

CCCLXXXIII.—*The Modes of Addition to Conjugated Unsaturated Systems. Part IV. Further Remarks and Observations on the Additions of Pseudo-acids.*

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General.—A statement of the position of this and the preceding paper in the general scheme of these investigations necessitates reference to the classification of additions to conjugated unsaturated systems which prefaced the brief review given in Part I (J., 1928, 910). This classification, which is based on the nature of addenda and the structural influences affecting unsaturated systems, may be restated in the following modified form :

Case 1. Both parts of addendum stable as anions [*e.g.*, Br₂, ICl]. Structural influences (*a*) favour, (*b*) inhibit anionotropy.

Case 2. One part of addendum stable as anion and the other as kation, the kationic component being the more reactive [*e.g.*, HBr]. Structural influences (*a*) favour, (*b*) inhibit anionotropy.

Case 3. One part of addendum stable as anion and the other as kation, the anionic component being the more reactive [*e.g.*, HCN, CH₂(CO₂Et)₂].

Case 4. Both parts of addendum stable as kations [*e.g.*, H₂].

Although cases 2 and 3 were not formally separated in Part I, the basic reason was given for effecting such a separation : it is that the mechanism of addition is different, reaction being initiated by kation-attack in case 2 and by anion-attack in case 3. One consequence of this is that the place of anionotropic phenomena in the orientation theory of case 2 is taken by reversibility effects in case 3. An alternative statement is that whilst, in case 2, the electromeric displacements which determine the distribution of the anion take place in a first-formed kation, which, after co-ordination, yields the molecular products, in case 3 they occur in the original unsaturated molecule, which, after co-ordination, gives the anions of the products ; in short, the distribution of the anion is determined in the final stage of addition in case 2, but in the initial stage of addition in case 3. A second, dependent difference is that, whereas in case 2 the anion-affinity required for the addition of the anionic component of the

addendum is furnished by the positive charge introduced in the first stage of addition, in case 3 the mechanism does not thus automatically furnish the necessary form of reactivity and hence some kind of electron-sink must be present originally in the unsaturated molecule. The effect of this on the classification is that the sub-division of case 2 according to the character of the structural influences contained in the unsaturated complex has no counterpart in case 3, in which electropolar nature of the dominating constitutional effect is predetermined. It still remains true that the analogies between the two cases in regard to the orientation effects they exhibit are very close; nevertheless the difference of mechanism leads to distinctions which, it is now considered, are of sufficient importance to justify the separation indicated.

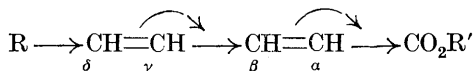
Cases 1a, 2a, and 3 of the revised classification were briefly reviewed in Part I. Further consideration was given to cases 1a and 2a in the preceding paper, and this communication continues the discussion of case 3.

Addition of Pseudo-acids to Derivatives of Conjugated Poly-enes.

In connexion with the general outline, given in Part I, of the orientation theory of these reactions, reference was made to the addition (Michael's reaction) of malonic ester to sorbic ester. The choice of this as a standard case with which to illustrate the principles submitted was deliberate. It had long been known that the main product of this reaction is the $\alpha\delta$ -addition compound, and, at that time (1928), four independent investigations (Vorländer, 1906; Farmer, 1924; Kohler and Butler, 1926; Farmer and Healey, 1927) had been carried out with the object of detecting the simultaneous production of an $\alpha\beta$ -addition isomeride—all without success. Further, the analogous addition of malonic ester to vinylacrylic ester had been independently studied by Kohler and Butler (1926) and by Farmer and Healey (1927) with completely parallel results: $\alpha\beta$ -addition could not be detected. Finally, Farmer and Healey (1927) had investigated the effect of replacing methyl malonate by ethyl methylecyanoacetate in both these reactions; the results were exactly the same; and, summarising their experience with all these reactions, the last-named investigators stated: "In no experiment could any divergence from the ($\alpha\delta$) type of addition be observed, and in particular, there is little doubt of the entire absence of $\alpha\beta$ -products." Despite this body of consistent experience, theoretical considerations indicated that, in the case of sorbic ester (and the same could have been said of any δ -monoalkylvinylacrylic ester), the addition products with malonic and cyanoacetic esters should contain

significant amounts of the $\alpha\beta$ -isomerides; and thus the authors of Part I, being unable to convince themselves that the cause of the discrepancy lay with the theory, stated their conclusions with respect to sorbic ester, and directed attention to the contrary indication of recorded observation. Since Part I was published, Farmer and Mehta have shown (J., 1930, 1610) that, notwithstanding the previous failures to detect $\alpha\beta$ -addition compounds,* the product of the addition of methyl malonate to methyl sorbate does indeed contain $8.5 \pm 1.5\%$ of the $\alpha\beta$ -isomeride.

A serious difficulty having been resolved by this important experimental demonstration, it is possible to continue the discussion, initiated in Part I, of the group of examples represented by the esters of vinylacrylic acid and its alkyl and aryl derivatives. The elementary theory is that the conductivity of unsaturated ions, including dipolar ions, guarantees the distribution between C_δ and C_β of the positive charge produced by the primary polarisation, whilst the greater lability of double bond electrons than of single bond electrons determines the dominant reactivity of C_δ :



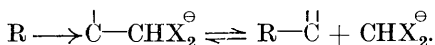
This holds provided the conditions of substitution in the $C_\delta : C_\gamma$ - and $C_\beta : C_\alpha$ -units, which determine the respective degrees of reversibility of the corresponding addition reactions, are comparable, and it is for this reason that sorbic ester, in which both C_δ and C_β are tertiary, rather than vinylacrylic ester, was selected as a test case in Part I, and is now treated as the point of departure.

Sorbic and Crotonylidenemalonic Esters.—Reference has already been made to Farmer and Mehta's result for the addition of methyl malonate to methyl sorbate. We have shown that ethyl cyanoacetate and ethyl sorbate yield an addition product containing $10 \pm 2\%$ of the $\alpha\beta$ -isomeride. It follows that the replacement of methyl malonate by a more reactive ψ -acid has little effect on the orientation of addition. We have also examined the addition product of methyl cyanoacetate and methyl crotonylidenemalonnate and find that it contains $16 \pm 2\%$ of the $\alpha\beta$ -compound. This shows that the increased efficacy of the α -situated electron-sink does not alter the type of orientation, though it diminishes the disparity between the proportions of the isomerides.

Vinylacrylic Ester.—The influence of δ -alkylation may be envisaged as a simple application of the effect (Cooper, Ingold, and

* Detailed references to the previous literature will be found in this paper.

Ingold, J., 1926, 1868) of the β -alkylation of acrylic esters in repressing Michael-equilibria* in favour of the factors,



In the more complex case of vinylacrylic esters, $\alpha\delta$ -addition would be selectively repressed by δ -alkylation, the double equilibrium, $\alpha\delta$ -products \rightleftharpoons factors \rightleftharpoons $\alpha\beta$ -products, being shifted towards the right. Accordingly methyl vinylacrylate and methyl malonate should give considerably less than 8.5% of $\alpha\beta$ -addition product, and, in conformity with previous experience of this reaction (above), we find that the proportion of $\alpha\beta$ -isomeride is certainly under 2%.

δ -Methylsorbic Ester.—Analogously, the product of addition of malonic ester to this ester should contain substantially more than 8.5% of the $\alpha\beta$ -compound. This inference still awaits verification.

γ -Methylsorbic Ester.—Not only β -alkylation in acrylic esters, but α -alkylation also is known to repress Michael-equilibria in favour of the factors (Cooper, Ingold, and Ingold, *loc. cit.*), the alkyl group in

this case acting through an unsaturated linking, $R \longrightarrow \overset{\curvearrowright}{\underset{\curvearrowleft}{\text{C}}}=\overset{\curvearrowright}{\underset{\curvearrowleft}{\text{C}}}-\text{CHX}_2$.

It follows that the effect of γ -alkylation in vinylacrylic esters should be qualitatively similar to that of δ -alkylation. In particular, γ -alkylsorbic esters, in reaction with cyanoacetic esters, ought to yield a considerably higher proportion than 10% of $\alpha\beta$ -addition product. Farmer and Mehta have in fact shown (*loc. cit.*) that the proportion of $\alpha\beta$ -isomeride in the product of addition of methyl cyanoacetate to methyl γ -methylsorbate is much more nearly 50%.†

* Regarding the establishment of these equilibria, see Vorländer (*Ber.*, 1900, **33**, 3185) and Ingold and Powell (*J.*, 1921, **119**, 1976). The last-named authors regret that at the time of the publication of their paper, and indeed for some years afterwards, they remained unaware that the general phenomenon to which they had directed attention had been observed by Vorländer many years earlier.

† Since this paper was written a further publication by the same authors has appeared (this vol., p. 1904) in which they give 70—74.5% as the proportion of $\alpha\beta$ -isomeride formed from ethyl cyanoacetate and ethyl γ -methylsorbate. The authors also confirm their earlier result for methyl sorbate and ours for ethyl β -methylsorbate (using, however, ethyl malonate, whereas we used ethyl cyanoacetate), and, by showing that crotonylideneacetone and methyl malonate yield 27—29% of $\alpha\beta$ -product, they provide a new instance of the effect (p. 2767) of increasing the efficacy of the α -situated electron-sink. Incidentally, several of the points in the paragraph on the relative facility of addition (p. 2770) are illustrated; notably, the positions assigned to β -methylsorbic and $\beta\delta$ -dimethylsorbic esters in the alkyl-substituted series, and the relation of β -methylsorbic ester to its phenyl analogue, β -styryl-cinnamic ester, are substantiated. Thus these most recent results are consistent both with the observational data now recorded and with our general interpretation of the conjugative additions of pseudo-acids.

β-Methylsorbic Esters.—An entirely similar argument shows that β -alkylation in vinylacrylic esters should selectively repress $\alpha\beta$ -addition. As an example, the proportion of $\alpha\beta$ -isomeride in the product of the addition of ethyl cyanoacetate to ethyl β -methylsorbate should be definitely less than 10%. We find that, although appreciable, it is not more than 2%.

α-Methylsorbic Esters.—Analogously, the product of addition of ethyl cyanoacetate to ethyl α -methylsorbate should contain substantially less than 10% of the $\alpha\beta$ -compound. We find that the proportion is appreciable but is actually not more than 2%.

Cinnamylideneacetic and Cinnamylidenemalonic Esters.—The very great electron-releasing power of the δ -phenyl substituent in these compounds would be expected (compare Part I) strongly to repress $\alpha\delta$ -addition and thus to cause the formation of high proportions of $\alpha\beta$ -addition products. So far as cinnamylideneacetic esters are concerned, Vorlander and Groebel (*Annalen*, 1906, **345**, 206) showed that this is so, the products of addition with malonic esters consisting wholly or almost wholly of the $\alpha\beta$ -isomerides; we have, indeed, confirmed this result using a different experimental method. With regard to methyl cinnamylidenemalonate, it is known that $\alpha\beta$ -addition products are formed with hydrogen cyanide (Thiele and Meisenheimer, *Annalen*, 1899, **306**, 247) and with nitromethane (Kohler and Engelbrecht, *J. Amer. Chem. Soc.*, 1919, **41**, 764), and that, in the latter case at least, the isomeride isolated is substantially the only one produced. The reaction with methyl malonate pursues a complicated course which is at present the subject of investigation. The reaction with methyl cyanoacetate is also complex, but in this case we are able to show that it is initiated by $\alpha\beta$ -addition, since the actual products, methyl α -cyanocinnamylideneacetate and methyl malonate, whilst they have no intelligible connexion with a product of $\alpha\delta$ -addition, are the substances to be expected from the incursion of a retrograde Michael reaction following the formation of the $\alpha\beta$ -isomeride.

β-Styrylcinnamic Ester.—The presence of phenyl substituents in both δ - and β -positions is expected strongly to repress both $\alpha\delta$ - and $\alpha\beta$ -addition, and it is therefore scarcely surprising that, using cyanoacetic ester, we were unable to obtain practicable yields of addition products. Should it be possible to find a sufficiently active ψ -acidic addendum, the products of addition, in contrast to those derived from cinnamylideneacetic ester, should consist largely of 1 : 4-addition compounds.

Muconic Ester.—The β -positions should evidently be the more reactive towards the anions of ψ -acids, and this is consistent with the known mode of attachment of cyanoacetic and malonic esters

(Farmer, J., 1922, **121**, 2015; 1923, **123**, 3324; Farmer and Mehta, this vol., p. 1762). The formation of a dicyclopropyl ester rather than a cyclopentadiene ester from methyl $\alpha\alpha'$ -dichloromuconate and methyl malonate (Farmer, J., 1923, **123**, 3332) is closely allied and is also consistent.

Facility of Additions.—The preceding considerations enable us to foretell the effect of structural changes in the unsaturated substance on the facility of addition in simple cases, *i.e.*, the relative yields in which addition products should be formed with a given addendum under given conditions of temperature and concentration. Thus for substitution by methyl the order should be,

vinylacrylic ester > sorbic ester > α - and β -methylsorbic esters >
 γ - and δ -methylsorbic esters > $\beta\delta$ -dimethylsorbic esters

and for substitution by phenyl it should be,

vinylacrylic ester > cinnamylideneacetic ester > β -styrylcinnamic ester.

The recorded facts confirm the first sequence to the following extent:

vinylacrylic ester > sorbic ester > α - and β -methylsorbic esters >
 γ -methylsorbic ester,

the positions of δ -methyl- and $\beta\delta$ -dimethyl-sorbic esters being as yet unknown.* The second sequence is completely confirmed by experiment. It can also be foreseen that the disparities in the second sequence should be greater than those in the corresponding methyl-sequence, *viz.*,

vinylacrylic ester > sorbic ester > β -methylsorbic ester,

and this also is fully confirmed by experimental results.

EXPERIMENTAL.

Addition of Methyl Malonate to β -Vinylacrylate.—The addition product (Kohler and Butler, *op. cit.*) was first examined by ozonolysis in conjunction with Schryver's test for formaldehyde, by which it was found possible to detect 1 part of this substance in the presence of 500 parts of acetaldehyde in solutions of concentration 0.2—2.0% with respect to the latter. Acetaldehyde was present in the volatile ozonolysis product, but formaldehyde could not be detected with certainty. The less volatile products were treated with cold hydrogen peroxide and the acids were isolated, and esterified with methyl alcohol. Malonic and succinic acids were obtained on fractionation of the esters and saponification of the fractions.

On reduction in aqueous acetic acid by means of hydrogen and platinum-black the addition product yielded *methyl pentane- $\alpha\alpha\alpha$ -*

* See footnote, p. 2768.

tricarboxylate, b. p. 172—176°/19—20 mm. (Found: C, 53·3; H, 7·4. $C_{11}H_{18}O_6$ requires C, 53·6; H, 7·3%), which on boiling for 8 hours with 20% hydrochloric acid gave almost pure pimelic acid (m. p. and mixed m. p.). Since β -vinylacrylic acid is now preparable in quantity (Burton and Ingold, J., 1929, 2028), the yield in the Michael reaction is 75%, and the subsequent processes are practically quantitative, this series of reactions seems to constitute a method at least as convenient as any which exist for the preparation of pimelic acid. β -Ethylglutaric anhydride could not be separated from the unpurified pimelic acid by digestion with acetic anhydride and subsequent distillation.

Addition of Ethyl Cyanoacetate to Ethyl Sorbate.—The addition, carried out by a method based on that of Kohler and Butler (*op. cit.*), gave in 76% yield a product, b. p. 180—189°/15—16 mm., subsequently shown to consist of a mixture of *ethyl α -cyano- β -methyl- Δ^{γ} -pentene- $\alpha\epsilon$ -dicarboxylate* and *ethyl α -cyano- β -propenylglutarate* (Found: C, 61·3; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%). It was completely hydrolysed by boiling first with dilute sulphuric acid until carbon dioxide ceased to be evolved, and then with aqueous sodium hydroxide in order to complete the elimination of nitrogen as ammonia. The oily acid was left in contact with hydriodic acid (8 parts; prepared by saturating the commercial acid with hydrogen iodide below 0°) at the ordinary temperature for 1 day, and the solution was then slightly diluted with water, mixed with phosphorus (0·25 part), and heated at 140° for 6 hours. The acid product, which was further reduced by zinc dust and acetic acid in order to eliminate some combined iodine, after complete distillation in the vacuum of an oil-pump, was obtained as a colourless oil from which β -methylpimelic acid, m. p. 47—48°, could be obtained by cooling and seeding. The over-all yield of the distilled mixture of acids based on the original addition product was, in the two best experiments, 85% and 87%, and it is considered that the loss was mainly mechanical, because, in a control experiment in which each process was duplicated before proceeding to the next, the over-all yield was lower but the composition the same. The samples of distilled acid (Found: C, 55·5; H, 7·8; *M*, by titration, 175, 175. Calc. for $C_8H_{14}O_4$, dibasic: C, 55·2; H, 8·0%; *M*, 174) were dehydrated with acetic anhydride and the β -*n*-propylglutaric anhydride was separated from the polymolecular β -methylpimelic anhydride by distillation (this method of separation is due to Farmer and Mehta, *loc. cit.*), and converted into its anilic acid, on the yield of which (m. p. 128°. Found: C, 67·4; H, 7·5. Calc.: C, 67·4; H, 7·6%) the figure for the proportion of $\alpha\beta$ -addition given in the introduction is based. The methylcyclohexan-3-one, obtained by completing the distillation at

a higher pressure, was identified as its semicarbazone (m. p. and mixed m. p. 191°).

Addition of Methyl Cyanoacetate to Methyl Crotonylidenemalonate.—The addition reaction, carried out analogously, yielded a viscous oil, b. p. 182—187°/2 mm., 190—200°/3 mm., 211—220°/9 mm., shown later to consist of a mixture of *methyl α -cyano- β -methyl- Δ^{γ} -pentene- $\alpha\epsilon$ -tricarboxylate* and *methyl α -cyano- α -carboxy- β -propenyl-glutarate* (Found: C, 55.2; H, 5.8. $C_{13}H_{17}O_6N$ requires C, 55.1; H, 6.0%). It was hydrolysed, the hydrolysis product was reduced, and the reduced acids (Found: C, 55.2; H, 7.9%) were separated exactly as described above.

Addition of Ethyl Cyanoacetate to Ethyl β -Methylsorbate.—Ethyl β -hydroxy- β -methyl- Δ^{γ} -hexenoate (Burton and Ingold, J., 1929, 2029) was distilled under ordinary pressure, and the *ethyl β -methylsorbate* thus obtained was taken up in ether, dried with calcium chloride, and distilled. It had b. p. 102—104°/17—18 mm. (Found: C, 70.1; H, 9.2. $C_9H_{14}O_2$ requires C, 70.1; H, 9.1%). The addition, carried out by the general method already mentioned, gave an oil (yield, 65%), b. p. 195—200°/5—16 mm., shown later to consist essentially of *ethyl α -cyano- $\beta\gamma$ -dimethyl- Δ^{γ} -pentene- $\alpha\epsilon$ -dicarboxylate* (Found: C, 62.6; H, 7.8. $C_{14}H_{21}O_4N$ requires C, 62.9; H, 7.8%). On hydrolysis, reduction and dehydration by the method already described, it yielded no separable quantity of a substituted glutaric anhydride. The semicarbazone of the ketone had m. p. 191—195° (Found: C, 59.2; H, 9.2. Calc.: C, 59.0; H, 9.3%), and its oxime m. p. 72—73° (Knoevenagel, *Annalen*, 1897, 297, 163, records 190—196° and 73° for the m. p.'s of these derivatives of 1 : 3-dimethylcyclohexan-3-one).

The hydrolysis product on ozonolysis yielded methylsuccinic acid in quantity (m. p. and mixed m. p.). Acetone and acetaldehyde were qualitatively detected, and the *p*-nitrophenylhydrazone of the latter was obtained in quantity sufficient for confirmatory identification (m. p. and mixed m. p.).

Addition of Ethyl Cyanoacetate to Ethyl α -Methylsorbate.—The addition product (yield, 67%), consisting essentially of *ethyl α -cyano- $\alpha\epsilon$ -dimethyl- Δ^{γ} -pentene- $\alpha\epsilon$ -dicarboxylate*, had b. p. 196—200°/17—18 mm. (Found: C, 62.8; H, 7.7. $C_{14}H_{21}O_4N$ requires C, 62.9; H, 7.8%), and, on degradation as in the preceding example, gave similar results. The ketone had b. p. 174—176°, and its semicarbazone (Found: C, 58.8; H, 9.1. Calc.: C, 59.0; H, 9.3%) m. p. 166—167° (Harding, Haworth, and Perkin, J., 1908, 93, 1970, record 174—177° as the b. p. of 1 : 4-dimethylcyclohexan-2-one and 167° as the m. p. of its semicarbazone).

The hydrolysis product when ozonised gave a large amount of

methylsuccinic acid (m. p. and mixed m. p.), and a very small amount of acetaldehyde which was isolated as its *p*-nitrophenylhydrazone (m. p. and mixed m. p.).

Addition of Methyl Malonate to Methyl Cinnamylideneacetate.—The product of this reaction (Vorländer and Groebel, *loc. cit.*) was hydrolysed, decarboxylated at 160°, and examined by the method of ozonolysis. The ozonide, prepared in chloroform, was decomposed with water and the products were oxidised with hydrogen peroxide. The products were tricarballic acid, which was isolated as its lead salt and identified as such and as its anhydro-acid (m. p.'s and mixed m. p.'s), and benzoic acid.

Addition of Methyl Cyanoacetate to Methyl Cinnamylidenemalonate.—This reaction proceeded rapidly in the cold in the presence of small proportions of sodium methoxide, and methyl α -cyanocinnamylideneacetate separated in large yield as a yellow crystalline solid, m. p. 143–145° (Found: C, 73.1; H, 5.2; N, 7.0. $C_{13}H_{11}O_2N$ requires C, 73.2; H, 5.2; N, 6.6%). Methyl malonate was obtained from the alcoholic liquid and identified by conversion into malonamide (m. p. and mixed m. p.).

The cyano-ester was independently synthesised by adding a few drops of sodium methoxide solution to a mixture of cinnamaldehyde and methyl cyanoacetate. The mixture rapidly set to a yellow mass, which, having been drained and crystallised from methyl alcohol, was found to be identical with the previous specimen (m. p. and mixed m. p.).

Formation and Properties of Ethyl β -Styrylcinnamate.—Chalkone (10.4 g.), ethyl bromoacetate (10 g.), and zinc (4 g.) were heated together in dry benzene (30 c.c.) until the zinc began to dissolve: the source of heat was then removed and the reaction was allowed to proceed spontaneously. After the spontaneous reaction had ceased, the mixture was heated for 30 minutes, cooled, poured into dilute sulphuric acid, and extracted with benzene. The residue obtained by drying and evaporating the solvent, on crystallisation from benzene, gave ethyl β -hydroxy- β -phenyl- β -styrylpropionate, needles, m. p. 93°, in almost theoretical yield (Found: C, 77.2; H, 6.8. $C_{19}H_{20}O_3$ requires C, 77.0; H, 6.6%). When this ester was heated for 1 hour with half its weight of potassium hydrogen sulphate, and the ethereal extract of the product was dried and distilled, ethyl β -styrylcinnamate was obtained in excellent yield as a pale yellow oil, b. p. 237°/10 mm. (Found: C, 82.3; H, 6.3. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%). Attempts to combine this ester with ethyl cyanoacetate in the presence of various proportions of sodium ethoxide uniformly resulted in the recovery of unchanged materials.

Miscellaneous Observations.—(i) *p*-Bromobenzyl cyanoacetate, pre-

pared by boiling a benzene solution of *p*-bromobenzyl bromide with silver cyanoacetate, separated from benzene in prisms, m. p. 84—85° (Found : C, 47·3; H, 3·1. $C_{10}H_8O_2NBr$ requires C, 47·3; H, 3·2%).

(ii) *Methyl γ -benzoyl- β -phenyl- α -carboxybutyrate*, prepared from chalkone and methyl malonate in the presence of piperidine, crystallised from methyl alcohol in prisms, m. p. 104° (Found : C, 70·9; H, 5·9. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%). Its constitution follows from its hydrolysis to γ -benzoyl- β -phenylbutyric acid (Vorländer and Knotsch, *Annalen*, 1897, **294**, 332), which was identified by its m. p., and that of its oxime.

(iii) β -*Styrylcinnamic acid* was prepared by boiling its ethyl ester (above) for 2 hours with 10% aqueous-alcoholic potassium hydroxide, precipitating the acid with hydrochloric acid, and crystallising it from alcohol or acetic acid, from which it separated in rhombic prisms, m. p. 145° (Found : C, 81·4; H, 5·5. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%). On treatment of the acid with 2 atoms of bromine in cold chloroform combination slowly took place, and, on removal of the solvent, a viscous liquid was obtained which solidified only after rubbing with ether. The solid product, a *bromo- β -styrylcinnamic acid*, crystallised from alcohol in needles, m. p. 170° (Found : C, 61·5; H, 4·0. $C_{17}H_{13}O_2Br$ requires C, 62·0; H, 4·0%). The reduction of β -styrylcinnamic acid will be described in a later communication.

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