479. *Anionotropic Systems. Part V.* A Kinetic Investigation of the Rearrangement of 1-Phenylallyl Esters in Non-aqueous Solvents.*

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The kinetics of the anionotropic rearrangement of 1-phenylallyl *p*-nitrobenzoate in chlorobenzene and, less extensively, acetic anhydride have been investigated. The reaction is of the first order, has a finite rate in the initial absence of acid, and is accompanied by the formation of small amounts of *p*-nitrobenzoic acid. The rate is directly proportional to the concentration of added *p*-nitrobenzoic acid. The rearrangement is intramolecular with respect to added ionic bromide but in the presence of acetic acid cinnamyl acetate is formed. 1-Phenylallyl acetate and benzoate isomerize more slowly in chlorobenzene than the *p*-nitrobenzoate and the ease of migration of leaving groups is shown to be: hydroxyl < acetate < benzoate < *p*-nitrobenzoate ≪ chloride.

A technique is described for the determination of small amounts of water in chlorobenzene.

The rearrangement of 1-phenylallyl *p*-nitrobenzoate, $CH_2{:}CH{\cdot}CHPhX$ ($X = O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$), to *trans*-cinnamyl *p*-nitrobenzoate, $Ph{\cdot}CH{:}CH{\cdot}CH_2X$, has played a prominent part in the development of the theory of anionotropy. The reaction was first investigated by Burton [1] and by Meisenheimer and Schmidt,[2] and more recently has been re-examined by Catchpole and Hughes.[3] Our interest in it arose from a kinetic study [4] of the acid-catalyzed isomerization of allylic alcohols.

The reaction proceeds essentially to completion and since the two isomers have considerably different light absorption at 2535 Å the system is suitable for application of the spectrokinetic method previously used.[4] Previous workers used a wide variety of organic solvents, but we have found only chlorobenzene to satisfy the necessary requirements of non-reactivity, thermal stability, and reasonable transparency to light of the appropriate

* Part IV, *J.*, 1953, 3138.

[1] Burton, *J.*, 1928, 1650; 1934, 1268.
[2] Meisenheimer and Schmidt, *Annalen*, 1933, **501**, 131.
[3] Catchpole and Hughes, *J.*, 1948, 1.
[4] Braude and Jones, *J.*, 1944, 436 *et seq.*; Braude, *Ann. Reports*, 1949, **46**, 114; *Quart. Rev.*, 1950, **4**, 404.

wavelength. A few runs were carried out with acetic anhydride as solvent but its reactivity rendered it unsuitable.

The reaction occurs at a reasonable rate in chlorobenzene at 130° and is kinetically of the first order with respect to ester, with an activation energy, derived from the limited data given in Table 1, of about 26 kcal./mole, confirming Meisenheimer and Schmidt's

TABLE 1. *Rearrangement of* 1-*phenylallyl* p-*nitrobenzoate in chlorobenzene containing acid. The effect of temperature.* (*Ester concn.*, 0·157 *mole/l.*).

Temp.	100°	100°	130°	130°
$[NO_2 \cdot C_6H_4 \cdot CO_2H]$ (mole/l.)	0·0021	0·0214	0·0032	0·0214
10^4k (min.$^{-1}$)	0·043	0·28	1·0	4·0

results.[2] The rate depends on the purity of the ester and of the solvent, and a side reaction affords *p*-nitrobenzoic acid, which can be extracted with water and estimated titrimetrically. A much larger quantity of *p*-nitrobenzoic anhydride is obtained from runs in acetic anhydride, probably produced by the reaction of the acid with the solvent. The elimination of *p*-nitrobenzoic acid, discussed below, was also noted by Meisenheimer and Schmidt, who claimed, however, that the addition of acid has little effect on the rate of rearrangement in ether although increasing it considerably in the absence of solvents. In chlorobenzene, however, addition of *p*-nitrobenzoic acid considerably increases the rate, and the first-order rate constant k is directly proportional to the acid concentration (Fig. 1). It was very difficult to obtain reproducible rate constants at acid concentrations less than 0·005M and reasonable values were only obtained by working with highly purified materials *in vacuo* to avoid, in particular, the presence of moisture and traces of acids. Under these conditions and in the initial absence of *p*-nitrobenzoic acid the rearrangement exhibits a finite rate which increases as the reaction proceeds, a consequence of the acid-producing reaction. This provides an unambiguous demonstration of a purely thermal anionotropic rearrangement of an allylic ester. Since the preliminary publication of this work [5] Goering and Silversmith [6] have shown that 5-methyl*cyclo*hex-2-enyl *p*-nitrobenzoate undergoes isomeric rearrangement, which is not catalysed by the *p*-nitrobenzoic acid produced, concurrently with solvolysis in aqueous acetone.

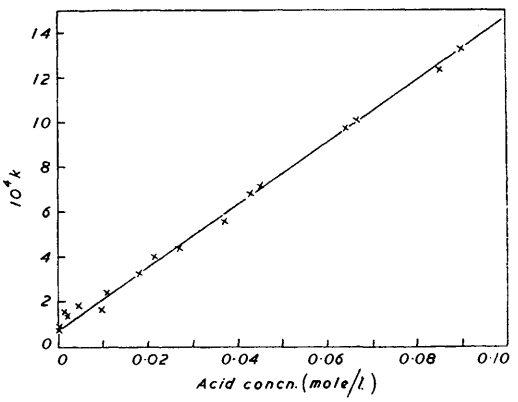


FIG. 1.

The simplest rate law fitting our results has the form:

$$\text{Rate} = k_1[\text{Ester}] + k_2[\text{Ester}][\text{Acid}]$$

i.e., the rearrangement involves a unimolecular process, $k_1 = 0{\cdot}78 \times 10^{-4}$ min.$^{-1}$, and a bimolecular process involving *p*-nitrobenzoic acid $k_2 = 1{\cdot}4 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$. Further experiments designed to elucidate the precise mechanism of these two reactions are reported in the following paper.

The effect of high concentrations of foreign and common (*p*-nitrobenzoate) anions has been investigated respectively by Burton [1] and Catchpole and Hughes.[3] Burton sought to prove complete ionization of the *p*-nitrobenzoate group by showing that some cinnamyl acetate is formed when the rearrangement is carried out in the presence of acetate ions.

[5] Braude, Turner, and Waight, *Nature*, 1954, **173**, 863.
[6] Goering and Silversmith, *J. Amer. Chem. Soc.*, 1955, **77**, 6249.

He later showed that this replacement does not occur after rearrangement. Catchpole and Hughes showed that the addition of lithium *p*-nitrobenzoate causes a small increase in rate which they attributed to a salt effect, indicating that bimolecular substitution with rearrangement (S_N2') by *p*-nitrobenzoate ions is unlikely. We have confirmed these semiquantitative results by observing that in the presence of lithium *p*-nitrobenzoate (0·116M) 10^4k is about 8·8 min.$^{-1}$ in acetic anhydride at 100° compared with 3·2 min.$^{-1}$ in the absence of the salt. However, in our opinion the interpretation of Burton's experiment is equivocal in view of the well-known tenacity with which the salt used, tetramethylammonium acetate, retains water or acetic acid of crystallization.[7] Acetic acid either already present in the salt or produced by hydrolysis of the solvent (acetic anhydride) may well be an important factor since cinnamyl acetate is also produced when the ester is heated in chlorobenzene containing acetic acid. Burton's result may have been due to direct reaction of acetic acid with the ester rather than to competition between free acetate and *p*-nitrobenzoate ions for the phenylallyl cation.

In an attempt to discover the effect of added anions in the absence of large amounts of free acid the rearrangement has been carried out in chlorobenzene in the presence of di*iso*pentylammonium bromide. No cinnamyl bromide was detected in the products, the sole effect of the salt being to increase the amount of *p*-nitrobenzoic acid formed and thus the rate of rearrangement. Under these conditions the rearrangement is thus essentially intramolecular. The effect of other anions such as *p*-nitrobenzoate has not been tested since it has not been possible to find a salt which is reasonably soluble in chlorobenzene and yet thermally stable. This failure is not surprising since the cation will be only weakly stabilized by solvating chlorobenzene molecules and the salt is thus likely to decompose to uncharged products, in the case of a quaternary ammonium compound to a tertiary amine and an alkyl ester, or olefin and carboxylic acid.

The Relative Mobility of Migrating Groups in Anionotropy.—Burton and Ingold's conclusion that mobility of a migrating group in an anionotropic system increases with its stability as an anion [8] has been widely accepted although not hitherto quantitatively investigated. Some rate measurements for the anionotropy of 1-phenylallyl alcohol and its acetate and benzoate in chlorobenzene are reported in Table 2. In view of the slowness of these reactions the reasonable assumption has been made that the kinetic features of the rearrangements of the acetate and benzoate are the same as for the *p*-nitrobenzoate, namely, that essentially pure cinnamyl isomers are produced by a first-order (with respect to ester) process and that the rates are directly proportional to acid concentration. It has also been assumed that the very slow increase in intensity of light absorption at 2510 Å of 1-phenylallyl alcohol in chlorobenzene is due to the formation of cinnamyl alcohol. As is well known, the anionotropy of alcohols is dependent on catalysis by proton donors [4] or Lewis acids,[9] and in the present case the acid catalyst is derived by slight decomposition, possibly hydrolysis, of the chlorobenzene.

TABLE 2. *Rearrangements of* 1-*phenylallyl compounds in chlorobenzene at* 130°.

Compound	Concn. (mole/l.)	Acid concn. (mole/l.)	10^4k (min.$^{-1}$)
Alcohol	0·332	~0·001	~0·015
Acetate	0·089	0·015	0·038
Benzoate	0·089	0·0013	0·14
p-Nitrobenzoate	0·157	0·0036	1·0

The ease of rearrangement is in the sequence: alcohol < acetate < benzoate < *p*-nitrobenzoate, *i.e.*, the order of stability of the leaving group as an anion, as claimed by Burton and Ingold. Although different amounts of acid are eliminated from each ester, the

[7] Collie and Lawson, *J.*, 1888, **53**, 625; Willstätter and Kahn, *Ber.*, 1902, **35**, 2757; Steigmann and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2540.
[8] Burton and Ingold, *J.*, 1928, 904.
[9] Braude and Gore, *Nature*, 1954, **173**, 1091.

differences between the rates recorded and the calculated uncatalysed rates are, for the acetate and benzoate, negligibly small (10^4k for the isomeric rearrangement of 1-phenylallyl chloride in chlorobenzene at 100° is 50 min.$^{-1}$, about a thousand times greater than the value for the *p*-nitrobenzoate under the same conditions [10]).

The Acid-elimination.—*p*-Nitrobenzoic acid is not continuously produced during rearrangement of the ester but appears to reach a constant concentration long before the rearrangement is complete. One of us suggested that the acid may arise from a 1 : 2-elimination to give phenylallene which polymerizes to the small amount of petroleum-insoluble tar obtained in about the same yield as the acid.[4] Elemental analyses and infrared spectra now indicate that this is not the case and that the material is mainly

TABLE 3.

State of chlorobenzene	H_2O concn. (mole/l.)	Acid concn. (mole/l.)
(*a*) Saturated with H_2O	0·032	0·007
(*b*) Dried and distilled, handled in air	0·0072—0·023	0·0015—0·0026
(*c*) Dried and distilled in sealed apparatus	0·001	0·0007—0·001

cinnamyl *p*-nitrobenzoate rendered insoluble in petroleum by a very small amount of tar. The acid probably arises by hydrolysis of the ester by small amounts of water present in the solvent, a correlation between the amount of acid produced and the amount of water present being evident from the results given in Table 3. The much larger amounts of acid produced from the fused ester are clearly unlikely to arise by hydrolysis, but could result from autoxidation, since aldehydes have been reported as by-products,[2] or by ionic polymerization as suggested for the decomposition of benzyl toluene-*p*-sulphonate.[11]

EXPERIMENTAL

Light-absorptions refer to EtOH solutions.

Materials.—1-*Phenylallyl* p-*nitrobenzoate.* 1-Phenylallyl alcohol [12] (5 g.) was added to a suspension of *p*-nitrobenzoyl chloride (7 g.) in dry pyridine (10 ml.) at 0°. The mixture was kept at room temperature for 72 hr., then poured into aqueous sodium hydrogen carbonate. The ester (7·9 g., 75%) was filtered off, washed with water, and crystallized from methanol. It had m. p. 45—46° (Burton [1] gives m. p. 45—46°, Meisenheimer and Schmidt [2] give m. p. 46·2°), and $\lambda_{max.}$ 2565 Å (ε 13,800). Some specimens had slightly different m. p.s and extinction coefficients. Samples of the ester crystallized from light petroleum gave anomalous values for rate constants, apparently owing to the presence of small amounts of *p*-nitrobenzoic acid which are precipitated with the ester under these conditions but remain in solution when methanol is used as solvent.

Cinnamyl p-*nitrobenzoate.* This was prepared as above from *trans*-cinnamyl alcohol and *p*-nitrobenzoyl chloride and, crystallized from ethanol, had m. p. 77—78° (Hill and Nason [13] give m. p. 78°, Meisenheimer and Schmidt [2] give m. p. 76·5°), $\lambda_{max.}$ 2535 Å (ε 30,700).

1-*Phenylallyl acetate.* 1-Phenylallyl alcohol (20 g.), acetic anhydride (acid-free, see below) (20 g.), and pyridine were heated at 65° for 1 hr., then distilled. The acetate (15·4 g., 59%) had b. p. 82—84°/0·1 mm. (Meisenheimer and Link [14] give b. p. 110—112°/16 mm.), n_D^{20} 1·5110, $\lambda_{max.}$ 2510, 2560 Å (ε 550, 520).

Cinnamyl acetate. *trans*-Cinnamyl alcohol (10 g.), acetic anhydride (10 g.), and pyridine (9 g.) were heated at 100° for 3 hr., then distilled. The product (8·4 g., 64%) had b. p. 94—95°/1 mm., $n_D^{21\cdot5}$ 1·5427 (Bert and Dorier [15] give b. p. 141°/18 mm., n_D^{12} 1·5442), $\lambda_{max.}$ 2500 Å (ε 17,300).

[10] Braude, Valkanas, and Waight, *Chem. and Ind.*, 1956, 314.
[11] Drahowzal and Klamann, *Monatsh.*, 1951, **82**, 460; Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3443.
[12] Braude and Jones, *J.*, 1946, 396.
[13] Hill and Nason. *J. Amer. Chem. Soc.*, 1924, **46**, 2236.
[14] Meisenheimer and Link, *Annalen*, 1930, **479**, 211.
[15] Bert and Dorier, *Compt. rend.*, 1930, **191**, 332.

1-*Phenylallyl benzoate.* 1-Phenylallyl alcohol (10 g.) was added to benzoyl chloride (10·5 g.) in pyridine at 0°. After 72 hr. at room temperature the mixture was poured into aqueous sodium hydrogen carbonate, and the benzoate extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and distilled. The ester (8·5 g., 50%) had b. p. 130—138°/0·05 mm. (Rupe and Miller [16] give b. p. 182°/12 mm.), n_D^{21} 1·5639, $\lambda_{max.}$ 2560, 2650, 2720, 2810 Å (ε 1120, 970, 970, 830).

Cinnamyl benzoate. *trans*-Cinnamyl alcohol (6·7 g.), benzoyl chloride (8 g.), and pyridine (10 g.) were kept at room temperature for 72 hr., then poured into water. The product was extracted with ether, washed with dilute hydrochloric acid and water, dried (Na_2SO_4), recovered, and distilled. The benzoate (6·8 g., 60%), b. p. 140—160°/0·005 mm. (Rupe and Miller [16] give b. p. 209°/13 mm.), solidified and, recrystallized from light petroleum (b. p. 60—80°), had m. p. 36—37°, $\lambda_{max.}$ 2465, 2510 Å (ε 21,600, 21,300).

Diisopentylammonium bromide. This was obtained by reaction of tri*iso*pentylamine and *iso*pentyl bromide at 230° (sealed tube). Recrystallized from ethyl acetate–methanol, it had m. p. 318—320° (Heilbron and Bunbury [17] give m. p. 315°).

Lithium p-*nitrobenzoate.* A solution of *p*-nitrobenzoic acid in aqueous methanol was neutralized with methanolic lithium hydroxide to Methyl Red, then evaporated slowly to dryness and dried *in vacuo*.

p-*Nitrobenzoic acid.* A commercial sample was used without further purification.

Chlorobenzene. This was kept for some time over calcium chloride and then distilled from a trace of either anhydrous potassium carbonate or sodium.

Acetic anhydride. This was kept over sodium at room temperature for 48 hr., then refluxed under reduced pressure. Distillation under reduced pressure from the mixture of sodium and sodium acetate produced yielded acetic anhydride free from acetic acid.

Kinetic Measurements.—The method of Braude and Jones [4] was modified in a few respects. As the reactions were slow the conventional oil-thermostat was replaced by a jacketed vessel, consisting essentially of a long-necked flask (A) (capacity 50 ml.), fitted with a cold-finger, sealed into a 1 l. flask (B) provided with a reflux condenser. A suitable liquid was boiled in flask (B) by means of an electrical heating mantle. *iso*Pentyl alcohol and water were used as the heating liquids for runs at 130° and 100° respectively, care being taken to avoid overheating by ensuring that the flask (A) was not immersed in the heating liquid itself. *p*-Nitrobenzoic acid, accurately weighed, was placed in the flask (A), which was heated to the appropriate temperature. A weighed amount of 1-phenylallyl *p*-nitrobenzoate was dissolved in the correct volume of solvent (usually 25 ml.) and poured into flask (A). After 10 min., when all the acid had dissolved and the solution had reached the correct temperature, a 1 ml. sample was withdrawn by inserting a long narrow-stem pipette through the neck of the flask (A) after temporary removal of the cold-finger, and the time noted. The sample was diluted with ethanol, the pipette was washed with ethanol, and the solution and washings were made up to 50 ml. The intensity of light absorption at 2535 Å of the solution was measured on a Beckman spectrophotometer (model DU). Further samples were taken at appropriate intervals. When acetic anhydride was used as solvent samples were diluted into chloroform. In runs involving the liquid 1-phenylallyl esters the above procedure was altered. The weighed ester, contained in a short specimen tube, was dropped into the solvent already heated to the correct temperature. The apparatus was shaken vigorously and the first sample taken immediately.

First-order rate constants are calculated from the expression,

$$k = (2{\cdot}3/t) \log_{10}[(a - x_0)/(a - x)],$$

where k is the rate constant (min.$^{-1}$), t is the time (min.), a is the final intensity, x_0 the initial intensity, and x the intensity of light absorption at time t.

In the runs tabulated the light absorption of the solvent has been subtracted from extinction coefficients given. In very slow runs the reaction was not followed to completion and the values taken for a (marked with an asterisk) assume complete rearrangement to the cinnamyl compound. Concentrations are corrected for solvent expansion.

Rearrangement of 1-*Phenylallyl* p-*Nitrobenzoate under Conditions of High Purity.*—Ten Pyrex ampoules were each charged with 54·8 mg. of the ester, and sealed on to the apparatus

[16] Rupe and Miller, *Helv. Chim. Acta*, 1921, **4**, 841.

[17] Heilbron and Bunbury (Eds.), "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.

as shown in Fig. 2. A thick ampoule containing potassium hydroxide (100 mg.) was sealed on as at *B*, and all air in the apparatus displaced by nitrogen.

Rearrangement of 1-*phenylallyl* p-*nitrobenzoate in chlorobenzene*, 130°. *Ester concn.*, 0·157 *mole/l.* p-*Nitrobenzoic acid concn.*, 0·0107 *mole/l.*

t (min.)	0	690	1380	2820	4270	5705	10,010	
$E^{1\%}_{1\ cm.}$	480	567	633	734	854	895	1040	
10^4k (min.$^{-1}$)	—	2·44	2·31	2·14	2·58	2·35	—	(mean 2·4)

Rearrangement of 1-*phenylallyl acetate in chlorobenzene*, 130°. *Ester concn.*, 0·089 *mole/l.*

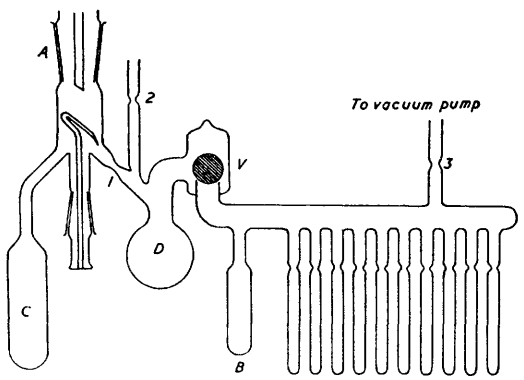
t (min.)	0	15,865	30,450	78,100	148,100	—	
$E^{1\%}_{1\ cm.}$	52	102	157	286	455	960 *	
10^4k (min.$^{-1}$)	—	0·035	0·040	0·038	0·040	—	(mean 0·038)

Rearrangement of 1-*phenylallyl benzoate in chlorobenzene*, 130°. *Ester concn.*, 0·089 *mole/l.*

t (min.)	0	5775	9810	15,575	24,200	38,600	—	
$E^{1\%}_{1\ cm.}$	93	156	181	225	315	394	820 *	
10^4k (min.$^{-1}$)	—	0·16	0·13	0·13	0·15	0·14	—	(mean 0·14)

Meanwhile purified chlorobenzene (100 g.) had been refluxing gently with sodium (1 g.) in a flask to which was attached a fractionating column (18 in., Fenske-ring packed) and vacuum take-off head delivering into the apparatus at *A*. After 24 hr. the rate of heating was increased

FIG. 2.



until distillation commenced. The first fraction (20 ml.) was rejected into *C* and the next (50 ml.) collected in *D*. The tubes at the points of sealing 1 and 2 were swept with nitrogen to remove any chlorobenzene and sealed. The chlorobenzene was then frozen and the apparatus evacuated. After several alternate meltings of the chlorobenzene and evacuation, the apparatus was sealed off at 3 with as hard a vacuum as could be obtained (about 2×10^{-3} mm. Hg) with the potassium hydroxide molten and the magnetic valve *V* (a ball bearing on a ground-glass seating) held open. After the chlorobenzene had warmed to room temperature one ml. was distilled into each ampoule in turn by cooling with liquid nitrogen and the ampoule sealed off. In order to prevent pyrolysis of the solvent vapour at the seal, the valve *V* was closed during the operation of sealing, and the ampoule kept at liquid-nitrogen temperature. After being heated at 130° for various times, the ampoules were cooled in ice and opened, and 0·04 ml. was removed by a micrometer syringe. This was diluted with ethanol for spectrometric analysis. The remaining 0·96 ml. was titrated in water with alkali by the cathode-ray polarographic procedure.

t	Acid concn. (μmole/ml.)	$E^{1\%}_{1\ cm.}$	10^4k (min.$^{-1}$)	t	Acid concn. (μmole/ml.)	$E^{1\%}_{1\ cm.}$	10^4k (min.$^{-1}$)
0	—	482	—	13,380	0·8	886	0·96
1725	<0·1	553	0·78	21,720	1·58	1024	—
3090	0·2	613	0·86	30,240	1·63	1040	—
6030	0·4	733	1·02	40,220	1·87	—	(mean) 0·91

Reaction Products of the Rearrangement of 1-*Phenylallyl* p-*Nitrobenzoate.*—(i) *Chlorobenzene solution.* A solution of the ester (2·5 g.) in chlorobenzene (25 ml.) was heated at 130° for 21 days. The solvent was evaporated under reduced pressure and the residue extracted with light petroleum (b. p. 60—80°), leaving an insoluble gum (150 mg.) with an infrared spectrum similar to that of cinnamyl *p*-nitrobenzoate (Found: C, 65·8; H, 5·0. Calc. for $C_{16}H_{13}O_4N$: C, 67·5; H, 4·6%). The petroleum solution was evaporated to dryness, and the solid dissolved in ether and extracted with aqueous sodium carbonate (5 × 25 ml.). The ethereal solution was dried (Na_2SO_4) and distilled, leaving a solid (2·35 g., 94%) which after crystallization had m. p. 77—78° undepressed by *trans*-cinnamyl *p*-nitrobenzoate. The light absorption max. was at 2535 Å (ε 30,700). The aqueous sodium carbonate extract was acidified with concentrated hydrochloric acid and extracted with ether (5 × 25 ml.). The ether extract was washed once with water, dried (Na_2SO_4), and distilled. The residue (17·7 mg.), crystallized from water, had m. p. 238—240°, undepressed by *p*-nitrobenzoic acid. A fresh specimen of 1-phenylallyl *p*-nitrobenzoate treated in the above manner yielded none of the acid.

(ii) *Acetic anhydride solution.* The ester (1·25 g.) in acid-free acetic anhydride (25 ml.) was heated at 100° for 17 days. The solvent was then distilled under reduced pressure. No cinnamyl acetate was obtained. The residue was extracted with light petroleum (b. p. 80—100°), leaving an insoluble solid (200 mg.), which after crystallization from ethyl acetate had m. p. 176—177°, undepressed by *p*-nitrobenzoic anhydride, prepared by refluxing *p*-nitrobenzoic acid in acetic anhydride for 65 hr. Evaporation of the petroleum extract yielded cinnamyl *p*-nitrobenzoate.

(iii) *Chlorobenzene solution containing acetic acid.* A solution of the ester (2·5 g.) and dry acetic acid (1·0 ml.) in chlorobenzene (25 ml.) was heated at 130° for 4 days. The cold solution was diluted with ether and extracted several times with aqueous sodium hydrogen carbonate solution. The aqueous layer was acidified as above, yielding *p*-nitrobenzoic acid (480 mg.) (extraction with ether yielded a further 70 mg. of the acid). The ethereal extract was dried (Na_2SO_4) and distilled, giving cinnamyl acetate (300 mg.), b. p. 72°/0·1 mm., n_D^{26} 1·5373, $\lambda_{max.}$ 2510 Å (ε 17,100). The residue (1·32 g.) was cinnamyl *p*-nitrobenzoate.

(iv) *Chlorobenzene containing di*isopentylammonium *bromide.* The ester (1·252 g.) and di*iso*pentylammonium bromide (1·670 g.) in chlorobenzene (50 ml.) were heated at 130° for 5 days. The solution became dark brown and crystals separated on cooling. The semisolid mass was dissolved in chloroform, and the solution evaporated, leaving a dark brown residue, which was heated at 160°/0·1 mm. No cinnamyl bromide distilled. The residue was extracted with ether, leaving the insoluble salt (850 mg.). The ether solution was extracted with aqueous sodium hydrogen carbonate (5 × 25 ml.), and the aqueous solution acidified as above, yielding *p*-nitrobenzoic acid (250 mg.), m. p. 240—241°. The ethereal solution contained cinnamyl *p*-nitrobenzoate and some polymeric material.

Assay and Separation of p-*Nitrobenzoic Acid* (*for Low and Medium Concentrations*).—The acid was detected in aqueous solution by cathode-ray polarography. The " wave " due to hydrogen-ion reduction at a platinum microelectrode was observed on a cathode-ray polarograph at a rate of potential increase of 10 v/sec. and a sweep repetition frequency of 2 per sec. At this rate of increase of potential, the wave height was insensitive to stirring of the solution, and no undue " broadening " of the wave due to slowness of reduction was found. The use of such a high rate of sweep was made feasible by capacity current compensation by a novel method.

In the region of interest, from *ca.* 0 to −0·6 v (with respect to the saturated calomel electrode used as working anode), it was found that the behaviour of the microelectrode (a 5 mm. long platinum wire of 0·001 in. diam.) in the supporting electrolyte alone (0·1N-potassium chloride) could be simulated by a capacitance and resistance in parallel. The currents resulting from the application of the sweep potential to the polarographic cell and to an equivalent RC network were subtracted electronically, leaving only the signal due to reducible ions.

Potassium hydroxide solution (0·5M) was added from a micrometer syringe to the rapidly stirred mixture of supporting electrolyte (5 ml.) and chlorobenzene solution of *p*-nitrobenzoic acid (1 ml.) until the hydrogen-ion " wave " continuously observed on the cathode-ray tube disappeared. Only at high acid concentrations was the speed of titration seriously limited by the slow establishment of partition equilibrium of the acid between the two solvents. The end-point was determined by graphical interpolation, the values of " wave height " (on an arbitrary scale) being plotted against titre. The smallest quantity of acid which could be titrated by this method was 2×10^{-7} mole, corresponding to a concentration in the aqueous

phase of 10^{-5} mole/l. Determinations were reproducible to 10^{-7} mole. The acid produced during the reaction was also determined by adding 1 ml. samples of the chlorobenzene solution to water (25 ml.) and titrating them with 0·001M-ammonia to Methylene Blue–Neutral Red used as a " flash-indicator."

Determination of Traces of Water in Chlorobenzene.—Methanol dried by magnesium turnings was distilled into a dropping funnel containing freshly dried potassium nitrate on a wad of glass wool just above the tap. The resultant anhydrous solution had sufficient electrolytic conductivity to permit its use for polarographic measurements. A suitable volume (1—5 ml.) was run directly into the polarograph cell without exposure to air, and excess of Karl Fischer reagent was added from a micrometer syringe, stirring being by dry nitrogen. Two platinum electrodes were immersed in the solution, one large and relatively unpolarisable (3 cm. long, 0·2 mm. thick), and one small (2 mm. long, 0·01 mm. thick). Application of a linearly increasing potential between the electrodes (the microelectrode becoming negative) produced an iodine diffusion peak which was observed on the cathode-ray polarograph, as described for acid assay. The iodine peak height was found to be proportional to the iodine concentration, and hence to the excess concentration of Karl Fischer reagent. Addition of a water-containing solution reduced this peak height and sufficient Karl Fischer reagent was then added to restore it to its previous value or to the appropriate new value if an appreciable volume change resulted. The Karl Fischer reagent was standardized independently by titration of a standard solution of water containing 5 mg./ml.; 0·1 ml. of the standard solution of water required 0·119 ml. of Karl Fischer reagent. Since 0·119 ml. were delivered by 595 divisions on the micrometer syringe, 1 division is equiv. to 0·84 μg. of water.

Four samples of chlorobenzene were prepared, of decreasing degrees of wetness: (*a*) Untreated chlorobenzene was shaken with distilled water for 24 hr. and separated. (*b*) Chlorobenzene was dried ($CaCl_2$) and distilled, and then left in a glass-stoppered bottle for some months. (*c*) Chlorobenzene was freshly dried ($CaCl_2$) overnight and distilled, without special precautions. (*d*) Chlorobenzene from (*c*) was redistilled from sodium directly into the polarographic cell in an apparatus sealed against moisture. Results are tabulated.

Chlorobenzene (ml.)	Karl Fischer (div.)	H_2O (10^{-6} g.)	Mean H_2O concn. (mole/l.)
(*a*) 0·03, 0·03	18·5, 19·5	15·5, 16·3	0·032
(*b*) 0·01	5	4·2	0·023
(*c*) 0·295, 0·295, 0·11, 0·15	32·6, 53, 17·8, 19·1	27·4, 44·5, 14·9, 16·1	0·0072
(*d*) 1·0, 0·5, 1·0, 1·0, 1·0	22·4, 7·35, 17·8, 10·9, 39·8	18·9, 6·15, 15·0, 9·14, 33·5	0·0010

Acid Production from 1-*Phenylallyl* p-*Nitrobenzoate in Wet Chlorobenzene.*—The ester (200 mg.) was dissolved in chlorobenzene (*a*) (4 ml.), and the solution sealed into two 2 ml. ampoules and heated at 130° (1) for 7200 min. and (2) for 23,000 min. The ampoules were cooled and the acid produced measured by polarographic titration: (1) 0·95 μmole/ml., (2) 7·0 μmole/ml.

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