The Mechanism of the Gas-phase Pyrolysis of Esters. Part IV.[1] Effects of Substituents at the β-Carbon Atom †

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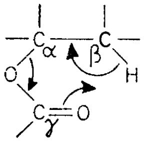
Rates of gas-phase thermal decomposition of some 2-substituted ethyl acetates and 3-substituted propyl acetates into acetic acid and substituted alkenes have been measured between 368.7 and 429.2 °C. The data for 2-arylethyl acetates give a Hammett correlation with ρ +0.2 at 650 K, which taken along with previous data for the effect of α-aryl substituents (ρ −0.63 at 625 K) confirm that electron return to the β-carbon does not compensate for the electron withdrawal from the α-carbon during the transition state for the reaction so that the process is not fully concerted. These data, and comparison of rates of elimination of 2-substituted ethyl acetates with those of the corresponding 3-substituted propyl acetates provides the first unified and consistent interpretation of the effects of β-substituents on the rates of pyrolysis of esters. The data show that the conjugative effects of β-substituents play a major role in determining the overall rate of elimination for compounds with β-substituents, and that the anomalous activating effect of β-alkyl substituents is not due to the stabilising effect upon the incipient α-carbonium ion as reported in the literature, but rather to steric acceleration.

ALTHOUGH a very large number of thermal β-eliminations are known,[2,3] much remains to be learned about the detailed mechanism of these reactions and in particular the extent to which charge is developed in the transition state (I). In this series of papers we seek to evaluate this latter factor more precisely and thus far we have been able to show that the reaction is not *fully* concerted [*i.e.* the electron pairs in (I) do not move at exactly the same time], that the amount of resultant heterolytic character increases along the series: acetates < phenylacetates < benzoates < carbamates < carbonates,[1,4] and increases along the series: primary < secondary < tertiary.[1] We have also shown that the β-deuterium isotope effect is not a secondary effect arising from hyperconjugative stabilisation of the incipient carbonium ion formed at the α-carbon.[5]



(I)

Studies of the effects of substituents of various kinds at the α- and γ-carbon atoms in the transition state (I) are now both extensive and consistent with each other. Studies of the effects of substituents at the β-carbon are by contrast more limited and do not show the same measure of accord. For example, preliminary studies (on less sophisticated apparatus) of the effects of β-aryl substituents in 2-aryl-1-phenylethyl acetates and 2-arylethyl acetates showed differing ρ factors of +0.08 and +0.3, respectively;[6] in this paper we report an accurate value for the elimination from 2-arylethyl acetates. Other studies of the effects of β-substituents appear to show more serious qualitative inconsistencies (described in detail below) and this could be due to a conflict between the following five factors: (a) the inductive and mesomeric effects of the substituents (which may themselves be in conflict); (b) the primary effect of the substituent upon the breakage of the C–H bond (aided by electron withdrawal); (c) the secondary effect of the substituent upon breakage of the more remote C–O bond (aided, and to a greater extent by electron supply); (d) the effect upon the stability of the forming alkene; (e) the possibility of steric acceleration through a decrease in steric hindrance between substituents in the product alkene compared with the starting ester. Point (e) has been almost totally neglected in discussions of the effects of substituents on β-eliminations.

Before describing our kinetic results it is both appropriate and revealing to document the relevant existing data for the effects of β-substituents, and to draw attention to the inconsistencies which exist, many of which are not evident in influential reviews of the subject.[3,7]

(i) Our preliminary studies of the effects of 2-aryl substituents showed that electron withdrawal in the ring increased the rate. Therefore one could expect that electron-withdrawing substituents attached directly to the β-carbon should increase the rate. The phenyl group has a −*I* effect and thus we find that 2-phenylethyl acetate is 6.9 times as reactive (per β-hydrogen atom) as ethyl acetate at 600 K. However, at the same temperature 1,2-diphenylethyl acetate is only 3.95 times as reactive per β-hydrogen atom as 1-phenylethyl acetate. Both results may be contrasted with the absence of any effect of a β-phenyl substituent reported from the pyrolysis of alkyl chlorides.[8]

(ii) One could expect that other −*I* substituents should also increase the rate. Thus the carbonyl substituent causes 1-methyl-3-oxobutyl acetate to be more reactive

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† No reprints available.

[1] Part III, H. B. Amin and R. Taylor, *J.C.S. Perkin II*, 1975, 1802.

[2] C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.

[3] G. G. Smith and F. W. Kelly, *Progr. Phys. Org. Chem.*, 1971, **8**, 75.

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

[5] R. Taylor, *J.C.S. Perkin II*, 1972, 165.

[6] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817; G. G. Smith, F. D. Bagley, and R. Taylor, *ibid.*, 1961, **83**, 3647.

[7] A. Maccoll and P. J. Thomas, *Progr. Reaction Kinetics*, 1967, **4**, 119.

[8] D. V. Banthorpe, ' Elimination Reactions,' Elsevier, Amsterdam, 1963, p. 183.

than 1-methylpropyl acetate but by an astonishingly high factor of 240 (per β-hydrogen atom adjacent to the carbonyl group) at 582 K.[9] (Again this contrasts sharply with the factor of 2.4 observed for pyrolysis of the corresponding chlorides.[7]) The large effect of the β-carbonyl substituent in acetate pyrolysis is also indicated by the facts that *trans*-1-acetoxy-2-methoxycarbonylcyclohexane eliminates acetic acid to give 97% of 1-methoxycarbonylcyclohexene and only 3% of the 3-isomer,[10] that 2-ethoxycarbonyl-1-methylethyl acetate gives 3-ethoxycarbonylprop-1-ene on elimination,[11] and that 1-methyl-2-nitroethyl acetate gives 1-nitroprop-1-ene on elimination.[11] These results show that the statement [9] that 'electron release enhances the rate (of ester pyrolysis) whereas electron withdrawal decreases it' is clearly incorrect.

(iii) Oxygen-containing substituents in the β-position (*i.e.* methoxy and ethoxy) decrease the rate of elimination. This was claimed to be due to the electron-withdrawing ($-I$) effect of the oxygen upon the more remote incipient α-carbonium ion.[12] This cannot be correct in view of the results obtained with the much more powerful electron-withdrawing groups described under (ii) above.

(iv) Since a phenyl group increases the rate, a vinyl group (σ_I 0.15,[13] *cf.* 0.10 for phenyl [14]) could be expected to do likewise. This is true to the extent that $\mathrm{Me{\cdot}CHOAc{\cdot}CH_2CH{=}CH_2}$ eliminated 3·3 times as fast (per β-hydrogen adjacent to the vinyl group) as isopropyl acetate.[9,15] A quantitative inconsistency however is the fact that $\mathrm{Bu^t{\cdot}CHOAc{\cdot}CH_2{\cdot}CH{=}CH_2}$ eliminated 8.6 times as fast (per β-hydrogen) as $\mathrm{Bu^t{\cdot}CHOAc{\cdot}CH_3}$,[15] so clearly some other factor must be involved. Since a β-vinyl substituent increases the rate, a β-ethynyl substituent (σ_I 0.20 [16]) should do the same. The compound $\mathrm{Me{\cdot}CHOAc{\cdot}CH_2C{\equiv}CH}$ should therefore produce predominantly the conjugated product upon elimination whereas it is reported to produce none of this.[17]

TABLE 1

Rate per β-hydrogen atom due, and adjacent to, the group R [12,15]

		R		
$\mathrm{H{-}\underset{\underset{OAc}{\mid}}{CH}{-}R}$	Me	Et	$\mathrm{Pr^i}$	T/°C
	1	1.37	1.32	489
$\mathrm{CH_3{-}\underset{\underset{OAc}{\mid}}{CH}{-}R}$	Me	Et	CH·Me(Et)	
	1	2.6	3.8	411
$\mathrm{CH_3{-}\underset{\underset{OAc}{\mid}}{C}CH_3{-}R}$	Me	Et	$\mathrm{Pr^i}$	
	1	3.5	3.05	311
$\mathrm{Bu^t{-}\underset{\underset{OAc}{\mid}}{CH}{-}R}$	Me	Et	$\mathrm{Pr^i}$	
	1	2.61	1.40	330

(v) It follows from the above that $+I$ substituents should decrease the rate of elimination. This however is not observed, though some confusion on this point exists in the review literature. Maccoll and Thomas state that β-methylation decreases the rate for primary esters but increases it for secondary and tertiary esters.[7] In fact, when allowance has been made for the number of β-hydrogen atoms available, all ester types are made more reactive by monomethylation at the β-position; further methylation produces conflicting results (Table 1). The effect of β-methylation has been explained in terms of a stabilising effect upon the remote incipient α-carbonium ion,[12] but as we have seen from the above this cannot be correct otherwise strongly electron-withdrawing groups would decrease the rate. It is evident from Table 1 that we have to explain not only the initial rate decrease due to β-methylation, but also the attenuated increase on further substitution.

RESULTS AND DISCUSSION

Tables 2 and 3 show the rate coefficients, thermodynamic parameters, and log k_{rel} values for the 2-arylethyl acetates (relative to 2-phenylethyl acetate) and other substituted ethyl acetates (relative to ethyl acetate) respectively; the log k_{rel} values are interpolated from the Arrhenius diagrams at 650 K. Figure 1 shows the Arrhenius diagram for the substituted ethyl acetates; that for the 2-arylethyl acetates is not shown because of the difficulties arising from the very small ρ factor.

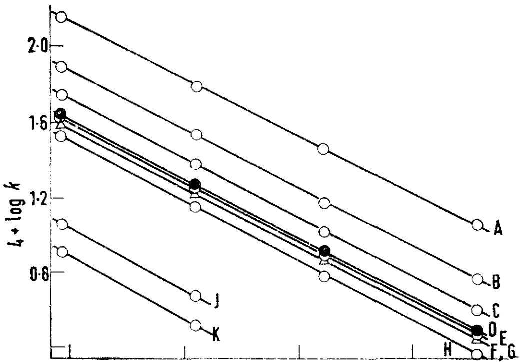

FIGURE 1 Arrhenius plot for β-substituted ethyl acetates: β-substituents, A, Ph; B, $\mathrm{CH_3COCH_2}$; C, $\mathrm{PhOCH_2}$; D, $\mathrm{PhCH_2}$; E, $\mathrm{CH_3CH_2}$; F, H; G, $\mathrm{CH_3OCH_2}$ (F and G coincident); H, $\mathrm{CH_3}$; J, PhO; K, $\mathrm{CH_3O}$

A plot of the log k_{rel} values for the 2-arylethyl acetates against σ values is shown in Figure 2 (upper curve). With the exception of the *p*-fluoro-point a reasonable correlation is obtained with ρ +0.2, *i.e.* in general, electron-supplying substituents decrease the rate and electron-withdrawing substituents increase it. The ρ factor

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[9] E. V. Emovon and A. Maccoll, *J. Chem. Soc.*, 1964, 227.

[10] W. J. Bailey and R. A. Baylouny, *J. Amer. Chem. Soc.*, 1954, **81**, 2126.

[11] W. J. Bailey and C. King, *J. Org. Chem.*, 1956, **21**, 858.

[12] J. C. Scheer, E. C. Kooyman, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 1123.

[13] G. B. Ellam and C. D. Johnson, *J. Org. Chem.*, 1971, **36**, 2284.

[14] R. W. Taft, N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, 1958, **9**, 287.

[15] G. Chuchani, S. P. de Chang, and L. Lombana, *J.C.S. Perkin II*, 1973, 1961.

[16] C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 857.

[17] R. Paul and S. Tchelitcheff, *Compt. rend.*, 1951, **233**, 1116.

of +0.3 obtained in a preliminary study [5] is therefore no longer applicable. Since the ρ factor is less than those which describe the effects of aryl substituents at the α- and γ-carbon atoms (I) our conclusions regarding the timing of the electron movements in the transition state are unchanged.[5]

TABLE 2

Pyrolysis of compounds $RC_6H_4CH_2CH_2OAc$

		$10^3k/s^{-1}$										
R	$T/°C$	429.2	427.2	420.8	409.9	402.7	394.9	368.7	log (A/s^{-1})	E/kcal mol^{-1}	$\Delta S^‡$/cal $mol^{-1}\,K^{-1}$ [a]	log k/k_0 [b]
2-CF_3		20.7		13.8		5.96		0.931	12.545	45.7	−2.5	0.125
3-CF_3		19.1		12.9		5.24		0.879	12.41	45.4	−3.1	0.088
3-F		17.7		11.8		5.01		0.810	12.385	45.4	−3.3	0.062
4-Cl		17.4		11.1		4.73		0.775	12.41	45.7	−3.1	0.038
H		15.55	14.3	10.4	6.16	4.26	2.78	0.700	12.48	45.8	−2.8	0.0
2,3,4,5,6-F_5		15.1		10.0		4.11		0.684	12.46	45.8	−2.9	−0.014
4-F		14.5	13.6	9.89	5.85	4.02	2.73	0.665	12.46	45.8	−2.9	−0.020
4-Me		14.5		9.75		3.97		0.650	12.50	46.0	−2.7	−0.029
4-MeO		13.4	12.4	9.06	5.26	3.76	2.55	0.601	12.51	46.0	−2.7	−0.062
2-F		13.0		8.64		3.57		0.553	12.44	46.1	−3.0	−0.090

[a] Calc. at 600 K. [b] Calc. at 650 K.

TABLE 3

Pyrolysis of compounds RCH_2CH_2OAc

		$10^4k/s^{-1}$						
R	$T/°C$	427.2	410.3	394.9	377.3	log(A/s^{-1})	E/kcal mol^{-1}	log k/k_0 [a]
H		39.0	16.6	7.30	2.78	12.5	47.7	0
CH_3		33.9	14.0	6.15	2.29	12.65	48.5	−0.075
CH_2CH_3		42.5	17.8	8.10	3.05	12.6	48.1	+0.030
Ph		See Table 2						+0.615
CH_2Ph		45.0	18.8	8.30	3.09	12.6	48.1	+0.05
OMe		8.0 [b]	3.3 [b]			12.9	51.2	−0.73
CH_2OMe		33.5	13.9	6.25	2.28	12.65	48.5	0.0
OPh		11.5 [b]	4.8 [b]			12.5	49.4	−0.56
CH_2OPh		55.1	23.6	10.5	4.05	12.7	47.8	+0.16
CH_2COCH_3		79.0	34.0	15.1	5.75	12.8	47.5	+0.32

[a] At 650 K. [b] Because of the accompanying decomposition of acetic acid (see text) these rate coefficients may be accurate to only ±10%.

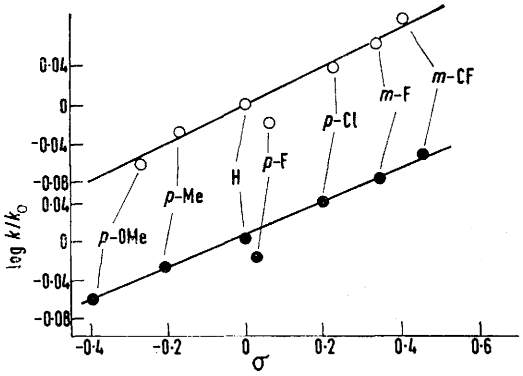
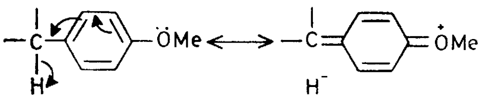


FIGURE 2 Plot of log k_{rel} values for pyrolysis of 2-arylethyl acetates against σ (open circles) and σ + 0.25 (σ^+ − σ) (filled circles)

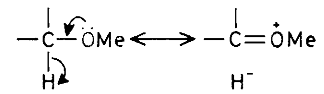
It is however evident from Figure 2 that the correlation is not of the quality generally obtained in gas-phase eliminations of esters, and inspection shows that substituents with a $+M$ effect produce enhanced deactivation; this was evident in a preliminary study [6] and also from the measurements of the reactivities of 2-aryl-1-phenylethyl acetates wherein the *p*-methoxy substituent produced greater deactivation than predicted by its σ value.[6] A plot (Figure 2, lower curve) of the data against σ + 0.25 (σ^+ − σ) is a better line and this suggests that resonance interactions of the substituent play a significant role in accounting for the overall reactivities. It might be argued that the deviations are not very much greater than the possible experimental error. However, the reality of the effect is more dramatically demonstrated as we shall show, by comparison of the effects of other substituents when attached to the β-carbon, and when insulated from it by a methylene group (Table 3).

The resonance effect cannot be operating on the incipient α-carbonium ion (since in this case *p*-methoxy would increase the rate, not decrease it) and the more logical and simple explanation is that conjugation increases the electron density at the β-carbon [as in (II)] which either reduces the ability of the C–H bond to polarise with a positive charge on the hydrogen, or hinders formation of the alkene; the latter seems the less likely in view of the activating effect of $+M$ substituents when attached to the other side of the forming double bond *i.e.* at the α-carbon.

We are now in a position to reconsider the deactivating effect of an alkoxy-group attached directly to the β-carbon [see (iii) above]. We have already seen that the effect cannot be ascribed to deactivation of the incipient α-carbonium ion, and since it is precisely the same as when attached to the phenyl ring, the deactivating effect must come from the same lone pair delocalization, as in (III). Our data show a reactivity ratio of 5.4 ± 0.5 for ethyl acetate: 2-methoxyethyl acetate at 650 K [*cf.* 3.2 (≡ 4.0 at 650 K) obtained by Scheer *et al.* at a higher temperature [12]] so that the methoxy-group deactivates by a factor of 8.1 per adjacent β-hydrogen. Likewise the phenoxy-group deactivates by a factor of 5.4 per adjacent β-hydrogen.



(II)



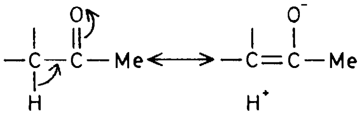
(III)

These results are completely consistent with each other and our explanation. The phenoxy-group has a larger $-I$ effect and a weaker $+M$ effect than methoxy, therefore it should be less deactivating than methoxy. Nevertheless, the $+M$ effect is larger than the $-I$ effect (since σ_p is -0.32) [18] so deactivation should be, and is observed.

If these groups are now insulated from the β-carbon by a methylene group, then the $+M$ effect is prevented from operating and only the $-I$ effect remains. According to our arguments these groups should now activate; the data in Table 3 show that the CH_2OPh and CH_2OMe groups activate 2.17 and 1.5 times respectively, per β-hydrogen atom. The greater $-I$ effect of the phenoxy-group relative to methoxy shows up in the greater activation by the former.

One further point requires comment. Scheer *et al.*[12] found that the methoxy-group was considerably less deactivating when substituted at the β-position of a secondary ester than at the corresponding position of a primary one. We believe this reflects the greater ionic character of the transition state for pyrolysis of secondary esters so that C–H bond breaking (or alkene formation) plays a less significant role in determining the overall reactivity; more examples (described below) confirm this.

Consider now the effect of the acetyl group, the very strong activation by which [(ii) above] can now be seen



(IV)

to arise not merely from the $-I$ effect, but more importantly from the $-M$ effect which is greater, as shown by the σ_I and σ_R values of 0.28 and 0.55, respectively.[19] The contribution from structure (IV) is therefore very significant and we have now demonstrated this by measuring the rate of elimination of 3-acetylpropyl acetate, wherein the carboxy-group is insulated from the β-carbon by methylene. This is only 3.14 times as reactive per β-hydrogen atom as ethyl acetate, a result which would be wholly inconsistent with the previous results for 2-acetylethyl acetate [see (ii) above] if inductive effects were solely responsible since these are well known to diminish by a factor of only *ca.* 2.8 per intervening carbon atom.[20] Our observation is confirmed by the fact that 1-acetoxy-3-methoxycarbonylcyclohexane gives 58% of 3- and 42% of 4-methoxycarbonylcyclohexane [10] which may be compared with the much more dramatic effect observed with the 2-isomer in (ii). The much diminished effect of a β-acetyl group in halide pyrolysis noted in (ii) may be reconciled with the lower degree of C–H bond breakage and double bond formation in the more heterolytic transition state that applies in this reaction.

Thus far the effects of electron-withdrawing or -supplying substituents attached directly to the β-carbon or to a phenyl group attached to the β-carbon have been parallel. This is not true for the alkyl substituents and we confirm that β-alkylation increases the reaction rate, the factors derived from the data in Table 3 being 1.60 and 1.26 per β-hydrogen for the effect of the methyl and ethyl groups respectively. Since it is evident from the Hammett correlation for the effects of 2-aryl substituents that the alkyl group acts normally when substituted in the phenyl ring, it follows that when attached directly to the β-carbon its effect is abnormal and cannot be electronic at all. We have already seen under (v) above that interpretation of the effect in terms of long range stabilisation of the incipient α-carbonium ion,[12] a view favoured by Maccoll and Thomas is incorrect. The explanation must therefore be a steric one and we believe that steric acceleration, proposed many years ago by Benkeser *et al.*[21] to account for the relative proportions of alkenes formed from various esters is responsible. In the transition state the hybridisation at both α- and β-carbon atoms changes from sp^3 to sp^2 and this relieves the strain which will exist between substituents on these carbon atoms. As the substituents are made larger, so the relief of hindrance and the rate enhancement will be greater. This effect is shown very clearly by the data in Table 1 whereby the rate enhancement on substituting the β-carbon becomes greater, the more substituted is the α-carbon. The tendency for the rate to diminish on increasing the branching of the β-alkyl substituent (confirmed by our data) is wholly consistent with a gradual compensation of the steric acceleration by the increased $+I$ effect of the alkyl group.

The rate data for the vinyl and ethynyl substituents

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

[19] J. Shorter, 'Correlation Analysis in Organic Chemistry,' Clarendon, Oxford, 1973, p. 18.

[20] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436.

[21] R. A. Benkeser, J. J. Hadra, and M. L. Burrows, *J. Amer. Chem. Soc.*, 1959, **81**, 5374.

can now be properly interpreted. The greater acceleration in the vinyl compound that has a t-butyl group compared with that which has a methyl group substituted at the α-carbon [see (iv) above] can be seen to arise simply from the greater steric acceleration that will result. The poorer activation by vinyl compared to phenyl, even though the former has a larger $-I$ effect, can be related to the lower steric acceleration produced by the smaller substituent (coupled maybe with the lower ability to exhibit $-M$ electron withdrawal). The absence of any rate acceleration by the ethynyl group accords with the linearity of this substituent so that it produces little if any hindrance compared to the hydrogen atom it replaces.

The activating effect of a phenyl group cannot be due to its $-I$ effect alone since intervention of a methylene group reduces the activating effect per β-hydrogen from 6.9 to 1.68 which is considerably greater than the inductive fall-off factor. Activation by $-M$ electron-withdrawal (and possibly steric acceleration) must also be involved. The former would account for the lesser activation by the β-phenyl group in 1,2-diphenylethyl acetate and the negligible effect in halide pyrolysis, since along this series the heterolytic diameter of the reaction increases and the extent of C–H bond breakage and alkene formation in the transition state decreases.

We had hoped to use the pyrolysis of 2-arylethyl acetates as a means of determining σ values for heterocycles. However, the interplay of the factors described above renders the reaction unsatisfactory for this purpose. In addition, a test pyrolysis of 2-(2-pyridyl)ethyl acetate showed that this compound at least tended to eliminate *via* the intervention of surface-catalysed reactions.

The abnormally low reactivity of the *o*-fluoro-compound merits comment. The fact that the *p*-fluoro-compound was also less reactive than expected suggests that fluorine is particularly effective here in supplying electrons by a $+M$ effect. Any explanation of the *ortho*-effect must be speculative, but it is relevant that this substituent is well placed for hydrogen bonding with a hydrogen attached to either the α- or β-carbon atoms, leading to a six- or five-membered ring respectively. The former would provide a direct path to destabilizing the incipient α-carbonium ion, whilst the latter renders the β-hydrogen less susceptible to attack by the carbonyl group. It may be significant that the pentafluorophenyl group (in which only one *ortho*-fluorine can form a hydrogen bond) the log k_{rel} factor (-0.014) is much less than the predicted factor (-0.076), based on additivity.

EXPERIMENTAL

For the majority of preparations of 2-arylethyl acetates, the intermediate alcohol was obtained by the Grignard procedure from the aryl halide and ethylene oxide. Acetylations were carried out with acetic anhydride and pyridine. All products were purified by fractional distillation until only a single peak was produced on g.l.c. analysis.

The standard preparative procedure gave the following products: 2-phenylethyl acetate, b.p. 105° at 160 mmHg, n_D^{20} 1.4978 (lit.,[6] 118° at 17 mmHg, n_D^{25} 1.4968); 2-(4-methoxyphenyl)ethyl acetate, b.p. 136° at 60 mmHg, n_D^{20} 1.5054 (lit.,[6] 158—159° at 27 mmHg, n_D^{25} 1.5070), 2-(4-methylphenyl)ethyl acetate, b.p. 157° at 60 mmHg, n_D^{20} 1.4972 (lit.,[6] 121° at 11 mmHg, n_D^{25} 1.4976); 2-(4-*chlorophenyl*)*ethyl acetate*, b.p. 94° at 1 mmHg, n_D^{20} 1.5140 (Found: C, 60.9; H, 5.85. $C_{10}H_{11}ClO_2$ requires C, 60.5; H, 5.6%); 2-(3-*trifluoromethylphenyl*)*ethyl acetate*, b.p. 140° at 60 mmHg, n_D^{20} 1.4483 (Found: C, 56.6; H, 4.35. $C_{11}H_{11}F_3O_2$ requires C, 56.8; H, 4.75%); 2-(2-*trifluoromethylphenyl*)*ethyl acetate*, b.p. 138° at 60 mmHg (Found: C, 56.5; H, 4.7%); 2-(4-*fluorophenyl*)*ethyl acetate*, b.p. 158° at 60 mmHg, n_D^{20} 1.4817 (Found: C, 66.1; H, 6.3. $C_{10}H_{11}FO_2$ requires C, 65.95; H, 6.05%); 2-(3-*fluorophenylethyl*) *acetate*, b.p. 158° at 60 mmHg, n_D^{20} 1.4836 (Found: C, 66.3; H, 6.0%).

2-(2,3,4,5,6-*Pentafluorophenyl*)*ethyl Acetate*.—Two attempts to prepare this compound from iodopentafluorobenzene failed to produce any product, extensive carbonisation accompanying distillation during work up. However, using bromopentafluorobenzene as starting material the standard procedure yielded 2-(2,3,4,5,6-*pentafluorophenyl*)-*ethyl acetate*, b.p. 44° at 0.3 mmHg, n_D^{20} 1.4310 (Found: C, 47.0; H, 3.05. $C_{10}H_7F_5O_2$ requires C, 47.25; H, 2.8%).

2-(2-*Fluorophenyl*)*ethyl Acetate*.—The standard procedure yielded a product which had too high a b.p. and appeared from spectral analysis to be either a diacetate or a mixture of acetates, and this probably stems from the ability of fluorine, when *ortho* to bromine, to be removed during the Grignard reaction.[22] An attempted preparation by reacting the Grignard reagent from *o*-fluorobenzyl chloride with paraformaldehyde gave, after acetylation of the crude intermediate, 2-fluorophenylmethyl acetate, indicating failure to form the Grignard reagent initially.

The required product was successfully made in the following way. 2-Fluorobenzyl cyanide (20 g, 0.15 mol) dissolved in absolute ethanol (150 ml) was refluxed with excess sodium hydroxide solution under nitrogen during one week. Acidification yielded 2-fluorophenylacetic acid (together with an unidentified solid of m.p. >360°). Standard esterification yielded ethyl 2-fluorophenylacetate, b.p. 62° at 0.65 mmHg, n_D^{20} 1.4829. Reduction of this ester with lithium aluminium hydride (1.3 g), acetylation of the intermediate alcohol and work up yielded 2-(2-fluorophenyl)ethyl acetate, b.p. 145° at 60 mmHg, n_D^{20} 1.4825. (Found: C, 66.3; H, 7.06%).

2-(2-*Pyridyl*)*ethyl Acetate*.—Acetylation of 2-(2-hydroxyethyl)pyridine gave after work up, 2-(2-*pyridyl*)*ethyl acetate*, b.p. 84° at 0.25 mmHg, n_D^{20} 1.4957 (Found: C, 65.6; H, 6.9; N, 8.6. $C_9H_{11}NO_2$ requires C, 65.45; H, 6.65; N, 8.5%).

2-*Methoxyethyl Acetate*.—Commercial 2-methoxyethanol produced, on acetylation with acetic anhydride in pyridine, the required product, b.p. 78° at 60 mmHg, n_D^{20} 1.4030 (lit.,[12] 86° at 100 mmHg, n_D^{20} 1.4020). This ester obtained from the acetylation mixture by direct distillation since its extreme solubility in water precludes the usual work-up procedure.

3-*Methoxypropyl Acetate*.—Acetylation of commercial 3-methoxypropanol as above gave 3-methoxypropyl acetate, b.p. 112° at 60 mmHg, n_D^{20} 1.4078; this is also very water soluble.

2-*Phenoxyethyl Acetate*.—Acetylation of 2-phenoxyethanol, work up, and fractional distillation gave the

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[22] R. Taylor, Ph.D. Thesis, University of London, 1959.

required product, b.p. 184° at 60 mmHg, n_D^{20} 1.5069 (lit.,[23] 241—243° at 760 mmHg).

3-*Phenoxypropyl Acetate*.—3-Phenoxypropyl bromide (10.5 g, 0.05 mol) was treated with excess of sodium hydroxide (20%) and ethanol (50 ml) during 2 h. The crude product was acetylated as above and work up followed by fractional distillation gave an unidentified fraction, b.p. 162° at 60 mmHg, and 3-phenoxypropyl acetate, b.p. 175° at 60 mmHg, n_D^{20} 1.4999, identified by its n.m.r., i.r., and mass spectra.

3-*Phenylpropyl Acetate*.—Acetylation of commercial 3-phenylpropanol as above gave the required product, b.p. 166° at 60 mmHg, n_D^{20} 1.4959 (lit.,[24] 136° at 21 mmHg).

3-*Acetylpropyl Acetate*.—Acetylation of commercial 3-acetylpropanol as above gave the required product, b.p. 142° at 60 mmHg, n_D^{20} 1.4253 (lit.,[25] 91° at 12 mmHg, n_D^{14} 1.4295).

The standard kinetic procedure as described previously [26] was employed. All the esters were liquids and were injected into the reactor as such. Because of the higher temperatures employed in this study compared to previous work, decomposition of the acetic acid produced in the primary reaction became appreciable with the most unreactive compounds studied. Consequently at the time that the primary elimination is complete (10 half-lives) a small pressure increase continued to occur [except for the 2-methoxy- and 2-phenoxy-esters (see below)]. Rate coefficients were therefore calculated using the value of the pressure at 10 half-lives. Rate coefficients could be duplicated in this way to within ±2% and excellent Arrhenius plots were obtained.

For the 2-methoxy- and 2-phenoxy-esters (the least reactive which have ever been studied in a static system) the extent of the accompanying decomposition of acetic acid was such that the rate coefficients for the primary reaction are not considered to be accurate to better than ±10% and the rates were measured at the two highest temperatures only because of the slowness of the runs.

For the 2-pyridyl ester, kinetics were not of good first-order and neither were they reproducible due to the incursion of surface-catalysed reactions; no rate data are therefore reported.

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