

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Process for the Production of Araliphatic Sulphoxides

We, CASSELLA FARBWERKE MAINKUR AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 6 Frankfurt/Main-Fechenheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a process for the production of araliphatic sulphoxides.

It is known that, when sodium hydride or alkali metal alcoholates are allowed to act on dimethyl sulphoxide, the anion formed by loss of a proton from dimethyl sulphoxide is capable of addition to arylconjugated olefines or styrenes with the formation of araliphatic sulphoxides.

Surprisingly, we now have found that arylconjugated olefines or styrenes can likewise be added, with very good yields, to methyl sulphoxides by replacing the alkali metal alcoholate or sodium hydride, which are difficult to handle on a technical scale, with potassium hydroxide and by carrying out the reaction at a temperature of 75—150°C., preferably 100—120°C.

For use as the catalyst, potassium hydroxide of a technical grade, as well as the pure grade is suitable. It may be employed in catalytic or stoichiometric amounts. It is of advantage to use 0.01 to 1 mole potassium hydroxide per 1 mole of the unsaturated compound.

Suitable methyl sulphoxides are, for example, dimethyl sulphoxide, methylethyl sulphoxide, methylphenyl sulphoxide, methylbenzyl sulphoxide, and methyl- α -propylphenyl sulphoxide.

The arylconjugated olefines or styrenes which may be employed for the process under [Price 4s. 6d.]

the present invention are chiefly styrene, α -methylstyrene, β -methylstyrene, α -phenylstyrene, β -butylstyrene, β -hexylstyrene, vinyltoluenes as well as vinylpyridines and vinylthiophenes. Moreover, such arylolefines are also suitable as undergo displacement of the double bond, in an alkaline reaction medium so as to give arylconjugated olefines, such as, for example, allylbenzene.

The fact, that an addition can be brought about in the presence of potassium hydroxide acting as a catalyst must be considered especially surprising because it was not known that alkali metal hydroxides are really suited for converting methyl sulphoxides into the corresponding deprotonated methyl sulphoxide anions and that the addition reaction does not take place with sodium hydroxide. Moreover, using potassium hydroxide, the reaction temperatures are higher than in the known utilisation of sodium hydride or alkali metal alcoholates and thus already come within the range of the pyrolytic decomposition temperatures of the reaction products. However as may be gathered from the high yields of the process under this invention, this decomposition does not take under the reaction conditions of the invention.

The products under the process of the present invention are suited as starting materials for the preparation of dyestuffs and pharmaceuticals.

The following examples are given for the purpose of illustrating the present invention. Unless otherwise stated, all temperatures given are in degrees Centigrade.

EXAMPLE 1:

56 g. pulverised potassium hydroxide are introduced, with thorough stirring, into 500 c.c. dimethyl sulphoxide of a technical grade

and the mixture is heated to 115—120°. At this temperature, 104 g. styrene are dropwise added in the course of one hour and the mixture is then stirred for a further hour at the same temperature. Subsequently, the excess dimethyl sulphoxide is distilled off under vacuum, the residue from distillation is admixed with ice, neutralised with 10 N. hydrochloric acid and extracted with chloroform. After drying using anhydrous sodium sulphate, the resultant chloroform solution is liberated under vacuum from the solvent. Thus, 152 g. (83.5% of the theoretical) of methyl- ω -phenylpropyl sulphoxide are obtained in the form of a brownish oil that crystallises entirely in the course of time. For further purification, the product may either be recrystallised from a mixture of cyclohexane and benzene, whereby colourless needles are obtained having a melting point of 44—45°, or be purified by distillation (boiling point: 143—145°/0.01 mm Hg.).

Analysis: (C₁₁H₁₆OS) Calculated: C 67.4% H 8.2% S 16.4%
determined: C 67.6% H 8.0% S 16.5%

EXAMPLE 3:

At a temperature of 120°, 35 g. pulverised potassium hydroxide of a technical grade are stirred together with 400 c.c. dimethyl sulphoxide of a technical grade. From this mixture are subsequently distilled off 100 c.c. dimethyl sulphoxide at a boiling point of 83°/16 mm Hg. in order to remove the water brought in. After cooling down to 40°, 156g. styrene of a technical grade are added dropwise and the reaction mixture is then stirred for 2 hours, at a temperature of 100—110°. Subsequently, the excess dimethyl sulphoxide is distilled off under vacuum and the resultant residue is buffered by saturation with carbon dioxide. The crude oil obtained is filtered by suction through kieselguhr and the filtrate fractionated by distillation. At a boiling point of 156°/0.2 mm Hg., 207 g. (74% of the theoretical) of methyl- ω -phenylpropyl sulphoxide are distilled off in the form of a light, viscous oil that crystallises fully after inoculation. The product is identical with that obtained according to Example 1.

EXAMPLE 2:

56 g. pulverised potassium hydroxide are introduced, with thorough stirring, into 400 c.c. dimethyl sulphoxide of a technical grade and the mixture is heated to 110°. At this temperature 118 g. α -methystyrene are dropwise added in the course of 2 hours and the mixture is then stirred for a further 5 hours at the same temperature. The resultant reaction mixture is added, with stirring, into 1500 c.c. iced water and neutralised with hydrochloric acid. Hereby, an oily organic layer separates which is dissolved in chloroform. After washing of the chloroform solution with water, drying using anhydrous sodium sulphate, and removal of the solvent under vacuum, 151 g. (77% of the theoretical) of crude methyl-phenylbutyl sulphoxide are obtained. The product may be further purified by way of vacuum distillation (boiling point: 145—150°/0.1 mm Hg.) and becomes thereafter a colourless, somewhat viscous oil.

WHAT WE CLAIM IS:—

1.—Process for the production of araliphatic sulphoxides by a base-catalysed addition of arylconjugated olefines or styrenes to methyl sulphoxides of the aliphatic or aromatic series characterised by using potassium hydroxide as a basic catalyst and carrying out the reaction at a temperature of 75—150°C.

2.—Process as claimed in claim 1 wherein the reaction temperature is between 100 and 120°C.

3.—Process for the production of araliphatic sulphoxides as described hereinbefore and with reference to any of the foregoing Examples.

4.—Araliphatic sulphoxides whenever prepared by the process of any of claims 1—3.

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