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AROMATIC REARRANGEMENTS IN THE BENZENE SERIES[1]—II[2]

THE FRIES REARRANGEMENT OF 4-BIPHENYLYL BIPHENYL-4-CARBOXYLATE

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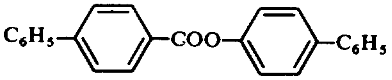
Abstract The title compound has been shown to rearrange under the influence of anhydrous aluminium bromide in homogeneous solution in chlorobenzene. The products are similar to those obtained in the rearrangement, under analogous conditions, of phenyl benzoate, except that migration to the *para*-position in the case of the title ester has not been established. The relevance of the results obtained to the problem expounded in Part I of this series is explained.

Part I[2] of this series outlined a theory[3a, b] proposed to account for the very rapid rearrangement reactions undergone by certain suitably constituted aromatic compounds. Two tests of this theory were proposed, and Part I of this series described the investigation of the application of the more important test, under selected conditions, to the rearrangement of phenyl benzoate and to the reverse process, i.e. the benzoylation of phenol. In this paper, the second test of the theory is applied: an attempt to rearrange the 4,4′-diphenyl-substituted phenyl benzoate, under the same selected conditions referred to above.

The starting material, 4-biphenylyl biphenyl-4-carboxylate, (4-biphenylyl 4-phenylbenzoate), (I), has not previously been reported: it was prepared by acylation of 4-hydroxybiphenyl with 4-biphenylcarbonyl chloride. Since reaction of the ester (during the attempted rearrangement) with the solvent chlorobenzene might give rise to the acylation products 4-(2-chlorobenzoyl) biphenyl, (II), and 4-(4-chlorobenzoyl) biphenyl, (III), as in the case of the corresponding reactions of phenyl benzoate,[2] these compounds were also synthesised.



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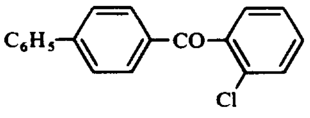

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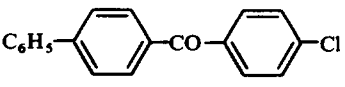

III

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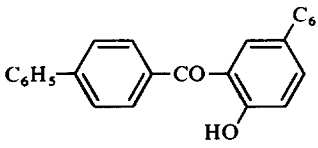
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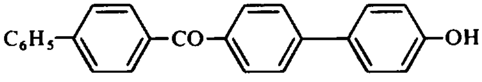
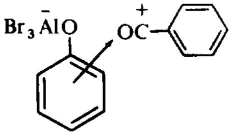

V

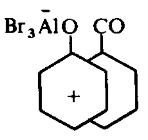
The rearrangement of the ester (I) under the influence of anhydrous aluminium bromide in homogeneous solution in chlorobenzene was investigated using one and two molar proportions of catalyst per mole of ester. (The rearrangement reactions discussed in this paper are referred to as the 1:1 and 2:1 rearrangement reactions, as in Part I[2] of this series.)

In both these reactions, considerable amounts of ester remained unchanged, (more in the 1:1 rearrangement reaction), and some of the ester was cleaved to 4-hydroxybiphenyl and 4-biphenylcarboxylic acid, (more in the 2:1 rearrangement reaction). However, in both processes, the ester rearranged, with migration of the acyl group to the *ortho-* position, to give IV, i.e. 4′, 5-diphenyl-2-hydroxybenzophenone. The formation of the *para*-rearrangement product (V), i.e. 4-(4-hydroxphenyl)-4′-phenylbenzophenone, was not definitely established, although it appeared to have been formed in one of the 2:1 rearrangement reactions performed. In the 1:1 rearrangement reaction, no attack on the solvent occurred: in the 2:1 rearrangement reaction, the solvent was acylated, with the formation of the expected chloroketones (II and III), the latter predominating, as would be expected. This behaviour is entirely analogous to that of phenyl benzoate under similar conditions.[2]

Quantitative analysis of the products of the rearrangement reactions was not undertaken, largely because of the analytical problems involved (Experimental), and because the main point of interest, in the context of these investigations, is the fact that the ester rearranges.

We have already shown[2] that phenyl benzoate can undergo rearrangement, catalysed by anhydrous aluminium bromide (in suitable quantity) in homogeneous solution in chlorobenzene, through an intermediate which may well be a "normal" π-complex (VI): but that a "sandwich" π-complex[3a,b] (VII) is unlikely to be involved. The work reported here supports this latter conclusion, as the title ester, substituted in both the *para*-positions by bulky groups, still undergoes rearrangement, contrary to what the theory[3a,b] involving a "sandwich" π-complex intermediate would predict, (introduction in Part I[2]). The recent work of Shine[4a,b,c] on the rearrangement of 4-hydrazobiphenyl should also be noted in this connection.


VI


VII

On the basis of our work, therefore, we suggest that the Fries Rearrangement of phenyl benzoate can occur (i) via a π-complex intermediate, leading to an exclusively *ortho*-oriented intramolecular rearrangement; and (ii) via other intermediates, represented (see the reaction schemes shown in Part I[2]) as the precursors of acylium ions, leading to *ortho*- and *para*- oriented migrations. Thus the various mechanisms operating depend on the different postulated intermediates, formation of which is in turn governed by the reaction conditions used. The reaction conditions relevant to the formation of any particular proposed intermediate have been defined in Part I[2] of this series.

We intend to extend our investigations to esters of other types differing from the wholly aromatic ones on a study of the rearrangements of which our conclusions are based.

EXPERIMENTAL

Synthetic work. Complete details of all experimental work are given in Ref. 1: see also Ref 2 for details of micro-analyses, etc.

The title ester was prepared from the chloride of 4-biphenylcarboxylic acid and 4-hydroxybiphenyl. The acid itself was prepared from the nitrile, as the attempted carbonation of the Grignard reagent from 4-bromobiphenyl was consistently unsuccessful,[1] and oxidation of 4-acetylbiphenyl was unsatisfactory.[1]

4-Bromobiphenyl (B.D.H.) was converted (in 76% yield) to 4-cyanobiphenyl according to the directions of Friedman and Shechter, (Method A),[5] (except that ether was used for extracting the product at the end of the synthesis). The nitrile melted at 84°, (cf. 84–88°[6a, b]), and depressed the m.p. of 4-bromobiphenyl (89°[7]) strongly.

The nitrile (15 g, 0·084 mole) was stirred with H_2SO_4 (60%, 200 ml) which was brought slowly to the boil and allowed to boil for 5 min. The carboxylic acid began to separate from the boiling soln as a white solid, and the whole mixture, after being cooled, was slowly added to ca. 1·5 l. cold water, and left to stand for 30 min. The product was filtered off, partially dried between filter papers, and recrystallized from alcohol, after treatment with a little charcoal. The first recrystallization gave 15 g (90% yield) of material, m.p. 212°, (values quoted in the lit. range from 208–228°[6a, 8, 9a–1]), and was considered to be pure enough for further use. A small amount of the acid was recrystallized further from alcohol, m.p. 223°.

4-Biphenylcarboxylic acid (2 g, 0·01 mole) was mixed with $SOCl_2$ (5 ml) and DMF[10] (2 drops) and the soln refluxed for 4 hr on the water-bath (although the evolution of HCl was largely complete after ca. 30 min). The excess of $SOCl_2$ was distilled off under reduced press, and the residue solidified· The crude acid chloride was refluxed with light petroleum, (b.p. 80–100°; 25 ml), and the hot soln filtered through a little activated charcoal. The chloride crystallized from the filtrate in yellow needles, m.p. 111°, 1·5 g being obtained (69% yield). A further recrystallization from the same solvent gave long white needles, m.p. 112°, (cf. 113–115°[11]). This preparation of the acid chloride worked equally well on a larger scale.

4-Biphenylyl biphenyl-4-carboxylate was prepared by esterifying 4-hydroxybiphenyl with the above acid chloride. The acid chloride was mixed with a 3-fold excess of 4-hydroxybiphenyl, and the two were heated together without a solvent at 160–170° for 4 hr. The ester was obtained in 80–85% yield.

The products are easily separated, as the ester is virtually insoluble in EtOH, while 4-hydroxybiphenyl dissolves readily. Extraction of the crude reaction product with hot EtOH leaves the ester unaffected, and it can then be recrystallized from benzene. It is also soluble in hot $CHCl_3$, and in a rather large volume of cold $CHCl_3$.

The purified ester, m.p. 217–218° depressed the m.p. of 4-biphenylcarboxylic acid, which has a similar m.p., sharply: unlike the acid, it does not sublime. (Found: C, 85·9; H. 5·1; O, 9·1; mol. wt. (Rast) 333. $C_{25}H_{18}O_2$ requires: C, 85·7; H, 5·2; O, 9·1%; mol. wt. 350·4); λ_{max}^{EtOH} 276 nm, $E_{1\,m}^{1\%}$ 1168; λ_{min}^{EtOH} 237 nm, $E_{1\,cm}^{1\%}$ 508; ν_{max}^{KBr} 1733, 1489, 1287, 1084, 1005, 741 cm^{-1}. (A small amount of the ester was initially prepared by heating the acid chloride and the phenol (above) in dekalin. When the solvent was partially removed after several hr, and the residual soln cooled, the ester deposited. Attempts to synthesize the ester directly from the acid and the phenol, using dicyclohexylcarbodi-imide as condensing agent,[12] were unsatisfactory. Some ester was formed, but the best method of separating the rather low yields of this compound from the other reaction products involved TLC).

4-(2-Chlorobenzoyl)biphenyl, (II) has been prepared by the Friedel-Crafts reaction between 2-chlorobenzoyl chloride and biphenyl in the presence of anhyd $AlCl_3$.[13] The synthesis was performed in accordance with the procedure of Long and Henze.[14] The reaction appeared to have been incomplete, as there was a strong smell of acyl halide in the reaction product. The acyl halide was removed by boiling the crude product with 2N NaOH. The ketone was crystallized from alcohol, but still had a yellow tint, and melted at 90°. The yield obtained was 24% of the theoretical value.

A small amount of the product was recrystallized further from aqueous MeOH, giving a white crystalline product, m.p. 92–92·5°, (cf. 94°[13]). (Found: C, 77·9; H, 4·6; Cl, 12·0; O, 5·3; Calc. for $C_{19}H_{13}ClO$: C, 78·0; H, 4·5; Cl, 12·1; O, 5·5%); λ_{max}^{EtOH} 294 nm, $E_{1\,cm}^{1\%}$ 857; λ_{min}^{EtOH} 250 nm, $E_{1\,cm}^{1\%}$ 216; ν_{max}^{KBr} 1669, 1294, 1055, 1005, 931, 742 cm^{-1}.

4-(4-Chlorobenzoyl)biphenyl, (III), was prepared by a method entirely analogous to that used for the 2-chloroketone above, and was obtained in 39% yield. The chloroketone crystallized as a yellow solid from $CHCl_3$, m.p. 169°. The product was very sparingly soluble in EtOH, from which it crystallized almost white, but with hardly any change in the m.p. (now 169–169·5°).

Bachmann and Moser[15] quote a b.p. of 300°/10 mm for this ketone, but give no m.p. (Found: C, 78·0; H, 4·6; Cl, 12·0; O, 5·2. Calc. for $C_{19}H_{13}ClO$: C, 78·0; H, 4·5; Cl, 12·1; O, 5·5%); λ_{max}^{EtOH} 290 nm, $E_{1\,cm}^{1\%}$ 896; λ_{min}^{EtOH} 243 nm, $E_{1\,cm}^{1\%}$ 492; ν_{max}^{KBr} 1644, 1301, 1091, 1015, 932, 857, 744, 689 cm^{-1}. IR absorption spectra of I and II and III are given in Ref. 1.

Rearrangement reactions

The rearrangement of the title ester was examined in homogeneous soln in chlorobenzene, using anhyd $AlBr_3$ as catalyst. Quantitative analyses have not been made, mainly because of the analytical problems involved, and partly because of the low solubility of the ester in chlorobenzene (see below). For details of the preparation and/or purification of the solvent and catalyst, as well as details of the apparatus and techniques used in carrying out this work, see Part I.[2]

The ester (0·1753 g, 0·0005 mole) was dissolved in chlorobenzene (5 ml) and a molal soln of $AlBr_3$ in chlorobenzene, (containing 0·2668 g, 0·0001 mole catalyst), was added. (Even the relatively large volume of chlorobenzene used would only dissolve the ester on warming, although the ester is very much more soluble in chlorobenzene in the presence of the catalyst.) The soln was heated at 110° in a constant-temp oil-bath for 2 hr, and then hydrolysed by being poured into cold dil HCl. The products were extracted with $CHCl_3$, and the solvent layer was washed with water and dried. The $CHCl_3$ was evaporated.

Analysis of the products

Thin-layer chromatography. The reaction products were submitted to TLC, using a silica plate and a solvent consisting of CH_2Cl_2 (93 parts) and di-isopropyl ether (7 parts). Five "spots" or fractions were obtained when the plate was viewed under UV light or sprayed with an appropriate locating agent. Authentic samples of the ester, 4-hydroxybiphenyl, and 4-biphenylcarboxylic acid were chromatographed on the same plate as the reaction products. The first fraction of the reaction products, which had hardly moved from the origin of the plate, was 4-biphenylcarboxylic acid. The third fraction, which was a major constituent of the reaction products, was 4-hydroxybiphenyl. The fifth fraction, which had travelled the furthest, was the ester itself. (As an additional check, the separation was repeated on the preparative scale. Samples of the various fractions were removed from the plate, separated from the adsorbent, and their IR absorption spectra determined. Comparison of the spectra of the first, third and fifth fractions with the spectra of the authentic materials confirmed the identities of these three fractions.)

The second and fourth fractions remained to be identified. Of these, fraction No. 2, present only to a very small extent in the reaction products, was a white substance, soluble in alkali, (giving a yellow soln), and whose UV absorption maxima showed a pronounced shift in alkaline soln—i.e. this fraction was most probably a phenolic rearrangement product. The "spot" on the original (i.e. analytical scale) plate, corresponding to this substance, turned blue when sprayed with a ferricyanide reagent, ($Fe^{3+} + Fe(CN)_6^{3-}$), a reaction typical of a phenol. (This reaction was also given by the third fraction, 4-hydroxybiphenyl.) Fraction No. 4, present to a considerable extent in the reaction products, was a bright yellow. Its "spot" did not give a blue colour when sprayed with the ferricyanide reagent, but in alcoholic soln, this material gave a brilliant yellow colour when NaOHaq was added.

The fourth fraction, the bright yellow material, was classified as the *ortho*-rearrangement product, and the white second fraction as the *para*-rearrangement product, partly by analogy with the simple monohydroxybenzophenones. 2-Hydroxybenzophenone is bright yellow, 4-hydroxybenzophenone pale yellow, but both give coloured anions, a different shade of yellow from the parent phenols. Secondly, the *ortho*-rearrangement product will almost certainly be intramolecularly hydrogen bonded, like 2-hydroxybenzophenone, and will therefore be less polar than the *para*-rearrangement product, and likely to travel further on a plate of this nature than the *para*-rearrangement product, under the same circumstances. Thirdly, when 2-hydroxybenzophenone and 2-hydroxyacetophenone were chromatographed on a similar plate and sprayed with the ferricyanide locating reagent, these two hydroxyketones also failed to give blue spots. This is most probably a consequence of the strong internal H-bonding displayed by these compounds, the effect of which is observable in other of their physical and chemical properties. Thus the second and fourth fractions are believed to be V and IV respectively, i.e. the *para-* and *ortho-* rearrangement products respectively.

Fraction No. 4 also gave the impression of not being homogeneous, but to consist of a small amount of a very bright yellow material, mixed with a large amount of a white substance. (On a preparative plate, this fourth fraction was partially resolved into two components.) By analogy with the rearrangement of phenyl benzoate in the presence of two molar proportions of catalyst,[2] one would expect to find the products resulting from acylation of the solvent, viz. II and III (see earlier). However, these had not so far been detected.

Gas–liquid chromatography. A sample of the reaction products was submitted to GLC analysis, using the equipment referred to previously,[2] but with a 1′-column containing 5% "Embaphase" silicone oil on acid-washed 60–100 mesh kieselguhr ("Embacel") as solid support. The column was operated at 206° (using tetralin as heating liquid) and a carrier-gas inlet pressure of 4 lb, with on-column injection of samples. The chromatogram of the above-mentioned sample showed three peaks: two were partially resolved, and sharp, with retention times of 7 and 9 min, (the material with the higher retention time being present in very much greater quantity than the other); the third peak was badly distorted, and had a retention time of ca. 55 min. Silylation[2] of the reaction mixture, followed by chromatography of the products, showed that the first two peaks were unaffected, whilst the third substance was converted to material with a higher retention time still (ca. 75 min). It was considered that the first two peaks were the *ortho-* and *para-* chloroketones (II and III) respectively, and that the third peak was the *ortho*-hydroxyketone (IV). When authentic samples of the chloroketones were chromatographed under the same conditions, they had the same retention times as the two constituents of the reaction products suspected of being these ketones. (This, of course, is not conclusive proof of the identity of the reaction products.)

The fourth fraction from the preparative plate (above) also showed the presence of the materials with retention times of 7, 9, and 55 min, and the amount of substance with the retention time of 55 min was quite small. The principal constituent of this fraction was the substance with the retention time of 9 min, i.e. the suspected III.

On an alumina plate, with EtOH as solvent, the fourth fraction (above (I) was resolved into two parts. The yellow material remained near the origin, whilst the white product travelled up the plate. It was not possible to separate a synthetic mixture of the two chloroketones by preparative layer chromatography, although a partial separation, (without proper identification), was achieved on the analytical scale.

A synthetic mixture of II and III could be reasonably well separated by extraction with cold alcohol, in which II dissolves quite readily, whilst III is only sparingly soluble. The progress of the separation is easily followed by GLC as above.

(With the column and operating conditions (described in Part I[2]) normally used for the work on phenyl benzoate, 4-hydroxybiphenyl had originally been identified as a reaction product. A sample of the rearrangement product mixture showed, when chromatographed, a peak with the same retention time as authentic 4-hydroxybiphenyl. When a sample of the reaction product was silylated,[2] and rechromatographed, the above peak disappeared, and was replaced by one having the same retention time as authentic 4-trimethylsilyloxybiphenyl.) All the chromatograms relevant to the above work are shown in Ref. 1.

Column chromatography. The ester (0·8422 g, 0·0024 mole) was mixed with chlorobenzene (5 ml) and largely dissolved by warming. A molal soln of $AlBr_3$ in chlorobenzene (containing 1·2871 g, 0·00483 mole catalyst, in 5·1229 g solvent) was added, and the whole soln heated at 110° for 4 hr. The reaction mixture was hydrolysed in the usual way, filtered, (see below), and the aqueous mixture extracted thoroughly with $CHCl_3$. The solvent layer was washed and dried in the usual way, and the solvent evaporated. (When the reaction mixture is hydrolysed, a solid product separates. This is mainly, if not entirely, unchanged ester, which is not very soluble in chlorobenzene. The other reaction products are more soluble in chlorobenzene. and in cold $CHCl_3$, than the ester, and if the residue from the filtration is rinsed briefly with $CHCl_3$, and the washings are added to the filtrate, the ester has been effectively separated from the other reaction products, avoiding complications later in the analysis of the reaction products. This process is even more useful in the 1 : 1 rearrangement reaction, (see below), where more unchanged ester is present in the reaction products).

A small portion of the residue was redissolved in the minimum amount of $CHCl_3$, and applied to the top of an alumina column, c. 1" × 8". The *ortho*-rearrangement product (see below) was adsorbed as a bright yellow band at the top of the column, which was then eluted with EtOH. The yellow band spread gradually down the column, but elution was stopped before the hydroxyketone reached the bottom of the column. The eluate was submitted to GLC, and found to contain the substances with retention times of 7 and 9 min, (see above).

The eluate was evaporated to dryness, then dissolved in a little $CHCl_3$, and shaken with dil NaOH aq, to remove any 4-hydroxybiphenyl which might also have been eluted. The $CHCl_3$ solution was washed with a little water, dried, and the solvent removed. The residue was powdered, and extracted 3 times with small quantities of cold alcohol, the alcoholic extracts being pooled. The residue was recrystallized from a large volume of alcohol, and its m.p., and mixed m.p. with an authentic sample of 4-(4-chlorobenzoyl)-biphenyl, was 169°, (see synthetic work above). The IR absorption spectrum of the purified material was *identical with that of the authentic chloroketone.*

The combined ethanolic extracts (above) were concentrated to about half the volume, and, when the soln was cooled, a small amount of material crystallized, and was filtered off. GLC showed that this was more of the 4-chloroketone, and that the filtrate was almost entirely the suspected 2-chloroketone. The filtrate was evaporated to dryness. Careful recrystallization of the residue from aqueous MeOH gave a product, m.p. 91–92°, the mixed m.p. with an authentic sample of 4-(2-chlorobenzoyl)biphenyl being 92°, (see synthetic work above). The IR absorption spectrum of the purified material was identical with that of the authentic chloroketone.

Thus, the formation of the chloroketones which would result from acylation of the solvent chlorobenzene has been established in the reaction in which two molar proportions of catalyst per mole of ester are used.

The phenolic material was eluted from the column, using acidified alcohol, and the aqueous alcohol evaporated. However, when a sample of the residue was submitted to TLC as before, no material corresponding to the suspected *para*-rearrangement product, i.e. fraction No. 2, was found, nor was any indication of the presence of this substance found in the products of subsequent reactions.

Rearrangement reactions—the phenolic product

In an attempt to isolate the suspected *ortho*-rearrangement product, another rearrangement reaction was performed using only one molar proportion of catalyst per mole of ester. The ester (1·3940 g, 0·00398 mole) was mixed with a molal soln of $AlBr_3$ in chlorobenzene, (containing 1·0615 g, 0·00398 mole catalyst, dissolved in 3·9797 g chlorobenzene). Chlorobenzene (3 ml) was added, and the mixture heated at 110° for 6 hr. (A homogeneous soln of the reactants was rapidly obtained after the tube was immersed in the oil-bath.) The reaction mixture was hydrolysed in the normal way, the aqueous mixture was filtered to remove unchanged ester, and then extracted with $CHCl_3$. The $CHCl_3$ layer was washed with a little water and dried, and the solvent evaporated. GLC of the residue showed that the chloroketones resulting from reaction of the ester with the solvent were absent.

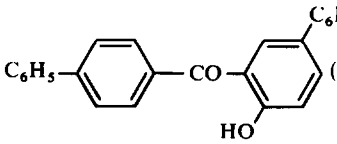
The residue was redissolved in a small amount of $CHCl_3$ and shaken with $NaHCO_3$ aq, to convert any 4-biphenylcarboxylic acid, which might be present, to its Na salt. The $CHCl_3$ layer was then washed with water, dried, and the solvent was evaporated. The residue was dissolved in boiling EtOH, giving a yellow soln. A yellow solid formed on cooling the soln, and more of this material was obtained from the mother liquor. (4-Hydroxybiphenyl is readily soluble in alcohol, and did not interfere with the isolation of the yellow product; apart from which, less of the 4-hydroxybiphenyl is formed under the conditions of the above rearrangement than when two molar proportions of catalyst are used per mole of ester).

The yellow solid had a retention time of ca. 55 min when submitted to GLC under the conditions used previously (see earlier). TLC showed that the substance was homogeneous, and no indication of the presence of the suspected *para*-rearrangement product was found.

Recrystallization of the product from EtOH gave bright yellow crystals, m.p. 135°. (Found: C, 85·7; H, 5·2; O, 9·3; mol. wt. (Rast) 338; $C_{25}H_{18}O_2$ requires: C, 85·7; H, 5·2; O, 9·1≈ ; mol. wt. 350·4).

Thus, on the basis of its mode of formation, its chemical behaviour, and the physico-chemical properties exhibited during its separation, this compound is identified as the hydroxyketone *4′,5-diphenyl-2-hydroxy-*

benzophenone



(IV); λ_{max}^{EtOH} 249 nm, $E_{1\,cm}^{1\,\%}$ 1025; λ_{min}^{EtOH}, 228 nm, $E_{1\,cm}^{1\,\%}$ 731; $\pi_{max}^{N\cdot 10\ NaOH}$ 288, 405 nm, $E_{1\,cm}^{1\,\%}$ 1035, 115; $\pi_{min}^{N\cdot 10\ NaOH}$ 244, 354 nm, $E_{1\,cm}^{1\,\%}$ 450, 50; ν_{max}^{KBr} 1629, 1477, 1334, 1220, 1006, 948, 764, 698 cm^{-1}.

A quantitative study of the rearrangement would be difficult, as the reaction products are not all equally amenable to GLC analysis, and the reactions themselves are complicated by the low solubility of the ester in chlorobenzene. The use of large volumes of chlorobenzene to dissolve the ester is not a satisfactory solution, as this means that very dilute solns of the reactants are being used; nor is it a satisfactory alternative to heat the solid ester with the catalyst soln. Although the ester is very much more soluble under these conditions, it is questionable how reproducible (quantitatively) such an approach would be.

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