878. *Intermediates in Allylic Rearrangements. Part II.*[1] *Rates and Mechanism of Exchange and Rearrangement in* 1- *and* 3-*Phenylallyl Benzoate.*

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The isomerisation of 1- to 3-phenylallyl benzoate in chlorobenzene is of first order in ester, is unaffected by added pyridine, and shows linear catalysis with added benzoic acid. The overall rates of loss of ^{18}O from labelled benzoic acid or saline benzoate during the rearrangement of the 1-ester approximate to the isomerisation rates, while under similar conditions the rates of isotopic exchange with the 3-ester are negligible. The loss of tracer from benzoic acid is accounted for by exchange taking place during the rearrangement of the 1-ester and leading to isotopic enrichment into the 1- and the 3-position, *i.e.*, with and without rearrangement.

The rate of production of ^{18}O-labelled 3-ester from normal 1-ester and labelled saline benzoate is only 70—75% of the isomerisation rate, so that about 25—30% of the isomerisation proceeds with no isotopic exchange. The rate at which tracer is introduced into the 1-ester is about 15—20% of the isomerisation rate. An explanation in terms of ion-pair intermediates is proposed.

The isomerisation of 1- to 3-phenylallyl *p*-nitrobenzoate, in the absence of added acid, in chlorobenzene, is a unimolecular process (see Part I) which may in principle be inter- or intra-molecular. The present investigation attempts to distinguish between these alternatives with the help of ^{18}O isotopic tracer experiments. The corresponding allylic benzoates were used because partial separation from a mixture containing the two isomers and subsequent pyrolysis proved to be experimentally easier. An additional advantage is that the problem of a possible dilution of ^{18}O derived from the carboxylic group by the normal oxygen atoms of the nitro-group, during the high-temperature pyrolysis which precedes the mass-spectrometric analysis, does not arise.

As for *p*-nitrobenzoates,[1] the marked difference in ultraviolet light absorption of 1- and 3-phenylallyl benzoate made it convenient to follow the rearrangement spectrophotometrically. Measurements carried out on synthetic mixtures in absolute ethyl alcohol show that the compounds behave as independently absorbing mixtures. Optical-density

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[1] Part I, preceding paper.

measurements were carried out in the region 240—255 mμ, and the values at 250 mμ were used for calculating first-order rate coefficients. In some cases these were checked against values calculated from measurements at other convenient wavelengths, and the agreement was good. The rearrangement of 1- to 3-phenylallyl benzoate in dry chlorobenzene at 155·5° gives good first-order rate coefficients which are practically identical for a variation of 1 : 1000 in the initial 1-ester concentration (see Table 1).

TABLE 1. *First-order rate coefficients k_1 (in sec.$^{-1}$) for the rearrangement of* 1-*phenylallyl benzoate* (Ph·CO$_2$R) *in chlorobenzene at* 155·5°, *with and without added pyridine* (P).

10^3[Ph·CO$_2$R]	0·35	3·5	35	350
10^6k_1	0·99	1·02	0·99	1·00

A partly isomerised sample containing initially 15·6% of 3-phenylallyl benzoate gives 10^6k_1 = 0·99 sec.$^{-1}$.

[Ph·CO$_2$R] = 0·035M

[P]	0·02	0·045	0·103
10^6k_1	1·00	1·00	1·08

The amount of benzoic acid produced under kinetic conditions during the first 20% of reaction was too small to be detected. The rate of neutral rearrangement of 1-phenylallyl benzoate in chlorobenzene at 155·5° is 11·6 times less than the rate for the corresponding *p*-nitrobenzoate. This result accords with what would be expected on the basis of Burton and Ingold's theory,[2] *i.e.*, that the ease of rearrangement increases in the order of stability of the anion. This order is indicated, in turn, by the strength of the corresponding acids.

Added Pyridine.—Pyridine in concentration up to 0·045M (Table 1) had no observable effect on the isomerisation rate. This concentration was 1·3 times larger than that of 1-isomer originally introduced, and therefore overwhelmingly larger than the traces of acid which might be formed during the isomerisation. These observations support the value given in the previous section for the rate of neutral isomerisation. The relatively negligible increase in rate observed with 0·103M-pyridine shows that a bimolecular attack with rearrangement, an S_N2' reaction, does not take place to any kinetically significant extent at these concentrations.

Added Benzoic Acid.—The addition of benzoic acid catalyses the rearrangement (see Table 2). The catalysis is linear with respect to stoicheiometric acid concentration. The overall first-order rate coefficient, k_1^{R}, can be expressed by the equation: $k_1^{\mathrm{R}} = k_0^{\mathrm{R}} + k^{\mathrm{R}}_{\mathrm{Ph\cdot CO_2H}}$[Ph·CO$_2$H], where k_0^{R} is the first-order rate coefficient for neutral rearrangement ($10^6k_0^{\mathrm{R}} = 0{\cdot}99$ sec.$^{-1}$ at 155·5°), and $k^{\mathrm{R}}_{\mathrm{Ph\cdot CO_2H}}$ is the catalytic coefficient for benzoic acid ($10^6k^{\mathrm{R}}_{\mathrm{Ph\cdot CO_2H}} = 34{\cdot}4$ l. mole^{-1} sec.$^{-1}$ at 155·5°).

Exchange with ^{18}O-Benzoic Acid.—When 1-phenylallyl benzoate is heated in the presence of ^{18}O-benzoic acid in chlorobenzene at 155·5°, the acid recovered at various intervals shows a steady diminution of its ^{18}O content. The amount of acid was shown to remain constant throughout the various heating periods, thereby excluding any decomposition of the ester to 1-phenylallene and benzoic acid[3] of natural isotopic abundance. The ^{18}O content found in the mixture of isomers corresponds practically quantitatively to the isotopic dilution found in the acid, proving that isotopic exchange takes place. On the other hand, when the rearranged isomer, the 3-phenylallyl benzoate, is heated with ^{18}O-labelled benzoic acid for periods up to 120 hr. at 155·5° there is practically no isotopic dilution of the acid [*e.g.*, heating 0·198M-3-phenylallyl benzoate with ^{18}O-enriched 0·224M-benzoic acid for 0, 72, 96, and 120 hr. gave values of β′ (^{18}O atoms % excess above normal) = 1·69, 1·70, 1·68, and 1·68, respectively]. The observed exchange with 1-phenylallyl benzoate must therefore take place either before or during rearrangement. The rates of isotopic equilibration between enriched benzoic acid and 1-phenylallyl benzoate of normal abundance were determined for a given ester concentration and varying acid concentration

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[2] Burton and Ingold, *J.*, 1928, 904.

[3] Braude, *Ann. Reports*, 1949, **46**, 125; *Quart. Reviews*, 1950, **4**, 404.

in chlorobenzene at 155·5°. Under these conditions the rearranged isomer can undergo only a negligible amount of isotopic exchange after formation. First-order rate coefficients for exchange, k_1^{E}, are therefore calculated with respect to 1-phenylallyl benzoate left after various periods of heating. The results are given in Table 2.

TABLE 2. *First-order rate coefficients of rearrangement* (k_1^{R} *in* sec.$^{-1}$) *and exchange* (k_1^{E} *in* sec.$^{-1}$) *for the reaction of* 1-*phenylallyl benzoate* (1-Ph·CO_2R) *with varying amounts of benzoic acid in chlorobenzene at* 155·5°.

[1-Ph·CO_2R] = 3·50 × 10^{-2}M

10^2[Ph·CO_2H]	0·00	0·90	1·80	2·90	4·42	5·00	6·20	6·63	7·00	7·48
$10^5 k_1^{\mathrm{R}}$	0·99	1·30	1·60	1·99	2·52	2·70	3·12	3·30	3·49	3·56
10^2[Ph·CO_2H]	1·99	4·42	6·20	7·48						
$10^6 k_1^{\mathrm{E}}$	1·5	2·3	2·7	3·1						

The first-order rate coefficient for overall exchange, k_1^{E}, can be expressed by the linear equation:

$$k_1^{\mathrm{E}} = k_0^{\mathrm{E}} + k^{\mathrm{E}}_{\mathrm{Ph\cdot CO_2H}}[\mathrm{Ph\cdot CO_2H}]$$

where the first-order rate coefficient for neutral exchange, k_0^{E}, is about 0·9 × 10^{-6} sec.$^{-1}$ and the catalytic coefficient for exchange with benzoic acid, $k^{\mathrm{E}}_{\mathrm{Ph\cdot CO_2H}}$, is about 0·29 × 10^{-4} l. mole^{-1} sec.$^{-1}$. The ratio of exchange to rearrangement rates under neutral conditions, $k_0^{\mathrm{E}}/k_0^{\mathrm{R}}$, is approximately 0·90, and the ratio of the corresponding catalytic coefficients, $k^{\mathrm{E}}_{\mathrm{Ph\cdot CO_2H}}/k^{\mathrm{R}}_{\mathrm{Ph\cdot CO_2H}}$, is approximately 0·85.

Added Tetra-n-*butylammonium* [^{18}O]*Benzoate.*—The importance of an S_N2' mechanism under non-acidic conditions was tested by studying the effect of a benzoate salt (tetra-*n*-butylammonium [^{18}O]benzoate) on the rates of isomerisation and exchange of 1-phenylallyl benzoate. At the high temperature used (155·5°) a relatively mobile equilibrium is set up between the salt and its decomposition products, *n*-butyl benzoate and tri-*n*-butylamine, so that any isotopic exchange between enriched benzoate salt ion-pairs and 1-phenylallyl benzoate of normal abundance is almost immediately equilibrated with *n*-butyl benzoate. Exchange rates were therefore evaluated on the assumption that all the ^{18}O initially present in the benzoate salt is readily available for isotopic equilibration.

The first-order rate coefficient for the isomerisation of 0·248M-1-phenylallyl benzoate in the presence of originally introduced 0·0887M-Ph·$CO_2NBu^n_4$ in chlorobenzene at 155·5° is 1·25 × 10^{-6} sec.$^{-1}$, the corresponding rate of exchange being 1·16 × 10^{-6} sec.$^{-1}$. Increases of about 25% in the corresponding rates of rearrangement and exchange in the presence of a relatively high salt concentration are compatible with ion-pair catalysis on a reaction whose transition state is more polar than its initial state. Any attempt by benzoate ion-pairs or tri-*n* butylamine to by-pass the rate-determining step of the unimolecular isomerisation (*e.g.*, *via* an S_N2' process) must be relatively small. The ratio of rate of exchange to that of rearrangement in the presence of benzoate salt ion-pairs (and possibly very minor Bu^n_3N catalysis) is 0·94, in good agreement with 0·9, the value obtained for the neutral region by extrapolation (previous section).

Isotopic Product Analysis.—1-Phenylallyl benzoate (0·0340M) of normal abundance and ^{18}O-enriched benzoic acid (0·062M) or tetra-*n*-butylammonium benzoate (0·0977M) were heated in chlorobenzene at 155·5° to 50% rearrangement. The mixture of isomers was partly separated into fractions rich in 1- and 3-phenylallyl benzoate. A portion of each fraction was quantitatively pyrolysed to benzoic acid, and the carbon dioxide obtained from the decomposition of the corresponding silver salts was mass-spectrometrically analysed. With both acid and benzoate salt the 1-isomer was found to contain about one-fifth * of the ^{18}O atoms excess above normal lost by the acid or salt, while the 3-isomer contained the remaining four-fifths. Account being taken of the ratio of the rate

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* This result is qualitatively similar to that obtained by Meisenheimer and Beutter (*Annalen*, 1934, **508**, 58) who found that 3-phenylallyl chloride in acetic acid produces a mixture of acetates containing 18% of the 1-phenylallyl compound.

[redacted]

rearrangement proceeds with isotopic exchange and about 25—30% must proceed intramolecularly.

Discussion of Mechanism.—(1) Isotopic exchange between acid (HX*) and ester (RX) *before* rearrangement followed by intramolecular isomerisation: [5]

$$\mathrm{RX} + \mathrm{HX^*} \rightleftharpoons \mathrm{RX^*} + \mathrm{HX}$$

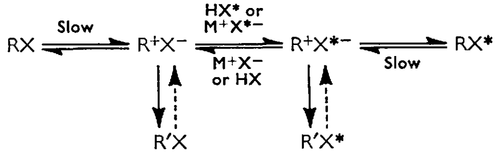
$$\mathrm{RX^*} \xrightarrow{S_{\mathrm{N}}\mathrm{i}} \mathrm{R'X^*}$$

is largely excluded by observations (*a*) and (*b*): (*a*) The total rate of exchange contains a relatively large zero-order component in benzoic acid (*e.g.*, $k_0^{\mathrm{E}} = 0{\cdot}9k_0^{\mathrm{R}}$), whereas this mechanism demands $k_0^{\mathrm{E}} = 0$. (*b*) The amount of enrichment in the 3-isomer is larger than that found in the unrearranged material. Also, contrary to the present results, the expected order of reactivity for $S_{\mathrm{N}}2$ reactions is primary > secondary.

(2) Isotopic exchange *after* rearrangement,[5] *viz.*,

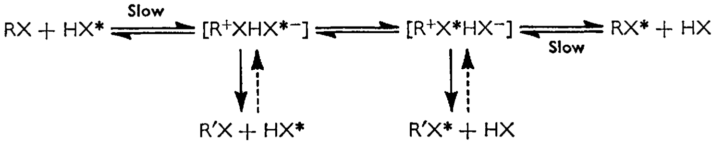
$$\mathrm{RX} \xrightarrow{S_{\mathrm{N}}\mathrm{i}} \mathrm{R'X}$$

$$\mathrm{R'X} + \mathrm{HX^*} \rightleftharpoons \mathrm{R'X^*} + \mathrm{HX}$$



The transition state for ion-pair collapse with rearrangement is only somewhat lower in energy than the corresponding transition state for ion-pair return with exchange, and bears no relation to the large energy of conjugation of a phenyl with a vinyl system which affects only the position of equilibrium.

The acid-catalysed component can be explained in terms of an electrophilic catalysis of the slow ionisation process:



That the acid-catalysed component is mechanistically similar to the neutral rearrangement is supported by the observation that the ratios k^{E}/k^{R} and $k^{E}_{Ph\cdot CO_2H}/k^{R}_{Ph\cdot CO_2H}$ are not very different, so that the electrophilic catalysis of ionisation does not affect the possible fates of the carbonium benzoate ion-pairs.

EXPERIMENTAL

Materials.—The purification of chlorobenzene, pyridine, and ethyl alcohol is described in the preceding paper.

1-Phenylallyl benzoate was prepared by adding to a cooled mixture of 1-phenylallyl alcohol [redacted] and pure 3-phenylallyl benzoate respectively, all at the same dilution. Sample runs are given below:

[1-Phenylallyl benzoate] = 0·035M; D_∞ (theor.) = 2·400.

t (min.)	0	1200	1500	2200	3000	3600	4800	6000	6600	8000	10,000
D	0·220	0·376	0·404	0·494	0·577	0·630	0·771	0·875	0·918	1·04	1·20
10^6k_1 (sec.$^{-1}$)...	—	1·02	0·98	1·01	0·99	0·96	1·01	0·99	0·97	0·98	0·995

[1-Phenylallyl benzoate] = 0·035M; [Pyridine] = 0·045M; D_∞ (theor.) = 1·450.

t (min.)	0	1500	3960	4500	6000	8000	9000	11,400	13,020
D	0·133	0·430	0·580	0·600	0·669	0·778	0·798	0·888	0·934
10^6k (sec.$^{-1}$)	—	0·955	1·03	0·995	0·982	1·045	0·985	1·00	0·983

Isotopic Measurements.—(a) *Analysis of* ^{18}O *content of benzoic acid.* Samples isolated at various times were pumped off, leaving a mixture of 1- and 3-phenylallyl benzoate and benzoic acid. The acid was extracted with insufficient alkali hydroxide (to ensure that no hydrolysis takes place). (Extraction with alkali hydrogen carbonate and then working up of the solution at pH 5—6 resulted in dilution of tracer, probably because of the difficulty of removing the last traces of carbon dioxide at this pH.) Silver benzoate was precipitated from sodium benzoate at pH ~5—6, washed with water, alcohol, and ether, dried at 110—120°, and kept in a vacuum-desiccator. Samples (10—30 mg.) were decarboxylated by heat *in vacuo*; the carbon dioxide entered the mass spectrometer through a trap at −80°. The isotopic abundance of the oxygen was measured by comparing masses 44 and 46 corresponding to $^{12}C^{16}O^{16}O$ and $^{12}C^{16}O^{18}O$. The contribution to mass 46 from $^{13}C^{16}O^{17}O$ was neglected. If R is the ratio of the peaks 44 and 46, the abundance in atoms % of ^{18}O is given by $\beta = 100/(2R + 1)$. The values quoted, β', are excess above normal in carbon dioxide. These measurements were carried out in a 180° mass spectrometer of 10 cm. radius of curvature and a single collector with voltage scanning.

Calculation of isotopic results. The change in the concentration of labelled benzoic acid [HX*] with time equals the total concentration of benzoic acid [HX] multiplied by the change in excess abundance with time:

$$-\mathrm{d}[\mathrm{HX}^*]/\mathrm{d}t = -[\mathrm{HX}]\,\mathrm{d}\beta'/\mathrm{d}t$$

Since the 3-isomer, once formed, undergoes only a negligible amount of exchange (see first example below) the change in concentration of labelled benzoic acid with time is proportional to the concentration of the 1-isomer left at time t and to the excess abundance at time t of the labelled benzoic acid:

$$-\mathrm{d}[\mathrm{HX}^*]/\mathrm{d}t = k_1^{\mathrm{E}}\,[\mathrm{RX}]_t\,\beta'_t$$

This leads to $-[\mathrm{HX}]\,\mathrm{d}\beta'/\mathrm{d}t = k_1^{\mathrm{E}}\,[\mathrm{RX}]_t\,\beta'_t$, where $[\mathrm{RX}]_t = [\mathrm{RX}]_0 \exp\,(-k_1^{\mathrm{R}}t)$, so that

$$-\int_0^t \mathrm{d}\beta'/\beta' = k_1^{\mathrm{E}}\,\frac{[\mathrm{RX}]_0}{[\mathrm{HX}]}\int_0^t \exp\,(-k_1^{\mathrm{R}}t)$$

or

$$2{\cdot}303\,\log_{10}\,(\beta_0'/\beta'_t) = k_1^{\mathrm{E}}\,\frac{[\mathrm{RX}]_0}{[\mathrm{HX}]}\,\frac{1 - \exp\,(-k_1^{\mathrm{R}}t)}{k_1^{\mathrm{R}}}$$

For calculating the isotopic results the above formula was used.

Examples:

[3-Phenylallyl benzoate] = 0·198M; [^{18}O]benzoic acid = 0·224M. Temp. 155·5°; chlorobenzene solution.

t (hr.)	0	72	96	120
β'	1·69	1·70	1·68	1·68

[1-Phenylallyl benzoate] = 0·035M; β'_0 (benzoic acid) = 1·92.

$10^2[\mathrm{Ph{\cdot}CO_2H}]$	1·99	4·42	6·20	7·48
t (min.)	1680	1500	1200	1200
β'_t	1·486	1·654	1·733	1·75
$1 - \exp\,(-k^{\mathrm{R}}t)$	0·154	0·201	0·200	0·226
$10^6k_1^{\mathrm{E}}$ (sec.$^{-1}$)	1·5	2·3	2·7	3·1

(b) *Analysis of* ^{18}O *content of the isomeric esters.* 1- and 3-Phenylallyl benzoate were converted into carbon dioxide in two steps. The first step was the virtually quantitative [12, 13] pyrolysis of the esters at 600° in a stream of purified, oxygen-free, dry nitrogen into benzoic acid and a mixture of unsaturated hydrocarbons, a pyrolysing unit being used similar to that employed by Bender.[13] The decomposition products collected in the liquid-air trap appeared to be a mixture of hydrocarbons and benzoic acid. The second step consisted in preparing and decarboxylating silver benzoate (see above).

The reliability of this method was tested as follows: 1-Phenylallyl benzoate (0·576M) and labelled benzoic acid (0·484M) were heated in chlorobenzene until the extinction coefficient at 250 mμ of the mixed isomers rose from 2080 to 17,700. During the same period the enrichment of benzoic acid in ^{18}O atoms % excess above normal, β', decreased from 1·96 to 1·156. After extraction of the benzoic acid, the purified ester mixture (ε 17,700) was pyrolysed ($\beta' = 0{\cdot}662$). The expected enrichment $\beta' = (1{\cdot}96 - 1{\cdot}156)0{\cdot}484/0{\cdot}576 = 0{\cdot}674$.

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[12] Biltger and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 823.

[13] Bender, *ibid.*, 1951, **73**, 1626.