aniline was obtained from nitrolevulinanilide. 4-Amino-2-nitrotoluene was obtained from nitro 4-methyllevulinanilide. From the hydrolysis of the other nitrolevulinanilides (R = Cl, Br, COOH, $COOC_2H_5$), 4-chloro-2-nitroaniline, 4-bromo-2-nitroaniline, 4-amino-3-nitrobenzoic acid, and ethyl 4-amino-3-nitrobenzoate, respectively, were obtained. 4-Acetamido-2-nitrolevulinanilide was hydrolyzed with barium hydroxide solution by the method of Bülow and Mann[3] to obtain 4-amino-3-nitroacetanilide.

Four of the compounds, in which the nitro groups were located in the 2 position, were reduced with iron powder and dilute hydrochloric acid in ethanol to form the corresponding amino derivatives.

Only two of the four amino compounds could be converted to benzimidazoles by Phillips procedure.[4] The amino compounds and 2-acetylethylbenzimidazoles are listed in Table V.

EXPERIMENTAL

General method for preparation of 4-substituted levulinanilides. The 4-substituted aniline (0.1 mole) was mixed with 0.1 mole of γ-acetoxy-γ-valerolactone[2] and 20–50 ml. of 50% aqueous ethanol. The mixture was allowed to stand for 3 to 4 days at room temperature with occasional shaking. The crystals, which separated, were removed and washed with 50% aqueous ethanol. The product was then recrystallized from a suitable solvent.

General method for preparation of nitro 4-substituted levulinanilides. The 4-substituted levulinanilide (0.04 mole) was added gradually to 50 ml. of concentrated sulfuric acid with cooling (−10 to −20°) and vigorous stirring. Then a mixture of 10 ml. of concentrated sulfuric acid and 3.2 ml. of concentrated nitric acid and a small amount of urea was added dropwise, with cooling and stirring. After 30 min., the mixture was poured onto cracked ice, at which point a yellow precipitate formed. After washing with cold water and drying, the product was recrystallized from a suitable solvent.

General method for preparation of amino 4-substituted levulinanilides. The nitro compound (0.04 mole), 12 g. of reduced iron powder, and 4.5 ml. of 2*N* hydrochloric acid was added to 40 ml. of ethanol and the mixture heated for 8 hr. on a steam bath. The reaction mixture was neutralized with 2*N* sodium hydroxide solution. The hot solution was filtered and the filtrate evaporated under reduced pressure. The crude product, so obtained, was recrystallized from a suitable solvent.

General method for preparation of 2-acetylethylbenzimidazoles. One g. of the 2-aminolevulinanilide derivative was dissolved in 10 ml. of 4*N* hydrochloric acid and the solution was refluxed for 2 hr. The solution was neutralized with ammonium hydroxide. A gummy precipitate was formed. The mixture was allowed to remain in the refrigerator (2–3 hr.) until the gummy product became solid. The crude product was then recrystallized from hot water with the aid of decolorizing carbon. The products are soluble in 1*N* hydrochloric acid and in 2*N* sodium hydroxide solution.

General method for determining the position of the nitro group. One g. of the 4-substituted nitrolevulinanilide was dissolved in 5 ml. of 95% ethyl alcohol and 5 ml. of 2*N* hydrochloric acid. The solution was refluxed for 1 hr. and cooled to yield crystals of the corresponding nitroaniline. The products were purified by recrystallization from hot water. They were identified by melting point and mixed melting point determinations.

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Syntheses of Some β-Aroyl-α- and β-methylacrylic Acids

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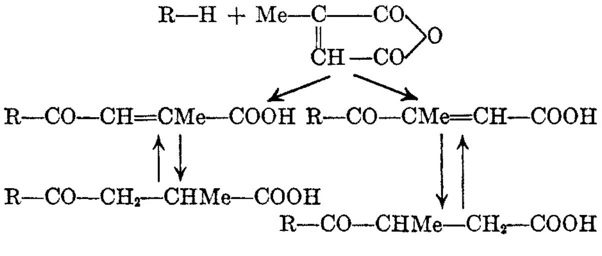
The condensation of citraconic anhydride with anisole, *p*-cresyl methyl ether, diphenyl, and fluorene has been studied. Powdered anhydrous aluminum chloride (2 equiv.) was added portionwise to the mixture of citraconic anhydride (1 equiv.) and the aromatic compound (1 equiv.) in *s*-tetrachloroethane or nitrobenzene as solvent. In each case, the reaction product was a mixture of two isomeric acids: R—CO—CH═CMe—COOH (type A) and R—CO—CMe═CH—COOH (type B). The structure of both acids is established by one of the following methods: (i) Reduction of the obtained β-aroylacrylic acids (A or B) with hydrogen in palladium chloride solution and activated charcoal to the corresponding β-aroylpropionic acids.(1) These have been found to be identical with authentic specimens prepared by the action of methylsuccinic anhydride on the corresponding aromatic compound.[2–4] (2) The synthesis of β-aroylacrylic acids (A or B) by bromination of the corresponding β-aroylpropionic esters followed by dehydrobromination and hydrolysis.[5] This is illustrated in the following scheme:



Acids of type A were predominant and less soluble (*cf.* ref. 4), those of type B were more soluble and hence comparatively difficult to purify.

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EXPERIMENTAL

Anisole and citraconic anhydride. Powdered aluminum chloride (26.7 g., 0.2 mole) was added portionwise to the mixture of anisole (10 g., 0.09 mole) and citraconic anhydride (10 g., 0.08 mole) in *s*-tetrachloroethane (80 ml.) at room temperature (25°). The reaction mixture was left for 2 days and decomposed with ice-cooled 6*N* HCl, the organic solvent was floated with benzene, then shaken with an aqueous solution of sodium carbonate. Acidification of this sodium carbonate extract yielded 20 g., (100%) of a material melting at 70–90°. This wide range indicates that the product consisted of a mixture of isomeric acids. Fractional crystallization from benzene (*ca.* 60 ml.) gave a crystalline precipitate (9 g.), m.p. 113–115° which, on recrystallization from benzene, gave β-*p*-anisoyl-α-methylacrylic acid, m.p. 119–120°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.65; H, 5.55.

The benzene mother liquor was evaporated, the residue was purified by dissolving in sodium carbonate solution, boiling with charcoal, filtering, and acidifying. Repeated crystallization from light petroleum (b.p. 50–60°) gave β-*p*-anisoylcrotonic acid, m.p. 93–95°, depressed to 80–85° on admixture with the above isomeric acid.

Anal. Found: C, 65.35; H, 5.50.

Determination of structure. (*1*). β-*p*-Anisoyl-α-methylacrylic acid (1 g.) was dissolved in sodium carbonate solution (10%) and 6 ml. of a 0.01% solution of palladium chloride and 0.4 g. of activated charcoal added. Hydrogen under normal pressure was passed in for 2 hr. The acid obtained on acidification had m.p. 145–146° and when mixed with β-*p*-anisoyl-α-methylpropionic acid, (m.p. 145–146°) melted at 145–146° (cf. ref. 2).

(*2*) β-*p*-Anisoylcrotonic acid when similarly treated afforded β-*p*-methoxybenzoylbutyric acid, m.p. 70–71°.[6] This acid was converted into the corresponding semicarbazone, in the normal manner, which had m.p. 179–180°, not depressed when mixed with an authentic specimen, m.p. 179–180°, prepared as mentioned in ref. 2.

p-Cresylmethyl ether and citraconic anhydride. The product from *p*-cresylmethyl ether (10 g., 0.08 mole), citraconic anhydride (9.2 g., 0.08 mole) and aluminum chloride (24.3 g., 0.18 mole) in *s*-tetrachloroethane (80 ml.), had m.p. 85–105° and weighed 2.5 g. (13%). It was digested with light petroleum (b.p. 50–60°) several times and the residue was crystallized from benzene–light petroleum (b.p. 50–60°) to give β-(2-methoxy-5-toluyl)-α-methylacrylic acid (1.4 g.), m.p. 155–156°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.35; H, 5.86. This acid on hydrogenation, in the usual manner, gave β-(2-methoxy-5-toluyl)-α-methylpropionic acid, m.p. 129°, and when mixed with an authentic specimen (m.p. 129°) melted at 129° (cf. ref. 3).

The other keto-acid which, after the digestion of the crude reaction product, remained in the mother liquor was purified by crystallization from light petroleum (b.p. 80–100°) to give β-(2-methoxy-5-toluyl)crotonic acid (0.5 g.), m.p. 122–125°.

Anal. Found: C, 66.30; H, 5.77.

When nitrobenzene was used as a solvent instead of *s*-tetrachloroethane, an inseparable mixture of acids was obtained.

Diphenyl and citraconic anhydride. Aluminum chloride (26.2 g., 0.19 mole) was added portionwise to the mixture of diphenyl (13.7 g., 0.09 mole) and citraconic anhydride (10 g., 0.08 mole) in *s*-tetrachloroethane (100 ml.) with stirring. The product was decomposed with HCl in the usual manner after one night and sufficient ether added to float the organic solvent which was extracted with sodium carbonate solution. Acidification gave a solid (21 g., 89%), m.p. 146–154°. This was dissolved in sodium carbonate solution (10%) and left to cool at 50°. A crystalline precipitate was removed by filtration, suspended in water, and acidified. The acid obtained had m.p. 151–152° (18 g.). The sodium carbonate mother liquor, at 0°, gave an additional crop of precipitate which, after acidification, yielded another 0.7 g. of an acid, m.p. 150–152°. The combined material on crystallization from benzene–light petroleum (b.p. 50–60°) afforded β-*p*-phenylbenzoyl-α-methylacrylic acid, m.p. 152–153°, undepressed when mixed with an authentic specimen.

Anal. Calcd. for: $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 76.51; H, 5.30.

The sodium carbonate mother liquor remaining after removal of the second crop was acidified giving a colorless product (1 g.), m.p. 116–118°. Crystallization from light petroleum (b.p. 80–100°) gave β-*p*-phenylbenzoylcrotonic acid, m.p. 119–120°, identical to an authentic specimen.

Anal. Found: C, 76.49; H, 5.35.

Authentic specimen of β-phenylbenzoyl-α-methylacrylic acid. 4-Crotonyldiphenyl. Freshly distilled crotonyl chloride (10.4 g., 0.1 mole) was gradually added to the mixture of diphenyl (15.4 g., 0.1 mole) and aluminum chloride (13.4 g., 0.1 mole) in nitrobenzene (120 ml.) at 5°. After being left overnight, the reaction mixture was poured in cold 6*N* HCl and steam-distilled. The residue was taken in ether, dried, and the solvent removed. The product (22 g., 99.5%) was crystallized from light petroleum (b.p. 50–60°) to give 4-crotonyldiphenyl, m.p. 82–84°.

Anal. Calcd. for: $C_{16}H_{14}O$: C, 86.48; H, 6.30. Found: C, 86.19; H, 6.47.

The mother liquor was investigated and no other isomer was found. The ketone on oxidation with sodium hypobromite (10%), gave diphenyl-4-carboxylic acid, identical to an authentic specimen (cf. ref. 4).

α-Phenylbenzoyl-β-cyanopropane. 4-Crotonyldiphenyl was converted into the nitrile, as mentioned in Hann & Lapwerth's procedure.[7] This after crystallization from ethanol gave α-phenylbenzoyl-β-cyanopropane, m.p. 140–141° in 89% yield.

Anal. Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.49.

α-Methyl-β-p-phenylbenzoylpropionic acid. The above nitrile was hydrolyzed by heating with 10% methanolic KOH for 10 hr. on the steam bath. The acid obtained after acidification was crystallized from ethanol to give α-methyl-β-*p*-phenylbenzoylpropionic acid, m.p. 209–210°, undepressed when mixed with an authentic sample (cf. ref. 4).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.00. Found: C, 75.68; H, 6.2.

β-p-Phenylbenzoyl-α-methylacrylic acid. The methyl ester of α-methyl-β-*p*-phenylbenzoylpropionic acid, obtained by the action of methanol and concentrated sulfuric acid (5 hr. on the steam bath), was treated with bromine (1 mole) in chloroform and heated for 3 hr. on the steam bath. The resulting bromoester, without purification, was dehydrobrominated by treatment with potassium acetate in methanol (cf. ref. 5). The product of hydrolysis (methanolic KOH (5%) and heating for 1 hr.) gave β-*p*-phenylbenzoyl-α-methylacrylic acid, m.p. 152–153°.

β-*p*-Phenylbenzoylbutyric ester, prepared as mentioned above, on bromination and dehydrobromination afforded β-*p*-phenylbenzoylcrotonic acid, m.p. 119–120° (cf. ref. 4).

Fluorene and citraconic anhydride. The mixture of fluorene (8.3 g., 0.05 mole) and citraconic anhydride (5.6 g., 0.05 mole) in nitrobenzene (100 ml.) was treated with aluminum chloride (13.4 g., 0.1 mole) at 0–5°. After 2 days the reaction mixture was decomposed with 6*N* HCl and the organic solvent was removed by steam distillation. The product (8 g., 42%) was fractionally crystallized from chloroform. The less soluble fraction (6 g.) was recrystallized from chloroform

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to give β-2-fluorenoyl-α-methylacrylic acid as yellowish crystals, m.p. 181–182°, identical to an authentic sample.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.69; H, 5.03. Found: C, 77.25; H, 4.91.

The mother liquor was evaporated and the residue crystallized from light petroleum (b.p. 80–100°) to give β-2-fluorenoylcrotonic acid (1 g.), m.p. 139–141° (m.p. and mixed m.p.). Found: C, 77.32; H, 4.95. When this reaction was repeated using *s*-tetrachloroethane as solvent, the mixture of isomeric acids was obtained in higher yield. However, the two acids were difficult to separate. Authentic samples of both keto-acids were prepared from the corresponding α- and β-methylpropionic acids as previously stated (cf. ref. 4).

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Preparation and Polymerization of *p*-Vinylphenol

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Recently, syntheses of *p*-vinylphenol have been reported[1,2] by the decarboxylation of *p*-benzoxycinnamic acid followed by hydrolysis of the resulting ester, and by hydrogenation of *p*-acetoxyacetophenone followed by dehydration-hydrolysis. In view of this, it is of interest to describe the successful direct synthesis of *p*-vinylphenol by the decarboxylation of *p*-hydroxycinnamic acid. Although this route to the monomer has been reported to yield only traces of the desired product[3,4] in contrast to the smooth conversion of *o*-coumaric acid to the *o*-vinylphenol,[5] it was found that by use of the decarboxylation procedure of Wiley and Hobson,[6] wherein the cinnamic acid in quinoline is added dropwise to an evacuated, heated vessel containing catalyst and the product immediately distilled out, yields as high as 40% were obtained. The usual decarboxylation procedures even when carried out *in vacuo* gave resinous products.[7–9]

The separation of the monomer from the distillate and its purification are extremely difficult because of the ease with which it polymerizes, especially in the presence of acidic reagents. Best yields were obtained when the distillate was carefully acidified in the cold in the presence of extractant to remove monomer immediately. Extraction with aqueous caustic followed by neutralization with acid or carbon dioxide gave lower yields. The physical properties and color tests of the monomer agreed with those described.[3] Analysis of the monomer with standard bromine–carbon tetrachloride or bromate-bromide solutions indicated that four atoms of bromine were added per mole of monomer.

Attempts to prepare vinylphenols by the reaction of vinyl chloride with phenol in the presence of aluminum chloride as described by Seymour were unsuccessful.[10]

p-Vinylphenol readily polymerizes on standing, even at 0°, or in the presence of free-radical or cationic initiators. The latter may be predicted on the basis of the presence of the electron-releasing phenolic group. Benzene solution viscosities indicated low molecular weight. Addition of the monomer to a mixture of sulfuric and acetic acids gave a swellable but insoluble cross-linked polymer, possibly from alkylation reactions.

Since phenols are generally inhibitors for the radical addition polymerization of vinyl monomers, consideration was given to other modes of polymerization, such as the addition of the double bond of one molecule of vinylphenol to the benzene ring of another molecule. However, the infrared spectra of the polymer obtained with catalytic amounts of either azobisisobutyronitrile or sulfuric acid were essentially identical and indicated vinyl-type addition polymerization.[11] The monomer and polymer spectra are shown in Figs. 1 and 2 for comparison.

Radical initiated polymeric *p*-vinylphenol which sintered at 207–215° and melted at 229° was obtained as a white powder on purification by reprecipitation. Ionic initiation generally gave lower melting polymers in the 175–220° range. A copolymer of styrene and *p*-vinylphenol was prepared from a mixture containing 10 mole % vinylphenol, and resulted in a polymer containing approximately 19 mole % vinylphenol as deduced from absorption spectra and carbon-hydrogen analysis. Its softening range was 164–198°.

EXPERIMENTAL

p-Hydroxycinnamic acid. The method of Vorsatz[12] was used except that aniline was used as the catalyst as sug-

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