Electrophilic Aromatic Reactivities *via* Pyrolysis of Esters. Part 18.[1] Pyrolysis of 1-Aryl-1-methylethyl Acetates: the High Polarisability of the *meta*-Methyl Substituent

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Rates of pyrolysis of a range of 1-aryl-1-methylethyl acetates, measured between 590.8 and 529.6 K, give a very good correlation with σ^+ values. The ρ factor (-0.743 at 550 K) is almost exactly the same as in pyrolysis of the much less reactive 1-arylethyl acetates and this contrasts with S_N1 solvolyses of the corresponding chlorides where increased electron supply by the methyl groups to the side-chain α-carbocation produces less demand for stabilisation of the transition state by the aryl substituents and a smaller ρ factor. In the elimination the cation is only partially formed and the electron supply from the extra methyl groups of the tertiary esters facilitates C–O bond breakage and a more polar transition state: the opposing effects of the methyl substituents therefore produce no nett change in ρ factor. The transition-state charge difference is confirmed by the (statistically corrected) tertiary : secondary reactivity ratio of 77 which is much greater, relative to the ρ factor, than the difference between the rates of S_N1 solvolysis of the corresponding tertiary and secondary chlorides.

The *meta* methyl substituent is confirmed as being of exceptional polarisability in the absence of solvent; in both the present reaction and phenyl carbonate pyrolysis a σ^+ value of -0.13 is required to correlate its effect.

The reactivity of 1-(2-pyridyl)-1-methylethyl acetate is less than predicted from the corresponding data for 1-arylethyl acetates and 1-arylethyl methyl carbonates, and reasons for this are considered. This anomaly apart, data from all three ester types confirm that the σ^+ values for the pyridine free base are (positions in parentheses): 0.77(2), 0.295(3), and 0.86(4) and that the larger values obtained in most solution reactions refer to the hydrogen-bonded species.

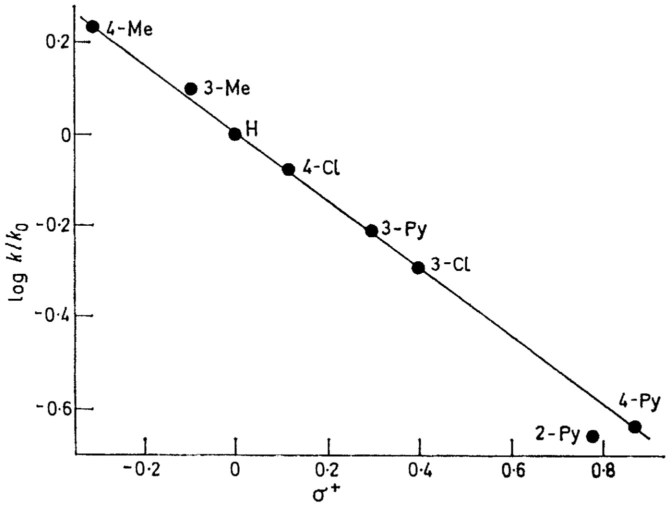
THE pyrolysis of 1-arylethyl acetate is well established as a model reaction for determining the quantitative electrophilic reactivity of aromatic molecules. In order to extend the general technique to measuring the reactivities of very unreactive heterocycles it may be necessary to use other types of esters because the secondary decomposition of acetic acid in the time taken for the primary elimination becomes significant enough to interfere with the kinetics. One alternative could be to use 1-arylethyl methyl (or phenyl) carbonates, *i.e.* to increase the ease of C–O bond breaking by increasing the electronegativity of the group attached to the acyl carbon. This also causes the secondary decomposition to become instantaneous leading to an overall stoicheiometry of 3.0 and no kinetic complication.

Another method, which we have investigated in this paper is to use tertiary esters in which the elimination rate is increased not only by increased electron supply to the α-carbon by the extra methyl group, but also because there are a greater number of β-hydrogen atoms. Moreover, measurement of the elimination rates of the tertiary esters should provide an additional test of our proposal[2-5] that (contrary to an earlier belief[6]) the charge developed in the transition state for ester pyrolysis is not constant but varies according to the electron supply to the α-carbon.

RESULTS AND DISCUSSION

The kinetic data are given in Table 1 which show that compared to pyrolysis of the corresponding 1-arylethyl acetates, the log (A/s^{-1}) values are slightly larger (*ca.* 0.5 units). This is to be expected since less reorganisation of structure is necessary before the acetoxy-group can become *cis*-coplanar to a β-hydrogen. The activation energies are however considerably less (*ca.* 5 kcal mol^{-1}) than for 1-arylethyl acetates since the 1-aryl-1-methylethyl acetates are much more reactive, and it is a general feature of these pyrolyses that higher reactivity is correlated with a lower activation energy.[7,8]

The data give a good Hammett correlation against σ^+ values (Figure 1) and ρ is -0.743 at 550 K ($\equiv -0.68$ at 600 K) which is only slightly greater than for pyrolysis of 1-arylethyl acetates (-0.66 at 600 K). These values are shown in Scheme 1 together with those for S_N1 solvolysis of the corresponding chlorides at 25 °C.[9,10] It is apparent that in solvolysis, going from a secondary to a tertiary compound causes a decrease in the ρ factor because the α-carbocation receives additional stabilisation by the extra methyl group, and so requires less



Hammett plot for pyrolysis of 1-aryl-1-methylethyl acetates at 550 K

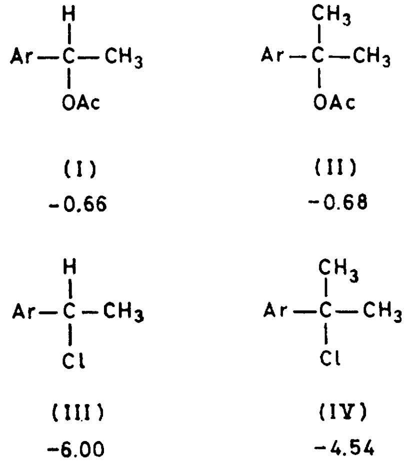
Table 1

Pyrolysis of compounds $ArCMe_2OAc$

Ar	T/K	10^3k/s^{-1}	log (A/s^{-1})	$\frac{E}{\text{kcal mol}^{-1}}$	Corr. coeff.	log k/k_0 ^{a}
4-MeC_6H_4	583.7	73.9	12.87	37.4	0.999 75	0.234
	575.2	42.7				
	559.4	17.0				
	542.7	6.30				
	529.6	2.64				
3-MeC_6H_4	583.7	54.2	13.03	38.2	0.999 98	0.098
	575.2	33.0				
	559.4	13.1				
	542.7	4.46				
	529.6	1.88				
H	583.7	43.6	13.00	38.4	0.999 95	0
	575.2	26.4				
	559.4	10.6				
	542.7	3.57				
	529.6	1.48				
4-ClC_6H_4	583.7	37.8	13.08	38.7	0.999 95	−0.077
	575.2	22.2				
	559.4	8.72				
	542.7	2.97				
	529.6	1.23				
3-ClC_6H_4	583.7	23.35	13.22	39.7	0.999 96	−0.295
	575.2	14.3				
	559.4	5.48				
	542.7	1.76				
	529.6	0.719				
3-Pyridyl	590.8	42.4	13.23	29.5	0.999 99	−0.213
	583.7	28.2				
	575.1	17.1				
	559.7	6.57				
	542.8	2.17				
4-Pyridyl	590.8	17.6	13.56	41.4	0.999 94	−0.642
	583.7	11.9				
	575.1	6.77				
	559.7	2.53				
	542.8	0.789				
2-Pyridyl	590.8	16.9	13.65	41.6	0.999 79	−0.660
	583.7	11.7				
	575.1	6.75				
	559.7	2.39				
	542.8	0.759				

^{a} At 550 K.

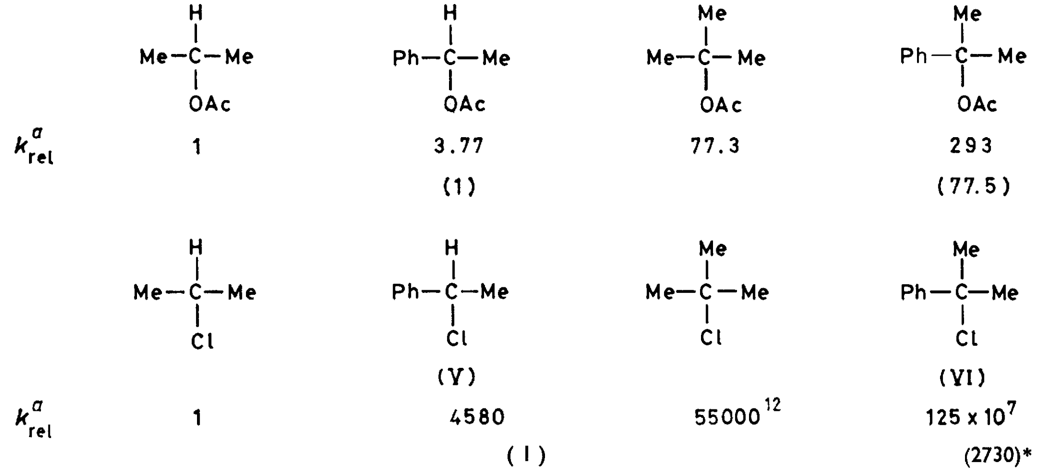
stabilisation by the adjacent aryl group. Numerous examples of this effect (termed the ' tool of increasing electron demand ') have recently been collated by H. C. Brown.[11] This does not happen in the elimination and the reason confirms our earlier analysis of the transition-state charge structure in ester pyrolysis. Unlike the solvolysis, the transition state charge is not the same for the secondary and tertiary esters, but is greater in the latter due to the extra electron release by the additional methyl group. This methyl group stabilizes the extra charge which it creates with the nett result that the amount of charge to be stabilized by the aryl group remains approximately the same as does the ρ factor.



Scheme 1 ρ Factors for elimination of acetates (at 600 K) and for S_N1 solvolysis of chlorides (at 298 K)

The difference in polarities of the transition states for pyrolysis of secondary and tertiary esters is also evident from comparing their differences in reactivities with those for the corresponding S_N1 solvolyses of chlorides. The statistically corrected values for elimination are given along with those for solvolysis in Scheme 2. The consistency of the tertiary : secondary rate ratios in the elimination stems from the general relatively insensitivity of these ratios to the type of ester,[2] and from the similar reactivity of the phenyl- and methyl-containing esters so that the transition state charge will be similar. Two features follow from these data. (i) In each case the phenyl group activates more than the methyl group it replaces. However in the solvolysis, this activation is 4 580 × for the secondary chlorides and 227 × for the tertiary chlorides, the lower value being obtained with the latter because there is less nett positive charge to be stabilized (as indicated by the differences in the ρ factors). For the esters however a constant value of *ca.* 3.78 is obtained in both the secondary and tertiary series because the nett positive charge is the same in both series (as also indicated by ρ factors).

(*ii*) The differences in reactivity of the secondary and corresponding methylated tertiary chlorides in the solvolysis are 55 000 and 2 730. The approximate value *F* that should apply in the pyrolysis can be calculated from the ratios of the average ρ factors and average of these reactivity differences thus: *F* = antilog [log 29 000 × (0.67/5.3)] = 3.7. The value observed in the elimination (77.4) is very much greater than this because the transition state is more polar for the tertiary esters than for the secondary esters.



[a] Statistically corrected to allow for the number of β-hydrogens

SCHEME 2 Relative reactivities in pyrolytic elimination of acetates and S_N1 solvolysis of chlorides

* This can be calculated in two ways: k_{VI} (25°) = 12.4 × 10^{-5} s^{-1} in 90% aqueous acetone,[13] and k_V (25°) is estimated in the literature as 5.86 × 10^{-7} s^{-1} in 80% aqueous acetone.[14] The difference in the two media is reported to give a reactivity difference of 12.9 at 25 °C,[15] so the (VI) : (V) reactivity difference is (12.4 × 12.9)/0.0586 = 2 730. The value of k_V (25°) can also be calculated from the rate of solvolysis of (V) in 80% aqueous ethanol at 25 °C (1.04 × 10^{-5} s^{-1}) [9] and the reactivity difference of 17 between 80% aqueous ethanol and 80% aqueous acetone.[16] The rate coefficient for (V) is then (1.04 × 10^{-5}) s^{-1}/ 17 = 6.12 × 10^{-7} s^{-1} in good agreement with the above value.

These data show that the reactivity of (VI) relative to that of isopropyl chloride (2.6 × 10^8) given in ref. 11, p. 198, is wrongly calculated.

The Effect of the m-*Methyl Substituent.*—It is apparent from the Figure that the *m*-methyl substituent activates more than predicted by its σ^+ value (even using the value of −0.098, redefined from the pyrolysis of 1-arylethyl acetates). This behaviour is not just confined to the present results and the values of σ^+ required to correlate this substituent effect in four gas-phase eliminations are given in Table 2. The persistence of the deviation rules out experimental error or one arising from surface-catalysed elimination. Moreover, these esters were not derived from a common precursor, so impurity in that is not responsible. Nor is rearrangement prior to or during the pyrolysis because this would be most effective at the highest temperatures whereas the deviations are most significant with the eliminations studied at lowest temperatures. (Such rearrangement would lead also to poor first-order kinetics, in contrast to the experimental observations.) Since the value of σ^+ (*m*-Me) tends to increase with increasing charge in the transition state we are led to the conclusion that the *m*-methyl substituent is able to exhibit exceptional polarisability in the gas-phase by a mechanism not available to the *p*-methyl substituent. At present we have no idea what this mechanism can be. Since it is now known that the inductive and hyperconjugative effects of alkyl groups in the same direction[17] it is reasonable to suppose that for alkyl groups in general $\sigma_p^+ - \sigma_m^+$ = constant. For t-butyl $\sigma_p^+ = -0.365$, and $\sigma_m^+ = -0.19$, so this difference = −0.175. Applying this to methyl we obtain σ_m^+ (predicted) = −0.311 − (−0.175) = −0.136, so the exalted value obtained in some of the eliminations appears not unreasonable. The present work shows even more emphatically, the extent to which the electronic effect of *m*-alkyl groups in solution reactions is masked by steric hindrance to solvation.[18]

TABLE 2

Values of σ^+ (*m*-Me) required in ester pyrolysis

Reaction	ρ at 600 K	σ^+	Ref.
1-Arylethyl acetates	−0.06	−0.098	17
1-Arylethyl benzoates	−0.72	−0.115	8
1-Arylethyl phenyl carbonates	−0.84	−0.130	7
1-Aryl-1-methylethyl acetates	−0.68	−0.130	This work

The Effect of the 2-*Pyridyl Group.*—From the pyrolysis of 1-arylethyl acetates σ^+ values were determined for each position of pyridine as shown in Table 3.[19] These values gave excellent and quantitative correlation with theoretical predictions. The values derived from the pyrolysis of 1-aryl-1-methylethyl acetates are also given in Table 3 from which it is seen that the constants for the 3- and 4-positions are confirmed precisely, whereas the constant for the 2-position appears anomalously large. In order to ascertain the reason for this, we have pyrolysed the corresponding 1-arylethyl methyl carbonates, for which ρ may be calculated as —0.71 at 600 K from the data given in ref. 20. The kinetic data are given in Table 4 and yield σ^+-values (Table 3) which agree precisely with those obtained for 1-arylethyl acetates, and further indicate that the value for the 2-position of pyridine in pyrolysis of 1-aryl-1-methylethyl acetates is anomalous and possible explanations are as follows. (i) The deactivation of the 2-position may derive substantially from a direct field effect which could be more important because of the greater charge which develops at the side chain α-carbon in pyrolysis of 1-aryl-1-methylethyl acetates. Against this argument must be set: (*a*) the fact that the ρ factor shows that the *nett* charge for delocalisation by the aromatic ring in the propyl esters is the same as for the ethyl esters and (*b*) the nett charge at the side-chain α-carbon for the carbonate pyrolysis is greater than for the acetates, yet the 2-pyridyl substituent behaves normally in carbonate pyrolysis.

TABLE 3

σ^+-Values for pyridine, determined from gas-phase pyrolysis of ester

Position			
2	3	4	Esters
0.78	0.295	0.87	1-Arylethyl acetates
0.89	0.285	0.86	1-Aryl-1-methylethyl acetates
0.76	0.30	0.85	1-Arylethyl methyl carbonates

TABLE 4

Pyrolysis of 1-arylethyl methyl carbonates, $ArCHCH_3OCOOMe$

	$10^7k/s^{-1}$				
T/K	Ar =	2-Py	3-Py	4-Py	Ph
665.4		62.4	128	52.8	
650.4		30.5	61.6	25.8	45.0
634.5		13.55	28.9	11.7	15.2
613.8		4.44	9.44	3.80	6.51
599.3			4.11		2.23
579.9					
Correlation coefficient		0.999 99	0.999 94	0.999 97	0.999 76
log (A/s^{-1})		12.46	12.61	12.31	12.56
E/kcal mol^{-1}		41.61	41.11	41.36	40.395
log k/k_0 (at 600 K)		−0.5405	−0.212	−0.604	0

(ii) The lone pair on the nitrogen sterically prevents the methyl groups lying in the plane of the aromatic ring as is required for maximum overlap of the incipient p-orbital at the α-carbon with those of the ring. However it seems improbable that the lone pair will be any bulkier than an *ortho*-C–H bond.

Thus we cannot properly account for the anomaly at this time, and conclude that the use of 1-aryl-1-methylethyl acetates as a means of evaluating reactivities of very unreactive heterocycles is less satisfactory than the use of carbonates.

Comparison of the gas-phase σ^+ values (and which describe the reactivity of the free base) with those which have been obtained in solution[21] (positions in parentheses): 0.74(2), 0.55(3), and 1.15(4) show that whereas the value for the 2-position agrees well, the solution values for the 3- and 4-positions are approximately 0.25 σ units too positive. This we believe is because the latter values refer to the hydrogen-bonded species and not the free base. However, when the probe group (CHMeCl) is attached to the 2-position, hydrogen bonding is likely to be sterically hindered, so that the value determined in solution (0.74) agrees well with the gas-phase value. Indeed it is significant that the average values of σ (which are unlikely to be very different from σ^+) that have recently been obtained in polar media[22] are: 0.76(2), 0.57(3), and 1.04(4) and again the value for the 2-position agrees well with the gas-phase value, but the others are more positive. On the other hand, the σ values obtained in non-polar solvents agree more closely for each position with the gas-phase values.[22] The notion[22] that the σ values are independent of solvent would seem to be difficult to sustain in the light of these results.

EXPERIMENTAL

1-*Phenyl*-1-*methylethyl Acetate*.—Acetophenone was converted *via* reaction with methylmagnesium bromide into 1-phenyl-1-methylethanol which was acetylated with pyridine and acetic anhydride, and worked up in the usual way. Fractional distillation gave 1-*phenyl*-1-*methylethyl acetate* (38% based on ketone), b.p. 52—54 °C at 0.8 mmHg, n_D^{20} 1.498 2 (Found: C, 74.4; H, 7.75. $C_{11}H_{14}O_2$ requires C, 74.1; H, 7.92%), τ(CCl_4) 2.81 (5 H, m, ArH), 8.14 (s, $COCH_3$), and 8.32 [s, $C(CH_3)_2$].

1-(4-*Methylphenyl*)-1-*methylethyl Acetate*.—4-Methylacetophenone was converted as above into crude 1-(4-methylphenyl)-1-methylethyl acetate (48% based on ketone). This compound is thermally very unstable and could not be fractionally distilled without very extensive decomposition. However, reasonable purification was achieved by very slow distillation at 60 °C and 0.5 mmHg pressure using a Buchi rotary still. This gave a colourless product which n.m.r. showed to contain a small amount of α,4-dimethylstyrene; τ(CCl_4) 2.92 (4 H, m, ArH), 7.75 (s, $ArCH_3$), 8.12 (s, $COCH_3$), and 8.33 [s, $C(CH_3)_2$]. This, however, does not interfere with the kinetic studies since it is the pyrolysis product. An attempt to make the corresponding 4-methoxy-compound by this method was unsuccessful.

1-(3-*Methylphenyl*)-1-*methylethyl Acetate*.—The reaction between acetone and *m*-tolylmagnesium bromide gave crude 1-(3-methylphenyl)-1-methylethanol which was acetylated as above to give 1-(3-*methylphenyl*)-1-*methylethyl acetate* (63% based on *m*-bromotoluene), b.p. 48—50 °C at 0.2 mmHg, n_D^{20} 1.495 7 (Found: C, 75.0; H, 8.3. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.39%), τ(CCl_4) 2.99 (4 H, m, ArH), 7.70 (s, $ArCH_3$), 8.10 (s, $COCH_3$), and 8.33 [s, $C(CH_3)_2$].

1-(4-*Chlorophenyl*)-1-*methylethyl Acetate*.—The reaction between acetone and *p*-chlorophenylmagnesium bromide gave crude 1-(4-chlorophenyl)-1-methylethanol which was acetylated as above to give 1-(4-*chlorophenyl*)-1-*methylethyl* *acetate* (80% based on *p*-bromochlorobenzene), b.p. 62—64 °C at 0.4 mmHg, n_D^{20} 1.510 8 (Found: C, 62.5; H, 6.25. $C_{11}H_{13}ClO_3$ requires C, 62.1; H, 6.16%), $\tau(CCl_4)$ 2.82 (4 H, m, ArH), 8.10 (s, $COCH_3$), and 8.33 [s, $C(CH_3)_2$].

1-(3-*Chlorophenyl*)-1-*methylethyl Acetate*.—The reaction between acetone and *m*-chlorophenylmagnesium bromide gave crude 1-(3-chlorophenyl)-1-methylethanol which was acetylated as above to give 1-(3-*chlorophenyl*)-1-*methylethyl acetate* (79% based on *m*-bromochlorobenzene), b.p. 50—52 °C at 0.2 mmHg, n_D^{20} 1.512 9 (Found: C, 62.3; H, 6.26%), $\tau(CCl_4)$ 2.82 (4 H, m, ArH), 8.08 (s, $COCH_3$), and 8.32 [s, $C(CH_3)_2$].

1-(2-*Pyridyl*)-1-*methylethyl Acetate*.—2-Acetylpyridine was treated with methylmagnesium bromide to give crude 1-(2-pyridyl)-1-methylethanol which was acetylated as above to give 1-(2-*pyridyl*)-1-*methylethyl acetate* (31% based on ketone), b.p. 60 °C at 0.8 mmHg, n_D^{20} 1.493 8 (Found: C, 67.2; H, 7.16. $C_{10}H_{13}NO_2$ requires C, 67.0; H, 7.31%), $\tau(CCl_4)$ 1.58, 2.72 (4 H, m, ArH), 8.04 (s, $COCH_3$), and 8.29 [s, $C(CH_3)_2$].

1-(3-*Pyridyl*)-1-*methylethyl Acetate*.—Reaction of 3-acetylpyridine as above gave 1-(3-*pyridyl*)-1-*methylethyl acetate* (44% based on ketone), b.p. 77 °C at 0.7 mmHg, n_D^{20} 1.499 8 (Found: C, 67.3; H, 7.31%), $\tau(CCl_4)$ 1.49, 1.75, 2.48, 2.92 (4 H, m, ArH), 8.08 (s, $COCH_3$), and 8.30 [s, $C(CH_3)_2$].

1-(4-*Pyridyl*)-1-*methylethyl Acetate*.—Reaction of 4-acetylpyridine as above gave 1-(4-*pyridyl*)-1-*methylethyl acetate* (43% based on ketone), b.p. 77 °C at 0.8 mmHg, n_D^{20} 1.501 4 (Found: C, 67.2; H, 7.29%), $\tau(CCl_4)$ 1.48, 2.82 (4 H, m, ArH), 7.99 (s, $COCH_3$), and 8.29 [s, $C(CH_3)_2$].

The 1-(*X*-pyridyl)ethyl methyl carbonates were each prepared from the corresponding alcohols by heating the latter to reflux with an excess of methyl chloroformate and pyridine during 2 h. Esterification is very slow and the esters showed a marked tendency to decompose so that longer reaction times were avoided. This resulted in some of the esters containing substantial quantities of alcohol from which they could not be separated by fractional distillation, again due to decomposition. Purification from other impurities was, however, effected by distillation on a Buchi rotary still, and the presence of the alcohols was not a problem since these are inert under the pyrolytic conditions. 1-(3-Pyridyl)ethyl methyl carbonate and 1-(4-pyridyl)ethyl methyl carbonate were distilled at 90 °C at 0.4 mmHg and 60 °C at 0.2 mmHg respectively. Pure 1-(2-*pyridyl*)*ethyl methyl carbonate*, b.p. 60 °C at 0.2 mmHg, n_D^{20} 1.488 0 was obtained by this method (Found: C, 59.6; H, 6.1. $C_9H_{11}NO_3$ requires C, 59.9; H, 6.1%).

1-Phenylethyl methyl carbonate was available from a previous study.[23]

Kinetic Studies.—These studies were carried out in the general manner described previously,[24] and excellent first-order kinetic plots, linear to beyond 95% of reaction were obtained with each ester. Even with the most unreactive ester the rate of the primary elimination is so fast compared to the rate of decomposition of acetic acid, that the latter is not observed; in this respect the reaction is superior to pyrolysis of the corresponding 1-arylethyl acetate. The tendency to undergo surface-catalysed decomposition is, however, rather greater and very thorough deactivation of the surface is necessary (*via* multiple injections of but-3-enoic acid at 700 K). The absence of surface-catalysed elimination was demonstrated by the reproducibility of rate coefficients, linearity of the Arrhenius plots (over a 50 °C range) and constancy of the log (A/s^{-1}) values; rate coefficients were also independent of a 3-fold variation in the initial pressure for a given ester. As in the case of pyrolysis of 1-arylethyl acetates, variations in rate are governed by activation energies rather than by the activation entropies the variation of which is within the limits of experimental error.

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