



The type of combination with the catalyst necessary to bring about the removal of X was left undetermined, and the further question therefore arose whether the production of a co-ordinate link is required, or whether the formation of residual electrovalencies arising from attraction due to external molecular fields ("molecular combination," "dipole association," etc.) would suffice. Furthermore, the volatile, non-salt-like character of the anionotropic substances described in Part I indicated that the ionisation of X might not be followed by dissociation of the ions, so that  $X^{\ominus}$  might, throughout the isomeric change, remain in electrovalent association with the cation of the molecule which gave rise to it. Thus the possible modifications of mechanism (II) are :

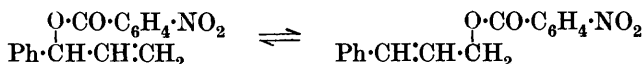
(IIa) Covalent interaction with catalyst, and ionic dissociation.

(IIb) Molecular association with catalyst, and ionic dissociation.

(IIc) Covalent interaction with catalyst; ionisation but no dissociation.

(IId) Molecular association with catalyst; ionisation but no dissociation.

A suitable example for detailed study is the conversion of  $\alpha$ -phenylallyl *p*-nitrobenzoate into cinnamyl *p*-nitrobenzoate :



The advantages offered by this example are : (1) Both isomerides are crystalline and are easily identified. (2) In three-carbon systems terminated by a single phenyl group the reaction proceeds substantially in one direction and experimental complications arising from a considerable retrograde reaction are avoided (compare Part I). (3) The mobility is of the right order of magnitude for detailed study, interchange occurring at an elevated temperature, and not taking place at an appreciable speed at the ordinary temperature in the presence of any of the reagents or solvents used in this investigation; the equilibrated system, therefore, can be "fixed" by rapid cooling, and disturbances during the isolation of the products obviated.

The main portion of this work has therefore been carried out with the substances mentioned, although experiments with a number of other anionotropic individuals are described. The stages in which the investigation has proceeded are :

(1)  $\alpha$ -Phenylallyl *p*-nitrobenzoate was left for some months without change in solution in acetic acid, acetic acid containing a few drops of 30% hydrobromic acid, and alcoholic hydrochloric acid. These observations tell against mechanisms (I), (IIa), and (IIc),

for which either a weak or a strong acid ought to furnish the best possible catalyst.

(2) In boiling acetic anhydride  $\alpha$ -phenylallyl *p*-nitrobenzoate passes smoothly into its isomeride. This appears to exclude mechanism (I), according to which the products of the change should be cinnamyl acetate and *p*-nitrobenzoic-acetic anhydride. There is, however, one other alternative, namely, that the mixed anhydride might react with cinnamyl acetate, yielding cinnamyl *p*-nitrobenzoate and acetic anhydride.

(3) If this were so,  $\alpha$ -phenylallyl alcohol on treatment with an equivalent of the mixed anhydride in acetic anhydride solution should yield only cinnamyl *p*-nitrobenzoate. Actually both cinnamyl acetate and cinnamyl *p*-nitrobenzoate are formed, so mechanism (I) is definitely eliminated.

(4) Final confirmation was obtained by heating cinnamyl acetate with an equivalent of *p*-nitrobenzoic-acetic anhydride under the conditions used in the experiments of sections (2) and (3). No double decomposition occurred.

(5) Carbonyl groups are well known for the facility with which they form co-valency addition compounds with anions, *e.g.*, in the alkaline hydrolyses of esters (*Ann. Reports*, 1927, 24, 157), and the catalytic activity of acetic anhydride might therefore be due to this cause (hypotheses II*a* and II*c*). The dielectric constant of acetic anhydride is 20.5, and the external electrostatic field, as measured by the molecular dipole moment, must be considerable, and might also be the cause of its catalytic activity (hypotheses II*b* and II*d*). Benzonitrile has about the same dielectric constant as acetic anhydride, namely, 26, but chemical evidence shows that the ability of the cyano-group to form covalency addition compounds with anions, if not nil, is at least negligible in comparison with that of carbonyl. Substitution of benzonitrile for acetic anhydride as solvent for the isomerisation showed that conversion occurred equally smoothly and completely. These experiments favour mechanisms II*b* and II*d* and are against II*a* and II*c*.

(6) Unsuccessful attempts were made to find an inert solvent having a dielectric constant of 20 or more, in which covalent union with an anion is structurally impossible. Chlorobenzene fulfils the necessary structural requirements, although its dielectric constant is only 11 (dipole moment  $1.58 \times 10^{-18}$  E.S.U.). Isomeric change occurred smoothly and substantially completely in this solvent, although definitely more slowly than in the solvents having dielectric constants of about 20. Mechanisms II*a* and II*c* were thus excluded, II*b* or II*d* confirmed.

(7) On either of the latter views it is to be expected that in

*p*-xylene (dielectric constant 2) the change would proceed with difficulty or not at all, since there are no pre-formed dipoles in this substance, although the anion itself might cause some polarisation. Actually under conditions comparable with those used in (6), a slow and partial isomerisation occurs, together with simultaneous decomposition, the products of which, rather than the xylene, may be responsible for catalysing the interconversion observed.

(8) Finally, decision between mechanisms II*b* and II*d* was obtained by heating  $\alpha$ -phenylallyl *p*-nitrobenzoate in acetic anhydride as under (2), except that an equivalent of acetate ions was introduced in the form of tetramethylammonium acetate. If the ionisation and subsequent re-co-ordination of the *p*-nitrobenzoyloxy-group is intramolecular (hypothesis II*d*), the presence of the tetramethylammonium acetate should make no difference to the isomeric change (excepting in so far as it might alter the dielectric constant of the medium); on the other hand, if ionisation is followed by dissociation (hypothesis II*b*), the recombination of the anion with the cation will be inhibited by the competition of the acetate ions, and a large proportion of cinnamyl acetate should be produced. Actually the product was a mixture of cinnamyl acetate and cinnamyl *p*-nitrobenzoate, in which the former preponderated, the ionic dissociation hypothesis thus being confirmed.

*Conclusions.*—The study of the mechanism of anionotropic change divides itself into two portions :

(1) The behaviour of the electrons in the electromeric cation under different conditions of structure, (2) the behaviour of the eliminated anion under different conditions of catalysis. Aspect (1) was studied in Part I (*loc. cit.*), and as regards aspect (2) it is now shown that the mobile group undergoes ionic dissociation promoted by some molecular property of the solvent closely related to its dielectric constant. It is suggested that the anion combines electrostatically with the catalyst by means of the pre-existing, plus the induced, dipolar field of the latter.

#### EXPERIMENTAL.

*Conversion of  $\alpha$ -Phenylallyl p-Nitrobenzoate into Cinnamyl p-Nitrobenzoate.*—A mixture of  $\alpha$ -phenylallyl *p*-nitrobenzoate (10 g.) and acetic anhydride (20 c.c.) was boiled for 6 hours and then poured into water. The precipitate (8 g.), m. p. 75° after being washed with water and cold alcohol, gave after one crystallisation from alcohol pure cinnamyl *p*-nitrobenzoate, m. p. and mixed m. p. 77—78°. The alcoholic washings contained a dark oil, but the quantity was too small for examination.

*Simultaneous Formation of Cinnamyl Acetate and Cinnamyl p-Nitrobenzoate from  $\alpha$ -Phenylallyl Alcohol.*—A mixture of  $\alpha$ -phenylallyl alcohol (4.6 g.), *p*-nitrobenzoyl chloride (6.4 g.), dry sodium acetate (2.82 g.), and acetic anhydride (20 c.c.) was boiled for 6 hours. The mixture was poured into water, and the semi-solid precipitate washed with cold alcohol. The residue (4.85 g.) contained cinnamyl *p*-nitrobenzoate (1.35 g.), which was isolated by washing with dilute sodium hydroxide solution, and the alcoholic washings yielded 3 g. of cinnamyl acetate, b. p. 140°/16 mm., and a further quantity (0.65 g.) of the nitrobenzoate.

When cinnamyl acetate was acted on by a mixture of *p*-nitrobenzoyl chloride and sodium acetate under the above conditions, it was recovered unchanged.

*Other Methods of converting  $\alpha$ -Phenylallyl p-Nitrobenzoate into Cinnamyl p-Nitrobenzoate.*—(a) A solution of the nitrobenzoate (5 g.) in benzonitrile (10 c.c.) was heated at 140° for 6 hours. When the dark solution was poured into an excess of petrol, 0.2 g. of a dark, flocculent precipitate remained undissolved. The filtrate slowly deposited colourless crystals of cinnamyl *p*-nitrobenzoate (1 g.), m. p. 77—78°, and a further quantity (2.5 g.) was obtained by steam distillation of the mother-liquor to remove volatile products, and trituration of the partly solid residue with alcohol.

(b) Solutions of the nitrobenzoate (2.5 g.) in chlorobenzene (5 c.c.) were boiled for 6 and 72 hours, respectively. The cinnamyl derivative was not formed in recognisable amount in the first case, but formed the major part of the product in the second.

(c) Experiments (b) were repeated with *p*-xylene in place of chlorobenzene. No change was observed after 6 hours, but when reaction took place for 72 hours and the resulting dark brown solution was steam-distilled, a semi-solid residue was obtained. This was dissolved in alcohol, and after 2 days crude cinnamyl *p*-nitrobenzoate (0.85 g.) separated; no definite product could be isolated from the mother-liquor.

$\alpha$ -Phenylallyl *p*-nitrobenzoate decomposes when it is heated at 140° for 6 hours with glycerol or chlorohydrin.

*Formation of Cinnamyl Acetate from  $\alpha$ -Phenylallyl p-Nitrobenzoate.*—A mixture of  $\alpha$ -phenylallyl *p*-nitrobenzoate (10 g.), tetramethylammonium acetate (4.7 g.), and acetic anhydride (20 c.c.) was boiled for 6 hours. The dark reaction mixture was either (a) fractionated, the bath being heated to 200° to ensure that the last trace of cinnamyl acetate was given off (yield of crude acetate, 4 g.; b. p. 134°/10 mm.), or (b) poured into warm water, and the precipitated *p*-nitrobenzoic acid separated and washed with ether. The ethereal washings together with the ethereal extract of the aqueous filtrate yielded

on evaporation a further quantity of the acid; total, 3.5 g. The residue on distillation gave 4.0 g. of cinnamyl acetate, b. p. 134°/10 mm., leaving 2.5 g. of crude cinnamyl *p*-nitrobenzoate in the flask.

Further examples of transformations similar to those recorded on p. 1653 are the production of *p*-chlorocinnamyl *p*-nitrobenzoate and 3-methylcinnamyl *p*-nitrobenzoate from  $\alpha$ -*p*-chlorophenylallyl *p*-nitrobenzoate and  $\alpha$ -*m*-tolylallyl *p*-nitrobenzoate, respectively.

*Attempted Transformations in Other Solvents.*—A solution of  $\alpha$ -phenylallyl alcohol or its *p*-nitrobenzoate in chloral (compare Part I, p. 909) was heated at 65° for 6 hours, and a solution of  $\alpha$ -phenylallyl alcohol in benzonitrile was treated as described on p. 1654. In no case was isomerisation into the cinnamyl derivative noticed.

$\alpha$ -*p*-Chlorophenylallyl Alcohol,  $C_6H_4Cl \cdot CH(OH) \cdot CH \cdot CH_2$ .—The Grignard reagent prepared from magnesium (6 g.), *p*-chloriodobenzene (60 g.), ether (100 c.c.), and a trace of iodine was cooled below 0° and treated during 1 hour with a solution of acetaldehyde (14 g.) in ether (72 c.c.). The mixture was well stirred for a further 3 hours and then decomposed by ice and dilute hydrochloric acid. The oil obtained after extraction with ether, washing with sodium bicarbonate solution, drying, and evaporation was distilled, and a fraction (20 g.), b. p. 125—128°/12 mm., collected. The alcohol boils at 122—123°/10 mm. (Found: Cl, 21.4.  $C_9H_9OCl$  requires Cl, 21.05%). The high value for chlorine is probably due to a small amount of impurity (see below) which cannot be eliminated by repeated distillation. The *p*-nitrobenzoate was prepared as described for the phenylallyl analogue (Burton and Ingold, *loc. cit.*), but it was necessary to crystallise the crude product five times from methyl alcohol, colourless, glistening plates, m. p. 81—82°, being formed (Found: C, 60.5; H, 3.9.  $C_{16}H_{12}O_4NCl$  requires C, 60.45; H, 3.8%), and when the mother-liquors were partly evaporated in a vacuum a small quantity of a substance was obtained which separated from ethyl alcohol in long, silky needles, m. p. 170° after previous softening (Found: C, 56.5, 56.5; H, 3.4, 3.3%).

*Conversion of  $\alpha$ -p-Chlorophenylallyl Alcohol into p-Chlorocinnamyl Alcohol.*—A mixture of  $\alpha$ -*p*-chlorophenylallyl alcohol (11.5 g.) and acetic anhydride (12 c.c.) was boiled for 6 hours and then distilled, 3.7 g. of the unchanged alcohol and 8 g. of an acetate, b. p. about 155°/11 mm., being obtained. The latter, on hydrolysis with 5% alcoholic potassium hydroxide (200 g.) for 3 hours, yielded *p*-chlorocinnamyl alcohol, which crystallised from ligroin (b. p. 40—60°) in clusters of long, colourless needles, m. p. 57—58° (Found: C, 64.2; H, 5.55.  $C_9H_9OCl$  requires C, 64.1; H, 5.4%). The *p*-nitrobenzoate, prepared by the pyridine method, crystallised from alcohol in

almost colourless, prismatic needles, m. p. 130—131° (Found : C, 60.5; H, 3.9.  $C_{16}H_{12}O_4NCl$  requires C, 60.45; H, 3.8%).

*Bromide from  $\alpha$ -p-Chlorophenylallyl Alcohol (p-Chlorocinnamyl Bromide,  $C_6H_4Cl\cdot CH:CH\cdot CH_2Br$ ).*—To the alcohol (8.4 g.), cooled in ice, a cold solution of hydrogen bromide in glacial acetic acid (30%; 50 g.) was added gradually. After solution occurred, a colourless, crystalline mass separated, which was poured into water, collected, washed free from acetic acid, and dried (yield 10 g.). The bromide dissolves readily in hot glacial acetic acid and separates, on cooling, in colourless plates, m. p. 62—63° (Found : 0.1910 gave 0.2732  $AgCl + AgBr$ .  $C_9H_8ClBr$  requires  $AgCl + AgBr = 0.2732$ ). The same bromide was obtained from *p*-chlorocinnamyl alcohol. Ozonolysis of a chloroform solution of the bromide (see Burton and Ingold, *loc. cit.*) gave *p*-chlorobenzoic acid and bromoacetaldehyde.

*$\alpha$ -m-Tolylallyl Alcohol,  $C_6H_4Me\cdot CH(OH)\cdot CH:CH_2$ .*—The Grignard reagent prepared from magnesium (12 g.), *m*-iodotoluene (109 g.), ether (250 c.c.), and a trace of iodine was treated with a solution of acetaldehyde (28 g.) in ether (100 c.c.) as described for the chloro-compound. The gummy reaction product was decomposed with ice and dilute acetic acid, and the oil obtained fractionated. The alcohol boils at 115—117°/11 mm., and is a colourless mobile oil (yield, 30%). The *p*-nitrobenzoate, prepared by the pyridine method, crystallised from alcohol in almost colourless, glistening plates, m. p. 53° (Found : C, 68.75; H, 4.7.  $C_{17}H_{15}O_4N$  requires C, 68.7; H, 5.1%).

*$\alpha$ -3-Methylcinnamyl Alcohol,  $C_6H_4Me\cdot CH:CH\cdot CH_2\cdot OH$ .*—The transformation of  $\alpha$ -*m*-tolylallyl alcohol into 3-methylcinnamyl acetate, b. p. about 145°/13 mm., was complete after 6 hours' boiling with acetic anhydride. Hydrolysis of the acetate furnished 3-methylcinnamyl alcohol, b. p. 137—140°/11 mm., as a colourless, mobile oil, which could not be induced to solidify. The *p*-nitrobenzoate separated from alcohol in almost colourless, prismatic needles, m. p. 63—64° (Found : C, 68.5; H, 4.8.  $C_{17}H_{15}O_4N$  requires C, 68.7; H, 5.1%).

*Bromide from  $\alpha$ -m-Tolylallyl Alcohol.*—The bromide was prepared, in a similar manner to the corresponding *p*-chloro-compound, from the tolylallyl alcohol (7.5 g.) and an acetic acid solution of hydrobromic acid (30%; 50 g.); after 15 minutes, the dark solution was poured into water. The bromide, extracted with ether and washed free from acids by sodium bicarbonate solution, was a straw-coloured oil, b. p. 138—140°/11 mm. (with slight decomp.), which slowly decomposed into a black, viscous mass. Ozonolysis of a chloroform solution of a freshly prepared specimen, and subsequent decomposition of the oily ozonide with boiling water, gave mainly *m*-toluic

acid and bromoacetaldehyde, together with a small quantity of a volatile aldehyde (formaldehyde?).

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THE UNIVERSITY, LEEDS.

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