Patented Nov. 29, 1949

2,489,884

UNITED STATES PATENT OFFICE

2,489,884

RESOLUTION OF TAR BASES

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No Drawing. Application December 22, 1945, Serial No. 637,080

8 Claims. (Cl. 260—290)

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This invention relates to separation of 3-picoline from closely-related heterocyclic nitrogen compounds.

The picolines, other homologs of pyridine, and pyrrole are customarily extracted, along with pyridine, from coal tar oils and other sources of these heterocyclic nitrogen compounds by means of an aqueous solution of a mineral acid, usually sulfuric acid, and are liberated from the acid solution by the addition of alkali hydroxide or carbonate. Mixtures of the nitrogen compounds thus liberated are then fractionally distilled. Bases such as pyridine, boiling point 116° C., and 2-picoline, boiling point 129.4° C., can generally be obtained in reasonably pure form by fractional distillation, but for the most part the remaining compounds cannot be separated by distillation methods alone. Instead, the fractions obtained, even when they are of relatively narrow boiling range, contain increasing numbers of pyridine homologs and their isomers. Mixtures of this kind have found but limited practical application, mainly as special solvents, and are of relatively low economic value. An individual compound such as 3-picoline, however, if it could be readily isolated, would be of far greater value, for example, in the preparation of derivatives, especially pharmaceutical products and dyes; thus nicotinic acid, a member of the vitamin B complex, may be readily obtained by oxidation of 3-picoline. The requirements for raw material purity in these fields, however, are often quite rigid.

The potentially valuable 3-picoline is found in coal tar nitrogen compound fractions boiling within the range of about 140° to 148° C. But when mixtures of heterocyclic nitrogen compounds are recovered from most types of coal tar, the fractions taken within the range 140° to 148° C., even closely cut fractions within this boiling range, in general contain as components three pyridine homologs of substantially the same boiling point in roughly equal proportions; i. e. 2,6-lutidine, boiling point 143.8° C., 3-picoline (beta-picoline), boiling point 143.9° C., and 4-picoline (gamma-picoline), boiling point 144.8° C. Mixtures of heterocyclic nitrogen compounds recovered from some of the less common coal tars may contain substantial proportions of pyrrole instead of, or in addition to, the 2,6-lutidine, since, although pyrrole alone boils at 129.8° C., with 3- and 4-picolines it forms high boiling azeotropes boiling about 145° to 148° C., the components of which are inseparable by ordinary distillation methods.

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Since the three components making up the usual nitrogen base fractions in which 3-picoline is found (2,6-lutidine, 3-picoline, and 4-picoline) have substantially the same boiling points, and since pyrrole, present in some of these fractions, forms azeotropes with these bases, ordinary fractional distillation is obviously unsatisfactory as a means for separating the 3-picoline from such mixtures. Other methods of separating 3-picoline heretofore described in the published prior art have been generally unsatisfactory in regard to products, yields, and production costs.

An object of this invention is to provide a process whereby 3-picoline of a high degree of purity may be recovered from mixtures thereof with like-boiling nitrogen compounds.

I have discovered that high yields of the commercially valuable 3-picoline may be recovered in substantially pure form from mixtures of this base with like-boiling closely-related heterocyclic nitrogen bases such as 4-picoline and 2,6-lutidine, by treating such mixtures with copper sulfate, whereupon a complex addition compound of copper sulfate and 3-picoline is precipitated to the substantial exclusion of other nitrogen base complexes. The precipitated material is separated from the liquid phase material and the 3-picoline may then readily be liberated from the copper sulfate addition compound thereof.

The 3-picoline mixtures that may advantageously be treated by the process of my invention include the various nitrogen base fractions containing 3-picoline and like-boiling closely-related heterocyclic nitrogen bases such as 4-picoline and 2,6-lutidine. I find it advantageous to treat fractions containing from 15% to 85% by weight of 3-picoline, the remainder of the mixture consisting essentially of one or both of the bases 4-picoline and 2,6-lutidine, and sometimes pyrrole as well.

In all such mixtures, when treated with copper sulfate in accordance with the process of my invention, the 3-picoline reacts preferentially with the copper sulfate to precipitate a complex addition compound, the formula of which is believed to be $2(3\text{-picoline}).CuSO_4$. In the usual commercial 3-picoline fractions as above described, generally boiling within the range of 140° to 148° C. and generally consisting roughly of about one-third 3-picoline, up to 65% of the 3-picoline may be precipitated in the form of its copper sulfate addition compound and, upon separation of the precipitated material and treatment to recover 3-picoline therefrom, a 3-picoline product of purity as high as 95% to 97% may be

obtained. A 3-picoline product of such purity is entirely suitable as a starting material for the various products such as pharmaceuticals, etc. for which 3-picoline is in great demand.

In a preferred method of carrying out the process of my invention, a 3-picoline fraction of the type above described is mixed with an aqueous copper sulfate solution. The use of from 1 to 3 mols of copper sulfate per mol of 3-picoline in the mixture being treated has been found advantageous but satisfactory results are obtained employing larger or smaller amounts of copper sulfate; about 1.5 mols of copper sulfate per mol of 3-picoline is preferred. The aqueous solution of copper sulfate may be of any practicable concentration, e. g. from 50% to 60% copper sulfate by weight. I have found it convenient to warm the mixture somewhat to decrease liquid viscosity and bring about more rapid and complete mixing of the reactants.

When mixing is complete, the reaction mixture is cooled to approximately room temperature or below and filtered, e. g. by centrifuging. In order to obtain the highest purity of 3-picoline, particularly when a substantial concentration of 2,6-lutidine was present in the initial mixture treated, it is desirable to reslurry the filter cake once with water and refilter.

The solid 3-picoline-copper sulfate addition product may then be decomposed by any suitable means; for example the addition of alkali converts the copper sulfate to copper oxide and releases the 3-picoline. The 3-picoline thus released may be removed from the copper mixture by steam distillation whereupon a distillate consisting of a water solution of 3-picoline is obtained. The 3-picoline may be readily salted out from its aqueous solution by addition of sodium chloride, caustic soda or the like. Other methods of liberating the 3-picoline from its copper sulfate addition compound involve passing dry ammonia through the slurry of the addition compound and steam distilling off the liberated 3-picoline; or adding ammonium hydroxide, containing, for example, 28% ammonia to the slurry, and recovering the oil which separates and washing the liberated oil.

After liberation and separation of the 3-picoline, the copper may be recovered from the residue and reconverted to copper sulfate for reuse in the process. For example, when the 3-picoline has been liberated by causticization, the copper oxide formed in the process may be separated by filtration and washed to remove sodium sulfate also formed in the causticization step. The copper oxide is then reacted with sulfuric acid to form copper sulfate.

The following examples are illustrative of the process of my invention:

Example 1

A 3-picoline fraction of coal tar bases boiling in the range 140° to 145° C. and containing about 38.7% 3-picoline, 37.0% 4-picoline, 22.1% 2,6-lutidine was employed in this run. Copper sulfate ($CuSO_4.5H_2O$) was dissolved in an equal weight of water, warmed to about 70° C., and added slowly to the tar base mixture which had been similarly warmed, until about 1.5 mols of copper sulfate had been added for each mol of 3-picoline present. After the addition was complete and the reactants thoroughly mixed the mixture was cooled to 20° C. and centrifuged. The filter cake was slurried with an equal weight of hot water, cooled and again centrifuged.

The filter cake from the second centrifuging was sludged with water and 20% aqueous sodium hydroxide solution was added in amount slightly in excess of that required to convert all the copper sulfate to copper oxide. The resulting mixture was subjected to steam distillation and distillate was collected until no more nitrogen base was coming over from the still. Solid sodium chloride was added to the distillate thus obtained to the point of saturation. The supernatant layer of nitrogen base was withdrawn and dried with solid caustic soda. 66% of the 3-picoline present in the original coal tar base fraction was thus separated and a 3-picoline product of 95.7% purity was obtained.

A mixture of the 4-picoline and 2,6-lutidine originally present in the fraction treated was obtained by causticizing and distilling the mother liquor from precipitation of the copper sulfate addition compound.

Example 2

Following the same procedure as in Example 1 and employing the same coal tar base fraction, the addition of copper sulfate solution was stopped when about 0.82 mol of copper sulfate had been added for each mol of 3-picoline in the base mixture. The copper sulfate addition compound was separated and treated as described in the previous example. In this run 55% of the 3-picoline present in the original coal tar base fraction was recovered as a product of 97% purity.

Example 3

Employing the same coal tar base fraction as in the previous examples and the same procedure, 1.7 mols of copper sulfate were added for each mol of 3-picoline in the nitrogen base mixture. In this run 63% of the 3-picoline present in the original base mixture was eventually recovered as a product of 95.8% purity.

Example 4

Employing the same coal tar base fraction as in the previous examples and the same procedure, 2.6 mols of copper sulfate were added for each mol of 3-picoline. In this run 57% of the 3-picoline present in the original base mixture was eventually recovered as a product of 96% purity.

Example 5

This example illustrates the resolution of a 3-picoline-4-picoline-2,6-lutidine mixture into its three components by the process of the invention combined with preliminary steps.

The above-described 3-picoline fraction containing 4-picoline and 2,6-lutidine in addition to the 3-picoline was treated with a 50% aqueous solution of zinc chloride in approximately the stoichiometric amount for reaction of the zinc chloride with both picolines to form the addition compound $ZnCl_2.2$(picoline). The reaction mixture was cooled, filtered and the filter cake thoroughly washed with water. Substantially all the 2,6-lutidine present in the original base mixture was thus separated in the filtrate. The 2,6-lutidine could be recovered from this filtrate by causticization and steam distillation as above described in connection with 3-picoline. The picolines were similarly liberated and recovered from the solid zinc chloride addition compound.

The mixture of 3- and 4-picolines thus obtained was treated with copper sulfate solution as described in Example 1 above, employing 1.5 mols of copper sulfate for each mol of 3-picoline present in the mixture. The copper sulfate ad-

dition compound was separated and treated as described in Example 1. Over 77% of the 3-picoline was thus recovered as a product of approximately 95% purity.

The mother liquor from precipitation of the copper sulfate addition compound was also causticized and distilled as above described in connection with 3-picoline. From this distillate a 4-picoline product of 87% purity was obtained.

Example 5 illustrates the step of precipitating the $CuSO_4$ addition compound of 3-picoline from its mixtures with 4-picoline only, while the other examples illustrate precipitation of the 3-picoline complex from its mixtures with both 4-picoline and 2,6-lutidine. The 3-picoline complex is similarly precipitated from its mixtures with 2,6-lutidine alone, and from other mixtures of 3-picoline with one or both of these closely-related pyridine homologs; for example, a 95% 3-picoline product was obtained by the process of Example 1 from a 3-picoline-4-picoline-2,6-lutidine fraction containing 15% pyrrole.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A process for separation of 3-picoline from a mixture thereof with at least one of the bases 4-picoline and 2,6-lutidine, which comprises treating the base mixture with copper sulfate to precipitate 3-picoline in the form of its copper sulfate addition compound, and separating the addition compound thus precipitated.

2. A process for separation of 3-picoline from a mixture thereof with at least one of the bases 4-picoline and 2,6-lutidine, which comprises treating the base mixture with copper sulfate to precipitate 3-picoline in the form of its copper sulfate addition compound, separating the addition compound thus precipitated, and treating the separated addition compound to liberate 3-picoline therefrom.

3. In a process for separation of 3-picoline from a heterocyclic nitrogen compound mixture boiling within the range 140° to 148° C., containing from 15% to 85% by weight of 3-picoline and a substantial proportion of at least one of the bases 4-picoline and 2,6-lutidine, the steps that comprise treating the base mixture with copper sulfate to precipitate 3-picoline in the form of its copper sulfate addition compound, and separating the addition compound thus precipitated.

4. A process for resolving into its components a nitrogen base mixture containing from 15% to 85% by weight of 3-picoline and substantial proportions of the bases 4-picoline and 2,6-lutidine, which comprises treating the base mixture with zinc chloride to form picoline addition compounds of the zinc chloride, separating said addition compounds, liberating the picolines therefrom, treating the picoline mixture thus recovered with copper sulfate to precipitate 3-picoline in the form of its copper sulfate addition compound, separating the addition compound thus recipitated, treating the separated addition compound with a reagent capable of reacting with the copper sulfate to liberate 3-picoline therefrom, and distilling off the liberated 3-picoline.

5. A process for separation of 3-picoline from a mixture thereof with pyrrole and at least one of the bases 4-picoline and 2,6-lutidine, which comprises treating the base mixture with copper sulfate selectively to precipitate 3-picoline in the form of its copper sulfate addition compound, and separating the addition compound thus precipitated.

6. In a process for separation of 3-picoline from a heterocyclic nitrogen compound mixture boiling within the range 140° C. to 148° C., containing from 15% to 85% by weight of 3-picoline and a substantial proportion of at least one of the bases 4-picoline and 2,6-lutidine, the steps which comprise adding to the nitrogen base mixture an aqueous solution of copper sulfate containing between about 1 and about 3 mols of copper sulfate per mol of 3-picoline present in the mixture, to precipitate 3-picoline in the form of its copper sulfate addition compound and separating the addition compound thus precipitated.

7. In a process for separation of 3-picoline from a heterocyclic nitrogen compound mixture boiling within the range 140° C. to 148° C., containing from 15% to 85% by weight of 3-picoline and a substantial proportion of at least one of the bases 4-picoline and 2,6-lutidine, the steps which comprise adding to the nitrogen base mixture at a temperature of about 70° C. an aqueous solution of copper sulfate having a copper sulfate concentration between about 50% and about 60% and containing between about 1 and about 3 mols of copper sulfate per mol of 3-picoline present in the mixture, to precipitate 3-picoline in the form of its copper sulfate addition compound, cooling the mixture to a temperature of about 20° C., and separating the precipitated addition compound.

8. In a process for separation of 3-picoline from a heterocyclic nitrogen compound mixture boiling within the range 140° C. to 148° C., containing from 15% to 85% by weight of 3-picoline and a substantial proportion of the base 4-picoline and 2,6-lutidine, the steps which comprise adding to the nitrogen base mixture at a temperature of about 70° C. an aqueous solution of copper sulfate having a copper sulfate concentration between about 50% and about 60% and containing between about 1 and about 3 mols of copper sulfate per mol of 3-picoline present in the mixture, to precipitate 3-picoline in the form of its copper sulfate addition compound, cooling the mixture to a temperature of about 20° C., separating the precipitated addition compound by filtration, reslurrying the filter cake with water and refiltering.

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