

The extent of addition to the anil linkage is significantly increased when ethyl α -bromopropionate is used. In this case there is obtained an 85% yield of the β -lactam of α -methyl- β -anilino- β -phenylpropionic acid. The Reformatsky reaction with anils appears to be broad in scope, and more complete details will be published later.

Experimental

β -Lactam of β -Anilino- β -phenylpropionic Acid.—A solution of 36.2 g. (0.2 mole) of benzalaniline in 200 cc. of sodium-dried toluene was heated to boiling with 13.5 g. (0.21 g. atom) of sandpapered zinc foil and a crystal of iodine. Three cc. of ethyl α -bromoacetate was added and on stirring an exothermic reaction set in. Twenty more cc. (a total of 0.21 mole) of the bromo-ester was now added at such a rate as to maintain gentle refluxing. When the addition was completed, the mixture was boiled gently for one-half hour. Hydrolysis was effected with 200 cc. of concd. ammonium hydroxide. The toluene layer was then washed with water, dilute hydrochloric acid, sodium bisulfite solution, and again with water. After distillation of the solvent, and two recrystallizations from methanol, a 56% yield of lactam melting at 153–154° was obtained.

Ketene³ was treated with 0.1 mole of benzalaniline following the directions of Staudinger.³ After a number of recrystallizations from methanol, the product melted at Staudinger's value of 153–154°. A mixed melting point determination showed the compounds to be identical.

Reaction without Hydrolysis.—A mixture of 11.1 cc. (0.1 mole) of ethyl α -bromoacetate and 18.1 g. (0.1 mole) of benzalaniline in 100 cc. of toluene reacted with 6.6 g. (0.1 g. atom) of zinc. After the reaction, the mixture was diluted with 500 cc. of dry ether. The precipitate was allowed to settle and the supernatant liquid then decanted. After distillation of the solvent, the residue was twice recrystallized from anhydrous methanol. The melting point of the product was 154°, and there was no depression when this compound was mixed with lactam prepared from ketene.

β -Lactam of α -Methyl- β -Anilino- β -phenylpropionic Acid.—Using the same general procedure as in the first reaction, but substituting 0.21 mole of ethyl α -bromopropionate for the ethyl α -bromoacetate, an 85% yield of lactam melting at 109–110° was obtained. Crystallization was from methanol.

Reaction with Benzyl α -Bromoacetate.—A solution of 18.1 g. of benzalaniline (0.1 mole) in 100 cc. of toluene reacted with 6.6 g. of zinc (0.1 g. atom) and 23 g. (0.1 mole) of benzyl α -bromoacetate. The product was isolated and purified by the procedure of the first reaction. A 40% yield of lactam melting at 153–154° was obtained. This compound was identified by a mixed melting point determination with the lactam obtained from ketene.

(3) Hurd, "Organic Syntheses," 4, 39 (1925).

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4-Phenylphenyl Iodoacetate

BY LEE C. HENSLEY AND STEWART E. HAZLET

Bromine previously¹ has been shown to convert 4-phenylphenyl chloroacetate to 4-phenylphenyl bromoacetate by a reaction in specially prepared acetic acid in the presence of a trace of iron. We have now prepared the corresponding iodoacetate by the reaction of potassium iodide with the chloro or bromo compound.

Preparation of 4-Phenylphenyl Iodoacetate from 4-Phenylphenyl Bromoacetate.—Four and seventy-five

(1) Hazlet, Hensley and Jass, *THIS JOURNAL*, 64, 2449 (1942).

hundredths grams of the bromoacetate was dissolved in 40 ml. of acetone. This solution was added in small portions to 275 ml. of acetone saturated with potassium iodide and containing an excess of 0.5 g. of undissolved potassium iodide. At first a cloudiness appeared but, as more of the solution containing the ester was added, small granules formed and precipitated. The mixture was set aside at room temperature for thirty-six hours; Norite was added and the mixture was then allowed to stand for an additional six hours. Boiling, filtering, and removing about one-half of the acetone on the steam-bath followed. The remaining solution was poured into 600 ml. of water, and a flocculent precipitate was formed. This product represented a 77.8% yield of 4-phenylphenyl iodoacetate; m. p. 113–114°. Two recrystallizations from methanol followed by two from 70–90° ligroin raised the melting point to 113.5–114.3°.

Anal. Calcd. for $C_{14}H_{11}O_2I$: I, 37.53. Found: I, 37.76.

Preparation of 4-Phenylphenyl Iodoacetate from 4-Phenylphenyl Chloroacetate.—The same procedure, applied to the bromoacetate, gave 18.3% yield of the iodo product.

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The Hydrolysis of Nicotinonitrile by Ammonia

BY CHARLES F. KREWSON AND JAMES F. COUCH

It is well known that the action of potassium or sodium hydroxide on nitriles leads directly to the formation of the corresponding acids.¹ The amides, postulated as intermediate products in this reaction, are obtained when hydrogen peroxide is added to the mixture.²

The action of ammonium hydroxide has not been extensively studied. Schlieper reported that it did not react with valeronitrile. The idea that ammonium hydroxide reacts with nitriles to form amidines possibly stems from Berntsen's³ discovery that amine hydrochlorides react with certain nitriles to form amidine hydrochlorides. Ammonium chloride, however, did not react in this way. We have found that ammonium hydroxide reacts with nicotinonitrile to form nicotinamide.

Procedure.—A mixture of nicotinonitrile (20 g.) prepared either by the Woodward, Badgett and Willaman process⁴ or from nicotinamide by the method of LaForge,⁵ and 120 ml. (9 moles) of concentrated ammonium hydroxide solution in a cylindrical glass bulb made of 60-mm. Pyrex glass tubing, to one end of which is sealed a short piece of 10-mm. tubing, is cooled in ice, and the small tube drawn down to a spiral capillary. The bulb is then placed in a 500-cc. steel bomb along with 100 cc. of concen-

(1) (a) A. Schlieper, *Ann. Chem. Pharm.*, 59, 1–23 (1846); (b) E. Frankland and H. Kolbe, *ibid.*, 65, 288–304 (1848).

(2) (a) Br. Radziszewski, *Ber.*, 17, 1289–1290 (1884); 18, 355–356 (1885); (b) L. McMaster and F. B. Langreck, *THIS JOURNAL*, 39, 103–109 (1917); (c) L. McMaster and C. R. Noller, *J. Indian Chem. Soc.*, 12, 652–653 (1935); *C. A.*, 30, 1736 (1936).

(3) A. Berntsen, *Ann. Chem. Pharm.*, 184, 321–370 (1876); 192, 1–60 (1878); *Ber.*, 10, 1235 (1877).

(4) In course of publication.

(5) F. B. LaForge, *THIS JOURNAL*, 50, 2477 (1928).