Aromatic Rearrangements in the Benzene Series. Part 5.[1] The Fries Rearrangement of Phenyl Benzoate: the Rearranging Species. The Effect of Tetrabromoaluminate Ion on the *ortho/para* Ratio: the Non-involvement of the Proton as a Co-catalyst

Ian M. Dawson, Julia L. Gibson, Lionel S. Hart,* and Catherine R. Waddington
Department of Organic Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

Kinetic studies show that in the rearrangement of phenyl benzoate catalysed by anhydrous $AlBr_3$ in homogeneous solution in chlorobenzene, the actual species undergoing rearrangement is $PhCO_2Ph{\cdot}AlBr_3$ (when a 1:1 molar ratio of catalyst: ester is used). Addition of $AlBr_4^-$ to the reaction mixture (as $Bu_4N^+AlBr_4^-$, which itself causes no rearrangement) gives lower *ortho/para* ratios than are found in the absence of this ion, the ratio decreasing as the quantity of $AlBr_4^-$ increases. In the absence of deliberately added $AlBr_4^-$, ^{27}Al n.m.r. spectroscopy shows that $AlBr_4^-$ is undetectable at the beginning of the 1:1 rearrangement reaction (1 $AlBr_3$:1 $PhCO_2Ph$), though it accumulates during the reaction; but that *ca.* 0.8% of the $AlBr_3$ is present as this ion at the start of the closely related 1:1:1 acylation reaction (1 $AlBr_3$: 1 PhCOBr: 1 PhOH), accumulating during the course of this reaction also. Thus, the different behaviour of the rearrangement and acylation reactions (as indicated by their *o*:*p* ratios, and the variation of these with time) is explained by the initial absence of $AlBr_4^-$ from, or its initial presence in, the various reaction mixtures. Rearrangement reactions carried out with a stream of nitrogen bubbled through them to remove HBr show *o*:*p* ratios which support the above conclusion, but more rigorous proof comes from acylation reactions involving PhCOBr and PhO^-Na^+ (rather than PhOH), which give only $PhCO_2Ph$ and NaBr, *i.e.* H^+ and (soluble) Br^- are not formed. Under the influence of $AlBr_3$, these reactions then mimic the 1:1 rearrangement reactions, but if $Bu_4N^+Br^-$ is also added with the $AlBr_3$, the subsequent rearrangements mimic the 1:1:1 acylation reactions. This excludes H^+ as a co-catalyst in the 1:1 rearrangement reaction. Finally, calorimetric measurements provide data supporting the proposed mechanism of the first stage of the 1:1 rearrangement (set out in Part 3 of this series), and investigations of the initial stages of the 1:1 rearrangement and 1:1:1 acylation reactions are described.

In Part 1[2] of this series, we described the anhydrous aluminium bromide-catalysed rearrangement of phenyl benzoate in homogeneous solution in chlorobenzene (specifically, the 1:1 rearrangement reaction, involving 1 mol of $AlBr_3$ per mol of ester), and the acylation of phenol by benzoyl bromide using the same catalyst and solvent (specifically, the 1:1:1 acylation reaction, involving 1 molar proportion each of $AlBr_3$, benzoyl bromide, and phenol). The 1:1 rearrangement gave an *ortho/para* (*o*:*p*) ratio (*i.e.* of 2- and 4-hydroxybenzophenone) which decreased with increasing time. In contrast, the 1:1:1 acylation, which proceeded, to more than 90%, *via* the first-formed ester, showed an effectively constant *o*:*p* ratio (though it reached this constant value from a very low *o*:*p* ratio in the initial stages of this reaction). The 1:1 rearrangement was interpreted[2] as involving two processes: the first-stage reaction, giving 2-hydroxybenzophenone only (and consequently considered to be intramolecular[3]), and the second-stage reaction, giving 2- and 4-hydroxybenzophenone in constant ratio (and considered to proceed through an ion-pair type of intermediate). The second-stage reaction of the 1:1 rearrangement was identical with the 1:1:1 acylation. This, essentially, was our view[2] of the mechanisms of these reactions under the specified reaction conditions.

Our recent work[4] using isotopically labelled phenyl benzoates confirmed our original interpretation,[2] except that the first-stage reaction is actually intermolecular, and we proposed a bimolecular process involving a cyclic six-membered transition state for this reaction. The second-stage reaction involves heterolysis of a catalyst–ester complex to give a tight ion pair ($Ph\overset{+}{C}O\ PhO\bar{A}lBr_3$) from which 2- and 4-hydroxybenzophenone result in constant ratio, the formation of these acylphenols occurring to some extent before full solvation of the ion pair occurs ('pseudointramolecular'[2] or 'extra-molecular'[5] rearrangement).

Having thus established the nature of the first- and second-stage reactions, we now show why there is so striking a difference (described above) between the rearrangement of the ester itself (the 1:1 rearrangement) and rearrangement of the ester formed *in situ* (the 1:1:1 acylation).

The difference between the 1:1 rearrangement and the 1:1:1 acylation was attributed[2] to the presence, from the start, in the latter reaction mixture, of HBr, formed as outlined in Scheme 1,

$$PhCOBr + PhOH \xrightarrow{AlBr_3} PhCO_2Ph + HBr$$

Scheme 1.

and responsibility was initially[2] attached specifically to the proton. (The earliest suggestion that proton catalysis played a role in the Fries rearrangement was made by Amin and Shah,[6] though they presented no experimental evidence to substantiate this proposal. Their idea was taken up in the 1950's by Gerecs and his coworkers, and discussed at length in his 1964 review[7]). We long sought evidence[8] for the proposal that H^+ was the cause of the difference between the 1:1 rearrangement and

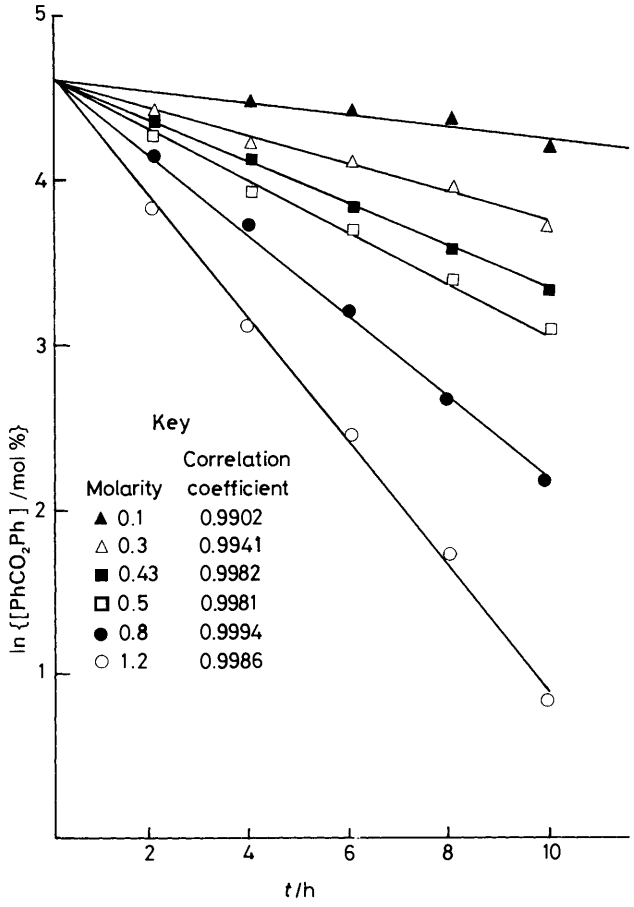


Figure 1. First-order plot for varying initial concentrations of phenyl benzoate.

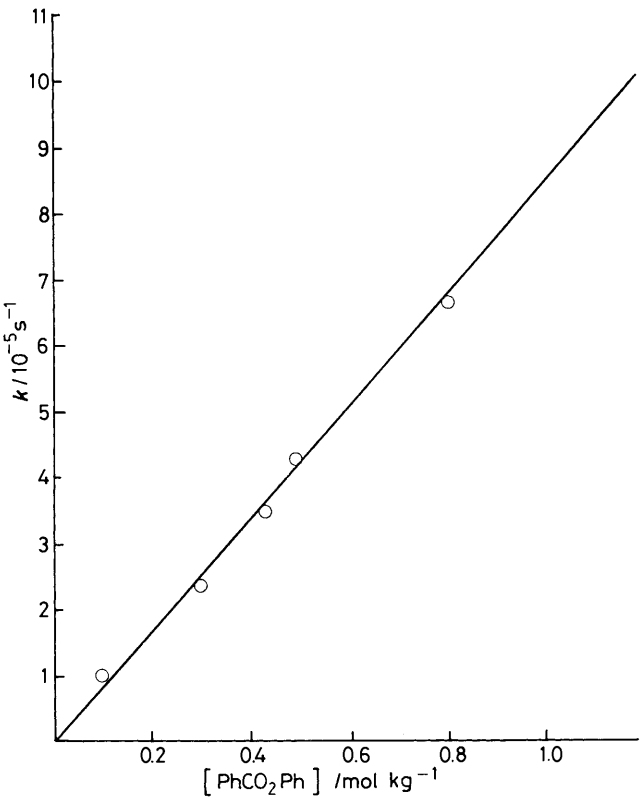


Figure 2. First-order rate constants *vs.* initial concentrations of phenyl benzoate. $k_2 = (8.44 \pm 0.17) \times 10^{-5}$ kg mol^{-1} s^{-1}; correlation coefficient 0.9991.

1:1:1 acylation, but as the results were unconvincing, we began to seek other explanations.

As HBr is produced in Scheme 1, the other possibility is that Br^- has an important role in the rearrangement, probably as $AlBr_4^-$, formed by reaction with $AlBr_3$. This paper describes a systematic investigation of the effect of added $AlBr_4^-$ on the 1:1 rearrangement, and a search, using ^{27}Al n.m.r. spectroscopy, for the presence of this ion in rearrangement and acylation reaction mixtures. Attempts to remove HBr formed during a 1:1 rearrangement, and the effect of this on the *o*:*p* ratio, are also described, but a more rigorous test of our proposals is provided by two series of 1:1:1 acylation reactions, in the first of which both Br^- and H^+ are prevented from being present at the start of the reaction, and in the second of which Br^- is deliberately added, but H^+ is still initially absent. These situations were achieved *via* reactions (*a*) and (*b*) in Scheme 2, respectively:-

$$\text{PhCOBr} + \text{PhO}^-\text{Na}^+ \xrightarrow{\text{PhCl}} \text{PhCO}_2\text{Ph} + \text{NaBr}\downarrow \xrightarrow{\text{AlBr}_3} \text{rearrangement} \quad (a)$$

$$\text{PhCOBr} + \text{PhO}^-\text{Na}^+ + \text{Bu}_4\text{N}^+\text{Br}^- \xrightarrow{\text{PhCl}} \text{PhCO}_2\text{Ph} + \text{NaBr}\downarrow + \text{Bu}_4\text{N}^+\text{Br}^- \xrightarrow{\text{AlBr}_3} \text{rearrangement} \quad (b)$$

Scheme 2.

We also describe the results of analyses of the early stages of the 1:1 rearrangement and 1:1:1 acylation reactions, as these are relevant to our mechanistic proposals, and a calorimetric investigation of the interaction of phenyl benzoate and $AlBr_3$, for its relevance to our mechanistic proposals in Part 3 of this series.[4] The composition of the rearranging species in the 1:1 rearrangement[9] is also discussed.

Results and Discussion

The Rearranging Species.—Investigation of a series of 1:1 rearrangements gave the results shown in Figure 1. Plots of the reciprocal of the ester concentration *vs.* time were curved. The first-order rate constants were proportional to the initial concentration of the ester (Figure 2), so that the kinetic form is given by equation (1), where [Z] is a constant concentration

$$\text{rate} = k[\text{PhCO}_2\text{Ph}][\text{Z}] \quad (1)$$

equal to the initial concentration of ester or of $AlBr_3$; but Z cannot be the ester as the reaction is first order in $PhCO_2Ph$. If $AlBr_3$ (or some other species of equivalent catalytic ability, *e.g.* $ArOAlBr_2$) remains effectively constant in concentration throughout the reaction, then the rearranging species would be $PhCO_2Ph{\cdot}AlBr_3$, though the structure of this entity is not known: we shall return to this point later.

(Furka and Szell[10] performed detailed kinetic studies of the rearrangement of thymyl acetate caused by $AlCl_3$ in homogeneous solution in nitrobenzene. Cullinane and his co-workers[11] had also studied the kinetics of various Fries rearrangements, and the results of these workers' investigations are discussed in references 3(*b*) and 12. These investigators agree that rearrangement involves a catalyst–ester complex, but detailed interpretations beyond this point differ—even as to the composition of the complex—and we do not wish to draw comparisons between the results of our own reactions and the results of those carried out under substantially different experimental conditions).

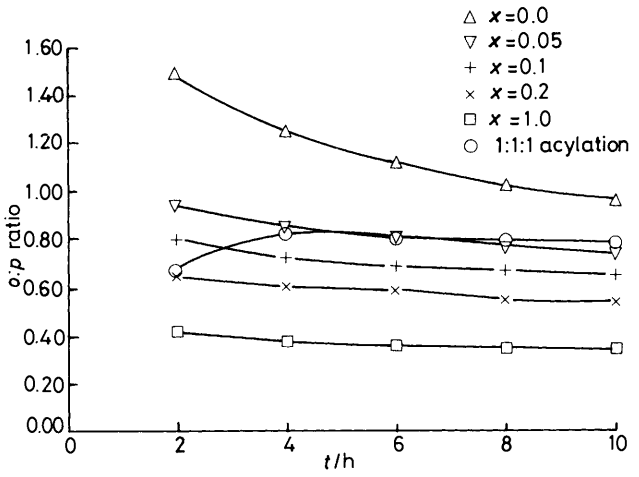


Figure 3. *o*:*p* ratio *vs.* time, *x* varying.

Table 1. Effect of varying the alkyl groups in $R_4N^+Br^-$: $(1 + x):1:x$ rearrangements (x = 0.1; 4 h, 110 °C).

	R				
	Et	Pr^n	Bu^n	n-C_5H_{11}	n-C_6H_{13}
$PhCO_2Ph$[a]	63.5	64.1	64.7	64.4	66.0
2-OH[a,b]	13.1	12.5	12.8	12.8	12.4
4-OH[a,c]	16.4	16.3	17.3	17.1	16.8
(2-OH + 4-OH)[a]	29.5	28.7	30.1	29.9	28.9
Return[a,d]	93.0	92.9	94.7	94.3	95.1
o:*p* ratio	0.80	0.77	0.74	0.75	0.74

[a] All quantities are mol %, and the average of four determinations. [b] 2-Hydroxybenzophenone. [c] 4-Hydroxybenzophenone. [d] $PhCO_2Ph$ + 2-OH + 4-OH.

Table 2. 1:1 Rearrangement reaction with nitrogen stream (4 h, 110 °C).[a]

	Reaction			
	I	Control I	II	Control II
$PhCO_2Ph$[a]	66.4	65.8	65.4	68.4
2-OH[a,b]	12.5	12.9	11.1	12.0
4-OH[a,c]	8.2	11.2	7.8	10.0
(2-OH + 4-OH)[a]	20.7	24.2	18.9	22.0
Return[a,d]	87.1	89.9	84.3	90.4
o:*p* ratio	1.53	1.15	1.44	1.19

[a] Footnotes as in Table 1. Reactions I and II were carried out under a stream of dry nitrogen.

The second-order rate constant obtained for rearrangement at 110 °C under our conditions is $(8.44 \pm 0.17) \times 10^{-5}$ kg mol^{-1} s^{-1}.

The Effect of Added Bromide Ion.—When Br^- is added to the 1:1 rearrangement reaction mixtures, as $Bu_4N^+Br^-$,[13] $AlBr_4^-$ is produced *via* the reaction in Scheme 3.

$$Br^- + AlBr_3 \longrightarrow AlBr_4^-$$

Scheme 3.

When a 1 molar proportion of $Bu_4N^+Br^-$ was included in such a reaction mixture, no detectable rearrangement subsequently occurred even after 10 h at 110 °C (see Experimental): all of the $AlBr_3$ had been sequestered as $AlBr_4^-$, which is thus, by itself, incapable of bringing about the Fries rearrangement of phenyl benzoate, at least under our experimental conditions. Likewise, the Bu_4N^+ ion is inert. We then performed a series of $(1 + x):1:x$ rearrangements, this expression representing the molar proportions of $AlBr_3$, $PhCO_2Ph$, and $Bu_4N^+Br^-$ respectively. In all cases, the molar ratio of 'free' $AlBr_3$: $PhCO_2Ph$ remained fixed at 1:1, the additional AlB_3 and $Bu_4N^+Br^-$ combining immediately to give x moles of Bu_4N^+ $AlBr_4^-$. Figure 3 shows the striking effect of added Br^- (as $AlBr_4^-$). As the amount of $AlBr_4^-$ increases, the *o*:*p* ratio at any given time decreases, eventually becoming almost constant over the reaction period studied, but still showing to a very much reduced extent the upward concavity characteristic of 1:1 rearrangements. Figure 3 also shows that the ultimate *o*:*p* ratio obtained in the 1:1:1 acylation reaction (see earlier) is reproduced when *ca.* 5 mol % of $AlBr_4^-$ is present in the 1:1 rearrangement, *i.e.* if *ca.* 5% of the HBr produced in Scheme 1 is retained in the reaction mixture as $AlBr_4^-$, the difference in *o*:*p* ratios between the 1:1 rearrangement and 1:1:1 acylation could be accounted for. The effect of varying the cation of the added bromide $R_4N^+Br^-$ was examined by fixing the value of x and the reaction time and using a series of tetra-alkylammonium bromides. The results are shown in Table 1. The *o*:*p* ratio is little affected, so that the size of the alkyl groups in R_4N^+ cannot play an important part (*e.g. via* steric hindrance) in determining the *o*:*p* ratios in these reactions.

Attempts to Remove HBr.—1:1 Rearrangements were carried out with a slow stream of dry nitrogen passing through the reaction mixture, a normal rearrangement being performed simultaneously as a control. The results are shown in Table 2. The *o*:*p* ratios show substantial increases in those reactions through which nitrogen was bubbled: partial removal of HBr from the reaction mixture has reduced the quantity of $AlBr_4^-$ formed, delaying the onset, or reducing the contribution, of the second-stage reaction, so that the *o*:*p* ratio is larger, as predicted.

Determination of $AlBr_4^-$ *in the Reaction Mixtures by* ^{27}Al *N.M.R. Spectroscopy.*—None of the above experimental work proves that $AlBr_4^-$ is actually present in any of the reaction mixtures when the rearrangements or acylations are performed in the normal way (*i.e.* as unmodified 1:1 rearrangements or 1:1:1 acylations). Killen[8f] had shown $AlBr_4^-$ to be present in various reaction mixtures by using far i.r. absorption spectrophotometry. The ion was found to be present in 1:1 rearrangements after 4 and 8 h, but not after 5 min, nor was it detected in 1:1:1 acylations after 5 min. The method was inconvenient, qualitative, and not very sensitive. ^{27}Al N.m.r. spectroscopy proved a more satisfactory method of analysis. The symmetrical $AlBr_4^-$ ion gave a sharp signal, obscured by the broad signal from unsymmetrical aluminium-containing species (*i.e.* $AlBr_3$, presumably both free and combined with phenyl benzoate or rearrangement products). Once a procedure enabling the $AlBr_4^-$ signal to be 'extracted' and integrated had been achieved (see Appendix), the amounts of $AlBr_4^-$ present at different times in 1:1 rearrangement and 1:1:1 acylation reaction mixtures were determined, and are shown in Figure 4. 5 min after the start of a 1:1 rearrangement, no $AlBr_4^-$ could be detected (20,000 scans) in the reaction mixture, but at the same time, a 1:1:1 acylation reaction reproducibly contained *ca.* 0.8% (of the $AlBr_3$ as) $AlBr_4^-$. This technique has the advantage that the reaction mixtures are not disturbed in any way before being analysed.

All the above work (addition of $AlBr_4^-$ to rearrangements, removal of HBr using a nitrogen stream, and ^{27}Al n.m.r. spectroscopy) implies that the $AlBr_4^-$ ion both causes the difference between the 1:1 rearrangement and the 1:1:1 acylation reactions, and also triggers the second-stage of the 1:1 rearrangement.

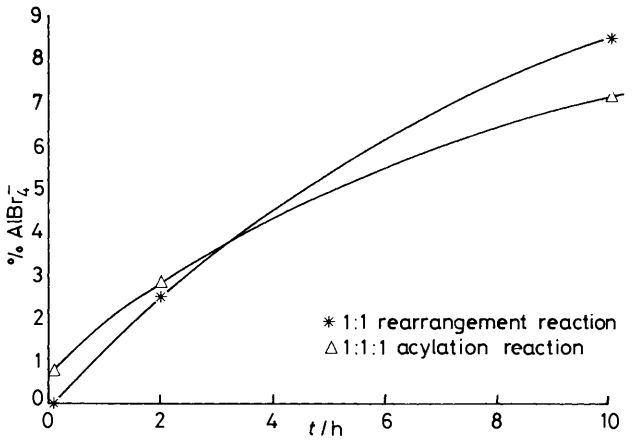


Figure 4. Determination of $[AlBr_4^-]$ by ^{27}Al n.m.r. spectroscopy.

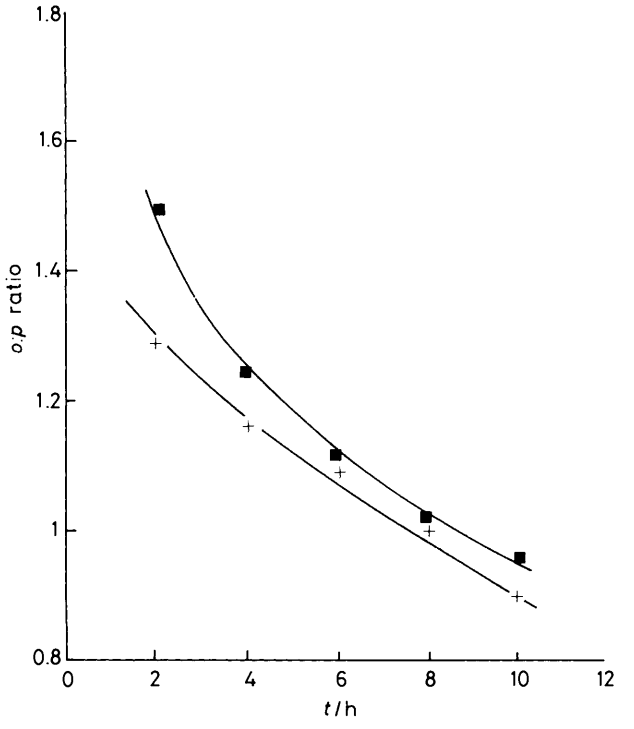


Figure 5. *o*:*p* ratio *vs.* time; ■ 1:1 rearrangement; + 1:1:1 Acylation: HBr absent.

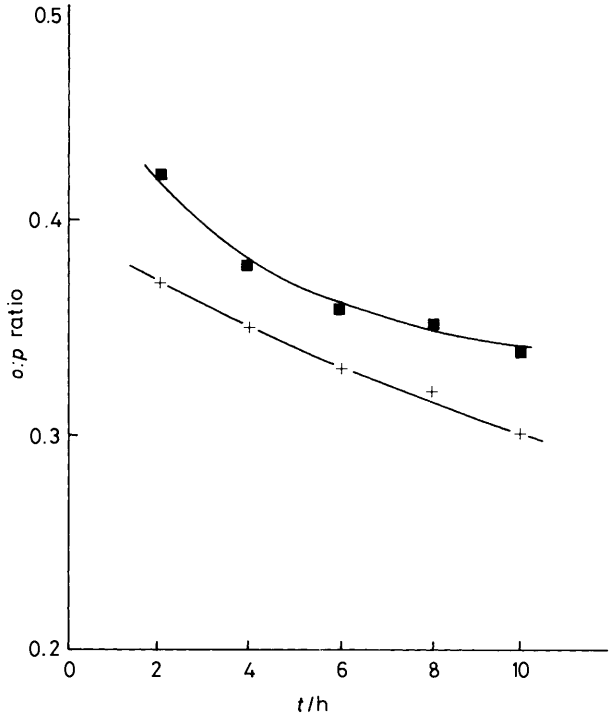


Figure 6. *o*:*p* Ratio *vs.* time; ■ 1:1 rearrangement, $AlBr_4^-$ added; + 1:1:1 acylation, H^+ absent, Br^- added.

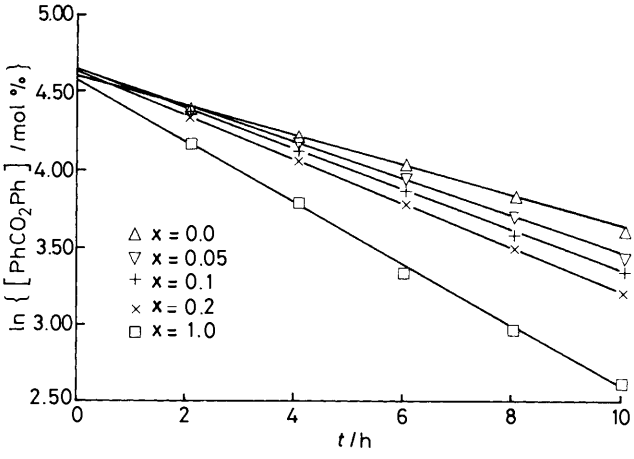


Figure 7. $(1 + x):1:x$ Rearrangements, x varying. First-order plots.

As a further test, we performed acylations from which HBr was excluded at the beginning of the reaction, and similar reactions to which Br^- was deliberately added, (Scheme 2). In both series of reactions, benzoyl bromide reacted with sodium phenoxide in chlorobenzene to give phenyl benzoate and a precipitate of NaBr. A sample of the solution (containing ester but no bromide) was then removed, and $AlBr_3$ was added, so that effectively a 1:1:1 acylation was carried out in the initial absence of both H^+ and Br^-. However, in one series of reactions, $Bu_4N^+Br^-$ was also added, so that effectively a 1:1:1 acylation was now performed in the presence of $AlBr_4^-$, but in the absence of H^+. Figures 5 and 6 show clearly that the acylation initially free of H^+ and Br^- resembles a 1:1 rearrangement, whilst the acylation initially free of H^+ but containing Br^- resembles a normal acylation reaction. Thus, we have both confirmed the interpretation above—that the presence of $AlBr_4^-$ is a crucial factor in establishing the chemical behaviour of the two reacting systems (rearrangements and acylations)—and simultaneously ruled out the proton's having any effect.

Figure 3 shows that the plots of *o*:*p* ratio *vs.* time are all still slightly concave upwards, even when large amounts of $AlBr_4^-$ are present in the rearrangement mixtures. This implies that in all these reactions, there is still a contribution from the first-stage (*i.e.* solely *ortho*-directed) reaction of the 1:1 rearrangement, even though it is substantially attenuated when larger amounts of $AlBr_4^-$ are present. Presumably, therefore, there must be a very small contribution from the process giving *ortho*-rearrangement product only, in the early stages of the 1:1:1 acylation, as there is in the 1:1 rearrangement reaction, since at the start of the 1:1:1 acylation, the amount of $AlBr_4^-$ present is small (*ca.* 0.8% of the $AlBr_3$ present—see above).

The Function of $AlBr_4^-$.—The above work does not, however, define the actual role of the $AlBr_4^-$ ion. Graphs of ln $[PhCO_2Ph]$ *vs.* time give a set of first-order plots (see Figure 7) and first-order rate constants, which are plotted against $[AlBr_4^-]$

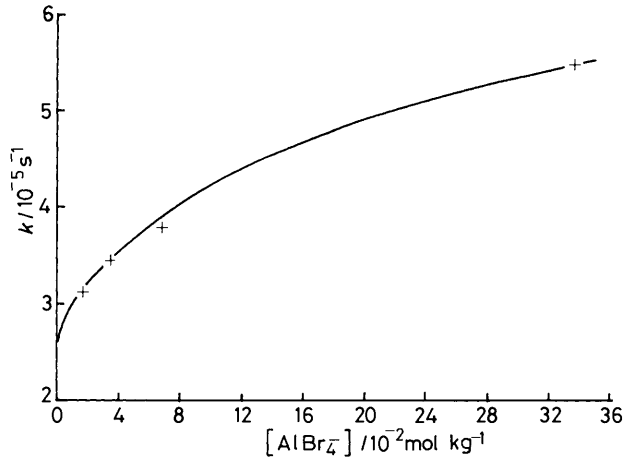


Figure 8. $(1 + x):1:x$ Rearrangements, x varying. First-order rate constants *vs.* $[AlBr_4^-]$ added.

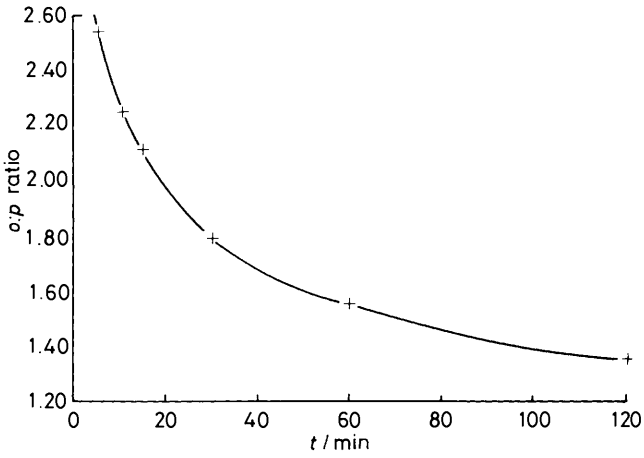


Figure 9. 1:1 Rearrangement, early stages; *o*:*p* ratio *vs.* time.

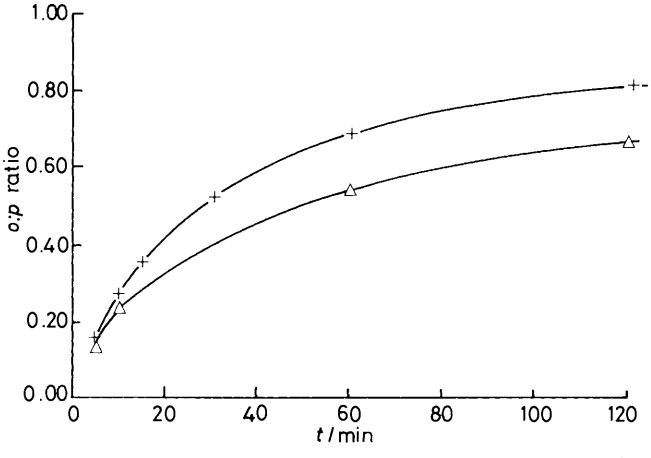
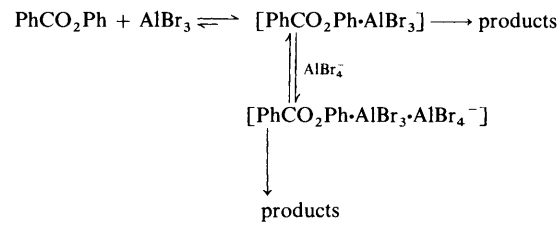


Figure 10. 1:1:1 Acylation, early stages; *o*:*p* ratio *vs.* time. +, sampled reaction; △, undisturbed reaction.

in Figure 8. No simple kinetic relationship is apparent, but the general shape of the curve is similar to that obtained in Michaelis–Menten kinetics,[14] and implies that a second complex is involved in the rearrangement (Scheme 4).

However, the system is not identical with that involved in Michaelis–Menten kinetics because of the side reactions, *e.g.* the first-stage reaction which involves rearrangement of ester



Scheme 4.

without the intervention of $AlBr_4^-$,[4] and the formation of the ketoester 4-benzoylphenyl benzoate.[2] As yet, a simple kinetic interpretation of the system is not possible.

In Scheme 4, specific bonding of $AlBr_4^-$ to the first $AlBr_3$–ester complex (thus involving penta-co-ordinate aluminium) is not at present being suggested, but no firm explanation of the structure of the second complex is offered. A speculative interpretation is as follows. The initial co-ordination of $AlBr_3$ occurs at the ester's carbonyl oxygen (see Experimental), but it is difficult to see how this species could then fragment to give $PhC\overset{+}{O}\cdot PhO\overset{-}{A}lBr_3$ (as the second-stage reaction requires[4]). If rearrangement actually occurred instead *via* the intermediate $PhCO\text{–}\overset{+}{O}(Ph)\text{–}\overset{-}{A}lBr_3$ this could easily give the above ion pair. Perhaps the $AlBr_4^-$ assists in the removal of the elements of $AlBr_3$ from the carbonyl oxygen and their addition to the phenoxy oxygen, so aiding the second-stage reaction, and re-routing the rearrangement *via* this process, away from the first-stage reaction. The actual mode of action of $AlBr_4^-$ in the rearrangement is currently being investigated.

Calorimetric Investigations.—We conducted some additional investigations to round out earlier work. The mechanism of the first-stage reaction proposed in Part 3[4] requires the presence of free (*i.e.* uncomplexed) phenyl benzoate in the 1:1 rearrangement reaction mixture at 110 °C. FTIR spectrometry showed that only a very small amount of free ester is present in the 1:1 rearrangement reaction mixture at room temperature (as shown by absorption at 1 740 cm^{-1}: see Experimental). If the amount of free ester at 25 °C is estimated, and the heat of complexation between ester and $AlBr_3$ determined by calorimetric measurements, simple thermodynamic considerations give the amount of free ester present at 110 °C. We found that if 1% of free ester were present at 25 °C, then there would be *ca.* 35% present at 110 °C; whilst if only 0.1% of the free ester were present at 25 °C, there would then be *ca.* 6% present at 110 °C. There is thus adequate free ester present at 110 °C as our proposed mechanism[3] requires. (Two determinations of the enthalpy of complexation of phenyl benzoate and $AlBr_3$ gave the values −89.3 and −96.6 kJ mol^{-1} (−21.3 and −23.1 kcal mol^{-1}, respectively). Russian workers[15] using a more complex procedure obtained values of −37.8 kcal mol^{-1} for complexation of $AlBr_3$ with benzophenone and with ethyl benzoate, taking into account the energy of dimerisation of the $AlBr_3$(−13.3 kcal mol^{-1}), so that our results are in quite good agreement with these values (obtained with comparable Lewis bases).

The Early Stages of the 1:1 *Rearrangement and* 1:1:1 *Acylation Reactions.*—Finally, we examined the rearrangement and acylation reactions in the period 5–120 min from the start of the reaction. A 1:1 rearrangement was sampled at intervals, and the *o*:*p* ratio of the hydroxybenzophenones determined by glc. A 1:1:1 acylation was treated similarly, but we also performed undisturbed acylations which were allowed to run for specified times without being sampled, and then worked-up in the normal way. Figures 9 and 10 show the results. In the 1:1 rearrangement, the *o*:*p* ratio is *ca.* 2.4 after 5 min, this high value

supporting the existence of the first-stage reaction giving only 2-hydroxybenzophenone. The acylations were slightly more complicated, the sampled reactions giving consistently higher *o*:*p* ratios than the undisturbed ones. We attributed this to traces of moisture adsorbed on the Pasteur pipettes used for sampling the reactions (though the pipettes had been dried), the result being decomposition of some $AlBr_4^-$ and the (partial) removal of its influence. In the undisturbed acylations, the *o*:*p* ratio was *ca.* 0.14 after 5 min (*cf.* the value of 0.24 after 2 min found in Part 1[2]), and this most probably represents direct *C*-acylation of phenol by benzoyl bromide at the beginning of the reaction, in contrast to the main process, *O*-acylation to give the ester, which subsequently rearranges.

This raises an important point. It might be argued that the approximately constant *o*:*p* ratio eventually attained in the 1:1:1 acylation is lower than that attained in the 1:1 rearrangement because at the beginning of the acylation, there is a very low *o*:*p* ratio, the effect of which is still apparent after longer reaction times, just as the effect of the very high (actually, infinite) *o*:*p* ratio at the beginning of the 1:1 rearrangement is carried forward to longer reaction times. This argument would deny any role to the $AlBr_4^-$ ion in creating the differences between the rearrangement and acylation reactions. However, our own work disproves this interpretation. In those acylations in which PhCOBr reacts with PhO^-Na^+, there is no detectable *C*-acylation at all at the start of the reaction (in which at least 95% of ester is formed). Thus, the lower *o*:*p* ratios observed in the subsequent rearrangements, when Br^- (as $Bu_4N^+Br^-$) is added to such reactions, compared with the higher *o*:*p* ratios observed in such reactions to which no Br^- is added, support our identification of the presence of the $AlBr_4^-$ ion as the distinguishing feature of these processes.

Experimental

Materials.—Anhydrous $AlBr_3$, chlorobenzene, phenyl benzoate, 2-, 3-, and 4-hydroxybenzophenone, and benzoyl bromide were all synthesised and/or purified as described previously.[2] 4-Bromobiphenyl (Eastman) and phenol were recrystallised from light petroleum (b.p. 40–60 °C). Sodium phenoxide was synthesised as described previously.[1] The quaternary ammonium salts $R_4N^+Br^-$ (where R = Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_6H_{13}) were all commercially available (the first four from Aldrich, the fifth from Eastman) and were dried in a desiccator before use, without further purification.

Rearrangement and Acylation Reactions.—Detailed descriptions of these appear in refs. 9 and 13(*b*), but a brief summary of the essential points was given in ref. 2: a similar procedure was adopted, weight-in-weight (molal) solutions being used throughout. For the reactions involving added $AlBr_4^-$, calculated quantities of $Bu_4N^+Br^-$ and $AlBr_3$ were used such as to leave the $AlBr_3$: $PhCO_2Ph$ molar ratio at 1:1 with the chosen value (*x*) of $AlBr_4^-$ present.

For the kinetic studies, 1:1 rearrangements were carried out in the normal way at 0.1, 0.3, 0.8, and 1.2 molal concentrations with respect to $AlBr_3$ and $PhCO_2Ph$. For 0.3, 0.8, and 1.2 molal solutions, reaction periods of 2,4,6, 8, and 10 h were used; for 0.1 molal solutions 4, 6, 8, 10 and 12 h reactions were performed. (The results of reactions which were 0.43[2] and 0.5[8f] molal were available from earlier investigations).

For reactions carried out in a nitrogen stream, the procedure was as follows. The large Quickfit tube in which the reactions occurred was fitted with a side-arm, to allow a Pasteur pipette attached to a nitrogen line to be inserted into the reaction mixture. The gas was dried by passage first through silica gel and then through a 4 Å molecular sieve, previously dried in a furnace at 350 °C in a stream of dry nitrogen. A two-necked adaptor was fitted to the top of the reaction tube so that a water-cooled cold-finger condenser could be inserted above the surface of the reaction mixture (to minimise losses of PhCl in the gas stream) and also to provide the normal outlet *via* a silica-gel drying tube. Reactions were performed at 110 °C for 4 h, simultaneously with a duplicate normal rearrangement (*i.e.* without the nitrogen stream).

For acylations in the absence of HBr or of H^+, PhCOBr and PhO^-Na^+ were stirred magnetically and refluxed in chlorobenzene in an oil-bath at *ca.* 150 °C for *ca.* 1.5 h. (Lower temperatures and shorter reaction times led to lower conversions to phenyl benzoate). Under these conditions, the yield of ester (as determined by glc) was 95—98%, and no detectable amounts of 2- or 4-hydroxybenzophenone were formed. A portion of the supernatant liquid was removed, centrifuged to remove any residual suspended NaBr, and a weighed sample taken. To this was added the calculated amount of $AlBr_3$ (and $Bu_4N^+Br,^-$ if this also were being used), and the rearrangement was then performed in the usual way.

For the investigation of the early stages of the 1:1 rearrangement and 1:1:1 acylation reactions, the normal procedure was adopted, with samples being removed (by Pasteur pipette) after 5, 10, 15, 30, 60, and 120 min. A duplicate reaction was left undisturbed in the oil-bath for 2 h as a control. Undisturbed acylation reactions were also performed, from which no samples were removed, the whole reaction mixture being left for the requisite times (5, 10, 60, and 120 min). In analysing these reactions, an *o*:*p* ratio was obtained directly by glc without carrying out a complete quantitative analysis (*i.e.* including that of the ester as well). The conversions after such short reaction times were small, and complete quantitative analyses would have involved larger errors than we normally consider acceptable in this work. A response factor for 2- and 4-hydroxybenzophenone was obtained by injecting a known weight ratio of these compounds and measuring the resultant peak-height ratio on the gas chromatogram. The average of several injections was used (see below).

Analytical Work.—The products of the kinetic studies[9] were analysed by glc as described in ref. 4. All subsequent g.l.c. was performed on a Hewlett–Packard 5710A dual-channel gas chromatograph. The columns were glass, 0.9 m long and 2 mm i.d., packed with 25% May and Baker 'Embaphase' silicone oil on 100–120 mesh Gas Chrom Q (Applied Science Laboratories). The oven temperature was 193 °C, and on-column injection at 200 °C was used with a detector (f.i.d.) temperature of 250 °C, the carrier gas being dry, oxygen-free nitrogen at 20 psi inlet pressure. The internal standard method of quantitative analysis was used, with 4-bromobiphenyl as internal standard for the ester, and 3-hydroxybenzophenone as internal standard for its 2- and 4-isomers. Reaction mixtures were silylated (using *N*,*O*-bis-(trimethylsilyl) acetamide) before use. Further details are given in refs. 2, 12, and 13.

^{27}Al *N.M.R. Spectroscopy.*—The ^{27}Al n.m.r. spectra were recorded at room temperature on a JEOL FX90Q Fourier transform spectrometer. An external deuterium lock of [$^2H_6$]-DMSO in a small capillary tube was added to the sample tube. Details of the analysis are given in the Appendix.

FTIR Spectroscopy.—Spectra were recorded at room temperature on a Nicolet 7199 Fourier-transform instrument. A cell with BaF_2 windows was used. Spectra (in PhCl) of phenyl benzoate and of $AlBr_3$ and phenyl benzoate (1:1 molar ratio) were recorded. The carbonyl-stretching absorption of the ester appeared at 1 740 cm^{-1}, shifting to 1 623 cm^{-1} when a 1 molar proportion of $AlBr_3$ was also present. A very small quantity of free ester was detectable in the catalyst-ester solution.

Calorimetry.—Routine calorimetric techniques were used. A detailed description, with all measurements and calculations, is given in ref. 13(*b*)

Appendix

The determination by ^{27}Al n.m.r. spectroscopy of the amounts of $AlBr_4^-$ present in solution was performed as follows. For each sample, a spectrum was recorded with a small delay between the pulse and the acquisition of the spectrum (A), and a further spectrum was obtained with a longer delay (B). The longer delay was of such duration that the signal due to the component(s) giving a broader peak (*i.e.* $X \longrightarrow AlBr_3$, $X \neq Br$) had decayed to half its intensity in the first spectrum.

Let: sharp = signal due to $AlBr_4^-$
broad = signal due to all other Al-containing species
sharp′ = signal due to $AlBr_4^-$ slightly reduced during longer delay

Then A = sharp + broad
B = sharp′ + (broad/2)
C = (A − B) = (broad/2)
(B − C) = sharp′

and $$\frac{(B - C)}{2C} = \frac{\text{sharp}'}{\text{broad}} = r$$

The percentage of the sharp peak (due to $AlBr_4^-$) relative to the total signal (broad + sharp, due to total A), is $r/(1 + r) \cdot 100\%$. Since r is small, this expression approximates to $(r \times 100)\%$, and the r values plotted in Figure 4 have been taken as the percentage (of the $AlBr_3$ added) of $AlBr_4^-$ present (see Results and Discussion). It is noteworthy that at the start of the 1:1 rearrangement, no $AlBr_4^-$ could be detected after 20,000 accumulated scans.

Acknowledgements

We are very grateful to Dr. R. J. Goodfellow for devising the method of measuring $[AlBr_4^-]$ by ^{27}Al n.m.r. spectroscopy, and Miss R. Silvester for recording the spectra. We thank Dr. P. L. Goggin for the FTIR spectra, the late Mr. A. J. B. Cruickshank for suggesting the calorimetric measurements, Dr. A. R. Hillman for advice on carrying them out, and Dr. J. S. Littler for helpful discussions. We thank the SERC for Research Studentships (to I. M. D., C. R. W., and J. L. G.).

References

1 Part 4, L. S. Hart and C. R. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1607.
2 M. J. S. Dewar and L. S. Hart, *Tetrahedron*, 1970, **26**, 973.
3 (*a*) M. J. S. Dewar, in 'Theoretical Organic Chemistry,' Papers presented to the Kekulé Symposium, London, 1958; Butterworths Scientific Publications, London, 1959, p. 179; (*b*) M. J. S. Dewar, in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, London, 1963, p. 295.
4 I. M. Dawson, L. S. Hart, and J. S. Littler, *J. Chem. Soc., Perkin Trans 2*, 1985, 1601.
5 K. Schofield, personal communication.
6 G. C. Amin and N. M. Shah, *J. Univ. Bombay*, 1948, **17A**, 5 (*Chem. Abstr.* 1949, **43**, 6593).
7 A. Gerecs, in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. III, part I, p. 499.
8 (*a*) G. A. Mackee, B.Sc. Thesis, University of Bristol, 1973; (*b*) C. R. J. Killen, B.Sc. Thesis, University of Bristol, 1974; (*c*) K. D. Saunders, B.Sc. Thesis, University of Bristol, 1976; (*d*) J. B. G. Tarrant, B.Sc. Thesis, University of Bristol, 1977; (*e*) I. M. Dawson, B.Sc. Thesis, University of Bristol, 1978; (*f*) C. R. J. Killen. Ph.D. Thesis, University of Bristol, 1978; (*g*) L. O. Whittaker, B.Sc. Thesis, University of Bristol, 1979.
9 I. M. Dawson, Ph.D. Thesis, University of Bristol, 1983.
10 (*a*) A. Furka and T. Szell, *J. Chem. Soc.*, 1960, 2312; (*b*) T. Szell and A. Furka, *J. Chem. Soc.*, 1960, 2321.
11 N. M. Cullinane, B. F. R. Edwards, and V. V. Bailey-Wood, *Recl. Trav. Chim. Pays-Bas*, 1960, **79**, 1174, and refs. therein.
12 L. S. Hart, Ph.D. Thesis, University of London, 1967.
13 C. R. Waddington, (*a*) B.Sc. Thesis, University of Bristol, 1982; (*b*) Ph.D. Thesis, University of Bristol, 1985.
14 A. A. Frost and R. S. Pearson; 'Kinetics and Mechanism,' John Wiley and Sons Inc., New York, London, 2nd edn., 1961, p. 193.
15 L. A. Ganyushin, I. P. Romm, E. N. Gur'yanova, E. S. Isaeva, V. M. Ryaboi, and E. S. Shcherbakova, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1980, **50**, 1735.

Received 15*th November* 1988; *Paper* 8/04550J