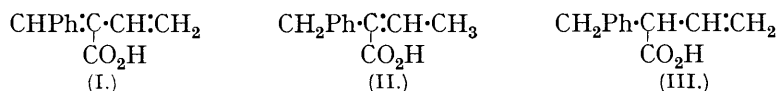


159. *The Modes of Addition to Conjugated Unsaturated Systems.*
Part VIII. Reduction of α -Vinylcinnamic Acid.

By CHRISTOPHER K. INGOLD and MAURICE A. T. ROGERS.

THE publication of Part VI completed a general survey of conjugative additions from the point of view of Burton and Ingold's orientation theory of additions; two examples of long standing in which a reported experimental result appeared to present difficulty were considered in Part VII, and we have now examined a recent example.

Kuhn and Deutsch (*Ber.*, 1932, **65**, 817) investigated the reduction of α -vinylcinnamic acid (I) by sodium amalgam; they reported the substantially exclusive formation of the 1:4-dihydro-derivative, α -benzylcrotonic acid (II). They suggested that, according to Burton and Ingold's theory, the primary dihydro-product should, on the contrary, be the 1:2-isomeride, β -phenyl- α -vinylpropionic acid (III), no trace of which was detected.



We accept this application of our views, and return to the matter below. Kuhn and Hoffer (*Ber.*, 1933, **66**, 1263), however, attempted to strengthen their criticism of the theory by the production of a second example: they reduced β -phenylsorbic acid by means of sodium amalgam, and obtained both the 1:2- and the 1:4-dihydro-compound, in proportions which they determined. They stated that according to Burton and Ingold's theory the 1:2-dihydro-isomeride should be produced exclusively. Now *this* is incorrect; and the conclusion, apparently reached by applying a statement detached from context and implied restrictions, suggests imperfect appreciation of the limitations of the theory. The case, indeed, belongs to a class which, as Burton and Ingold indicated (*loc. cit.*, p. 2025, footnote), is too complicated for theoretical diagnosis. We therefore pass over the criticisms

based on this example, and revert to Kuhn and Deutsch's case, where the issue between theory and reported fact is definite.

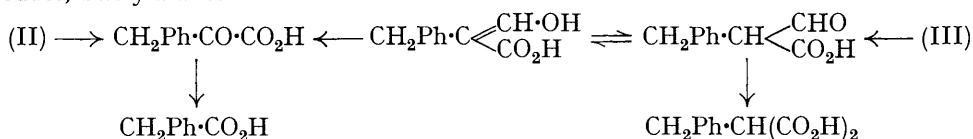
Reduction of α -Vinylcinnamic Acid.—Kuhn and Deutsch reduced the conjugated acid with sodium amalgam in the presence of carbon dioxide. They described the dihydro-acid as a liquid which on distillation (7 mm.) passed into the known crystalline α -benzylcrotonic acid, m. p. 99°. They suggested that the liquid undistilled acid might contain the unknown geometrical isomeride of the crystalline acid. They considered the presence of β -phenyl- α -vinylpropionic acid to be excluded because (1) on oxidation with chromic acid the liquid acid gave acetic acid in yield equal to that obtained from authentic α -benzylcrotonic acid, and (2) on ozonolysis the liquid acid gave acetaldehyde but no formaldehyde. We have reinvestigated the matter.

Our reductions of the conjugated acid were carried out with sodium amalgam both in carbonated alkaline, and in acid, solution, and also with aluminium amalgam in neutral solution. All three methods gave similar results. The dihydro-product consisted partly of α -benzylcrotonic acid, m. p. 99°, and partly of a liquid acid. The proportion in which these appeared varied considerably even when the conditions of reduction were as nearly as possible identical. The liquid acid on repeated distillation (14—15 mm.) underwent no change. It was, however, quantitatively converted into α -benzylcrotonic acid, m. p. 99°, when treated with sodium hydroxide. These observations are much more strongly suggestive of prototropic change (a possibility considered by Kuhn and Deutsch) than of geometrical isomerisation (see later). Incidentally, the last experiment proves the absence of the tetrahydro-derivative.

We have excluded the hypothesis that the properties of the liquid dihydro-acid arise from the presence of a labile geometrical isomeride. This isomeride (this vol., p. 723) has m. p. 107°, and none of its mixtures with the acid of m. p. 99° are liquid near the ordinary temperature. Furthermore, the new isomeride is stable, not only thermally, but also on treatment with sodium hydroxide, under conditions more drastic than those of the experiments with the liquid dihydro-acid.

The oxidative degradation of the liquid acid was accomplished partly by Burton and Ingold's method (J., 1929, 2022) and partly by Fischer, Düll, and Ertel's (*Ber.*, 1932, 65, 1467); the former yielded an acid corresponding to the aromatic fragment of the unsaturated molecule, and the latter an aldehyde representing the aliphatic fragment. We show by both methods that the essential constituent of the liquid acid is indeed β -phenyl- α -vinylpropionic acid (III).

Burton and Ingold's method consists in ozonolysis combined with oxidation by hydrogen peroxide. Probably all specimens of the liquid acid contained some dissolved α -benzylcrotonic acid, not wholly removed by freezing or by fractional solution in water, and the oxidation product from this acid was phenylacetic acid. The β -phenyl- α -vinylpropionic acid also yielded some phenylacetic acid, especially when alkali was present during the oxidation of the aldehydes; but under suitably adjusted conditions, it gave its characteristic product, benzylmalonic acid:

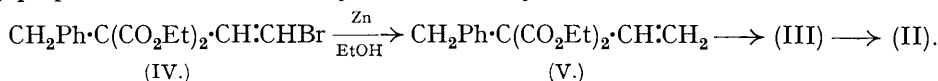


The intervention of the hydroxymethylene tautomeride of the aldehydic acid is assumed in order to account for effect of alkalis on the course of the oxidation of β -phenyl- α -vinylpropionic acid.

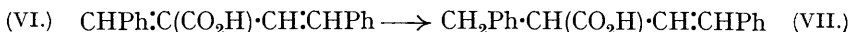
It appears, as might have been expected from the constitution of β -phenyl- α -vinylpropionic acid, that its ozonide is thermally unstable: the liquid dihydro-acid, on ozonolysis under ordinary conditions, yields only a little acetaldehyde, derived from the dissolved α -benzylcrotonic acid, but no formaldehyde. Fischer, Düll, and Ertel's method of ozonolysis is particularly valuable in cases of this kind (cf. Bradfield, Francis, and Simonsen, J., 1934, 188), and on applying it to the liquid acid we obtained formaldehyde in good yield.

These results prove that the liquid dihydro-compound consists essentially of β -phenyl- α -vinylpropionic acid (III). Its conversion into the Δ^a -tautomeride (II) has already been described and below we give synthetic confirmation of the facility with which this change takes place. We also show that in the reduction of a simple analogue of α -vinylcinnamic acid, for which, however, the change corresponding to (III) \longrightarrow (II) is much less facile, the sole dihydro-product is the 1 : 2-derivative, as theory requires.

Formation and Decarboxylation of Ethyl Benzylvinylmalonate.—The preparation was based on Cope and McElvain's discovery (*J. Amer. Chem. Soc.*, 1932, **54**, 4311) that dibromethylene has an appreciable reactivity towards sodiomalonic esters. Condensation with ethyl potassibenzylmalonate yielded the *bromovinyl* ester (IV), which on reduction with zinc and alcohol gave the *vinyl* ester (V). On hydrolysis of this, with either alkalis or acids, decarboxylation took place accompanied by complete isomerisation of the β -phenyl- α -vinylpropionic acid to the ordinary form of α -benzylcrotonic acid :



Reduction of α -Styrylcinnamic Acid.—The theory that the primary product of amalgam reductions of α -vinylcinnamic acid should be the 1 : 2-dihydro-compound applies equally to any substitution product of this acid, provided that it does not contain an additional substituent comparable in function with the carboxyl group; and amongst such substitution products some should be discoverable for which the transformation of the 1 : 2- into the 1 : 4-dihydro-derivative is much less facile than for α -vinylcinnamic acid itself. An example exists in α -styrylcinnamic acid (VI). Thiele reduced this substance by means of sodium amalgam in acid solution, and obtained only the 1 : 2-dihydro-compound (VII) (*Annalen*, 1899, **306**, 225). We have confirmed this observation, and also have carried out the reduction in alkaline solution with an identical result.



Concluding Remarks.—It will be appreciated that the theory of amalgam reductions is part of a more general theory of addition, in conformity with the principles of which it is assumed that the hydrogen adds, not in an atomic, but in an ionic, manner, the components ($\overset{+}{\text{H}} + 2e$) of the unstable ion ($\bar{\text{H}}$) being fixed before the complementary, stable ion ($\overset{+}{\text{H}}$) is taken up. Kuhn and Hoffer (*loc. cit.*) reject this conception in favour of that of the addition of hydrogen atoms or sodium atoms, and in their argument they allude to the statistical improbability of triple collisions, to the occurrence of pinacol-like reduction, and to known effects of the purity of amalgams. In reply we would direct attention to the statistical equivalence of three-body and successive two-body collisions (Hinshelwood, "Kinetics of Homogeneous Gas Reactions," 1933, p. 157). We should also emphasise that in our view the hydrogenation is essentially a wall-reaction, and that, in conformity with well-established conceptions, the metal surface is assumed to be present throughout the rate-affecting stage, normally the fixation of $\bar{\text{H}}$. Even the pinacol-like reduction products are formed only when two neighbouring adsorbed molecules, each having acquired but one electron from the metal, can be desorbed in combination; and when secondary changes succeed addition, as in the example of α -vinylcinnamic acid, they may also occur before or during desorption. The effect of purity in amalgams is automatically covered. Electrically conducting impurities provide weak places in the work-function of the metal-electrolyte interface, and, if these suffice for the electrons to escape into the electrolyte without using the reducible organic substance as a path, the amalgam will have poor efficiency. On the other hand, if, owing to the absence of electrically conducting impurities, the potential wall is nearly electron-proof, the discharge will be dependent on the adsorption of a molecular electrical conductor, *i.e.*, an unsaturated compound, and the reducing efficiency will be high. The theory is, indeed, in excellent agreement with the available facts, and one of its advantages over atomic theories of amalgam reductions is that it can be closely linked with contemporary views on overpotential.

EXPERIMENTAL.

α-Vinylcinnamic Acid.—This was prepared as recommended by Kuhn and Ishikawa (*Ber.*, 1931, **64**, 2347) except that an atmosphere of nitrogen was maintained above the reaction mixture in order to avoid the formation of coloured oxidation products. Amorphous by-products were removed by crystallising the crude acid from a large volume (*e.g.*, 24 l. for 15 g. of acid) of water below 75°, this limit of temperature being necessary to avoid polymerisation. The acid then separated from light petroleum in stout needles, and from acetic acid in plates, *m. p.* 92°. The yield was variable, and seldom above 20%.

Reduction of α-Vinylcinnamic Acid.—The sodium amalgam (2.5%) was in a readily friable form, prepared under paraffin in porcelain vessels. Various samples of aluminium were used for the preparation ("Houben," II, 256) of aluminium amalgam, one of the most satisfactory being a foil supplied by Messrs. Harrington Bros. The *α*-vinylcinnamic acid was reduced by sodium amalgam in alkaline and in acid solution and by aluminium amalgam in neutral solution. A typical reduction of each kind is described below, but the proportion of liquid product varied in the different experiments of each series.

(a) A solution of the acid (4.3 g.) in 2*N*-sodium carbonate (1 equiv.) was diluted with water (200 c.c.), treated with a stream of carbon dioxide, and stirred for 3.5 hours, during the first 2 hours of which the amalgam (450 g.) was gradually introduced. Hydrochloric acid was added to the filtered solution at 0°. The precipitate, which was washed with much water and crystallised from this solvent, consisted of *α*-benzylcrotonic acid, and a further small quantity, isolated along with the liquid acid, was separable below 0° (*m. p.* and mixed *m. p.* 99°; yield, 2.1 g.). The liquid acid, obtained by extraction of the aqueous liquors with ether, was purified by two distillations (*b. p.* 119–122°/2 mm., 174°/19 mm.; yield, 1.5 g.) (Found: C, 74.7; H, 6.9. C₁₁H₁₂O₂ requires C, 75.0; H, 6.8%).

(b) For the reductions in acid solution the solvent was a mixture of 95% ethyl alcohol (80 c.c.) and glacial acetic acid (60 c.c.). At the end of the reduction the mixture was filtered, and the residues washed with hot alcohol and acetic acid. Water was added to the solution, the alcohol boiled off, and hydrochloric acid added at 0°. The products, isolated as under (a), were *α*-benzylcrotonic acid (0.75 g., *m. p.* 99°), and the liquid acid (2.25 g., *b. p.* 166°/15 mm.), from which no further *α*-benzylcrotonic acid could be separated.

(c) A neutral solution of the acid (5.7 g.) in 2*N*-aqueous sodium hydroxide was diluted with water (500 c.c.) and reduced for 18 hours with aluminium amalgam (13 g.). The products were *α*-benzylcrotonic acid (3.5 g.) and the liquid acid (1.3 g.).

Properties of the Liquid Dihydro-Acid.—Specimens from which further *α*-benzylcrotonic acid could not be separated by freezing or otherwise could not be caused to yield that acid by distillation (15 mm.), followed by cooling and seeding. They were, however, quantitatively converted into the pure crystalline acid by treatment with 2*N*-aqueous sodium hydroxide for 15 minutes on the water-bath. The same reagent effected conversion, although more slowly, at room temperature. The liquid acid and *α*-benzylcrotonic acid were comparably hydrogenated in 95% ethyl alcohol in the presence of Adams's platinum catalyst; both absorbed nearly 4 mols. of hydrogen and the times occupied in the absorption were similar.

Oxidation of the Liquid Dihydro-acid.—(a) The acid was treated with 3% ozonised oxygen in chloroform solution at 0°, and after removal of the solvent the ozonides were decomposed with water. Volatile aldehydes were carried by means of a stream of air into a solution of 2:4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The precipitated arylhydrazones appeared to be impure, but by crystallisation from alcohol and benzene gave acetaldehyde-2:4-dinitrophenylhydrazone. The remaining products of the ozonolysis were oxidised with hydrogen peroxide (Burton and Ingold, *loc. cit.*). The acids, obtained by extraction with ether, were lixiviated with water, which removed the more soluble benzylmalonic acid, and this was then extracted from the aqueous washings with ether and crystallised from benzene (*m. p.* and mixed *m. p.* 115°) (Found: C, 62.0; H, 5.2. Calc.: C, 61.9; H, 5.2%). The acid which was less soluble in water was crystallised from ligroin and shown to be phenylacetic acid (*m. p.* and mixed *m. p.* 76°). If sodium carbonate or hydroxide was added before the decomposition of the ozonides with water, the sole acid product was phenylacetic acid.

(b) The acid was treated with 3% ozonised oxygen in ethyl acetate at –80°, and the ozonides were reduced with hydrogen after the addition of palladised barium sulphate (Fischer, Düll, and Ertel, *loc. cit.*). The filtered solution was extracted with water, and formaldehyde was isolated from the aqueous extract in the form of methylenedimethone (Vorländer, *Z. anal. Chem.*, 1929, **77**, 241) (*m. p.* and mixed *m. p.* 188–189°).

Ethyl α -Vinylcinnamate.—Silver α -vinylcinnamate (20 g., prepared from a neutral solution of the ammonium salt), ethyl iodide (26 g.), and benzene (100 g.) were heated together on the water-bath for 1.5 hours, and the filtered solution was dried and evaporated. The drying was necessary because it was not found possible to remove water completely from the silver salt by exposure over phosphoric oxide in a vacuum, and it is undesirable to heat the salt. The ester was a sweet-smelling liquid, b. p. 106—108°/1 mm. (Found: C, 76.9; H, 6.9. $C_{13}H_{14}O_2$ requires C, 77.2; H, 6.9%). On reduction with an equal weight of aluminium amalgam in moist ether, a *dihydro*-derivative, b. p. 134—144°/13—14 mm., was obtained (Found: C, 76.1; H, 8.1. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.9%).

Reduction of α -Styrylcinnamic Acid.—(a) The reduction by sodium amalgam in alcoholic acetic acid, described originally by Thiele (*loc. cit.*), was repeated with the same results; the β -phenyl- α -styrylpropionic acid, m. p. 124°, obtained in good yield, was converted by means of bromine into 2-bromo-1-phenyl-*ac*-tetrahydronaphthalene-3-carboxylic acid.

(b) Thiele stated that reduction in alkaline solution is precluded by the sparing solubility of sodium styrylcinnamate in water. Trial showed that the sodium salt is soluble enough, but that the acid is so weak that it is precipitated from an alkaline solution by carbon dioxide; it is, indeed, soluble in sodium carbonate, but not in sodium hydrogen carbonate, so an excess of carbon dioxide cannot be passed during the reduction. We therefore reduced the acid without carbonating. It was dissolved (3 g.) in 2*N*-sodium carbonate (12 c.c.), and the solution, diluted to 1 l., was treated during 3 hours with 3% sodium amalgam (50 g.). Rapid stirring was maintained, and after a further 2 hours the filtered solution was acidified. The precipitated product was treated as under (a) with the same results.

β -Phenyl- α -styrylpropionic acid remained substantially unchanged when heated under reflux for 2 hours with excess of 5*N*-aqueous sodium hydroxide.

Ethyl Benzyl- β -bromovinylmalonate.—No product of even approximately the correct bromine content could be obtained from *s*-dibromoethylene and ethyl sodiobenzylmalonate (cf. Cope and McElvain, *loc. cit.*). The bromovinyl compound was, however, obtained in a sufficiently pure form for further work by the following method. An ethereal solution of ethyl benzylmalonate (75 g.) was warmed with potassium (11.7 g.) under reflux until the metal had completely dissolved, and dibromoethylene (112 g.) was then added. The reaction appeared to begin readily, notwithstanding that a large amount of unchanged material was always recovered. The mixture was heated under reflux with continuous stirring for 18 hours, and the ethereal solution was then washed with dilute hydrochloric acid and with sodium chloride solution and dried with sodium sulphate. The ether and unchanged dibromoethylene were distilled off at ordinary pressure, and the unchanged ethyl benzylmalonate in the vacuum of a water pump. The condensation product, isolated by distillation up to about 165° at pressures below 0.1 mm., was obtained by redistillation as a pale yellow, viscous oil, b. p. 130—140°/0.05—0.07 mm. (Found: Br, 20.4. $C_{16}H_{19}O_4Br$ requires Br, 22.6%). The yields were about 7% of the theoretical.

Ethyl Benzylvinylmalonate.—A mixture of the bromo-ester (7 g.), 95% ethyl alcohol (15 c.c.), and zinc dust (4 g.) was enclosed in a stout sealed tube, which was clamped perpendicularly to a shaft by means of which it was slowly rotated for 10 hours in an air-bath at 170°. The cooled tube was opened (a considerable pressure was released), and the filtered solution was evaporated. The product from two experiments was washed in ethereal solution with hydrochloric acid, dried, and distilled. The required ester (4.5 g.) was collected at 100—110°/0.14 mm. (Found: C, 69.5; H, 7.2. $C_{16}H_{20}O_4$ requires C, 69.6; H, 7.2%).

The ester was hydrolysed with ethyl-alcoholic potassium hydroxide, aqueous-alcoholic sodium hydroxide, aqueous barium hydroxide, and hydrochloric acid in aqueous acetic acid. The sole product in all cases was α -benzylcrotonic acid (m. p. and mixed m. p. 99°).

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