolysis of compounds ArCHMe·OAc

Substituent in Ar	10^3k (sec.$^{-1}$) at temperature (°K) shown 408·8°	395·8°	380·4°	373·7°	361·7°	352·3°	343·7°	342·1°	log A	E_{act} (kcal. mole^{-1})	$\Delta S^{\ddagger}$ (cal. mole^{-1} deg.$^{-1}$)	log k/k_0 (at 600 °K)
2-PhO		39·1	18·7	13·3 [a]	6·74		2·62	2·28	12·5	42·5	−2·7	0·08
4-PhO	116·5	64·8	31·2		11·6		4·74		12·5	41·9	−2·7	0·35
2-PhS		30·4			5·20	3·03	1·89		12·8	43·7	−1·4	−0·05
3-PhS		28·0		9·37	4·73	2·84	1·65		12·8	43·9	−1·4	−0·095
4-PhS	78·2	42·9	20·6		7·62	4·40			12·9	42·5	−0·9	0·12
2-MeS		33·1	15·9		5·84		2·09		12·65	43·3	−2·1	0·01
4-MeS		46·6	21·9		8·28		3·10		12·6	42·8	−2·3	0·17
2-Me		48·0	22·3 [b]				3·09		12·65	42·8	−2·1	0·175
2-$PhCH_2$		47·1	22·5		8·66 [c]		3·21	2·86	12·6	42·5	−2·3	0·18
4-$PhCH_2$	86·0	48·3	22·8	16·5	8·70	5·15			12·6	42·5	−2·3	0·18

[a] 373·8°. [b] 380·3°. [c] 361·9°. [d] 395·7°.

para-*Methoxy-, -Phenoxy-, and -Benzyl-substituents.*—The pyrolysis of 1-arylethyl acetates has previously been shown [2,6] to have an r factor of *ca.* 1·0 in a Yukawa–Tsuno analysis; [7] thus σ^+ constants can be obtained directly in this reaction. Our data predict values of −0·76, −0·53, and −0·27 for *p*-MeO, *p*-PhO, and *p*-$PhCH_2$, respectively. The first value is close to the standard value of −0·778, which applies to a large number of reactions. For the other two substituents, however, data from other reactions are limited and have not previously been analysed in quantitative terms. For *p*-PhO, σ^+ values required to correlate the data for each reaction are as follows: −0·53 (hydrogen exchange [8]), *ca.* −0·47 (nitration [9]), −0·57 (mercuration [10]), −0·555 (solvolysis of diarylmethyl chlorides [11]), −0·66 (molecular bromination [12]), −0·42 (protodesilylation [13]), and −0·40 (protodegermylation [14]). The first four reactions require an average σ^+ value of −0·53, in precise agreement with the prediction for the pyrolysis reaction. Bromination and the demetallations require higher and lower σ^+ values, respectively; this arises because the r factors for these reactions are correspondingly higher and lower than 1·0. The Yukawa–Tsuno treatment of the data for these reactions shows that the observed substituent effect can be predicted precisely from our σ^+ value by using a σ value for *p*-PhO of −0·17; the predicted value seems theoretically reasonable, being 0·1 unit more positive than for *p*-MeO.

The effect of *p*-$PhCH_2$ has only been measured in hydrogen exchange [15] and protodesilylation,[16] which require σ^+ values of −0·25 and −0·195, respectively. The former value is in good agreement with ours, and the lower value for the desilylation can be shown to arise from the lower r factor for this reaction.

para-*Methylthio- and* meta- *and* para-*Phenylthio-substituents.*—The order of activation is *p*-MeS > *p*-PhS, as found in hydrogen exchange [8,17] and protodesilylation.[13,18] However, data from the present reaction predict σ^+ values of −0·26 and −0·18 for these substituents, for which required values are −0·58 and −0·47 (hydrogen exchange) and −0·275 and −0·225 (protodesilylation); for *p*-MeS alone, solvolysis of α-cumyl chlorides [19] requires −0·605, solvolysis of 9-aryl-9-chlorofluorenes [20] −0·59, acetylation [21] −0·51, and bromination [21] −0·675. The pyrolysis apart, the values for the thiomethyl substituent from each reaction correlate well with each other, deviations from a standard σ^+ value of *ca.* −0·59 being in accord with the reaction r factors (that for acetylation [6] is 0·81). The low σ^+ values in pyrolysis cannot, however, be explained in these terms since the r factor for the reaction is *ca.* 1·0.

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We have recently proposed that the abnormal response of sulphur to demands for resonance arises from the existence of d_π–p_π conjugation between the sulphur atom and the aromatic π-electrons in the ground state, so that in going to the transition state sulphur passes from being conjugatively electron-withdrawing to conjugatively electron-supplying.[18] For the gas-phase reaction, conjugation in the ground state seems to be abnormally high compared with the solution reactions. A possible explanation is that in the latter, solvent partially satisfies the electron requirement of the substituent in the ground state, thereby facilitating greater electron release on passing to the transition state. We are not however wholly inclined to this view because it suggests that no correlation of sulphur substituent effects in solution reactions should be possible, contrary to observation.

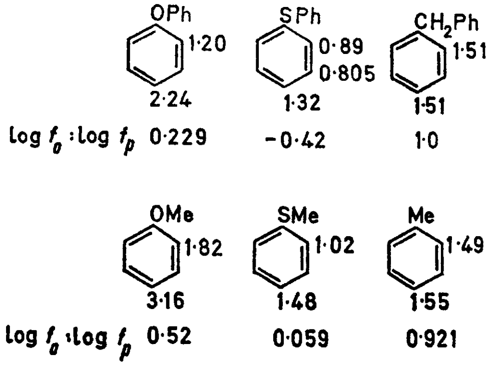

FIGURE 2 Partial rate factors for pyrolysis of 1-arylethyl acetates

The effect of d_π–p_π conjugation is probably not important for *meta*-substituents, so we may deduce a value of +0·145 for $\sigma^+_{m\text{-PhS}}$. No other measurement of the effect of this substituent has been made, but the value seems reasonable since $\sigma^+_{m\text{-PhO}}$ can be deduced as +0·1 from the desilylation data of Eaborn and Jackson,[22] and the deactivation by the sulphur-containing substituent would be expected to be greater.

Ortho-*Substituents*.—The electronic effects of the *ortho*-substituents are most accurately assessable in terms of the log f_o : log f_p ratios shown in Figure 2. In the case of the phenoxy- and phenylthio-substituents, the ratios are considerably less than in hydrogen exchange and protodesilylation,[18] these being the only reactions for which these values have been measured. For methylthio- the ratio is similarly considerably less than those found for hydrogen exchange[18] (0·88), protodesilylation[18] (0·70), bromination[21] (0·78), and acetylation[21] (0·64).

The ratio for the methoxy-substituent has been most widely measured; for electrophilic substitutions we have 0·805 (molecular bromination[23]), 0·885 (molecular chlorination[24]), 0·795 (desilylation[25]), 0·840 (degermylation[14]), and 0·92 (detritiation[17]); mercuration, which is known to be subject to severe steric hindrance, gives a value of 0·68.[10] For side-chain reactions we have 0·45 (solvolysis of α-cumyl chlorides[26]), 0·42 (acid-catalysed dehydration of 1-aryl-2-phenylethanols[27]), 0·37 (solvolysis of 9-aryl-9-chlorofluorenes[20]), 0·54 (pyrolysis of 1-arylethyl carbonates[4]), 0·49 (pyrolysis of 1-arylethyl benzoates[4]), 0·52 (benzoyl ion formation[28]), —0·01 (acid-catalysed hydration of phenylacetylenes[29]), and —0·1 (acid cleavage of arylethynyl germanes[30]). As a class the reactions with side-chain α-carbonium ion transition states all give rise to lower ratios than do electrophilic substitutions. This may not be solely attributable to steric hindrance to attainment of coplanarity of the substituent and carbonium ion p-orbitals with those of the ring, because *ortho*-halogeno-substituents in the acetate pyrolysis and other side-chain reactions are also abnormally deactivating compared to electrophilic substitutions; for these substituents, steric hindrance to attainment of coplanarity was shown not to apply.[1]

The low ratio observed for the oxygen- and sulphur-containing substituents in pyrolysis (relative to desilylation and hydrogen exchange) is apparently part of a much more widely occurring phenomenon, and we predict that as more substituent-effect data become available it will fit into the pattern described. It is significant that all of these substituents are, like the halogens, of the $-I$ type. For the halogens we proposed that this extra deactivation arose from the particular effectiveness of the direct field effect in operating between the *ortho* and side-chain α-positions, there being neither bonds nor (for the gas-phase reactions at least, if not generally) solvent molecules in the intervening space, and we propose that this accounts substantially for the present results as well.

Our conclusions are particularly important because it has recently been proposed[4] on the basis of the good correlation of the *ortho*-methoxy-substituent effect in the pyrolysis reactions, and[27] on the basis of a similar correlation in solvolysis of α-cumyl chlorides and acid-catalysed dehydration of 1,2-diarylethanols, that a $\sigma^+_{o\text{-MeO}}$ value could be obtained; these workers proposed values of —0·411 and —0·33 respectively. Unfortunately, no attempt was made to see if these values actually *correlated* data for electrophilic substitutions of anisole; the foregoing discussion shows that they do not, and can not. Values required are —0·66 (molecular bromination), —0·68 (molecular chlorination), —0·57 (mercuration), —0·55 (desilylation), and —0·59 (degermylation); the mercuration value would be higher

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but for steric hindrance, and the demetallation values are low (just as they are for *p*-MeO in these reactions) merely because of the low *r* factors.

It might be supposed that since both halogen and oxygen- and sulphur-containing substituents in the *ortho*-position for side-chain reactions produce abnormal deactivation because of the direct field effect, then methyl groups should produce a corresponding rate enhancement. However, Taft has shown that the average inductive substituent constants for methyl, methoxy-, and chloro-substituents are −0·03, +0·28, and +0·45 respectively.[31] Furthermore, the electropositive hydrogen atoms of the methyl group are as near to the carbonium ion as the negative end of the C–C dipole; consequently it would not be surprising to find the methyl group producing no effect, or even abnormal deactivation, in the side chain reactions. Such an effect, which has been proposed to account for the anomalous behaviour of alkyl groups in ^{19}F n.m.r. spectra of aromatic compounds,[32] would also enhance the deactivating direct field effect of the *ortho*-methoxy- and -thiomethyl-substituents. Analysis of the experimental data is more difficult here because there is evidence that for methyl-substituted compounds steric hindrance to attainment of coplanarity of side-chain carbon *p*-orbitals with those of the ring may be important, in contrast for example, to the chloro-substituted compounds.[33] Nevertheless, for the gas-phase reaction, steric hindrance is probably small since, one of the side chain α-substituents is hydrogen, and the $\log f_o : \log f_p$ value of 0·92 (similar values are obtained for carbonate and benzoate pyrolysis [4]) is comparable to those obtained in electrophilic substitutions (values range from 0·76 to 1·11 in reactions for which steric hindrance is believed to be unimportant [34]).

The *ortho*-benzyl substituent is abnormally activating in pyrolysis, so that the $\log f_o : \log f_p$ ratio is greater than for other reactions.[18] Indeed *ortho*-benzyl is more activating than *ortho*-methyl, whereas the reverse should be the case. We tentatively attribute this abnormality to interaction between the π-electrons of the substituent phenyl ring and the incipient carbonium ion, in a manner similar to that proposed to account for the abnormally high reactivity of *ortho*-phenyl- and -trifluoromethyl-substituted compounds.[1] If this is correct then it should also apply to the *ortho*-phenoxy- and -phenylthio-substituents, and must therefore be outweighed by the direct field effect in these cases. We hope to investigate this further.

Lithiation of diphenyl sulphide and coupling of the intermediate with acetaldehyde produced, in addition to the expected *ortho*-compound, *ca.* 40% of *meta*-product (see Experimental section), in contrast to other coupling reactions which appear to produce little or none of the latter.[18] Caution in the use of the lithiation reaction for the preparation of specific isomers is obviously necessary.

EXPERIMENTAL

The apparatus and general method of the pyrolytic kinetic studies have been described.[1] In the following preparations, all fractionations were monitored by g.l.c. and the nature of the products was confirmed by i.r. spectroscopy.

1-(2-*Phenoxyphenyl*)*ethyl Acetate*.—Diphenyl ether (34·0 g., 0·2 mole) was metallated with n-butyl-lithium (1·35M-solution in heptane; 150 ml.); the mixture became warm during the addition of the latter, and was refluxed for a further 8 hr. An excess of acetaldehyde was added slowly, and the mixture was heated under reflux for a further 2 hr. Hydrolysis and work-up gave crude 1-(2-phenoxyphenyl)ethyl alcohol, which was acetylated directly with acetic anhydride (40 ml.) in pyridine (80 ml.) under reflux during 3 hr. Work-up gave 1-(2-*phenoxyphenyl*)*ethyl acetate* (32%), b.p. 112°/0·3 mm., n_D^{20} 1·5489 (Found: C, 75·1; H, 6·4. $C_{16}H_{16}O_3$ requires: C, 75·0; H, 6·3%).

1-(4-*Phenoxyphenyl*)*ethyl Acetate*.—Diphenyl ether (34·0 g., 0·2 mole) was converted into 4-acetylphenyl phenyl ether (71%), m.p. 49—50° (lit.,[35] 45°; lit.,[36] 50°; lit.,[37] 53°) by the normal Friedel–Crafts procedure. The crude alcohol obtained by reduction with sodium borohydride was acetylated as before to give, after work-up, 1-(4-*phenoxyphenyl*)*ethyl acetate* (81% based on ketone), b.p. 128°/0·4 mm., n_D^{20} 1·5515 (Found: C, 75·3; H, 6·4%).

1-(2-*Phenylthiophenyl*)*ethyl Acetate and* 1-(3-*Phenylthiophenyl*)*ethyl Acetate*.—Diphenyl sulphide (37·0 g., 0·2 mole) was treated with n-butyl-lithium as for the oxygen analogue and likewise converted into the ester. However, g.l.c. analysis of the product showed two peaks in *ca.* 3 : 2 ratio, both of which had lower retention times than the *para*-compound and both of which, like the *para*-compound, gave *m*/*e* values of 272 in a mass spectral analysis. These compounds were therefore the *ortho*- and *meta*-isomers, the former (lower retention time) being present in the larger quantity. Careful fractionation yielded pure 1-(2-*phenylthiophenyl*)*ethyl acetate* (2·8%), b.p. 130°/0·5 mm., n_D^{20} 1·5875 (Found: C, 71·0; H, 6·3. $C_{16}H_{16}O_2S$ requires: C, 70·6; H, 5·9%). Further fractionation yielded pure 1-(3-*phenylthiophenyl*)*ethyl acetate* (2%), b.p. 118°/0·2 mm., n_D^{20} 1·5882 (Found: C, 70·9; H, 6·15%).

1-(4-*Phenylthiophenyl*)*ethyl Acetate*.—Diphenyl sulphide (18·6 g., 0·1 mole) was converted by the Friedel–Crafts procedure into 4-acetylphenyl phenyl sulphide; reduction, and acetylation of the crude alcohol as before gave 1-(4-*phenylthiophenyl*)*ethyl acetate* (13% based on ketone), b.p. 142°/0·3 mm., n_D^{20} 1·5914 (Found: C, 70·2; H, 6·2%). The low overall yield in the last two stages arose from the tendency of the ester to decompose (to phenyl 4-vinylphenyl sulphide and acetic acid) during fractionation. Use of a shorter fractionating column than that (1 m.) used in these preparations, and a higher vacuum, would probably increase this yield.

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1-(2-*Methylthiophenyl*)*ethyl Acetate*.— 2-Bromothioanisole[18] (15·5 g., 0·055 mole) was converted *via* the Grignard reagent (in tetrahydrofuran) into crude 1-(2-methylthiophenyl)ethyl alcohol, which was acetylated as before to give 1-(2-*methylthiophenyl*)*ethyl acetate* (77·5% overall), b.p. 86°/0·4 mm., n_D^{20} 1·5435 (Found: C, 62·8; H, 6·6. $C_{11}H_{14}O_2S$ requires: C, 62·8; H, 6·7%).

1-(4-*Methylthiophenyl*)*ethyl Acetate*.— 4-Bromothioanisole (34 g., 0·17 mole) was converted like the 2-isomer into 1-(4-*methylthiophenyl*)*ethyl acetate* (31% overall), b.p. 98—100°/0·3 mm., n_D^{20} 1·5569 (Found: C, 62·6; H, 6·75%).

1-(2-*Benzylphenyl*)*ethyl Acetate*.—α-(2-Bromophenyl)toluene, b.p. 94°/0·4 mm. (lit.,[38] 192—198°/32 mm.), prepared[39] in 30% yield from bromobenzene and 2-bromobenzyl bromide, was metallated with n-butyl-lithium in the usual way. The α-(2-lithiophenyl)toluene so obtained was treated with an excess of acetaldehyde, and the crude alcoholic product was acetylated as before to give 1-(2-*benzylphenyl*)*ethyl acetate* (50%), b.p. 102—105°/0·4 mm., n_D^{20} 1·5513 (Found: C, 80·5; H, 7·35. $C_{18}H_{18}O_2$ requires: C, 80·3; H, 7·15%).

1-(4-*Benzylphenyl*)*ethyl Acetate*.—α-(4-Bromophenyl)toluene, b.p. 104°/0·4 mm. (lit.,[40] 162°/13 mm., 128°/3 mm.), prepared[39] in 46% yield from bromobenzene and 4-bromobenzyl bromide, was converted like the 2-isomer into 1-(4-*benzylphenyl*)*ethyl acetate* (63%), b.p. 142°/0·4 mm., n_D^{20} 1·5484 (Found: C, 80·3; H, 7·45%).

1-(o-*Tolyl*)*ethyl Acetate*.—This was available from a previous[2] preparation.

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