As, in this instance, the method of thermal polymerization *in alto vacuo* was not feasible because of the high decomposition temperature, polymerization was carried out in solution, using pyridine,[4] nitrobenzene[5] and dimethylformamide as solvents.

III, on being dissolved in dry pyridine or nitrobenzene, polymerized rapidly and the solution turned into a gel. Owing to the sparse solubility even of low-chain polymers of N^{β}-benzyl-*dl*-asparagine (IV) in these solvents, the resulting substances had an average chain length of 10 to 13 only. As these were, however, soluble in dimethylformamide, polymerization was carried out in the latter solvent leading to polymer preparations with an average chain length of 24 units (molecular weight about 5000), which were already insoluble in dimethylformamide and precipitated on standing.

The above polymers were soluble in hot glacial acetic acid, but practically insoluble in water, as well as in dilute mineral acids and alkali. A positive biuret reaction could, therefore, be obtained only on prolonged contact of the substance with the reagent solution, or when adding some dimethylformamide which dissolved lower fractions. On boiling with ninhydrin solution, the solid particles of the substance attained a blue color.

Attempts to remove the benzyl group have, so far, not been successful.

Experimental

Microanalyses are by Drs. Weiler and Strauss. Melting points were determined in a Fisher–Johns apparatus.

N-Carboxy Anhydride of N^{β}-Benzylasparagine (III).—N^{β}-Benzylasparagine (II) was obtained from N^{α},N^{β}-dibenzylasparagine (I),[3] by hydrogenolysis with a palladium chloride on carbon catalyst (30%) in glacial acetic acid at 60°. A 10% catalyst[2] gave only poor results. After reduction, the organic material which adhered to the catalyst was extracted with cold formic acid. Removal of the latter *in vacuo* gave II in 77% yield.

Eight grams of II (which had been dried at 100°), was suspended in 250 ml. of dry dioxane in a three-necked flask to which a reflux condenser, a gas inlet tube and a stirrer had been attached. Phosgene was bubbled into the suspension and stirring commenced, while the bath temperature was maintained at 55°. After about 30 minutes, a clear solution resulted. Excess of phosgene and the dioxane were removed *in vacuo* at 40° and the resulting white crystalline substance was washed with ether and dried over phosphorus pentoxide. The yield was 7 g. (78.5%).

Anal. Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.1; H, 4.8; N, 11.3. Found: C, 58.0; H, 4.8; N, 11.4.

Polymerization of the N-Carboxy Anhydride of N^{β}-Benzylasparagine (III) in Pyridine.—III was dissolved in varying amounts of pyridine (which had been dried by reflux with potassium hydroxide) and left at room temperature (*cf.*, Table II). The solutions became gradually more viscous while CO_2 was evolved and finally turned into gels. The polymers were isolated, after different periods of time, by precipitating them through addition of ether or water. They were then filtered, washed with some more ether or water respectively and dried *in vacuo*. The average chain length of all polymeric preparations was determined by analysis of amino-nitrogen in a Van Slyke manometric apparatus.

Polymerization in Nitrobenzene.—The procedure was similar to the above and polymers were precipitated by the addition of ether.

Polymerization in Dimethylformamide.—Polymerization was carried out at temperatures of about 5° and isolation of the polymer effected by addition of water. Results are summarized in Table II.

TABLE II

		In pyridine			1n nitro-bz.	In dimethyl-formamide	
Amt. III, g.		1	0.5	1	3	5	1
Sol., ml.		4	20	15	20	40	10
1sold. after, days		15 min.	9	19	18	24 hr.	21
Amino N, %	Calcd.	0.62	0.68	0.68	0.52	0.75	0.29
	Found	0.62	0.67	0.71	0.53	0.75	0.30
Carbon,[6] %	Calcd.	64.3	64.1	64.1	64.3	64.1	64.5
	Found	63.1	63.9	62.8	62.6	64.2	62.0
Hydrogen,[6] %	Calcd.	5.9	5.9	5.9	5.9	5.9	5.9
	Found	5.8	5.9	6.0	5.9	6.6	6.0
Nitrogen,[6] %	Calcd.	13.6	13.6	13.6	13.6	13.6	13.6
	Found	14.2	12.9	13.6	13.5	13.3	13.1
Chain length		11	10	10	13	9	24

Hydrolysis of Poly-N^{β}-benzyl-*dl*-asparagine.—0.019 g. of the polymer ($n = 24$) was boiled under reflux with 5 ml. of hydrochloric acid (6 *N*) for 19 hours. The resulting clear solution was transferred quantitatively into a 25-ml. volumetric flask, neutralized with 6 *N* sodium hydroxide solution against methyl orange and water added up to the 25-ml. mark. Aliquot parts of this solution were analyzed for free amino-nitrogen and values of 13.0% obtained (theor. 13.7%). This indicated complete hydrolysis to aspartic acid and benzylamine. Confirmation of this fact was obtained by paper partition chromatography of the hydrolysate (phenol–water as mobile phase), giving the characteristic spots for aspartic acid and benzylamine.

---

[4] V. Go and H. Tani, *Bull. Chem. Soc.* (*Japan*), **14**, 510 (1939); W. E. Hanby, S. G. Waley and J. Watson, *Nature*, **161**, 132 (1948); *J. Chem. Soc.*, 3239 (1950).

[5] W. E. Hanby, S. G. Waley and J. Watson, *ibid.*, 3009 (1950).

[6] As is generally known, analyses of polymers, especially as regards carbon, are not always satifactory (see for instance ref. 5 and C. S. Marvel, Cooke and J. C. Cowan, THIS JOURNAL, **62**, 3497 (1940)).

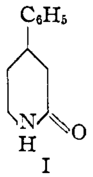
DEPARTMENT OF ORGANIC CHEMISTRY
THE HEBREW UNIVERSITY
JERUSALEM, ISRAEL

Syntheses from 4-Phenyl-2-piperidone[1]

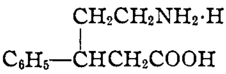
BY C. F. KOELSCH AND ROBERT W. DENET

RECEIVED APRIL 2, 1953

Having developed a method for preparing 4-phenyl-2-piperidone (I),[2] we considered it of some interest to investigate various chemical transformations of the substance. The present note describes conversion of I through II, III and IV, into V.

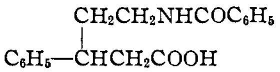


I



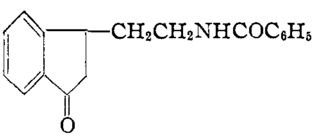
$$\overset{\displaystyle CH_2CH_2NH_2\cdot HCl}{\overset{|}{C_6H_5\text{—}CHCH_2COOH}}$$

II

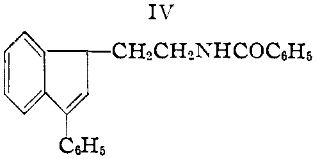


$$\overset{\displaystyle CH_2CH_2NHCOC_6H_5}{\overset{|}{C_6H_5\text{—}CHCH_2COOH}}$$

III



IV



V

---

[1] From the M.S. Thesis of R. W. DeNet, December, 1947.

[2] C. F. Koelsch, THIS JOURNAL, **65**, 2459 (1943).

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.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINNESOTA

Polymerization of Esters of Cinnamic Acid[1]

BY C. S. MARVEL AND G. H. MCCAIN

RECEIVED MARCH 7, 1953

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.

---

(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.