

### 384. *Topochemistry. Part II.\* The Photochemistry of trans-Cinnamic Acids.*

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The photo-dimerisation of the two crystal modifications of *trans*-cinnamic acid has been re-investigated and clarified. The stable ( $\alpha$ ) form gives  $\alpha$ -truxillic acid only; the metastable ( $\beta$ ) form yields pure  $\beta$ -truxinic acid at temperatures where the  $\beta \longrightarrow \alpha$  phase transformation of the monomer is sufficiently slow; at higher temperatures  $\alpha$ -truxillic acid is also formed from the  $\alpha$ -modification which arises *via* the  $\beta \longrightarrow \alpha$  phase change.

The dimers of *o*-hydroxycinnamic acid and of its methyl, *n*- and isopropyl, and allyl ethers have been related to  $\alpha$ -truxillic acid. The ethoxy-acid occurs in three modifications: one form ( $\gamma$ ) is light-stable; the second ( $\alpha$ ) gives an  $\alpha$ -truxillic acid derivative; the third (least stable)  $\beta$ -form gives mainly a  $\beta$ -truxinic acid if irradiation is conducted at temperatures at which the phase transformation  $\beta \longrightarrow \alpha$  is slow. The 5-bromo-2-hydroxy-, 5-bromo-2-methoxy-, and 5-chloro-2-methoxy-derivatives of cinnamic acid dimerise to derivatives of  $\beta$ -truxinic acid.

*m*- and *p*-Hydroxy-*trans*-cinnamic acids dimerise to dihydroxy- $\alpha$ -truxillic acids while their methyl ethers are light-stable.

The photochemical behaviour of *o*-, *m*-, and *p*-nitro-*trans*-cinnamic acids has been re-investigated; *o*-, ( $\beta$ ) *m*-, and ( $\beta$ ) *p*-nitrocinnamic acids give dimers which have been identified as truxinic rather than the  $\alpha$ -truxillic acids suggested by Tanasescu and Hodosan. Light-stable modifications of *m*- and *p*-nitrocinnamic acids are described.

*o*-, ( $\beta$ ) *m*-, *p*-Chloro-, 2,4-, 3,4-, 2,6-dichloro-, *o*-, ( $\beta$ ) *m*-, and *p*-bromo-*trans*-cinnamic acids give photo-dimers all of which are derivatives of  $\beta$ -truxinic acid. *m*-Chloro- and *m*-bromo-cinnamic acids also occur in light-stable ( $\gamma$ ) modifications.

*o*-Methylcinnamic acid is light-stable while the *p*-isomer dimerises to the corresponding  $\alpha$ -truxillic acid.

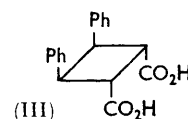
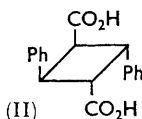
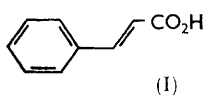
As part of the study of the effect of topochemical factors on solid-state reactions of organic compounds (see Part I \*) we report the results of work on the photo-dimerisation of *trans*-cinnamic acid and certain of its ring-substituted derivatives. In view of the expected effect of crystal-lattice geometry on the course of these reactions the objectives of this work

\* Part I, preceding paper.

have been the search for polymorphic forms of these acids, their preparation in high crystallographic purity, and the analysis of the photoreaction product(s), if any, arising from the monomer in each of its polymorphic modifications.

Our choice of derivatives of cinnamic acid has been based on the following considerations: first, we have repeated and extended previous work. Secondly, in preparation for the X-ray structural work reported in Part III (following Paper) we have studied the photochemistry of chloro- and bromo-substituted acids. Thirdly, to determine the effect of "steric inhibition" a few *ortho*-substituted acids have been irradiated. Fourthly, we have tested the photo-behaviour of several hydroxycinnamic (coumaric) acids in which the additional hydrogen bond must not only have a bigger effect on molecular packing than halogens or even alkoxy-groups, but may conceivably also set up a barrier to the molecular motion required for dimerisation. We have in fact covered a reasonably comprehensive range of substituents with the major exception of the amino-group: the photochemistry of the aminocinnamic acids will be reported later.

*Cinnamic Acid.*—Both the dimorphism and the solid-state dimerisation of *trans*-cinnamic acid (I) have been known for many years; nevertheless, the precise details of the solid-state reaction were never agreed by the several schools of investigators (*e.g.*, Stobbe,<sup>1</sup> and de Jong<sup>2</sup>), and even a recent study<sup>3</sup> failed to settle the problem. There is no need to review the earlier literature (see, *e.g.*, ref. 4); we note here the general consensus that the stable ( $\alpha$ ) form of acid (I) gives  $\alpha$ -truxillic acid (II) exclusively; controversy centres around



the reaction products of the metastable ( $\beta$ ) form of acid (I) which is reported to yield varying amounts of  $\beta$ -truxinic acid (III) and of  $\alpha$ -truxillic acid (II). Analysis of the controversial papers suggests that both the method of preparation of the metastable form and the conditions of photochemical reaction are open to suspicion. Most workers have prepared the  $\beta$ -form by precipitation from solutions of sodium cinnamate by mineral acid without adequate checks of the crystallographic purity of such a specimen. Again, the  $\beta$ -form was often irradiated in aqueous suspensions over long periods of time, apparently without the realisation that, because of the significant solubility of cinnamic acid in water, conversion of the metastable into the stable form can occur and may vitiate the experiment. Finally, the conditions of irradiation of dry materials (temperature, type of radiation) have frequently been inadequately specified and consequently are not always comparable.

In our re-investigation of the problem each of the two crystalline forms was prepared by several methods, and the purity of each phase checked. Pure  $\alpha$ -form can be grown in large crystals either by evaporation of a solution of the *trans*-acid (I) in ether, or from a solution in benzene by slow cooling. We have found that the  $\beta$ -form can best be prepared from concentrated solutions in ether which are rapidly filtered through a cotton plug previously washed with ether, and are then carefully overlaid with two to three volumes of light petroleum (b. p. 30–60°), the whole operation being carried out at 0°; large single crystals of the  $\beta$ -form grow over a period of a few days. Specimens thus produced must be checked for homogeneity: the small plates of the  $\alpha$ -form which are found in occasional preparations alongside the long laths of the  $\beta$ -form, can be distinguished by eye. The

<sup>1</sup> Stobbe, *Ber.*, 1922, **55**, 2225; 1925, **58**, 2415.

<sup>2</sup> de Jong, *Ber.*, 1922, **55**, 463; 1923, **56**, 818.

<sup>3</sup> Bernstein and Quimby, *J. Amer. Chem. Soc.*, 1943, **65**, 1845.

<sup>4</sup> Bachér, in "Handbuecher der biologischen Arbeitsmethoden," ed. Abderhalden, Urban, und Schwarzenberg, Berlin-Vienna, 1929, Abt. I, Teil 2, II, 1, p. 1829.

conventional method of preparation of  $\beta$ -cinnamic acid (by precipitation with mineral acid from sodium cinnamate solution) is adequate provided the solution is first filtered to remove traces of undissolved cinnamic acid which act as seeds of the  $\alpha$ -form.

Care is necessary in establishing methods of preparing samples for irradiation and the method of irradiation itself. Thermal stability of the metastable form was checked; powder samples were heated on a hot stage and their  $X$ -ray patterns taken at frequent intervals. It was found that  $\beta$ -cinnamic acid undergoes a phase transformation to the  $\alpha$ -form at a noticeable rate near  $50^\circ$ , and that the rate of this transformation is not only a function of temperature but also of crystal size. A routine check by  $X$ -ray powder photographs on the method of preparation of powdered specimens showed that long grinding in a mortar produces partial transformation of the metastable to the stable form, presumably as the result of the heat of friction. Grinding was therefore either omitted or reduced to the absolute minimum consistent with acceptable powder photographs.

The results of a large number of irradiation experiments can be summarised as follows:  $\alpha$ -*trans*-cinnamic acid dimerises to  $\alpha$ -truxillic acid only;  $\beta$ -*trans*-cinnamic acid dimerises to  $\beta$ -truxinic acid only, provided the irradiation experiment is carried out at a sufficiently low temperature ( $<50^\circ$ ), where the (thermal)  $\beta \rightarrow \alpha$ -transformation does not occur. If, on the other hand, the temperature during irradiation is high enough to permit the phase transformation to proceed at a rate comparable to that of dimerisation, the product of the photo-reaction will be a mixture of the dimers (II and III) resulting from the two modifications. Powder photographs taken during exposure to light at temperatures above  $50^\circ$  show the presence of the  $\alpha$ -modification of the monomer.

We conclude that the correlations  $\alpha$ -*trans*-cinnamic acid  $\rightarrow$   $\alpha$ -truxillic acid, and  $\beta$ -*trans*-cinnamic acid  $\rightarrow$   $\beta$ -truxinic acid, are well established, and that the conflicting experimental results of previous workers are explained in terms of crystallographic impurity of the  $\beta$ -phase and working conditions in a temperature range where the  $\beta$ -phase transforms thermally to the  $\alpha$ -phase.

*Hydroxycinnamic Acids.*—In our re-investigation of the photochemistry of *o*-hydroxycinnamic acid and its ethers (methyl, ethyl, *n*- and iso-propyl, allyl) we have based our work on that of Ström.<sup>5</sup> Our results agree with his except for the ethoxy-derivative of which additional crystal forms have been discovered. We have extended Ström's work by showing that the dimers of these alkoxy-acids, with the exception of one of the two dimers of the *o*-ethoxy-acid (see below) are derivatives of the dicoumaric acid which is obtained by the solid-state dimerisation of the hydroxy-acid itself. This identification was effected both by the dealkylation (in acid medium) of these dimers to dicoumaric acid as well as, conversely, by alkylation (in alkaline medium) of dicoumaric acid. The crystallographic constants of the dimethyl ester of the dimer of *o*-methoxycinnamic acid show that this ester has a molecular centre of symmetry; it therefore is a derivative of  $\alpha$ -truxillic acid, as must also be the dimers of *o*-hydroxycinnamic acid and of the alkoxy-acids referred to above. The configuration of the dimer of *o*-hydroxycinnamic acid has also been proved independently by Anet.<sup>6</sup>

The ethoxy-acid was found also in a light-stable ( $\gamma$ ) and in a second photo-active ( $\beta$ ) modification. The latter form is unstable: it is sensitive to grinding and changes to the  $\alpha$ -form at a measurable rate at  $30^\circ$ . Irradiation of this acid gave a mixture of dimers (IV) and (V) whose ratio was a function of the temperature during irradiation. Dimer (IV) was identical with that obtained from the  $\alpha$ -form and is therefore 2,2'-diethoxy- $\alpha$ -truxillic acid; dimer (V) has been identified as 2,2'-diethoxy- $\beta$ -truxinic acid (see below). Since the  $\alpha$ -monomer pattern replaces the original  $\beta$ -lines in the early stages of irradiation at  $50^\circ$ , the formation of the truxillic acid at this temperature may be ascribed to the  $\alpha$ -form produced by the thermal  $\beta \rightarrow \alpha$  phase transformation. This explanation, invoked already in the instance of  $\beta$ -cinnamic acid, is supported by the fact that on irradiation at

<sup>5</sup> Ström, *Ber.*, 1904, **37**, 1385.

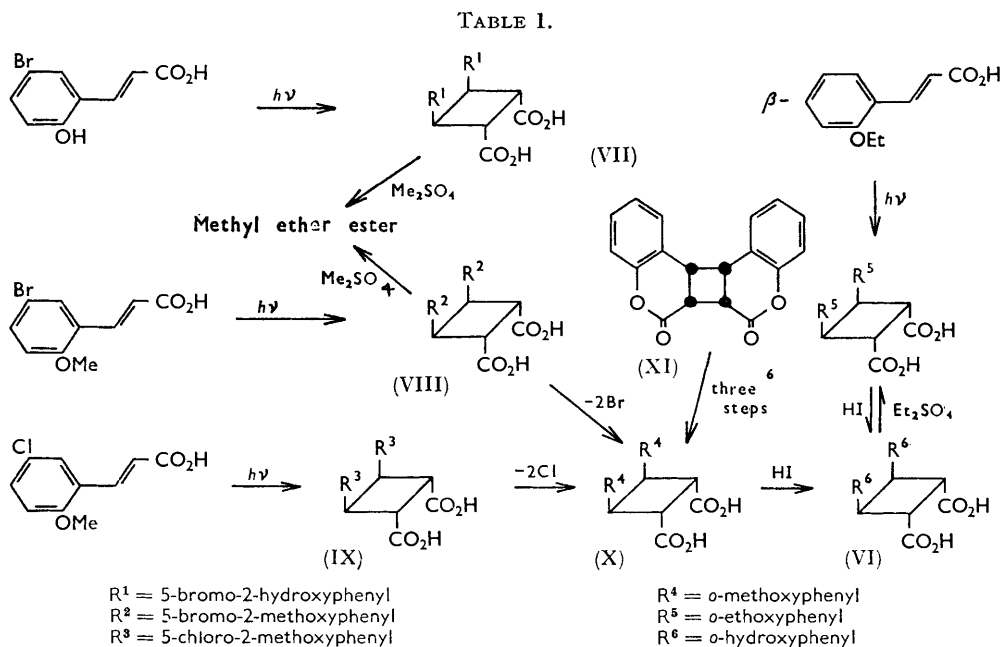
<sup>6</sup> Anet, *Canad. J. Chem.*, 1962, **40**, 1249.

25°, where no  $\alpha$ -pattern is observed, the product ratio (V) : (IV) is 20 : 1 as compared with 1 : 1 at 50°.

A third crystal form of *o*-ethoxycinnamic acid, obtained by recrystallisation from ethanol-water, proved to be light-stable: no change in melting point or powder diagram could be observed after 26 days' irradiation. We have thus established the following correlation:  $\alpha$ -modification  $\rightarrow$  2,2'-diethoxy- $\alpha$ -truxillic acid,  $\beta$ -modification  $\rightarrow$  2,2'-diethoxy- $\beta$ -truxinic acid;  $\gamma$ -modification, light-stable.

The structure of (V) was derived as follows. On treatment with hydrodic acid it gave a dihydroxy-acid (VI), from which it was recovered by ethylation and partial hydrolysis. Treatment of the dihydroxy-acid (VI) with boiling acetic anhydride afforded a five-membered cyclic anhydride diacetate ( $\nu_{\max}$  in KBr, at 1780, 1860, and 1760  $\text{cm}^{-1}$ ), rather than a mono- or di-lactone. The two carboxyl groups are therefore attached *cis*-1,2 to the cyclobutane ring and *trans*- to both *o*-hydroxyphenyl groups; product (V) is therefore 2,2'-diethoxy- $\beta$ -truxinic acid.

The 5-bromo-2-hydroxy-, ( $\beta$ ) 5-bromo-2-methoxy-, and 5-chloro-2-methoxy-derivatives of *trans*-cinnamic acid, whose photochemistry has not been previously investigated, dimerise to (VII), (VIII), and (IX), respectively; these dimers are  $\beta$ -truxinic acids, since on the dehalogenation they give a compound (X), which can be converted into the dihydroxy-acid (VI) by demethylation with HI. Anet,<sup>6</sup> independently, prepared compound (X) from *cis*-*syn*-dicoumarin (XI) by methylation, double epimerisation, and hydrolysis, and derived its structure by n.m.r. methods. The inter-relationship of compounds (V)—(XI) is summarised in Table I.

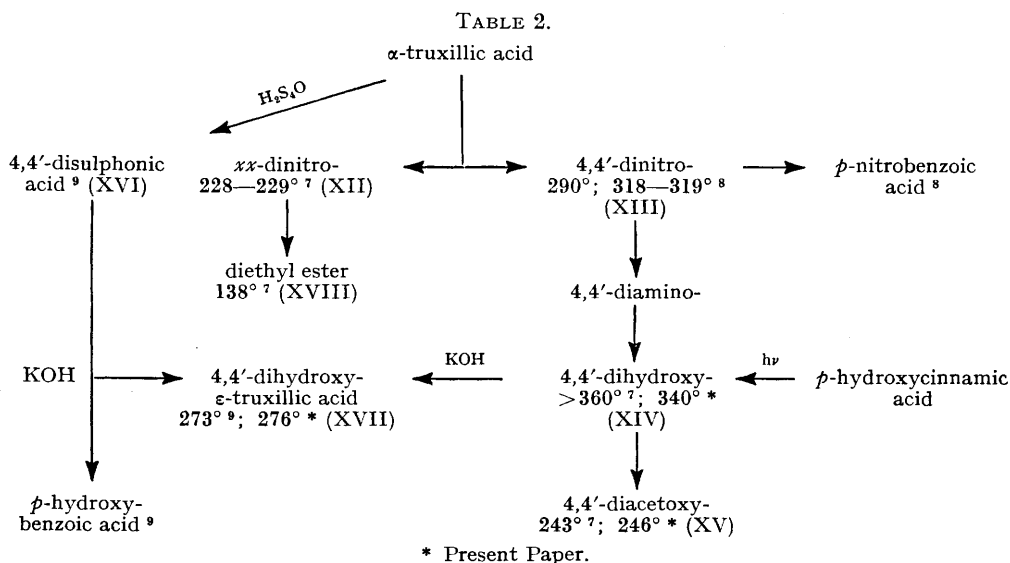


Of these three halogenated acids the 5-bromo-2-methoxy-derivative has been observed also in a light-stable ( $\gamma$ ) modification.

*m*- and *p*-Hydroxy-*trans*-cinnamic acids give photo-dimers which, according to their crystallographic constants, are likely to be  $\alpha$ -truxillic acid derivatives. The proof of the chemical structure of the dimer of the *p*-isomer is based on the following argument: Homans, Steltzner, and Sukow<sup>7</sup> have prepared a dihydroxy- $\alpha$ -truxillic acid from the

<sup>7</sup> Homans, Steltzner, and Sukow, *Ber.*, 1891, **24**, 2590, 2592.

higher-melting isomer of their dinitration products [m. p. 228—229°, (XII) and m. p. 290° (decomp.) (XIII)] of  $\alpha$ -truxillic acid, *via* reduction and diazotisation. Since Schenck<sup>8</sup>



has shown compound (XIII) to be the 4,4'-derivative, their dihydroxy-acid is identified as (XIV). Its melting point is recorded<sup>7</sup> as above 360°; we find that our photo-dimer melts at 340° if heated rapidly, but does not melt below 360° if heated slowly. The melting point of the diacetate (XV) is reported<sup>7</sup> as 243° which corresponds to our value of 246°. Identity of the photo-dimer of *p*-hydroxycinnamic acid with (XIV) is therefore established.

Liebermann and Bergami<sup>9</sup> recorded a compound, m. p. 273°, prepared by potassium hydroxide fusion of the 4,4'-disulphonic acid of  $\alpha$ -truxillic acid (XVI) and claimed to be (XIV); while substitution of the 4- and 4'-positions was demonstrated by degradation to *p*-hydroxybenzoic acid the stereochemistry of this compound was not established. Indeed, it is unlikely to correspond to that of  $\alpha$ -truxillic acid, which is known to invert to  $\epsilon$ -truxillic acid on fusion with potassium hydroxide (Stoermer and Emmel<sup>10</sup>). To clarify this point we have subjected (XIV) to short treatment with fused potassium hydroxide and have obtained in excellent yield an acid, m. p. 276°, most probably identical with Liebermann and Bergami's acid and likely to be 4,4'-dihydroxy- $\epsilon$ -truxillic acid (XVII). Table 2 summarises these relationships.

The methyl ethers of the *m*- and *p*-hydroxy-acids were each obtained in light-stable ( $\gamma$ ) modifications only.

**Nitrocinnamic Acids.**—The photochemical behaviour of *o*-, *m*-, and *p*-nitro-*trans*-cinnamic acids has been reported by Tanasescu and Hodosan;<sup>11</sup> they state that *o*- and *p*-nitrocinnamic acids dimerise to derivatives of  $\alpha$ -truxillic acid whereas *m*-nitrocinnamic acid on irradiation undergoes partial resinification rather than dimerisation.

Our own results do not agree with their findings. We have obtained from *o*-nitrocinnamic acid (crystal modification from *t*-pentyl alcohol) a compound (m. p. 225—227°) isolated from the crude reaction mixture by the method described.<sup>11</sup> We may presume this compound to be identical with the dimer (m. p. 222—223°) obtained by the previous authors, particularly in view of the close correspondence of the melting points of the methyl

<sup>8</sup> Schenck, *Ber.*, 1934, **67**, 1691.

<sup>9</sup> Liebermann and Bergami, *Ber.*, 1889, **22**, 783.

<sup>10</sup> Stoermer and Emmel, *Ber.*, 1920, **53**, 499.

<sup>11</sup> Tanasescu and Hodosan, *Rev. Chim., Acad. R.P.R.*, 1956, **1**, No. 2, **39**.

and ethyl esters obtained in the two laboratories (methyl ester, m. p. 183—184°,<sup>11</sup> m. p. 186—187°; ethyl ester, m. p. 128—129°,<sup>11</sup> m. p. 130—131°). Tanasescu and Hodosan suggested the  $\alpha$ -truxillic acid configuration on the grounds that *o*-nitrocinnamic acid, m. p. 240°, is the most stable form of this acid and hence, by analogy with the stable ( $\alpha$ ) modification of *trans*-cinnamic acid, likely to give the corresponding  $\alpha$ -truxillic acid. The argument is unfounded in theory as well as unsupported by crystallographic data (see Part III, succeeding Paper). Since the dimer on treatment with acetic anhydride yields a five-membered cyclic anhydride ( $\nu_{\max}$  in KBr, 1780 and 1865  $\text{cm}^{-1}$ ) which can be hydrolysed back to the original diacid, we have identified it as one of the three isomers of 3-di-2-nitrophenylcyclobutane-1,2-*cis*-dicarboxylic acid.

*m*-Nitrocinnamic acid crystallised in two modifications of which one ( $\gamma$ ), obtained from the reaction mixture in pyridine, is light-stable; the second form ( $\beta$ ) (from aqueous acetic acid) yields, after three weeks' irradiation in sunlight, a compound of m. p. 205.5—206.5° which, according to the analysis and molecular-weight determination of its diethyl ester, is a dimer; since it contains no aliphatic double bond (no reaction with potassium permanganate or bromine solutions) it is identified as a cyclobutane derivative. It is converted by boiling acetic anhydride into a five-membered anhydride ( $\nu_{\max}$  in KBr, 1780 and 1865  $\text{cm}^{-1}$ ) from which it can be recovered after short treatment with 2% potassium carbonate solution. The dimer could be reduced, by means of hydrazine hydrate and Raney nickel,<sup>12</sup> to a diamino-derivative which was tetrazotised and converted with cuprous chloride into 3,3'-dichloro- $\beta$ -truxinic acid, described below. The dimer of *m*-nitrocinnamic acid is therefore 3,3'-dinitro- $\beta$ -truxinic acid.

*p*-Nitrocinnamic acid is reported<sup>11</sup> to dimerise to a cyclobutane derivative, m. p. 226—227°, whose diethyl ester melts at 134.5—135.5°. Tanasescu and Hodosan consider this dimer to be 4,4'-dinitro- $\alpha$ -truxillic acid (XII) on the ground that the melting points of their diacid and its diethyl ester agree with those of the dinitration product (XII), m. p. 228—229°, of  $\alpha$ -truxillic acid and its diethyl ester (XVIII), m. p. 138° (see Table 2), first obtained by Homans *et al.*<sup>7</sup> and mistakenly identified by Jessen<sup>13</sup> as the 4,4'-dinitro-derivative. Tanasescu and Hodosan overlooked Schenck's later correction,<sup>8</sup> according to which 4,4'-dinitro- $\alpha$ -truxillic acid melts at 318—319° (see Table 2). Tanasescu's structure proof cannot, therefore, be accepted.

We have obtained a photo-dimer of m. p. 219—221° (diethyl ester, m. p. 136—137°) from *p*-nitrocinnamic acid recrystallised from acetic acid ( $\beta$ -form); a second modification of the monomer obtained from aqueous alcohol is light-stable ( $\gamma$ -form). Nitration of  $\beta$ -truxinic acid yields a dinitro- $\beta$ -truxinic acid<sup>7</sup> of previously unknown constitution which we could show to be identical with the dimer of *p*-nitrocinnamic acid; both compounds are therefore identified as 4,4'-dinitro- $\beta$ -truxinic acid. The close correspondence in melting points of our and Tanasescu's photo-dimers of their diethyl esters suggests that the two compounds are identical.

*Halogenocinnamic Acids.*—Since the presence of a heavy atom, such as chlorine or bromine, in an organic molecule often simplifies X-ray structure analyses we have investigated the photochemical behaviour of some halogenocinnamic acids. All six ring-substituted chloro- and bromo-acids dimerise; the *m*-derivatives also exist in light-stable modifications ( $\gamma$ ). The six dimers are derivatives of  $\beta$ -truxinic acid since they can be dehalogenated to the parent acid.

In order to test the influence of several large substituents 2,4-, 3,4-, and 2,6-dichloro-*trans*-cinnamic acids have been prepared and tested; all three dimerise to the corresponding tetrachloro- $\beta$ -truxinic acids, identified as such by dechlorination to the parent acid.

Methyl derivatives frequently crystallise in structures isomorphous with those of

<sup>12</sup> Houben-Weyl, "Methoden der organischen Chemie," G. Thieme, Stuttgart, 4th edn., 1957, Vol. 11/1, p. 455.

<sup>13</sup> Jessen, *Ber.*, 1906, **39**, 4087.

correspondingly substituted chloro- and/or bromo-compounds, and such isomorphism is of help in X-ray analyses; the *o*- and *p*-methylcinnamic acids were consequently prepared. Although their crystal structures turned out not to be related in an obvious manner to the corresponding chloro-acids, their photochemical behaviour was nevertheless investigated: the *o*-methyl acid was found to be inactive, whereas the *p*-isomer gave a dimer which was identified by its crystallographic constants as 4,4'-dimethyl- $\alpha$ -truxillic acid.

*Summary of Experimental Results.*—(1) Each crystalline phase gives its own characteristic photo-dimer or else is light-stable.

(2) In the series of ring-substituted cinnamic acids photo-dimerisation leads to  $\alpha$ -truxillic and  $\beta$ -truxinic acids only. We have detected no other products than the ones reported here, by using working-up procedures (fractional crystallisation, powder photography) whose limits of accuracy we estimate at 5% of converted material.

(3) Where two dimers are formed ( $\beta$ -cinnamic acid,  $\beta$ -form of *o*-ethoxycinnamic acid) it has been shown that the ratio of  $\alpha$ -truxillic to  $\beta$ -truxinic acid is temperature-dependent, that the dimer increasingly formed at higher temperature is derived from a second crystal modification of the monomer, and that this second modification is formed from the first by a thermal phase transformation at a sufficient rate to account for the appearance of its dimer.

(4) Steric effects due to *o*-substituents, in so far as they have been investigated, appear to play no role whatsoever since both *o*-bromo- and 2,6-dichloro-cinnamic acids dimerise. Both compounds yield overcrowded  $\beta$ -truxinic acids rather than isomers (such as  $\alpha$ -truxillic acid) with less severe internal strain.

(5) Intermolecular hydrogen-bonding presents no barrier to dimerisation. The parallelism of photo-reaction of the chalcones ( $\text{Ar}\cdot\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{Ar}$ )<sup>14</sup> and the cinnamic acids negates any effect on reactivity by the carboxyl hydrogen bonds; the ready dimerisation of the hydroxycinnamic acids described in this Paper is further evidence.

(6) No clear-cut correlation between photo-dimerisation or light-stability on the one hand and ring substituents on the other emerges from our work. Indeed, no "chemical" generalisation of any kind seems possible at this stage; it follows qualitatively from the different behaviour of each phase of polymorphic acids [see (1) and (3) above], and will be shown quantitatively in Part III (succeeding Paper), that dimerisation or light-stability and the structure of the reaction product are determined by the geometry of the molecular assembly, *i.e.*, the crystal lattice, rather than by the molecule itself. (Whether substituents affect rates of reaction by virtue of their electronic or other effects must be left a question for further work; our present data, while indicating wide variations in rate, are too crude to permit any conclusions.)

## EXPERIMENTAL

*Preparation of Materials.*—The cinnamic acids other than some *o*-coumaric acids were prepared from the correspondingly substituted benzaldehydes by condensation with freshly dried malonic acid in dry pyridine in the presence of small amounts of piperidine (*e.g.*, ref. 15); certain *o*-coumaric acids were obtained from coumarin (or substituted coumarins) by hydrolysis and isomerisation with yellow mercuric oxide.<sup>16</sup>

The compounds were first checked for polymorphism by recrystallisation from solvents of differing polarity (water, acetic acid, ethanol, nitromethane, methylcyclohexane, benzene, petroleum); crystals were grown by slow cooling (24—36 hr.) of solutions from the boiling point to room temperature. Sudden cooling of solutions was tested as a method of preparation

<sup>14</sup> Schönberg, "Präparative Organische Photochemie," Springer Verlag, Berlin, 1958, p. 26.

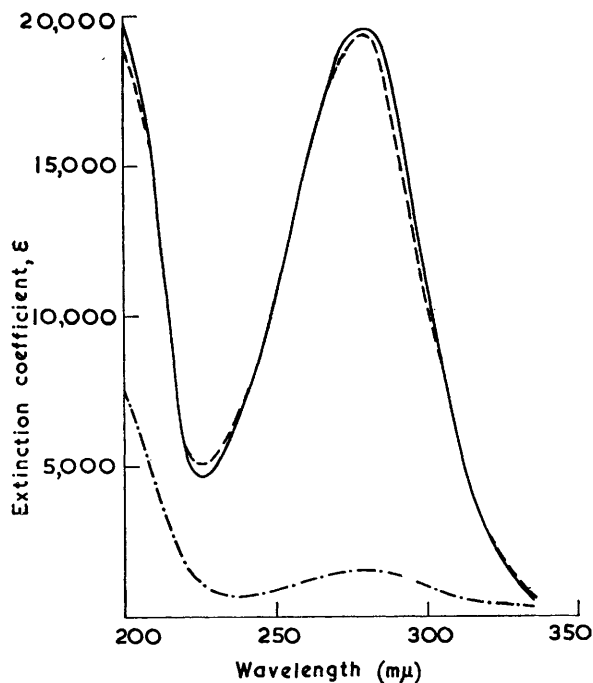
<sup>15</sup> Horning, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1955, Coll. Vol. III, p. 425.

<sup>16</sup> Chakravarti and Majumdar, *J. Indian Chem. Soc.*, 1933, **16**, 398; Seshadri and Rao, *Proc. Indian Acad. Sci.*, 1936, **3A**, 293.

of forms stable at high temperature and preserved by quenching. Single crystals were taken from crystallographically homogeneous specimens checked by microscopic methods, and their crystallographic constants measured in the usual way (see Table I, Part III); powder samples prepared from such specimens were photographed in a "Nonius" Guinier powder camera with Cu-K $\alpha$  radiation, and these photographs used as standards.

*Progress of Reaction.*—Bulk-recrystallised samples (10–20 g. lots) were checked for phase purity on the Guinier camera and, if pure, exposed to sunlight in Cellophane-covered Petri-dishes or in "Pyrex" cylinders. The powder was turned continuously (automatically) or

Ultraviolet absorption spectra of *m*-chloro-*trans*-cinnamic acid in ethanol; —, unirradiated; — · — · —, irradiated  $\beta$  crystal modification; - - - -, irradiated  $\gamma$  crystal modification.



once or twice daily (manually). Samples were withdrawn before, and at intervals during, irradiation and photographed on the Guinier camera. Progress of reaction was also followed by ultraviolet-absorption measurements. Irradiation was discontinued when no further change could be observed by these checks. The Figure shows the ultraviolet spectra of *m*-chlorocinnamic acid and of the irradiation product of its  $\beta$ -modification ( $\epsilon_{\text{apparent}}$  is calculated on the assumption of monomer molecular weight for both starting and irradiated materials). The "light-stable" crystal modifications show no change on irradiation, whether in powder pattern, ultraviolet spectrum, or melting point. The Figure shows the ultraviolet spectrum of the product of irradiation (21 days) of the  $\gamma$ -form of *m*-chlorocinnamic acid.

Materials appearing in more than one photo-active crystal form were irradiated with and without water cooling. The temperature of the non-cooled samples rose to (maximally) 50° depending upon the season of the year, while water-cooled materials were at all times held below 30°.

Table 3 lists the monomers in their various polymorphic forms and their photo-properties.

*Work-up of Irradiated Materials.*—Dimeric materials present in the irradiation product were separated from residual monomer (as also from oxidation or isomerisation products, if any) either by Soxhlet extraction or by direct recrystallisation. Certain dimers and more particularly the  $\beta$ -truxinic acids show a marked tendency to retain solvent of crystallisation; hence analyses were occasionally performed on derivatives rather than on the photo-products themselves. Infrared spectra were measured in potassium bromide unless otherwise stated. Identity of compounds was established by m. p., mixed m. p., and powder photography.



TABLE 3.

Cinnamic acid <sup>a</sup>	Ref.	Crystal form <sup>b</sup>	Crystallised from	Period of irradiation <sup>c</sup> days rate of change	Photo-product	Yield (%)
MT1 Cinnamic acid		$\alpha$	EtOH	15 fast	D1	74
MT2 "		$\beta$	precipitate	15 " fast	D1, <sup>h</sup> D2	20°: 3, 80 50°: 46, 30
MT3 <i>o</i> -HO-	16	$\alpha$	EtOH	21 fast	D3	90
MT4 <i>o</i> -MeO-	17	$\alpha$	MeOH	32 fast	D4	83
MT5 <i>o</i> -EtO-	18	$\alpha$	EtOAc	26 fast	D5	93
MT6 "		$\beta$	C <sub>6</sub> H <sub>6</sub> /pet	26 fast	D5, <sup>h</sup> D6	20°: 5, 90 50°: 36, 32
MT7 "		$\gamma$	EtOH-H <sub>2</sub> O	26 —	None	—
MT8 <i>o</i> -Pr <sup>n</sup> O-	17	$\alpha$	EtOAc	36 fast	D8	94
MT9 <i>o</i> -Pr <sup>t</sup> O-	17, 18	$\alpha$	AcOH-H <sub>2</sub> O	36 fast	D9	97
MT10 <i>o</i> -Allyloxy-		$\alpha$	EtOH-H <sub>2</sub> O	36 fast	D10	93
MT11 5-Br,2-HO- <sup>d</sup>	19	$\beta$	AcOH	45 slow	D11	30
MT12 5-Cl,2-MeO- <sup>e</sup>	16	$\beta$	EtOH	42 fast	D12	85
MT13 5-Br,2-MeO- <sup>e</sup>	20	$\beta$	EtOH	10 fast	D13	50 <sup>d</sup>
MT14 "		$\gamma$	EtOH-H <sub>2</sub> O	28 —	none	—
MT15 <i>m</i> -HO- <sup>e</sup>	21	$\alpha$	H <sub>2</sub> O	27 slow	D15	76
MT16 <i>m</i> -MeO- <sup>e</sup>	22	$\gamma$	C <sub>6</sub> H <sub>6</sub>	41 —	none	—
MT17 <i>p</i> -HO-	23	$\alpha$	MeNO <sub>2</sub>	27 slow	D17	78
MT18 <i>p</i> -MeO- <sup>e</sup>	24	$\gamma$	EtOH	40 —	none	—
MT19 <i>o</i> -NO <sub>2</sub> - <sup>e</sup>	25	$\beta$	Pe <sup>h</sup> OH	49 slow	D19	27 <sup>d</sup>
MT20 <i>m</i> -NO <sub>2</sub> - <sup>e</sup>	26	$\beta$	AcOH-H <sub>2</sub> O	21 fast	D20	60
MT21 "		$\gamma$	<sup>g</sup>	56 —	none	—
MT22 <i>p</i> -NO <sub>2</sub> - <sup>e</sup>	25	$\beta$	AcOH	28 fast	D22	70
MT23 "	25	$\gamma$	EtOH	28 —	none	—
MT24 <i>o</i> -Cl- <sup>e</sup>	27	$\beta$	EtOH-H <sub>2</sub> O	42 fast	D24	85
MT25 <i>m</i> -Cl- <sup>e</sup>	28	$\beta$	EtOH	77 fast	D25	70
MT26 "		$\gamma$	AcOH	70 —	none	—
MT27 <i>p</i> -Cl- <sup>e</sup>	29	$\beta$	AcOH	49 fast	D27	71
MT28 <i>o</i> -Br- <sup>e</sup>	30	$\beta$	AcOH-H <sub>2</sub> O	30 fast	D28	82
MT29 <i>m</i> -Br- <sup>e</sup>	31	$\beta$	AcOH-H <sub>2</sub> O	60 fast	D29	91
MT30 "		$\gamma$	EtOH	30 —	none	—
MT31 <i>p</i> -Br- <sup>e</sup>	31	$\beta$	EtOH-H <sub>2</sub> O	60 fast	D31	90
MT32 2,4-di-Cl- <sup>e</sup>	32	$\beta$	AcOH	90 slow	D32	78
MT33 2,6-di-Cl- <sup>e</sup>	28	$\beta$	AcOH	90 slow	D33	70
MT34 3,4-di-Cl- <sup>e</sup>	33	$\beta$	AcOH	90 slow	D34	60
MT35 <i>o</i> -Me- <sup>e</sup>	34	$\gamma$	C <sub>6</sub> H <sub>6</sub>	50 —	none	—
MT36 <i>p</i> -Me- <sup>e</sup>	34	$\alpha$	C <sub>6</sub> H <sub>6</sub>	50 fast	D36	95

<sup>a</sup> Superscript letters refer to method of preparation (Experimental). <sup>b</sup> For definition of crystal forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) see Part III (following Paper). <sup>c</sup> Periods of irradiation are only roughly comparable because of unequal conditions of irradiation during the different seasons of the year. <sup>d</sup> See Experimental. <sup>e</sup> By Doebner condensation (Experimental). <sup>f</sup> See Introduction. <sup>g</sup> As obtained from the reaction mixture in pyridine without recrystallisation. <sup>h</sup> The dimer is formed from the stable form of the monomer which is produced thermally during irradiation. The proportion of this product decreases at lower temperature (see Introduction). <sup>i</sup> Because of the unusually slow rate of reaction, irradiation was stopped before the end point had been reached.

<sup>17</sup> Stoermer, *Ber.*, 1911, **44**, 644.

<sup>18</sup> Hach and Protiva, *Chem. Listy*, 1957, **51**, 2099.

<sup>19</sup> Dey and Row, *J.*, 1924, **125**, 562.

<sup>20</sup> Büllman and Rimbert, *Bull. Soc. chim. France*, 1923, [4], **33**, 1478.

<sup>21</sup> Posner, *J. prakt. Chem.*, 1910, [2], **82**, 428.

<sup>22</sup> Helfer, *Helv. Chim. Acta*, 1924, **7**, 947.

<sup>23</sup> von Konek and Pacsu, *Ber.*, 1918, **51**, 856.

<sup>24</sup> Roth and Stoermer, *Ber.*, 1913, **46**, 269.

<sup>25</sup> Vanino, "Handbuch der präparativen Chemie," F. Enke, Stuttgart, 1923, Vol. II, p. 593.

<sup>26</sup> Gilman and Blatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1944, Coll. Vol. I, p. 399.

<sup>27</sup> Stoermer, *Ber.*, 1911, **44**, 657.

<sup>28</sup> Böck, Lock, and Schmidt, *Monatsh.*, 1934, **64**, 406, 409.

<sup>29</sup> van der Lee, *Rec. Trav. chim.*, 1926, **45**, 680.

<sup>30</sup> Reich and Chaskelis, *Bull. Soc. chim. France*, 1916, [4], **19**, 290.

<sup>31</sup> Gabriel, *Ber.*, 1882, **15**, 2297, 2301.

<sup>32</sup> Newman, Fones, and Renoll, *J. Amer. Chem. Soc.*, 1947, **69**, 719.

<sup>33</sup> Walling and Wolstirn, *J. Amer. Chem. Soc.*, 1947, **69**, 853.

<sup>34</sup> Kröber, *Ber.*, 1890, **23**, 1920.

*Cinnamic Acid (MT1, MT2).*—The two crystal forms of cinnamic acid were prepared as described above. Some preliminary data on the heat stability of the  $\beta$ -form are given in Table 4.

TABLE 4.  
Thermal stability of the  $\beta$ -form of cinnamic acid.

$T$ ( $^{\circ}\text{C}$ ) .....	25 $^{\circ}$	45 $^{\circ}$	51 $^{\circ}$	64 $^{\circ}$	64 $^{\circ}$
Time (hr.) .....	100	9	26	2	4
$\beta$ : $\alpha$ .....	100:0	100:0	$\sim$ 50:50	$\sim$ 50:50	0:100

Samples of  $\alpha$ -cinnamic acid (MT1) were irradiated in Petri-dishes and in a rotating "Pyrex" cylinder. The powder lines of  $\alpha$ -truxillic acid (D1) appeared after 2 days' irradiation. After 15 days the reaction was complete. Samples of  $\beta$ -cinnamic acid (MT2), exposed under similar conditions, were rapidly transformed into  $\alpha$ -cinnamic acid whose powder pattern predominated after 3 days' irradiation. The product obtained after 15 days' irradiation was a mixture of  $\alpha$ -truxillic acid,  $\beta$ -truxinic acid (D2), and small amounts of  $\alpha$ -cinnamic acid.  $\beta$ -Cinnamic acid was also irradiated in a double-walled, water-cooled quartz container; powder pictures taken after 2, 6, and 11 days showed the gradual replacement of the original  $\beta$ -cinnamic acid lines by the pattern of  $\beta$ -truxinic acid. At no stage could the lines of either  $\alpha$ -cinnamic or  $\alpha$ -truxillic acid be seen. Conversion into  $\beta$ -truxinic acid was almost complete after 18 days' irradiation.

*o-Hydroxycinnamic Acid (MT3).*—Soxhlet extraction with ether of the irradiation product left insoluble material (D3), m. p. 320 $^{\circ}$  (from acetic acid), actually the m. p. of  $\alpha$ -dicoumarin<sup>35</sup> formed by double lactonisation of the dimeric acid on being heated or treated with boiling acetic acid. Methylation of the dimer with dimethyl sulphate,<sup>36</sup> gave  $\alpha$ -dicoumaric acid dimethyl ether dimethyl ester, m. p. 134—135 $^{\circ}$  (from methanol) (lit.,<sup>35</sup> m. p. 133—134 $^{\circ}$ ). According to its crystallographic data ( $a = 9.71$ ,  $b = 5.90$ ,  $c = 17.76$  Å,  $\beta = 93.5^{\circ}$ ; space group  $P2_1/c$ ;  $d_{\text{calc.}} = 1.257$ ;  $n = 2$ ) it possesses a molecular centre of symmetry.

*o-Methoxycinnamic Acid (MT4).*—Soxhlet extraction with ether of the irradiation product gave insoluble material (D4) (m. p. 260 $^{\circ}$ ) which after recrystallisation from acetic acid melted at 264—265 $^{\circ}$  (lit.,<sup>35,37</sup> m. p. 261—262 $^{\circ}$ ). The dimer D4, 2,2'-dimethoxy- $\alpha$ -truxillic acid was demethylated to  $\alpha$ -dicoumaric acid with boiling 57% hydriodic acid; it was also prepared from  $\alpha$ -dicoumaric acid by methylation and subsequent hydrolysis of the diester with boiling 10% sodium hydroxide.

*o-Ethoxycinnamic Acid (MT5, MT6, MT7).*—Large crystals of the  $\alpha$ -form (MT5) were obtained from a hot concentrated solution in ethyl acetate; the  $\beta$ -modification (MT6) was grown from benzene by slow evaporation, or by precipitation with light petroleum (b. p. 60—80 $^{\circ}$ ) from cold dilute solutions in benzene; long thin needles of the  $\gamma$ -form (MT7) were obtained by slow cooling of a solution in aqueous ethanol. The  $\beta$ -form is extremely unstable; it changed to the  $\alpha$ -phase at an appreciable rate at room temperature, and was sensitive even to short grinding. The  $\alpha$ -phase generally contaminated samples crystallised by addition of light petroleum to benzene; small amounts of the  $\gamma$ -form accompanied the  $\beta$ -phase obtained by slow evaporation.

The powder pattern of the  $\alpha$ -form irradiated in Petri-dishes changed within the first 2 days. The dimer D5, 2,2'-diethoxy- $\alpha$ -truxillic acid, obtained as the insoluble fraction by Soxhlet extraction with ether, had m. p. 285—287 $^{\circ}$  (from acetic acid) (lit.,<sup>5</sup> 273—274 $^{\circ}$ ). The dimer was dealkylated with hydriodic acid to  $\alpha$ -dicoumaric acid, from which it was also prepared by ethylation with diethyl sulphate and subsequent partial hydrolysis.

Samples of the  $\beta$ -modification were irradiated with and without water cooling. In the latter experiment a powder picture taken after 2 days' irradiation showed a diffuse  $\alpha$ -monomer pattern and no lines of the  $\beta$ -monomer. The irradiation product (39.56 g.), m. p. 200—280 $^{\circ}$ , was extracted with ether (1.5 l.). The insoluble fraction (14.25 g., 36%) had m. p. 282—284 $^{\circ}$  and was 2,2'-diethoxy- $\alpha$ -truxillic acid (D5). On concentration of the yellow extract to one half its volume a crystalline solid (12.68 g., 32%; m. p. 206—209 $^{\circ}$ ) was obtained: D6, 2,2'-diethoxy- $\beta$ -truxinic acid, m. p. 210—212 $^{\circ}$  [from ether—light petroleum (b. p. 60—80 $^{\circ}$ )] (Found: C, 68.8; H, 6.3.  $\text{C}_{22}\text{H}_{24}\text{O}_6$  requires C, 68.7; H, 6.3%).

<sup>35</sup> de Jong, *Rec. Trav. chim.*, 1924, **43**, 319.

<sup>36</sup> Brederbeck, Hennig, and Rau, *Chem. Ber.*, 1953, **86**, 1085.

<sup>37</sup> Bertram and Kürsten, *J. prakt. Chem.*, 1895, [2], **51**, 323.

Powder photographs taken after 1 and 2 days' irradiation of a water-cooled sample of the  $\beta$ -modification still showed a clear  $\beta$ -monomer pattern; after 6 days the powder pattern corresponded mainly to D6. Separation with ether gave 5% of D5, the remainder being mainly D6 and very little residual monomer. D6 was treated with boiling acetic anhydride for 2 hr., excess of anhydride evaporated, and the solid residue recrystallised from ether–light petroleum: 2,2'-diethoxy- $\beta$ -truxinic anhydride had m. p. 100–101° (Found: C, 72.2; H, 6.1.  $C_{22}H_{22}O_5$  requires C, 72.1; H, 6.05%);  $\nu_{\max}$  (chloroform) 1865 and 1780  $cm^{-1}$  (five-membered ring anhydride<sup>38</sup>). Hydrolysis of the anhydride with aqueous 2% potassium carbonate gave D6, proving the 1,2-*cis*-attachment of the carboxyl groups. D6 (5 g.) was refluxed with hydriodic acid (18 ml.) for 3 hr. The undissolved starting material (44%) was recovered; dilution of the filtrate precipitated a solid (2.12 g.) which, after recrystallisation from ethyl acetate–chloroform, had m. p. 186–187°. This material was recovered unchanged (m. p., mixed m. p., and infrared spectra) after treatment with boiling acetic acid; the relative positions of the hydroxyl and carboxyl groups therefore do not permit lactonisation. This compound is thus 2,2'-dihydroxy- $\beta$ -truxinic acid. Analyses results failed to agree with the expected values, probably because of retention of solvent; the acid was therefore converted into 2,2'-diacetoxy- $\beta$ -truxinic anhydride by treatment (2 hr.) with boiling acetic anhydride; it had m. p. 230–231° (from benzene) (Found: C, 67.0; H, 4.5.  $C_{22}H_{18}O_7$  requires C, 67.0; H, 4.6%);  $\nu_{\max}$  1780, 1860, 1760  $cm^{-1}$ .

The dihydroxy-acid was treated with diethyl sulphate in dilute sodium hydroxide solution, and the diester obtained hydrolysed to the diacid with 10% aqueous sodium hydroxide. The product was identical with D6.

*o*-Propoxy-cinnamic Acid (MT8).—The dimer D8, 2,2'-dipropoxy- $\alpha$ -truxillic acid, was obtained as the insoluble fraction (m. p. 255–260°) by Soxhlet extraction of the irradiated material with ether; m. p. 258–260° (from acetic acid) (lit.,<sup>5</sup> m. p. 254°). Treatment with hydriodic acid converted the dimer into  $\alpha$ -dicoumaric acid from which it was also obtained by alkylation with propyl iodide and partial hydrolysis.

*o*-Isopropoxy-cinnamic Acid (MT9).—The dimer D9, 2,2'-di-isopropoxy- $\alpha$ -truxillic acid, was obtained as the insoluble fraction by Soxhlet extraction with ether of the irradiated material; it had m. p. 272–273° (lit.,<sup>5</sup> m. p. 264°). Dealkylation gave  $\alpha$ -dicoumaric acid, from which the dimer could be obtained by treatment with isopropyl iodide and partial hydrolysis.

*o*-Allyloxy-cinnamic Acid (MT10).—Methyl coumarate (30 g.) was dissolved in a solution of sodium ethoxide [from sodium (4.2 g.) and ethanol (150 ml.)]. Allyl bromide (20 g.) was added dropwise to the boiling solution, and refluxing continued for another 3 hr. The ester was hydrolysed with boiling 10% aqueous sodium hydroxide giving the acid (32 g.) in 76% yield, m. p. 122–123° (from EtOH/H<sub>2</sub>O) (Found: C, 70.65; H, 6.0.  $C_{12}H_{12}O_3$  requires C, 70.6; H, 5.9%). D10, 2,2'-diallyloxy- $\alpha$ -truxillic acid, was isolated as the insoluble fraction by Soxhlet extraction with ether of the irradiated monomer; m. p. 238–239° (from acetic acid) (lit.,<sup>5</sup> m. p. 236°). Dealkylation transformed the dimer into  $\alpha$ -dicoumaric acid, from which it could be obtained by alkylation with allyl bromide and partial hydrolysis.

5-Bromo-2-hydroxycinnamic Acid (MT11).—6-Bromocoumarin (12 g.) was dissolved in a hot solution of sodium hydroxide (8 g.) in water (100 ml.). After cooling to room temperature and stirring with yellow mercuric oxide<sup>16</sup> (1 g.) for 1 hr. we obtained 5-bromocoumaric acid in quantitative yield. The irradiated product (9.47 g.) was extracted with ether (3  $\times$  20 ml.) leaving undissolved material (5.90 g., 62%) identified as unchanged monomer. From the extract taken to dryness a solid was obtained which after trituration with chloroform and two recrystallisations from nitromethane had m. p. 201–202°: D11, 5,5'-dibromo-2,2'-dihydroxy- $\beta$ -truxinic acid; on methylation it gave dimethyl 5,5'-dibromo-2,2'-dimethoxy- $\beta$ -truxinate (see later) of m. p. 134–135° (from methanol) (Found: C, 48.9; H, 4.0; Br, 29.5.  $C_{22}H_{22}Br_2O_6$  requires C, 48.7; H, 4.1; Br, 29.5%).

5-Chloro-2-methoxycinnamic Acid (MT12).—The dimer D12, 5,5'-dichloro-2,2'-dimethoxy- $\beta$ -truxinic acid, was isolated from the irradiation product by two crystallisations from acetic acid; m. p. 242–245°. Treatment of D12 with acetic anhydride for 2 hr. gave 5,5'-dichloro-2,2'-dimethoxy- $\beta$ -truxinic anhydride, m. p. 211.0–211.5° (from benzene) (Found: C, 58.8; H, 4.2; Cl, 17.4.  $C_{20}H_{16}Cl_2O_5$  requires C, 59.0; H, 4.0; Cl, 17.4%);  $\nu_{\max}$  1780 and 1860  $cm^{-1}$ . Hydrolysis of the anhydride gave the original dimer, proving the 1,2-*cis*-attachment of the

<sup>38</sup> Jones and Sandorfy, "Technique of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," ed. West, Interscience Publishers Inc., New York, 1956, p. 211.

carboxyl groups. The dimer was demethylated, the reaction mixture taken to dryness in a vacuum on a water-bath, and the residue treated with acetyl chloride and stannic chloride at room temperature.<sup>39</sup> The mixture was poured into ice-water and 2,2'-diacetoxy-5,5'-dichloro- $\beta$ -truxinic acid precipitated in quantitative yield, m. p. 197—198° (from acetic acid) (Found: C, 55.1; H, 3.9; Cl, 14.5.  $C_{22}H_{18}Cl_2O_8$  requires C, 54.9; H, 3.8; Cl, 14.7%). The dimer (2.00 g.) was dechlorinated by treatment of its solution in 3% aqueous sodium hydroxide (5 moles) with hydrogen at atmospheric pressure in the presence of 2% palladium-calcium carbonate catalyst,<sup>40,41</sup> when 231 ml. of hydrogen were absorbed (calc. 229 ml.). The chlorine-free product obtained was 2,2'-dimethoxy- $\beta$ -truxinic acid, m. p. 207—208° (from aqueous acetic acid) (lit.,<sup>6</sup> m. p. 202°) (Found: C, 67.1; H, 5.5. Calc. for  $C_{20}H_{20}O_6$ : C, 67.4; H, 5.65%). This acid was demethylated, and the vacuum-dried product treated with acetic anhydride; 2,2'-diacetoxy- $\beta$ -truxinic anhydride was obtained, identical with that described above.

*5-Bromo-2-methoxycinnamic Acid (MT13).*—The photo-active ( $\beta$ ) modification can be prepared on the large scale only if special care is taken to avoid contamination with seeds of the stable ( $\gamma$ ) form (MT14). The following procedure is adequate: a dilute solution of the acid in ethanol, filtered through paper of small pore-size, is added slowly to very rapidly stirred cold water to which seeds of the  $\beta$ -form have been added. However, formation of the  $\gamma$ -phase could not be entirely avoided; its presence in the irradiated samples did not permit exact evaluation of the yield of the photo-dimer. D13, 5,5'-dibromo-2,2'-dimethoxy- $\beta$ -truxinic acid was obtained from the reaction product as the ethanol-soluble fraction; it had m. p. 241—244° (from dioxan-water). The dimer (0.50 g.) was debrominated (hydrogen uptake, 45.0 ml.; calc. 47.5 ml.) to 2,2'-dimethoxy- $\beta$ -truxinic acid, m. p. 207—208° (see above). D13 was treated with thionyl chloride and methanol to give dimethyl 5,5'-dibromo-2,2'-dimethoxy- $\beta$ -truxinate, m. p. 134—135° (see above).

*m-Hydroxycinnamic Acid (MT15).*—The dimer D15, 3,3'-dihydroxy- $\alpha$ -truxillic acid, isolated from the irradiation product as the insoluble fraction by Soxhlet extraction with ether, had m. p. 284°. Crystallographic data obtained on crystals from water suggest that the dimer molecule is centrosymmetric ( $a = 16.23$ ,  $b = 5.64$ ,  $c = 19.80$  Å,  $\beta = 91.0^\circ$ ; space group  $A2/a$ ;  $d_{\text{calc.}} = 1.204$ ;  $n = 4$ ); the alternative molecular symmetry 2, also compatible with the symmetry requirements of this space group, is less probable since it would require the molecule to lie with its twofold axis along the short  $b$  axis.

Treatment with dimethyl sulphate transformed D15 into *dimethyl 3,3'-dimethoxy- $\alpha$ -truxillate*, m. p. 130—131° (from methanol) [Found: C, 68.45; H, 6.3%;  $M$  (in camphor), 380.  $C_{22}H_{24}O_6$  requires C, 68.7; H, 6.3%;  $M$ , 384].

*p-Hydroxycinnamic Acid (MT17).*—The dimer D17, 4,4'-dihydroxy- $\alpha$ -truxillic acid, isolated as the insoluble fraction by Soxhlet extraction with ether, had m. p. about 340° (fast heating). When heated slowly it did not melt below 360°. It is insoluble in most of the common solvents, and sparingly soluble in ethanol. *Dimethyl 4,4'-dimethoxy- $\alpha$ -truxillate* (from methanol) has m. p. 129—130° [Found: C, 68.6; H, 6.1%;  $M$  (in camphor), 378.  $C_{22}H_{24}O_6$  requires C, 68.7; H, 6.3%;  $M$ , 384]. Hydrolysis of this ester with 10% sodium hydroxide at 60° for 1 hr. yielded 4,4'-*dimethoxy- $\alpha$ -truxillic acid*, m. p. 260.5—262.5° (from aqueous acetic acid) (Found: C, 67.4; H, 5.5.  $C_{20}H_{20}O_6$  requires C, 67.4; H, 5.7%). Its crystallographic constants suggest that this acid is centrosymmetric ( $a = 10.70$ ,  $b = 5.22$ ,  $c = 8.34$  Å;  $\alpha = 112.1^\circ$ ,  $\beta = 88.2^\circ$ ,  $\gamma = 95.1^\circ$ ; space group  $P1$  or  $P\bar{1}$ ;  $d_{\text{calc.}} = 1.362$ ;  $n = 1$ ). Acetylation of D17 according to Homans *et al.*<sup>7</sup> gave 4,4'-diacetoxy- $\alpha$ -truxillic acid, m. p. 245—246° (from acetic acid) (lit.,<sup>7</sup> m. p. 244°). Fusion of D17 with potassium hydroxide yielded a compound, m. p. 276—277°, probably identical with the acid (m. p. 273°) prepared by Liebermann and Bergami<sup>9</sup> by alkali fusion of the disulphonation product of  $\alpha$ -truxillic acid, and likely to be 4,4'-dihydroxy- $\alpha$ -truxillic acid.

*o-Nitrocinnamic Acid (MT19).*—The dimer D19, 3,4-di-2-nitrophenylcyclobutane-1,2-*cis*-dicarboxylic acid, was isolated from the irradiation product by Tanasescu and Hodosan's method.<sup>11</sup> Obtained in 14% yield it had m. p. 225—227° (from acetic acid). Boiling acetic anhydride converted D19 into an *anhydride*, m. p. 253—254° (from chlorobenzene) (Found: C, 58.8; H, 3.1; N, 7.4.  $C_{18}H_{12}N_2O_7$  requires C, 58.7; H, 3.3; N, 7.6%);  $\nu_{\text{max}}$ . 1780 and 1865

<sup>39</sup> Hill, *J. Amer. Chem. Soc.*, 1953, **75**, 3020.

<sup>40</sup> Busch and Stöve, *Ber.*, 1916, **49**, 1063.

<sup>41</sup> Rosenmund and Zetzsche, *Ber.*, 1918, **51**, 578.

cm.<sup>-1</sup>. Hydrolysis of the anhydride regenerated D19. The photo-product can be isolated from the mixture in higher yield (27%) by treatment of the irradiation product with boiling acetic anhydride for 2 hr.; on cooling the anhydride separates in large crystals. No monomer was recovered from the irradiated material; the residue was a red-brown non-crystalline material of unidentified constitution which may have arisen <sup>11</sup> entirely or in part from the dimer. The actual yield of D19 may therefore be much higher than the figures recorded.

*m-Nitrocinnamic Acid (MT20).*—The dimer D20, 3,3'-dinitro- $\beta$ -truxinic acid, isolated by repeated extraction of the irradiation product with acetone, had m. p. 205.5—206.5° (from acetic acid). It did not decolorise potassium permanganate and bromine solutions. Boiling acetic anhydride converted D20 into 3,3'-dinitro- $\beta$ -truxinic anhydride, m. p. 172—173° (from benzene) (Found: C, 58.6; H, 3.5; N, 7.7. C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>7</sub> requires C, 58.7; H, 3.3; N, 7.6%);  $\nu_{\max}$ . 1780 and 1865 cm.<sup>-1</sup>. Hydrolysis of the anhydride regenerated D20. *Dimethyl 3,3'-dinitro- $\beta$ -truxinate* had m. p. 120.0—120.5° (from methanol) (Found: C, 57.7; H, 4.5; N, 6.6. C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub> requires C, 58.0; H, 4.4; N, 6.8%). *Diethyl 3,3'-dinitro- $\beta$ -truxinate* had m. p. 85—86° (from ethanol) [Found: C, 59.6; H, 4.9; N, 6.1%; *M* (in camphor), 448. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>8</sub> requires C, 59.7; H, 5.0; N, 6.3%; *M*, 442]. D20 was dissolved in 5% aqueous sodium carbonate and reduced with hydrazine monohydrate (3 moles) and Raney nickel at 60°. <sup>12</sup> After filtration the reaction mixture was taken to dryness in a vacuum, and the product separated by extraction with hot ethanol. On cooling, 3,3'-diamino- $\beta$ -truxinic acid was deposited on the walls of the flask; it was very hygroscopic, and was immediately and without further purification tetrazotised in 20% hydrochloric acid with sodium nitrite. The product was added to a boiling solution of cuprous chloride in hydrochloric acid. A solid which separated from the reaction mixture on cooling was dissolved in ether; after addition of light petroleum (b. p. 30—40°) the solution slowly deposited white crystals of 3,3'-dichloro- $\beta$ -truxinic acid (D25, see later).

*p-Nitrocinnamic Acid (MT22, MT23).*—Preparations of the  $\gamma$ -modification of this acid, obtained by Soxhlet crystallisation with ethanol, were invariably contaminated with small amounts of the photo-active form. The pure  $\gamma$ -modification (MT23) could only be obtained by irradiation of a mixture of both forms and extraction of the dimer formed from the photo-active modification with ethanol, in which the monomer is very sparingly soluble. D22, 4,4'-Dinitro- $\beta$ -truxinic acid, m. p. 219—221° (from acetic acid), was separated from the irradiation product (of MT22) by Tanasescu and Hodosan's method; <sup>11</sup> it was identical with the dinitration product, m. p. 219—222° (from acetic acid) (lit., <sup>7</sup> m. p. 216°), of  $\beta$ -truxinic acid prepared according to Homans *et al.* <sup>7</sup> Treatment with boiling acetic anhydride converted D22 into 4,4'-dinitro- $\beta$ -truxinic anhydride, m. p. 190—191° (from chlorobenzene) (Found: C, 58.4; H, 3.3; N, 7.5. C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O<sub>7</sub> requires C, 58.7; H, 3.3; N, 7.6%);  $\nu_{\max}$ . 1780 and 1865 cm.<sup>-1</sup>. *Dimethyl 4,4'-dinitro- $\beta$ -truxinate* had m. p. 125—126° (from methanol) [Found: C, 58.0; H, 4.3; N, 6.6%; *M* (in camphor), 452. C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub> requires C, 58.0; H, 4.4; N, 6.8%; *M*, 414]. The diethyl ester had m. p. 136—137° (from ethanol).

*o-Chlorocinnamic Acid (MT24).*—The dimer D24, 2,2'-dichloro- $\beta$ -truxinic acid, was isolated by recrystallisation of the irradiation product from aqueous ethanol; it had m. p. 200—204° (from acetic acid) (Found: C, 59.1; H, 3.7; Cl, 19.3. C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 59.2; H, 3.9; Cl, 19.4%). The dimer (0.236 g.) was dechlorinated (hydrogen uptake 33.6 ml.; calc. 34.4 ml.), giving  $\beta$ -truxinic acid in 86% yield.

*m-Chlorocinnamic Acid (MT25).*—The dimer D25, 3,3'-dichloro- $\beta$ -truxinic acid, was isolated from the irradiation product by extraction of the monomer with hot benzene; it had m. p. 175—176° (from acetic acid) [Found: C, 59.4; H, 3.7; Cl, 19.6 (after being dried at 0.1 mm./90° for 3 days). C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub> requires C, 59.2; H, 3.9; Cl, 19.4%]. D25 (0.236 g.) was dechlorinated (hydrogen uptake 32.4 ml.; calc. 34.5 ml.) to  $\beta$ -truxinic acid in 83% yield.

*p-Chlorocinnamic Acid (MT27).*—The dimer D27, 4,4'-dichloro- $\beta$ -truxinic acid, was isolated from the irradiation product by 2 recrystallisations from acetic acid (m. p. 190°, after sintering at 160°). Analysis figures suggested the inclusion of solvent; the dimer was therefore converted into its *potassium salt* with alcoholic potassium hydroxide [Found: C, 48.7; H, 2.85; Cl, 16.3; K, 17.3 (after being dried in a high vacuum over P<sub>2</sub>O<sub>5</sub> at 70°). C<sub>18</sub>H<sub>12</sub>Cl<sub>2</sub>K<sub>2</sub>O<sub>4</sub> requires C, 49.0; H, 2.7; Cl, 16.1; K, 17.7%]. Chlorine was determined after fusion of the salt with metallic potassium. The dimer (0.245 g.) was dechlorinated (hydrogen uptake 31.0 ml.; calc. 32.1 ml.) to give  $\beta$ -truxinic acid in 84% yield.

*o-Bromocinnamic Acid (MT28).*—The dimer D28, 2,2'-dibromo- $\beta$ -truxinic acid, was isolated

as the insoluble fraction by extraction with ether; it had m. p. 218—219° (from acetic acid) (mixed m. p. with monomer 190—196°). The dimer (0.50 g.) was debrominated (hydrogen uptake 52.4 ml.; calc. 53.7 ml.) to  $\beta$ -truxinic acid. *Dimethyl 2,2'-dibromo- $\beta$ -truxinate* had m. p. 150—151° (from methanol) (Found: C, 49.6; H, 3.8; Br, 33.2.  $C_{20}H_{18}Br_2O_4$  requires C, 49.8; H, 3.8; Br, 33.15%).

*m-Bromocinnamic Acid (MT29)*.—The dimer D29, 3,3'-dibromo- $\beta$ -truxinic acid, was isolated by extraction of the monomer with hot benzene; it had m. p. 151° (from acetic acid). Debromination (0.454 g.; hydrogen uptake 48.0 ml.; calc. 49.1 ml.) gave  $\beta$ -truxinic acid. *Dimethyl 3,3'-dibromo- $\beta$ -truxinate* had m. p. 87.5—88.5° (from methanol) (Found: C, 49.8; H, 3.9; Br, 32.9.  $C_{20}H_{18}Br_2O_4$  requires C, 49.8; H, 3.8; Br, 33.15%).

*p-Bromocinnamic Acid (MT31)*.—The dimer D31, 4,4'-dibromo- $\beta$ -truxinic acid, was isolated from the irradiation product by extraction of the monomer with benzene; it had m. p. 219—220° (from acetic acid). Debromination (0.227 g.; hydrogen uptake 22.2 ml.; calc. 24.2 ml.) gave  $\beta$ -truxinic acid. *Dimethyl 4,4'-dibromo- $\beta$ -truxinate* had m. p. 136° (from ethanol) (Found: C, 49.5; H, 3.5; Br, 33.1.  $C_{20}H_{18}Br_2O_4$  requires C, 49.8; H, 3.8; Br, 33.15%).

*2,4-Dichlorocinnamic Acid (MT32)*.—The dimer D32, 2,2',4,4'-tetrachloro- $\beta$ -truxinic acid, was isolated from the irradiation product by extraction of the monomer with benzene; it had m. p. 230—232° (decomp.) (from acetic acid) (Found: C, 49.9; H, 2.8; Cl, 32.5.  $C_{18}H_{12}Cl_4O_4$  requires C, 49.8; H, 2.8; Cl, 32.7%). Dechlorination (0.434 g.; hydrogen uptake 95.0 ml.; calc. 98.5 ml.) yielded  $\beta$ -truxinic acid.

*2,6-Dichlorocinnamic Acid (MT33)*.—The dimer D33 2,2',6,6'-tetrachloro- $\beta$ -truxinic acid, was isolated from the irradiation product by extraction of the monomer with benzene; it had m. p. 237° (from aqueous acetic acid) (Found: C, 49.9; H, 2.8; Cl, 32.8.  $C_{18}H_{12}Cl_4O_4$  requires C, 49.8; H, 2.8; Cl, 32.7%), and was dechlorinated 0.436 g.; hydrogen uptake 83.4 ml.; calc. 98.9 ml.) to  $\beta$ -truxinic acid.

*3,4-Dichlorocinnamic Acid (MT34)*.—The dimer D34, 3,3',4,4'-tetrachloro- $\beta$ -truxinic acid, was isolated from the irradiation product by extraction with acetic acid; it had m. p. 146—147° (from benzene-acetic acid), and was dechlorinated (0.435 g.; hydrogen uptake 88.8 ml.; calc. 98.7 ml.) to  $\beta$ -truxinic acid. *Dimethyl 3,3',4,4'-tetrachloro- $\beta$ -truxinate* had m. p. 106.5—107.0° (from methanol) (Found: C, 52.2; H, 3.55; Cl, 30.4.  $C_{20}H_{16}Cl_4O_4$  requires C, 52.0; H, 3.5; Cl, 30.7%).

*p-Methylcinnamic Acid (MT36)*.—The dimer D36, 4,4'-dimethyl- $\alpha$ -truxillic acid, was isolated from the irradiation product by Soxhlet extraction of the monomer with benzene; it had m. p. 281—282° (from ethanol-water) (Found: C, 74.1; H, 6.1.  $C_{20}H_{20}O_4$  requires C, 74.1; H, 6.2%). The crystallographic constants ( $a = 17.9$ ,  $b = 8.56$ ,  $c = 5.65$  Å,  $\beta = 94.0^\circ$ ; space group  $P2_1/a$ ;  $d_{\text{calc.}} = 1.250$ ;  $n = 2$ ) show the presence of a molecular centre of symmetry.

In conclusion we should like to enter the plea that workers in solid-state chemistry specify in sufficient detail the reacting crystalline phase: solvents and conditions of crystallisation, crystallographic (preferably X-ray) data, thermal stability with respect to other phases, and temperature conditions of the solid-state reaction. Homogeneity and stability of the reactant phase are important parameters of the reaction which must be checked as well as recorded.

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