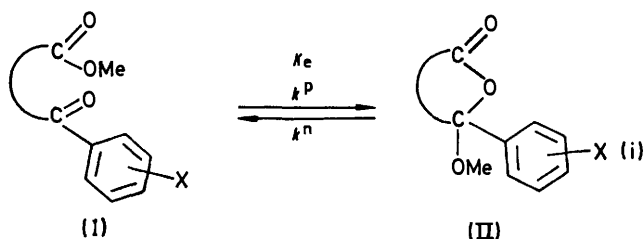# Ring–Chain Tautomerism. Part 6. [1] Base- and Acid-catalysed Rearrangement of Pseudo to Normal Methyl 8-(3- or 4-Substituted benzoyl)-1-naphthoates and 2-(3- or 4-Substituted benzoyl)benzoates

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Rate coefficients have been measured for both the base- and acid-catalysed rearrangements of a series of methyl pseudo-8-benzoyl-1-naphthoates and pseudo-2-benzoylbenzoates in methanol at 60.0 °C to form the corresponding normal esters. The entropies and enthalpies of activation for the parent pseudo-esters have been evaluated, as have the solvent isotope and solvent (methanolic dioxan and dimethyl sulphoxide) effects for these esters. The reaction constants ρ for the methoxide anion-catalysed rearrangement are ca. 2.1 (naphthoates) and 1.1 (benzoates), respectively. The evidence is consistent with a stepwise mechanism in which the formation or decomposition of tetrahedral intermediates is rate-determining: for the pseudo-benzoates, the formation by addition of methoxide to the pseudo-ester carbonyl group; for the pseudo-naphthoates, the decomposition by dissociation of methoxide from the normal ester carbonyl group. This mechanistic switch appears to arise from greater strain in the five-membered ring affecting its initial state and primary addition product stabilities. The reaction constants ρ for the acid-catalysed rearrangement are ca. −0.1 (naphthoates) and −0.2 (benzoates), respectively. All the evidence for the latter reaction indicates an $A_{AC}2$ path and likely transition states are discussed.

IT has been known for some time that both normal and pseudo-esters of 2-benzoylbenzoic and 8-benzoyl-1-naphthoic acids exist.[2] This nucleophilic tautomerism occurs between the normal (chain) (I) and pseudo (ring) (II) methyl esters as shown in the equilibria (i). Although qualitative observations have been made on several systems, only a quantitative study of *both* the equilibrium constants and the rate coefficients for acid- and base-

(I)   (II)

catalysed interconversion of normal and pseudo methyl 2-acylbenzoates has been made.[3] However, for benzoyl esters, the normal esters are very much more stable than

the pseudo-esters and the position of equilibrium is thus very difficult to detect.[3,4]

We have now measured the rates of base- and acid-catalysed rearrangement of both methyl pseudo-8-(3- and 4-substituted benzoyl)-1-naphthoates and pseudo-2-(3- and 4-substituted benzoyl)benzoates. A series of kinetic mechanistic probes have been used to study the mechanism of both these reactions.

RESULTS AND DISCUSSION

At equilibrium, for all the benzoyl esters studied here, the normal esters are *very* much more stable than the pseudo-esters. The equilibrium constant, K_3, can be estimated to be <0.02. The rate coefficients for the formation of the normal from the pseudo-ester have been measured in the presence of base or acid catalyst and are shown in Tables 1—3.

Base-catalysed Rearrangement.—The reaction was found to be first order both in the substrate, the pseudo-ester, and in methoxide anion. Rate coefficients for the

[1] Part 5, K. Bowden and A. M. Last, *J.C.S. Perkin II*, 1973 1144.
[2] P. R. Jones, *Chem. Rev.*, 1963, **63**, 461.
[3] K. Bowden and G. R. Taylor, *J. Chem. Soc. (B)*, 1971, 1395.
[4] M. S. Newman and C. Courduvelis, *J. Org. Chem.*, 1965, **30**, 1795.

TABLE 1

Rate coefficients (1 mol^{-1} s^{-1}) for the catalysed rearrangement of methyl pseudo-2-(substituted benzoyl)-1-naphthoate and pseudo-2-(substituted benzoyl)benzoate in methanol at 60.0 °C *

Naphthoate substituent	Methoxide-catalysed $10k_2$	Acid-catalysed 10^4k_2	λ/nm †
H	1.25	3.25	325
4-Me	0.831	3.54	324
3-Me	1.04	3.42	325
4-Cl	4.45	2.91	325
3-Cl	8.56	2.94	325
4-Br	5.29	3.14	325
3-CF$_3$	12.0	3.07	325
Benzoate substituent			
H	40.5	27.4	245
4-Me	38.3	30.2	260
4-CHMe$_2$	34.1	28.4	258
4-CMe$_3$	32.4	33.3	260
4-OMe	38.9	32.0	285
4-F	81.1	30.4	248
4-Cl	94.5	24.4	255
4-I	95.5	20.4	275
3-NO$_2$	270.5	23.7	240/ 230

* Rate coefficients were reproducible to within ±3%·
† Used in kinetic measurements (not λ$_{max}$ values for the esters)

TABLE 2

Rate coefficients (1 mol^{-1} s^{-1}) for the methoxide-catalysed rearrangement of methyl pseudo-8-benzoyl-1-naphthoate and pseudo-2-benzoylbenzoate *

$10k_2$

	In methanol				In MeOD
	30.0 °C	40.0 °C	50.0 °C	60.0 °C	60.0 °C
Naphthoate	0.176	0.328	0.661	1.25	2.35
Benzoate	9.18	15.8	27.1	40.5	67.9

In mole% methanolic dioxan at 60.0 °C

	0	10.62	24.06	41.62	65.56
Naphthoate	1.25	1.76	3.88	10.7	19.0
Benzoate	40.5	43.7	74.8	221	436

In mole% methanolic DMSO at 60.0 °C

	0	12.48	27.57	46.13	69.55
Naphthoate	1.25	1.85	4.03	11.9	31.6
Benzoate	40.5	72.7	122	330	785

* Rate coefficients were reproducible to within ±3%.

TABLE 3

Rate coefficients (1 mol^{-1}s^{-1}) for the acid-catalysed rearrangement of methyl pseudo-8-benzoyl-1-naphthoate and pseudo-2-benzoylbenzoate *

10^4k_2

	In methanol				In MeOD
	40.4 °C	50.2 °C	55.1 °C	60.0 °C	60.0 °C
Naphthoate	0.940	1.74	2.35	3.25	2.70
Benzoate	9.02	16.2	22.0	27.4	22.7

In mole% methanolic dioxan at 60.0 °C

	0	10.62	24.06	41.62	65.56
Naphthoate	3.25	3.22	2.77	1.87	0.736
Benzoate	27.4	26.9	22.4	11.8	5.16

* Rate coefficients were reproducible to within ±3%.

methoxide-catalysed rearrangement of the methyl pseudo-esters in methanol at 60.0 °C are shown in Table 1. Table 2 shows the rate coefficients for the parent pseudo-esters at several temperatures in methanol, in MeOD, in methanolic dioxan, and in methanolic dimethyl sulphoxide (DMSO) at 60.0 °C. The activation parameters of the parent esters are shown in Table 4.

TABLE 4

Activation parameters for the catalysed rearrangement of methyl pseudo-8-benzoyl-1-naphthoate and pseudo-2-benzoylbenzoate in methanol at 30.0 °C *

	Catalyst	$\Delta H^{\ddagger}/$ kcal mol^{-1}	$\Delta S^{\ddagger}/$ cal mol^{-1} K^{-1}
Naphthoate	Methoxide	12.6	−25
	Acid	12.2	−38
Benzoate	Methoxide	9.4	−28
	Acid	11.3	−36

* Values of $\Delta H^{\ddagger}$ are accurate to within ±400 cal mol^{-1} and $\Delta S^{\ddagger}$ to within ±1 cal mol^{-1} K^{-1}.

Bowden and Taylor [3] have indicated a likely mechanistic path (ii). The pathway is shown as proceeding
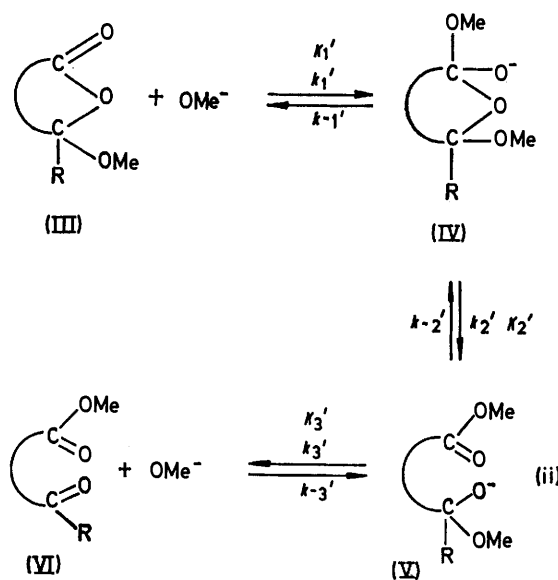
through discrete tetrahedral intermediates, but a single step, concerted process is possible.

Substituent Effects.—The effect of meta- and para-substitution in the benzoyl ring can be assessed using the Hammett equation [5] using both σ and σ^n [6,7] and the results are shown in Table 5. Excellent correlations are obtained with both substituent constants, but those with σ^n are slightly better. The ρ value for the naphthoate system is ca. 2.1 and contrasts markedly with that of ca. 1.1 for the benzoate. As shown in (ii), the rate-determ-

[5] C. D. Johnson, ' The Hammett Equation,' Cambridge University Press, London, 1973.
[6] D. H. McDaniel and H. C. Brown, J. Org. Chem., 1958, 23, 420.
[7] H. van Bekkum, P. E. Verkade, and B. M. Wepster, Rec. Trav. chim., 1959, 78, 815.

ining step could be either k'_1, k'_2, or k'_3 and the observed rate coefficient would be equal to either k'_1, $K'_1 k'_2$, or $K'_1 K'_2 k'_3$, respectively. A single step, concerted process would result in a transition state with negative charge distributed on the four oxygens. The ρ value is a measure of the stabilising or destabilising effect of substituents on the transition compared with the initial state. Two

TABLE 5

Hammett reaction constants for the catalysed rearrangement of methyl pseudo-8-benzoyl-1-naphthoate and pseudo-2-benzoylbenzoate in methanol at 60.0 °C *

System	Catalyst		ρ	$\log k_0$	r	s	n
Naphthoate	Methoxide	(a)	2.041	−0.810	0.996	0.112	7
		(b)	2.108	−0.846	0.999	0.060	7
	Acid	(a)	−0.123	−3.480	0.878	0.030	7
		(b)	−0.125	−3.479	0.870	0.032	7
Benzoate	Methoxide	(a)	0.952	0.751	0.990	0.074	9
		(b)	1.087	0.674	0.996	0.062	9
	Acid	(a)	−0.172	−2.551	0.771	0.054	9
		(b)	−0.182	−2.541	0.731	0.064	9

* r is the correlation coefficient, s is the standard deviation and n is the number of substituents used. Correlations (a) is that using σ and (b) that using σ^n.

comparisons should be noted. First, the methoxide anion-catalysed methanolysis of labelled methyl benzoates in methanol at 60.0 °C has a ρ value of ca. 2.0.[8] Secondly, the ρ values for the alkaline hydrolysis of the normal methyl esters of both the 2-benzoylbenzoates and 8-benzoyl-1-naphthoates in 70% (v/v) dioxan–water at 60.0 °C are ca. 2.0 and 1.9, respectively,[9,10] whereas, those for the alkaline hydrolysis of the pseudo-esters of the two systems are ca. 0.6 and 0.8, respectively.[11] The exchange reaction and the normal ester hydrolyses involve rate-determining attack at the carbonyl group carbon bonded to the substituted phenyl group, contrasting with the pseudo-ester hydrolyses which involve rate-determining attack at the carbonyl group carbon bridged by oxygen to the carbon bonded to the phenyl group. Thus the transition state for the rearrangement of the pseudo-naphthoates must be close to the intermediate (V), with the negative charge on the carbonyl oxygen bonded to the substituted phenyl group, and that for the pseudo-benzoates must be close to the intermediate (IV), with the negative charge on the oxygen bonded to a carbon bridged by oxygen to the substituted phenyl group. It is thus suggested that k'_1 and k'_3 are the rate-determining steps for the pseudo-benzoates and -naphthoates, respectively (see also below). If the reaction pathway is concerted, the same reasoning applies to indicate the distribution of charge. However, the evidence here is both consistent with and appears to favour the stepwise path. An energy profile can be outlined for the methoxide anion-catalysed rearrangement of the methyl pseudo-esters by consideration of the following points: (i) the pseudo-esters are very much less stable than the normal esters; (ii) according to the principle of micro-

scopic reversibility,[12] the path going from pseudo to normal ester must be the same as the reverse; (iii) the rearrangement is first order in both substrate and methoxide anion. Further, it may be assumed that $k'_2 > k'_{-1}$. k'_{-1} Involves the loss of methoxide anion from (IV), whereas k'_2 involves the loss of a better leaving group, the hemiacetal anion, together with ring-fission which releases strain energy. This is shown in the Figure. The formation of the transition states TSI and TSIII, can be rate-determining. The present evidence indicates that the naphthoates follow the path shown by the broken line in the Figure whereas the benzoates follow the path

Reaction co-ordinate
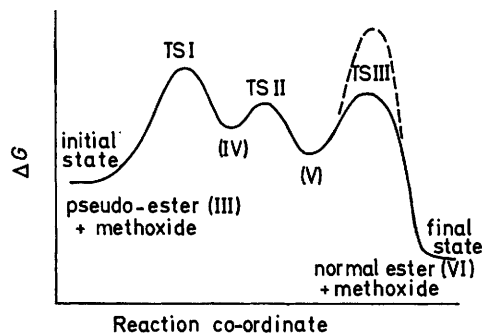
Free energy profile for the base-catalysed rearrangements

shown by the continuous line. This switch arises from the interactions in TSI and TSIII differing for the benzoates and naphthoates because of ring strain, steric ' bulk ', and resonance interactions being a function of the particular system under study (cf. refs. 1 and 11).

Relative Reactivities and Activation Parameters.—The rearrangement of the parent pseudo-benzoate was found to be ca. 32 times faster than that of the pseudo-naphthoate. The rate coefficient for the rearrangement of methyl pseudo-2-pivaloylbenzoate at 20 °C in methanol[3] has been found to be 3.08×10^{-3} l mol^{-1} s^{-1}. This is considerably slower than the extrapolated value for methyl pseudo-2-benzoylbenzoate. The rate decrease appears to be a function of the combination of unfavourable polar and steric effects of the t-butyl, as opposed to the phenyl, substituent.

The relative rates and activation parameters of the reactions of pseudo-benzoates and -naphthoates refer to different rate-determining steps. The activation parameters are typical of those for bimolecular methoxide anion-catalysed reactions of esters.[8,13,14] The greater reactivity of the benzoate clearly arises from the greater strain in the five-membered ring[1] and results in the considerably lower enthalpy of activation.

Solvent and Solvent Isotope Effects.—As shown in Table 2, the kinetic solvent isotope effect, $k_2^{\text{MeOD}}/k_2^{\text{MeOH}}$, for the parent benzoate and naphthoate pseudo-esters were

[8] L. B. Jones and T. M. Sloane, *Tetrahedron Letters*, 1966, 831.
[9] K. Bowden and G. R. Taylor, *J. Chem. Soc. (B)*, 1971, 145.
[10] K. Bowden and A. M. Last, *J.C.S. Perkin II*, 1973, 345.
[11] K. Bowden and F. A. El-Kaissi, *J.C.S. Perkin II*, 1977, 526.

[12] W. P. Jencks, ' Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969.
[13] R. W. Taft, M. S. Newman, and F. H. Verhoek, *J. Amer. Chem. Soc.*, 1950, 72, 4511.
[14] C. G. Mitton, R. Schowen, M. Gresser, and J. Shapley, *J. Amer. Chem. Soc.*, 1969, 91, 2036.

1.7 and 1.9 at 60 °C, respectively. These compare closely with those found for the methoxide-catalysed methanolysis of 4-substituted phenyl acetates in range 1.6—2.1 at 25 °C.[15] The results for variation in the composition of methanolic dioxan and DMSO at 60 °C are shown in Table 2. Plots of log k_2 against mole % non-aqueous
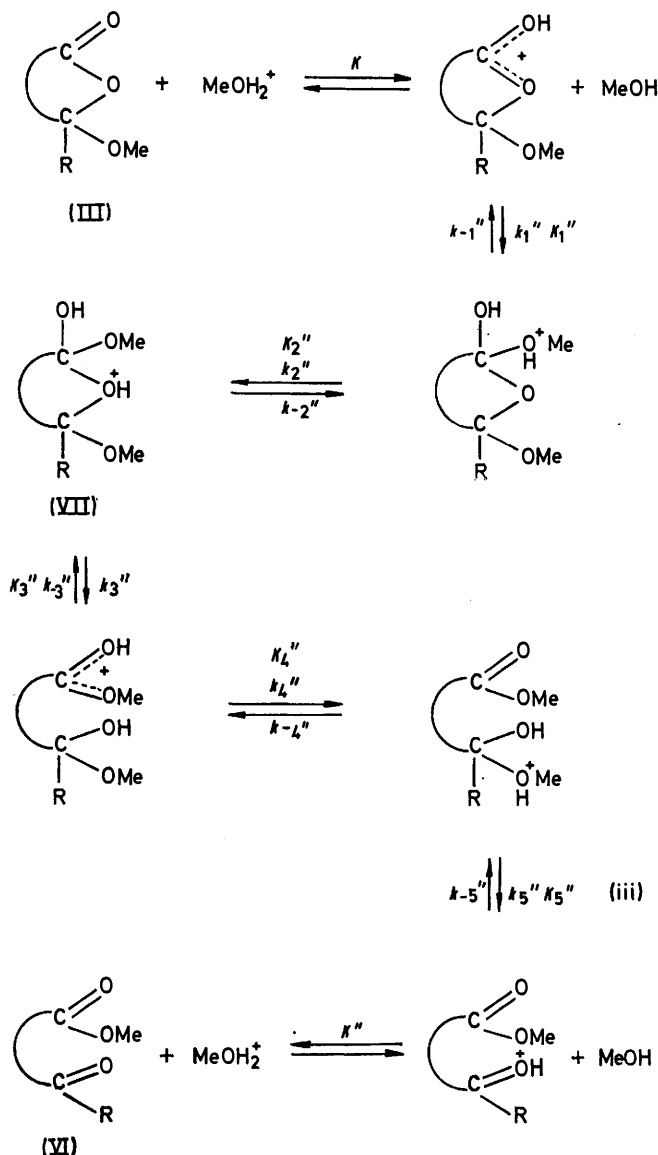
component are linear with slopes of $ca.$ 2.0 × 10⁻² and 1.8 × 10⁻² for both systems in methanolic DMSO and dioxan, respectively.

These results indicate a transition state composed of the ester and a methoxide anion. The decrease protic solvation requirement of the transition state relative to the initial state gives rise to all these rate enhancements.

Acid-catalysed Rearrangement.—The reaction was found to be first order in the substrate, the pseudo-ester, and in the acid catalyst. Rate coefficients for the acid-catalysed rearrangement of methyl pseudo-esters in methanol at 60.0 °C are shown in Table 1. Table 3 shows the rate coefficients for the parent pseudo-esters at several temperatures in methanol, in MeOD, and in methanolic dioxan at 60.0 °C. The activation parameters of the parent esters are shown in Table 4. Mechanism (iii), related to that suggested previously,[3] is proposed. Again a concerted process is possible.

Related Rates.—The five-membered ring pseudo-esters are more reactive by a factor of $ca.$ 8 at 60.0 °C than the six-membered system. This is much closer to the rate ratio for these esters in their alkaline hydrolysis reaction than that for their methoxide anion-catalysed rearrangement. A comparison of the rates of the acid-catalysed rearrangement for methyl pseudo-2-acylbenzoates at 40 °C in methanol[3] indicates that the benzoyl ester reacts at rate between that of the isobutyryl and pivaloyl esters. Clearly steric ' bulk ' factors of the substituents mainly control reactivity here and, for the benzoyl esters, there are no resonance interactions between the keto-carbonyl and the phenyl group present in the transition state.

Substituent Effects.—It can be noted from the results shown in Table 1 that substituents have *very* little effect on the rates for either series. Correlations using the Hammett equation,[5] as shown in Table 5 either using σ or σⁿ values, give apparently poor results. However, the appearance of the latter is really a function of ρ being close to zero.[16] The result itself is both meaningful and reliable. Similar results, with ρ close to zero but negative, have been previously found for the acid-catalysed esterification or ester hydrolysis of substituted benzoic acids.[17] The pathway shown in (iii) is closely related to the accepted $A_{AC}2$ pathways for the latter reactions.[18] Thus, for the pseudo-esters and benzoates in these types of reactions, the opposing effects on equilibrium protonation and nucleophilic attack by methanol by polar substituents would tend to cancel (*cf.* ref. 19). This behaviour is in sharp contrast to that of methyl pseudo-2-benzoylbenzoates and pseudo-8-benzoyl-1-naphthoates in their acid-catalysed hydrolysis.[20] Weeks *et al.*[20] have suggested an A-1 pathway *via* a carbonium ion. In methanol such a pathway would simply result in reforming the pseudo-ester by reaction of the ion with the solvent. The entropies of activation of $ca.$ −37 cal mol⁻¹ K⁻¹ for both systems in their acid-catalysed methanolysis, shown in Table 4, are clearly indicative of a bimolecular process, in contrast to the results of Weeks *et al.*[20,21] for the acid-catalysed hydrolysis of the pseudo-benzoate and

[15] C. G. Mitton, M. Gresser, and R. Schowen, *J. Amer. Chem. Soc.*, 1969, **91**, 2045.

[16] W. H. Davis and W. A. Pryor, *J. Chem. Educ.*, 1976, **53**, 285.

[17] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[18] C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, ch. XIV.

[19] J. Hine, ' Physical Organic Chemistry,' McGraw-Hill, New York, 1962, ch. 12.

[20] D. P. Weeks and J. Crane, *J. Org. Chem.*, 1973, **38**, 3375; D. P. Weeks and G. Zuorick, *J. Amer. Chem. Soc.*, 1969, **91**, 477; D. P. Weeks, J. Cella, and L. T. Chen, *J. Org. Chem.*, 1973, **38**, 3383.

[21] D. P. Weeks, A. Grodski, and R. Fanucci, *J. Amer. Chem. Soc.*, 1968, **90**, 4958.

-naphthoate, the entropies being -19 and 1 cal mol^{-1} K^{-1}, respectively.

Solvent and Solvent Isotope Effects.—The solvent isotope ratio k_2^{MeOD}/k_2^{MeOH} for the acid-catalysed rearrangement of the parent pseudo-benzoate and -naphthoate at $60.0°$ is *ca.* 0.8. For reactions involving pre-equilibrium protonation of esters and pseudo-esters in water, k^{D_2O}/k^{H_2O} has been found to be equal to *ca.* 1.6—2.8.[20-22] A number of general base-catalysed reactions of esters in water, in which the rate-determining step involves concerted proton removal and nucleophilic attack on the ester carbonyl group, have k^{H_2O}/k^{D_2O} *ca.* 1.9—4.[23] As similar results would be expected for reactions in methanol, the likely rate-determining step appears to be a process in which the protonated substrate undergoes a proton transfer at or subsequent to the nucleophilic attack by methanol.

A plot of log k_2 for both pseudo-esters against the mole % dioxan gives a curve showing decreased rate with increasing dioxan content. This behaviour appears to arise mainly from the decrease in effective concentration of the methanol, which is the nucleophile. Studies [24] of both bimolecular and unimolecular acid-catalysed hydrolyses in aqueous dioxan indicate different behaviour for the different classes of reaction, $A1$, A-S_E2, or $A2$. Our study for methanolic dioxan closely corresponds to that observed for the $A2$ process.

All the present evidence for the acid-catalysed rearrangements of both pseudo-esters indicates a reaction pathway similar to that shown in (iii), the rate-determining step being equal to or subsequent to the nucleophilic attack by methanol. A cyclic transition state has been considered likely for the $A_{AC}2$ hydrolysis of esters.[25] An analogous structure can be drawn for the present study; but there is, as yet, no compelling evidence for a choice between the various possible transition states. It needs to be more 'crowded' than the initial state, have no resonance interaction between the keto-carbonyl and phenyl group, and have some proton

transfer involved. Thus, the formation of (VII) in mechanism (iii) appears to be attractive and k_{obs} would then be equal to $KK_1''k_2''$.

EXPERIMENTAL

Methyl pseudo-8-(substituted benzoyl)-1-naphthoates and pseudo-2-(substituted benzoyl)benzoates were prepared and purified as previously described,[11] as were the corresponding normal esters.[10,26] Solvents were purified as described previously,[27,28] as were solutions of hydrogen chloride and sodium methoxide in methanol.[3] MeOD (methan[^{2}H]ol) was obtained from Ryvan Chemicals Ltd., and purified as for methanol. Fresh solutions were always employed in the measurements and were stored, when necessary, at -10 °C under dry nitrogen.

Kinetic Procedure.—Rate coefficients for the acid- or base-catalysed rearrangement of the pseudo-esters were determined spectrophotometrically by use of a Unicam SP 800 or 8000 spectrophotometer. The cell temperature was controlled to ± 0.05 °C by means of a Churchill thermocirculator. The reactions were followed at suitable wavelengths, as shown in Table 1, which were normally those having the greatest difference between the pseudo and normal ester. The procedure followed that described previously [28] using a Beckmann 1005 chart recorder. The substrate, sodium methoxide, and acid (hydrogen chloride) concentrations were in the range 5×10^{-5}—1×10^{-4}, 5×10^{-4}—1×10^{-2} and 1×10^{-1}—1M, respectively. The reactions were found to be first order in substrate, without deviation over at least three 'half lives', and first order in methoxide or acid. The products of the reaction were found to be the corresponding normal ester in quantitative yield. The latter was confirmed spectrophotometrically by comparison of the spectrum of the normal ester in base or acid with that of the reaction product. No significant change in the spectrum of the normal esters could be noted on addition of base or acid. The ^{1}H n.m.r. of the product was identical with that of the normal ester so that the K_e value for the tautomeric equilibrium of the pseudo and normal esters will be <0.02 (*cf.* ref. 3).

[22] R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 275.
[23] E. K. Euranto in 'The Chemistry of Carboxylic Acids and Esters,' ed. S. Patai, Interscience, New York, 1969.
[24] A. Kankaanpera, M. Lahti, and M. Merilahti, *Acta Chem. Scand.*, 1970, **24**, 360; A. Kankaanpera and M. Merilahti, *ibid.*, 1972, **26**, 685.

[25] C. A. Lane, *J. Amer. Chem. Soc.*, 1964, **86**, 2521; C. A. Lane, M. F. Cheung, and G. F. Dorsey, *ibid.*, 1968, **90**, 6492.
[26] K. Bowden and G. R. Taylor, *J. Chem. Soc.* (B), 1971, 145.
[27] K. Bowden, M. Hardy, and D. C. Parkin, *Canad. J. Chem.*, 1968, **46**, 2929.
[28] K. Bowden and M. J. Price, *J. Chem. Soc.* (B), 1971, 1784.