

Anal. Calcd. for $C_{26}H_{26}O_4$: C, 82.8; H, 5.0. Found: C, 83.0; H, 5.0.

When 0.9 g. of this substance was boiled and stirred for five hours with 125 ml. of acetic acid containing 14 g. of chromic anhydride and 5 ml. of concd. sulfuric acid, it gave 0.96 g. (96%) of crude dibasic acid, m. p. 400° with decomposition. The substance was insoluble in aqueous or alcoholic alkali and in all organic solvents except hot quinoline. Recrystallized from quinoline and then digested with boiling alcohol for thirty minutes, the *p,p',p''*-quinquebenzone-*p,p'*-dicarboxylic acid formed a colorless powder that sintered at 400° and melted at $405\text{--}410^\circ$ with decomposition.

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 74.2; H, 3.8. Found: C, 74.9; H, 3.9.

Distillation of 0.2 g. of the acid from copper chromite at 10 mm. gave 0.1 g. of *p,p',p''*-quinquebenzone, colorless platelets from pyridine, m. p. $285\text{--}286^\circ$. The same compound was obtained in a yield of 79% from 2 g. of *p*-terbenzone-*p,p'*-dicarbonyl chloride, 3 g. of aluminum chloride, and excess benzene.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 82.6; H, 4.5. Found: C, 82.7; H, 4.3.

No pure product (*cyclopentabenzoylene*) other than a minute amount of quinquebenzone, could be isolated from the red liquid that was formed when a mixture of 0.3 g. of *p,p',p''*-quinquebenzone-*p,p'*-dicarboxylic acid and 0.3 g. of calcium oxide was heated at $390\text{--}400^\circ$.

Summary

Dibasic acids of the structure $HO(COC_6H_4)_nCOOH$, where $n = 3, 4$ and 5 and where the phenylene groups are all *para* substituted, have been prepared, but attempts to obtain cyclopoly-

benzoylenes, $\square(COC_6H_4)_n$, where $n = 5, 6$ and 8 , from them have failed. It is suggested that the dibasic acids have nearly linear structures through resonance of the linking carbonyl groups with the benzene rings.

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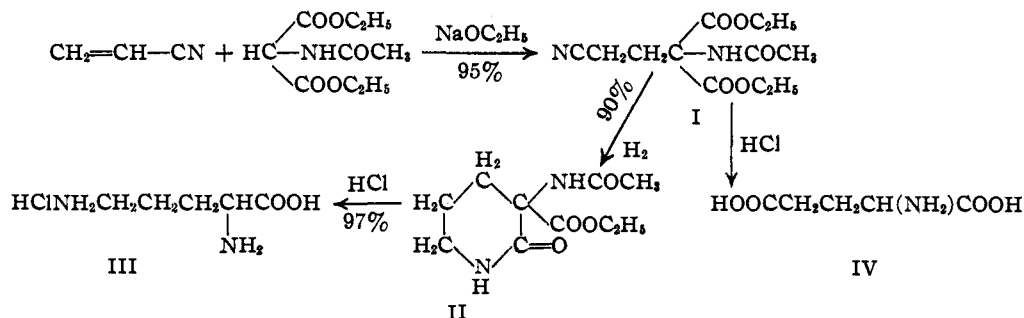
NOTES

A Synthesis of *dl*-Ornithine Hydrochloride

BY N. F. ALBERTSON AND S. ARCHER

Although several syntheses of ornithine are recorded in the literature, most of them are long and give the final product in small yield. The most recent¹ was patterned after the synthesis of lysine as described by Eck and Marvel.² Seven steps were required to give the dibasic amino acid in 12% over-all yield.

A more convenient and economical synthesis, which gave *dl*-ornithine hydrochloride in 83% over-all yield, based on ethyl acetamidomalonate, is illustrated by the following equations



Acrylonitrile was condensed with ethyl acetamidomalonate in the presence of a small quantity of sodium ethylate to give the crystalline

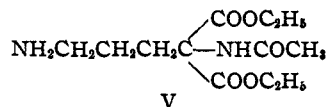
(1) Fox, Dunn and Stoddard, *J. Org. Chem.*, **6**, 411 (1941). A bibliography of the earlier work is listed here.

(2) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 76, 74, 374.

ethyl α -acetamido- α -carbethoxy- γ -cyanobutyrate (I) in 95% yield. The structure of the ester was confirmed by hydrolysis with hydrochloric acid to *dl*-glutamic acid in 66% yield. In agreement with Snyder³ we found that the product resulting from the condensation of methyl acrylate and ethyl acetamidomalonate was a liquid which could be hydrolyzed to *dl*-glutamic acid.

The reduction of I to II was carried out in the presence of Raney nickel catalyst at 68° and 600 lb. of hydrogen. We preferred the piperidone structure for the following reasons. The compound showed no basic properties and the elementary analyses agreed more closely with II

than with V. The compound was a nicely



(3) Snyder, *et al.*, *THIS JOURNAL*, **67**, 310 (1945).

crystalline substance of definite melting point and was quite soluble in water. The tendency of compounds such as V to undergo intra- rather than intermolecular condensation is indicated by the work of E. Fischer.⁴ When ornithine was treated with methanolic hydrogen chloride β -aminopiperidone resulted rather than the bimolecular condensation product, bis-(γ -aminopropyl)-diketopiperazine. These facts militated against a possible polymeric structure.

The piperidone, II, was hydrolyzed by refluxing with hydrochloric acid. After neutralization and removal of ammonium chloride, *dl*-ornithine monohydrochloride was isolated in 97% yield. For identification purposes the amino acid was converted to the dipicrate, m. p. 195.5–196.5°, and to ornithuric acid, m. p. 184–185°.⁵

Experimental

Ethyl α -Acetamido- α -carboxy- γ -cyanobutyrate (I).—To a solution of 1 g. of sodium in 500 ml. of absolute alcohol there was added 217 g. (1 m.) of ethyl acetamidomalonate. The resulting slurry was stirred and cooled while 60 g. of acrylonitrile was added dropwise over a period of twenty minutes. The clear solution was allowed to stand at room temperature for one hour. It was chilled and the solid that separated collected on a filter. The filtrate was poured into cold water whereupon a further quantity of material separated. The solids were combined and dried. The yield of ester, m. p. 92–94°, was 256.5 g. (95%).

Anal. Calcd. for $C_{12}H_{18}O_5N_2$: N, 10.37. Found: N, 10.27.

β -Acetamido- β -carboxypiperidone (II).—A quantity of 127 g. of the nitrile (I) was dissolved in 400 ml. of alcohol and reduced in the presence of Raney nickel catalyst at 600 lb. initial pressure at 68°. After one and one-half hours the reduction was complete. The catalyst was removed and the filtrate concentrated *in vacuo* to a small volume. It was chilled thoroughly and filtered. The solid was washed with a small quantity of cold alcohol and then with ether. The yield of glistening white prisms, m. p. 136–138.5°, was 96 g. (90%). A sample was crystallized from ethanol, m. p. 138.5°.

Anal. Calcd. for $C_{13}H_{22}O_5N_2$: C, 52.54; H, 8.09; N, 10.21. Calcd. for $C_{10}H_{16}O_4N_2$: C, 52.62; H, 7.07; N, 12.28. Found: C, 52.86; H, 7.28; N, 12.12.

Ornithine Monohydrochloride.—A quantity of 22.8 g. (0.1 mole) of the piperidone was refluxed with 100 ml. of concentrated hydrochloric acid for four hours and then evaporated to dryness. The residue was taken up in 60 ml. of alcohol and treated with 14 ml. of concentrated ammonium hydroxide. After cooling in ice for one hour the solid was collected. It was suspended in 150 ml. of alcohol, boiled for several minutes, filtered, and washed with two 20-ml. portions of alcohol. After drying, the amino acid melted at 225° and weighed 16.4 g. (97.4%).

***dl*-Glutamic Acid.**—The nitrile (I) (23.5 g.) was refluxed with 75 ml. of concentrated hydrochloric acid for six hours. The solution was then taken to dryness. The residue was taken up in water (25 ml.) and neutralized to pH 3 with concentrated ammonium hydroxide. After purification by the method of Dunn and Stoddard,⁶ there was obtained 8.4 g. (86%), m. p. 199°.

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(4) Fischer, *Ber.*, **42**, 4886 (1909).

(5) Adamson, *J. Chem. Soc.*, 1564 (1939), reported the m. p. of ornithine dipicrate as 198–200° and the m. p. of ornithuric acid as 186–187°.

(6) Dunn and Stoddard, *J. Biol. Chem.*, **121**, 527 (1937).

The Copolymerization of Styrene and Maleic Anhydride

BY TURNER ALFREY AND EDWARD LAVIN

The general theory of vinyl copolymerization recently has been discussed by several investigators.^{1,2,3} The essential feature of such copolymerization reactions is that four distinct chain propagation processes are involved. A monomer of type A can add to an active chain-end of type A; a monomer B can add to such an active chain; a monomer A can add to a B chain end, and a monomer B can add to a B chain end. These four processes are governed by the propagation rate constants: k_2^{aa} , k_2^{ab} , k_2^{ba} , k_2^{bb} . The chemical composition and chain structure of the copolymer is determined by two ratios of these rate constants: $\alpha = k_2^{ab}/k_2^{aa}$; $\beta = k_2^{bb}/k_2^{ba}$. A monomer mixture containing the two monomers in the molar ratio (B/A) yields an initial copolymer with the molar ratio b/a , below:

$$\frac{b}{a} = \frac{B}{A} \cdot \alpha \cdot \frac{\beta B + A}{\alpha B + A} \quad (1)$$

The essential correctness of equation (1) has been experimentally verified in a number of cases.^{2,4}

Certain symmetrically substituted ethylenic compounds—maleic anhydride, maleic esters, etc.—exhibit a very special polymerization behavior. These monomers do not polymerize alone or at least polymerize only very slowly to yield products of low polymerization degree. In the presence of an ordinary vinyl monomer, however, they often *co-polymerize* very readily and may actually accelerate the polymerization rate. The most reasonable explanation of this apparent anomaly—and indeed the only explanation which also explains the other effects described in this note—is the following: Such monomers have practically no tendency to add to free radicals of similar structure but will add readily to free radicals of the ordinary vinyl type. Whether this is the result of steric or electronegativity effects, it is impossible to say.

When a vinyl monomer (A) such as styrene is copolymerized with a monomer of the maleic anhydride type (B), the normal set of four propagation processes is reduced to 3, since k_2^{bb} is effectively zero. In this special case, the equations relating polymer composition and monomer composition take on a very simple form, since $\beta = 0$. The simplified equation can best be written

$$\frac{a}{b} = 1 + \frac{1}{\alpha} \cdot \frac{A}{B} \quad (2)$$

Equation (2) indicates that (if B is known to be a monomer of the class possessing a vanishing k_2^{bb}) a single experiment at one monomer ratio will

(1) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205–209 (1944).

(2) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944).

(3) Wall, *ibid.*, **66**, 2050 (1944).

(4) Alfrey, Merz and Mark. Paper presented at A. C. S. meeting, New York, 1944.