Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Esters. Part 16.[1] The Effects of the Acetoxy and Acylamino Substituents

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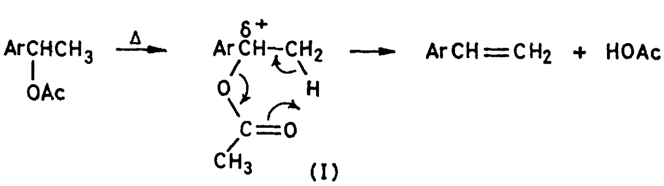
The rates of gas-phase elimination of acetic acid from the appropriate 1-arylethyl acetates have been measured to determine σ^+ values for the following substituents: *p*-OAc (−0.12), *m*-OAc (0.335), *p*-NHAc ($\ngtr -0.62$), *m*-NHAc (0.08). The numerical values, and the differences between them and those reported for molecular chlorination, are discussed in terms of electronic effects.

RECENTLY, de la Mare and his co-workers studied the molecular chlorination of 4-substituted acetanilides.[2] Comparison of the rates of substitution *ortho* to the acetylamino substituent with that for the corresponding position in acetanilide yielded f_m values for the 4-substituent. A plot of log f_m *versus* σ_m^+ values (determined from the solvolysis of 2-aryl-2-chloropropanes [3]) gave a fairly good straight line with ρ −5.3, and from this correlation new σ_p^+ values were obtained for the *m*-OAc (0.26) and *m*-NHAc (0.13) substituents. From the rate and isomer distribution in chlorination of acetoxybenzene σ_p^+ for *p*-OAc was determined as −0.19;[2] likewise from data for chlorination of acetanilide[4] the value of σ_p^+ for *p*-NHAc may be calculated as −0.64. Since, in a (so far) unsuccessful attempt to measure the σ^+ value of the *p*-OH substituent in the gas phase *via* pyrolysis of 1-arylethyl acetates(I) we had prepared the *p*-acetoxy-substituted 1-arylethyl acetate, it seemed timely to measure the effect of this substituent and, for completeness, of the *m*-OAc, *p*-NHAc, and *m*-NHAc substituents as well.



(I)

RESULTS AND DISCUSSION

The rate and Arrhenius data for the elimination are given in Supplementary Publication No. SUP 22298 (3 pp.); † data for 1-phenylethyl acetate have been given in previous parts of this series, from which the rate coefficient for elimination at 650 K may be interpolated as 12.8×10^{-3} s^{-1}. At 650 K the ρ factor for the elimination may be calculated from the value of −0.66 at 600 K (*via* the $\rho T = \rho' T'$ relationship) to be −0.61. Use of this value gives the σ^+ values listed in the Table along with those determined from molecular chlorination,

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[1] Part 15, E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 1541.

[2] P. B. D. de la Mare, N. S. Isaacs, and M. J. McGlone, *J.C.S. Perkin II*, 1976, 784.

[3] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[4] P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 1958, 1519.

and the corresponding σ values.[5] There is in general quite good agreement in the two sets of σ^+ values but it is relevant to consider the differences that do exist and probable reasons for these. The main points are as follows.

δ Parameters for acetoxy and acylamino substituents

Substituent	σ	σ^+ (pyrolysis)	σ^+ (molecular chlorination)
m-OAc	0.39	0.335	0.26
p-OAc	0.31	−0.12	−0.19
m-NHAc	0.21	0.08	0.13
p-NHAc	0	$\not> -0.62$ [a]	−0.64

[a] This is a maximum value, see Experimental section.

(i) The *p*-AcO substituent is slightly less activating in pyrolysis but this is not unexpected because the overall effect of this substituent represents a delicate balance between a strong $-I$ effect (as shown by the σ values for both *m*- and *p*-OAc substituents) and a strong $+M$ effect (as shown by the large difference between σ_p and σ_p^+). The overall effect will be very susceptible to the extent of conjugation between the substituent and the reaction site. Similar arguments account for the differences in the σ^+ and σ values for the *p*-NHAc substituent.

(ii) The discrepancies in the values for the *meta*-substituent cannot be similarly explained. Possible reasons for the discrepancy are indicated by considering the differences in the σ_m^+ and σ_m values since these reflect the extent of secondary relay of the conjugative effect to the *meta*-position and should be greater for NHAc than for OAc. This is true for the pyrolysis data, $\sigma^+ - \sigma = 0.055$ (OAc), 0.13 (NHAc), but not for the chlorination data, $\sigma^+ - \sigma = 0.13$ (OAc), 0.08 (NHAc). Furthermore the ratio of the σ_m^+ values deduced from molecular chlorination (2.0) is *not* the same as the ratio of the $\log f_m$ values in that reaction (2.5) whereas of course it should be. The reason for this appears to be that the scatter in the $\log f_m$—σ^+ plot is such that the line of best fit does not pass through the origin (though one would expect that the data for acetanilide itself must be the most accurate). However, if one uses the σ_m^+ values determined in the gas phase for the Me (−0.098),[6,7] Ph (0.0),[8] and NO_2 (0.73) [9] substituents (and which give a better correlation of *all* electrophilic substitution data than do the values derived from solvolysis), the correlation is very significantly improved, and ρ becomes −4.7 and the σ_m^+ values for the OAc and NHAc substituents become 0.24 and 0.095, respectively (ratio 2.5). The data for the *m*-NHAc substituent in both reactions are now in very good agreement but the value for *m*-OAc still seems much too small in chlorination. It seems possible that the method of determining *meta*-reactivities in molecular chlorination is unsatisfactory due, as de la Mare *et al* have suggested,[2] to interaction between the substituents; in 1,4-diacetoxybenzene an even smaller σ^+ value for *m*-OAc is required to predict accurately the overall reactivity.

EXPERIMENTAL

1-(4-*Acetoxyphenyl*)*ethyl Acetate*.— 4-Hydroxyacetophenone was reduced by sodium borohydride in aqueous ethanol, and the intermediate alcohol thought to be obtained was acetylated with acetic anhydride in pyridine to give a product, b.p. 100° at 0.5 mmHg. The n.m.r. spectrum indicated that this compound was in fact 1-(4-acetoxyphenyl)ethyl ethyl ether and this was confirmed by its failure to undergo elimination. Evidently the excess of sodium borohydride in the reduction step facilitates ether formation at the aliphatic oxygen.

To circumvent this, reduction by sodium borohydride was carried out in a rapidly stirred mixture of ether and water to give, after work up, 1-(4-hydroxyphenyl)ethyl alcohol, m.p. 130° (lit.,[10] 130—131°). Acetylation of this alcohol with acetic anhydride and pyridine gave after work up and fractional distillation, 1-(4-*acetoxyphenyl*)*ethyl acetate*, b.p. 100° at 0.5 mmHg, n_D^{20} 1.497 2, m.p. 57° (after standing), $\tau(CCl_4)$ 2.90 (4 H, A_2B_2, m, ArH), 4.22 (q, *J* 6.5 Hz, CH), 7.85 (s, $ArOCOCH_3$), 8.07 (s, $COCH_3$), and 8.54 (d, *J* 6.5 Hz, CH_3) (Found: C, 65.0; H, 6.4. $C_{12}H_{16}O_4$ requires C, 64.85; H, 6.35%).

1-(3-*Acetoxyphenyl*)*ethyl Acetate*.—3-Hydroxyacetophenone was reduced as above and the intermediate alcohol was acetylated to give after work up and fractional distillation, 1-(3-*acetoxyphenyl*)*ethyl acetate*, b.p. 108° at 0.6 mmHg, n_D^{20} 1.496 4, $\tau(CCl_4)$ 2.95 (4 H, m, ArH), 4.25 (q, *J* 6.5 Hz, CH), 7.87 (s, $ArOCOCH_3$), 8.08 (s, $COCH_3$), and 8.56 (s, *J* 6.5 Hz, CH_3) (Found: C, 65.1; H, 6.3%).

1-(4-*Acetylaminophenyl*)*ethyl Acetate*.—This compound was prepared as previously described [11] and melted at 102° thereby confirming that the earlier literative value [12] of 192° was in error.

1-(3-*Acetylaminophenyl*)*ethyl Acetate*.—3-Aminoacetophenone, dissolved in aqueous ethanol, was reduced by sodium borohydride and the crude alcohol acetylated as above to give after work up and fractional distillation, 1-(3-*acetylaminophenyl*)*ethyl alcohol*, b.p. 185° at 0.5 mmHg, as a yellow, very viscous oil, $\tau(CCl_4)$ 0.71 (s, NH), 2.79 (4 H, m, ArH), 4.35 (q, *J* 6.5 Hz, CH), 8.00 (s, $ArNCOCH_3$), 8.11 (s, $COCH_3$), and 8.63 (d, *J* 6.5 Hz, CH_3) (Found: C, 64.5; H, 7.8. $C_{12}H_{17}NO_3$ requires C, 64.5, H. 7.7%).

Kinetics.—These were carried out in the manner previously described,[13] and rate coefficients (derived from kinetic plots which were linear to >90% reaction) could be duplicated to within ±2% for the *m*- and *p*-OAc, and *m*-NHAc compounds. However, this was not the case for the *p*-NHAc ester. We had previously attempted to measure the rate of elimination of this ester but found that it appeared to be particularly sensitive to the condition of the surface of the reactor,[11] and this was true in the present case also. Surface effects can be minimised by measuring elimination rates at the highest possible temperature. However, with this ester its very low volatility means that a significant time is taken for it to volatilize after injection into the reactor whereas with most esters, this process is effectively instantaneous. Consequently at higher temper-

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[5] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[6] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1463.

[7] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 681.

[8] R. Taylor and G. G. Smith, *Tetrahedron*, 1963, **19**, 937.

[9] H. B. Amin and R. Taylor, *Tetrahedron Letters*, 1978, 267.

[10] U.S.P. 2,276,139/1940 (*Chem. Abs.*, 1942, **36**, 4732).

[11] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

[12] M. L. Rousset, *Bull. Soc. chim. France*, 1894, **11**, 322.

[13] R. Taylor, *J. Chem. Soc.* (*B*), 1967, 1397.

atures, the rate of elimination (measured in our system as the rate of pressure increase at constant volume) becomes confused with the pressure increase due to volatilization. This in itself would not be serious since the time elimination rate could be determined over the latter portion of the observed pressure–time plot. However a further complication is that this ester is very insoluble in chlorobenzene, the inert solvent used for injecting solid esters into the reactor. Hence the pressure increase obtained in a kinetic run is sufficiently small to render determination of rate coefficients from the latter portion of a run rather inaccurate. As a result of these complications, rate coefficients were measured only over a very small temperature range and only the minimum values obtained at a given temperature are reported; these however give an identical $k_{\text{rel.}}$ value to that which we obtained from the minimum rate coefficients in an earlier but unpublished study (see ref. 11). We may therefore with some confidence state that the $k_{\text{rel.}}$ value is unlikely to be greater than that reported, but could, since we have been unable to carry out a full study to show the absence of surface effects, be smaller. The derived σ^+ value is therefore a maximum.

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