

8.5 g. (0.13 mole) of solid sodium azide. The solution was stirred for 30 min., filtered, and methanol removed *in vacuo*. Mesityl azide distilled at 56° (0.5 mm.), 7.4 g. (61%). It was thermally unstable above 100° and was not attacked by cold concentrated sulfuric acid whereas rapid decomposition occurred in this solution above 100°. Elemental analysis was not attempted; nitrogen and sulfur were detected by sodium fusion analysis. Infrared absorption (cm.^{-1}) from a four per cent chloroform solution was observed at 4310 (w), 4149 (w), 3922 (w), 3546 (w), 3279 (w), 3021 (w), 2924 (w), 2500 (w), 2336 (m), 2137 (s) (azide), 1613 (w), 1449 (w), 1406 (m), 1361 (s), 1326 (s), 1156 (s), 1095 (w), 1003 (m), 966 (s).

For methanesulfonyl chloride, $d_{20} = 1.4805$; $n_D^{20} 1.4464$; M_R (obs.) 20.65. This allowed an assignment of 14.68 as the M_R contribution from the methanesulfonyl group. For methane-sulfonyl azide, $d_{20} = 1.4024$; $n_D^{20} 1.4532$; M_R (calcd.) 23.58, M_R (obs.) 23.35.

Reaction of *p*-toluenesulfonylazide with sodium alkoxide. To a solution of 2.3 g. (0.10 mole) of sodium in 160 ml. of absolute methanol, 19.7 g. (0.10 mole) of tosyl azide was slowly added with stirring. The mixture was heated at reflux temperature for 24 hr. as an azide odor was detected and colorless crystals of sodium tosylate, 19.0 g. (98%), separated. From 1.0 g. of this salt suspended in 5 ml. of absolute ether saturated with dry hydrogen chloride a colorless precipitate of *p*-toluenesulfonic acid was obtained, m.p. 104°¹⁰ after recrystallization from benzene. The m.p. of its *o*-toluidine salt was 190°.¹¹

The reaction was repeated with 14.4 g. (0.15 mole) of sodium butoxide in 200 ml. refluxing ether. A solution of 19.7 g. (0.10 mole) of tosyl azide in 50 ml. of ether was added dropwise with stirring. The mixture was held at reflux temperature for 12 hr., cooled, and filtered. The solid, 5.3 g. (81.5%), was identified as sodium azide by a positive azide test with ferric chloride solution. An oil residue, 10.4 g. (46%), from the ether layer was dried over anhydrous sodium sulfate and identified as *n*-butyl tosylate, b.p. 100° (0.2 mm.)¹² and $n_D^{25} 1.5042$.¹² After storage in the refrigerator in a stoppered bottle for four weeks redistillation of 8.0 g. was attempted at 0.2 mm. When the heating bath was at about 70° a violent explosion occurred. The ester apparently had become contaminated with the corresponding acid since a fine white precipitate was noted in the distillation flask just prior to the explosion.¹³ A portion of *n*-butyl tosylate was hydrolyzed to *p*-toluenesulfonic acid, m.p. and mixture m.p. 106–107°.¹⁰

Reaction of methyl tosylate with sodium azide in methanol. To a solution of 18.6 g. (0.1 mole) of methyl tosylate in 160 ml. of absolute methanol was added 6.5 g. (0.1 mole) of solid sodium azide. With efficient stirring the reaction mixture was refluxed for 24 hr. during which time an azide odor was detected. Solid sodium tosylate, 15.4 g. (80%), was separated from the cold mixture and identified by the m.p. and mixture m.p. 104° for the corresponding acid monohydrate and m.p. and mixture m.p. 190° for its *o*-toluidine salt.

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(10) K. H. Slotta and W. Franke, *Ber.*, **63**, 678 (1930).

(11) N. D. Cheronis and J. B. Entrikin, *Semi-micro Qualitative Organic Analysis*, T. Y. Crowell, New York, 1947, pp. 442–444.

(12) H. Gilman and N. J. Beaber, *J. Am. Chem. Soc.*, **47**, 518 (1925) reported b.p. 163–165° (3.0 mm.) and $n_D^{20} 1.5050$. K. Slotta and W. Franke¹⁰ reported b.p. 146° (1.0 mm.) and 191–192° (17 mm.).

(13) H. Gilman and N. J. Beaber¹² reported that decomposition rapidly commenced after this precipitation became evident. They found that *sec*-butyltosylate decomposed without distilling.

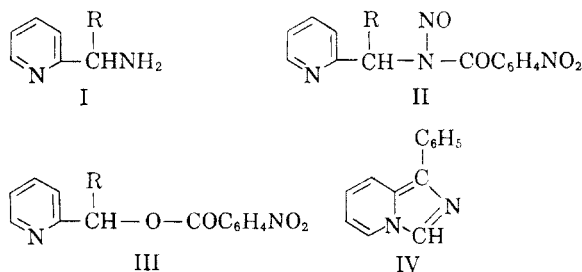
Diazotization of 2-Pyridylmethyl Amine¹

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Received December 6, 1957

An oxidation was observed upon attempted diazotization of 2-pyridylmethyl amine (I, R = H).^{3,4} The pyrolysis of *N*-*p*-nitrobenzoyl-*N*-nitroso-2-pyridylmethyl amine (II, R=H) into 2-pyridylmethyl *p*-nitrobenzoate (III, R=H) has now been realized and offers a more successful method for the transformation of this amine into the corresponding carbinol. An *N*-nitroso derivative of *N*-benzoyl phenyl(2-pyridyl)methyl amine could not be obtained.

Catalytic reduction of α -cyanopyridine and the oxime of 2-benzoylpyridine are efficient methods for the synthesis of 2-pyridylmethyl amine and phenyl(2-pyridyl)methyl amine, respectively. A Leuckhart reduction of 2-benzoylpyridine apparently occurs with cyclization and the formation of a product to which the structure of 1-phenyl-2:3a-diazaindene (IV) has been assigned.⁵ Attempted reduction of phenyl 2-pyridyl ketoxime with zinc and acetic acid is unsuccessful.⁶



(1) Partial support of this work under National Institutes of Health Grants Nos. H-2295 and CY-2895 is gratefully acknowledged. Presented at the 133rd Meeting, American Chemical Society, San Francisco, April 1958.

(2) Texas Eastman Fellow, 1955–1956.

(3) J. H. Boyer, R. Borgers, and L. T. Wolford, *J. Am. Chem. Soc.*, **79**, 678 (1957).

(4) C. Niemann, R. N. Lewis, and J. T. Hays, *J. Am. Chem. Soc.*, **64**, 1679 (1942) reported a successful diazotization of 2-pyridylmethyl amine in the presence of concentrated hydrochloric acid.

(5) Cyclization during Leuckart reductions of aromatic acylloins was found to be general and produced 4,5-diaryl-imidazoles [A. Novelli, *Anales Assoc. quim. Arg.*, **27**, 161 (1939); *Chem. Abstr.*, **34**, 1659 (1940)]. W. H. Davies and A. T. Rogers, *J. Chem. Soc.*, 126 (1944). Upon heating α -hydrazinopyridine with formic acid a similar ring closure brought about the formation of 1,2,4-pyridotriazole [R. G. Fargher and R. Furness, *J. Chem. Soc.*, **107**, 688 (1915); see reference 4]. In a similar reaction, 2:3a-diazaindene was prepared by cyclization with dehydration using phosphorus chloride of *N*-formyl 2-pyridylmethyl amine [J. D. Bower and G. R. Ramage, *J. Chem. Soc.*, 2834 (1955)].

(6) F. B. LaForge, *J. Am. Chem. Soc.*, **50**, 2484 (1928) successfully reduced phenyl 3-pyridyl ketoxime by this method.

EXPERIMENTAL⁷

Phenyl 2-pyridyl ketoxime, m.p. 126–140°, as a mixture of the geometrical isomers, was prepared from 2-benzoylpyridine.⁸

According to the method of Kolloff and Hunter,⁹ α -cyano-pyridine was reduced, using Raney nickel,¹⁰ to *2-pyridylmethyl amine*, b.p. 102–104° (26 mm.)¹¹ in 57% yield.

In a similar procedure phenyl 2-pyridyl ketoxime was hydrogenated over 24 hr. The product, *phenyl-2-pyridylmethyl amine*, distilled as a yellow liquid, b.p. 110–114° (0.1 mm.), 6.0 g. (54%). Attempted redistillation led to polymerization and/or decomposition. A *picrate* derivative separated from 95% ethanol as yellow needles and was further purified by recrystallization from ethyl acetate and hexane mixtures. A sample, m.p. 181–182° (dec.), was analyzed.

Anal. Calcd. for $C_{12}H_{12}N_2 \cdot C_6H_3N_3O_7$: C, 52.31; H, 3.66; N, 16.94. Calcd. for $C_{12}H_{12}N_2 \cdot C_6H_3N_3O_7 \cdot \frac{1}{2}H_2O$: C, 51.19; H, 3.82; N, 16.58. Found: C, 51.15; H, 3.63; N, 16.71.

Reduction of 2-benzoylpyridine by the Leuckart reaction. According to a general procedure of Crossley and More¹² for the Leuckart reaction, 35 g. (0.57 mole) of 28% ammonium hydroxide and 29.3 g. (0.57 mole) of 90% formic acid were added to a three-necked flask equipped with a dropping funnel, thermometer, and distilling condenser. As water was removed by distillation, the temperature was raised to 160° and 21.0 g. (0.115 mole) of 2-benzoylpyridine was added all at once. The mixture was held at 160–170° for 9 hr., cooled, treated with 40 ml. of concentrated hydrochloric acid, refluxed for 8 hr., cooled, diluted with 70 ml. of water, and extracted with benzene. The aqueous layer was treated with a little charcoal and made alkaline with concentrated ammonium hydroxide. An oil was extracted into benzene, washed with water, dried over sodium sulfate, and distilled. Benzene was removed at 1 atm. and 2.8 g. (12.6%) of a viscous yellow liquid, b.p. 168–174° (0.5 mm.) was obtained. It rapidly darkened upon standing. The structural assignment, 1-phenyl-2:3a-diazaindene was in agreement with elemental analyses of its *picrate* derivative, m.p. 209–212° (dec.) in a bath preheated to 204°. Blue fluorescence under ultraviolet light was reported for 2:3a-diazaindene⁴ and was also observed for 1-phenyl-2:3a-diazaindene.

Anal. Calcd. for $C_{13}H_{10}N_2 \cdot C_6H_3N_3O_7$: C, 53.90; H, 3.10; N, 16.55. Found: C, 54.14; H, 3.39; N, 16.56.

Preparation of amides. One ml. of benzoyl chloride was added dropwise to a solution of 1.0 g. (0.005 mole) of phenyl 2-pyridylmethyl amine in 10 ml. of dry pyridine and 20 ml. of dry benzene. The mixture was heated at 60–70° for 30 min., poured into 200 ml. of water, the aqueous layer separated and washed with benzene. The combined benzene layer and washings were washed with 20 ml. of water and 20 ml. of 5% sodium carbonate solution, dried over anhydrous sodium sulfate, concentrated to 10 ml., and added to 20 ml. of hexane whereupon *N-benzoyl phenyl(2-pyridyl)methyl amine* separated as colorless needles, m.p. 124–125°, 0.76 g. (49%), and was recrystallized from aqueous ethanol.

Anal. Calcd. for $C_{13}H_{10}N_2O$: C, 79.13; H, 5.59; N, 9.92; O, 5.55. Found: C, 79.25; H, 5.65; N, 9.91; O, 5.47.

(7) Semi-micro analyses by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim (Ruhr), Germany.

(8) E. H. Huntress and H. C. Walter, *J. Am. Chem. Soc.*, **70**, 3702 (1948) reported m.p. 116–145°.

(9) H. G. Kolloff and J. H. Hunter, *J. Am. Chem. Soc.*, **63**, 490 (1941).

(10) R. Mozingo, D. E. Wolf, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **65**, 1013 (1943).

(11) A b.p. 81° (12 mm.) for a sample from the reduction of α -cyanopyridine with lithium aluminum hydride was reported.⁴

(12) F. S. Crossley and M. L. More, *J. Org. Chem.*, **9**, 529 (1944).

N-p-nitrobenzoyl 2-pyridylmethyl amine, m.p. 135–137°,¹³ was prepared in a similar manner from 2-pyridylmethyl amine and *p*-nitrobenzoyl chloride.

N-nitrosoamides. To a solution of 0.85 g. (0.003 mole) of *N-p*-nitrobenzoyl 2-pyridylmethyl amine in 3 ml. of acetic acid and 17 ml. of acetic anhydride cooled to 0°, 5.0 g. (0.07 mole) of sodium nitrite was added over a period of 4 hr. The mixture was then kept at 0° for 10 hr., poured into ice water, and extracted with ether. The ether layer was washed with water, 5% sodium bicarbonate, again with water, and dried over anhydrous sodium sulfate. Upon removal of solvent *in vacuo*, an unstable orange oil, assumed to be *N-2-picoyl-N-nitroso-p-nitrobenzamide*, was dissolved in 30 ml. of toluene and heated at 100–110° for 5 hr. The mixture was extracted with 5% sodium bicarbonate solution, and then with 5% hydrochloric acid. Upon neutralization of the combined acid extracts crude *2-pyridylmethyl p-nitrobenzoate* precipitated. It recrystallized from ethanol as colorless needles, 0.17 g. (20% based on *N-p*-nitrobenzoyl 2-pyridylmethyl amine), m.p. and mixture m.p. 90–92°.¹⁴

In attempts to nitrosate *N*-benzoyl phenyl(2-pyridyl)methyl amine with nitrogen tetroxide or with isoamyl nitrite starting material was quantitatively recovered. Impure unidentified products were obtained upon all attempts to combine nitrous acid and either phenyl 2-pyridylmethylamine or 2-pyridylmethylamine in aqueous media. An unidentified yellow liquid, b.p. 94–98° (3.2 mm.), was obtained from 2-pyridylmethyl amine and isoamyl nitrite in glacial acetic acid. It solidified upon standing and then decomposed into a dark oil. A *picrate* derivative after repeated recrystallizations had a melting range 155–163°.

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(13) R. Graf, G. Perathoner, and M. Tatzel, *J. prakt. Chem.*, **146**, 88 (1936) reported 136°.

(14) The ester was identical with the product obtained from *p*-nitrobenzoic acid and pyridotriazole [J. H. Boyer and L. T. Wolford, *J. Am. Chem. Soc.*, **80**, 2741 (1958)].

Hydrogenation of Thiophene Compounds with Hydrogen and Carbon Monoxide and a Cobalt Catalyst

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Received December 9, 1957

Previous attempts to hydrogenate the thiophene nucleus to thiolane have been only partly successful.⁴ Thiophenes have been reduced to thiolanes over a palladium catalyst, but very large quantities of catalyst were required to overcome the poisoning effect.⁵ Alkyl derivatives of thiophene and thiolane

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(3) Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio.

(4) H. D. Hartough, *Thiophene and Its Derivatives*, Interscience Publishers, Inc., New York, 1952, p. 167.

(5) R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffine, Jr., N. R. Easton, and K. Folkers, *J. Am. Chem. Soc.*, **67**, 2092 (1945).