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.

Ketene[3] was treated with 0.1 mole of benzalaniline following the directions of Staudinger.[2] 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.

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

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4-Phenylphenyl Iodoacetate

By Lee C. Hensley and Stewart E. Hazlet

Bromine previously[1] 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 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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[1] Hazlet, Hensley and Jass, This Journal, **64**, 2449 (1942).

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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 Bernthsen's[3] 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 process[4] 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-

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[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. Bernthsen, *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).

trated ammonium hydroxide. The bomb is then closed and heated at 107–109° for twelve hours, cooled, and the reaction mixture transferred to a desiccator and evaporated. The non-volatile product, 21.2 g., m. p. 114–122°, contains 80.5% of nicotinamide,[6] the remainder being nicotinic acid.[7] The yield of amide is 72.66%. After two recrystallizations from ethyl acetate, the amide melts at 129–130°, and the mixed melting point with pure nicotinamide shows no depression.

Anal. Calcd. for $C_6H_6ON_2$: C, 59.01; H, 4.95; N, 22.94. Found:[8] C, 58.97, 59.06; H, 4.9, 5.11; N, 22.80, 22.82.

The amide may, however, be extracted directly in the reaction mixture in very pure condition by ethyl acetate. Using this procedure, we have obtained a product containing 98.93% of amide and melting at 129–130°.

Addition of sodium hydroxide to the reaction mixture results in markedly speeding up the reaction, with an increased production of nicotinic acid and a corresponding decrease in the yield of amide.

Hydrogen peroxide (3.5 moles in 30% solution) added to the ammonium hydroxide (2 moles) and nitrile (1 mole) shortens the reaction time and gives increased yields (94 and 96%). The product, however, contains more nicotinic acid and melts over a wide range of temperature.

Hydrogen peroxide (3.5 moles in 30% solution), sodium hydroxide (0.3 mole), and the nitrile (1 mole) heated for six hours at 50° gives yields of 89 and 93%. The product is discolored and is less easily purified than the product obtained by the use of ammonia alone.

The observation that ammonium hydroxide may hydrolyze nitriles to the corresponding amide without the use of hydrogen peroxide may make it possible to obtain amides from nitriles oxidized or polymerized by the peroxide.

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(6) C. F. Krewson, *Am. J. Pharm.*, **115**, 122–125 (1943).

(7) The evaporation of solutions of nicotinic acid in ammonia results in dissociation of any ammonium nicotinate present and leaves a residue of nicotinic acid free from ammonia.

(8) C and H determined by D. M. Mortimore; N by C. L. Ogg.

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The Stereochemistry of Coördination Number Eight. Isomers for the Trigonal Prism with Symmetry C_2^v

BY LOUIS E. MARCHI

In a previous paper[1] four likely configurations for compounds of elements exhibiting coördination number eight were considered. In the light of one referee's comments about the radius ratio the trigonal prism considered in that paper seems to be a very unlikely configuration for coördination number eight.[2] The trigonal prism with two extra bonds along the normals to two of the rectangular faces and with symmetry C_2^v, Fig. 1, previously suggested by Hoard and Nordsieck, and Kimball,[3] is now considered.

The possible isomers for all classes containing only monodentate groups are given in Table I.

TABLE I

ISOMERS FOR MONODENTATE GROUPS

	Configuration, *T*	Optically active	Optically inactive	Total
8a	M	0	1	1
7ab	M	2	2	4
6a2b	M	12	4	16
6abc	M	26	2	28
5a3b	M	22	6	28
5a2bc		78	6	84
5abcd		168	0	168
4a4b	M	32	6	38
4a3bc		134	6	140
4a2b2c		204	12	216
4a2bcd		414	6	420
4abcde		840	0	840
3a3b2c		268	12	280
3a2bcd		560	0	560
3a2b3cd		828	12	840
3a2bcde		1,680	0	1,680
3abcdef		3,360	0	3,360
2a2b2c2d		1,252	22	1,274
2a2b2cde		2,508	12	2,520
2a2bcdef		5,040	0	5,040
2abcdefg		10,080	0	10,080
abcdefgh		20,160	0	20,160

M indicates that the isomer count was also determined by the construction of models and it was found in agreement with the number obtained by the use of Lunn and Senior's method.[4]

TABLE II

SPECIAL CLASSES OF BIDENTATE GROUPS

AA6b	6	3	9
AB6c	16	1	17
2AA4b	38	6	42
3AA2b	50	5	55
4AA	10	1	11

For the bidentate groups the same restrictions were imposed as with the other configurations. The isomer numbers for the limited number of classes containing bidentate groups, which were considered, are given in Table II. (The classes 2AB 4C, 3AB 2C and 4AB have not been considered because a preliminary study of these classes has shown that the isomer count is probably greater than for the corresponding classes in the other configurations).

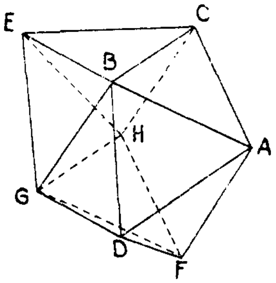

Fig. 1.—The trigonal prism is outlined by ABCFGH; D and E are the two extra bonds.

It is apparent that the number of isomers for class 4AA of this trigonal prism and of the dodecahedron, is exactly the same. Consequently

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(1) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, THIS JOURNAL, **65**, 329 (1943).

(2) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, *ibid.*, ref. 5 d.

(3) Marchi, Fernelius and McReynolds, *ibid.*, ref. 5.

(4) Lunn and Senior, *J. Phys. Chem.*, **33**, 1027 (1929).