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PRODUCTION OF BENZYL SULPHONYL CHLORIDES

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This invention relates to the manufacture of benzyl sulphonyl chlorides, by an improved method, which does not involve the use of dangerous and unpleasant substances as phosphorus compounds or mercaptans.

Aralkyl sulphonyl halides have heretofore been prepared either by the action of phosphorus halides on sodium alkyl sulphonates, or by the action of halogen on an aqueous solution of aralkyl pseudothioureas (Johnson U. S. Patents 2,146,744 and 2,147,346) and on an aqueous solution of sodium aralkyl thiosulphates (Douglass and Johnson, J. A. C. S., 60, 1486 (1938).)

We have found that both the processes described by Johnson, the chlorination of benzyl pseudothiourea and sodium benzyl thiosulphate in water solution, yield a mixture of the desired product, benzyl sulphonyl chloride, and two intermediate oxidation products, benzyl disulphide and benzyl disulphoxide (benzyl benzylthiosulphonate.) This crude mixture which comes from the chlorination in aqueous medium melts over a range of 10°–15° C. from 70° to about 85° C. It possesses a very sharp unpleasant odor which is absorbed by the skin and hair of persons working with it. The product in order to be used as an intermediate at the point of manufacture, or to be shipped to consumers must be recrystallized from a suitable solvent. This is an expensive, wasteful operation.

We have discovered that, by the use of admixtures of water and a suitable non-reactive, water miscible substance containing oxygen, particularly a lower fatty acid as acetic acid, we can obtain 80% of theory or better yields of aralkyl sulphonyl chlorides by the chlorination of solutions of water soluble aralkyl thio-compounds.

The products are pure aralkyl sulphonyl chlorides and can be used as intermediates in this form. This use of water miscible solvents improves the yields and the quality of the aralkyl sulphonyl chlorides to such an extent as to make their economic manufacture possible.

This invention will be further understood from a consideration of the following examples in which the parts are given by weight, and which illustrate the way in which the invention has been practiced.

Example I

Preparations of benzyl sulphonyl chloride

A mixture of 25.2 parts of benzyl chloride, 49.6 parts of sodium thiosulphate pentahydrate, 50 parts of methanol and 50 parts of water was heated to the boiling temperature and refluxed until a homogeneous solution had been formed which required three hours. This solution, containing the sodium benzyl thiosulphate, was distilled to remove most of the methanol, and the residue, 125 parts, was mixed with 125 parts of glacial acetic acid, cooled to 5° C. with an ice bath and treated with gaseous chlorine. Good stirring was maintained throughout the oxidation and chlorination. The white solid was benzyl sulphonyl chloride. After dilution with 100 parts of water, the suspension was filtered and washed by decantation. The product was air dried. It weighed 38 parts (99% of theory) and melted at 91–92° C.

Example II

Preparation of benzyl sulphonyl chloride

A mixture of 252 parts of benzyl chloride, 496 parts of sodium thiosulphate pentahydrate, and 100 parts of water was heated to the boiling temperature and refluxed until a homogeneous solution was obtained which required eight hours. This solution weighing about 850 parts was mixed with 1500 parts of glacial acetic acid, cooled to 5° C. with an ice bath and treated with gaseous chlorine until the solution became yellow green and the vapor above the reaction solution contained chlorine. Good mixing of the gas and the solution was maintained throughout. The product was filtered, suspended in 2000 parts of water and stirred vigorously. Upon filtering again and drying, it weighed 250 parts (65% of theory) and melted at 91–92° C. The acetic acid filtrate which could have been used for the next preparation, was diluted with 2500 parts of water and yielded 100 parts of benzyl sulphonyl chloride. The total yield was 350 parts (92% of theory), melting at 91–92° C.

Example III

Preparation of benzyl sulphonyl chloride

A mixture of 12.6 parts of benzyl chloride, 7.6 parts of thiourea were warmed on a steam bath for one half hour. The mixture was removed for a second half hour and then replaced for a full hour longer to complete the formation of the benzyl pseudothiourea. When cool, 50 parts of water were added, and the contents warmed to effect solution. Oil droplets indicated incomplete reaction. The solution was divided into two equal portions, the subsequent procedure indicated as (1) and (2).

(1) To portion (1) was added 75 parts of water. The mixture was cooled to 5° C. and chlo-

rine passed in until the suspension was yellow green in color. The precipitated crude benzyl sulphonyl chloride was filtered and dried in the air. It melted at 84 to 87° C. and possessed a sharp unpleasant odor.

(2) To portion (2) was added 75 parts of glacial acetic acid. Chlorine was passed in at 5° C. as in portion (1). To this suspension 100 parts of water were added. The suspension was filtered and washed by decantation with 50 parts of water. Upon drying it melted at 92–93° C. and was essentially free of odor.

EXAMPLE IV

Preparation of o-chlorobenzyl sulphonyl chloride

A mixture of 80.5 parts of o-chlorobenzyl chloride, 124 parts of sodium thiosulphate pentahydrate, and 100 parts of 50% methanol were heated at the boiling point until the solution became homogeneous. This solution was mixed with 1000 parts of glacial acetic acid, cooled to 7° C. with an ice bath and treated with gaseous chlorine until the solution became yellow-green. The mixture was diluted with 1500 parts of cold water and the white needles which were formed were filtered off, and washed with water and dried in a vacuum dryer. The yield was 90 parts (80% of theory) melting at 62–64° C.

EXAMPLE V

Preparation of p-chlorobenzyl sulphonyl chloride

A mixture of 16.1 parts of p-chlorobenzyl chloride, 24.8 parts of sodium thiosulphate pentahydrate, and 20 parts of 50% methanol were heated at the boling point until the solution became homogeneous. This solution was mixed with 150 parts of glacial acetic acid, cooled to 7° C. with an ice bath and treated with gaseous chlorine until the solution became green yellow. The mixture was diluted with 200 parts of cold water and the white needles which were formed were filtered off, and dried. The yield was 18 parts (80% of theory), melting at 89–91° C.

EXAMPLE VI

Preparation of benzyl sulphonyl chloride

A solution of 46 parts of sodium benzyl thiosulphate in 100 parts of water was mixed with 250 parts of propionic acid and the mixture cooled to 5° C. Chlorine was passed through the solution until it became green yellow. The mixture was diluted with four times its volume of water. The benzyl sulphonyl chloride formed upon dilution was filtered, washed with water and dried. The yield was 38 parts (99% of theory), melting at 89–90° C.

EXAMPLE VII

Preparation of benzyl sulphonyl chloride

A solution of 46 parts of sodium benzyl thiosulphate in 100 parts of water was mixed with 300 parts of methanol and the mixture cooled to 5° C. Chlorine was passed through the solution until it became green yellow. The mixture was diluted with four times its volume of water. The benzyl sulphonyl chloride formed upon dilution was filtered, washed with water and dried. The yield was 38 parts (99% of theory), melting at 88–91° C.

EXAMPLE VIII

Preparation of benzyl sulphonyl chloride

A solution of 46 parts of sodium benzyl thiosulphate in 100 parts of water was mixed with 250 parts of dioxane and the mixture cooled to 5° C. Chlorine was passed through the solution until it became green yellow. The mixture was diluted with four times its volume of water. The benzyl sulphonyl chloride formed upon dilution was filtered, washed with water and dried. The yield was 36 parts (95% of theory) melting at 88–91° C.

In addition, other aralkyl sulphonyl chlorides and bromides could be made by this process. Examples of these are p-nitrobenzyl sulphonyl bromide, o-carboxybenzyl sulphonyl chloride, p-phenyl benzyl sulphonyl chloride, α-naphthyl methyl sulphonyl chloride, and β-phenyl ethyl sulphonyl chloride.

Any water miscible, non-reactive oxygen containing substance such as acetic acid, propionic acid, methanol, dioxane, ethyl alcohol, ethylene glycol, diethylene glycol, ethylene chlorohydrin, glycerine, glycerine chlorohydrins, B-methoxy ethyl alcohol, acetone, methyl cyanide, B-ethoxy ethyl alcohol, B-butoxy ethyl alcohol, n-butyric acid, etc., is of use in this improvement. By non-reactive, we mean one that does not react appreciably with the reactants or the products under the conditions outlined in the examples and specified in the body or the claims. We prefer to chlorinate a solution which is 50% or higher with respect to the water miscible substance.

These compounds are useful intermediates for dyes, plastic and other organic preparations.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and an oxygen containing, water miscible, non-reactive substance which is a solvent for compounds containing sulphur and oxygen.

2. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and a non-reactive water miscible fatty acid which is a solvent for compounds containing sulphur and oxygen.

3. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and acetic acid which is a solvent for compounds containing sulphur and oxygen.

4. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and propionic acid which is

a solvent for compounds containing sulphur and oxygen.

5. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and a non-reactive water miscible alcohol which is a solvent for compounds containing sulphur and oxygen.

6. The improved method of producing a benzyl sulphonyl chloride, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. a solution of an aralkyl thiosulphate salt, soluble in water, and of the formula $C_6H_4RCH_2.S.SO_2.OX$, where R is selected from the group consisting of hydrogen and halogen, and X is an alkali metal, in a mixture of water and methanol which is a solvent for compounds containing sulphur and oxygen.

7. The improved method of producing benzyl sulphonyl chlorides, which comprises subjecting to the action of gaseous chlorine at 0° to 10° C. solutions of sodium salts of benzyl thiosulphates of the formula $C_6H_4RCH_2.S.SO_2.ONa$, where R is selected from the group consisting of hydrogen and halogen, in a mixture of water and a compound selected from the group of oxygen containing, water miscible, non-reactive substances consisting of acetic acid, propionic acid, methanol, and 1,4-dioxane.

8. The improved method of producing benzyl sulphonyl chloride, which comprises subjecting an aqueous solution of sodium benzyl thiosulphate containing a compound selected from a group of oxygen containing, water miscible, non-reactive substances consisting of acetic acid, propionic acid, methanol, and 1,4-dioxane of at least 50% concentration, to the action of gaseous chlorine at 0° to 10° C.

9. The improved method of producing benzyl sulphonyl chloride which comprises subjecting a solution of sodium benzyl thiosulphate in aqueous acetic acid of at least 50% concentration to the action of gaseous chlorine at 0° to 10° C.

10. The improved method of producing benzyl sulphonyl chloride which comprises subjecting a solution of sodium benzyl thiosulphate in aqueous methanol of at least 50% concentration to the action of gaseous chlorine at 0° to 10° C.

11. The improved method of producing benzyl sulphonyl chloride which comprises subjecting a solution of sodium benzyl thiosulphate in aqueous propionic acid of at least 50% concentration to the action of gaseous chlorine at 0° to 10° C.

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