

ence in the configuration of the chains is probably due to rotation of the glucose residues about the glucosidic link. The helical configuration would suggest that the (CH₂OH) groups on neighboring glucose residues are *cis* to each other, while the extended form of the chain must represent a *trans* arrangement.⁸

Little further can be said of the actual arrangement of the glucose residues in the helices. However, models built by Freudenberg, *et al.*,⁹ indicate that it is possible to construct helical starch chains only if the normals to the planes of the glucose rings are normal to the helix axis. The periodicity along the helix should then equal the width of a glucose residue. Space models of a glucose ring have a width of about 8 Å., the periodicities found for the helix in the wet and dried precipitates and in the starch-iodine complex^{2c} are in good agreement with this value. This width was also found for the glucose residue in the extended starch chains of the "B" modification.⁸ Freudenberg's

(9) K. Freudenberg, E. Schaaf, G. Dumpert and T. Floetz, *Naturwissenschaften*, **27**, 850 (1939).

model of the helix is then very probably correct in the above particular.

Summary

Diffraction patterns from wet and dried butanol-precipitated amylose confirm a helical starch chain with a helix diameter of about 13.7 Å., a length per turn of about 8 Å., and six glucose residues per turn. The helices approximate a close-packed arrangement in both the wet and dried precipitates, with alternate helices directed in opposite directions. The space group for both structures is probably D₂⁴-P₂1₂2₁.

The spacial relations between the starch-iodine complex and the dried butanol precipitate confirm the proposal² that in the starch-iodine complex the iodines occupy the interior of the helices, and it is suggested that in butanol-precipitated amylose the butanol occupies the interior of the helix.

The cell previously reported for the starch-iodine complex^{2c} must be a pseudo-cell with only pseudo-hexagonal symmetry.

AMES, IOWA

RECEIVED AUGUST 16, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

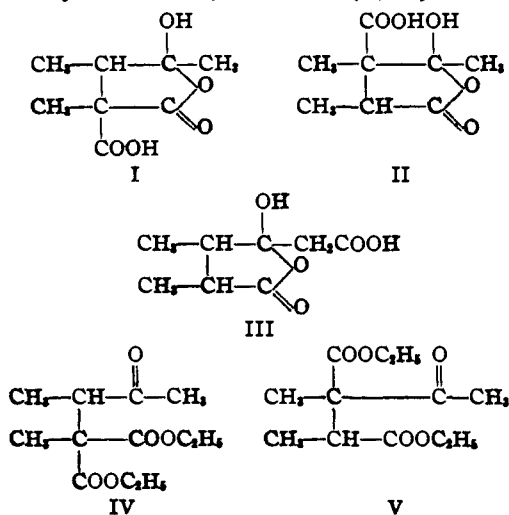
Structure of Monocrotaline. X. Monocrotalic Acid¹

BY ROGER ADAMS AND J. M. WILKINSON, JR.²

Monocrotalic acid, which is obtained by the hydrogenolysis of the alkaloid monocrotaline,³ was assigned three possible structural formulas I, II and III. The failure of either ethyl α -carbethoxy- α,β -dimethyllevulinate (IV) or ethyl β -carbethoxy- α,β -dimethyllevulinate (V) to yield mono-

crotalic acid but instead dimethyllevulinic acid on acid saponification, introduced some doubt as to the correctness of either I or II as possible structures.^{1b}

After the initial researches,^{1a,3} two reasons for not favoring structure III for monocrotalic acid were offered. The first was the difficulty encountered in attempting to esterify the acid with methanol and sulfuric acid or with methanol saturated with hydrogen chloride.^{1a} Such behavior seemed indicative of a tertiary carboxyl group. The second was that methyl anhydromonocrotalate (VI), which is the unsaturated



(1) For previous papers see (a) Adams, Rogers and Long, *This Journal*, **61**, 2822 (1939); (b) Adams and Long, *ibid.*, **62**, 2289 (1940).

(2) An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

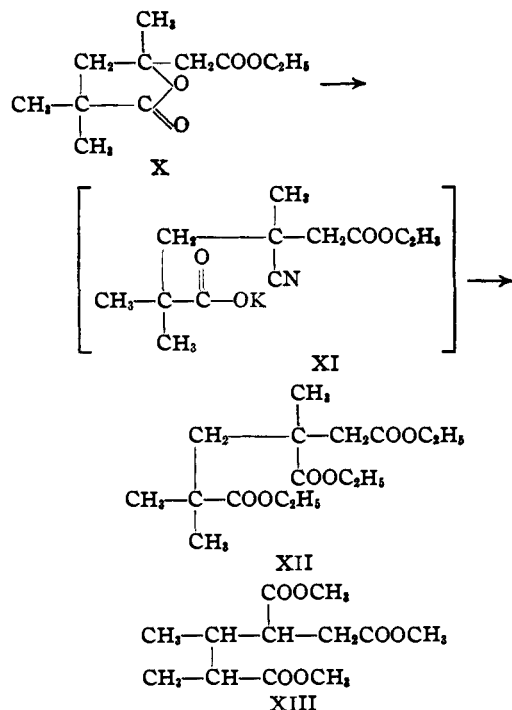
(3) Adams and Rogers, *This Journal*, **61**, 2815 (1939)

ester derived from monocrotalic acid of structure III, did not give a Legal test which was considered to be specific for β,γ -unsaturated γ -lactones containing a free hydrogen in the α -position.⁴

Recent investigations have cast doubt as to the specificity of the Legal test for β,γ -unsaturated lactones.⁵ As to the esterification, it now appears that the failure to obtain satisfactory yields of the ester by the use of methanol and hydrogen chloride may be attributed not to the unreactivity of the carboxyl group in monocrotalic acid but rather

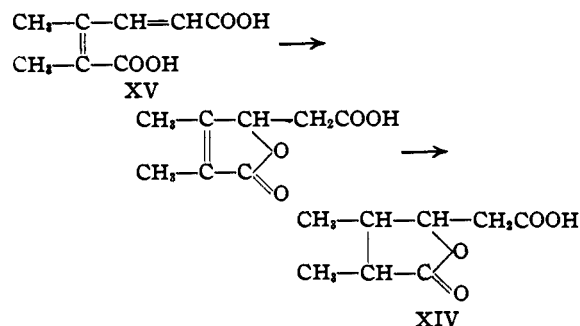
(4) Jacobs and Hoffman, *J. Biol. Chem.*, **61**, 333 (1925).

(5) Paist, Blout, Uhle and Elderfield, *J. Org. Chem.*, **6**, 273 (1941)

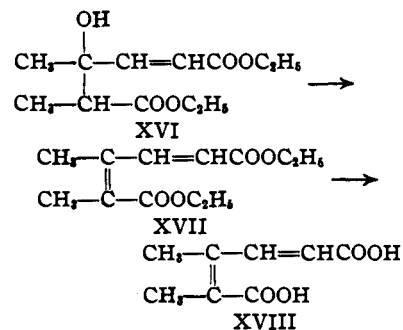
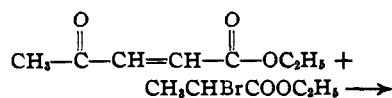


acid, m. p. 131–132°, $[\alpha]^{20}_D +3.80^\circ$.^{1b} It is probable that the new product is merely a stereoisomeric form of dihydroanhydromonocrotalic acid formed possibly by opening of the lactone ring and epimerization of the γ -carbon atom.

Studies have been started to prepare synthetically dihydroanhydromonocrotalic acid of structure XIV. Since alkyl substituted muconic acids are known to lactonize,¹⁰ the synthesis and lactonization of α,β -dimethylmuconic acid (XV) might serve as an expeditious route to structure XIV.

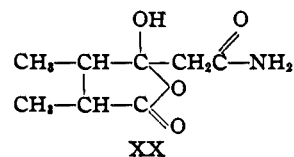
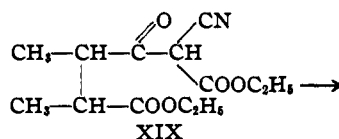


An approach to the synthesis of α,β -dimethylmuconic acid is indicated in the following series of reactions (XVI–XVIII).



The condensation of ethyl β -acetylacrylate with ethyl α -bromopropionate did not proceed smoothly. A 30% yield of product which analyzed for XVI resulted. However, both phosphorus pentoxide and phosphorus oxychloride failed to dehydrate the product to the ester of α,β -dimethylmuconic acid so that doubt is indicated for the proposed structure of the initial condensation.

Still another synthetic approach to monocrotalic acid is under study. β -Carbomethoxy- α,β -dimethyl propionyl chloride was condensed with sodium-ethyl cyanoacetate in ether to give ethyl δ -carbomethoxy- δ -cyano- α,β -dimethyllevulinate (XIX). The product, however, has not yet been con-



verted by either acid or alkaline hydrolysis to the amide of monocrotalic acid (XX).

Experimental

Monocrotalyl Chloride.—A suspension of 1.0 g. of monocrotalic acid in 3 cc. of purified thionyl chloride¹¹ was heated under reflux for one hour. At the end of this time the acid had gone into solution completely. The reaction mixture solidified on cooling to room temperature, and 5 cc. of dry benzene was added. The benzene was then removed under diminished pressure, and a further 5 cc. of benzene was added which was likewise removed. The residue was purified by recrystallization from dry ether: white needles, m. p. 145–146° (cor.); yield, 1.0 g. (91%).

Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{O}_4\text{Cl}$: C, 46.55; H, 5.36. Found: C, 46.42; H, 5.41.

A solution of 0.5 g. of the above acid chloride was refluxed gently with 5 cc. of anhydrous methanol for thirty minutes. Evaporation of the methanol under diminished pressure left an oily residue which soon crystallized. The product, after recrystallization from ether, melted at 79–80° (cor.); yield, 0.4 g. (78%). The mixed melting point with an authentic sample of methyl monocrotalate was 79–80° (cor.).

Anhydromonocrotalic Acid.—A suspension of 2.0 g. of monocrotalic acid in 10 cc. of purified thionyl chloride was

(10) Baker and Laufer, *J. Chem. Soc.*, 1342 (1937); Nuenhoeffer, *Ber.*, 68, 255 (1935); Böseken, Metz and Pluim, *Rec. trav. chim.*, 54, 345 (1935); Pauly and Will, *Ann.*, 416, 1 (1918).

(11) L. F. Fieser, "Experiments in Organic Chemistry," Part 2, D. C. Heath and Company, New York, N. Y., sec. ed., 1941, p. 381.

refluxed for five hours. At the end of this time, the reaction mixture had become a deep red in color. The solution was allowed to cool to room temperature, and 10 cc. of ether was added. The ether was then removed under diminished pressure, and an additional 10 cc. of ether was added which was likewise removed. The residue, which did not crystallize, was distilled at 2 mm. (temperature not recorded). The distillate slowly crystallized on standing under the influence of a stream of air which contained sufficient moisture to hydrolyze the acid chloride. The product was purified by recrystallization from benzene-petroleum ether (b. p. 60–110°): white leaflets, m. p. 115–117° (cor.); yield, 1.14 g. (64%).

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.44; H, 5.93. Found: C, 56.28; H, 6.06.

Rotation: 0.2788 g. made up to 10 cc. with absolute ethanol at 28° gave $\alpha_D +5.45^\circ$; $l, 2$; $[\alpha]^{25}_D +196.0^\circ$.

It was found in later procedures that it was not necessary to distill the product, but rather evaporation of an ether solution of the crude reaction product by means of a stream of air caused the material to crystallize. Moisture in the air served to hydrolyze the acid chloride.

Anhydromonocrotalic acid decomposes gradually upon standing several weeks at room temperature.

Although anhydromonocrotalic acid was prepared several times by this method, later attempts to repeat the preparation were unsuccessful and only an oil was obtained.

A solution of 1.0 g. of the anhydromonocrotalic acid in 20 cc. of ether was cooled in an ice-bath to 5°, and an ether solution of diazomethane was added until the solution had become a light yellow. The reaction mixture was allowed to stand in the ice-bath for an additional thirty minutes with occasional shaking. Evaporation of the ether under diminished pressure left a yellow oil.

The yellow oil was dissolved in 10 cc. of ether and hydrogenated at 125° and 2000 lb. pressure with Raney nickel for six hours. The nickel was separated, and the ether was removed by evaporation in a stream of air. The oily residue was then hydrolyzed by boiling with 5 cc. of concentrated hydrochloric acid for four hours. Evaporation of the water under reduced pressure left a white crystalline solid. Purification by recrystallization from benzene gave 0.8 g. (81%) of pure acid: white crystals, m. p. 131–132° (cor.); mixed melting point with pure dihydroanhydromonocrotalic acid^{1a} was 131–132° (cor.).

Reaction of Monocrotalyl Chloride with Diazomethane: Preparation of the Diazoketone.—A solution of 1.0 g. of monocrotalyl chloride in 50 cc. of dry ether was cooled to 5° in an ice-bath, and an ether solution of diazomethane was added with stirring until an excess was present as evidenced by the yellow color of the resulting solution. The solution was then allowed to stand in the cold for one hour and at room temperature for fifteen to twenty minutes. The ether was removed under diminished pressure, and the yellow residue was purified by recrystallization from absolute ether: yellow plates, m. p. 132–134° (dec.) (cor.); yield, 0.80 g. (78%).

Anal. Calcd. for $C_8H_{12}O_4N_2$: C, 50.94; H, 5.66; N, 13.20. Found: C, 50.84; H, 5.80; N, 12.85.

Attempts to rearrange the diazoketone with silver oxide into the homologous acid or its ester were unsuccessful. The products were invariably dark, viscous liquids which resisted all attempts to cause them to crystallize and which were present in such small amounts that purification by distillation was not feasible.

Reaction of Hydrogen Chloride with the Diazoketone Prepared from Monocrotalyl Chloride. Preparation of the Chloroketone.—A solution of 5 cc. of concentrated hydrochloric acid in 5 cc. of water was added to the crude diazoketone made from 0.8 g. of monocrotalyl chloride. There was a vigorous reaction, and a gas was evolved. Removal of the water by means of a stream of air left an oil which soon crystallized. The product on recrystallization from petroleum ether (b. p. 60–110°) gave white crystals, m. p. 97–99° (cor.); yield, 0.7 g. (75%).

Anal. Calcd. for $C_8H_{10}O_4Cl$: C, 49.10; H, 5.91; Cl, 16.00. Found: C, 49.03; H, 6.11; Cl, 16.14.

An attempt to remove the halogen from the chloroketone by the use of palladium and hydrogen was unsuccessful. The product was unchanged chloroketone.

Oxidation of Monocrotalic Acid with Nitric Acid.—A solution of 1.5 g. of monocrotalic acid in 5 cc. of 70–75% nitric acid (sp. gr. 1.42) was refluxed for eighteen hours. The reaction mixture was then diluted with 5 cc. of distilled water, and on standing at room temperature it deposited a white crystalline solid. The crystals were separated and purified by recrystallization from water: white plates, m. p. 95–96° (cor.); yield, 0.25 g. A mixed melting point with an authentic sample of α, β -dimethylmaleic anhydride was 95–96°.

Anal. Calcd. for $C_8H_6O_3$: C, 57.14; H, 4.76; neut. equiv., 72. Found: C, 57.12; H, 4.99; neut. equiv., 71.0.

The filtrate from which the α, β -dimethylmaleic anhydride had separated was made exactly neutral with 10% aqueous sodium hydroxide. The solution was then extracted with ether. The ether layer was dried over anhydrous sodium sulfate, and removal of the ether under diminished pressure left a small amount of a yellow-green oil. The odor of the material strongly indicated biacetyl.

In another oxidation, the precipitated dimethylmaleic anhydride was removed by filtration, and the filtrate was distilled at atmospheric pressure. Acetic acid was indicated in the distillate as shown by a positive lanthanum nitrate test⁷ since, when 1 cc. of the distillate was treated successively with 1 cc. of 5% aqueous lanthanum nitrate, 1 cc. of 0.02 *N* aqueous iodine, and a few drops of 1 *N* aqueous ammonia, and warmed on a steam-bath, a brownish-blue solution resulted. No similar test could be obtained by the use of dimethylmaleic anhydride.

Oxidation of Monocrotalic Acid with Potassium Permanganate.—A solution of 2.0 g. of monocrotalic acid, 0.85 g. of potassium permanganate, and 0.5 cc. of concentrated sulfuric acid in 15 cc. of water was heated with stirring for six hours in a water-bath at 50°. The precipitated manganese dioxide was then removed by filtration, and the filtrate was distilled until 10 cc. of distillate had been collected. The distillate was neutralized with 0.1 *N* sodium hydroxide and was evaporated to dryness on a steam cone.

The solid residue, which weighed about 0.2 g., was dissolved in 5 cc. of water, and the aqueous solution was made acidic with two drops of dilute hydrochloric acid. Two-tenths of a gram of *p*-bromophenacyl bromide and 5 cc. of ethanol were added, and the solution was heated under reflux for one hour. The reaction mixture was allowed to cool to room temperature, and a white solid separated which, after recrystallization from dilute ethanol, gave 0.07 g. of white plates, m. p. 85° (cor.). A mixed melting point between this material and an authentic sample of the *p*-bromophenacyl ester of acetic acid showed no depression.

The residual solution, from which the 10 cc. of distillate had been collected, was extracted continuously with ether for twenty-four hours. The ether extract was dried over anhydrous sodium sulfate, and removal of the ether under diminished pressure left 0.96 g. of white crystalline solid, m. p. 180–181° (cor.). A mixed melting point between this material and monocrotalic acid was 180–181°.

The Amide of Monocrotalic Acid.—A solution of 0.50 g. of methyl monocrotalate^{1a} in 10 cc. of 16 *N* aqueous ammonia was allowed to stand at room temperature for seventy-two hours. The water was removed by means of a stream of air, and the product was purified by recrystallization from methyl ethyl ketone: white needles, m. p. 209–211° (cor.); yield, 0.31 g. (65%).

Anal. Calcd. for $C_8H_{13}O_4N$: C, 51.50; H, 6.95; N, 7.50. Found: C, 51.43; H, 6.83; N, 7.40.

Rotation: 0.1235 g. made up to 10 cc. with absolute ethanol at 29° gave $\alpha_D -0.07^\circ$; $l, 1$; $[\alpha]^{25}_D -5.70^\circ$.

The Amide of Anhydromonocrotalic Acid.—To 1.0 g. of methyl anhydromonocrotalate^{1a} was added 10 cc. of 16 *N* aqueous ammonia. The mixture was shaken vigorously, and within a few minutes, a white solid separated. The solid was collected on a filter and purified by recrystalliza-

tion from benzene: white crystals, m. p. 146–147° (cor.); yield, 0.82 g. (88%).

Anal. Calcd. for $C_8H_{11}O_2N$: C, 56.80; H, 6.55; N, 8.28. Found: C, 57.01; H, 6.47; N, 8.44.

The Amide of Dihydroanhydromonocrotalic Acid.—To a solution of 0.8 g. of methyl dihydroanhydromonocrotalate¹² in 3 cc. of absolute ethanol was added 10 cc. of 16 *N* aqueous ammonia, and the resulting solution was allowed to stand at room temperature for seventy-two hours. Evaporation of the water by a stream of air left an oil which soon crystallized. The product was purified by recrystallization from ether–petroleum ether (b. p. 30–60°): white crystals, m. p. 130–132° (cor.), with softening at 125°; yield, 0.4 g. (55%).

Anal. Calcd. for $C_8H_{11}O_2N$: C, 56.14; H, 7.60; N, 8.12. Found: C, 55.42; H, 6.93; N, 8.50.

Reaction of Potassium Cyanide with Methyl Dihydroanhydromonocrotalate: Attempted Preparation of α,β -Dimethyl- γ -carboxyadipic Acid.—The procedure was similar to that employed by Ranganathan in his addition of potassium cyanide to the lactone of γ -hydroxy- α,α,γ -trimethyladipic acid.⁹

A mixture of 1.0 g. of methyl dihydroanhydromonocrotalate¹² and 0.5 g. of potassium cyanide was heated under reflux for nine hours at 200–220° (bath temperature). The reaction mixture was allowed to cool to room temperature, and a mixture of 5 cc. of methanol and 1.5 cc. of concentrated sulfuric acid was added. The solution was then heated under gentle reflux for one week. An additional 5 cc. of methanol was added, and a solid separated, apparently potassium sulfate, which was removed by filtration. The methanolic filtrate was evaporated in a stream of air and left a residual oil.

The dark yellow oil was refluxed for five hours with 5 cc. of concentrated hydrochloric acid. The water was evaporated under diminished pressure, and a white solid crystallized. The residue was extracted four times with ether, and evaporation of the combined ether extracts left an oil which partially crystallized. The residue was dissolved in carbon tetrachloride, and on slow evaporation of the resulting solution in a stream of air, a white solid was deposited. The product was purified by successive recrystallizations from carbon tetrachloride: white plates, m. p. 111–112° (cor.); yield, 0.65 g.

Anal. Calcd. for $C_8H_{11}O_4$: C, 55.78; H, 6.96; neut. equiv., 172. Found: C, 55.36; H, 6.97; neut. equiv., 173.3.

Rotation: 0.2083 g. made up to 5 cc. with ethanol at 27° gave $\alpha_D -2.32^\circ$; l , 1; $[\alpha]_D^{27} -55.7^\circ$.

The product was apparently a stereoisomeric form of dihydroanhydromonocrotalic acid.¹² A mixed melting point of the product and the latter was 95–96°. Dihydroanhydromonocrotalic acid melts at 131–132°.

Ethyl α,β -Dimethylhydrogensuccinate.—The method employed was similar to that used by Bone, Sudborough and Sprankling¹³ for the preparation of the half methyl ester.

A solution of 64.0 g. (0.5 mole) of *cis*- α,β -dimethylsuccinic anhydride in 92.0 g. (2.0 moles) of absolute ethanol was heated under reflux for five hours. The excess ethanol was removed by distillation, and the residue was made slightly alkaline with a saturated solution of sodium bicarbonate. The aqueous solution was extracted twice with ether, and the ether extracts were discarded. The aqueous layer was acidified strongly with concentrated hydrochloric acid and was extracted several times with ether. The ether extracts were combined and dried over anhydrous sodium sulfate. Removal of the ether under diminished pressure left an oil which was distilled: colorless liquid, b. p. 115–117° (3 mm.). n_D^{20} 1.4345; yield, 77.0 g. (88%).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.09. Found: C, 54.76; H, 7.94.

(12) Bone, Sudborough and Sprankling. *J. Chem. Soc.*, **85**, 539 (1904).

β -Carbethoxy- α,β -dimethylpropionyl Chloride.—To 71.0 g. (0.47 mole) of monoethyl α,β -dimethylhydrogensuccinate was added cautiously 120.0 g. (0.58 mole) of pulverized phosphorus pentachloride. After the initial reaction had subsided, the mixture was heated on a steam-bath for two hours. The phosphorus oxychloride was removed by distillation under reduced pressure, and the residue was fractionated: colorless liquid, b. p. 96–97° (15 mm.), n_D^{20} 1.4462; yield, 47.0 g. (52%).

There was some tendency for the product to revert to the anhydride as indicated by the fact that a portion of the distillate crystallized toward the end of the distillation. The solid material which separated melted at 87° which was identical with the melting point of the anhydride as shown by a mixed melting point. Therefore, in subsequent experiments, it was found advantageous to remove the phosphorus oxychloride by distillation under reduced pressure and to utilize the crude half ester acid chloride without purification.

Condensation of Ethyl Cyanoacetate with β -Carbethoxy- α,β -dimethylpropionyl Chloride: Ethyl δ -Carbethoxy- δ -cyano- α,β -dimethyllevulinate.—In a one-liter three-necked flask equipped with a mercury-sealed stirrer, dropping funnel, and a reflux condenser carrying a calcium chloride tube was placed a solution of 26.0 g. (0.23 mole) of ethyl cyanoacetate in 200 cc. of dry ether and 5.28 g. (0.23 mole) of powdered sodium. The sodium salt soon precipitated, and after stirring the solution vigorously for four hours, most of the sodium disappeared.

A solution of 22.0 g. (0.115 mole) of β -carbethoxy- α,β -dimethylpropionyl chloride in 100 cc. of dry ether was then added dropwise, with stirring, at such a rate as to maintain gentle refluxing. Stirring was continued at room temperature for five hours after the addition of the acid chloride. At the end of this time, the reaction mixture was maintained at reflux on a steam-bath for an additional five hours with stirring.

The reaction mixture was poured cautiously into 300 cc. of ice water which contained 5 cc. of concentrated sulfuric acid. The ether layer was separated, and the aqueous layer was extracted several times with ether. The ether extracts were combined and dried over anhydrous sodium sulfate. Removal of the ether under diminished pressure left an oil which was fractionated: colorless liquid, b. p. 136–138° (2 mm.), n_D^{20} 1.4726; yield, 15.0 g. (42%).

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 57.98; H, 7.11; N, 5.22. Found: C, 57.68; H, 6.98; N, 5.81.

Numerous attempts to hydrolyze the ester to a crystalline lactic acid or amide using alkali and hydrogen peroxide,¹⁴ dilute alkali, or concentrated hydrochloric acid resulted in water-soluble oils as the only products. In all cases, the quantities of the ester were such that purification of the products by distillation was impossible. Attempts were made to characterize the products by means of their *p*-bromophenacyl esters, but no such derivatives could be obtained.

Ethyl β -Acetylacrylate.—Ethyl β -acetylacrylate prepared according to the method of Wolff¹⁴ was a pale yellow liquid, b. p. 65–67° (2 mm.); n_D^{20} 1.4492.

To 1 cc. of the keto-ester was added 10 cc. of water and sufficient ethanol to effect solution. After the addition of 1.0 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate, the solution was heated on a water-bath for a few minutes. The solution was cooled, and the precipitated semicarbazone was purified by recrystallization from 95% ethanol giving 1.26 g. of white crystals, m. p. 205–207° (cor.).

Anal. Calcd. for $C_8H_{13}O_2N_2$: C, 48.24; H, 6.58; N, 21.09. Found: C, 48.61; H, 6.66; N, 21.25.

Condensation of Ethyl β -Acetylacrylate with Ethyl α -Bromopropionate.—In a 200-cc. three-necked flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser was placed 9.2 g. (0.14 mole) of granulated zinc (20-mesh). A solution of 20.0 g. (0.14 mole) of ethyl

(13) Radziazewski, *Ber.*, **16**, 355 (1885).

(14) Wolf. *Ann.*, **264**, 248 (1891).

β -acetylacrylate and 25.4 g. (0.14 mole) of ethyl α -bromopropionate in 100 cc. of a mixture of dry benzene and toluene, which contained equivalent amounts of benzene and toluene, was added dropwise with stirring. The reaction started after gentle warming; however, the reaction mixture soon set to a gel and failed to reflux spontaneously. The mixture was then maintained at reflux by means of an oil-bath, and the remainder of the reactants was added dropwise with stirring. Stirring and refluxing were continued for three hours after all the benzene-toluene solution had been added.

The reaction mixture was poured into iced sulfuric acid, and the benzene-toluene layer was separated. The aqueous layer was extracted with ether. The ether and benzene-toluene extracts were combined, washed with 5% sodium carbonate solution, and dried over anhydrous sodium sulfate. Removal of the solvents under diminished pressure left an oil which was distilled: colorless liquid, b. p. 121–122° (2 mm.); n_D^{20} 1.4579; yield, 10.5 g. (30%).

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 59.02; H, 8.25. Found: C, 59.40; H, 8.18.

Attempts to transform the product into diethyl α,β -dimethylmuconate by means of phosphorus oxychloride or phosphorus pentoxide in benzene resulted in recovery of the material unchanged.

Summary

1. It has been demonstrated that under proper conditions, monocrotalic acid can be esterified with methanol and hydrogen chloride. Methyl monocrotalate and its derivatives, methyl anhydromonocrotalate and methyl dihydroanhydromonocrotalate, react very readily in the cold with aqueous ammonia to give the corresponding

amides. These two reactions lead to the deduction that monocrotalic acid contains a primary carboxyl group.

2. Monocrotalic acid forms with thionyl chloride monocrotalyl chloride which gives methyl monocrotalate with methanol. With diazomethane the acid chloride gives the diazoketone. This product with hydrogen chloride gives the chloroketone but could not be made to rearrange with silver oxide to the homologous acid.

3. Prolonged heating of monocrotalic acid with thionyl chloride gives anhydromonocrotalic acid. In turn this could be esterified with diazomethane to methyl anhydromonocrotalate.

4. Oxidation of monocrotalic acid with nitric acid gives dimethylmaleic anhydride and traces of acetic acid. Acid permanganate gives acetic acid.

5. Treatment of methyl dihydroanhydromonocrotalate with potassium cyanide in order to convert it to an adipic acid derivative gives apparently merely a stereoisomer of the original compound.

6. By the condensation of the monoethyl ester monoacid chloride of dimethyl succinic acid with ethyl cyanoacetate, the ethyl- δ -carbethoxy- δ -cyano- α,β -dimethyllevulinate presumably was formed but could not be hydrolyzed to the monocrotalic acid amide.

URBANA, ILLINOIS

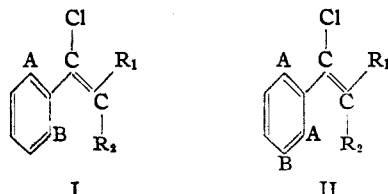
RECEIVED JULY 2, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Aryl Olefins. VII. A New Synthesis of Hindered β -Substituted- β -Arylacrylic Acids

BY ROGER ADAMS AND C. W. THEOBALD¹

Recent work on the study of optical activity resulting from restricted rotation has led to the preparation and resolution of several acrylic acid derivatives of types I and II,² in which R_1 or R_2 is a carboxyl and A and B represent a variety of groups.



The same general synthetic procedure has been used in preparing all of these compounds. It is,

(1) An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry: Eastman Kodak Fellow. 1942–1943.

(2) Adams and Miller, *THIS JOURNAL*, **63**, 53 (1940); Adams, Anderson and Miller, *ibid.*, **63**, 1589 (1941); Adams and Binder, *ibid.*, **63**, 2773 (1941); Adams and Gross, *ibid.*, **64**, 1786 (1942); Adams, Binder and McGrew, *ibid.*, **64**, 1791 (1942); Adams, Miller, McGrew and Anderson, *ibid.*, **64**, 1795 (1942).

however, not adaptable to the preparation of compounds in which the chlorine atom in I or II is replaced at will by other atoms or groups. The last step in the method consists in the conversion of a β -keto acid by means of phosphorus pentachloride to the corresponding β -chloroacrylic acid. Preliminary experiments to convert the keto acid to the β -bromoacrylic acid by means of phosphorus tribromide failed. With the exception of the introduction of the methoxyl group in the β -position of the acrylic acid, no feasible reactions are available for conversion of β -keto acids to β -substituted acrylic acids with varying β -substituents. As a consequence a new synthesis has been sought which would allow the formation of such acids, so that the influence of the β -substituents on the restricted rotation might be determined and compared. Wittig, Oppermann and Faber,³ have reported recently the synthesis and resolution of the amino ester (III) which had a half-life of forty-three minutes at 20° in methanol. The procedure

(3) Wittig, Oppermann and Faber, *J. prakt. Chem.*, **158**, 81 (1941).