Reduction of ethyl α-carbethoxy-γ-cyano-β-phenylbutyrate to I[2] was found to proceed much better in a larger amount of solvent than used formerly. Thus, 60 g. of cyano-ester in 300 g. of alcohol gave 21 g. of crystalline I, m.p. 138°.

Experimental

δ-Amino-β-phenylvaleric Acid Hydrochloride (II).—A solution of 60 g. of I in 600 ml. of 6 *N* hydrochloric acid was boiled for three hours and then evaporated. Crystallization of the residue from alcohol–ether gave 57 g. of colorless plates, m.p. 184–186°.

The same hydrochloride was obtained by similar treatment of the sirupy by-product from the preparation of I. From 90 g. of sirup there was obtained 25 g. of pure amino-acid hydrochloride.

Anal. Calcd. for $C_{11}H_{16}ClNO_2$: C, 57.5; H, 7.0. Found: C, 57.8; H, 7.2.

Benzoylation.—Thirty grams of II, shaken with 250 ml. of 16% sodium hydroxide and 18 g. of benzoyl chloride, gave 26 g. of the benzoyl derivative III, crystals from ether–ligroin, m.p. 110–112°.

Anal. Calcd. for $C_{18}H_{19}NO_3$: C, 72.7; H, 6.4. Found: C, 72.8; H, 6.5.

N-Benzoyl-1-keto-3-indanethylamine (IV).—An attempt to cyclize III with concd. sulfuric acid at 90° gave only water-soluble products. However, a Friedel–Crafts cyclization was successful.

A mixture of 29.7 g. of III and 12.5 g. of thionyl chloride was heated in a water-bath at 60–70° for one hour at atmospheric pressure, and then for 15 minutes at 20 mm. The residue was dissolved in 400 ml. of benzene and treated with 28 g. of aluminum chloride. The mixture was stirred for one hour at 60–70° and then poured on ice. The product was washed with sodium carbonate and crystallized from benzene giving 24.5 g. of colorless crystals, m.p. 106–107°.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.4; H, 6.1. Found: C, 77.3; H, 6.3.

The **2,4-dinitrophenylhydrazone** formed red plates from nitromethane, m.p. 220–221°.

Anal. Calcd. for $C_{24}H_{21}N_5O_5$: C, 62.7; H, 4.6. Found: C, 62.7; H, 4.5.

N-Benzoyl-3-phenyl-1-indene-ethylamine (V).—A solution of 10 g. of IV in 100 ml. of benzene was added to 130 ml. of 1 *N* ethereal phenylmagnesium bromide, and the mixture was stirred and heated in a water-bath at 70° for one hour. Hydrolysis was effected with iced dilute sulfuric acid, and the crude product was washed with aqueous sodium carbonate. Volatile materials were removed by steam distillation, but the glassy residue could not be crystallized. It was therefore dehydrated by boiling it for five minutes with 50 ml. of acetic acid containing one drop of sulfuric acid. Crystallization from ether–ligroin and then from benzene gave 1.7 g. of V, colorless needles, m.p. 132–134°.

Anal. Calcd. for $C_{24}H_{21}NO$: C, 84.9; H, 6.2. Found: C, 85.4; H, 6.3.

Attempts to hydrolyze compounds IV and V, using either acids or bases, were all unsuccessful.

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Polymerization of Esters of Cinnamic Acid[1]

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In 1878 Erlenmeyer[2] reported that on heating ethyl cinnamate he obtained a powdery white solid which was insoluble in most solvents and decomposed before it melted. Liebermann[3] confirmed this observation and showed that this solid was not one of the possible dimeric truxillic esters. Later it was established[4] that other esters of cinnamic acid behaved similarly and the high melting products were described as cyclic trimers. More recently Shapiro, Linstead and Newitt[5] heated ethyl cinnamate for 240 hours at 125° under 4000 atmospheres pressure, and reported that they obtained, in 58% yield, a white powdery product which melted above 320°. They did not establish the molecular weight of this product but did demonstrate that it was non-crystalline.

We have now polymerized ethyl cinnamate by the usual bulk free-radical-initiated procedure and found that this polymer has the structure which one would expect in a vinyl-type polymerization product. By heating ethyl cinnamate to 60° with either benzoyl peroxide or 2,2′-azobisisobutyronitrile for varying times the yield of polymer was 10–11%. The product seems to be identical with the high melting products described as resulting from the thermal polymerizations. When 2,2′-azobisisobutyronitrile was used as the initiator the nitrogen content of the polymer approached the nitrile nitrogen content of the initiator used. Assuming that the polymerization is terminated by coupling of the growing radical chains, the nitrogen content of the polymer indicates a molecular weight of 7600. This product showed an amorphous X-ray pattern.[6] The infrared absorption spectrum of the polymer showed the non-conjugated ester carbonyl band at 1736 cm.$^{-1}$, the ester carbon–oxygen band at 1166 cm.$^{-1}$, and the monosubstituted phenyl ring bands at 744 and 699 cm.$^{-1}$.[7]

Under comparable conditions methyl cinnamate gave a low yield of a similar white solid which melts above 300°. This solid also gave an amorphous X-ray pattern.[6] Its infrared absorption spectrum shows the non-conjugated ester carbonyl band at 1733 cm.$^{-1}$, the ester carbon–oxygen band at 1194 cm.$^{-1}$, and the monosubstituted phenyl bands at 744 and 700 cm.$^{-1}$. In addition there is a very weak carbon–carbon double bond band at 1637 cm.$^{-1}$. The molecular weight calculated from the nitrogen content of the polymer made by initiation with 2,2′-azobisisobutyronitrile was about 2300.

An old laboratory sample of methyl cinnamate which had stood in a partly-filled brown bottle for at least a year was found to be partially polymerized to a white product of fibrous appearance. Its molecular weight was not determined. The polymers prepared in our laboratory were soluble in the corresponding monomers.

Experimental

Polyethyl Cinnamate.—Twenty grams of ethyl cinnamate, 0.10 g. of 2,2′-azobisisobutyronitrile and 0.025 g. of technical lauryl mercaptan were heated to 60° for about a month.

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] E. Erlenmeyer, *Ber.*, **11**, 150 (1878).

[3] C. Liebermann, *ibid.*, **22**, 2240 (1889).

[4] C. Liebermann and M. Zsuffa, *ibid.*, **44**, 841 (1911); C. Liebermann, G. Mühle and M. Kardos, *ibid.*, **48**, 1645 (1915).

[5] R. H. Shapiro, R. P. Linstead and D. N. Newitt, *J. Chem. Soc.*, 1784 (1937).

[6] We are indebted to Mr. W. E. Thatcher for this information.

[7] The infrared data reported in this work were determined by the Anderson Physical Laboratory, Champaign, Illinois.

The solution became somewhat viscous during this time. The solution was poured into ethanol to precipitate the polymer. A white powdery product which did not darken, decompose or melt below 300° was obtained in 10% yield. This product was insoluble in benzene, chloroform, ethyl acetate, dioxane, dimethyl formamide, ether and hot trichloroethylene. It was soluble in ethyl cinnamate.

Anal.[8] Calcd. for $C_{11}H_{12}O_2$: C, 75.02; H, 6.87. Found: C, 74.95; H, 7.04; N, 0.37.

This nitrogen content is equivalent to the nitrile nitrogen in 0.087 g. of 2,2′-azobisisobutyronitrile.

Polymer of a similar nature was obtained in low yield in cyclohexane solution.

Ten grams of ethyl cinnamate, 0.12 g. of benzoyl peroxide and 0.025 g. of technical lauryl mercaptan were heated at 60° for about a week. On isolation as before an 11.3% yield of polymer was obtained.

Polymethyl Cinnamate.—Twenty grams of methyl cinnamate and 0.10 g. of 2,2′-azobisisobutyronitrile were heated at 60° for about 10 days and then to 85° for 3 days. When the solution was poured into ethanol a white powder was obtained in 2% yield. This product was insoluble in common solvents and did not darken, melt or decompose when heated to 300°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 71.08; H, 6.43; N, 1.17.

The nitrogen content corresponds to that of 0.055 g. of initiator.

A sample of fibrous polymethyl cinnamate was isolated from an old sample of methyl cinnamate. Its physical properties and infrared spectrum were similar to those of the material made by 2,2′-azobisisobutyronitrile polymerization, except that it was obviously of higher molecular weight. Its low solubility has interfered with proper evaluation of this material.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 73.46; H, 6.37.

Attempts to use standard emulsion polymerization procedures for making these products are contemplated.

[8] We are indebted to Mrs. Ester Fett and Mr. Joseph Nemeth for the microanalyses reported here.

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Anion Exchange Studies. VIII.[1,2] Separation of Iron and Aluminum in Sulfate Solutions

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It had been shown in an earlier paper that Fe(III) can be strongly adsorbed from chloride solutions by the quaternary amine polystyrene divinyl benzene "strong base" anion-exchange resin Dowex-1.[3] A similar study of the adsorbability of Fe(III) from sulfuric acid and ammonium sulfate solutions has now been carried out. For these media, conditions of strong adsorption were found. However, in contrast with the behavior in chloride solutions, the maximum adsorption found was considerably smaller for sulfate than for chloride solutions, and adsorption was found to decrease greatly with acidity and slightly with sulfate concentration.

The sulfate form of the resin was prepared by washing the chloride form with 1–2 M H_2SO_4 until the effluent was chloride-free and then washing the resin with distilled water until the *p*H of the effluent was larger than 5. Since elution of the acid from the resin tends to tail strongly,[2] large volumes of water are necessary.

The adsorbability of Fe(III) was investigated by determining distribution coefficients D (amount Fe per kg. of resin/amount Fe per l. of solution) by shaking iron sulfate solutions with known amounts of resin, and determining the change in iron concentration spectrophotometrically.

In the sulfuric acid solutions significant adsorption was found only for M $H_2SO_4 < 0.1$. This adsorption increased rapidly with decreasing sulfuric acid concentration reaching values of $D = ca.\ 100$ in 0.001 M H_2SO_4.

Adsorbabilities in ammonium sulfate solutions were measured with some acid added (initially 0.01 M H_2SO_4) to prevent extensive hydrolysis of Fe(III) and possible hydrolytic polymerization. D was found to decrease from *ca.* 35 in 0.01 M $(NH_4)_2SO_4$ to *ca.* 10 in 4 M $(NH_4)_2SO_4$, and to be essentially independent of iron concentration in the range 10^{-5} to 10^{-3} M Fe(III) under conditions where loading of the resin with respect to iron is small.

The color of the adsorbed iron complex varies somewhat with concentration in the resin phase, becoming red-brown at high concentrations. The adsorbed species cannot readily be identified since, as pointed out in an earlier paper,[2] the resin adsorbs sulfuric acid, hence causing significant changes in the acidity of the solutions and in the composition of the resin phase. The strong dependence of adsorption on acidity suggests that a basic sulfate complex is involved.

The adsorption of Fe(III) can be utilized for separations. The principles of these separations are illustrated in experiments with Al(III) which is only weakly adsorbed under conditions where Fe(III) is strongly adsorbed. Thus, an Fe(III)–Al(III) solution containing 0.005 M $Fe_2(SO_4)_3$, 0.005 M $Al_2(SO_4)_3$ and 0.010 M H_2SO_4 was passed through a 0.488 cm.^{2} × 15.9 cm. Dowex-1 column in the sulfate form with flow rate 0.34 cm. min.$^{-1}$. Aluminum appeared in the effluent after *ca.* 4.2 cc. of solution had been passed through the column. The iron concentration of the solution was $< 10^{-6}$ M. Iron was adsorbed at first at the top of the column, slowly moved through it, and appeared after *ca.* 95 ml. in the effluent. Since the interstitial volume of the column is *ca.* 3.3 cc., while Al(III) appeared in the effluent after 4.2 cc., it appears that Al(III) is slightly adsorbed under these conditions. Possibly for these reasons Fe(III) appears in the effluent somewhat earlier when the same separation is carried out with more concentrated Al(III) solutions (*e.g.*, after 44 ml. with a 0.005 M $Fe_2(SO_4)_3$–0.48 M $Al_2(SO_4)_3$–0.005 M H_2SO_4 solution in a similar though slightly shorter column (15.0 cm.)).

Fe(III) can be eluted from the column by increasing the sulfuric acid concentration of the eluent. The experiments described in Fig. 1 illustrate the procedure. In these experiments, iron was adsorbed from 0.5-ml. samples of 5 × 10^{-3} M $Al_2(SO_4)_3$–5 × 10^{-3} M $Fe_2(SO_4)_3$–10^{-2} M H_2SO_4 solutions on 0.187 cm.^{2} × 9.3 cm. columns.

[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper, K. A. Kraus, F. Nelson and J. F. Baxter, THIS JOURNAL, **75**, 2768 (1953).

[3] G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).