Aromatic Rearrangements in the Benzene Series. Part 4.[1] Intramolecularity of both the *ortho*- and *para*-Rearrangements of Benzyl Phenyl Ether as shown by Labelling Experiments

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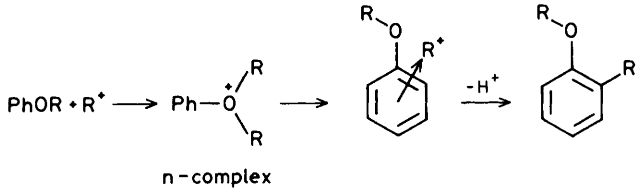
The rearrangement of a mixture of $Ph^{13}CH_2OPh$ and $PhCH_2{}^{18}OPh$ (with some unlabelled ether) catalysed by $AlBr_3$ in homogeneous solution in 1,2,4-trichlorobenzene and in nitrobenzene has been examined. The literature report of this reaction was shown to be substantially correct: the reaction is very rapid, and *ortho*-migration of the benzyl group predominates, but does not (in contrast to the earlier report) occur exclusively. The *ortho*:*para* ratio of the rearrangement products is *ca.* 11 in 1,2,4-trichlorobenzene and *ca.* 4.7 in nitrobenzene. The ether undergoes rearrangement in both solvents without prior scrambling of isotopic labels. In trichlorobenzene, the reaction appears to be almost completely intramolecular, even for *para*-rearrangement: *o*-benzylphenol is unscrambled, the *para*-isomer almost so. In nitrobenzene, *o*-benzylphenol is virtually unscrambled, the *para*-isomer *ca.* 25% so. A mechanism involving a tight ion-pair (from which some leakage occurs in nitrobenzene) is proposed, and possible explanations of the high *ortho*:*para* ratios are considered.

Although the acid-catalysed rearrangement of alkyl aryl ethers has been known for many years,[2] one of the most striking examples of this reaction was published in 1952, when Tarbell and Petropoulos[3] described the rearrangement of benzyl phenyl ether, catalysed by anhydrous $AlBr_3$, in homogeneous solution in chlorobenzene. They found that rearrangement occurred exclusively to 2-hydroxydiphenylmethane with simultaneous production of phenol, and that the 2-hydroxydiphenylmethane also underwent decomposition to phenol. The solvent was also benzylated, and the products underwent various further (disproportionation) reactions to give mixtures of dichlorodiphenylmethanes. No 4-hydroxydiphenylmethane was formed. The reaction was exceedingly fast, being complete in less than 5 s even at −40 °C, regardless of whether one or two moles of $AlBr_3$ were used per mole of ether. The ratio of phenol to 2-hydroxydiphenylmethane was hardly affected by use of either benzene or nitrobenzene in place of chlorobenzene. Shortly afterwards, Hart and his co-workers showed that (i) thermal rearrangement of alkyl aryl ethers could result in appreciable retention of optical activity in the products, even in the case of migration of the alkyl group to the *para*-position;[4] and (ii) in the case of rearrangement of α-phenylethyl *p*-tolyl ether under the influence of $AlBr_3$, the (*ortho*) migration occurred with *ca.* 76% retention of optical purity.[5]

These results, particularly those of Tarbell,[3] produced intense mechanistic speculation. Hart and Kosak[6] suggested that if an ion-pair intermediate were involved, then retention of configuration should be high in solvents of low ionising power (*e.g.* as in the case of PhCl) and low in solvents of high ionising power. However, Dewar[7] made the most novel and extensive mechanistic suggestions, in which he extended his π-complex theory of the mechanism of the benzidine rearrangement to the rearrangement of benzyl phenyl ether, and proposed that a mechanism involving a 'sandwich' π-complex may be general in the rearrangements of molecules of the type Ph-X-Y-Ph, where X = O, NH, S, and Y = CH_2, CO, SO_2.

Later investigations have shown that, at least in the rearrangement of various butyl phenyl ethers, a π-complex mechanism is untenable. Spanninger and von Rosenberg[8,9] examined the $AlCl_3$-catalysed rearrangement of n-butyl and s-butyl phenyl ethers[8] and found n-butylated and s-butylated n-butyl phenyl ethers and n- and s-butylphenols amongst the reaction products. They suggested that a higher *ortho*:*para* (*o*:*p*) ratio in homogeneous reactions without solvent may be due not only to an intramolecular process but also to an intermolecular reaction of initial ether followed by an intramolecular one (Scheme 1). The whole issue is complicated by heterogeneity of the reaction mixture so that reactions may occur in different phases, and a number of mechanisms may be operating.



Scheme 1.

The $AlBr_3$-catalysed rearrangement of s-butyl phenyl ether[9] in chlorobenzene led to *o*- and *p*-s-butylphenols with net inversion of configuration (14.1 and 52.0%, respectively). This process involved displacement of an active s-butyl group by unreacted ether from an n-complex (see Scheme 1) or ion-pair to give butylated ether which cleaved to give butylphenols with inverted configurations. The authors also found[9] that this masked an intramolecular rearrangement, since when the ether was added to $AlBr_3$ in chlorobenzene (rather than the other way round) the *o*-s-butylphenol was formed with net *retention* of configuration (54.2%) whilst the *p*-s-butylphenol was racemic. [With this inverse addition, the ether is never present in excess, so that the displacement reaction (above) is obviated.] In view of this and further evidence, the authors concluded that a π-complex mechanism was not involved, as this would require *complete retention* of configuration of the migrating s-butyl group to *both* the *o*- and *p*-positions, but that the reaction proceeds by a displacement by s-butyl phenyl ether on either the $AlBr_3$-complexed ether (the n-complex, above) or on the ion-pair $PhO\bar{A}lBr_3{\cdot}Bu^{s+}$. The work described[9] avoids all the problems of heterogeneity of reaction mixtures referred to above.[8]

One question raised in the above work[9] was whether a hydride shift might occur in the s-butyl cation, so leading to the degree of racemisation observed: this could occur even in an

Table 1. Rearrangement of benzyl phenyl ether (BPE) using $AlBr_3$ in chlorobenzene

Molar ratio $AlBr_3$:BPE	Time	% Conversion of BPE (estimated by g.l.c.)	*o*:*p* ratio for rearrangement products
1:1	15 min	99	5.9
1:1	<2 s	90	9.5
2:1	<2 s	95	7.5

Table 2. Interconversion of 2- and 4-hydroxydiphenylmethane (using $AlBr_3$ in chlorobenzene)

Reactant[a]	% Impurity in reactant	% product (reactant peak = 100%)	Approx. % interconversion[b,c]
2-OH	<0.1 4-OH	<0.1 4-OH	0
4-OH	0.5 2-OH	1.1 2-OH	0.6

[a] 2-OH and 4-OH are 2- and 4-hydroxydiphenylmethane respectively. [b] Later experiments (with a catalyst:ether molar ratio of 1:1 and a reaction time of 2 s) gave 2-OH 99.7% (unaltered), and 4-OH 100 → 99.8% (1,2,4-trichlorobenzene as solvent). [c] Phenol was formed in both reactions.

Table 3. Isotopic incorporations

$Ph^{13}CH_2OPh$	89.3%	($PhCH_2OPh$ 10.7%)
$PhCH_2{}^{18}OPh$	83.8%	($PhCH_2OPh$ 16.2%)

intramolecular rearrangement (involving a tight ion-pair). Dewar and Spanninger[10] tested this point (for the $AlBr_3$–PhCl system) by using s-butyl phenyl ether labelled with deuterium at the 2-position of the s-butyl group. Scrambling of the label was complete for the *p*-s-butylphenol and extensive though less than complete for the *o*-s-butylphenol. A π-complex mechanism was not upheld, the reactions being considered to involve a carbonium ion mechanism.

The work we describe in this paper is part of an investigation of Dewar's proposals[7] that rearrangement of compounds of the type Ph-X-Y-Ph (see above) might proceed through a 'sandwich-type' π-complex and be particularly facile. Earlier work[11,12] has already shown that in the case of the $AlBr_3$-catalysed rearrangement of phenyl benzoate (X = O, Y = CO) in homogeneous solution in chlorobenzene, the above idea is untenable: the rearrangement is not strikingly rapid, nor is the *o*:*p* ratio of the rearrangement products abnormally high. More recently, Dewar's suggestion that a high *o*:*p* ratio indicates an intramolecular rearrangement (either alone, or in addition to an intermolecular pathway) has been shown[1] by labelling experiments to be wrong: an exclusively *ortho*-directed rearrangement of phenyl benzoate involved a bimolecular (and thus necessarily intermolecular) reaction.

At this point, we felt it would be helpful to return to the original experiment,[3] the rearrangement of benzyl phenyl ether itself, and repeat the work using modern analytical techniques (particularly g.l.c.) to investigate the reaction products, with the minimum of chemical manipulation of these before analysis. The use of isotopically labelled starting material could provide information, more directly and certainly, which other workers have sought using optically active reactants.* We used a similar approach to that described in the preceding paper.[1] We prepared $Ph^{13}CH_2OPh$ and $PhCH_2{}^{18}OPh$, and rearranged a mixture of these (plus some unlabelled ether) using $AlBr_3$ in homogeneous solution in 1,2,4-trichlorobenzene (rather than in chlorobenzene itself, to simplify isolation of the rearrangement products and unrearranged benzyl phenyl ether itself – see later). Although we could separate benzyl phenyl ether and 2- and 4-hydroxydiphenylmethane by preparative layer chromatography, the amount of 4-hydroxydiphenylmethane formed was small, and in the event we used preparative g.l.c. to obtain clean samples of unrearranged ether and the *o*- and *p*-rearrangement products for mass spectrometric analysis, to determine the labelling patterns of unrearranged starting material and of products.

Results and Discussion

In this discussion, 'rearrangement' means the conversion of benzyl phenyl ether into 2- and 4-hydroxydiphenylmethane; 'scrambling' refers to mixing of isotopic labels by reactions between molecules or fragments of molecules; 'interchange' means the exchange of $PhCH_2$ and PhO groups between pairs of molecules to give benzyl phenyl ether (and is equivalent to scrambling of the ether when isotopically different fragments are involved).

Preliminary investigations[14] regarding the rearrangement products were carried out using synthetic unlabelled benzyl phenyl ether (see Experimental section) and $AlBr_3$ in chlorobenzene, as in the original work.[3] The following results were obtained (for reactions at 20 °C).

(1) Some 4-hydroxydiphenylmethane *is* formed, the *o*:*p* ratios being shown in Table 1.

(2) 2-Hydroxydiphenylmethane is not converted into the 4-isomer; 4-hydroxydiphenylmethane is converted into the 2-isomer to only a very small extent (when a catalyst:ether molar ratio of 2:1 is used with a reaction time of <5 s). The results are shown in Table 2.

Thus, the original report[3] is essentially correct: the reaction is extremely rapid, and *o*-benzylphenol is the major rearrangement product. However, the amount of the *para*-rearrangement product is not negligible; 2-hydroxydiphenylmethane is not (within experimental error) converted into 4-hydroxydiphenylmethane; and the extent of the conversion of 4-hydroxydiphenylmethane into the 2-isomer is very small indeed. Both hydroxydiphenylmethanes decompose to phenol under the reaction conditions used. The variation in the *o*:*p* ratio with time for the 1:1 $AlBr_3$–benzyl phenyl ether rearrangement could be explained by the differing rates of decomposition of the 2- and 4-hydroxydiphenylmethane to phenol, though we did not pursue this point in our investigations.

To simplify the separation of the reaction products (see later) we replaced chlorobenzene by 1,2,4-trichlorobenzene. This is less likely to undergo benzylation than PhCl (because of the additional chlorine atoms) and if any benzylation products *are* formed they are eluted beyond 4-hydroxydiphenylmethane (during g.l.c. of the reaction products), well away from unchanged ether, because of their increased molecular weight. 1,2,4-Trichlorobenzene has a dielectric constant of 3.98 at 20 °C[15] and a dipole moment of 1.25 D,[15] whilst chlorobenzene has a dielectric constant of 5.69 at 20 °C[16] and a dipole moment of 1.56 D,[17] so that polarity differences are small. In fact, the change of solvent had little effect: in several attempts at the rearrangement and separation of the products, the *o*:*p* ratio was consistently between 11 and 12 (always within the range 10.9—12.2; *cf.* 9.5 in chlorobenzene) and the trichlorobenzene was

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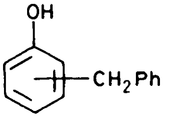
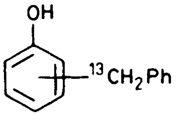
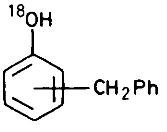
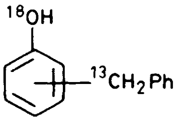
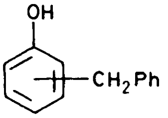
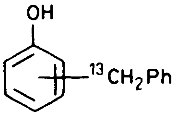
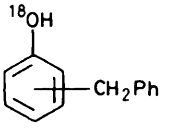
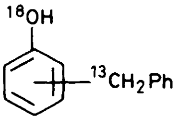
* For a discussion of the confusion and contradictions often met in published work on the related Fries rearrangement, which has an extensive history and literature, but relatively little published material involving modern analytical techniques, see ref. 13.

Table 4. Rearrangement in 1,2,4-trichlorobenzene

Molecular weight	Molecule	Composition (%)[a]				
		A	B	C	D	E
184	$PhCH_2OPh$ or 	11.6	10.4	13.1	13.9	31.1
185	$Ph^{13}CH_2OPh$ or 	45.4	46.8	44.5	42.3	25.9
186	$PhCH_2{}^{18}OPh$ or 	42.9	42.5	42.4	41.2	23.4
187	$Ph^{13}CH_2{}^{18}OPh$ or 	0	0	0	2.6	19.5

[a] See Part 3 [1] (Appendix) for a description of the treatment of the errors involved and method of calculation of the values in columns A and E. A, Initial benzyl phenyl ether mixture (calculated composition); B, isolated benzyl phenyl ether; C, isolated 2-hydroxydiphenylmethane; D, isolated 4-hydroxydiphenylmethane; E, 100% scrambled material (calculated composition).

Table 5. Rearrangement in nitrobenzene

Molecular weight	Molecule	Composition (%)[a]				
		A	B	C	D	E
184	$PhCH_2OPh$ or 	13.6	13.0	14.4	18.3	32.3
185	$Ph^{13}CH_2OPh$ or 	42.8	41.2	44.8	37.6	24.3
186	$PhCH_2{}^{18}OPh$ or 	43.3	45.1	40.7	39.2	24.8
187	$Ph^{13}CH_2{}^{18}OPh$ or 	0	0	0	4.9	18.6

[a] See Part 3 [1] (Appendix) for a description of the treatment of the errors involved and method of calculation of the values in columns A and E. A, Initial benzyl phenyl ether mixture (calculated composition); B, isolated benzyl phenyl ether; C, isolated 2-hydroxydiphenylmethane; D, isolated 4-hydroxydiphenylmethane; E, 100% scrambled material (calculated composition).

obviously a satisfactory solvent. Later, some rearrangements were carried out in nitrobenzene (dielectric constant 34.8 at 25 °C [18]) as solvent: the *o*:*p* ratio for these reactions was 4.7.

Results of Mass Spectrometric Measurements.—These are shown in Tables 3—5.

In Tables 4 and 5, column A gives the (calculated [1]) composition of the mixture of labelled benzyl phenyl ether molecules before the reaction; columns B—D respectively show the experimentally determined composition of the unrearranged benzyl phenyl ether and 2- and 4-hydroxydiphenylmethane isolated from the reaction mixture; and column E gives the

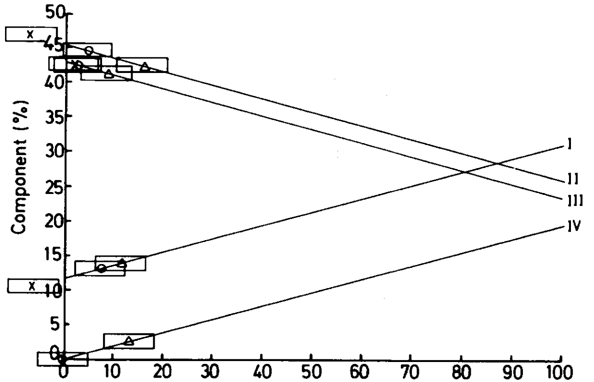


Figure 1. Rearrangement in 1,2,4-trichlorobenzene. I, mol. wt. 184; II, mol. wt. 185; III, mol. wt. 186; IV, mol. wt. 187. ×, Isolated benzyl phenyl ether; ○, isolated 2-hydroxydiphenylmethane; △, isolated 4-hydroxydiphenylmethane; ☐ , uncertainty

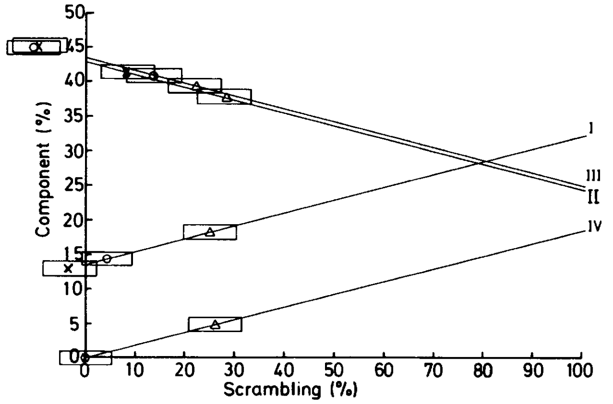


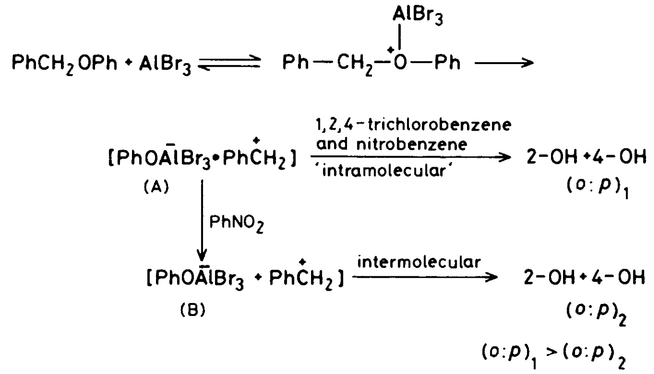
Figure 2. Rearrangement in nitrobenzene. I, mol. wt. 184; II, mol. wt. 185; III, mol. wt. 186; IV, mol. wt. 187. Symbols as in Figure 1.

calculated[1] composition of completely scrambled (*i.e.* interchanged or rearranged) molecules. (Primary kinetic isotope effects for carbon and oxygen have again been ignored.[1]) The same graphical treatment of the results has been used as in Part 3.[1] Using the calculated values in columns A and E (for each solvent) a graph of %-labelled molecule as ordinate and %-scrambling (or interchange, for the ether) as abscissa is readily plotted (Figures 1 and 2). The experimental values in columns B, C, and D have been plotted on the respective graphs. Table 6 shows the extent of scrambling for each molecule in each solvent.

Table 6 shows that, for rearrangement in trichlorobenzene, benzyl phenyl ether undergoes rearrangement without prior scrambling, the 2-hydroxydiphenylmethane is virtually unscrambled, and 4-hydroxydiphenylmethane has undergone scrambling to a small extent. In nitrobenzene, the result for the ether shows a large error margin. (There was only *ca.* 2.3% of ether left after the shortest reaction time attainable, and it proved difficult to isolate. The mass spectrum obtained was weak.) However, the 2-hydroxydiphenylmethane is again scarcely scrambled, but the 4-hydroxydiphenylmethane shows more scrambling than when trichlorobenzene was used, though three-quarters of this phenol is still unscrambled. In view of these results, it seems virtually certain that even in nitrobenzene the benzyl phenyl ether undergoes rearrangement without prior scrambling.

Table 6. Rearrangement reactions: average % scrambling of substrate and rearrangement products

	Average %-scrambling		
Solvent	Benzyl phenyl ether	2-Hydroxy-diphenyl-methane	4-Hydroxy-diphenyl-methane
1,2,4-Trichlorobenzene	−3 ± 4	4 ± 3	12 ± 3
Nitrobenzene	−1 ± 7	2 ± 8	25 ± 2



Scheme 2.

In summary then, benzyl phenyl ether undergoes rearrangement in both solvents without prior interchange; the *ortho*-rearrangement product is virtually or entirely unscrambled in both solvents, the *para*-rearrangement product has undergone scrambling, but not very extensively. The 4-hydroxydiphenylmethane is approximately twice as scrambled in the nitrobenzene reaction as in the trichlorobenzene reaction. The *o*:*p* ratio for reactions in nitrobenzene is rather less than half that for reactions in trichlorobenzene.

One explanation accounting for all the above observations is given in Scheme 2. A catalyst–ether complex is initially formed and gives a tight ion-pair (A). This leads to formation of unscrambled 2- and 4-hydroxydiphenylmethane as the fragments formed from any one molecule of ether react only with each other: this is implied in the term 'intramolecular'.* In the more dissociating solvent nitrobenzene, a solvent-separated ion-pair (B) is also formed, leading to reaction of the fragments from one ether molecule with those from another, giving rise to an intermolecular rearrangement and scrambled products. However, even in nitrobenzene, there is a substantial contribution from the 'intramolecular' reaction, because the extent of scrambling in the phenolic products is quite low. (Similarly, there is a very small contribution from the intermolecular reaction even in trichlorobenzene, as indicated by the slight scrambling of the 4-hydroxydiphenylmethane.) The *o*:*p* ratio drops in going from trichloro- to nitro-benzene [$(o{:}p)_1 > (o{:}p)_2$] because the solvated Ph$\overset{+}{C}H_2$ ion preferentially attacks the *para*-position in the ring of the phenolic moiety. [The decrease in *o*:*p* ratio with increasing dielectric constant of the solvent (noticeable even in going from 1,2,4-trichlorobenzene to chlorobenzene – see above) supports the views of Hart and Kosak[6] regarding the reaction mechanism.] The striking feature (in both cases) is the high *o*:*p* ratio. Dewar's explanation[7] of this in terms of a 'sandwich' π-complex may be

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* In Part 3,[1] such a process was described as 'pseudointramolecular' (see also ref. 11) or 'extramolecular' (see ref. 9 in Part 3[1]).

tenable for this reaction, or it may simply be the case that less reorganisation of the ion-pair is needed for *ortho*-substitution than for *para*. The latter explanation avoids the need for contact with Occam's razor.[19]

Experimental

Materials.—Anhydrous $AlBr_3$ was prepared, and PhCl purified, as described previously.[11] 1,2,4-Trichlorobenzene (Aldrich) was dried over P_2O_5 and distilled, the fraction boiling at 212—213 °C (lit.,[18] 213.5 °C) being collected. Nitrobenzene was dried (P_2O_5) and fractionally distilled, and boiled at 209—210 °C (lit.,[18] 210.8 °C). Tetrahydrofuran (THF) was distilled from potassium, and ethylene glycol dimethyl ether (glyme) was distilled from $LiAlH_4$ before use. 2-Hydroxydiphenylmethane (Aldrich) was used without further purification. G.l.c. (see below) showed it to be pure. 4-Hydroxydiphenylmethane (B.D.H.) was used without further purification. G.l.c. showed that it contained *ca.* 0.5% of an impurity with the same retention time as 2-hydroxydiphenylmethane. $Ph^{13}COOH$ (90 atom % ^{13}C) and $^{18}O_2$ (99 atom %) were obtained from Amersham International.

Benzyl Phenyl Ether (*Unlabelled*).—This was synthesised from $PhCH_2Cl$, PhOH, and Et_3N.[20] The product was distilled, and the fraction boiling at 94—104 °C and 0.3 mmHg collected. This crystallised on cooling (giving a 38% yield). The product was recrystallised from ethanol and dried. Its 100 MHz n.m.r. spectrum ($CDCl_3$) showed signals at δ 4.9 (s) and 6.8—7.4 in the ratio 1:5. G.l.c. showed that the recrystallised material had impurities with the retention times of 2- and 4-hydroxydiphenylmethane (arising from *C*-benzylation of the phenol) totalling *ca.* 6% of the product. The ether was chromatographed on a column of alumina, 8″ × 1″, with light petroleum (b.p. 60—80 °C)–CH_2Cl_2 (4:1) as eluant. A sample (10 g) was treated in this way, the progress of the ether being monitored by t.l.c. of the collected fractions, and then the process was repeated. The final product was >98% pure, the main impurity having the same retention time (g.l.c.) as 2-hydroxydiphenylmethane.

$Ph^{13}CH_2OPh$.—This was prepared from $Ph^{13}COOH$.[21] $Ph^{13}COOH$ (0.5 g, 4.1 mmol) was weighed into a two-necked flask (25 ml; oven-dried) containing a magnetic follower and fitted with a Suba seal, a condenser, and a mercury bubbler. A positive pressure of dry nitrogen was kept across the head of the condenser. Dry THF (1.5 ml) was added. The flask was cooled to 0 °C and BH_3·THF in THF (1M; 6 ml, 6 mmol) was added over 15 min. The flask was kept at 25 °C for 1 h whilst the contents were stirred vigorously. THF–H_2O (1:1; 1.5 ml) was then added carefully, and the precipitate of $B(OH)_3$ filtered off. The solvents (THF, H_2O) were distilled off under reduced pressure. To the residue ($Ph^{13}CH_2OH$) was added aqueous HBr (48%; 10 ml) and the mixture was refluxed for 1 h, then poured into water (50 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The organic layer was washed with saturated $NaHCO_3$ solution (20 ml) and dried ($MgSO_4$). The solution was filtered and the CH_2Cl_2 evaporated giving $Ph^{13}CH_2Br$ (0.629 g, 3.66 mmol, 89.8%). NaOH (0.16 g, 4 mmol) was dissolved in 85% aqueous MeOH (*ca.* 1 ml) and added to PhOH (0.38 g, 4.04 mmol) dissolved in MeOH (1 ml). The water and MeOH were removed using a rotary evaporator and the last traces of solvents and phenol were removed in a drying pistol at 78 °C for *ca.* 15 h. The calculated amount of $Ph\bar{O}Na^+$ in glyme (*ca.* 2.5 ml) was added to the synthetic $Ph^{13}CH_2Br$ in glyme (*ca.* 0.5 ml) and the mixture was left at room temperature for 4 days. The mixture was poured into water (15 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The organic layer was washed with NaOH solution (3M; 3 × 20 ml) then dried ($MgSO_4$), filtered, and the solvent was evaporated. The product was purified using a Kugelrohr (b.p. > 70 °C at 0.1 mmHg) and melted at 36—38 °C (lit.,[22] 38—39, 40 °C). The yield was 0.5325 g (2.83 mmol, 70.6% from $Ph^{13}COOH$). G.l.c. showed that the product was 98% pure. Incorporation of ^{13}C was 89.3% (see earlier). [The impurity in the ^{13}C-labelled ether was identified (by g.c.–m.s.) as 4-bromobutyl phenyl ether, presumably arising from ring-opening of traces of THF by the HBr to give $BrCH_2CH_2CH_2CH_2OH$ and conversion of this into 1,4-dibromobutane. Subsequently, reaction with PhO^-Na^+ gave $PhOCH_2CH_2CH_2CH_2Br$ (M^+ 228.230). This did not interfere with subsequent mass spectrometric analyses, nor with the rearrangement reaction itself, as it was still present (g.l.c.) after the rearrangement].

$PhCH_2{}^{18}OPh$.—$Ph^{18}OH$ was prepared from $^{18}O_2$ and PhMgBr as described previously.[1] The $Ph^{18}OH$ was then converted into its sodium salt and treated with the calculated amount of $PhCH_2Br$ (see above). The yield of $Ph^{18}OH$ was 82.9%, and of $PhCH_2{}^{18}OPh$ 67% overall; g.l.c. showed the ether to be 96% pure, the impurity most probably (*via* g.c.–m.s.) being dibenzyl ether. (This did not interfere subsequently with either the mass spectrometric analysis or the rearrangement reaction). Incorporation of ^{18}O was 83.8% (see earlier) from 99% labelled oxygen: as previously,[1] some atmospheric oxygen must have become incorporated during the synthesis.

Rearrangement Reactions.—These were performed essentially as described for phenyl benzoate,[1,11,13] but mixtures were hydrolysed as soon as the $AlBr_3$ and ether solutions were mixed. Equimolar proportions of $Ph^{13}CH_2OPh$ and $PhCH_2{}^{18}OPh$ were taken.

Analytical Work.—The products of rearrangement of unlabelled benzyl phenyl ether (in the exploratory runs), and the synthetic labelled materials, were analysed by g.l.c. using a Hewlett-Packard 5710A gas chromatograph fitted with a 0.9 m long, 2 mm i.d., glass column packed with 25% May and Baker Embaphase silicone oil on 100—120 mesh Gas Chrom Q (Applied Science Labs.). The oven temperature was 170 °C, and on-column injection at 200 °C and a detector (f.i.d.) temperature of 250 °C were used, with a nitrogen inlet pressure of 10 lb in^{-2}. An approximate relative response factor for the 2- and 4-hydroxydiphenylmethane was obtained by running a trimethylsilylated [*via NO*-bis(trimethylsilyl)acetamide] sample of these phenols in a 1:1 weight ratio. The labelled rearrangement products themselves were separated by preparative g.l.c. using a modified Pye 104 gas chromatograph fitted with a 7 ft long, 3/8 in. o.d. glass column packed with 10% Carbowax 20M on 80—100 mesh Chromosorb W at 170 °C with the injector at 250 °C, and the outlet at 207 °C. The samples were run without trimethylsilylation. [The above system was used for separation of the products of rearrangements carried out in trichlorobenzene. The reactions in nitrobenzene were carried out a little later and the original preparative column had meanwhile deteriorated, so that whilst benzyl phenyl ether could be eluted and trapped (though the amount was very small, *ca.* 2.3% of the products) and 2-hydroxydiphenylmethane could also be isolated satisfactorily, the 4-hydroxydiphenylmethane could not be properly resolved. It was accordingly chromatographed, as its trimethylsilyl ether, on a preparative-scale OV101 column (10% on 85—100 mesh Gas Chrom Q, and similar to the Carbowax column above in dimensions and operating conditions) on which the products were satisfactorily resolved. The 4-trimethylsilyloxydiphenylmethane was hydrolysed back to the free phenol using dilute HCl–Me_2CO, and then submitted to mass spectrometry in the normal way.] The purity of the collected fractions was checked by capillary g.l.c. using a Hewlett–Packard 5710A fitted with a 12.5 m methyl silicone fused-quartz capillary column. Operating conditions were as follows: oven, 100 °C (2 min) then at 4 °C min^{-1} to 250 °C; auxiliary zone 150 °C; detector 200 °C. Helium was used as carrier gas. Mass spectrometric analyses were carried out as described previously.[1] The errors in the quoted values of % intensities are (at most) ± 1. The treatment of errors and calculation of values shown in columns A and E of Tables 4 and 5, and in Table 6, were performed as described in the Appendix to Part 3.[1]

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