**480.** *Anionotropic Systems. Part VI.* *The Rearrangement of* 1-*Phenylallyl* p-*Nitrobenzoate in Chlorobenzene. Tracer Studies.*

By (the late) E. A. BRAUDE and D. W. TURNER.

The isomerisation of 1-phenylallyl *p*-nitrobenzoate has been shown * to involve (i) a unimolecular process and (ii) a bimolecular reaction with *p*-nitrobenzoic acid. By use of ^{18}O as tracer the former was shown to be intramolecular, in not producing equilibration of the carboxyl-oxygen atoms. By use of *p*-nitro[*carboxy*-^{14}C]benzoic acid the bimolecular reaction was shown to involve attack by essentially undissociated acid molecules at both positions 1 and 3 in the ester, as well as catalysis of the intramolecular reaction.

OF the three principal mechanisms proposed for anionotropic rearrangement, namely, unimolecular (S_N1'), intramolecular (S_Ni') and bimolecular (S_N2'), the last, understood as synchronous rearrangement by anions,[1] is rare, being readily observed only in systems where normal replacement (without rearrangement—S_N2) which tends to obscure it is much reduced,[2] or in isotopic exchange experiments.[3] This has been ascribed to the electrostatic repulsion between the negatively charged reagent and the double-bond π-electron system. It has been pointed out by one of us, however, that attack by a neutral reagent will not be thus hindered,[4] and examples of bimolecular rearrangement involving attack by amines are well known.[5,6] However, in the best authenticated example (involving a secondary amine) a hydrogen-bridge may be present in the transition state and such a reaction is best regarded as of the S_Ni' type.[7]
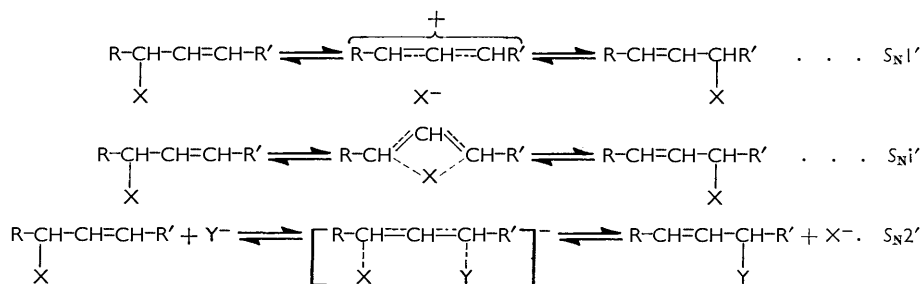
It has been shown [8] in these laboratories that rearrangement of allylic alcohols in aqueous organic media is essentially acid-catalysed and may involve bimolecular attack of a solvent molecule on the oxonium ion. Previous studies of the rearrangement of allylic esters have been carried out under conditions involving in all probability the presence of significant amounts of acids. The first indubitable demonstration of a purely thermal rearrangement of an allylic ester, described in the previous paper, required refined techniques to secure exclusion of water, acids, and oxygen. The purpose of the present paper is to describe the investigation of this thermal rearrangement by means of ^{18}O as

* Part V, preceding paper.

[1] Hughes, *Trans. Faraday Soc.*, 1938, **34**, 194.
[2] de la Mare and Vernon, *J.*, 1952, 3325, 3331, 3628.
[3] England and Hughes, *Nature*, 1951, **168**, 1002.
[4] Braude, *Ann. Reports*, 1949, **46**, 125.
[5] Young, Webb, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076; Young, Clement, and Shih, *ibid.*, 1955, **77**, 3061.
[6] Stork and White, *ibid.*, 1953, **75**, 4119.
[7] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953.
[8] Braude, Jones, and Stern, *J.*, 1946, 396; Braude, *J.*, 1948, 794; Braude and Coles, *J.*, 1951, 2085.

tracer, and of the acid-catalysed rearrangement by means of *p*-nitrobenzoic acid labelled with ^{14}C in the carboxyl position.

EXPERIMENTAL

p-*Nitro*[carboxy-^{14}C]*benzoic Acid.*—Potassium [^{14}C]cyanide (0·4 mc) was dissolved in distilled water (3 ml.) containing inactive potassium cyanide (61 mg.) as carrier. A solution of copper sulphate (150 mg.) in distilled water (3 ml.) was added and the solution gently boiled to expel cyanogen liberated in the decomposition of the cupric cyanide. The cyanogen (carrying half of the initial ^{14}C) was trapped in sodium hydroxide solution. The slurry of cuprous cyanide was transferred to a small Soxhlet extractor fitted with a sintered-glass disc in place of the usual thimble, filtered, and washed twice with distilled water. A 5 ml. flask was attached and the solid dried by connection to a vacuum-line. Dry air was admitted and the solid extracted by refluxing dry pyridine (3 ml.). Pure cuprous cyanide was extracted into the flask and left as yellow crystals after removal of the pyridine in a vacuum. Dry *p*-bromonitrobenzene (100 mg.) was added and fresh dry pyridine (0·25 ml.) was vacuum-distilled in from a pellet of potassium hydroxide. The mixture was heated at 180—190° under nitrogen for 22 hr., then cooled, syrupy phosphoric acid (1 ml.) and diethylene glycol diethyl ether (0·3 ml.) were added, and the whole was reheated to 160° for 1 hr. After cooling, the solid was triturated with water (2 ml.) and filtered off. *p*-Nitrobenzoic acid, isolated by repeated extraction with aqueous sodium hydroxide solution followed by acidification with hydrochloric acid, was washed with ice-cold water, crystallised twice from aqueous methanol, and dried *in vacuo* (m. p. and mixed m. p. 142°).

The combined yield from two such preparations was 58·4 mg., (29% based on total potassium cyanide used). This product was dissolved in redistilled acetone (25 ml.) to yield a stock solution. The specific activity of this solution was $1·26 \times 10^5$ counts per min. per ml. when counted in the standard manner (see below) and the acid thus had a specific molar activity of 9000 counts per min. per 10^{-6} mole.

1-*Phenylallyl* p-*Nitro*[carbonyl-^{18}O]*benzoate.*—Water (0·44 g.) containing 9·69 atoms % of ^{18}O was added to a solution of *p*-nitrobenzoyl chloride (4·48 g.) in pyridine (10 ml.). After the initial reaction had subsided, the mixture was stirred on the steam-bath for 3 hr. in order to complete exchange between the two carboxyl-oxygen positions. Ether (8 ml.) was added to the cooled mixture, and the precipitated solids were separated on the centrifuge, washed twice with ether, and dried in a vacuum. The dry solid was added in small portions to excess of thionyl chloride boiling under reflux, and the mixture heated for 2 hr. The remaining thionyl chloride was then removed by distillation and the removal completed by addition and distillation of carbon tetrachloride (2 × 2 ml.).

The residue (9·3 g.) (mainly *p*-nitrobenzoylpyridinium chloride) was stirred into dry pyridine (10 ml.) and cooled in ice, and 1-phenylallyl alcohol (3·2 g.) was added with stirring. After 2 days at room temperature, the 1-phenylallyl *p*-nitrobenzoate was separated and purified as described in the previous paper. Material twice recrystallised from methanol (1·9 g., 28%) had m. p. 47·5°, $\lambda_{max.}$ 2595 Å (ε 14,100).

Cinnamyl *p*-nitro[^{18}O]benzoate was prepared in the same manner from cinnamyl alcohol.

Kinetic Procedure.—Runs were carried out at 130° as described in the preceding paper.

A quantity of unlabelled recrystallised *p*-nitrobenzoic acid (m. p. 140—141°) sufficient to bring the acid concentration to the desired value was weighed in a short specimen tube, an aliquot part (usually 1 ml.) of the acetone solution of labelled acid was added, and after all had dissolved the acetone was removed in a gentle stream of nitrogen. The tube and contents were dropped into chlorobenzene (25 ml.) in the heated reaction vessel, and the mixture well shaken to complete dissolution. 1-Phenylallyl *p*-nitrobenzoate (1·37 g.) in a similar specimen tube was then added and one minute of vigorous shaking was allowed for temperature equilibration. The first samples were then removed, this being taken as zero time. 1 ml. samples were removed for spectrometric assay as described in the preceding paper. 1 ml. samples were taken for exchange measurements at frequent intervals, and after about 500 min. (at *t'*) 7 ml. of solution were removed for ester radioactivity analysis.

Measurement of Radioactivity.—An internal-sample proportional counter, flushed with methane at atmospheric pressure and operated at 3000 v, was employed.

After polarographic titration of the 1 ml. samples (for details see preceding paper), the neutralised chlorobenzene and aqueous layers were allowed to separate and a 1 ml. portion of

3 K

the aqueous layer was removed and evaporated to dryness on a nickel-coated dish (1 in. diam.). The residue was dissolved in NN-dimethylformamide (0·4 ml.) by gentle swirling and its activity determined. Such a sample was of " infinite thickness " and of very reproducible surface. Under these conditions, the observed count rate was proportional to the concentration of the active material per g. of solution. A standard procedure employing 0·4 ml. of solvent was adopted, a correction being made when large quantities of solute were introduced. Activities are expressed throughout as counts per min. per mg., or counts per min. per 10^{-6} mole, it being understood that 0·4 ml. of supporting solvent was used. The solvent used for assay of esters and of the free acid was diethylene glycol diethyl ether.

At the highest acid concentrations (0·05—0·09 mole l.$^{-1}$) 1 ml. samples were removed from the reaction mixture in a pre-heated pipette (to prevent immediate crystallisation of the acid) and run into light petroleum (b. p. 40—60°; 3 ml.) contained in a centrifuge tube. The precipitated acid was centrifuged, washed three times with light petroleum, and dried. Recovery was quantitative. The acid was dissolved in the ether (0·4 ml.) and transferred to a nickel-plated dish for counting.

Separation of Mixtures of Esters.—(i) *Sublimation.* The mixture of esters, from which the solvent had been removed under vacuum, was placed in a microsublimation apparatus (distance, sample to cold finger, 1·5 cm.) and sublimed at $60°/10^{-3}$ mm. for about 1 hr. The light absorption at 2535 Å and radioactivity in diethylene glycol diethyl ether (0·4 ml.) were measured. A portion of the mixture before sublimation was also assayed for radioactivity and, since the proportion of the two isomers (α and γ) in the mixtures was known from the light-absorption data, the specific activities of the individual isomers could be determined by solving the simultaneous equations for the specific activities of the two mixtures. Test sublimation of a synthetic mixture showed that rearrangement was not appreciable under the conditions used.

(ii) *Crystallisation.* The mixture of esters was crystallised from methanol between room temperature and $-15°$, giving a product in which the relative proportion of isomers (obtained by measurement of light absorption at 2535 Å) was altered. The specific activity of each isomer could be determined as above.

(iii) *By chromatography* [9] (*used in* ^{18}O *studies only*). The mixture of esters (50—200 mg.) was applied in light petroleum (b. p. 40—60°) to a column of silica gel (200 mesh; 2 cm. diam. × 12 cm. long contained in a Pyrex tube) rendered fluorescent by the admixture of activated Willemite (20 mg.). The esters were eluted with light petroleum (b. p. 40—60°) containing 2% of diethyl ether. Under irradiation by ultraviolet light (from a Hanovia mercury-vapour lamp) the esters were revealed as dark bands upon the white fluorescence of the column. The relative speeds of movement of the two bands were as 5·5 (band II) : 7·5 (band I). Band I on elution, and removal of the solvent, gave 1-phenylallyl p-nitrobenzoate, m. p. 45°, raised to 46·5° by recrystallisation from methanol. Band II similarly gave cinnamyl p-nitrobenzoate m. p. 68—72°, raised to 78° by recrystallisation from ethanol. Pure 1-phenylallyl p-nitrobenzoate was recovered quantitatively and showed less than 2% of rearrangement after chromatography under these conditions.

Determination of Carbonyl-^{18}O Enrichment.—A 1% w/v solution of labelled cinnamyl p-nitrobenzoate in carbon tetrachloride was contained in a micrometer cell (sodium chloride windows; Research and Industrial Instruments Co.) set to a path-length of 0·85 mm. and placed in the sample beam of an infrared double-beam spectrometer (Grubb-Parsons, Model S4). A similar cell containing a solution of pure unlabelled ester of the same strength was placed in the reference beam, and the path-length was adjusted to give identical absorption at all wavelengths (except near the 6 μ carbonyl band). The only absorption then remaining was a band at 1700 cm.$^{-1}$ due to $C=^{18}O$. Proportionality between enrichment (in excess of the natural enrichment) and the intensity of this band was confirmed by making accurate dilutions of a sample of labelled ester with unlabelled material.

	Relative concn. of labelled ester	Optical density at 1700 cm.$^{-1}$
Before dilution	1·00	0·037
1st dilution	0·49	0·018
2nd dilution	0·24	0·009

Accuracy.—The precision of the measurements made as above was limited by the finite width of the recorder trace and by noise, together equivalent to E ca. 0·002.

[9] Searse, *J. Amer. Chem. Soc.*, 1948, **70**, 3630.

Determination of the Molecular Weight of p-*Nitrobenzoic Acid in Chlorobenzene.*—The elevation of the b. p. of chlorobenzene on addition of p-nitrobenzoic acid was compared with that produced by anthracene. The boiling temperature was measured by a thermistor (resistance 2075 ohms at 132°) in one arm of a Wheatstone bridge. The b. p. elevations observed corresponded to M 175·0 and 175·5 at concentrations of 9·08 and 17·35 g. l.$^{-1}$ respectively (Calc. for $C_7H_5O_4N$: M, 167·05).

RESULTS

[14]C *Studies.*—The initial overall rate of exchange (R_e) of the p-nitrobenzoyl group between initially inactive 1-phenylallyl p-nitrobenzoate, and added radioactive p-nitrobenzoic acid in chlorobenzene at 130° was followed by measurements of the decrease in radioactivity of samples of the acid withdrawn from the reaction mixture. The relative contributions to this overall rate by exchange without rearrangement (S_N2?) at a rate referred to as R_3, and exchange with rearrangement, referred to as R_2, were deduced from the specific radioactivities of samples of the starting material and of the product of rearrangement, isolated shortly after the commencement of the reaction.

With no assumptions as to the mechanism of the individual steps, the increase of activity in α- and γ-esters was considered to arise in the manner summarised in the annexed schemes. R_1, R_2, R_3, and R_4 are the rates of formation of the various labelled products in mole l.$^{-1}$ min.$^{-1}$.
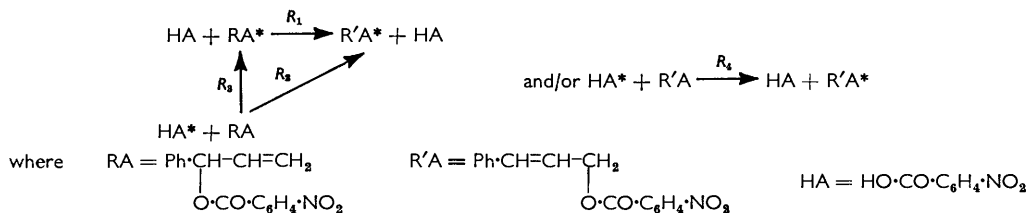
In order further to simplify the investigation, the contribution of exchange with the γ-ester was determined separately. It was negligible, the half-time of exchange between γ-ester (0·171 mole) and labelled p-nitrobenzoic acid (0·0096 mole) being not less than 4×10^4 min. That is, the exchange was more than 100 times slower than that with the α-ester under the same conditions. For the purpose of evaluation R_1, R_2, R_3, and, therefore, R_4 could be neglected.

Now, the specific molar activity of the γ-ester being produced at any instant was considered to be the sum of the instantaneous specific activity of the α-ester, multiplied by the fraction of ester produced by the intramolecular route, and the instantaneous specific activity of the acid, multiplied by the fraction of γ-ester produced by the bimolecular route:

$$y(i) = xR_1/R_{obs.} + AR_2/R_{obs.}$$

Where $y(i)$, x, and A were the instantaneous specific molar activities of the γ-ester, α-ester, and acid respectively, and $R_{obs.}$ was the total rate of rearrangement.

The observed specific activity (y) of the γ-ester after a time of reaction (t') was therefore:

$$y = \overline{x}R_1/R_{obs.} + \overline{A}R_2/R_{obs.}$$

where $\overline{x}$ and $\overline{A}$ are the mean specific molar activities from the start of the experiment to the time of determination of y:

$$\overline{x} = \frac{1}{t'}\int_0^{t'} x \, dt \qquad\qquad \overline{A} = \frac{1}{t'}\int_0^{t'} A \, dt$$

Now, since $R_{obs.} = R_2 + R_1$, rearrangement of the above expression for y gives:

$$R_2/R_{obs.} = (y - \overline{x})/(\overline{A} - x)$$

$\bar{x}$ was determinable from x, and $\bar{A}$ from the rate of loss of activity from the acid. The evaluation of R_2 (and hence R_1) rested then on the measurement of the specific molar activities of the α-ester and γ-ester at any single time after the commencement of exchange, between such limits that the ester activities should be high enough to measure, and that the rearrangement had not proceeded so far as to alter markedly the α-ester concentration. To this end, a portion of the reaction mixture was generally removed for ester analysis when exchange was between 50% and 80% complete.

x and y were not determined directly for the pure esters, since separation of a mixture containing more than a few per cent. of γ-ester was tedious. Since, however, the proportion of each ester in a mixture was readily found by light-absorption measurements, partial separation and comparison of the specific activities before and after separation gave simultaneous equations in x and y which were readily soluble.

The partial separation required was effected by crystallisation from cold ethanol or by sublimation in a high vacuum.

FIG. 1. *The influence of* p-*nitrobenzoic acid concentration on the rates of the reactions* R_1, R_2, R_3, R_r. *The curves (from top to bottom) relate to* R_r, R_1, R_3, R_2.
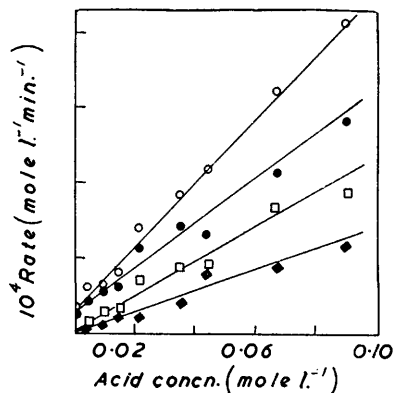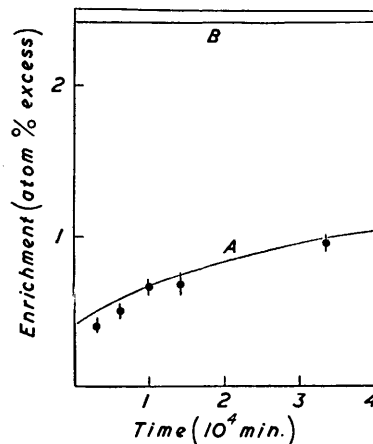
FIG. 2. *The time variation of the carbonyl-oxygen* ^{18}O *enrichment in cinnamyl* p-*nitrobenzoate. A, Calc. for Case* I *and Case* II *(see text). B, Calc. for complete oxygen equivalence during rearrangement.*

During sublimation, enrichment of α-ester in the sublimate took place, the γ-ester being much less volatile. Crystallisation produced enrichment of either α- or γ-ester depending on the proportions in which they were initially present and on the conditions of crystallisation. In all runs it was found that the two esters had specific activities of the same order of magnitude, that of the γ-ester tending to become higher than that of the α-ester by as much as four times at lower acid concentrations; this shows both α- and γ-attack by the labelled acid to take place. The difference between R_2 and the total rate of rearrangement (R_r) gave the rate of intramolecular rearrangement (S_Ni') referred to as R_1. The experimental data relating to fourteen kinetic experiments are summarised in the Table, and the derived values of R_1, R_2, and R_3 are plotted together with R_r *versus* acid concentration in Fig. 1.

^{18}O *Studies.*—The mechanism of the thermal rearrangement was investigated (at the suggestion of Dr. L. M. Jackman) by the use of ^{18}O to differentiate between the alkoxyl and carbonyl positions of the carboxylate group. The continued non-equivalence of these positions, *i.e.*, the lack of alteration of isotopic enrichment of the labelled position, can only be maintained in a carboxylate group which remains bound to the rest of the molecule throughout rearrangement. This criterion makes no distinction between a fully covalent cyclic process and the intermediate formation of a tight ion pair but may be used to detect the formation of kinetically free and mesomeric anions. Such a distinction has been obtained in an analogous case by Denny.[10]

[10] Denny, *J. Amer. Chem. Soc.*, 1955, **77**, 1706.

The isotopic enrichment (meaning the enrichment *in excess of* the natural ^{18}O content) in the carbonyl-oxygen position could be determined in both 1-phenylallyl and cinnamyl *p*-nitrobenzoate by infrared differential absorption measurements using the 6 μ carbonyl stretching

Acid concn. (M)	$\tau_{\frac{1}{2}}$ (min.)	$10^5 R_E$	x	y	A_0	A_∞	$\bar{x}$	$\bar{A}$	t'
0·00025	77	0·23	11·5	70·8	7150	12·5	7·9	1692	465
0·00025	86	0·20	10·7	104	8650	15·0	6·4	2557	405
0·00056	160	0·24	—	—	—	—	—	—	—
0·0013	200	0·45	—	—	—	—	—	—	—
0·0020	325	0·42	—	—	—	—	—	—	—
0·0045	310	0·98	12·0	58·0	810	20·8	7·6	424·8	580
0·0096	300	2·10	19·7	36·5	409	21·8	13·4	142·8	1320
0·015	300	3·20	13·5	63·0	275	22·2	7·8	180	440
0·018	330	3·43	—	—	—	—	—	—	—
0·027	325	4·98	13·0	30·8	231	31·4	5·14	163·4	420
0·037	315	6·70	5·60	15·7	77·2	13·8	3·04	56·3	390
0·045	280	8·80	6·50	36·6	117	24·5	3·4	88	325
0·067	240	13·9	7·90	21·2	82·5	23·2	4·2	63·1	305
0·090	264	15·3	6·95	14·4	51·8	17·9	3·8	40·6	330

band. Since the cinnamyl ester was the more readily purified after separation from reaction mixtures, the interchange of oxygen functions was followed by observations upon the carbonyl-^{18}O enrichment of this ester. The values found for various stages of rearrangement are plotted *versus* time in Fig. 2. The theoretical curve was derived on the assumption that " scrambling " of the oxygen atoms by way of carboxyl group exchange with traces of *p*-nitrobenzoic acid takes place at a rate suggested by the ^{14}C studies as follows:

The reactants were considered to have carboxyl isotopic contents shown:

$$\text{α-Ester:} \quad a\begin{cases} -O-C{=}^{18}O & y \\ -^{18}O-C{=}O & x \\ -O-C{=}O \end{cases} \qquad \text{Acid:} \quad b\begin{cases} O-C{=}^{18}O & zb/2a \\ -^{18}O-C{=}O & zb/2a \\ -O-C{=}O \end{cases}$$

where a, b, x, y, z ($= x + y$) are concentrations (mole l.$^{-1}$), R_e = rate of exchange (mole l.$^{-1}$ min.$^{-1}$) $= k_e a$, and k_r = 1st-order rate constant of rearrangement.

Case I: As a result of exchange without rearrangement (k_3):

$$dx/dt = R_e(a - x)z/2a^2 - R_e x(1 - z/2a)/a - k_r x$$

Since $z = z_0 \exp(-k_r t)$

$$dx/dt + (k_e + k_r)x = k_e z_0 \exp(-k_r t)$$

which can be integrated to

$$x = \tfrac{1}{2}z_0 \exp(-k_r t) + C \exp[-(k_e + k_r)t]$$

If $x = 0$ when $t = 0$, C (the constant of integration) $= -\tfrac{1}{2}z_0$, then

$$x = \tfrac{1}{2}z_0\{\exp(-k_r t) - \exp[-(k_e + k_r)t]\}$$

The concentration of carbonyl-labelled γ-ester produced by intramolecular rearrangement between t and $(t + dt)$ would be $k_r x_t \, dt$.

Hence the concentration of such ester produced from time 0 to t' would be $\displaystyle\int_0^{t'} k_r x \, dt$.

The enrichment of the γ-ester with reference to the carbonyl position would thus be $\displaystyle\int_0^{t'} (k_r x \, dt)/a_0[1 - \exp(-k_r t)]$, since $a_0[1 - \exp(k_r t)]$ would be the overall γ-ester concentration at t'; from above therefore

$$\text{Enrichment} = (z_0/2a_0)\{1 - k_r[1 - \exp(-k_e + k_r)t]/(k_e + k_r)[1 - \exp(-k_r t)]\} \quad . \quad (1)$$

Case II: As a result of exchange accompanied by rearrangement (R_2) (concn. of cinnamyl ester, $^-O-C{=}^{18}O = x'$):

$$dx'/dt = k_e z/2a \text{ (there being no reverse reaction)}$$

$$= \tfrac{1}{2}k_e z$$

and similarly

$$\text{Enrichment} = k_e z_0/2k_r a_0 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since the ^{14}C experiments indicated that both kinds of exchange were probable in the ratio k_e (Case I) : k_e (Case II) of $\sim$3 : 1 at low acid concentration, the enrichment resulting would be the sum of (1) and (2), the k_e appropriate in each case being used. The curve shown (Fig. 2) results from the substitution in the above expressions of the following values: k_e for reaction R_3 $0{\cdot}30 \times 10^{-4}$ min.$^{-1}$; k_e for reaction R_2 $0{\cdot}13 \times 10^{-4}$ min.$^{-1}$; k_r $0{\cdot}89 \times 10^{-4}$ min.$^{-1}$; *i.e.*, k_e (Case I) + k_e (Case II) = $0{\cdot}43 \times 10^{-4}$ min.$^{-1}$, which corresponds to a total rate of exchange of $0{\cdot}75 \times 10^{-5}$ mole l.$^{-1}$ min.$^{-1}$. This would require an acid concentration of *ca.* $4 \times 10^{-3}M$, a value consistent with our earlier findings (preceding paper).

DISCUSSION

If *p*-nitrobenzoic acid participated in the rearrangements in any way other than by simple proton-donation either with (as in the catalysis by halogen acids of the rearrangement of allylic alcohols) or without dissociation of the O–H bond, interchange of the carboxyl-^{14}C between the ester and the acid would be expected. In particular, if the rate-controlling step were ionisation of the ester to be followed by ion-recombination at either the α- or the γ-carbon atom, the rate of ^{14}C exchange could not depend in a simple linear manner on the concentration of the acid.

The rate (R) of isotopic exchange between two chemical species whose concentrations are [X] and [Y] respectively has been expressed by Duffield and Calvin [11] as:

$$R = 0{\cdot}693[X][Y]/\tau_{\frac{1}{2}}([X] + [Y])$$

If [X] and [Y] differ widely this leads in the case of a bimolecular exchange process $(R = k_2[X][Y])$ to nearly constant values of $\tau_{\frac{1}{2}}$ when as in this investigation the lesser of [X] and [Y] only is varied.

It is evident from the observed values of $\tau_{\frac{1}{2}}$ that for acid concentrations greater than about $0{\cdot}002M$ (that is, the minimum value reached under " normal " experimental conditions), an exchange (of anionic group) occurred between the ester and *p*-nitrobenzoic acid present, which was bimolecular (of the first order with respect to acid concentration). Further, the appearance of radioactivity in cinnamyl *p*-nitrobenzoate in the early stage of reaction cannot have been the result of rearrangement (intramolecularly) of exchange-labelled 1-phenylallyl *p*-nitrobenzoate since the specific activity of the rearranged product by this route could never at any instant be higher than that of the starting material. The generally higher specific activity of the former than of the latter isolated at a time not much greater than the half time of exchange (*i.e.*, when the specific activity of the acid is still significantly higher than that of the 1-phenylallyl *p*-nitrobenzoate) indicates direct participation of the acid in the act of rearrangement.

This, however, cannot have been the only route to cinnamyl *p*-nitrobenzoate; the total rate of exchange was always less than the total rate of rearrangement, and a large fraction of the former resulted in no rearrangement (to give radioactive 1-phenylallyl *p*-nitrobenzoate). Thus we were led to consider:

$$R_e = R_2 + R_3$$

$$R_r = R_1 + R_2$$

where rearrangement without exchange = R_1, rearrangement with exchange = R_2,

[11] Duffield and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 557.

exchange without rearrangement $= R_3$, and (possibly) exchange after rearrangement $= R_4$.

Except at the lowest concentration of acid, both R_2 and R_3 were found to be of the first order with respect to acid concentration. R_3 may be analogous to weakly alkaline hydrolysis in aqueous media which, contrary to the findings of Kenyon, Partridge, and Phillips,[12] takes place without rearrangement. Since it has been shown that anions are ineffective in promoting bimolecular rearrangement in this case (preceding paper), R_2 must involve both carboxylate anion and proton in a more or less concerted attack. The linear relation of rate to concentration suggests that undissociated p-nitrobenzoic acid acts as a kinetic unit. This interpretation is open to objection on the grounds of the known tendency of carboxylic acids to form dimers in this type of solvent. If this were so bimolecular reaction with the p-nitrobenzoic acid molecule would be linearly related to some fractional power of the total acid concentration. Dimer formation in carboxylic acids is known, however, to be reduced by increase of temperature, dielectric constant of the medium, and acid dissociation constant, and measurement of the elevation of the b. p. of chlorobenzene by p-nitrobenzoic acid showed no increase in the effective molecular weight of the latter greater than experimental error. We conclude therefore that bimolecular rearrangement is initiated by the combined attack of proton and anion. The manner in which a proton is shared between the anion and the attacked allylic system remains obscure since nothing is known of the dissociation of p-nitrobenzoic acid in this medium. It may, however, be conjectured that a more or less synchronous bond rearrangement results from the arrangement of the reagents to form a six-atom hydrogen-bridged ring analogous to that postulated for the rearrangement accompanying attack by primary and secondary amines: [5, 6]
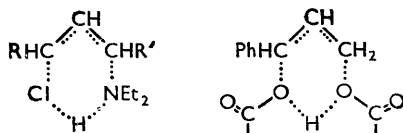
The acid-catalysis of rearrangement without exchange (R_1) is also undoubtedly to be attributed to an initial proton-attachment at the alkoxyl-oxygen atom, resulting in a weakening of the alkyl–oxygen link and partial redistribution of the electrons of the allylic double bond, as discussed for the proton-catalysed rearrangement of allylic alcohols.[8] This cannot, however, account for the whole of the rearrangement, as implied by the comment of De Wolfe and Young [13] on the preliminary communication of these results. It is, of course, most unlikely that in the solvent used, a " free " proton is at any stage obtained; its transfer from a molecule of p-nitrobenzoic acid to an ester molecule must result from an intimate colligation of the two—catalysis is bimolecular as the kinetic data show.

As the concentration of acid was progressively reduced, however, rearrangement tended to become entirely intramolecular in the sense that migration of the carboxyl group was not diverted by the few acid molecules present. We would not maintain that this evidence alone demonstrates this reaction to proceed without any charge development whatsoever; we hold, however, that to describe the fragments as ionic is to distort the original meaning of the term.

The investigation of this reaction by means of ^{18}O demonstrated clearly that the migrating group was not free in the ionic sense. The small amount of " scrambling " which took place in this case would be entirely explained in terms of exchange of carboxyl group with the inevitable trace of p-nitrobenzoic acid rapidly produced.

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[12] Kenyon, Partridge, and Phillips, *J.*, 1937, 207.
[13] De Wolfe and Young, *Chem. Rev.*, 1956, **56**, 776.