Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part 14.[1] Non-additivity of Methyl Substituent Effects: the Reactivity Selectivity Principle

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Rates of gas-phase elimination of acetic acid from polymethyl-substituted 1-arylethyl acetates, measured between 613.8 and 667.2 K, have shown that the effects of the methyl groups are not strictly additive in this reaction. The reactivity is *greater* than that calculated on the basis of the additivity principle, log $k_{rel.}$(obs.) − log $k_{rel.}$(calc.)/[log $k_{rel.}$(calc.)]^2 being approximately constant. This contrasts with the related electrophilic aromatic substitutions, in which the reactivities for polymethyl compounds are *less* than calculated from the additivity principle. The results confirm that the transition state for ester pyrolysis becomes more polar, the greater the electron supply to the α-carbon atom. Greater electron supply causes a shift in the transition state *away* from the ground state, whereas in electrophilic substitutions the transition state is shifted towards the ground state. These observations demonstrate the differences arising from the participation in the transition state of bond-breaking processes in the elimination as compared with bond-making processes in the substitution. As in solution reactions, the ratio of the reactivities of the 4- and 3-positions in *o*-xylene is less than that of the *para*- and *ortho*-positions in toluene, so this anomaly cannot arise from solvation effects.

THE principle of additivity of substituent effects has been tested in a wide range of reactions, particularly in electrophilic aromatic substitutions. For example, data are available for the methyl substituent in mercuriation,[2] protiodesilylation,[3] halogenation,[4] benzoylation,[5] acetylation,[6] nitration,[7] and hydrogen exchange.[8] Unfortunately, meaningful interpretation of the results can be beset with problems. Not only does the range of reactivities encompassed within a given reaction frequently mean that a range of solvent systems is necessary, leading to a lack of constancy in ρ, but also errors can be introduced by the 'overlap' technique necessarily involved. These difficulties are compounded by steric effects which differ for the poly- relative to the mono-substituted compounds, and, for nitration at least, the encounter rate is sometimes achieved, causing a breakdown in additivity.[9] This latter (rather than the explanation given in ref. 10) is almost certainly the cause of the breakdown in additivity in nitration of cycloalkyl-substituted compounds.[11]

Since the hydrogen-exchange reaction is freer of these complications than any other electrophilic substitution, the results for detritiation of polymethylbenzenes provide the most reliable test of the additivity principle for the methyl substituent. (For correct calculation of the additivity effect see ref. 12.) These show that the reactivity is less than that calculated, the deviation increasing with increasing reactivity. An explanation of these results is that the activating effect of an electron-supplying substituent in an aromatic system already containing an electron-supplying substituent will be less than in benzene itself; the aromatic system will require less electron supply from the additional substituent, or, in other terms, the transition state for reaction of the substituted aromatic compound will be nearer the ground state than will that for benzene.[13,14] Conversely, the transition state for reaction of an aromatic compound containing two electron-withdrawing substituents should be further from the ground state; deactivation by each substituent will be greater than in benzene itself, and the overall reactivity will be less than predicted,[13] and this has now been confirmed in nitration.[15] For aromatic systems containing an electron-withdrawing and one electron-supplying substituent, the reactivity should always be higher than calculated; the effect of the activating substituent placed in the aromatic system less reactive than benzene will be greater than in benzene itself: alternatively the effect of the deactivating substituent placed in the aromatic system more reactive than benzene will be less than in benzene itself. These latter predictions[13] have been confirmed in hydrogen exchange,[16] protiodesilylation,[17] and nitration[15,18] (under conditions where encounter control is not a problem).

Reactions producing side-chain carbocations in the

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[1] Part 13, E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1977, 678.

[2] H. C. Brown and C. W. McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 3210.

[3] C. Eaborn and R. C. Moore, *J. Chem. Soc.*, 1959, 3640.

[4] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421, 5157; R. M. Keefer and L. J. Andrews, *ibid.*, 1956, **78**, 5623.

[5] H. C. Brown, B. A. Bolto, and F. R. Jensen, *J. Org. Chem.*, 1958, **23**, 417.

[6] G. Marino and H. C. Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3308, 5929.

[7] A. Fischer, J. Vaughan, and G. J. Wright, *J. Chem. Soc.* (*B*), 1967, 368.

[8] K. E. Richards, A. L. Wilkinson, and G. J. Wright, *Austral. J. Chem.*, 1972, **25**, 2369.

[9] K. Schofield and S. R. Hartshorn, *Progr. Org. Chem.*, 1972, **8**, 278.

[10] L. M. Stock and P. E. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 4247.

[11] R. Taylor, Chem. Soc. Specialist Periodical Report: 'Aromatic and Heteroaromatic Chemistry,' 1974, vol. 2, pp. 247—248.

[12] Ref. 11, p. 236.

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

[14] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, 1965, pp. 298—299.

[15] R. Danielli, R. Ricci, H. M. Gilow, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 1477.

[16] R. Taylor, Chem. Soc. Specialist Periodical Report: 'Aromatic and Heteroaromatic Chemistry,' 1975, vol. 3, p. 227.

[17] C. Eaborn, Z. S. Salih, and D. R. M. Walton, *J. Organometallic Chem.*, 1972, **36**, 41.

[18] P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution: Nitration and Halogenation,' Butterworths, London, 1959, p. 90.

transition state are formally similar to electrophilic aromatic substitutions, and this is manifest in the linear free energy correlation of mono-substituent effects. However, the effects of polysubstitution in the former reactions have received little attention. A study of the solvolysis and thiosulphate reactions of 4-substituted α-chloro-3-nitrotoluenes showed that a change in mechanism from $S_{\rm N}1$ to $S_{\rm N}2$ occurred as the combined electron supply by the substituents decreased.[19] Such changes in mechanism from $S_{\rm N}1$ to $S_{\rm N}2$ are a common feature of the reactions of monosubstituted benzyl halides and related compounds in which there is insufficient electron supply to assure complete ionisation of the carbon–halogen bond.[20] A study of the additivity effects of 4-alkyl and 2-chloro-substituents in solvolysis of αα-dimethylbenzyl chlorides showed the overall reactivity to be considerably less than predicted, but to depend markedly on the alkyl group size,[21] *i.e.* solvation effects prevented any rigorous analysis here. By contrast, neither solvation nor overlap problems affect the determination of substituent effects in the gas-phase thermolysis of 1-arylethyl acetates. As far as we are aware there has been only one study of the additive effects of substituents in this or any other gas-phase elimination. Examination of the effects of the 4-methoxy-3,5-dimethyl-, 4-methoxy-3-methyl-, and 3,5-dimethyl-substitution in 1-arylethyl acetates showed that the first ester was abnormally unreactive owing to steric inhibition of conjugation between the methoxy-substituent and the aryl ring.[22] For the last ester, in which there can be no steric complication, the reactivity was abnormally high [$\log k_{\rm rel.}$ (616 K) $= 0.136 \equiv 0.1395$ at 600 K], the activating effect being more than twice that of the 3-methyl substituent which we have recently determined [23] as 0.065 at 600 K. This result is relevant to the present work and is discussed further below. We decided therefore to examine the effect of polymethyl-substitution in this reaction in which, in contrast to electrophilic aromatic substitutions, the positively charged transition state is formed *via* a bond-breaking rather than a bond-making process. Furthermore, this provided an opportunity to investigate the puzzling and abnormally low reactivity of the 4-positions of *o*-xylene and *o*-diethylbenzene in electrophilic aromatic substitution.[24-26] This has been explained in terms both of solvation effects,[24] and of steric inhibition of hyperconjugation,[18] this latter being considered more important at the 4-(*para*-)position than at the 3-(*ortho*-) position.

RESULTS AND DISCUSSION

Rates of pyrolysis of the methyl-substituted esters are given in the Table; the $\log k_{\rm rel.}$ value for the *ortho*-methyl ester agrees precisely with that previously reported by one of us [27] and is within 3% of the value determined by Smith *et al.*[28] The $\log k_{\rm rel.}$ values are illustrated in Figure 1, and these observed values are plotted against those calculated on the basis of additivity in Figure 2; the straight line in Figure 2 is the correlation line which would be obtained if additivity was adhered to, and Figure 2 also includes the value for the 3,5-dimethyl compound obtained by Smith and White.

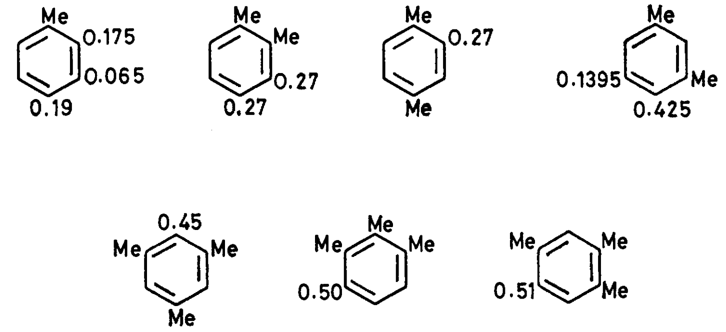

FIGURE 1 Values of $\log k_{\rm rel.}$ in pyrolysis of 1-arylethyl acetates

The main features of the results are as follows. (i) With the exception of the 2,4,6-trimethyl compound, each ester is more reactive than predicted. The deviation of the reactivity from that calculated increases progressively with increasing reactivity approximately according to equation (1), where $\text{D} = 0.38$. The reason

$$\log k_{\rm sel.}({\rm obs.}) - \log k_{\rm rel.}({\rm calc.})/[\log k_{\rm rel.}({\rm calc.})]^2 = {\rm D} \qquad (1)$$

for this deviation is evidently the fact (which we recently deduced from kinetic data for pyrolytic elimination of a range of ester types [29]) that the transition state for ester pyrolysis becomes more polar the greater the electron supply to the α-carbon atom (and also as the electron

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[19] R. Fuchs and D. M. Charlton, *J. Org. Chem.*, 1962, **27**, 1520.

[20] C. A. Bunton, ' Nucleophilic Substitution at a Saturated Carbon Atom,' Elsevier, Amsterdam, 1963, pp. 45—46.

[21] M. Hassan, A. Salama, and M. V. Bambala, *J.C.S. Perkin II*, 1972, 410.

[22] G. G. Smith and D. V. White, *J. Org. Chem.*, 1964, **29**, 3533.

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

[24] H. V. Ansell and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 526.

[25] P. J. McNulty and D. E. Pearson, *J. Amer. Chem. Soc.*, 1959, **81**, 612.

[26] A. Koeberg-Telder, A. J. Prinsen, and H. Cerfontain, *J. Chem. Soc.* (*B*), 1969, 1004.

[27] F. P. Bailey and R. Taylor, *J. Chem. Soc.* (*B*), 1971, 1446.

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

[29] R. Taylor, *J.C.S. Perkin II*, 1975, 1025; H. B. Amin and R. Taylor, *ibid.*, 1975, 1802.

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

Ar	T/°C	10^3k/s^{-1}	log A/s^{-1}	E kcal mol^{-1}	$\Delta S^\ddagger$ cal mol^{-1} K^{-1}	log k/k_0 (at 600 K)	Corr. coeff.
Ph[a]						0	
2-MeC_6H_4	368.8	12.5	13.1	44.4	0.1	0.175	0.999 8
	354.5	5.35					
	340.6	2.55					
3-MeC_6H_4[a]						0.065	
2,3-$Me_2C_6H_3$	394.0	51.6	12.7	42.9	−1.8	0.27	0.999 7
	369.2	15.6					
	354.5	6.85					
	340.6	3.12					
2,5-$Me_2C_6H_3$	394.0	52.85	12.9	43.4	−0.9	0.27	0.999 9
	369.2	15.3					
	354.5	6.99					
	340.6	3.09					
3,4-$Me_2C_6H_3$	394.0	53.45	12.8	43.3	−1.4	0.27	0.999 9
	369.2	15.4					
	354.5	6.82					
	340.6	3.185					
2,4-$Me_2C_6H_3$	394.0	72.55	12.9	43.1	−0.9	0.425	0.999 8
	369.2	21.9					
	354.5	9.74					
	340.7	4.38					
2,4,6-$Me_3C_6H_2$	394.0	77.1	13.0	43.5	−0.4	0.45	0.999 8
	369.2	22.9					
	354.5	10.15					
	340.7	4.55					
2,3,4-$Me_3C_6H_2$	393.2	79.8	12.6	42.1	−2.3	0.50	0.999 9
	368.8	24.7					
	354.5	11.3					
	340.6	5.35					
2,4,5-$Me_3C_6H_2$	394.0	88.6	13.0	43.2	−0.4	0.51	0.999 9
	369.2	25.9					
	354.5	11.55					
	340.7	5.32					

[a] Kinetic data for these compounds have been reported previously (E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1463).

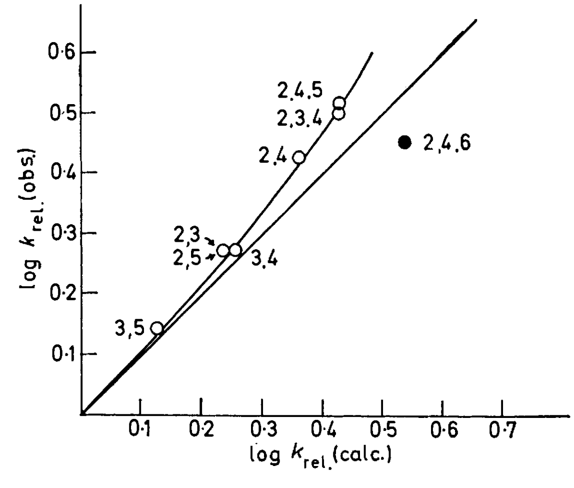

FIGURE 2 Plot of log $k_{rel.}$ (calc.) *vs.* log $k_{rel.}$ (obs.) for pyrolysis of polymethyl-substituted 1-arylethyl acetates at 600 K

withdrawal from the γ-carbon atom increases). Thus the transition state for elimination from a tertiary ester is more polar than that from a secondary ester, which is in turn more polar than that for elimination from a primary ester. Moreover, we showed that the less polar the transition state for a given ester type, the greater the effect of a change in electron supply or withdrawal on the transition state polarity. Hence on going from acetates through to carbonates, a series in which the electron withdrawal from the γ-carbon atom increases, the difference in reactivity between the primary and the secondary esters increased considerably more than did that between the secondary and the tertiary esters. The present results therefore confirm these previous deductions. The greater the electron supply in the aromatic ring, the more polar the transition state becomes and the observed substituent effect increases. The deviation should increase with increasing electron supply, and this we observe. A number of conclusions follow from this. (*a*) The transition state for pyrolysis of monosubstituted 1-arylethyl acetates (or related compounds) will become more polar with increasing electron supply from the substituent. Thus the quoted ρ factors are indicative of the *average* charge separation in the transition state. This conclusion has much wider relevance than merely to the mechanism of ester pyrolysis, and it is significant therefore that Lomas and Dubois have recently shown, in the solvolysis of aryl $\alpha\alpha$-di-t-butylaryl *p*-nitrobenzoates, that there is a continuous variation in the extent of charge separation with substituent.[30] Thus in both elimination and nucleophilic substitution the transition state structure can be modified in just the same way as we have argued it to be modified in electrophilic aromatic substitution according to the reactivity of both the electrophile *and*

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[30] J. S. Lomas and J. E. Dubois, *J. Org. Chem.*, 1975, **40**, 3303.

the aromatic system.[14,31] This relationship amongst reactivity, transition state structure, and substituent effects, otherwise known as the selectivity principle,* therefore applies unambiguously to elimination, but because the transition state is approached *via* bond breakage rather than bond formation (as in electrophilic substitution) an *increase* in reactivity here produces an *increase* in substituent effect.

(*b*) The extent to which the transition state can be modified by a change in electron supply and departure from additivity observed will depend upon the polarity of the transition state, *i.e.* a transition state that is already highly polar should not be susceptible to modification to the same extent as one which is relatively non-polar. Thus we predict that departure from additivity will be greatest for a series of primary esters and least for a series of tertiary esters; the former can only be tested for substituent effects at the γ-carbon atom.

(*c*) It follows that the ρ factor for pyrolysis of 1-arylethyl acetates is an average value and the *precise* correlation with σ^+ values is to some extent fortuitous since the more electron-supplying substituents activate more than they should relative to the effects of the other substituents. This explains the anomaly which we noted some years ago, *viz.* that although the ρ factor is small (-0.66) the *r*-factor is high (1.0).[33] At that time we suggested that this arose from the absence of solvent, so that, although there is a small charge in the transition state, the substituent is solely stabilizing this. This explanation still applies, but in addition the variation in transition state structure as described above will also produce an enhanced *r* factor. These conclusions in no way affect the validity of the gas-phase elimination as a model for quantitatively determining electrophilic substituent constants.

(*d*) Smith and White found that the additive effects of a 3-methyl- and a 4-methoxy-substituent came out to be almost exactly as predicted.[22] This was surprising in view of the expectation that the methoxy-group would be forced out of the plane of the aromatic ring. The reason for the discrepancy is now evident; in the disubstituted compound each substituent should have activated more than in the monosubstituted compound, so the observed value *is* lower than predicted when account is taken of the change in transition state structure.

(ii) The 2,4,6-trimethyl compound is considerably less reactive than predicted and this is due simply to the two *ortho* methyl groups preventing coplanarity and hence conjugation between the aromatic ring and the incipient carbocation at the side chain α-position.

(iii) 2,3-Dimethyl- and 3,4-dimethyl-substitution produce identical activating effects whereas the latter should be the more activating. Since 2,5-dimethyl-substitution produces the same effect as 2,3-dimethyl-substitution (as expected) it appears that 3,4-dimethyl-substitution is activating less than it should, and this is also indicated by Figure 2. The situation therefore parallels that in solution chemistry where the 4-position of *o*-xylene is less reactive than expected. Since solvent plays no part in the explanation, steric inhibition of hyperconjugation[8] may provide the answer, more especially since we have recently shown that 80% of the methyl group activating effect is hyperconjugative in conjugating situations.[1]

(iv) The 2,3,4-trimethyl ester is slightly less reactive than the 2,4,5-trimethyl ester (*ortho*-, *meta*-, and *para*-methyl substituent in each). This follows from buttressing in the former interfering with coplanarity between the incipient carbocation and the aryl ring.

EXPERIMENTAL

All esters were indicated to be >98% pure by g.l.c. analysis and the nature of each product was confirmed by i.r. spectroscopy.

1-Phenylethyl and 1-(2-methylphenyl)ethyl acetate were available from previous studies.[34] The preparation of 1-(3-methylphenyl)ethyl acetate has been described.[23]

1-(2,3-*Dimethylphenyl*)*ethyl Acetate*.—Treatment of the Grignard reagent from 1-bromo-2,3-dimethylbenzene (13.6 g, 0.073 mol) with an excess of acetaldehyde gave, after normal work-up involving fractional distillation, 1-(2,3-dimethylphenyl)ethyl alcohol (6.4 g, 58%), b.p. 112—113° at 5.5 mmHg. Acetylation of this alcohol with acetic anhydride and pyridine gave, after normal work-up and fractional distillation, 1-(2,3-*dimethylphenyl*)*ethyl acetate* (7.7 g, 92%), b.p. 109° at 4.5 mmHg, n_D^{20} 1.503 7 (Found: C, 75.1; H, 8.6. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.3%), τ (CCl_4) 2.94 (3 H, m, ArH), 3.92 (q, *J* 6.5 Hz, CH), 7.77 (s, $ArCH_3$), 8.04 (s, $COCH_3$), and 8.58 (d, *J* 6.5 Hz, CH_3).

1-(3,4-*Dimethylphenyl*)*ethyl Acetate*.—Treatment of the Grignard reagent from 3,4-dimethylbromobenzene (37 g, 0.2 mol) with acetaldehyde as above gave 1-(3,4-dimethylphenyl)ethyl alcohol (15.7 g, 52%), b.p. 111° at 6.0 mmHg. Acetylation as above gave 1-(3,4-*dimethylphenyl*)*ethyl acetate* (16.2 g, 84%), b.p. 101° at 2.7 mmHg, n_D^{20} 1.501 4 (Found: C, 74.9; H, 8.2%), τ (CCl_4) 2.95 (3 H, m, ArH), 4.01 (q, *J* 6.5 Hz, CH), 7.74 (s, $ArCH_3$), 8.09 (s, $COCH_3$), and 8.61 (d, *J* 6.5 Hz, CH_3).

1-(2,4-*Dimethylphenyl*)*ethyl Acetate*.—Reduction of 2′,4′-dimethylacetophenone (14.8 g, 0.092 mol) with sodium borohydride gave the crude intermediate alcohol which was acetylated as above to yield 1-(2,4-*dimethylphenyl*)*ethyl acetate* (13.5 g, 71% overall), b.p. 89° at 1.5 mmHg, n_D^{20} 1.498 3 (Found: C, 75.3; H, 8.1%), τ (CCl_4) 2.96 (3 H, m, ArH), 3.95 (q, *J* 6.5 Hz, CH), 7.76 (s, $ArCH_3$), 8.05 (s, $COCH_3$), and 8.60 (d, *J* 6.5 Hz, CH_3).

1-(2,5-*Dimethylphenyl*)*ethyl Acetate*.—Treatment of 2′,5′-dimethylacetophenone (15 g, 0.095 mol) as above gave

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* There have been recent criticisms of the reactivity–selectivity principle involving, in some cases, conclusions based upon data obtained *via* a substantial number of assumptions, extrapolations, and approximations (*e.g.* ref. 32). In our view there are sufficient unambiguous and accurate data, *e.g.* in aromatic hydrogen exchange (described above) to demonstrate the validity of the principle.

[31] R. Taylor, Chem. Soc. Specialist Periodical Report: ' Aromatic and Heteroaromatic Chemistry,' 1974, vol. 2, pp. 219—220.

[32] T. J. Gilbert and C. D. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 5846.

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

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

1-(2,5-*dimethylphenyl*)*ethyl acetate* (15.4 g, 84% overall), b.p. 84° at 1.5 mmHg, n_D^{20} 1.500 8 (Found: C, 75.3; H, 8.6%), τ (CCl_4) 2.96 (3 H, m, ArH), 4.03 (q, *J* 6.5 Hz, CH), 7.76 (s, $ArCH_3$), 8.10 (s, $COCH_3$), and 8.61 (d, *J* 6.5 Hz, CH_3).

1-(2,3,4-*Trimethylphenyl*)*ethyl Acetate*,—1,2,3-Trimethylbenzene (50 g, 0.42 mol) was acetylated by the method of Tokoroyama *et al.*; [35] normal work-up involving fractional distillation (twice, to ensure removal of the by-product, 3′,4′,5′-trimethylacetophenone) gave 2′,3′,4′-trimethylacetophenone (15.5 g, 25%), b.p. 78° at 0.2 mmHg (lit.,[35] 81° at 0.2 mmHg). Both g.l.c. and high pressure liquid chromatography indicated the presence of a single compound only. Reduction of this ketone (8.1 g, 0.048 mol) with sodium borohydride followed by acetylation of the intermediate alcohol gave 1-(2,3,4-*trimethylphenyl*)*ethyl acetate* (9.0 g, 90%), b.p. 86° at 0.35 mmHg, n_D^{20} 1.501 6 (Found: C, 76.3; H, 8.3. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.7%), τ (CCl_4) 2.93 (2 H, m, ArH), 3.88 (q, *J* 6.5 Hz, CH), 7.75 and 7.83 (s, $ArCH_3$), 8.02 (s, $COCH_3$), and 8.56 (d, *J* 6.5 Hz, CH_3).

1-(2,4,5-*Trimethylphenyl*)*ethyl Acetate*.—2′,4′,5′-Trimethylacetophenone (15.1 g, 0.1 mol) was reduced with sodium borohydride and the intermediate alcohol acetylated as above to give 1-(2,4,5-*trimethylphenyl*)*ethyl acetate* (13 g, 63% overall), b.p. 92° at 0.4 mmHg, n_D^{20} 1.503 4 (Found: C, 75.3; H, 8.5%), τ (CCl_4) 2.09 (2 H, m, ArH), 3.84 (q, *J* 6.5 Hz, CH), 7.71 and 7.82 (s, $ArCH_3$), 8.04 (s, $COCH_3$), and 8.54 (d, *J* 6.5 Hz, CH_3).

1-(2,4,6-*Trimethylphenyl*)*ethyl Acetate*.—2′,4′,6′-Trimethylacetophenone (15.1 g, 0.1 mol) was reduced with sodium borohydride and the intermediate alcohol acetylated as above to give 1-(2,4,6-*trimethylphenyl*)*ethyl acetate* (13.3 g, 65% overall), b.p. 98° at 0.8 mmHg, n_D^{20} 1.504 0 (Found: C, 75.1; H, 8.7%), τ (CCl_4) 3.22 (2 H, s, ArH), 3.83 (q, *J* 6.5 Hz, CH), 7.64 and 7.85 (s, $ArCH_3$), 8.10 (s, $COCH_3$), and 8.53 (d, *J* 6.5 Hz, CH_3).

Kinetic Studies.—The kinetic technique and apparatus have been described previously.[36] Excellent first-order kinetic plots were obtained to beyond 95% of reaction and rate coefficients could be duplicated to within ±1%.

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[35] T. Tokoroyama, S. Maeda, T. Nishikawa, and T. Kubola, *Tetrahedron*, 1969, **25**, 1047.

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