β-Naphthyl Mesitoate.—This ester was prepared in 96% yield from mesitoyl chloride and β-naphthol. It crystallized from alcohol in colorless needles; m. p. 112–113° (cor.).

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.42; H, 6.37.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
REYNOLD C. FUSON
STANLEY B. SPECK

RECEIVED NOVEMBER 27, 1944

The Inner Carbonate of 2,3-Butanediol

Hammond[1] and Mitchell[2] have patented methods for the preparation of the alkyl carbonates and chlorocarbonates by the interaction of the aliphatic monohydric alcohols and phosgene. These procedures have been applied by the present authors to the interaction of 2,3-butanediol and phosgene.

Procedure.—A vertical glass tube, 46 mm. by 450 mm. in dimensions, was filled with glass beads and electrically heated so that a thermometer imbedded in the glass beads was maintained at 150°. Liquid 2,3-butanediol was dropped into the top of the tube at the rate of 44 g. per hour while phosgene gas was introduced into the bottom of the tube at the rate of 200 ml. per minute. The products boiling above 150° were collected at the bottom of the tube. The resulting material was heated, on a boiling water-bath under a reflux condenser, for two hours to complete the reaction. During the heating period copious evolution of hydrogen chloride took place. The resulting product was distilled at reduced pressure, a large fraction distilling at 96° at 8 mm. pressure; yield, 75%.

Anal. Calcd. for $C_5H_8O_3$: C, 51.7; H, 7.0. Found: C, 51.5; H, 7.1.

Properties.—The molecular weight in phenanthrene was 116; $n^{26}{}_D$ 1.4226, $d^{26}{}_4$ 1.129, b. p. 240° (740 mm.). The compound is colorless and insoluble in water. It is an excellent solvent for cellulose nitrate and cellulose acetate.

CHEMISTRY DEPARTMENT
IOWA STATE COLLEGE
AMES, IOWA
J. J. KOLFENBACH
E. I. FULMER
L. A. UNDERKOFLER

RECEIVED DECEMBER 18, 1944

---

[1] J. A. Hammond, U. S. Patents 1,603,689 (October 19, 1926); 1,618,824 (February 22, 1927).

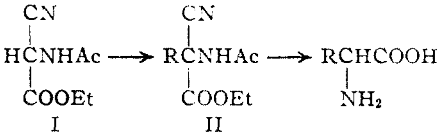
[2] H. G. Mitchell, U. S. Patents 1,603,703 (October 19, 1926); 1,638,014 (August 9, 1927).

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF AMINO ACIDS FROM ACETAMIDOCYANOACETIC ESTER

Sir:

Recently considerable interest has been shown in the preparation of amino acids from acetamidomalonic ester. We have found that ethyl acetamidocyanoacetate (I)[1] possesses even greater advantages as a general reagent. Alkylation is effected under the same conditions employed for acetamidomalonic ester.[2] Direct hydrolysis of the condensation product proceeds in either acid or basic media to yield the amino acid.



$$\underset{\text{I}}{\mathrm{HC(CN)(NHAc)COOEt}} \longrightarrow \underset{\text{II}}{\mathrm{RC(CN)(NHAc)COOEt}} \longrightarrow \mathrm{RCH(NH_2)COOH}$$

Alkylation of I with gramine gave 98% of ethyl α-acetamido-α-cyano-β-(3-indolyl)-propionate (II, R = skatyl), m. p. 196–198° (calcd. N, 14.02. Found: N, 13.78). Alkaline hydrolysis gave *dl*-tryptophan, m. p. 288–290° (cor.). A 71% yield of pure amino acid was obtained from crude indole.

When 4-chloromethylimidazole hydrochloride was condensed with I, a 66% yield of ethyl α-acetamido-α-cyano-β-imidazolepropionate (II, R = 4-imidazolemethyl), m. p. 100–103° anhydrous or 111° as monohydrate, was obtained (calcd. anhydrous: N, 22.39. Found: N, 21.98. Calcd. monohydrate: C, 49.25; H, 6.01. Found: C, 49.40; H, 5.89). Hydrolysis with sulfuric acid gave a 61% yield of *dl*-histidine, m. p. 285°. The dihydrochloride melted at 232°.[3] The overall yield of *dl*-histidine from cane sugar was 18%.

Methylation of monothioethylene glycol with dimethyl sulfate gave 80% of β-methylthiolethanol. Chlorination with thionyl chloride and condensation with I without isolation of the methylthiolethyl chloride or chlorination with hydrogen chloride followed by condensation with I gave 60% of the theoretical amount of ethyl α-acetamido-α-cyano-γ-methylthiolbutyrate (II, R = methylthiolethyl), m. p. 118° (calcd. N, 11.47. Found: N, 11.62). Basic hydrolysis gave 80% of recrystallized *dl*-methionine. The N-benzoyl derivative melted at 150°.

Alkylation of I with isopropyl bromide gave 66% of ethyl α-acetamido-α-cyano-β-methylbutyrate (II, R = isopropyl), m. p. 149° (calcd.: N, 13.20. Found: N, 13.52). Alkaline hydrolysis gave 65% of pure *dl*-valine, m. p. 289–290°. Acid hydrolysis gave an 80% yield, but the melting point was lower. The N-acetyl derivative melted at 147° and the N-benzoyl derivative at 131°.

Condensation of benzyl chloride with I gave 83% of ethyl α-acetamido-α-cyano-β-phenylpropionate (II, R = benzyl); m. p. 134° (calcd. N, 10.75. Found: N, 10.57). Hydrolysis with sodium hydroxide gave a 75% yield of *dl*-phenylalanine, m. p. 275–277°.

---

[1] Cerchez and Colesiu, *Compt. rend.*, **194**, 1954 (1932).

[2] (a) Albertson, Archer and Suter, THIS JOURNAL, **67**, 36 (1945); (b) Albertson and Archer, *ibid.*, **67**, 308 (1945).

[3] Pyman, *J. Chem. Soc.*, **99**, 1395 (1911).