

The material may also be prepared, but in lower yield (20-30%), by the hydrogenation of 2-amino-3-nitro-5-chloropyridine in alcohol at 5° using a platinum-on-charcoal catalyst.

6-Chloroimidazo[b]pyridine.—Five grams of 2,3-diamino-5-chloropyridine was dissolved in 25 cc. of 98-100% formic acid and the solution evaporated to dryness to yield a light tan, crystalline residue. This was recrystallized twice from water (Norit)⁸ to yield 4.50 g. (84%) of product as colorless, crystalline needles.

6-Chloropyrido[2,3-d]- ν -triazole.—Five grams of 2,3-diamino-5-chloropyridine was dissolved with warming in 150 cc. of water containing 5 cc. of concentrated sulfuric acid and the solution cooled to less than 10°. A second solution containing 2.5 g. of sodium nitrite in 10 cc. of cold water was then added with shaking. A yellow color developed immediately and the product separated rapidly as light yellow, crystalline needles. These were recrystallized from water (Norit) to yield 4.1 g. (76%) of material as colorless crystalline blades.

2-Hydroxy-6-chloroimidazo[b]pyridine.—A slow stream of phosgene was passed into a solution of 5.0 g. of 2,3-diamino-5-chloropyridine in 1:1 hydrochloric acid at ice-bath temperature for two hours to precipitate a crystalline phosgene adduct of the desired product. This was removed and decomposed by washing with water. The resulting granular product was recrystallized from 125 cc. of glacial acetic acid as colorless needles; yield, 2.73 g. (46%). An additional 1.0 g. (17%) of material was obtained by basifying the original acid filtrate and recrystallizing the resulting precipitate as above.

2-Thio-6-chloroimidazo[b]pyridine.—A mixture of 3.0 g. of 2,3-diamino-5-chloropyridine and 5 cc. of thiophosgene in 60 cc. of 1:1 hydrochloric acid was allowed to stand at room temperature for twenty-four hours. The crystalline precipitate which separated was washed with alcohol and dried. A satisfactory solvent for recrystallization was not found, but the material was purified in low yield by dissolving it in dilute ammonium hydroxide containing a trace of sodium hydrosulfite, treating the solution several times with Darco and reprecipitating the product with acetic acid; yield, 0.2 g. (5%).

Imidazo[b]pyridine.—A 3.3-g. sample of 6-chloroimidazo[b]pyridine and 3.5 g. of palladium hydroxide (5%) on calcium carbonate were placed in 75 cc. of water and shaken under 50 lb./sq. in. of hydrogen pressure at room temperature for seven hours. After removing the catalyst, the solution was concentrated to dryness and the residue sublimed under vacuum (2 mm.) at a bath temperature of 210° to yield 0.75 g. (29%) of product as colorless needles. The product was converted to its monohydrochloride by dissolving it in acetic acid, treating the solution with hydrochloric acid and precipitating with ethyl acetate. The salt separated slowly as colorless, crystalline blades.

2-Hydroxyimidazo[b]pyridine.—A mixture of 2.2 g. of 2-hydroxy-6-chloroimidazo[b]pyridine and 6.5 g. of palladium hydroxide (5%) on calcium carbonate in 100 cc. of alcohol was shaken under hydrogen pressure as in the previous example for eighteen hours. Removal of the catalyst and concentration of the alcohol solution gave a white solid. This was recrystallized twice from water to yield 1.0 g. (57%) of product as colorless needles.

Pyrido[2,3-d]- ν -triazole.—A 2.0-g. sample of 6-chloropyrido[2,3-d]- ν -triazole was added to 1.0 g. of platinum (10%) on charcoal and 1.0 g. of palladium (10%) on charcoal in 200 cc. of 1% sodium hydroxide solution and shaken for one hour at room temperature under 50 lb./sq. in. of hydrogen pressure. The theoretical hydrogen absorption was observed. The catalyst was removed and the filtrate neutralized with hydrochloric acid, treated with Darco and concentrated to 25 cc. On addition of a slight excess of hydrochloric acid and cooling the solution, the product crystallized as colorless needles. These were recrystallized from water; yield, 1.2 g. (76%).

Tetrahydropyrido[2,3-d]- ν -triazole.—A mixture of 1.0 g. of 6-chloropyrido[2,3-d]- ν -triazole and 3.0 g. of palladium hydroxide (5%) in 50 cc. of water was heated to 80° and

then shaken under hydrogen pressure as in the previous examples. The theoretical hydrogen absorption was obtained in one hour. The catalyst was removed and the filtrate concentrated to 10 cc. On cooling, 0.55 g. (68%) of product separated as colorless needles.

2,3,6-Triaminopyridine Dihydrochloride.—A 12.5-g. sample of 2,6-diamino-3-phenylazopyridine hydrochloride¹⁰ was placed in 100 cc. of water with 25 cc. of concentrated hydrochloric acid and 5 g. of platinum (10%) on charcoal and shaken under 50 lb./sq. in. of hydrogen pressure at room temperature for fifteen to twenty minutes to complete the reduction. The catalyst was removed and saved since it lost none of its activity. The filtrate was concentrated to 50 cc. and cooled to crystallize the product as stout needles; yield, 6.9 g. (70%). Recrystallization of these from constant-boiling hydrochloric acid (20.2%) gave 5.6 g. of pure material as colorless needles which decomposed indefinitely above 200°. The recorded melting point for this compound is 230°.¹¹

Anal. Calcd. for C₈H₈N₄·2HCl: C, 30.5; H, 5.1. Found: C, 30.5; H, 5.3.

5-Formylaminoimidazo[b]pyridine.—A mixture of 5.0 g. of 2,3,6-triaminopyridine dihydrochloride and 3.5 g. (2 equivalents) of sodium formate in 50 cc. of 98-100% formic acid was heated under reflux for one and one-half hours and then concentrated to dryness. The residue was washed well with cold water and crystallized from 50 cc. of glacial acetic acid (Darco) to yield 1.6 g. (39%) of product as colorless crystals.

5-Aminoimidazo[b]pyridine Dihydrochloride.—A 0.3-g. sample of 5-formylaminoimidazo[b]pyridine was placed in 3 cc. of concentrated hydrochloric acid and heated on a steam-bath for fifteen minutes. The clear solution was treated with Darco, filtered and diluted with two volumes of alcohol. On cooling, colorless crystalline needles separated; yield, 0.1 g. (26%). The product was recrystallized from a mixture of alcohol and concentrated hydrochloric acid.

Imidazo[b]pyridine-N-oxide Hydrochloride.—A solution of 5.0 g. of imidazo[b]pyridine in 100 cc. of dioxane was cooled to 15° and added slowly with stirring to a solution of 11.7 g. (1.5 equivalents) of monopero-phthalic acid¹² in 90 cc. of ether. The mixture was maintained at 15° in a water-bath. An oil separated rapidly and slowly crystallized over a two-hour period; yield, 8.8 g. (70%). A 5.0-g. sample of this colorless solid, which is an equimolecular complex of imidazo[b]pyridine-N-oxide and phthalic acid,¹³ was placed in 15 cc. of 10% hydrochloric acid and warmed gently for ten to fifteen minutes. On cooling the resulting solution, phthalic acid crystallized out in 75% yield (2.1 g.). The filtrate was concentrated to dryness and the residue purified by dissolving it in 100 cc. of alcohol and decolorizing with Darco. On addition of 200 cc. of acetone to the hot filtrate and cooling, the product separated slowly as crystalline blades; yield, 1.6 g. (56%), m. p. 225-230° (dec.). Concentration of the filtrate gave an additional 1.1 g. (37%) of material melting between 190-200° (dec.). The product was purified by two additional crystallizations from alcohol-acetone.

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Azeotrope in Cyclohexene-1,4-Dioxane System

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In the course of a systematic study of the deviations of binary liquid systems containing cyclo-

hexene from the laws of ideal solutions, an azeotrope in the system cyclohexene-1,4-dioxane was observed. To ascertain more fully the nature of this azeotropic system at atmospheric pressure, a further study on this pair of liquids has been made. A description of the vapor-liquid equilibrium has been obtained.

To ascertain the composition of vapor in equilibrium with the liquid solution, approximately 75 cc. of cyclohexene was placed in a 250-cc. round-bottom flask to which a distilling head was attached by a ground glass standard taper joint. A Liebig condenser was attached to the distilling head. The flask was almost totally immersed in a bath of paraffin oil. A boiling tube was kept in the flask to prevent bumping. The boiling point of the cyclohexene was measured with the bulb of the thermometer immersed in the liquid. A small amount of 1,4-dioxane was added and approximately 10 cc. was distilled from the solution. This distillate was removed and the next 2 cc. of the distillate was collected for analysis. The temperature of the boiling solution was observed during the collection of this latter portion of the distillate. A small sample of residue was removed immediately from the flask for analysis. The original 10 cc. of distillate was returned to the flask and a second small portion of the 1,4-dioxane added. The procedure was repeated until the composition remaining in the flask was approximately 50 mole per cent. of 1,4-dioxane. For compositions containing a greater proportion of 1,4-dioxane, a similar procedure was followed starting with pure 1,4-dioxane and adding small amounts of cyclohexene.

The analyses of the several solutions were made by means of an Abbe refractometer thermostated at 25°. In preliminary work, standard samples of these cyclohexene-1,4-dioxane solutions had been weighed out and the index of refraction of the several solutions measured. The data obtained in making up the reference solutions are given in Table I.

TABLE I

REFRACTIVE INDICES OF STANDARD SAMPLES OF CYCLOHEXENE-1,4-DIOXANE

Cyclohexene, mole %	n_D^{25}	Cyclohexene, mole %	n_D^{25}
100.0	1.4437	65.1	1.4339
95.2	1.4420	45.3	1.4290
89.8	1.4407	31.1	1.4260
86.8	1.4398	20.6	1.4235
80.3	1.4378	10.6	1.4216
69.9	1.4350	0.0	1.4198

In Table II are given the boiling temperatures of 21 solutions of 1,4-dioxane in cyclohexene and the composition of vapor in equilibrium with each of these solutions. A minimum-boiling azeotrope containing 84.3 mole per cent. of cyclohexene and boiling at 83.9° at 749.7 mm. pressure will be noted.

TABLE II

CYCLOHEXENE-1,4-DIOXANE SYSTEM (749.7 MM.)

Temp., ^a °C.	Cyclohexene, mole %		Temp., ^a °C.	Cyclohexene- mole %	
	Liquid	Vapor		Liquid	Vapor
84.35	100.0	100.0	87.6	41.9	61.5
84.00	91.3	89.9	89.5	34.0	53.0
83.95	88.0	97.9	90.6	30.0	49.9
83.90	86.8	86.5	93.0	23.1	42.0
83.90	84.3	84.3	94.5	18.0	36.9
84.3	73.9	77.0	96.2	13.0	32.0
84.6	69.0	73.8	97.0	10.3	28.2
84.5	69.9	73.8	97.9	8.9	27.0
85.3	61.0	69.1	99.9	5.0	13.9
85.9	55.7	68.2	101.0	3.0	9.0
86.4	51.1	65.0	102.0	0.0	0.0
86.9	47.5	62.8			

^a The boiling temperatures of the pure liquids with the thermometer bulb in the condensing vapor phase were 82.7° at 755.3 mm. for the cyclohexene and 101.5° at 751.2 mm. for the 1,4-dioxane.

The simple distilling assembly used is always more than one theoretical plate and the composition data on both sides of the azeotrope are only approximate. However, the azeotropic composition at 84.3 mole per cent. of cyclohexene should still be valid. The temperatures reported are approximately 1 to 1.5° higher than the actual values since the thermometer was totally immersed in the boiling liquid.

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Polarization of Ethylene Dichloride in Benzene

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Vernon, Wyman and Avery¹ reported the dielectric constants of ethylene dichloride-benzene mixtures over the complete range. It seemed worthwhile to determine the densities of these solutions and calculate the polarization of ethylene dichloride since the only reported measurements were made in very dilute solutions.^{2,3,4}

The only P_2 data are those reported by Gross.³

Ethylene dichloride and benzene were purified as previously reported¹ and the densities of the solutions were determined by the specific gravity bottle method.

An equation was established for the density-concentration curve

$$d = d_{Ax} + d_{Bx} - ax_{Ax}$$

where d = density, x = mole fraction, $a = 0.07345$ and subscripts A and B refer to benzene and ethylene dichloride, respectively. Table I gives the observed densities, the densities calculated according to the equation, P_{12} and P_2 values for

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