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2,979,503

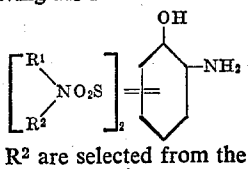
PROCESS FOR PRODUCING CERTAIN 2-AMINOPHENOLDISULFONAMIDES

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6 Claims. (Cl. 260—247.1)

This invention relates to novel compounds and to novel methods for producing same. More particularly, the compounds of the instant invention are 2-aminophenoldisulfonamides having the formula:

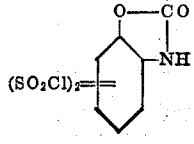


wherein R^1 and R^2 are selected from the group consisting of H, alkyl, aralkyl, cycloalkyl, and aryl, and when taken together, the atoms necessary to form a heterocycle. The compounds of the instant invention have been found to be highly effective as diazo components in the production of metallizible azo dyestuffs, as disclosed and claimed in our copending application Serial No. 704,312, filed on even date herewith.

In the above formula, R^1 and R^2 may be the same or different, and may be H, alkyl such as octadecyl, decyl, and preferably lower alkyl such as methyl, ethyl, propyl, isobutyl and hexyl, cycloalkyl such as cyclohexyl, aralkyl such as benzyl, aryl such as phenyl and biphenyl, and when taken together, morpholinyl, piperidinyl, pyridyl, and the like. It will be understood that R^1 and R^2 as above defined may contain inert substituents such as hydroxy, lower alkoxy such as methoxy, ethoxy, and the like.

The process of the instant invention for producing the above defined compounds comprises heating one mole of benzoxazolone with a minimum of about 4 up to about 12 moles of chlorosulfonic acid at a temperature of about 90 to 120° C. for about 3 to 10 hours, treating the resulting benzoxazolone disulfonylchloride with at least 4 moles of a compound of the formula R^1R^2NH, wherein R^1 and R^2 have the values given above, and then subjecting the resulting benzoxazolone disulfonamide to aqueous alkaline hydrolysis conditions.

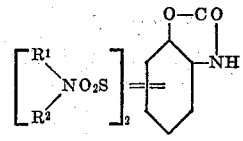
In carrying out the first step of the instant process, the benzoxazolone and chlorosulfonic acid are preferably admixed at a low temperature, i.e. less than about 10° C., and the temperature slowly raised and maintained at a temperature of 90 to 120° C. for sufficient time to complete the reaction, usually from about 3 to 10 hours. Temperatures above 10° C. and up to 120° C. may be employed for the initial admixture step, but are not preferred since the chlorosulfonic acid is more difficult to work at higher temperatures. Since this initial reaction probably proceeds in two stages, in the first of which the benzoxazolone disulfonic acid is first formed, and in the second of which the disulfonic acid reacts with two more moles of chlorosulfonic acid, 4 moles of chlorosulfonic acid are theoretically required to form the benzoxazolone disulfonylchloride, having the formula



However, an amount in excess of this theoretical amount, up to about 12 moles of the chlorosulfonic acid per mole of the benzoxazolone is preferred to prevent formation of undesirable by-products.

Reaction of the disulfonyl chloride with ammonia or an amine to produce the corresponding disulfonamide is readily carried out at ordinary temperatures by mere admixture. Here again, 4 moles of the amidating compound of the formula R^1R^2NH are theoretically required for each mole of the disulfonylchloride, although it is preferred to employ an excess of up to about 14 moles for neutralization of acidic substances and the like. As representative of suitable compounds for this amidation there may be mentioned ammonium hydroxide, ammonium carbonate; methylamine, ethylamine, methylethylamine, diethylamine, dimethylamine, propylamine, isobutylamine, ethanolamine, diethanolamine, propanolamine, hexylamine, decylamine, octadecylamine, methylethanolamine, benzylamine, methylbenzylamine, cyclohexylamine, aniline, toluidine, xylidine, anisidine, morpholine, piperidine, pyridine, and the lke.

In general, this amidating step may be carried out between the disulfonylchloride and the amidating compound alone or in aqueous or organic solvent solution or dispersion at temperatures ranging from about 5 to 30° C. for periods ranging from about 1 to 24 hours. Concentrated solutions of the ammonia or amine compound are preferred, but such concentrations may range from about 30 to 100% by weight of said compound. As compatible solvents which are inert under the conditions of amidation, there may be mentioned chlorobenzene, trichlorobenzene, nitrobenzene, toluene, dioxane, carbon tetrachloride, ether and the like. Upon completion of the amidating reaction, the disulfonamide is filtered and sucked dry. It has the formula



The final step in the reaction involves subjecting the benzoxazoline disulfonamide to aqueous alkaline hydrolysis conditions to produce the desired 2-aminophenoldisulfonamide. This may be readily accomplished by slurrying the benzoxazolone disulfonamide with caustic, usually employing about a 15 to 35% by volume caustic soda solution using a minimum of two equivalents of caustic up to about 300% of theory. Other alkaline substances may be employed, as for example, potassium hydroxide and the like. The hydrolysis is carried out at elevated temperatures, usually at or near the boil, for sufficient time to open the benzoxazolone ring, usually from about 1 to 10 hours. The hydrolysis medium is then neutralized with acid, for example by acidification to Congo acid followed by cooling, filtering and washing.

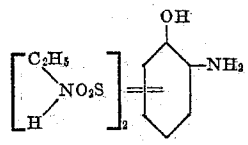
The following examples, in which parts are by weight unless otherwise indicated are illustrative of the instant invention and are not to be regarded as limitative.

Example 1

Charge to a 500 cc. 3-neck flask fitted with an agitator and thermometer, 350 g. chlorosulfonic acid. Cool to −5° C. Add 50 g. 100% benzoxazolone dry at such a rate that the temperature does not exceed 10° C. Allow to warm during 1 hour to room temperature. Heat to 100°–110° C. during 1 hour and hold at that temperature for 4 to 5 hours. Cool to room temperature and pour onto crushed ice. Filter and wash with ice water until almost neutral to Congo paper. Add the paste to an aqueous solution of ethylamine containing 70 g. of ethylamine which is kept below 10° C. during

addition of the paste. Stir cold 8 hours and add hydrochloric acid until acid to Congo paper. Filter. Add cake to 160 cc. water and 160 cc. sodium hydroxide (40% soln.) and heat to 100° C. for 4 hours. Cool to 90° C. Add nuchar, clarify and cool to below 40° C. Add hydrochloric acid to an acid reaction to Congo paper. Filter and wash with 100 cc. water.

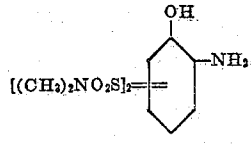
The product is a disulfonamide of the structure:



In the above example, the ethylamine may be replaced by ammonium hydroxide, methyl amine, dimethylamine, ethylamine, diethylamine, propylamine, isobutylamine, ethanolamine, diethanolamine, propanolamine, methylethanolamine, benzylamine, methylbenzylamine, cyclohexylamine, ammonium carbonate, morpholine, piperidine, pyridine and the like, as exemplified by the following examples.

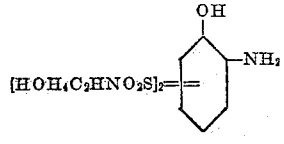
Example 2

Example 1 is repeated but substituting for the ethylamine, the same amount of dimethylamine. The product has the structure



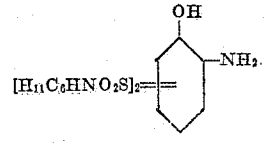
Example 3

Example 1 is repeated but substituting for the ethylamine, 95 g. ethanolamine. The product has the structure



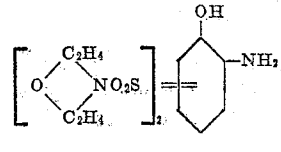
Example 4

Example 1 is repeated but substituting for the ethylamine, 153 g. cyclohexylamine. The product has the formula



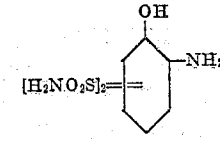
Example 5

Example 1 is repeated but substituting for the ethylamine 135 g. morpholine. The product has the formula



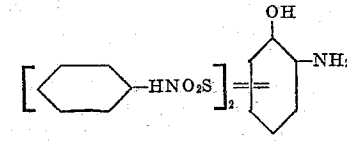
Example 6

Example 1 is repeated but substituting for the ethylamine, 102 cc. NH_4OH 29° Be'. The product has the formula



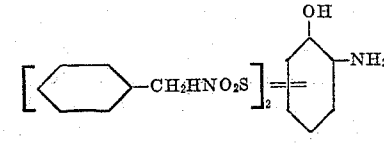
Example 7

Example 1 is repeated but substituting for the ethylamine, 140 g. aniline. The product has the formula



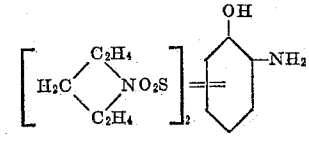
Example 8

Example 1 is repeated but substituting for the ethylamine, 160 g. benzylamine. The product has the formula



Example 9

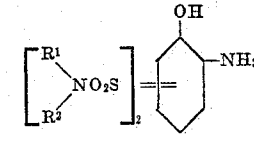
Example 1 is repeated but substituting for the ethylamine, 128 g. piperidine. The product has the formula



This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

We claim:

1. A process for producing a compound having the formula



wherein R^1 and R^2 are selected from the group consisting of H, alkyl, aralkyl, cycloalkyl, and aryl, and when taken together, the atoms necessary to form a heterocycle, comprising heating one mole of benzoxazolone with at least about 4 up to about 12 moles of chlorosulfonic acid at a temperature of about 90 to 120° C. for about 3 to 10 hours, treating the resulting benzoxazolone disulfonylchloride with at least 4 moles of an amine compound of the formula R^1R^2NH wherein R^1 and R^2 are selected from the group consisting of H, alkyl, aralkyl, cycloalkyl, and aryl, and when taken together, the atoms necessary to complete a heterocycle, and then subjecting the resulting benzoxazolone disulfonamide to aqueous alkaline hydrolysis conditions.

2. A process as defined in claim 1 wherein said amine compound is ethylamine.

3. A process as defined in claim 1 wherein said amine compound is dimethylamine.

4. A process as defined in claim 1 wherein said amine compound is cyclohexylamine.

5. A process as defined in claim 1 wherein said amine compound is morpholine.

6. A process as defined in claim 1 wherein said amine compound is ammonia.

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