Aromatic Rearrangements in the Benzene Series. Part 6.[1] The Fries Rearrangement of Phenyl Benzoate: The Role of Tetrabromoaluminate Ion as an Aluminium Bromide Transfer Agent

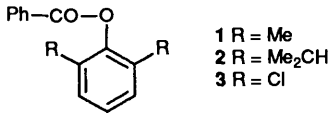
Julia L. Gibson and Lionel S. Hart *
School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

The ester $PhC^{17}O^{17}OPh$ was prepared, and its ^{17}O NMR spectra in PhCl were recorded alone, in the presence of $AlBr_3$ and in the presence of $AlBr_3 + AlBr_4^-$. Under similar conditions, ^{13}C NMR spectra of unlabelled $PhCO_2Ph$ were recorded, as were FTIR spectra of $PhCO_2Ph$ and benzoates of three 2,6-disubstituted phenols. The spectra show clearly that formation of the carbonyl-oxygen-coordinated complex $PhC(OPh){=}\overset{+}{O}{-}\overset{-}{Al}Br_3$ from $PhCO_2Ph$ and $AlBr_3$ is partially reversed in the presence of $AlBr_4^-$ (presumably by capture of $AlBr_3$ to give $Al_2Br_7^-$), with no detectable formation of any new intermediate. As this cannot increase the rate of rearrangement of $PhCO_2Ph$ by $AlBr_3$, which is the experimentally observed consequence of the addition of $AlBr_4^-$ to the 1 : 1 rearrangement reaction (1 $AlBr_3$: 1 $PhCO_2Ph$ in homogeneous solution in PhCl), the $AlBr_4^-$ must play an additional role. It is suggested that the $AlBr_4^-$ effectively transfers $AlBr_3$ from the carbonyl oxygen of the catalyst-ester complex (above) to the phenoxy oxygen, *via* a process involving a cyclic transition state, simultaneously resulting in fragmentation of the complex to give the ion-pair ($Ph\overset{+}{C}O{\cdot}PhO\overset{-}{Al}Br_3$), previously invoked as the intermediate involved in the second-stage reaction of the two-stage 1 : 1 rearrangement reaction (above).

In our investigations[2,3] of the mechanism of the Fries rearrangement of phenyl benzoate under the influence of anhydrous aluminium bromide in homogeneous solution in chlorobenzene, the most informative reactions are those involving one molar proportion each of $AlBr_3$ and ester (the 1 : 1 rearrangement), and one molar proportion each of $AlBr_3$, PhCOBr and PhOH (the 1 : 1 : 1 acylation), the latter reaction proceeding to >90% *via* the first-formed ester. We have shown[2,3] that the 1 : 1 rearrangement is a two-stage process, involving an intermolecular[3] first-stage reaction giving solely 2-hydroxybenzophenone *via* a cyclic transition state, and a faster, pseudo-intramolecular[2,3] second-stage reaction, involving[3] an ion-pair intermediate ($Ph\overset{+}{C}O{\cdot}PhO\overset{-}{Al}Br_3$), giving 2- and 4-hydroxybenzophenone in constant ratio. This second-stage reaction of the 1 : 1 rearrangement is identical with the (principal process of the) 1 : 1 : 1 acylation.[1] Recently, we showed[1] that $AlBr_4^-$ ($\equiv Br^-$) has a profound effect on the 1 : 1 rearrangement. Deliberate addition of $Bu_4\overset{+}{N}AlBr_4^-$ to a 1 : 1 rearrangement made it behave [as shown by the variation with time of the *ortho* : *para* (*o* : *p*) ratio of the hydroxybenzophenones] more like a 1 : 1 : 1 acylation, to an extent depending on the amount of $AlBr_4^-$ added. ^{27}Al NMR spectroscopy showed[1] that no $AlBr_4^-$ could be detected at the start of the 1 : 1 rearrangement, but that *ca.* 0.8% of the $AlBr_3$ was present as $AlBr_4^-$ at the beginning of the 1 : 1 : 1 acylation (by virtue of the HBr formed in the initial reaction between PhCOBr and PhOH). This was sufficient to cause the striking difference between the two processes, most readily observed when the *o* : *p* ratio of the products of either reaction is plotted against time.[2] $AlBr_4^-$ is generated in the course of the first-stage reaction of the 1 : 1 rearrangement, and then acts as a 'trigger' which brings into operation the second-stage reaction. Kinetic studies showed[1] that the rearranging entity is ($PhCO_2Ph{\cdot}AlBr_3$), and, from a series of reactions to which $AlBr_4^-$ was deliberately added, that the second-stage reaction involves some complex of the rearranging entity (above) and $AlBr_4^-$ ion. (The reaction displays Michaelis–Menten type kinetic behaviour.) Finally, we confirmed[1] the above effect of $AlBr_4^-$ ($\equiv Br^-$) by studying acylation reactions in which PhCOBr reacted with PhO^-Na^+ rather than with PhOH, and showed conclusively that H^+ had no effect on the reaction (*e.g.* as a co-catalyst with $AlBr_3$). Thus, Br^- (as $AlBr_4^-$), produced during the 1 : 1 rearrangement, or present from the start of the 1 : 1 : 1 acylation, dictates the behaviour of the reaction.

The actual role of the $AlBr_4^-$ remained to be identified. It was suggested[1] that this ion might in some way assist $AlBr_3$ coordinated to the carbonyl oxygen of the ester to move to the phenoxy oxygen, since $Ph{-}CO{-}\overset{+}{O}(Ph){-}\overset{-}{Al}Br_3$ can readily dissociate to the ion-pair needed for the second-stage reaction (above) of the 1 : 1 rearrangement, whilst it is difficult to see how the complex $PhC(OPh){=}\overset{+}{O}{-}\overset{-}{Al}Br_3$ could give this ion-pair. (In the extensive literature of the Fries rearrangement, there is no experimentally based information about the location of the Lewis acid catalyst in the actual rearrangement step. Various authors assume, without any supporting evidence, that it is located on the phenoxy oxygen. All that has been established is that the Lewis acid catalyst, initially at least, coordinates to the carbonyl oxygen—see below).

In an attempt to gain information about the site of the $AlBr_3$ molecule during the rearrangement, we prepared $PhC^{17}O{-}^{17}OPh$, and examined its ^{17}O NMR spectra in solution in PhCl: alone, in the presence of $AlBr_3$, and in the presence of $AlBr_3 + AlBr_4^-$. We also recorded ^{13}C NMR and FTIR spectra of unlabelled phenyl benzoate in PhCl solution: alone, and under the same conditions as for the labelled ester. The benzoates **1**–**3** of hindered phenols were also prepared, and their FTIR spectra recorded under the same conditions as above. The effects noted when R = H (*i.e.* for $PhCO_2Ph$ itself) were greatly magnified when R was a bulky substituent.



1 R = Me
2 R = Me_2CH
3 R = Cl

Table 1 Frequencies/cm^{-1} of C=O absorptions in the esters and catalyst-ester complexes

Absorption	$PhCO_2Ph$	DMPB[a]	DIPPB[b]	DCPB[c]
C=O	1738	1740	1738	1753
C=O + $AlBr_3$	1622	1620	1621	1629

[a] 2,6-Dimethylphenyl benzoate **1**. [b] 2,6-Diisopropylphenyl benzoate **2**. [c] 2,6-Dichlorophenyl benzoate **3**.

Table 2 Ratios of intensities of free and complexed carbonyl absorptions of phenyl benzoate and of benzoates of 2,6-disubstituted phenols

Reaction conditions[a]	$PhCO_2Ph$ Intensity ratio	DMPB[b] Intensity ratio	DIPPB[b] Intensity ratio	DCPB[b] Intensity ratio
A	0.84	0.30	0.50	0.57
B	0.96	0.47	1.04	0.97

[a] A: $AlBr_3$ + ester (1:1) in PhCl. B: $AlBr_3$ + ester + $AlBr_4^-$ (1:1:0.2, respectively) in PhCl, except for $PhCO_2Ph$ itself, for which A = $AlBr_3$ + ester (1:2) in PhCl, and B = $AlBr_3$ + ester + $AlBr_4^-$ (1:2:1, respectively) in PhCl. [b] Abbreviations as in Table 1.

Table 3 ^{17}O NMR chemical shifts/ppm of the carbonyl oxygen and phenoxy oxygen in $PhC^{17}O^{17}OPh$

Sample (in PhCl solution)	$\delta^{17}O$[a] $>C=^{17}O$	$Ph-^{17}O-$	Comments
$[^{17}O_2]PhCO_2Ph$	350	188	(1)
$AlBr_3$ + $[^{17}O_2]PhCO_2Ph$ (1:1)	228 (sh)	210	(2)
$AlBr_3$ + $[^{17}O_2]PhCO_2Ph$ + $AlBr_4^-$ (1:1:0.2, respectively)	239 (sh)	209	(2)

[a] All δ_0 values were measured relative to $D_2{}^{17}O$, δ_0 = 0.0. Note: $PhCO_2Ph$ C=O, $\delta^{17}O$ = 334 ppm;[4] C–O $\delta^{17}O$ = 193 ppm,[4] (both in $CDCl_3$ solution). (sh) = shoulder. The two oxygen signals overlap one another, but the chemical shift of the shoulder can be abstracted.

Table 4 ^{13}C NMR chemical shifts/ppm of the carbonyl carbon and phenoxy carbon in phenyl benzoate

Sample (in PhCl solution)	δ ^{13}C/ppm[a] $>C=O$	C–O
$PhCO_2Ph$	34.9	21.6
$AlBr_3$ + $PhCO_2Ph$ (1:1)	42.2	20.2
$AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$ (1:1:0.2, respectively)	41.5	20.4

[a] All δ_C values were measured relative to the *meta*-carbon of PhCl (δ_C 129.8)—see Experimental.

Results and Discussion

FTIR Spectra.—Spectra of solutions in PhCl of ($AlBr_3$ + $PhCO_2Ph$) and ($AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$) showed that when $AlBr_4^-$ was present, the intensities of absorptions of the free ester (1738 and 1265 cm^{-1}) increased a little relative to those of the catalyst-ester complex (1622, 1359 and 1314 cm^{-1}), but that there was no evidence for formation of any new species. In this particular case (see footnotes to Table 2), we used a 1:2 molar ratio of $AlBr_3$:$PhCO_2Ph$, respectively, and 1:2:1 molar proportions of $AlBr_3$:$PhCO_2Ph$:$AlBr_4^-$, respectively. Changes in the C=O stretching frequency in the presence of $AlBr_3$ are easily identified, unlike those associated with C–O absorptions, which were harder to assign. (A full discussion of attempts to make the latter assignments is given in ref. 5). By using an excess of the ester over the Lewis acid, we had hoped to have the C=O and C–O absorptions of both free and complexed ester represented at reasonable intensities in the same spectrum, and use of a molar equivalent of $AlBr_4^-$ relative to the catalyst-ester complex should magnify the effect of the anion, making it more readily discernible. In the event, only the C=O absorptions were informative, so that all other FTIR measurements were made using the same ratios of reagents as for the NMR measurements (see below).

For the 2,6-disubstituted phenyl benzoates, spectra were recorded of solutions in PhCl of the esters themselves, of ($AlBr_3$ + ester) (1:1), and of ($AlBr_3$ + ester + $AlBr_4^-$) (1:1:0.2, respectively). For all these esters, coordination of the $AlBr_3$ to the carbonyl oxygen was less complete than with $PhCO_2Ph$ itself, as expected because of steric hindrance. When $AlBr_4^-$ was added to the ($AlBr_3$ + ester) solution, the effect was as before: the C=O absorption of the free ester increased relative to the C=O absorption of the catalyst-ester complex. The change was more noticeable for **2** and **3** than for **1**. Thus, the behaviour of the 2,6-disubstituted phenyl esters corroborates and magnifies the effect found in the case of phenyl benzoate itself.

If the $AlBr_4^-$ reacted with the catalyst-ester complex to give a new species [*e.g.* the ion-pair ($PhC\overset{+}{O}{\cdot}PhO\bar{A}lBr_3$)] this would lead to new absorptions in the spectrum, and also to conversion of the free ester to catalyst-ester complex, to maintain the equilibrium between the free and complexed ester. The ratio of the intensities of the C=O absorptions due to the free and complexed ester would thus remain constant. Neither of these consequences is observed (see above and Table 2). In contrast, if the $AlBr_4^-$ converted the catalyst-ester complex back to free ester, disturbing the equilibrium between free and complexed ester, then the ratio of the intensities of the C=O absorptions due to free and complexed ester would increase. This is observed (see Table 2). The increase in the C=O absorption of the free ester relative to that of the complexed ester can readily be seen merely by inspection of the spectra. We tried to quantify the change as follows. There is a considerable error involved in integrating the areas under some of the absorption maxima because of uncertainty in the position of the baseline, caused by subtraction of the solvent absorption. Since all solutions were of the same concentration in the ester, and those for each ester were run consecutively under the same conditions, peak heights (which can be measured with greater precision) were used instead. Table 2 shows the ratios of the intensities of the C=O absorptions in the free ester and catalyst-ester complex, in the absence and presence of $AlBr_4^-$. In every case, addition of $AlBr_4^-$ causes an increase in the ratio, *i.e.* the amount of free ester has increased relative to the amount of catalyst-ester complex (the $AlBr_3$ presumably being converted to $Al_2Br_7^-$). The effect of the $AlBr_4^-$ is magnified in the 2,6-disubstituted phenyl esters. The same result has also been observed in the case of phenyl esters of 2,4,6-trisubstituted benzoic acids,[6] giving additional confirmation of the effect of $AlBr_4^-$.

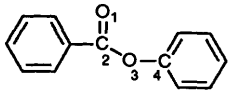
^{17}O NMR Spectra.—Spectra were recorded of solutions in PhCl of $[^{17}O_2]PhCO_2Ph$, ($AlBr_3$ + $[^{17}O_2]PhCO_2Ph$) (1:1), and ($AlBr_3$ + $[^{17}O_2]PhCO_2Ph$ + $AlBr_4^-$) (1:1:0.2, respectively). The results are shown in Table 3. When a molar proportion of $AlBr_3$ was added to the ester, the carbonyl oxygen signal showed a large upfield shift (from 350 to 228 ppm), and the phenoxy oxygen showed a smaller downfield shift (from 188 to 210 ppm), so that in the spectrum of the catalyst-ester

complex, the two signals overlapped. When $AlBr_4^-$ (0.2 molar proportion) was added, the carbonyl oxygen signal moved back downfield (from 228 to 239 ppm), and the phenoxy oxygen signal moved back upfield (from 210 to 209 ppm). The change for the carbonyl oxygen signal was the greater, reflecting the differences in the sizes of the changes observed when the $AlBr_3$ initially complexed with the ester. Given the time-averaged nature of NMR spectra, the effect of $AlBr_4^-$ seems to be either (*a*) to promote conversion of the catalyst-ester complex to some new species which contains oxygen atoms in very similar environments to those in the catalyst-ester complex (since they have chemical shifts very similar to those in the latter) or (*b*) to promote partial conversion of the catalyst-ester complex into some new species which is in rapid dynamic equilibrium with the catalyst-ester complex, and contains oxygens in very different environments from those in the latter species, *i.e.* a 'carbonyl' oxygen resonating at lower field, and a 'phenoxy' oxygen resonating at higher field. Taking into account the FTIR evidence above, (*a*) seems unlikely, since the IR spectra showed no new C=O or C–O absorptions close to the absorptions of the catalyst-ester complex. Similarly, (*b*) also seems unlikely, except in the special case where the 'new' species of very different nature from the catalyst-ester complex is simply the ester itself. The IR evidence rules out formation of the ion-pair (see above).

^{13}C *NMR Spectra.*—Spectra were recorded[7] of solutions in PhCl of $PhCO_2Ph$, ($AlBr_3$ + $PhCO_2Ph$) (1:1), and ($AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$) (1:1:0.2, respectively). The chemical shifts of the carbonyl carbon and the ring carbon of the C–O bond are shown in Table 4.

^{17}Oxygen chemical shifts have been interpreted[8] in terms of variation in the degree of π-bonding and/or the polarisation of carbon–oxygen bonds, where sp^3- and sp^2-hybridised oxygen is involved. It is reasonable to expect that the other nucleus of the bond, carbon, will experience some alteration in its local electron density, and hence its chemical shift, too, will change as $\delta^{17}O$ changes. De Jeu[9a] and Delseth and Kintzinger[9b] found fairly good correlations between $\delta^{13}C$ and $\delta^{17}O$ of the carbonyl group in a series of aldehydes and ketones, the correlation being greatest when the series of alkyl groups attached to the carbonyl groups were of similar nature. (There were some significant variations).

Consider structure **4**, with the atoms labelled as shown.



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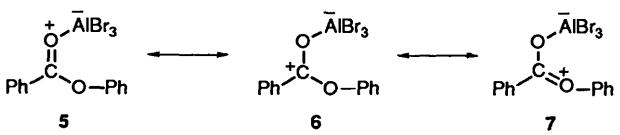
Figs.1 show plots of chemical shifts for the pairs of atoms 1 and 2, 1 and 3, 1 and 4, 2 and 3, 2 and 4, and 3 and 4. Each is a straight line. As noted by earlier workers,[9a,b;10] changes in $\delta^{13}C$ are small compared with those in $\delta^{17}O$. This may be partly due to the much greater chemical shift range for oxygen compared with that for carbon (~1500 ppm *vs.* ~650 ppm). It probably also indicates that canonical forms **5** and **7** contribute much more than form **6** to the structure of the catalyst-ester complex, **7** being an example of the so-called compensating conjugative effect[10] that a π-donor (OPh here) has on the carbonyl carbon, resulting in only small changes in that carbon's chemical shift.

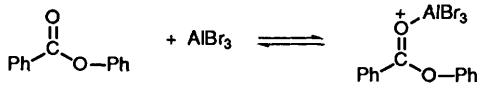
The significance of Figs. 1(*a–f*) lies in the information they



5 **6** **7**

provide about the role of the $AlBr_4^-$ ion. FTIR spectroscopy showed[1] that in a solution of $PhCO_2Ph$ + $AlBr_3$ (1:1) in PhCl at 25 °C, at least 99% of the ester is present as the catalyst-ester complex ($PhCO_2Ph{\cdot}AlBr_3$). If for convenience this figure is assumed to be 100%, then the points at the appropriate ends of the lines in the graphs represent 100% $PhCO_2Ph$ and 100% ($PhCO_2Ph{\cdot}AlBr_3$). Any points along the lines represent a mixture of free and complexed ester, and the position of such a point on the line is determined by the relative amounts of each of these compounds. Since, in all cases, the third point [*i.e.* for ($AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$, 1:1:0.2, respectively)] lies on the line between 100% free $PhCO_2Ph$ and 100% $PhCO_2Ph{\cdot}AlBr_3$ (within experimental error), this is strong evidence that $AlBr_4^-$ causes conversion of the catalyst-ester complex back to free ester. [If, rather than liberating free ester, the $AlBr_4^-$ were influencing production of a new species, it would be extremely unlikely that in every case the point for the solution containing ($AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$) would lie on the lines in Figs. 1(*a–f*), since this would require the new species to have exactly the same ratios of chemical shifts for all the pairs of atoms under consideration, as are found in $PhCO_2Ph$ itself]. Calculation shows that the effect of the 0.2 molar proportion of $AlBr_4^-$ is to produce (10 ± 2.4)% of free ester [the average of the six values obtainable from Figs. 1(*a–f*)]. This suggests that 0.2 mol of $AlBr_4^-$ generates *ca.* 10% (*ca.* 0.1 molar equivalent) of free ester from 1 mol of $PhCO_2Ph{\cdot}AlBr_3$ at 25 °C.

Thus, all the evidence from FTIR and ^{13}C and ^{17}O NMR spectroscopy cited above indicates that addition of $AlBr_4^-$ to a system containing $PhCO_2Ph$ and $AlBr_3$ causes the equilibrium (1) to move to the left and the question[3] of the role of $AlBr_4^-$ in promoting the second-stage reaction of the 1:1 rearrangement still remains. An increase in the amount of the free ester cannot assist the second-stage reaction: it would more reasonably be expected to promote the first-stage reaction, which requires attack of free $PhCO_2Ph$ on the catalyst-ester complex.[3]



(1)

If $AlBr_4^-$ removes $AlBr_3$ from the catalyst-ester complex, or combines with uncomplexed aluminium bromide, it presumably gives $Al_2Br_7^-$, though we have not established this point. Dubois[11] has shown the presence of $R_4\overset{+}{N}Al_2Br_7^-$ (R = Me, Et) and $R_4\overset{+}{N}AlBr_4^-$ in solutions of $R_4\overset{+}{N}Br^-$ and aluminium bromide in EtBr by conductivity measurements, and Akhrem[12] has used ^{13}C, ^1H and ^{17}O NMR spectroscopy to determine the structure of $MeCOBr{\cdot}2AlBr_3$ in solution, proposing that it existed either as $Me\overset{+}{C}OAl_2Br_7^-$ or $MeCOBr{\cdot}Al_2Br_6$, depending on concentration. Earlier work,[13] of course, showed the existence of $ArH_2^+Al_2Br_7^-$ in Friedel–Crafts alkylation reaction mixtures of ArH, $AlBr_3$ and HBr. It thus seems entirely reasonable that $Al_2Br_7^-$ may exist in solution in PhCl. However, the absence of thermodynamic data does not allow us to decide whether $AlBr_4^-$ strips $AlBr_3$ from the catalyst-ester complex, or reacts with Al_2Br_6 in solution. Either process, of course, necessarily produces more free ester at the expense of the catalyst-ester complex.

We suggest, therefore, another process in which $AlBr_4^-$ interacts with the catalyst-ester complex as shown in Scheme 1, in a mechanism involving a cyclic transition state.

This process produces the ion-pair ($Ph\overset{+}{C}O{\cdot}PhO\bar{A}lBr_3$), the intermediate in the second-stage reaction,[3] $AlBr_4^-$ effectively transferring $AlBr_3$ from the carbonyl oxygen to the phenoxy oxygen of the ester (see Introduction). The $AlBr_4^-$ is

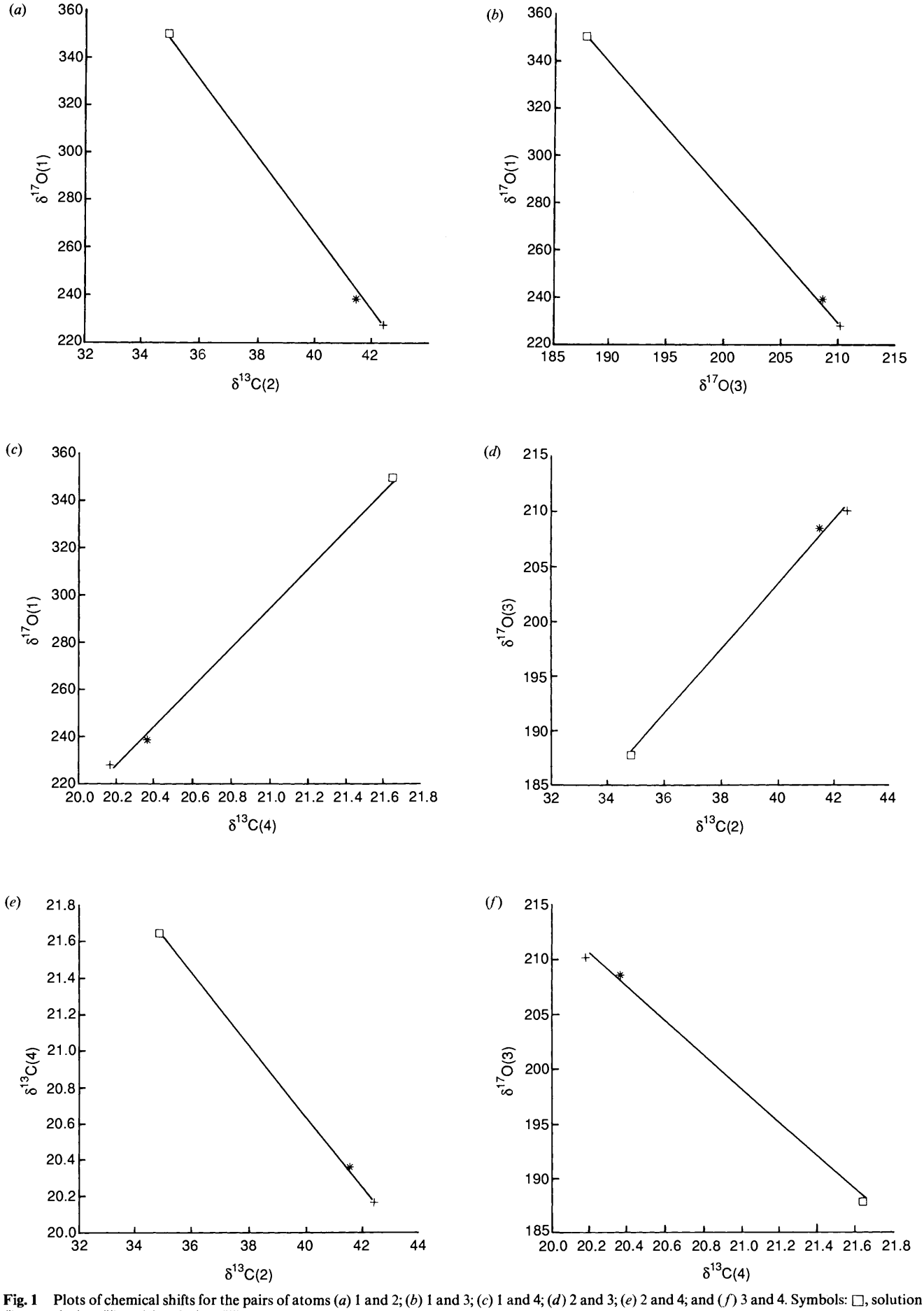
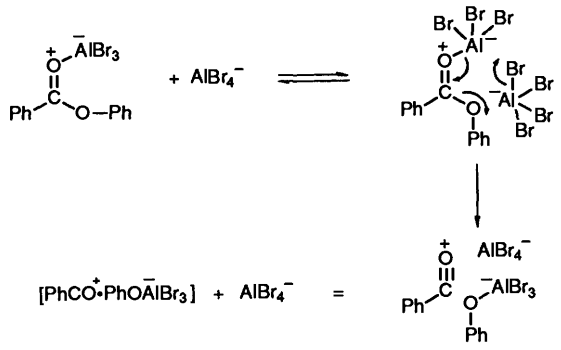


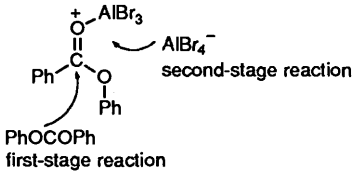
Fig. 1 Plots of chemical shifts for the pairs of atoms (*a*) 1 and 2; (*b*) 1 and 3; (*c*) 1 and 4; (*d*) 2 and 3; (*e*) 2 and 4; and (*f*) 3 and 4. Symbols: □, solution (i); +, solution (ii) and *, solution (iii).



Scheme 1

simultaneously regenerated, and can then react with another molecule of catalyst-ester complex. Approach of the $AlBr_4^-$ anion to the negatively polarised coordinated $AlBr_3$ may appear unfavourable, but the concerted movement of electrons in the cyclic transition state makes this unimportant, and the positive polarisation of the carbonyl group to which the $AlBr_3$ is initially coordinated will help to moderate any repulsive effect. Once the ion-pair is formed, it will react to give 2- and 4-hydroxybenzophenone. Rearrangement does not occur at room temperature,[14] at which all the spectroscopic measurements described above were made, so that at low temperatures, the activation energy for this process (or for the first-stage reaction [3]) is too high for rearrangement to proceed.

Is this proposal consistent with the established kinetics of the reaction? In Part 5,[1] we showed that the rearranging entity was ($PhCO_2Ph{\cdot}AlBr_3$), but that in the presence of added $AlBr_4^-$, the rate depended on [$AlBr_4^-$] in a manner reminiscent of Michaelis–Menten kinetics, implying an association complex of $AlBr_4^-$ with ($PhCO_2Ph{\cdot}AlBr_3$). At low concentrations of $AlBr_4^-$, dependence of the reaction rate on [$AlBr_4^-$] is strong, whereas at high concentrations of $AlBr_4^-$, the reaction rate is almost independent of [$AlBr_4^-$]. The proposed mechanism (Scheme 1) certainly involves an association complex of $AlBr_4^-$ with ($PhCO_2Ph{\cdot}AlBr_3$), albeit only a short-lived species. At very low concentrations of $AlBr_4^-$, the catalyst-ester complex will be present in great excess over $AlBr_4^-$ (even at 110 °C, *i.e.* allowing for the increased dissociation of the catalyst-ester complex). Hence, at low concentrations of $AlBr_4^-$, there will be a strong dependence on [$AlBr_4^-$], the limiting factor being availability of this ion. At higher concentrations of $AlBr_4^-$, the amount of this ion will no longer be such a limiting factor, especially since it converts the catalyst-ester complex back to free ester, thus reducing the relative amount of the complex. We have shown[1] that less than 10% of the $AlBr_3$ originally present in the 1:1 and 1:1:1 reactions is converted to $AlBr_4^-$ in 10 h.



Scheme 2

If our proposed mechanism is correct, it suggests that the first- and second-stage reactions can operate independently, since they involve attack by different species at different sites in the catalyst-ester complex (Scheme 2).

Experimental

Materials.—Anhydrous $AlBr_3$, chlorobenzene and (unlabelled) phenyl benzoate were all synthesised and/or purified as described previously.[2] $Bu_4\overset{+}{N}Br^-$ (Fluka), 2,6-dimethylphenol (BDH), 2,6-diisopropylphenol (Aldrich) and 2,6-dichlorophenol (Cambrian Chemicals) were all commercial products. The dimethyl- and dichloro-phenol were recrystallised from hexane before use. All three disubstituted phenols had mps close to the literature values. Two different batches of 22 atom-% [^{17}O]-labelled H_2O were used, the first from BOC, the second from Amersham International plc. The $^{17}O_2$ (21.9 atom-%) used also came from Amersham International plc.

The benzoates of the hindered phenols (1.73×10^{-2} mol) were obtained using PhCOCl (2 cm^3, 1.73×10^{-2} mol) in CH_2Cl_2 (15 cm^3) containing pyridine (2 cm^3), the solutions being left overnight. A normal work-up procedure gave the esters, those of the dialkylphenols being recrystallised from EtOH, and that of the dichlorophenol from light petroleum (b.p. 40–60 °C). All three esters had m.p.s in agreement with the literature values,[15–17] gave microanalytical data in accordance with calculated values, and showed the expected ^1H NMR spectroscopic data. Full details are given in ref. 5.

[$^{17}O_2$]$PhCO_2Ph$.—$Ph^{17}OH$ was prepared by the same route used for $Ph^{18}OH$,[3] *i.e.* by reaction of $^{17}O_2$ with PhMgBr. Two modifications of the earlier method were introduced. First, in the preparation of PhMgBr, the reflux period was reduced from 3 to 1.5 h.[3] This greatly reduced the formation of biphenyl as a byproduct. Second, in breaking the seal of the bulb containing $^{17}O_2$ (in this case, a 250 cm^3 glass bulb), a pointed steel plunger, 2 inches long, was used, instead of the ball-bearing used earlier. When the seal was broken and the PhMgBr reacted with the oxygen, solid material formed, and blocked the entrance to the bulb, preventing the continued injection of the Grignard reagent solution. The pointed plunger was much more effective than the ball-bearing at dislodging blockages. $Ph^{17}OH$ was obtained in 73% yield.

$PhC^{17}OCl$ was prepared by allowing unlabelled PhCOCl to react with $H_2{}^{17}O$, giving $PhCO^{17}OH$. This was dissolved in NaOH, the solution acidified with HCl, giving $PhCO^{17}OH$ and $PhC^{17}OOH$, and the acid re-converted to the acid chloride with $SOCl_2$, giving a mixture of $PhC^{17}OCl$ and unlabelled PhCOCl. PhCOCl (7.81 g, 5.56×10^{-2} mol) was weighed into a 100 cm^3 conical flask, and pyridine (20 cm^3) added. [^{17}O]H_2O (1 g, 5.49×10^{-2} mol) was added (using a syringe) and the [^{17}O]H_2O bottle washed with a little more pyridine (2×1 cm^3), the washings being added to the flask, which was left overnight. Concentrated HCl was added, and the solution extracted with Et_2O (5×20 cm^3). The total extract was dried, and the solvent evaporated. The residual crude benzoic acid was dissolved in NaOH (2 mol dm^3, 40 cm^3) and reprecipitated by addition of conc. HCl. The mixture was cooled, filtered and the acid dried in a desiccator before being refluxed with a large excess of $SOCl_2$ (70 cm^3). The excess of $SOCl_2$ was removed under reduced pressure, leaving the (labelled + unlabelled) benzoyl chloride (7.70 g, 98.5% yield).

A solution of $Ph^{17}OH$ (1.534 g, 0.0163 mol) in dry, distilled pyridine (2 cm^3) was added dropwise to the labelled benzoyl chloride (2.29 g, 0.0163 mol) with cooling in ice. The mixture was left overnight, then HCl (2 mol dm^{-3}, 50 cm^3) was added, and the solution extracted with Et_2O (5×30 cm^3). The ester was isolated in the normal way and recrystallised from EtOH. The [$^{17}O_2$]$PhCO_2Ph$ obtained (1.638 g, 51%) melted at 70.5–71 °C [*cf.* lit.,[18] ($PhCO_2Ph$) 71 °C]. It was found to be >99% pure by GLC. Mass spectrometry showed high levels of incorporation of ^{17}O in both positions in the ester [a little over 9% at the carbonyl oxygen (theoretical value ~11%), and a little over 21% at the phenoxy oxygen (theoretical value 22%). Detailed calculations are given in ref. 5].

Analytical Work

FTIR Spectroscopy.—Spectra were recorded at room temperature on a Nicolet 7199 FTIR spectrometer. A metal-free cell was used, and solutions were introduced into the cell using a glass syringe. (Earlier work [7] had shown that any contact of the $AlBr_3$-containing solutions with metal gave oddly-shaped artefact peaks in the IR spectra). The cell windows were BaF_2, and the path-length was 0.05 mm. Spectra were recorded in the range 800 or 900–1800 cm^{-1}, and signals due to the solvent PhCl were subtracted. The techniques used in preparing the various solutions were those used for carrying out rearrangements, and have been described previously (refs. 1–3). A detailed account appears in ref. 5. Spectra of PhCl solutions of ester, $AlBr_3$ + ester, and $AlBr_3$ + ester + $AlBr_4^-$ were recorded for $PhCO_2Ph$ and the benzoates of the 2,6-disubstituted phenols. In the case of $PhCO_2Ph$ itself, the $AlBr_3$:ester molar ratio was 1:2, and for $AlBr_3$:ester:$AlBr_4^-$ was 1:2:1. For the disubstituted esters, an $AlBr_3$:ester molar ratio of 1:1, and an $AlBr_3$:ester:$AlBr_4^-$ molar ratio of 1:1:0.2, was used (see Results and Discussion above).

^{17}O NMR Spectroscopy.—^{17}O NMR spectra of samples in PhCl were recorded on a JEOL JNM GX400 FT NMR spectrometer. ^{17}O-Enriched samples were submitted in 5 mm diameter tubes. Sealed glass capillaries filled with D_2O were placed inside the NMR tubes with the samples, to act as both external lock [19] and reference.[8] Spectra were recorded of $[^{17}O_2]PhCO_2Ph$, $AlBr_3$ + $[^{17}O_2]PhCO_2Ph$ (molar ratio 1:1), and $AlBr_3$ + $[^{17}O_2]PhCO_2Ph$ + $AlBr_4^-$ (molar ratio 1:1:0.2). A molecular weight for the $[^{17}O_2]PhCO_2Ph$ was calculated using the molecular weight distribution determined by mass spectrometry. Solutions were prepared as for FTIR spectroscopy. A detailed account appears in ref. 5.

^{13}C NMR Spectroscopy.—^{13}C NMR spectra of solutions in PhCl were recorded on a JEOL JNM FX200 FT NMR spectrometer. Chemical shifts were measured relative to the *meta*-carbon of PhCl:tetramethylsilane reacts with the $AlBr_3$ solutions, and could not be used as internal standard. Spectra of $PhCO_2Ph$, $AlBr_3$ + $PhCO_2Ph$ (molar ratio 1:1), and $AlBr_3$ + $PhCO_2Ph$ + $AlBr_4^-$ (molar ratio 1:1:0.2) were recorded.

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