877. *Intermediates in Allylic Rearrangements. Part I. The Anionotropy of* 1- *and* 3-*Phenylallyl* p-*Nitrobenzoate.*

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A detailed kinetic investigation of the anionotropic change of 1- to 3-phenylallyl *p*-nitrobenzoate in chlorobenzene at 155·5° is described. The marked difference in ultraviolet light absorption of the two esters made it convenient to follow the isomerisation spectrophotometrically. The rearrangement proceeds to more than 98% completion, is of first order in the ester and is subject to only a mild catalysis by added *p*-nitrobenzoic acid: this catalysis varies linearly with the stoicheiometric proportion of the acid.

Pyridine and *p*-nitrobenzoate salt in concentrations up to 4×10^{-3}M have no effect on the rate of isomerisation, and it is concluded that the isomerisation rate in the absence of any added acid is a purely unimolecular process. The direct proportionality between the acid-catalysed part and the stoicheiometric acid concentration indicates catalysis by monomeric *p*-nitrobenzoic acid molecules.

The general study indicated in the serial title is here begun with two papers on the kinetics of allylic rearrangements in chlorobenzene as solvent. The reaction chosen for investigation is the thermal isomerisation of 1- to 3-phenylallyl esters, which has been extensively investigated [1-4] in various solvents, found to proceed substantially to completion, and to be catalysed by acids. The relative importance of acid-catalysis was far from clear since the rearrangement of 1- to 3-phenylallyl *p*-nitrobenzoate which proceeds in the absence of any externally added acid has been described as being caused entirely,[4a] or at least largely,[4b] by a small amount of *p*-nitrobenzoic acid eliminated from the 1-ester on heating. As these observations were held to invalidate previous conclusions concerning the mechanism by which such isomerisations proceed,[3a,3b] it was important to try to establish unambiguously the existence or otherwise of a neutral isomerisation and its molecularity, as well as the magnitude and the kinetic order of the *p*-nitrobenzoic acid-catalysed reaction. These problems are discussed in the present paper; the nature of the reaction intermediates involved in the isomerisation is considered in Part II.

It is found that surface catalysis is negligible, as rates are practically unaffected by adding crushed glass or packing the reaction tubes with glass wool. The effect of oxygen is also negligible inasmuch as the reaction mixtures sealed in air with exclusion of moisture give practically the same rate as those sealed under dry nitrogen or " oxygen-free " dry nitrogen. The isomerisation rate is also unaffected by the amount of " free " space left above the liquid within the limits tested, *i.e.*, 20—60% of the volume of the reaction tube.

During the isomerisation of 1-phenylallyl *p*-nitrobenzoate in dry chlorobenzene minute quantities of *p*-nitrobenzoic acid are produced. The amount seems to depend on the ester concentration [RX] and on the heating period (see below):

[RX] (mole l.$^{-1}$)	[HX] (mole l.$^{-1}$) Isomerisation (%)		
	25	50	95
0·00312	$>10^{-6}$	—	$\sim 2 \cdot 7 \times 10^{-6}$
0·0312	$2 \cdot 2 \times 10^{-6}$	6×10^{-6}	4×10^{-5}
0·312	2×10^{-5}	5×10^{-5}	3×10^{-4}

However, even when the initial concentration of 1-ester is as high as 0·312M the amount of acid present during most of the isomerisation is too small to have a detectable effect

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[1] (*a*) Burton and Ingold, *J.*, 1928, 904; (*b*) Burton, *ibid.*, p. 1650; (*c*) *idem*, *J.*, 1934, 1268.

[2] Meisenheimer, Schmidt, and Schafer, *Annalen*, 1933, **501**, 131.

[3] (*a*) Catchpole and Hughes, *J.*, 1948, 1; (*b*) Catchpole, Hughes, and Ingold, *ibid.*, p. 8.

[4] (*a*) Braude, *Ann. Reports*, 1949, **46**, 125; *Quart. Rev.*, 1950, **4**, 404; (*b*) Braude, Turner, and Waight, *Nature*, 1954, **173**, 863 (Erratum, p. 1075).

on the rate (see Table 2). Accordingly the isomerisation reaction is not autocatalytic, as can be judged from the constancy in the first-order rate coefficients up to 85% isomerisation (see p. 4323).

The order with respect to 1-phenylallyl *p*-nitrobenzoate is unity. This is illustrated by the constancy in the first-order rate coefficients at various ester concentrations (Table 1). The test here illustrated is for a range of 1 : 1540 of 1-phenylallyl *p*-nitrobenzoate concentrations, and agrees with similar observations by Meisenheimer, Schmidt, and Schafer [2] for solutions in ether and pentane. The present results show that the importance of acid-catalysis has been overestimated; [4a, 4b] for, if *p*-nitrobenzoic acid had indeed been essential for rearrangement, the first-order rate coefficients should have increased both within any one run, and with the initial 1-phenylallyl *p*-nitrobenzoate concentration, the former conclusion arising because longer periods of heating increase the amount of acid produced, and the latter because, acording to the proposed elimination scheme,[4a] the amount of acid eliminated must be proportional to the initial concentration of 1-phenylallyl *p*-nitrobenzoate used.

TABLE 1. *First-order rate coefficients for the rearrangement of* 1-*phenylallyl* p-*nitrobenzoate* (RX) *in chlorobenzene at* 155·5°.

[RX] (M)	$2{\cdot}02 \times 10^{-4}$	$2{\cdot}02 \times 10^{-3}$	$2{\cdot}38 \times 10^{-3}$	$1{\cdot}17 \times 10^{-2}$
10^5k_1 (sec.$^{-1}$)	1·17	1·15	1·16	1·16
[RX] (M)	$2{\cdot}38 \times 10^{-2}$	$4{\cdot}44 \times 10^{-2}$	$1{\cdot}02 \times 10^{-1}$	$3{\cdot}12 \times 10^{-1}$
10^5k_1 (sec.$^{-1}$)	1·15	1·15	1·18	1·17

Added p-*Nitrobenzoic Acid.*—By using low concentrations of 1-phenylallyl *p*-nitrobenzoate we can investigate the effect of added *p*-nitrobenzoic acid in concentrations overwhelmingly large relative to the minute traces which may be formed on heating the esters in dry chlorobenzene. For a suitable concentration ($2{\cdot}02 \times 10^{-4}$M) it can be shown that, even when the ratio of added *p*-nitrobenzoic acid to the initial concentration of 1-phenylallyl *p*-nitrobenzoate is 2·2 : 1, there is practically no increase in the isomerisation rate. In chlorobenzene, saturated at room temperature with *p*-nitrobenzoic acid, the isomerisation rate increases at 155·5° by only about 16%, *i.e.*, from $10^5k_1 = 1{\cdot}16$ to $10^5k_1 = 1{\cdot}35$ sec.$^{-1}$ In order to extend the acid-catalysed region further, solubility measurements were carried out in chlorobenzene which indicate that quantities up to about 0·48M in *p*-nitrobenzoic acid can be dissolved at 155·5° In the present investigation, however, quantities were limited to 0·048M-*p*-nitrobenzoic acid since the high rate of dissolution of these lower concentrations (in less than 2 min. in sealed ampoules) ensured a high degree of reproducibility and a completely homogeneous acid-catalysis. Good first-order rate coefficients were obtained throughout any given run (see Table 2). For the presence of

TABLE 2. *First-order rate coefficients of the rearrangement of* 1-*phenylallyl* p-*nitrobenzoate* (RX) *with added* p-*nitrobenzoic acid* (HX) *in chlorobenzene at* 155·5°.

	$[RX] = 2{\cdot}02 \times 10^{-4}$M				$[RX] = 2{\cdot}02 \times 10^{-3}$M				
10^4[HX]	—	0·86	2·15	4·3	—	0·0287	0·718	2·15	4·31
10^5k_1 (sec.$^{-1}$)	1·17	1·14	1·15	1·16	1·15	1·17	1·18	1·18	1·15

	$[RX] = 4{\cdot}44 \times 10^{-2}$M										
10^2[HX]	—	0·04	0·07	0·21	0·30	0·50	0·96	1·40	2·10	3·30	4·57
10^5k_1 (sec.$^{-1}$)	1·16	1·16	1·20	1·30	1·36	1·49	1·78	2·08	2·53	3·34	4·19

	$[RX] = 1{\cdot}024 \times 10^{-1}$M							
10^2[HX]	—	0·23	0·43	0·62	0·71	0·86	1·05	1·20
10^5k_1 (sec.$^{-1}$)	1·15	1·32	1·37	1·57	1·63	1·72	1·86	1·95
10^2[HX]	1·38	1·60	1·89	2·46	2·63	3·22	3·56	3·99
10^5k_1 (sec.$^{-1}$)	2·06	2·22	2·42	2·78	2·88	3·28	3·52	3·80

	$[RX] = 3{\cdot}12 \times 10^{-1}$M							
10^2[HX]	—	0·12	0·15	0·26	0·45	0·60	0·70	1·2
10^5k_1 (sec.$^{-1}$)	1·16	1·24	1·25	1·32	1·46	1·54	1·62	1·94
10^2[HX]	1·37	1·50	1·71	2·08	2·60	3·40	3·80	4·27
10^5k_1 (sec.$^{-1}$)	2·09	2·15	2·29	2·54	2·84	3·40	3·68	4·02

added *p*-nitrobenzoic acid the overall first-order rate coefficient, k_1, can be expressed in the form $k_1 = k_0 + k_{\text{HX}}[\text{HX}]$, where k_0 is the first-order rate coefficient of the neutral rearrangement, k_{HX} is the catalytic coefficient, and [HX] the stoicheiometric acid concentration.

The values obtained for k_0 and k_{HX} from the different initial concentrations of 1-ester are practically the same, *viz.*, $10^5 k_0 = 1{\cdot}16 \pm 0{\cdot}02$ sec.$^{-1}$ and $k_{\text{HX}} = 6{\cdot}62 \times 10^{-4}$ l. sec.$^{-1}$ mole^{-1}. It should be noted that the k_0 value obtained on extrapolation to zero acid is practically identical with that independently established by following the isomerisation in the absence of any external added acid.

The linear form of the catalysis shows that the *p*-nitrobenzoic acid molecule is the acting catalyst, catalysis by species arising from dissociated or associated acid molecules being negligible. Electrophilic catalysis by one acid molecule followed by, or synchronous with, an attack by a second acid molecule at the 3-position is also ruled out. The observed linear catalysis is consistent with either an electrophilic catalysis of ionisation by acid molecules, as previously encountered in similar aprotic media,[5b] or with a hydrogen-bonded * S_N2' mechanism, in which one and the same molecule is bonded by hydrogen to the leaving group and attacks the 3-position of the allylic system. The distinction between these alternatives necessitates a comparison between rearrangement and isotopic exchange rates, and is discussed in the following paper (Part II).

Added Pyridine.—The isomerisation rate, as determined in chlorobenzene in the presence of added pyridine, is practically identical with that in the absence of any additive. The pyridine concentration is chosen to be small, yet comparable with the initial ester concentration, and therefore overwhelmingly large compared with the traces of *p*-nitrobenzoic acid formed during the isomerisation. Good first-order coefficients are obtained in any one run, and are independent of the pyridine concentration (see Table 3). In addition to their bearing on the problem of the neutral rate of isomerisation, these results indicate that, within the concentration range used, there is no bimolecular attack by pyridine at the 1- or 3-position of the 1-phenylallyl *p*-nitrobenzoate molecule with subsequent fast decomposition to form 3-phenylallyl *p*-nitrobenzoate and regenerate pyridine. The formation of a pyridinium intermediate following a unimolecular slow ionisation of the 1-ester is not, however, excluded, but limitations are imposed on such a process, for formation of the pyridinium intermediate is governed by the same rate-determining step as the neutral isomerisation, and its breakdown must be fast. Pyridine thus does not provide a by-pass to the rate-determining step of the normal unimolecular isomerisation.

TABLE 3. *First-order rate coefficients of the rearrangement of* 1-*phenylallyl* p-*nitrobenzoate* (RX) *in the presence of added pyridine* (P) *and tetra*-n-*butylammonium* p-*nitrobenzoate* ($\text{Bu}^{\text{n}}_4\text{NX}$) *and chlorobenzene at* 155·5°.

	[RX] = 2·02 × 10^{-3}M					[RX] = 2·38 × 10^{-3}M			
10^3[P]	—	1·50	1·82	3·65	$10^3[\text{Bu}^{\text{n}}_4\text{NX}]$	—	1·51	3·02	4·53
$10^5 k_1$ (sec.$^{-1}$)	1·16	1·15	1·17	1·16	$10^5 k_1$ (sec.$^{-1}$)	1·15	1·15	1·17	1·16

*Added Tetra-*n-*butylammonium* p-*Nitrobenzoate.*—Catchpole and Hughes [3] have shown that, in methyl cyanide and acetic anhydride, the effect of added lithium *p*-nitrobenzoate, though considerable, is no greater than can be accounted for as an activity effect of an added salt on a reaction whose rate is controlled by an ionic dissociation. The same test is applied in the present investigation but, since alkali and lower tetra-alkylammonium-*p*-nitrobenzoates are practically insoluble in chlorobenzene, tetra-*n*-butylammonium *p*-nitrobenzoate had to be employed. Unfortunately, at the high temperature used for

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* A hydrogen-bonded S_N2' rather than a simple S_N2' mechanism must be suggested because stronger nucleophilic agents ($\text{Bu}^{\text{n}}_3\text{N}$, C_5H_5N, and $p\text{-NO}_2{\cdot}C_6H_4{\cdot}CO_2NBu^{\text{n}}_4$) have practically no effect on the isomerisation rate.

[5] (*a*) Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206; (*b*) Hughes, Ingold, Mok, and Pocker, *ibid.*, p. 1238.

the isomerisation, ~30% decomposition sets in to produce tri-*n*-butylamine and *n*-butyl *p*-nitrobenzoate. Since, however, the rearrangement rate is practically unaffected by the added salt, one has to conclude that neither tetra-*n*-butylammonium *p*-nitrobenzoate ion-pairs nor tri-*n*-butylamine, at the concentrations used, attacks the 3-position with consequent rearrangement. Mechanism S_N2' is thus not operative under the conditions used, because one cannot by-pass the rate-determining step of the normal unimolecular isomerisation.

EXPERIMENTAL

Materials.—Chlorobenzene (B.D.H.), unless otherwise indicated, was dried ($CaCl_2$) for long periods, and fractionated in an all-glass, helix-packed column of about 20 theoretical plates, head and tail fractions being rejected; the middle fraction, b. p. 131·5—132°, was used. Chlorobenzene, fractionated as above, after treatment with phosphoric oxide or anhydrous potassium carbonate, gave practically the same isomerisation rates:

Drying agent	$CaCl_2$	P_2O_5	K_2CO_3
10^5k_1 (sec.$^{-1}$)	1·15	1·16	1·15

Chlorobenzene, purified as above and heated for two weeks at 155·5°, shows no change in its ultraviolet absorption spectrum, and tests for traces of hydrogen chloride are negative. An isomerisation run performed in this chlorobenzene at 155·5° gave $10^5k_1 = 1·15$ sec.$^{-1}$.

Pyridine (B.D.H.) was dried by the method of Burgess and Kraus [6] and subjected to the same fractionation as above. The middle fraction, b. p. 115·5°, was used. Pyridine was also dried over, and twice fractionated from, freshly fused potassium hydroxide, with exclusion of moisture. First-order rate coefficients of the rearrangements of 1-phenylally *p*-nitrobenzoate ($2·02 \times 10^{-3}$) in the presence of pyridine ($1·5 \times 10^{-3}$M) purified by either method gave:

Purification method	Burgess and Kraus	Fused KOH
10^5k_1 (sec.$^{-1}$)	1·16	1·16

Commercial methyl alcohol was purified by Bjerrum and Zechmeister's method,[7] and had n_D^{25} 1·3271 (lit.,[8] 1·3271).

Commercial ethyl alcohol was dried by Lund and Bjerrum's method [9] and fractionated with exclusion of moisture under oxygen-free nitrogen. This product was superior tor measurements in the ultraviolet region to the one purified, with similar precautions, by Smith's or Manske's procedure.[10a, b]

1-Phenylallyl alcohol was prepared by reaction of phenylmagnesium bromide [from magnesium (24 g.) in ether (600 ml.)] with an ethereal solution (300 ml.) of freshly distilled acraldehyde (56 g.) during 1 hr. at about −10° and then for 3 hr. at −5°, in dry oxygen-free nitrogen. The mixture was decomposed with cold saturated aqueous ammonium chloride. The combined extracts were dried (K_2CO_3) and distilled from a trace of this carbonate. The middle fraction, b. p. 52°/0·2 mm., n_D^{25} 1·5393, was used. The head fraction contained some diphenyl (a side product from the decomposition of phenylmagnesium bromide), and the tail fraction traces of cinnamyl alcohol. The light absorption of the middle fraction (in absolute ethanol) had max. at 2525 and 2580 Å (ε 285 and 280, respectively).

3-Phenylallyl alcohol (B.D.H.) was fractionated (b. p. 130°/15 mm.) and the middle fraction used (m. p. 36°).

1-Phenylallyl p-*Nitrobenzoate.*—1-Phenylallyl alcohol (10 g.) in dry pyridine (10 ml.) was added to a mixture of freshly distilled *p*-nitrobenzoyl chloride (11·1 g.) in dry pyridine (20 ml.) at −10°. After 2 days at room temperature, the mixture was poured into aqueous sodium hydrogen carbonate. The ethereal extracts were washed with bicarbonate solution, then water, and crystallised alternately from absolute methyl alcohol and light petroleum (b. p. 60—80°); the product had m. p. 46° (Burton and Ingold [1a] give 45—46°; Meisenheimer, Schmidt, and Schafer [2] give 46·2°); a light absorption max. (in absolute ethanol) was at 2585 Å (ε 14,000).

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[6] Burgess and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 706.
[7] Bjerrum and Zechmeister, *Ber.*, 1923, **56**, 894.
[8] Hughes and Vernon, *J. Phys. Colloid Chem.*, 1952, **56**, 927.
[9] Lund and Bjerrum, *Ber.*, 1931, **64**, 211.
[10] (*a*) Smith, *J.*, 1927, 1288; (*b*) Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106.

3-Phenylallyl *p*-nitrobenzoate, prepared in a similar manner, and recrystallised alternately from ethyl alcohol and light petroleum (b. p. 60—80°), had m. p. 76·5° (Hill and Nason [11] give 78°; Burton and Ingold [1] give 77—78°; Meisenheimer, Schmidt, and Schafer [2] give 76·5°); in absolute ethyl alcohol it had $\lambda_{\text{max.}}$ 2550 Å (ε 30,500).

p-*Nitrobenzoic Acid.*—The B.D.H. product was crystallised twice from water and twice from benzene and dried (over P_2O_5) under a good vacuum.

Tetra-*n*-butylammonium *p*-nitrobenzoate was prepared by exact neutralisation of the hydroxide with the acid. After evaporation to dryness the product was dried for one week over P_2O_5 under reduced pressure, and recrystallised from dry benzene. The pale yellow crystals were dried for 5 days under $\sim 10^{-5}$ mm., a liquid-air finger trap being kept above the crystals.

Spectrophotometry.—The marked difference in ultraviolet light absorption of 1- and 3-phenylallyl *p*-nitrobenzoates makes it convenient to follow the isomerisation spectrophotometrically. The measurements were carried out in a Unicam Quartz Spectrophotometer Model S.P. 500. The 656·3 mμ line from the hydrogen lamp was used for calibration, and the photometric accuracy of the instrument was checked with potassium hydrogen phthalate solutions: it fell within the range reported by Ewing and Parsons.[12] The optical density was measured in absolute ethanol in which the two esters, with and without *p*-nitrobenzoic acid, were shown to behave as independently absorbing substances. The rearrangement in carefully purified chlorobenzene is almost free from side reactions as indicated by a >98% conversion into the thermodynamically stable isomer.

The extinction coefficient, when 1-phenylallyl *p*-nitrobenzoate is left to rearrange in chlorobenzene for 10 half-life times, is 98% of the corresponding value for pure 3-ester; when left for 20 half-life times it is only 96% of the theoretical value. Pure 3-phenylallyl *p*-nitrobenzoate on similar treatment shows a reduction of 2% and 4% respectively in its extinction coefficient, which is largely due to the polymerisation of the styryl system. The isomerisation itself seems, therefore, to be practically complete, and for this reason the extinction coefficient of pure 3-phenylallyl *p*-nitrobenzoate was used as " infinity " in calculating rate coefficients.

Kinetic Measurements.—The thermostat was kept at 155·5° ± 0·02°. All-glass apparatus was baked for a long time at 160° before work with chlorobenzene solutions. Known amounts of 1-phenylallyl *p*-nitrobenzoate, either alone or with reagent, were dissolved in chlorobenzene at room temperature, and aliquot parts enclosed in ampoules and heated in the thermostat for various times. After the heating, known amounts of the mixture were pipetted into a series of bulbs specially constructed for vacuum-work. The bulbs were connected through a series of traps to a vacuum-system, and the solvent was removed at room temperature. The residue was dissolved in pure absolute ethanol, and the optical density recorded in the range 240—260 mμ. Point-by-point extinction measurements were made at 0·5 mμ intervals. The dilution was adjusted so as to bring the value of the optical density at 255 mμ into the most accurate range of the spectrophotometer. When quantities of *p*-nitrobenzoic acid in excess of their solubility at room temperature were used, the acid was weighed directly into each ampoule, aliquot parts of 1-ester in chlorobenzene were added, and the sealed ampoules heated for various periods. On cooling, the acid which crystallised was separated, and from known aliquot portions of the filtrate the solvent was removed as described above. The amount of rearrangement was then evaluated after subtraction of the corresponding optical density of the *p*-nitrobenzoic acid present. The acid was determined for each point in the run. This actually provided a double check, since the amount of acid left in solution on cooling to room temperature was practically constant. Independent tests have shown that the esters present in solution were not absorbed by the crystallising acid.

In runs in which tetra-*n*-butylammonium *p*-nitrobenzoate was employed the amount of rearrangement was calculated after correction of the change in optical density for the independently determined increase which accompanies the partial decomposition:

$$p\text{-}NO_2\cdot C_6H_4\cdot CO_2NBu^n_4 \rightleftharpoons Bu^n_3N + p\text{-}NO_2\cdot C_6H_4\cdot CO_2Bu^n$$

The first-order rate coefficients (k_1 in sec.$^{-1}$) were calculated from the formula

$$k_1 = (2\cdot303/t)\log_{10}(D_\infty - D_0)/(D_\infty - D_t)$$

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[11] Hill and Nason, *J. Amer. Chem. Soc.*, 1924, **76**, 2236.

[12] Ewing and Parsons, *Analyt. Chem.*, 1948, **20** 423.

where D_0, D_t, and D_∞ are the optical densities at 255 mμ and refer to readings at kinetic zero, time *t*, and pure 3-phenylallyl *p*-nitrobenzoate respectively, all at the same dilution. A sample run is given below.

[1-Phenylallyl *p*-nitrobenzoate] = 1·01 × 10^{-3}M

t (min.)	0	150	300	450	600	750	900	1200	1500	1800	3000	4000
D (255 mμ)	0·276	0·310	0·338	0·366	0·390	0·413	0·429	0·466	0·493	0·514	0·570	0·589
Rearrangement (%)	0	10·19	18·55	26·95	35·2	71·0	45·8	56·8	65·0	85·2	88	93·6
$10^5 k_1$ (sec.$^{-1}$)	—	1·17	1·14	1·16	1·16	1·17	1·13	1·17	1·16	1·15	1·18	1·15

k_1 (mean) = 1·16 × 10^{-5} sec.$^{-1}$.

After 8 days at 155·5°: D (255 mμ) = 0·603 (*i.e.*, 98% of theoretical infinity)
,, 16 ,, ,, D (255 mμ) = 0·598 (*i.e.*, 96% ,, ,,)
Theoretical infinity: D (255 mμ) = 0·610

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