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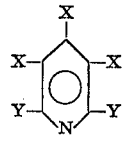
ELECTROLYTIC REDUCTION OF HALOGENATED PYRIDINES

Vernon D. Parker, Lawrence, Kans., assignor to The Dow Chemical Company, Midland, Mich.

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ABSTRACT OF THE DISCLOSURE

Halogenated pyridines of the formula



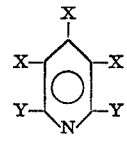
wherein each X is Cl or Br, and each Y is X or CN are electrolytically reduced to replace the halogen in the 4 position with hydrogen.

BACKGROUND OF THE INVENTION

The electrolytic reduction of halogenated aromatic compounds is known, see for example Sease et al. in J. Am. Chem. Soc., May 8, 1968. The reduction of a halogenated aromatic to give a specific predominance of a specific isomer, however, usually cannot be predicted, as indicated by Popp et al. in Chem. Reviews, 62, at p. 35.

SUMMARY OF THE INVENTION

It has now been found according to the present invention that compounds of the formula



wherein each X is Cl or Br, and each Y is X or CN can be selectively reduced electrolytically to replace the halogen in the 4 position with hydrogen. This electrolytic reduction is conveniently carried out in an ordinary electrolysis cell to give a surprisingly specific product.

The pyridine compound reduced in the present invention may be any of those compounds described by the formula above. The pyridines preferred in the invention contain halogens of chlorine, i.e., wherein each X is Cl and each Y is Cl or CN. Of special interest in the invention is the reduction of pentachloropyridine because of the commercially significant product which is used to make insecticides.

The desired electrolytic reduction of the invention is carried out by techniques that are generally known. These techniques are described below and exemplified in the Specific Embodiments. Broadly, the starting halogenated pyridine is dissolved in a suitable solvent containing an electrolyte, the solution is added to an electrolysis cell and current is passed through the cell until the desired degree of reduction is obtained.

The concentration of the reactants in the electrolytic cell may vary widely as different reactants and solvents are employed in the reaction. Preferably, the cell fluid is about saturated with the reactant at reaction temperature.

The design of the electrolysis cell used in the present invention is not critical. Numerous electrolytic cells known in the art may be readily employed in the present invention. Preferred electrolytic cells have cathodes of

mercury, lead, iron, tin or zinc, with lead or mercury being especially preferred. The anode may be essentially any chemically inert material, with graphite and platinum being especially preferred. Such preferred cell may be arranged in any conventional design.

The electrolyte used in the present invention may vary widely. Preferred electrolytes in the present invention are neutral and acidic salts. The use of strong bases may be detrimental to the progress of the reaction because of the tendency of such electrolytes to enter into substitution reactions with the halogens. Specific examples of preferred electrolytes include sodium p-toluenesulfonate, sodium acetate, ammonium p-toluenesulfonate, ammonium chloride, ammonium fluoride, tetramethylammonium chloride, and hydrochloric acid, sulfuric acid, acetic acid or phosphoric acid used alone or in combination with ammonia or a tertiary amine. Especially preferred is the use of ammonium acetate, H_2SO_4, acetic acid or HCl as the electrolyte. The concentration of the electrolyte may vary widely as different reactant concentrations, electrolytes, current densities and cathode potentials are employed.

The solvent employed in the electrolysis solution may vary widely as different reactants are employed in the electrolytic dehalogenation. The solvent should dissolve all or most of the starting material and the electrolyte and should be inert, or at least not detrimentally reactive, under the electrolysis conditions. Solvents preferred in the present invention include the lower alcohols, dialkyl and alkylene ethers, lower alkylene glycol monoalkyl ethers and dialkyl ethers and lower amides. Representative examples of these preferred solvents include: alcohols such as methanol, ethanol, isopropanol and isobutyl alcohol; dialkyl ethers and alkylene ethers such as diethyl ether, dipropyl ether, dioxane and tetrahydrofuran; lower alkylene glycol monoalkyl ethers and dialkyl ethers such as 2-methoxypropanol, ethoxyethanol, dimethoxyethane and 1,2-dimethoxypropane; lower amides such as dimethylformamide and acetamide, and other solvents such as sulfolane. These solvents of the present invention may be used either alone or preferably with up to about 30% by weight of water to assure proper solubility of the electrolyte.

In the operation of the electrolysis cell, the cathode potential is usually maintained between −0.5 and −2.5 volts versus the standard calomel electrode, with cathode potentials of −0.7 to −2.0 volts being especially preferred. A potential of about −1.7 volts is especially preferred for the reduction of pentachloropyridine. The applied voltage provided by the power source may vary widely depending upon the IR drop of the reaction medium. The IR drop is preferably minimized to prevent overheating of the reaction cell.

The current density may preferably range from about 0.01–5.0 amp./in.^{2} of electrode wtih 0.4 to 0.6 amp./in.^{2} being especially preferred. At higher current densities, the selectivity of the reaction decreases; therefore, the current density should be adjusted to give the desired minimization of by-products.

The temperature of the electrolysis reaction may vary widely. The temperatures may be varied to maintain the electrolysis mixture as a liquid phase, with temperatures from about 0° to about 100° C. or more being preferred and temperatures of about 40° to about 60° C. being especially preferred.

The reduction is usually and most conveniently taken to less than 100% conversion to minimize the over-reduction of the product under the reaction conditions. As a general rule, 70 to 95% of the reduction theoretically required gives the most favorable yields of the desired product with minimum by-product. After the electrolysis, the product may be isolated by any conventional method.

SPECIFIC EMBODIMENTS

Example 1.—Reduction of pentachloropyridine

An electrolytic cell was constructed in a jar of about 500 ml. volume. The cathode was a stirred pool of mercury on the bottom of the jar having a surface area of about 4 in.^{2}, and the anode was graphite protected from the migration of organic material by a glass barrier having a sintered glass disc on the end. The electrolysis cell was equipped with a power source and a calomel reference electrode. In the cell, a solution consisting of 20 g. of pentachloropyridine, 125 ml. of 1,2-dimethoxyethane, 100 ml. of methanol and 25 ml. of concentrated hydrochloric acid was electrolyzed. The electrolysis was started at a beginning temperature of 25° C., and was run at a current of 1.9 amps, except from 3 hours to 5 hours where the cell was run at 1 amp. After 5 hours, 50 ml. of methanol was added to the cell. The overall current efficiency was 38%. Periodic samples of the cell fluid were removed, stripped of solvent and analyzed. The results are shown in Table I.

TABLE I.—ELECTROLYTIC REDUCTION OF PENTACHLOROPYRIDINE USING DCL AS THE ELECTROLYTE

	Sample analysis	
Sample time, hr.	2, 3, 5, 6-tetra	Penta
1	33	67
2	43	57
3	57	43
5	65	35
7	80	20

Example 2.—Reduction of pentachloropyridine

In the cell of Example 1, a solution of 15 g. of pentachloropyridine, 125 ml. of 1,2-dimethoxyethane, 100 ml. of methanol and 25 ml. of 30% H_2SO_4 was electrolyzed at a current of 1.9 amps and a temperature of 25° C. The results of the reduction are shown in Table II. At 105 minutes, the current efficiency was 88%.

TABLE II.—ELECTROLYTIC REDUCTION OF PENTACHLOROPYRIDINE USING H_2SO_4 AS THE ELECTROLYTE

	Sample analysis, chloropyridine		
Sample time, min.	Tri	2, 3, 5, 6-tetra	Penta
45		32.6	67.4
60		50.9	49.1
90		78.1	21.9
105		89.0	11.0
115	0.6	94.5	4.9
129	2.7	97.3	Trace

Example 3.—Reduction of pentabromopyridine

In a cell similar to that of Example 1, without a cell divider, a solution of 4.73 g. pentabromopyridine, 75 ml. of methanol, 100 ml. of 1,2-dimethoxyethane and 20 ml. of 30% aqueous H_2SO_4 was electrolyzed. The temperature of the solution during the electrolysis ranged from 56° C. to 66° C. The applied voltage ranged from about 15 to 18 volts, the cathode potential was −1.06 to −0.95 volts and the current flow was 1.5 to 1.6 amps. The analysis of periodic samples from the cell after solvent removal are given in Table III.

TABLE III.—REDUCTION OF PENTABROMOPYRIDINE

	Sample analysis, bromopyridines		
Sample time, min.	Di plus tri	2, 3, 5, 6-tetra	Penta
16	3	38	59
31	6.7	52.6	40.7
42	8.7	65.2	26.1
55	12.5	75.0	12.5

Example 4.—Reduction of tetrachloro-2-cyanopyridine

In a cell similar to that of Example 1 having a volume of 1 liter, a solution of 25 g. tetrachloro-2-cyanopyridine, 750 ml. of ethanol and 30 ml. of concentrated aqueous HCl was electrolyzed. The solution was heated to 65° C. and electrolyzed at a constant current of 2.0 amps. Samples of the cell fluid were stripped of solvent and analyzed by vapor phase chromatography. The results of these analyses are shown in Table IV.

TABLE IV

Reduction of tetrachloro-2-cyanopyridine

Sample time, min.	Percent conversion to 3,5,6-trichloro-2-cyanopyridine
185	63
260	83
314	92
367	96

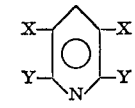
Example 5.—Reduction of trichloro-2,6-dicyanopyridine

In an electrolytic cell similar to that of Example 1, but having an anode of carbon and a cathode of mercury with a surface area of about 6 in.^{2}, a solution of trichloro-2,6-dicyanopyridine in 200 ml. of ethanol and 10 ml. of concentrated HCl was electrolyzed for 100 minutes. After the reaction, the solvent was removed in a rotary evaporator. 3,5-dichloro-2,6-dicyanopyridine was recovered in good yield and identified by mass spectography.

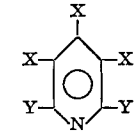
In the same manner as shown by the examples above, other electrolytic cells, other solvents, such as dioxane, acetic acid, isobutyl alcohol and sulfolane, other electrolytes, such as ammonium acetate and sodium p-toluene sulfonate, and other cathodes, such as lead, are used in the electrolysis to replace the halogen in the 4-position with hydrogen. Also, in the same manner as shown above, tetrabromo-2-cyanopyridine and tribromo-2,6-dicyanopyridine are reduced to give 3,5,6-tribromo-2-cyanopyridine and 3,5-dibromo-2,6-dicyanopyridine.

I claim:

1. The process for making



comprising electrolytically reducing a halopyridine of the formula



wherein each X is Cl or Br and each Y is X or CN, said process comprising preparing a solution of said halopyridine and a neutral or acidic electrolyte in an organic solvent which is essentially inert under the electrolysis conditions and which contains up to about 30% by weight of water and electrolyzing the solution in an electrolysis cell having an inert anode and a lead or mercury cathode at a cathode potential of about −0.5 to −2.5 volts and at a current density of about 0.01 to 5 amperes per square inch.

2. The process of claim 1 wherein each X is Cl and each Y is Cl or CN.

3. The process of claim 1 wherein the halopyridine is pentachloropyridine.

4. The process of claim 1 wherein the halopyridine is tetrachloro-2-cyanopyridine.

References Cited

J. Electroanal. Chem., vol. 22, pp. 407–412, by Evilia et al. (1969).

F. C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

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