[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

THE ISOMERIC 2-PHENYL-4-BENZYLIDENE-5-OXAZOLONES (AZLACTONES OF α-BENZAMIDOCINNAMIC ACID) AND RELATED COMPOUNDS[1]

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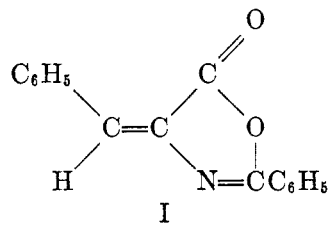
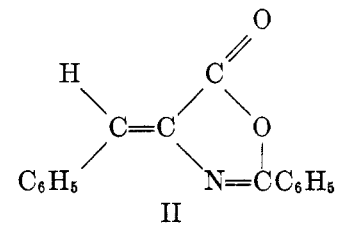
The two 2-phenyl-4-benzylidene-5-oxazalones (azlactones of α-benzamidocinnamic acid), which are geometric isomers, have been reported (1), but no assignment of configuration has been made. Azlactone I, m.p. 165–166°, appears to be the more stable and is the one predominantly formed in most synthetic methods. Azlactone II, m.p. 149–150°, is not only difficult to prepare free of I but is also easily isomerized to I by the action of anhydrous pyridine (1). The only reported (1) reactions of the two isomeric azlactones in which steric identity is maintained are the basic hydrolysis under very mild conditions to form the corresponding isomeric α-benzamidocinnamic acids and the basic alcoholysis to form the corresponding ethyl esters. Conversely each acid reacts with acetic anhydride to give the azlactone from which it was formed by hydrolysis.

On the basis of these results the present investigation has approached the problem of configuration assignment through the α-benzamidocinnamic acids. The acid (III) derived from I has m.p. 229–230°, and that (IV) from II has m.p. 199–200°. A comparison of these m.p.'s with those of the analogously substituted benzene derivatives; 4-benzamido-2-biphenylcarboxylic acid (V), m.p. 253–255°, and 2-benzamido-4-biphenylcarboxylic acid (VI), m.p. 231–233°, has led to the tentative assignment of configurations as shown by the structural formulas.



I



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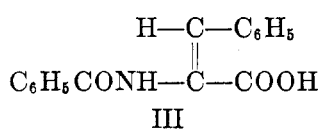
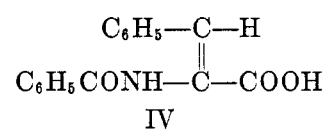
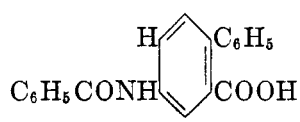


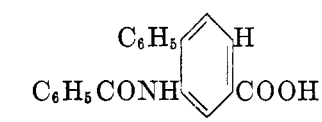
III



IV



V

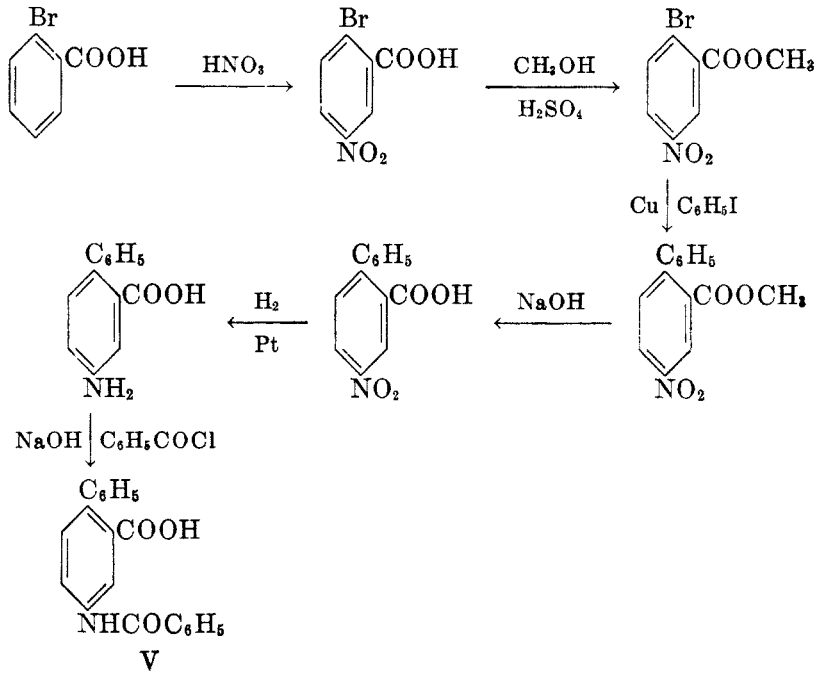


VI

[1] From the Ph.D. thesis of Robert Filler and the M.S. thesis of Lee Hilfman.

Such a comparison of m.p.'s is based on the fact that groups substituted *ortho* to each other on a benzene ring bear the same steric relationship as the same groups substituted *cis* to each other on a carbon-carbon double bond. A similar analogy exists between *para*-substitution and *trans*-substitution. It has been pointed out by Werner (2) that for symmetrically substituted ethylenes the *trans* is generally the isomer of higher m.p. just as the *para* isomer has a higher m.p. than the *ortho*. For unsymmetrically substituted ethylenes the comparison between the m.p.'s of the stereoisomers and those of the analogously substituted benzenes has likewise been applied for the assignment of configurations (2–5).

CHART I



V

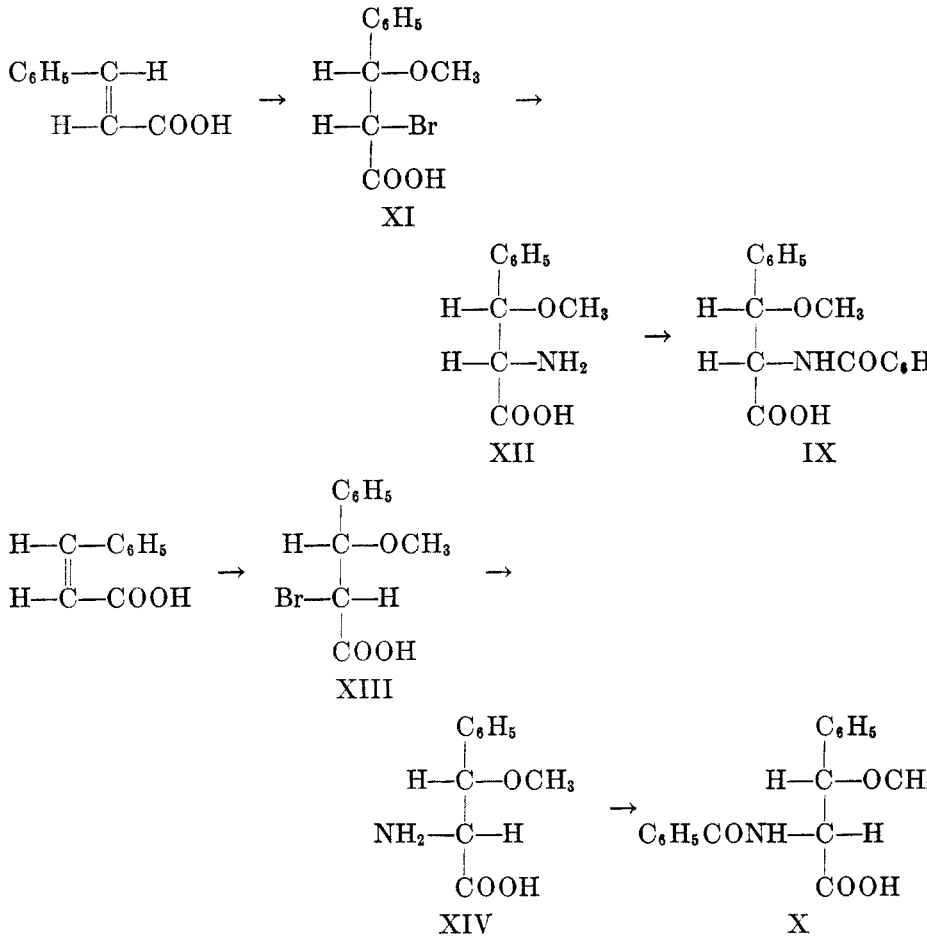
The reference compound V was prepared by the reactions outlined in Chart I. Compound VI was prepared by an entirely analogous series from *p*-bromobenzoic acid.

In Figure 1 are given the absorption spectra of the two α-benzamidocinnamic acids in absolute ethanol. Contrary to expectation the predominant peak shown by the lower-m.p. isomer (IV) is higher and nearer the visible than that of the higher-m.p. isomer (III). The spectrum of III agrees qualitatively with that already reported (6).

In Figure 2 are given the absorption spectra of the two azlactones in 95% ethanol. The wave lengths corresponding to maximum absorption are virtually the same for the two isomers. The isomer of lower m.p. (II) has much less in-

tense absorption in these regions, however. In the spectrum of azlactone I the position of the peaks and their relative heights correspond well with data already published (6, 7, 8), but do not agree with those of the spectrum reported by Schueler and Wang (9). Their spectrum showing peaks at 224 and 284 mμ is very close to the spectrum of α-benzamidocinnamic acid of higher m.p. (III) which is given in Figure 1. This correspondence would seem to indicate that

CHART II



hydrolysis or alcoholysis of the azlactone took place in their 95% ethanol solution. The ester would be expected to have an absorption spectrum very similar to that of the acid.

The reaction of the azlactone I with an equimolar amount of sodium methoxide in methanol was found to give the methyl ester (VII) of the α-benzamidocinnamic acid (III). This result parallels the reported reaction with sodium ethoxide (1). With excess sodium methoxide the methyl ester (VIII) of the

α-benzamido-β-methoxyhydrocinnamic acid of m.p. 220–221° (IX) was obtained along with VII. This result is analogous to that reported (10) for the reaction of 2-phenyl-4-ethylidene-5-oxazolone (azlactone of α-benzamidobutyric acid) with sodium methoxide. It was possible also to prepare VII by the action of diazomethane on III and in low yields by the acid-catalyzed methanolysis of I. The preparation of VII from I by the action of diazomethane in methanol

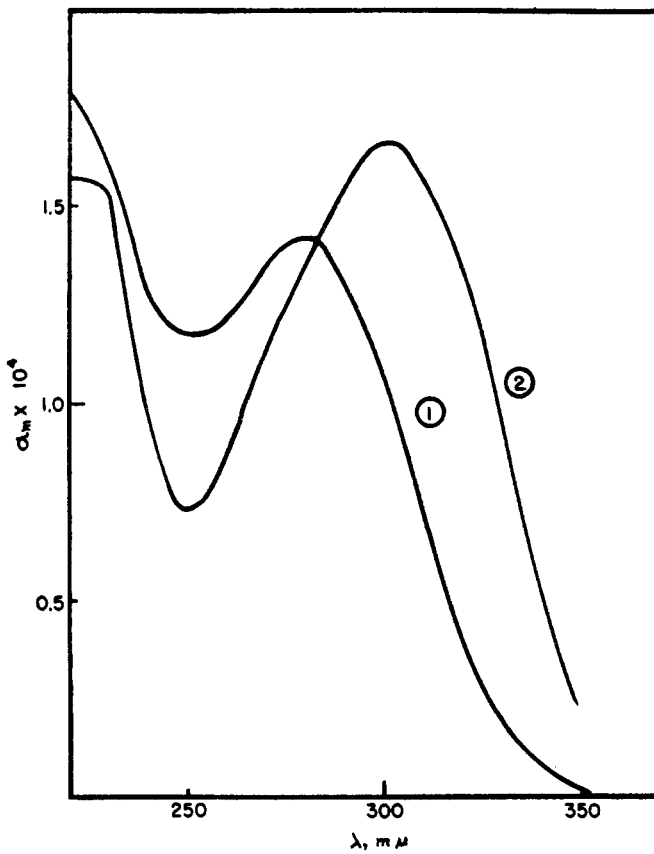


FIG. 1. ABSORPTION SPECTRA OF THE ISOMERIC α-BENZAMIDOCINNAMIC ACIDS IN ABSOLUTE ETHANOL. ① Isomer of m.p. 229–230° (III), conc'n, 6.60×10^{-5} *M*. ② Isomer of m.p. 199–200° (IV), conc'n, 3.96×10^{-5} *M*.

could not be repeated (11). The ester VIII was easily prepared by the action of diazomethane on IX or by the acid-catalyzed reaction of methanol with the α-benzamidocinnamic acid (III).

In the course of the investigation of the configurations of the α-benzamidocinnamic acids and their azlactones, reactions relating these compounds to *cis*- and *trans*-cinnamic acids were studied. The two racemic modifications of α-benzamido-β-methoxyhydrocinnamic acid (IX and X) have been shown to be derived from the cinnamic acids by reactions in which configurations were

maintained (12, 13). It was found, however, that either racemic modification of α-benzamido-β-methoxyhydrocinnamic acid (IX and X) reacted with acetic anhydride to give mixtures of the azlactones I and II.

Although the configurations of the α-benzamido-β-methoxyhydrocinnamic acids cannot be related to those of the azlactones by such results it is of interest to consider them from the standpoint of their relationship to those of the iso-

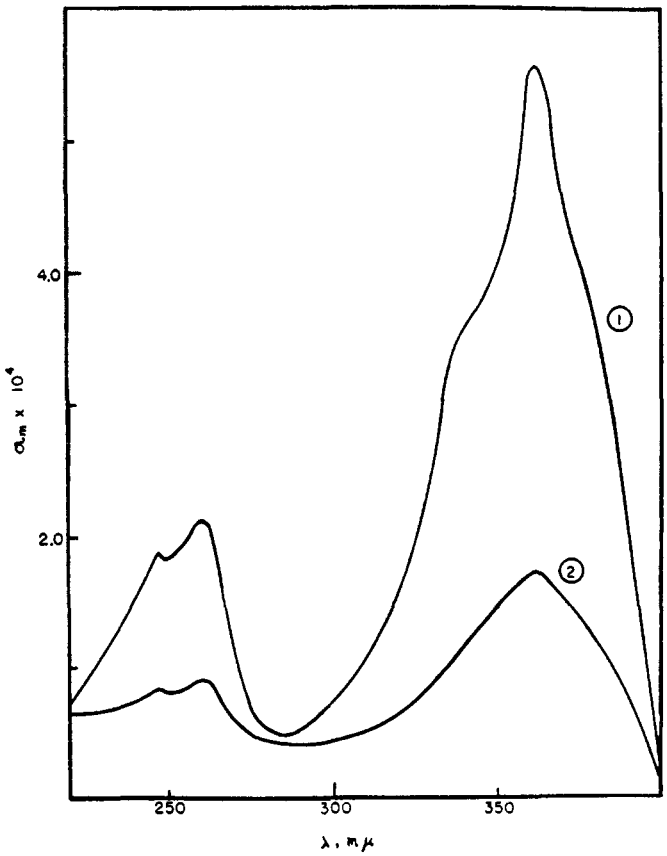


FIG. 2. ABSORPTION SPECTRA OF THE ISOMERIC 2-PHENYL-4-BENZYLIDENE-5-OXAZOLONES IN 95% ETHANOL. ① Isomer of m.p. 165–166° (I), conc'n, 1.784×10^{-5}. ② Isomer of m.p 149–150° (II), conc'n, 4.02×10^{-5}.

meric cinnamic acids. The racemic form of m.p. 220–221° (IX) has been derived from *trans*-cinnamic acid, and the racemic form of m.p. 160–162° (X) has been derived from *cis*-cinnamic acid by the addition of the elements of methyl hypobromite to the double bonds followed by the amination of the α-bromo-β-methoxyhydrocinnamic acids and the Schotten-Baumman reaction on the amino acids obtained (12, 13). In the present investigation these relationships were verified. N-Bromoacetamide in methanol was used as a source of the elements of methyl hypobromite for addition to the double bonds.

It would be expected that each amino acid would have the same configuration as the bromo acid from which it was prepared because of participation of the neighboring carboxyl groups during the displacement (14, 15, 16). If it be assumed that the usual *trans* addition to the double bond (17, 18) takes place, the configurations of compounds can be related as shown in Chart II.

By direct amination accompanied by retention of configuration, XII was obtained from XI, and XIV arose from XIII. On the other hand XIV was also prepared from XI by an application of the method used in the synthesis of threonine (19). The piperidide of XI was aminated with inversion of configuration to give the piperidide of XIV. Hydrolysis of this piperidide with 48% hydrobromic acid yielded XIV. No cleavage of the methoxyl group nor formation of β-phenylnaphthalene (13) was observed.

EXPERIMENTAL

2-Bromo-5-nitrobenzoic acid. Nitration of 40 g. (0.20 mole) of *o*-bromobenzoic acid in 160 ml. of fuming nitric acid (*sp. gr.* 1.60) for 5–10 minutes on a steam-bath yielded 28.5 g. (58%) of the 2-bromo-5-nitrobenzoic acid of m.p. 179–180°[2] (20).

4-Bromo-3-nitrobenzoic acid. Nitration of 30 g. (0.15 mole) of *p*-bromobenzoic acid in 200 ml. of fuming nitric acid (*sp. gr.* 1.60) for 1.5 hours yielded 30.6 g. (83%) of 4-bromo-3-nitrobenzoic acid of m.p. 201–202° (21).

Methyl 2-bromo-5-nitrobenzoate. Esterification of 24.6 g. (0.10 mole) of 2-bromo-5-nitrobenzoic acid in 70 ml. of boiling methanol containing 7 ml. of concentrated sulfuric acid for five hours yielded 24.6 g. (94%) of methyl 2-bromo-5-nitrobenzoate of m.p. 80–82° (22).

Methyl 4-bromo-3-nitrobenzoate. This ester was prepared in a manner analogous to that used for methyl 2-bromo-5-nitrobenzoate except that one hour of boiling the reaction mixture was sufficient. The yield was 23.5 g. (90%); m.p. 102–104° (22).

Methyl 4-nitro-2-biphenylcarboxylate. A mixture of 30.0 g. (0.115 mole) of methyl 2-bromo-5-nitrobenzoate, 73 g. (0.36 mole) of iodobenzene, and 40 g. of powdered copper was heated with stirring at 235° for one hour. The mixture was cooled and dissolved in chloroform. The copper was removed by filtration and the chloroform was removed by distillation. The liquid residue was distilled, b.p. 180–185 (2 mm.). Cooling the distillate induced solidification. Crystallization from methanol yielded 11.0 g. (37%) of methyl 4-nitro-2-biphenylcarboxylate, m.p. 69.0–69.5°. This compound with m.p. 70° has been reported as prepared by the action of bis(2-carbomethoxy-4-nitrobenzoyl)peroxide on benzene (23).

Methyl 2-nitro-4-biphenylcarboxylate. In a method completely analogous to that described above, 31.8 g. (0.122 mole) of methyl 4-bromo-3-nitrobenzoate was heated with 60 g. of powdered copper and 71.5 g. of iodobenzene at 220° for 1.5 hours. Distillation yielded 18.4 g. (59%) of methyl 2-nitro-4-biphenylcarboxylate, b.p. 185–192° (1.5 mm.), m.p. 94–95°.

Anal. Calc'd for $C_{14}H_{11}NO_4$: C, 65.3; H, 4.31; N, 5.44.

Found: C, 65.3; H, 4.28; N, 5.12.

4-Nitro-2-biphenylcarboxylic acid. A mixture of 9.0 g. (0.035 mole) of methyl 4-nitro-2-biphenylcarboxylate and 20 ml. of 6 *N* sodium hydroxide was boiled for 20 minutes under reflux. The clear, red solution was cooled and acidified to Congo Red with concentrated hydrochloric acid. The resulting solid was crystallized from glacial acetic acid to give 6.2 g. (73%) of 4-nitro-2-biphenylcarboxylic acid, m.p. 175–176.5°. This compound, m.p. 173°, has been reported (24) as prepared by the coupling of diazotized methyl 5-nitroanthranilate with benzene.

2-Nitro-4-biphenylcarboxylic acid. A mixture of 17.3 g. (0.067 mole) of methyl 2-nitro-4-biphenylcarboxylate and 40 ml. of 6 *N* sodium hydroxide was boiled under reflux for 45 minutes. At the end of this time the oily ester layer in the mixture had given way to the solid sodium salt which was removed and boiled with concentrated hydrochloric acid. Cool-

[2] All m.p.'s corrected.

ing yielded a solid which was crystallized from absolute ethanol to give 10.2 g. (63%) of 2-nitro-4-biphenylcarboxylic acid, m.p. 192–193°. This acid was also prepared in 30% overall yield from methyl 4-bromo-3-nitrobenzoate by an Ullmann reaction without isolation of the intermediate ester as has been reported before (25).

4-Amino-2-biphenylcarboxylic acid. A solution of 3.6 g. (0.015 mole) of 4-nitro-2-biphenylcarboxylic acid in 125 ml. of absolute ethanol was shaken for 45 minutes with hydrogen over platinum oxide. The crude acid (2.61 g., 82%) obtained by evaporation of the solvent was crystallized from absolute ethanol after treatment with decolorizing carbon. A 1.66 g. (52%) yield of 4-amino-2-biphenylcarboxylic acid, m.p. 182–183° was isolated. This acid of m.p. 182.5–183° has been reported (25) in low yields from the alkaline cleavage of 2-aminofluorenone.

4-Benzamido-2-biphenylcarboxylic acid (V). One gram of 4-amino-2-biphenylcarboxylic acid was shaken with 5 ml. of 6 *N* sodium hydroxide. Enough water was then added until all of the sodium salt went into solution. The solution was cooled and 4.8 g. of benzoyl chloride was added. The solution was shaken and cooled alternately until the evolution of heat ceased. Acidification yielded a white solid which was boiled with petroleum ether to remove any benzoic acid. The solid was crystallized from absolute alcohol to give 0.25 g. (17%) of 4-benzamido-2-biphenylcarboxylic acid (V), m.p. 253–255° (softened 200°).

Anal. Calc'd for $C_{20}H_{15}NO_3$: C, 75.7; H, 4.77; N, 4.41.

Found: C, 75.3; H, 4.79; N, 4.71.

2-Benzamido-4-biphenylcarboxylic acid (VI). A solution of 10.2 g. (0.042 mole) of 2-nitro-4-biphenylcarboxylic acid in 130 ml. of absolute ethanol was shaken with hydrogen over platinum oxide for three hours. Removal of the catalyst by filtration and the alcohol by evaporation left a crude yield of 2-amino-4-biphenylcarboxylic acid of 5.6 g. (63%), m.p. 195–197.5°. One gram of this crude acid was benzoylated exactly as described above to give 0.30 g. (20%) of 2-benzamido-4-biphenylcarboxylic acid (VI), m.p. 231–233°.

Anal. Calc'd for $C_{20}H_{15}NO_3$: C, 75.7; H, 4.77; N, 4.41.

Found: C, 75.4; H, 4.65; N, 4.81.

The isomeric 2-phenyl-4-benzylidene-5-oxazolones (I *and* II). The isomer of m.p. 165–166° (I) was prepared in 65% yield by the condensation of benzaldehyde with hippuric acid in acetic anhydride containing anhydrous sodium acetate (27). The isomer of m.p. 149–150° (II) was prepared in 54% yield from the isomer of α-benzamidocinnamic acid of m.p. 199–200° (IV) by the action of acetic anhydride (1).

A 96% yield of a mixture of azlactones I and II was obtained by the action of acetic anhydride on the α-benzamido-β-methoxyhydrocinnamic acid of m.p. 220–221° (IX) (1). In an analogous reaction the α-benzamido-β-methoxyhydrocinnamic acid of m.p. 160–162° (X) gave an 84% yield of a similar mixture.

The isomeric α-benzamidocinnamic acids (III *and* IV). The isomer of m.p. 229–230° (III) was prepared in 70% yield by the basic hydrolysis of the azlactone I (27). The isomer of m.p. 199–200° (IV) was obtained from the mixture of azlactones I and II by basic methanolysis followed by separation and hydrolysis of the esters as described by Carter and Risser (1).

An attempt to hydrolyze the two isomeric piperidides of α-benzamidocinnamic acid (28) in cold 4 *N* sodium hydroxide gave nearly 100% recovery of the starting material in each case. Hydrolysis at higher temperatures in an acidic medium had been reported (28) to yield only the α-benzamidocinnamic acid III in either case.

Reaction of azlactone I *with an equimolar amount of sodium methoxide.* To a solution of 2.3 g. (0.10 g.-atom) of sodium in 50 ml. of methanol was added a suspension of 25 g. (0.10 mole) of azlactone I in 100 ml. of benzene. The reaction mixture was kept at 5–10° during the addition and was then allowed to warm to room temperature. Acidification with 50 ml. of 1 *N* hydrochloric acid yielded a product which was crystallized twice from 50% ethanol to give 17.0 g. (60%) of methyl α-benzamidocinnamate (VII), m.p. 141–142°.

Anal. Calc'd for $C_{17}H_{15}NO_3$: C, 72.6; H, 5.38; N, 4.98.

Found: C, 72.4; H, 5.35; N, 4.96.

This ester is presumably identical with that reported (11) as obtained from the action of

diazomethane in methanol on azlactone I. The m.p. given was 133°. This method of preparation could not be repeated in the present instance, however.

Other methods of preparation of methyl α-benzamidocinnamate (VII). A suspension of 5.0 g. (0.019 mole) α-benzamidocinnamic acid (III) in 10 ml. of methanol was treated with the ether solution of diazomethane obtained from the treatment of 2.5 g. of N-methyl-N-nitrosourea in ether with excess aqueous potassium hydroxide. Removal of the ether by evaporation followed by the addition of water gave 4.0 g. (76%) of crude ester, m.p. 128–131°. Crystallization from 50% ethanol gave VII of m.p. 140–141°.

A mixture of 1.8 g. (0.0072 mole) of azlactone I, 3 ml. of concentrated sulfuric acid, and 15 ml. of methanol was heated on a steam-bath until a solution was obtained. The mixture was cooled immediately and water was added. The crude ester was crystallized from 50% ethanol to give 0.60 g. (30%) of VII, m.p. 140–141°.

All preparations of VII were shown to be identical by mixture m.p. analysis. Saponification of VII to the α-benzamidocinnamic acid (III) in about 90% yield was easily carried out.

Reaction of azlactone I *with excess sodium methoxide.* The procedure was that described for the reaction of I with an equimolar amount of sodium methoxide except that 4.6 g. (0.20 g.-atom) of sodium was used. The product was a mixture of m.p. 110–120°. Separation by crystallization was not successful. Hydrolysis in 1 *N* sodium hydroxide followed by acidification yielded a mixture of acids. Fractional crystallization from water yielded 7.5 g. (25%) of α-benzamido-β-methoxyhydrocinnamic acid (IX), m.p. 220–221°. The mother liquor on evaporation yielded a crude solid which was crystallized from 95% ethanol to give 10.8 g. (40%) of α-benzamidocinnamic acid (III), m.p. 228–230°.

Methods for the preparation of methyl α-benzamido-β-methoxyhydrocinnamate (VIII) This ester was prepared by the reaction of 5.0 g. (0.017 mole) of the acid IX with diazomethane as described for methyl α-benzamidocinnamate (VII). Crystallization from ligroin-benzene yielded 4.3 g. (80%) of VIII, m.p. 119–120°.

Anal. Calc'd for $C_{18}H_{19}NO_4$: C, 69.0; H, 6.11.

Found: C, 68.9; H, 5.74.

A solution of 3.0 g. (0.011 mole) of α-benzamidocinnamic acid (III) in 40 ml. of methanol containing 10 ml. of concentrated sulfuric acid was boiled under reflux for two hours. Dilution with water yielded a solid which was crystallized from ligroin-benzene to give 2.5 g. (71%) of VIII, m.p. 118–119°.

Cis-cinnamic acid. A 14.6 g. (0.10 mole) sample of phenylpropiolic acid in 10% sodium carbonate solution was hydrogenated (29) over palladium-on-barium sulfate to yield *cis*-cinnamic acid, m.p. 43–46°. The contaminating *trans*-isomer was removed by purification of the aniline salt (30). A 1.5–3.0 g. (10–20%) yield of *cis*-cinnamic acid, m.p. 65–66° was obtained.

α-Bromo-β-methoxyhydrocinnamic acid of higher m.p. (XI). To a suspension of 148 g. (1.0 mole) of *trans*-cinnamic acid in 500 ml. of methanol was added 138 g. (1 mole) of N-bromoacetamide (31). The reaction mixture became warm and assumed a light red, bromine color. After standing overnight the solution was yellow, and a solid product had precipitated. Recrystallization from ethanol yielded 143 g. (53%) of α-bromo-β-methoxyhydrocinnamic acid, m.p. 183–184° (XI).

α-Bromo-β-methoxyhydrocinnamic acid of lower m.p. (XIII). A solution of 0.50 g. (0.0034 mole) of *cis*-cinnamic acid in 5 ml. of methanol was treated with 0.50 g. (0.0036 mole) of N-bromoacetamide. Several drops of concentrated sulfuric acid was added to catalyze the reaction. The reaction mixture behaved in much the same way as in the synthesis of the isomer of higher m.p. Recrystallization from ethyl acetate gave 0.15 g. (17%) of α-bromo-β-methoxyhydrocinnamic acid, m.p. 140–141° (XIII).

Mixtures of the isomeric α-bromo-β-methoxyhydrocinnamic acids (XI *and* XIII). A sodium methoxide solution prepared from 5.0 g. (0.22 g.-atom) of sodium in 50 ml. of methanol was added to a suspension of 17.6 (0.052 mole) of ethyl α,β-dibromohydrocinnamate in 50 ml. of methanol. The ester dissolved rapidly; the mixture was allowed to stand at least half an hour after it became homogeneous. Water was added and the solution was heated.

Acidification yielded a product of m.p. 126–128°. This mixture was separated by fractional crystallization of the sodium salts from 10% aqueous sodium carbonate as described by Van Loon and Carter (32). The yields were 0.73 g. (5.3%) of the α-bromo-β-methoxyhydrocinnamic acid (XI), m.p. 183–184°, and 2.7 g. (20%) of the isomer XIII, m.p. 139–140°. This method of synthesis is analogous to that applied to the α-bromo-β-methoxybutyric acids (33).

A mixture of the isomeric acids was also prepared by the action of mercuric acetate on cinnamic acid in methanol followed by photochemical bromination of the mercurated derivative (32).

The isomeric α-amino-β-methoxyhydrocinnamic acids (XII *and* XIV). Aminations of the α-bromo-β-methoxyhydrocinnamic acids were carried out in concentrated aqueous ammonia for eight to ten hours at 80° in an autoclave as described by Carter and Van Loon (13). The high-melting bromo acid (XI) gave a 40% yield of α-amino-β-methoxyhydrocinnamic acid (XII), m.p. 252–254° (dec.). The low-melting bromo acid (XIII) gave a 42% yield of amino acid (XIV), m.p. 230–232° (dec.).

The isomeric α-benzamido-β-methoxyhydrocinnamic acids (IX *and* X). The acids were prepared by the Schotten-Baumann reaction as described for the synthesis of the α-benzamido-β-methoxybutyric acids (34). A 65% yield of IX, m.p. 220–221°, was obtained from the amino acid (XII) and a 52% yield of X, m.p. 160–162°, was obtained from the amino acid (XIV).

Amination of the piperidide of α-bromo-β-methoxyhydrocinnamic acid (XI). A mixture of 65 g. (0.25 mole) α-bromo-β-methoxyhydrocinnamic acid (XI) and 100 ml. of thionyl chloride was heated until the evolution of gas was completed. Distillation yielded 23.5 g. (34%) of the acid chloride, b.p. 159–162° (38 mm.). This product was added with shaking to a cooled mixture of 7.7 g. (0.090 mole) of piperidine and 5 g. of sodium hydroxide. After standing overnight the product was solid. Crystallization from alcohol yielded 15 g. (54%) of the piperidide of XI, m.p. 117.5–118.5°.

Anal. Calc'd for $C_{15}H_{20}BrNO_2$: C, 55.2; H, 6.18.

Found: C, 55.3; H, 5.77.

A solution of 1.00 g. (0.0031 mole) of the piperidide in 10 ml. of methanol to which 5 ml. of liquid ammonia had been added was heated for 18 hours, and the reaction product was hydrolyzed by 48% hydrobromic acid as described for the synthesis of threonine (19). Crystallization from 95% ethanol yielded 0.25 g. (42%) of α-amino-β-methoxyhydrocinnamic acid (XIV) m.p. 228–230° (dec.), no lowering when mixed with the product of the direct amination of XIII.

Absorption spectra. The absorbancies of solutions in calibrated silica cells of path length 1.000 ± 0.001 cm. were measured with a Beckman DU spectrophotometer. The molar absorbancy index, a_m, was plotted against wave length for each substance. The results are given in Figures 1 and 2. The uniform nomenclature and symbology suggested by the National Bureau of Standards (35) has been used.

SUMMARY

1. The α-benzamidocinnamic acid of m.p. 229–230° (III) and the azlactone, 2-phenyl-4-benzylidene-5-oxazolone of m.p. 165–166° (I), derived from it, have been tentatively assigned the configuration in which the carboxyl function is *cis* to the phenyl group. Conversely the α-benzamidocinnamic acid of m.p. 199–200° (IV) and its azlactone, m.p. 149–150° (II), have the carboxyl function *trans* to the phenyl. Assignment was based on the comparison of m.p.'s with those of the analogously substituted 4-benzamido-2-biphenylcarboxylic acid (V) and 2-benzamido-4-biphenylcarboxylic acid (VI).

2. The absorption spectra of the α-benzamidocinnamic acids and their azlactones have been measured.

3. Various chemical reactions relating the α-benzamidocinnamic acids and

their azlactones with the two racemic α-benzamido-β-methoxyhydrocinnamic acids have been investigated. They were found to be of no value in establishing the configurational relationships involved.

4. The racemic α-benzamido-β-methoxyhydrocinnamic acid of m.p. 220–221° (IX) has been tentatively assigned the *erythro* structure on the basis of its derivation from *trans*-cinnamic acid and the form of m.p. 160–162° (X) the *threo* structure on the basis of its derivation from *cis*-cinnamic acid.

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