Patented Jan. 4, 1938 2,104,407

UNITED STATES PATENT OFFICE

2,104,407

MANUFACTURE OF ARYL AMINES

Charles L. Thomas, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application September 23, 1933, Serial No. 690,761

5 Claims. (Cl. 260—130.5)

This invention relates more particularly to the manufacture of aryl amines containing alkyl-substituting groups in the nucleus.

In a more specific sense the invention has reference to an improved process for producing alkylated aryl amines whereby the number of separate steps is reduced and the yields of alkylated products are considerably higher than those obtainable by methods at present known in the art.

The aryl or aromatic amines, which term is used in its broadest sense to include mono or poly-nuclear ring hydrocarbons containing any number of amino groups, constitute an important class of compounds on account of their alkaline reaction which enables their ready solution in acids such as sulphuric, phosphoric and hydrochloric acids, which solutions may be made the starting point for the manufacture of different compounds, particularly the aniline dyes which are of great commercial importance. The aromatic amines are also the base materials for the manufacture of a large number of special synthetic chemicals such as various drugs, flavoring materials, perfumes, antiseptics, etcetera.

To develop the character of the present process as an improvement over older processes a brief mention will be made of the steps in some of the more generally known and commonly used methods of manufacturing the alkylated aryl amines which constitute its desired product.

The manufacture of alkylated aryl amines such as, for example, the toluidines which are simplest members of this class, may be accomplished (1) by the successive alkylation and aminization of the benzol ring, (2) the methylation of aniline or (3) the aminization of toluol. These steps in many cases conflict so that yields of toluidines representing the general class of alkylated aryl amines is too low for the process to be of any economic value.

In regard to the manufacture of alkylated aromatics, these may be produced by several methods, examples of which are: (1) The action of sodium on molecular mixtures of alkyl and aryl halides, and (2) the action of alkyl halides upon aromatics in the presence of aluminum and similarly acting chlorides.

One method of making alkylated aryl amines is exemplified by the production of toluidines from toluol, the last-named compounds representing the simplest members of the class of alkyl-substituted aromatics. Toluol is first nitrated by a mixture of sulfuric and nitric acids under proper conditions for forming maximum yields of mono nitro toluols, which are then recovered by crystallization from suitable solvents, and the nitro bodies are then reduced, for example, with iron powder and hydrochloric acid, to form the desired toluidine. The course of the reactions in these two general steps is indicated by the following equations:

$$\underset{\text{toluol}}{CH_3C_6H_5} + \underset{\text{nitric acid}}{HNO_3} \rightleftarrows \underset{\text{nitro-toluols}}{CH_3C_6H_4NO_2} + H_2O$$

$$CH_3C_6H_4NO_2 + 3H_2 \rightleftarrows \underset{\text{toluidines}}{CH_3C_6H_4NH_2} + 2H_2O$$

Another method of producing toluidines from toluol consists in first halogenating the ring and then converting the halogenated compound into the amine by treatment with ammonia under pressure. The steps in this process are shown by the following equations:

$$\underset{\text{toluol}}{CH_3C_6H_5} + \underset{\text{chlorine}}{Cl_2} \rightleftarrows \underset{\text{mono-chlor toluol}}{CH_3C_6H_4Cl} + \underset{\text{hydrochloric acid}}{HCl}$$

$$\underset{\text{mono-chlor toluol}}{CH_3C_6H_4Cl} + \underset{\text{ammonia}}{NH_3} \rightleftarrows \underset{\text{toluidine}}{CH_3C_6H_4NH_2} + HCl$$

A third method of manufacture consists in sulfonating the toluol with strong sulfuric acid and then treating the alkaline sulfonate with sodamide according to the following equations:

$$\underset{\text{toluol}}{CH_3C_6H_5} + \underset{\text{sulfuric acid}}{H_2SO_4} = \underset{\text{toluol sulfonic acid}}{CH_3C_6H_4SO_3H} + H_2O$$

$$\underset{\text{sodium toluol sulfonate}}{CH_3C_6H_4SO_3Na} + \underset{\text{sodamide}}{NaNH_2} = \underset{\text{toluidine}}{CH_3C_6H_4NH_2} + \underset{\text{sodium sulfate}}{Na_2SO_4}$$

This method is difficult and dangerous on account of the use of sodamide which reacts explosively with water which may accidentally be present.

Considerable difficulties are encountered in directly alkylating aromatic amines with olefins owing to their reactivity with the catalytic agents employed which are usually of an acid or metallic chloride character and may comprise such reagents as sulfuric acid, phosphoric acid, aluminum chloride, etcetera. For example, aniline readily reacts with sulfuric acid, phosphoric acid, hydrochloric acid, aluminum chloride, etcetera, to form water, alcohol or ether insoluble addition compounds and in the case of sulfuric acid also undergoes a certain amount of sulfonation depending upon the conditions of treatment. In the present process the alkaline characteristics of aryl amines are neutralized prior to alkylating

so that the common alkylating catalysts may be employed with good results.

In one embodiment the invention comprises the manufacture of alkylated aryl amines by the following steps: (1) Treatment of aryl amines with acetic acid to form acyl derivatives, (2) treatment of the acyl compounds with olefins in the presence of acid or metal salt catalyst, (3) hydrolysis of the alkylated acyl products to form alkylated aryl amines and regenerate acetic acid for reuse.

The three steps comprised in the present process are typified by the following equations which show the use of the simplest base compounds and typical catalytic and hydrolyzing reagents:

(1) $C_6H_5NH_2 + CH_3COOH =$ ($C_6H_5NH_2$: aniline; CH_3COOH: acetic acid)

$C_6H_5NHCH_3CO + H_2O$ ($C_6H_5NHCH_3CO$: acetanilide)

(2) $C_6H_5NHCH_3CO + C_2H_4 = C_2H_5C_6H_4NHCH_3CO$ (C_2H_4: ethylene; $C_2H_5C_6H_4NHCH_3CO$: ethyl acetanilide)

(3) $C_2H_5C_6H_4NHCH_3CO + H_2O =$

$C_2H_5C_6H_4NH_2 + CH_3COOH$ ($C_2H_5C_6H_4NH_2$: ethyl aniline; CH_3COOH: acetic acid)

Step (1) may be effected by using glacial acetic acid, acetic anhydride or acetyl chloride, with suitable variations in operating and treating conditions which are generally well known in the art. In step (2) various catalytic agents may be employed and in some cases improved results may be obtained when inert solvents are used along with the catalytic materials. As examples of catalytic agents which may be employed effectively may be mentioned sulfuric acid, phosphoric acid, aluminum chloride, etcetera. When using such reagents as strong sulfuric acid the acid-aromatic amine compound (e. g. acetanilide) is dissolved in the acid, the temperature is reduced to a suitable point, usually in the neighborhood of 0 to 40° C. and either a single olefin or a mixture of olefins such as may be present in the hydrocarbon gas mixtures produced in oil or gas cracking processes is introduced into the acid solution. To insure effective and complete action the solution should be mechanically agitated.

After completion of the alkylation the alkylated compound may be recovered either by diluting the acid with water, which throws the compound out of solution, or by extracting the acid with some suitable solvent such as, for example, carbon tetrachloride, ortho dichlorobenzol, etcetera, the desired compound then being recovered by boiling off the solvent.

A generally similar procedure to that outlined above may be followed with ortho phosphoric acid using concentrations from approximately 90 to 100%.

When using such alkylating catalysts as aluminum chloride which is solid at the preferred low temperatures employed, the alkylation may be aided by using various solvents which are inert to the compounds undergoing reaction and sufficiently fluid. Examples of such solvents are carbon tetrachloride, ethylene dichloride, ortho dichlorobenzene, chloroform, nitro benzol, etc. The procedure when using solvents consists in dissolving acyl-aromatic amines in the solvent, adding a finely divided metal chloride such as, for example, anhydrous aluminum chloride, maintaining intimate admixture of the solid and the solution by mechanical agitation and passing in olefin-containing gas until the absorption of olefins indicates that the desired degree of alkylation has taken place. The insoluble metal salt and any sludge reaction products are then allowed to settle, the solution of alkylated compound is decanted or filtered and the product recovered as before as a residue from the evaporation of the solvent. The alkylated acyl aromatic amines thus obtained are then subjected to hydrolysis with caustic alkalies to remove the acyl group and produce the desired aromatic amine.

A number of different catalytic reagents both of an acid and a saline character are mentioned above but the process is not limited to the specific reagents enumerated but may employ any catalyst of suitable condensing activity. The alternatives, however, will each exert its own peculiar effect upon the speed and course of the reactions in any given case so that they are not to be considered as exact equivalents.

The present process in one of its special application makes possible the production of alkylated derivatives of the nitrogen bases which occur in the tars produced by the distillation of various naturally occurring carbonaceous materials such as, for example, coal, lignite, peat, shale, etcetera. Without the step of acetylating the aromatic amines, their alkylation would be impossible by ordinary methods on account of the formation of stable and insoluble compounds with strong acids such as sulfuric and phosphoric acids and with condensing salts such as aluminum chloride.

The invention is not limited to the use of acetic acid in the first step as previously shown, but homologs of this acid such as propionic acid, butyric acid, etcetera, may be employed and also benzoic acid and its homologs. Thus, after the first step of the process compounds of the following character may be alkylated: Acetanilide, acetnaphthylamines, acetanthraquinoneamines, benzanilide, acet-toluidines, diacetbenzidine, etcetera.

In the second step of the process any olefin or mixture of olefins may be employed such as, for example, ethylene, propylene, the butylenes, amylenes, etcetera, and also compounds of a mixed olefinic-aromatic character such as indene and styrene.

The following examples are offered as illustrations of the results obtainable by utilizing the reactions comprised within the scope of the invention:

Example 1

100 parts by weight of acetanilide (produced by the direct interaction of aniline and acetic acid) is dissolved in approximately 400 parts by weight of carbon tetrachloride, and to the solution about 100 parts by weight of anhydrous aluminum chloride is added. The solution is then treated by introducing ethylene gas until a point is reached where the absorption rate is substantially zero.

The aluminum chloride sludge is settled, the carbon tetrachloride is distilled off and the recovered alkylated acetanilide then hydrolyzed to produce a mixture of ethyl anilines, the yield being between 85 and 90% of the theoretical corresponding to the production of 77 parts by weight of the alkylated amine.

Example 2

100 parts of acetanilide is dissolved in about 400 parts by weight of 100% phosphoric acid.

After warming to 40° C. to hasten solution, cooling is applied to maintain the temperature at approximately 30° C. during the introduction of gaseous propylene. After substantially complete saturation with propylene, the acid solution is diluted with about 6 volumes of water and extracted with carbon tetrachloride, the steps from this point being similar to those indicated in Example 1. The yield in this case is 85% of the theoretical and consists of 85 parts by weight of a mixture of isopropyl anilines, principally the ortho and para compounds. Approximately similar results are obtainable using concentrated sulfuric acid in place of phosphoric acid.

Example 3

100 part of propion anilide are dissolved in about 400 parts by weight of carbon tetrachloride and to the solution about 100 parts by weight of anhydrous aluminum chloride is added. The solution is then vigorously agitated and a mixture of butylenes is slowly added to insure substantially complete absorption, this reaction forming a mixture of butylene propion anilides. After the reactions are complete the semi-solid sludge is settled and the separated solution is distilled to remove solvent, the alkylated product being then recovered as a residue and subjected to hydrolysis to form the desired alkylated amine which in the present case is a mixture of various butyl anilines, the yield being 88% of the theoretical and corresponding to 59 parts by weight of the desired compounds.

The character of the present invention is disclosed in the preceding specification and its value is shown by a consideration of the numerical data presented but neither is to be considered in the light of imposing limitations upon its broad scope.

I claim as my invention:

1. A process for alkylating an alkyl-free aeromatic amine, which comprises treating a primary aryl amine with a mono-carboxylic acid to form an acyl derivative, subjecting the acyl derivative to treatment with an olefinic hydrocarbon in the presence of a condensation catalyst, and hydrolyzing the resultant compound to form the alkylated aryl amine.

2. A process for directly alkylating an alkyl-free aromatic amine, which comprises treating a primary aryl amine with a mono-carboxylic acid to form an acyl derivative, subjecting the acyl derivative to treatment with an olefin in the presence of a catalyst comprising essentially aluminum chloride, and hydrolyzing the resultant product to form the alkylated aryl amine.

3. A process for directly alkylating an alkyl-free aromatic amine, which comprises treating a primary aryl amine with a mono-carboxylic acid to form an acyl derivative, subjecting the acyl derivative to treatment with an olefin in the presence of a catalyst comprising essentially an inorganic non-oxidizing mineral acid, and hydrolyzing the resultant product to form the alkylated aryl amine.

4. A process for alkylating an alkyl-free aeromatic amine, which comprises treating a primary aryl amine with a mono-carboxylic acid to form an acyl derivative, subjecting the acyl derivative to treatment with an olefinic hydrocarbon in the presence of a condensation catalyst, and hydrolyzing the resultant compound to form the alkylated aryl amine while concurrently regenerating for reuse the acid employed.

5. A process for alkylating an alkyl-free aromatic amine, which comprises treating a primary aryl amine with acetic acid to form an acetyl derivative, subjecting the acetyl derivative to treatment with an olefinic hydrocarbon in the presence of a condensation catalyst, and hydrolizing the resultant compound to form the alkylated aryl amine.

CHARLES L. THOMAS.