Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Esters. Part 19.[1] Substituent Effects in Pyridine

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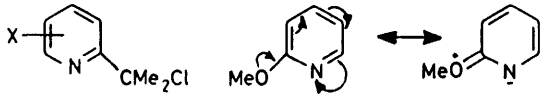
Rates of pyrolysis of some 4-, 5-, and 6-substituted 1-(2-pyridyl)ethyl acetates have been measured between 637.5 and 695.4 K. The data show that the electrophilic substituent constants which apply to substituted benzenes, do not describe the effects of these substituents in pyridine. For example, the 5-methyl and 5-chloro substituents, respectively, activate and deactivate the 2-position *less* than they affect a *para*-position in benzene, yet the 4- and 6-methyl substituents activate *more* than they affect a *meta*-position in benzene. Moreover the methyl substituent activates the 2-position more from the 6- than from the 4-position, as it does in the related S_N1 solvolysis of 2-aryl-2-chloropropanes. The differential effect is however proportionally much smaller in the gas phase indicating that steric hindrance of hydrogen bonding may be mainly responsible for the abnormally high reactivity of 6-substituted 2-chloro-2-(2-pyridyl)propanes in the solvolysis. Elimination of acetic acid from 1-(6-ethoxy-2-pyridyl)-ethyl acetate is accompanied by elimination of ethylene from the ethoxy group to give 6-vinyl-2-pyridone. This new gas-phase elimination is a nitrogen analogue of acetate pyrolysis.

ATTENTION has recently been focused on the transmission of substituent effects through pyridine compared to benzene.[2,3] The effects of substituents have been measured in a reaction with an electron deficient transition state by Noyce and Virgilio[4] who studied the S_N1 solvolysis of substituted 2-chloro-2-pyridylpropanes (I). They found that the compounds containing the 6-Me, 6-OMe, 6-OEt, 6-Cl, and 6-Ph substituents were all more reactive than predicted, and it has been suggested[2] that this arises from an interaction as shown in (II). However, an alternative explanation could be that the presence of a substituent in the 6-position



(I) (II)

coupled with a bulky group at the 2-position inhibits hydrogen bonding at nitrogen, thereby raising the overall reactivity.[5] Pyridine is strongly hydrogen bonded in solution, so much so that both σ and σ^+ values determined in hydrogen-containing solvents are all too positive (by *ca.* 0.25 σ units) relative to the true constants for the free base, measured either in the gas phase[6] or in carbon tetrachloride.[7] This deviation occurs for the β- and γ-positions rather than at the α-position where the probe substituent can sterically inhibit such bonding. For solvolysis of 2-chloro-2-pyridylpropanes,[8] the σ^+ constant for the α-position agrees well with that determined in the gas phase indicating that the bulk of the tertiary group at the α-position substantially prevents hydrogen bonding. Nevertheless, sufficient hydrogen bonding might remain as to cause the deviations observed, and we considered that the ultimate test for this would be to measure the reactivity of substituted pyridines in the gas phase, *via* pyrolysis of the appropriate 1-arylethyl acetates.

RESULTS AND DISCUSSION

The kinetic data are assembled in the Table along with the log k/k_0 values [*i.e.* logarithms of the rates relative to that of 1-(2-pyridyl)ethyl acetate] calculated at 650 K. Notable features of the results are as follows.

(i) The activating effect of the 5-methyl substituent (0.137 at 650 K $\equiv$ 0.148 at 600 K) is less than in pyrolysis of 1-(*p*-methylphenyl)ethyl acetate (0.19 at 600 K). This is due in part to the fact that the polarity of the transition state in ester pyrolysis varies according to the reactivity of the ester,[9] and so for the less reactive 1-(2-pyridyl)ethyl acetates a less polar transition state could be expected and hence a smaller ρ factor. From data for pyrolysis of polychloroarylethyl acetates we estimate that this effect would reduce the ρ factor by 15%. The reduction in log $k_{rel.}$ value we observe is however somewhat larger. Likewise in the S_N1 solvolysis (where the charge on the transition state is invariant), there is a similar discrepancy: log $k_{rel.}$ (calc.) = 1.245, log $k_{rel.}$ (obs.) = 1.15. Thus some factor other than a solvent effect appears to be operating, and this is also indicated in (ii).

(ii) The deactivating effect of the 5-chloro substituent (−0.033 at 650 K $\equiv$ −0.035 at 600 K) is substantially less than in pyrolysis of 1-(*p*-chlorophenyl)ethyl acetate (−0.07 at 600 K). Again this is the trend expected because of the less polar transition state, but the discrepancy is proportionally much larger than for the 5-methyl substituent. Again the solvolysis shows the same effect: log $k_{rel.}$(calc.) −0.456, log $k_{rel.}$(obs.) −0.13. There is thus no doubt that there is a solvent-independent anomaly and, taken in isolation, the data for the 5-Me and 5-Cl substituents indicate that the inductive effect is less easily transmitted in pyridine, but this may be a premature conclusion.

(iii) The 6-methyl substituent (log $k_{rel.}$ 0.074 at 650 K $\equiv$ 0.080 at 600 K) activates more than the 4-methyl substituent (log $k_{rel.}$ $\equiv$ 0.066 at 600 K) and the former activates significantly more than an *m*-methyl substituent in benzene (0.065 at 600 K). This difference in activation of the 4- and 6-methyl substituents is also found in the solvolysis, but here the difference between the log $k_{rel.}$ values is large (0.4) which predicts a difference for a reaction of ρ −0.66 of *ca.* 0.07 (*cf.* 0.015 observed). Thus the discrepancy is proportionally

greater in solvolysis so that inhibition of hydrogen bonding may be a contributory factor. Nevertheless there is evidently some other factor to be explained and it cannot be the interaction shown in (II) since this should be greater at the 4-position [2] whereas the reverse is the case. Moreover, in solvolysis the difference in the log $k_{rel.}$ values for the 4- and 6-chloro substituents (0.6) is greater than the discrepancy between the effects of the 1-arylethyl compounds is considerably harder than preparation of heterocyclic 1-aryl-1-methylethyl compounds because unwanted nucleophilic substitutions take place on converting the ethyl esters of heterocyclic carboxylic acids into the methyl ketones.) Nevertheless there are sufficient data to show that σ^+ constants for substituents in benzene do not apply to the same substituents in pyridine and that this is not simply a solvent effect.

Pyrolysis of compounds ArCHOAc·CH_3

Ar	T/K	$10^3\ k$/s^{-1}	log (A/s^{-1})	E / kcal mol^{-1}	Corr. coeff.	log k/k_0 [a]
2-Pyridyl	695.4	37.6	12.61	44.65	0.999 21	0
	694.8	34.9				
	682.5	20.4				
	678.5	18.9				
	667.4	10.0				
	667.1	9.78				
	653.5	4.555				
	652.6	4.62				
	637.5	2.02				
2-(5-Methylpyridyl)	695.4	51.35	12.68	44.44	0.999 89	0.137
	682.5	27.4				
	678.5	23.6				
	667.4	13.3				
	667.1	13.4				
	653.5	6.47				
	637.7	2.80				
2-(6-Methylpyridyl)	695.4	44.5	12.63	44.50	0.999 84	0.074
	694.8	43.1				
	678.5	20.7				
	667.1	11.0				
	653.5	5.67				
	637.5	2.40				
2-(4-Methylpyridyl)	695.4	43.8	12.73	44.81	0.999 86	0.061
	694.8	41.7				
	678.5	20.1				
	667.4	11.2				
	667.1	11.5				
	653.5	5.50				
	637.5	2.29				
2-(5-Chloropyridyl)	695.4	33.8	12.47	44.35	0.999 85	−0.033
	682.5	18.9				
	678.5	15.9				
	667.4	9.03				
	667.1	9.02				
	653.5	4.34				
	637.5	1.87				
2-(6-Ethoxypyridyl)	695.4	38.8	12.28	43.55	0.999 75	0.047
	678.5	19.1				
	667.1	10.6				
	653.5	5.27				
	652.6	4.82				
	637.5	2.30				
2-(4-Ethoxypyridyl)	695.4	37.5	12.38	43.88	0.999 85	0.027
	678.5	18.4				
	667.1	10.1				
	653.5	5.06				
	637.5	2.155				

[a] At 650 K.

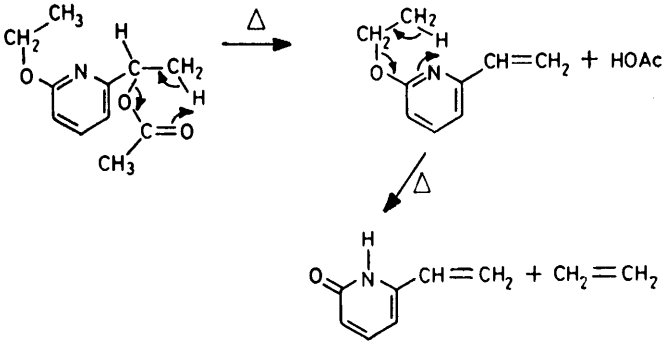
corresponding methyl substituents, yet the latter have the larger $+M$ effects. This again indicates that (II) cannot be the true explanation of the phenomenon.

(iv) The abnormality is confirmed by the results for the 4- and 6-ethoxy substituents, both of which activate (a small deactivation would have been expected) and the activation is greatest from the 6-position. In solvolysis both 6-ethoxy and 4-methoxy substituents produced slight activation.

Synthetic difficulties prevented us from examining a wider range of compounds. (Preparation of heterocyclic

A Side Reaction in Pyrolysis of 1-(6-*Ethoxy*-2-*pyridyl*)-*ethyl Acetate*.—During pyrolysis of this compound, the reaction stoicheiometry was found to be >2.0, and departure from the normal first-order kinetic form was obtained. This was more significant at higher temperatures and showed that a side-reaction of higher activation energy than the primary elimination was occurring. (At the highest temperatures employed this reaction took place to the extent of *ca.* 8% during the time of the primary elimination, and less at lower temperatures so that reasonably accurate rate coefficients for the primary

elimination could be obtained by using the calculated P_∞ values.) Separate experiments on 2-ethoxypyridine [10] have confirmed that this new reaction is a nitrogen analogue of acetate pyrolysis in which ethylene is eliminated giving 2-pyridone, and proceeds *via* a six-centre cyclic transition state involving the aromatic π-electrons. For the 6-ethoxy ester the overall elimination pathways are thus as shown in the Scheme.



SCHEME Pathway for pyrolysis of 1-(6-ethoxy-2-pyridyl)ethyl acetate

EXPERIMENTAL

1-(2-*Pyridyl*)*ethyl Acetate*.—This was available from a previous study.[6]

In the following preparations, work-up at each stage employed continuous liquid–liquid extraction with either chloroform or diethyl ether.

1-(5-*Methyl*-2-*pyridyl*)*ethyl Acetate*.—2-*Bromo*-5-*picoline*. 2-Amino-5-picoline (45.5 g, 0.42 mol) was converted *via* the literature method [11] into 2-bromopicoline (38.7 g, 54%), m.p. 46—48° (lit.,[11] 49—50°).

1-(5-*Methyl*-2-*pyridyl*)*ethanol*. 2-Bromo-5-picoline (8.6 g, 0.05 mol) was converted *via* reaction with n-butyl-lithium followed by the addition of excess of acetaldehyde and normal work-up with fractional distillation, into 1-(5-*methyl*-2-*pyridyl*)*ethyl alcohol* (2.5 g, 38%), b.p. 74—76° at 1 mmHg, n_D^{20} 1.524 0 (Found: C, 70.7; H, 8.11; N, 10.2. $C_8H_{11}NO$ requires C, 70.0; H, 8.08; N, 10.2%), τ(CCl_4) 8.02 (s, 1 H, ArH), 7.15 (m, 2 H, ArH), 5.29 (s, OH), 5.36 (q, *J* 6.5 Hz, CH), 7.78 (s, $ArCH_3$), and 8.66 (d, *J* 6.5 Hz, CH_3).

A further batch of alcohol was prepared and the total (7.9 g) was acetylated with excess of acetic anhydride in pyridine to give after normal work-up and fractional distillation, 1-(5-*methyl*-2-*pyridyl*)*ethyl acetate* (5.5 g, 87%), b.p. 58—60° at 0.12 mmHg, n_D^{20} 1.493 8 (Found: C, 67.0; H, 7.5; N, 7.8. $C_{10}H_{13}NO_2$ requires C, 67.0; H, 7.3; N, 7.8%), τ(CCl_4) 1.75 (s, 1 H, ArH), 2.78 (m, 2 H, ArH), 4.23 (q, *J* 6.5 Hz, CH), 7.75 (s, $ArCH_3$), 8.02 (s, $COCH_3$), and 8.51 (d, *J* 6.5 Hz, CH_3).

1-(6-*Methyl*-2-*pyridyl*)*ethyl Acetate*.—6-*Methyl*-2-*picolinic acid*. This acid, m.p. 127—129° (lit.,[12] 126.5—128°), was prepared in 77% yield from 2,6-dimethylpyridine by the method of Black *et al.*[13]

Ethyl (6-*Methylpyridyl*)-2-*carboxylate*.—6-Methyl-2-picolinic acid (16.0 g, 0.19 mol) was heated under reflux during 5 h with excess of ethyl alcohol (112 ml) and concentrated sulphuric acid (38 g). The cooled mixture was poured onto crushed ice, rendered alkaline (pH 8), and worked up in the usual way with fractional distillation to give *ethyl* (6-*methylpyridyl*)-2-*carboxylate* (20.6 g, 0.13 mol, 67%), b.p. 72—74° at 0.5 mmHg, n_D^{20} 1.507 7 (Found: C, 65.2; H, 6.8; N, 8.5. $C_9H_{11}NO_2$ requires C, 65.4; H, 6.8; N, 8.5%), τ(CCl_4) 2.32, 2.79 (3 H, m, ArH), 5.67 (q, *J* 8.0 Hz, CH_2), 7.46 (s, $ArCH_3$), and 8.61 (d, *J* 8.0 Hz, CH_3).

2-*Acetyl*-6-*methylpyridine*.—Ethyl (6-methylpyridyl)-2-carboxylate (7.5 g, 0.05 mol) was heated under reflux with a 5-fold excess of sodium ethoxide and ethyl acetate in toluene during 5 h. The crude sodium enolate, obtained by removal of volatiles under reduced pressure, was heated with an excess of 20% sulphuric acid (300 ml) during 2 h. The cooled mixture was poured onto ice and rendered alkaline (pH 8) with sodium carbonate. Work-up involving fractional distillation gave 2-*acetyl*-6-*methylpyridine* (4.1 g, 0.03 mol, 67%), b.p. 46° at 1 mmHg, n_D^{20} 1.515 3 (Found: C, 71.4; H, 6.7; N, 10.5. C_9H_9NO requires C, 71.7; H, 6.7; N, 10.4%), τ(CCl_4) 2.35, 2.81 (3 H, m, ArH), 7.42 (s, $COCH_3$), and 7.46 (s, $ArCH_3$).

1-(6-*Methyl*-2-*pyridyl*)*ethanol*.— 2-Acetyl-6-methylpyridine (4.1 g, 0.03 mol) was reduced with sodium borohydride in aqueous ethanol to give, after work up and fractional distillation, 1-(6-*methyl*-2-*pyridyl*)*ethanol* (2.20 g, 53%), b.p. 54—56° at 0.5 mmHg, n_D^{20} 1.521 8 (Found: C, 70.1; H, 8.3; N, 10.2%), τ(CCl_4) 2.83 (3 H, m, ArH), 5.30 (q, *J* 6.5 Hz, CH), 5.36 (s, OH), 7.53 (s, $ArCH_3$), and 8.60 (d, *J* 6.5 Hz, CH_3).

Acetylation of this alcohol as above gave 1-(6-*methyl*-2-*pyridyl*)*ethyl acetate* (1.64 g, 58%), b.p. 46—48° at 0.3 mmHg, n_D^{20} 1.492 1 (Found: C, 66.9; H, 7.15; N, 7.9%), τ(CCl_4) 2.82 (3 H, m, ArH), 4.24 (q, *J* 6.5 Hz, CH), 7.52 (s, $ArCH_3$), 7.98 (s, $COCH_3$), and 8.47 (d, *J* 6.5 Hz, CH_3).

1-(4-*Methyl*-2-*pyridyl*)*ethyl Acetate*.—2-*Bromo*-4-*picoline*. 2-Amino-4-picoline (45.5 g, 0.42 mol) was converted *via* the literature method [11] into 2-bromo-4-picoline (40.5 g, 56%), b.p. 42—44° at 0.6 mmHg (lit.,[14] 50° at 0.45 mmHg).

1-(4-*Methyl*-2-*pyridyl*)*ethanol*. 2-Bromo-4-picoline (25 g, 0.15 mol) was treated with n-butyl-lithium and acetaldehyde as above to give 1-(4-*methyl*-2-*pyridyl*)*ethanol* (8.7 g, 44%), b.p. 54—56° at 0.2 mmHg, m.p. 77—80° (after recrystallisation from light petroleum) (Found: C, 70.7; H, 8.05; N, 10.3%), τ(CCl_4) 1.86 (d, *J* 5.5 Hz, 1 H, ArH), 3.05 (s, 1 H, ArH), 3.23 (d, *J* 5.5 Hz, 1 H, ArH), 5.38 (q, *J* 6.5 Hz, CH), 5.73 (s, OH), 7.70 (s, $ArCH_3$), and 8.72 (d, *J* 6.5 Hz, CH).

Acetylation of this alcohol (8.0 g, 0.06 mol) as above gave 1-(4-*methyl*-2-*pyridyl*)*ethyl acetate* (6.7 g, 64%), b.p. 58—60° at 0.4 mmHg, n_D^{20} 1.493 7 (Found: C, 67.0; H, 7.75; N, 7.85%), τ(CCl_4) 1.73 (d, *J* 6.5 Hz, 1 H, ArH), 3.00 (s, 1 H, ArH), 3.14 (d, *J* 6.5 Hz, 1 H, ArH), 4.26 (q, *J* 6.5 Hz, CH), 7.72 (s, $ArCH_3$), 8.00 (s, $COCH_3$), and 8.52 (d, *J* 6.5 Hz, CH_3).

1-(5-*Chloro*-2-*pyridyl*)*ethyl Acetate*.—2-*Bromo*-5-*chloropyridine*. 2-Amino-5-chloropyridine (25 g, 0.19 mol) was converted [11] into 2-bromo-5-chloropyridine (18.5 g, 50%), m.p. 67—69° (lit.,[12] 70—71°).

1-(5-*Chloro*-2-*pyridyl*)*ethanol*. 2-Bromo-5-chloropyridine (18.5 g, 0.096 mol) was treated with n-butyl-lithium and acetaldehyde as above to give 1-(5-*chloro*-2-*pyridyl*)*ethanol* (5.3 g, 33%), b.p. 52—54° at 0.2 mmHg, τ(CCl_4) 1.59 (d, *J* 2 Hz, 2 H, ArH), 2.54 (s, 1 H, ArH), 5.23 (q, *J* 6.5 Hz, CH), 5.68 (s, OH), and 8.60 (d, *J* 6.5 Hz, CH_3).

Acetylation of this alcohol as above gave 1-(5-*chloro*-2-*pyridyl*)*ethyl acetate* (4.2 g, 65%), b.p. 52° at 0.2 mmHg, n_D^{20} 1.509 1 (Found: C, 54.2; H, 5.2; N, 6.85. $C_9H_{10}ClNO_2$ requires C, 54.2; H, 5.05; N, 7.0%), τ(CCl_4) 1.53

(d, J 2 Hz, 2 H, ArH), 2.58 (s, 1 H, ArH), 4.18 (q, J 6.5 Hz, CH), 7.96 (s, $COCH_3$), and 8.48 (d, J 6.5 Hz, CH_3).

1-(6-*Ethoxy*-2-*pyridyl*)*ethyl Acetate*.—6-*Hydroxy*-2-*methylpyridine*. 6-Amino-2-picoline (54 g, 0.5 mol) was converted [15] into 6-hydroxy-2-methylpyridine (54.1 g, 99%), m.p. 157—158° (lit.,[15] 158—159°).

6-*Chloro*-2-*methylpyridine*. 6-Hydroxy-2-methylpyridine (48.3 g, 0.44 mol) was converted [11] into 6-chloro-2-methylpyridine (38.8 g, 69%), b.p. 58—60° at 8 mmHg, n_D^{20} 1.527 0 (lit.,[16] b.p. 60—60.5° at 8 mmHg, n_D^{20} 1.527 6).

6-*Chloro*-2-*picolinic acid*. 6-Chloro-2-methylpyridine (38.8 g, 0.3 mol) was oxidised [17] to 6-chloro-2-picolinic acid (25.9 g, 61%), m.p. 190—192° (lit.,[17] 192—194°).

Ethyl (6-*chloropyridyl*)-2-*carboxylate*. 6-Chloro-2-picolinic acid was esterified with excess of ethanol and sulphuric acid to give, after work-up, ethyl (6-chloropyridyl)-2-carboxylate (30.7 g, 61%), b.p. 72—74° at 1 mmHg, m.p. 28—30° (lit.,[18] b.p. 118—125° at 7 mmHg, m.p.[19] 28—29°).

2-*Acetyl*-6-*ethoxypyridine*. It was hoped that 2-acetyl-6-chloropyridine would be obtained by treating ethyl (6-chloropyridyl)-2-carboxylate (34.5 g, 0.2 mol) with ethyl acetate and sodium ethoxide as above. However nucleophilic substitution occurred during this step so that the product was 2-acetyl-6-ethoxypyridine (4.3 g, 14%), b.p. 50—52° at 0.1 mmHg, m.p. 44—45° (lit.,[15] b.p. 110° at 10 mmHg, m.p. 42°).

1-(6-*Ethoxy*-2-*pyridyl*)*ethanol*. 2-Acetyl-6-ethoxypyridine (4.3 g, 0.03 mol) was reduced with sodium borohydride to give, after work-up, 1-(6-ethoxy-2-pyridyl)ethanol which was acetylated directly to give 1-(6-*ethoxy*-2-*pyridyl*)*ethyl acetate* (3.8 g, 70% based on ketone), b.p. 62—64° at 0.2 mmHg, n_D^{20} 1.487 1 (Found: C, 63.1; H, 7.25; N, 6.7. $C_{11}H_{15}NO_3$ requires C, 63.1; H, 7.2; N, 6.7%), $\tau(CCl_4)$ 2.61 (t, J 6.6 Hz, 1 H, ArH), 3.25, 3.54 (d, J 6.6 Hz, 2 H, ArH), 4.28 (q, J 6.5 Hz, CH), 5.72 (q, J 7.0 Hz, CH_3), 8.02 (s, $COCH_3$), 8.52 (d, J 6.5 Hz, CH_3), and 8.68 (t, J 7.0 Hz, CH_3).

1-(4-*Ethoxy*-2-*pyridyl*)*ethyl Acetate*.—4-*Chloropicolinic acid*. Picolinic acid (100 g, 0.81 mol) was converted [20] into picolinic acid hydrochloride (107 g, 83%), m.p. 228° (lit.,[20] 228°), and thence [20] to 4-chloropicolinic acid (64 g, 63%), m.p. 180—182° (lit.,[20] 182°).

Ethyl (4-*ethoxypyridyl*)-2-*carboxylate*. 4-Chloropicolinic acid (50 g, 0.32 mol) was esterified with excess of ethanol and sulphuric acid to give after work-up a mixture of ethyl (4-ethoxypyridyl)-2-carboxylate and ethyl (4-chloropyridyl)-2-carboxylate. Separation of these could not be affected at this stage.

2-*Acetyl*-4-*ethoxypyridine*. The above mixture of esters (21.7 g) was heated with sodium ethoxide and ethyl acetate as above. The partial nucleophilic substitution was completed at this stage to give a single product, 2-acetyl-4-ethoxypyridine (10 g, 0.066 mol), b.p. 62° at 0.2 mmHg.

1-(4-*Ethoxy*-2-*pyridyl*)*ethanol*. Reduction of 2-acetyl-4-ethoxypyridine (10 g, 0.066 mol) with sodium borohydride gave the crude alcohol which was acetylated as above to give the crude ester which n.m.r. analysis showed to contain 1-(2-pyridyl)ethyl acetate as a by-product, presumably through hydride ion replacement of ethoxide during the reduction stage. Careful fractional distillation gave 1-(4-*ethoxy*-2-*pyridyl*)*ethyl acetate* (2 g, 16%), b.p. 63° at 0.2 mmHg, n_D^{20} 1.494 9 (Found: C, 63.0; H, 7.65; N, 6.7%), $\tau(CCl_4)$ 1.79 (d, J 5 Hz, 1 H, ArH), 3.31 (d, J 2.4 Hz, 1 H, ArH), 3.46 (m, 1 H, ArH), 4.29 (q, J 6.8 Hz, CH), 6.02 (q, J 7.6 Hz, CH_2), 7.98 (s, $COCH_3$), 8.52 (d, J 6.8 Hz, CH_3), and 8.62 (t, J 7.6 Hz, CH_3).

Kinetic Studies.—These were carried out in the usual manner [21] and each compound except the 6-ethoxy ester gave excellent and reproducible first-order decompositions, and also excellent Arrhenius plots as indicated by the correlation coefficients given in the Table. The reason for the non-first order behaviour for the 6-ethoxy ester is described in the Discussion section.

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