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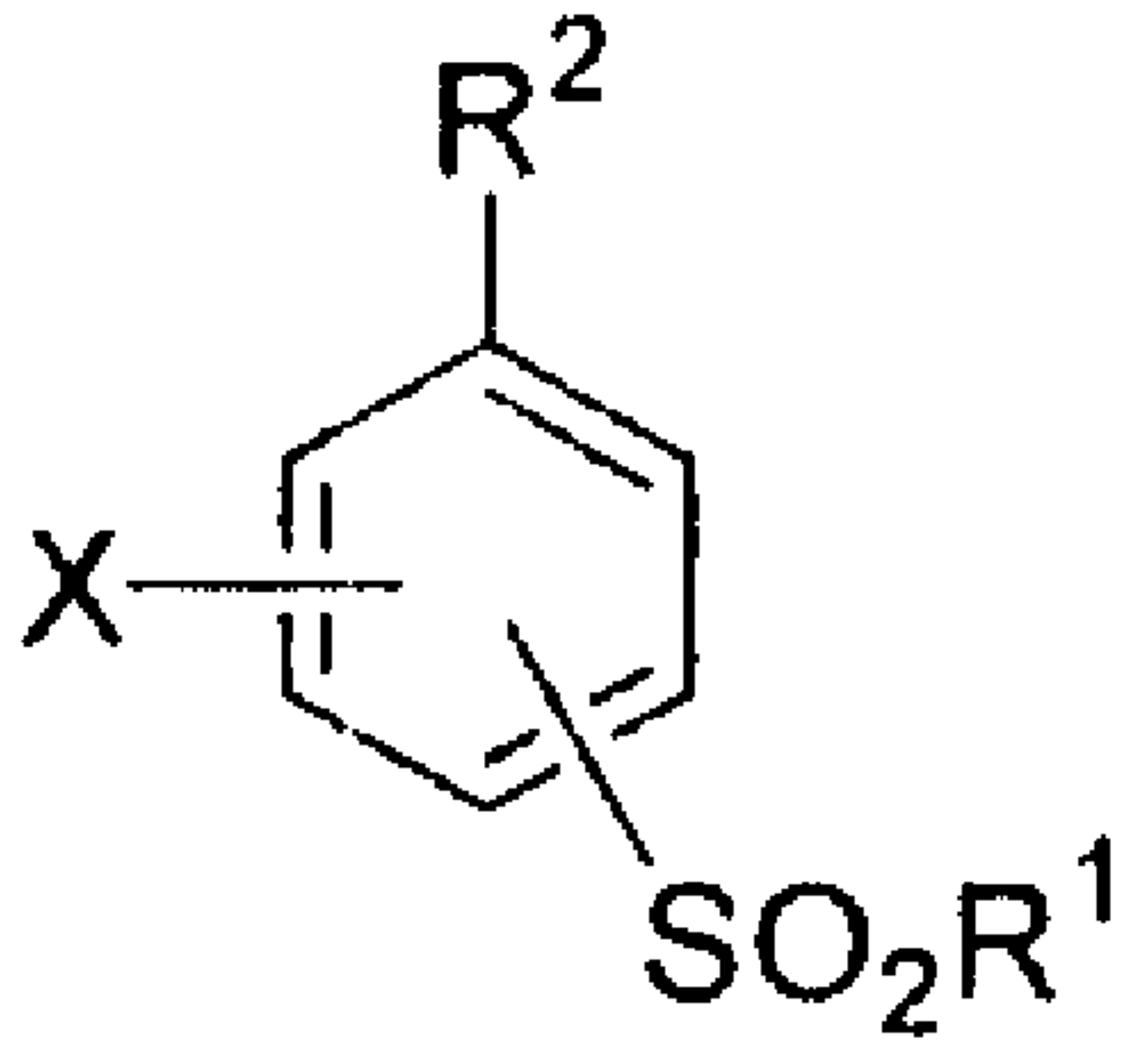
(54) Titre : METHODE DE PREPARATION D'ACIDES ALCANESULFONYLBENZOIQUES
(54) Title: PROCESS FOR THE PREPARATION OF ALKANESULFONYLBENZOIC ACIDS



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(57) Abrégé/Abstract:

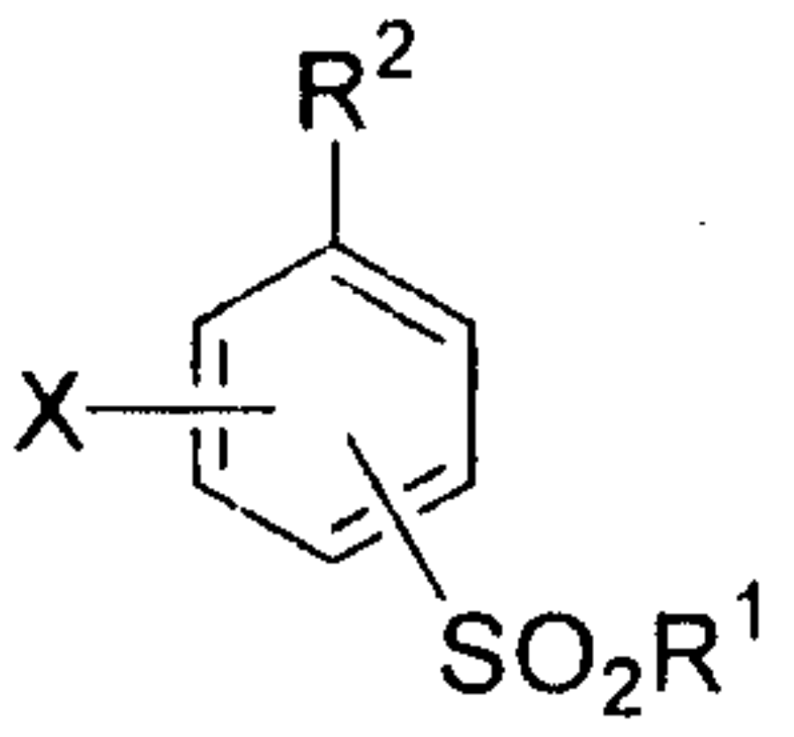
Process for the preparation of alkanesulfonyl-benzoic acids, characterized in that alkanesulfonyl-alkyl-benzenes of the formula (see formula I) in which R^1 and R^2 are identical or different and are alkyl having 1 to 4 carbon atoms, but R^2 has a meaning other than t-butyl, and X represents H, F, Cl, Br or NO_2, are oxidized under increased pressure at temperatures above 120°C with molecular oxygen in acetic and/or propionic acid in the presence of a catalyst soluble therein, which contains cobalt ions and bromine ions and, if R^2 has a meaning other than methyl, also manganese ions.

HOE 89/F 134

ABSTRACT:

Process for the preparation of alkanesulfonylbenzoic acids

Process for the preparation of alkanesulfonyl-benzoic acids, characterized in that alkanesulfonyl-alkyl-benzenes of the formula



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in which R^1 and R^2 are identical or different and are alkyl having 1 to 4 carbon atoms, but R^2 has a meaning other than t-butyl, and X represents H, F, Cl, Br or NO_2, are oxidized under increased pressure at temperatures above 120°C with molecular oxygen in acetic and/or propionic acid in the presence of a catalyst soluble therein, which contains cobalt ions and bromine ions and, if R^2 has a meaning other than methyl, also manganese ions.

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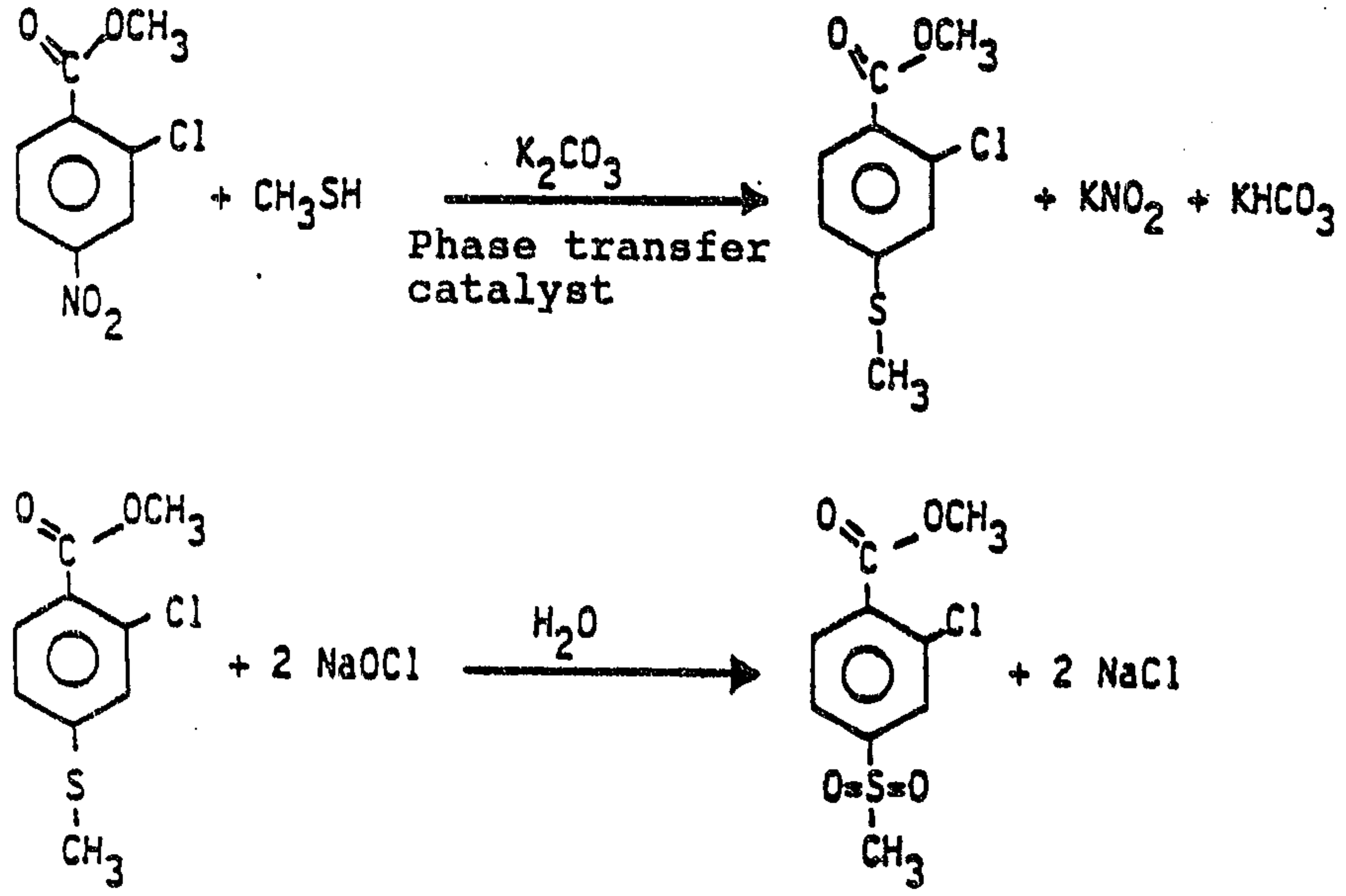
Description

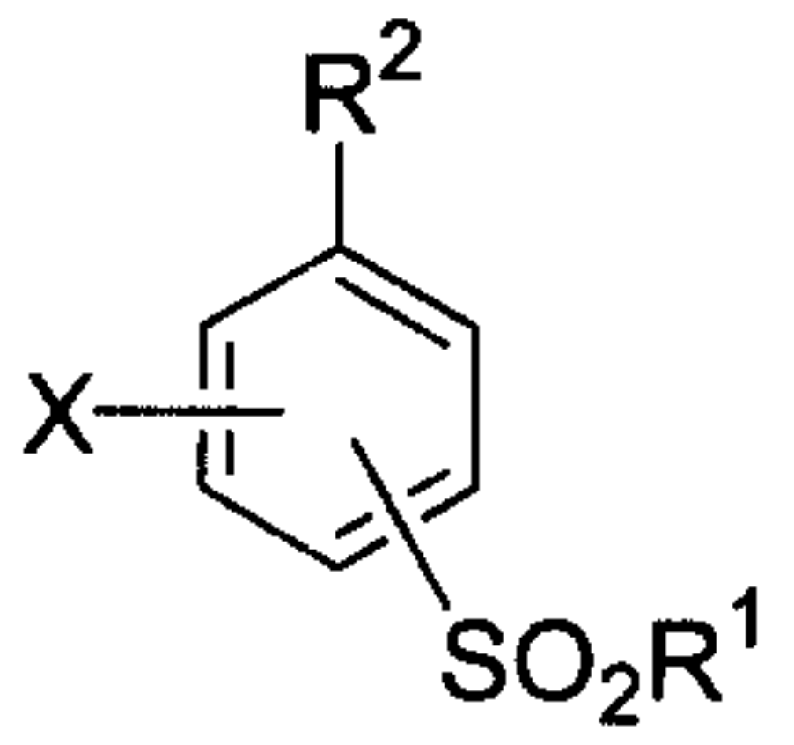
Process for the preparation of alkanesulfonylbenzoic acids

Alkanesulfonylbenzoic acids are precursors for pesticides and herbicides (US-PS 4,704,467 and EP-OS 203 428). According to the prior art to date, they are prepared, for example, by oxidation of alkylthiobenzoic acids with an oxidizing agent such as sodium hypochlorite or H_2O_2. The following route is described in US-PS 4,704,467 for methanesulfonylbenzoic acid:



The disadvantages of this procedure are the complicated introduction of the alkylthio radical, the use of mercaptans having an intensive smell and the oxidation with chemicals such as hypochlorite or H_2O_2.

It has now been found, surprisingly, that alkanesulfonylbenzoic acids can be prepared in a simple manner when alkanesulfonyl-alkyl-benzenes of the general formula I



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in which R^1 and R^2 are identical or different and are alkyl having 1 to 4 carbon atoms, but R^2 has a meaning other than t-butyl, and X represents H, F, Cl, Br, or NO_2, are oxidized under increased pressure at temperatures above 120°C with molecular oxygen in acetic and/or propionic acid in the presence of a catalyst soluble therein, which contains cobalt ions and bromine ions and, if R^2 has a meaning other than methyl, also manganese ions.

Possible alkyl groups for R^1 and R^2 are in each case methyl, ethyl, n- and iso-propyl and n-, sec.- and iso-butyl, and for R^1 additionally also t-butyl. During the oxidation, the radical R^2 is oxidized to the COOH group. 1.5 mol of oxygen are needed for oxidation of the methyl group R^2.

The starting compounds are readily accessible; for example, alkanesulfonyltoluenes can be prepared from toluenesulfonic acid by reduction to sodium toluenesulfinate and reaction thereof with dimethyl sulfate or diethyl sulfate.

Suitable starting compounds are, in addition to the compounds mentioned in the examples, for example, 2-[methanesulfonyl]-5-nitrotoluene, 3-nitro-4-[methanesulfonyl]-toluene and 6-chloro-3-nitro-4-[methanesulfonyl]toluene.

The present process is advantageously carried out under the conditions which are particularly effective for the oxidation of alkyl groups, such as are used, for example, for the oxidation of the two methyl groups of p-xylene to give terephthalic acid. By using these very effective oxidation conditions it is possible to oxidize the alkyl group on the benzene ring even if the benzene ring carries an additional deactivating substituent X in addition to the strongly electron-withdrawing alkanesulfonyl group. However, it is surprising that only the alkyl group on the benzene ring is oxidized under these oxidation conditions, while the alkanesulfonyl group on the other hand is retained. In contrast to the alkanesulfonyl group, the acetyl group of acetophenone, for example, is thus readily degraded by oxidation under these conditions.

The acetic and/or propionic acid is in general employed in anhydrous form; however, water is formed during the oxidation. Nevertheless, the reaction system in general contains not more than 15 % by weight of water, in particular not more than 5 % by weight. The use of acetic acid, in particular in anhydrous form, is preferred.

The presence of manganese ions is necessary for the desired oxidation of the ethyl, propyl and butyl group bonded to the aromatic, but is also expedient for the oxidation of the methyl group, although a combination of cobalt ions and bromine ions is also sufficient for the latter. The presence of manganese ions enables the amount of cobalt required to be reduced, for the same activity of the catalyst.

The ratio of the concentration of cobalt ions to manganese ions is in general 1:(0.2 to 3), preferably 1:(0.3 to 1.2). The ratio of the sum of the concentrations of the two metal ions to bromine ions is advantageously 1:(0.01 to 2), preferably 1:(0.1 to 1) and particularly preferably 1:(0.2 to 0.7). The sum of the concentrations of the two metal ions is advantageously in the range from 0.01 to 0.2 mol, preferably 0.02 to 0.1 mol and in particular 0.04 to 0.08 mol of metal ions per 1 of the liquid phase. The metal ions are preferably added in the form of the salts of the carboxylic acid in question. The bromide can be added in the form of an HBr solution, as an alkali metal bromide or advantagoeusly as cobalt bromide or manganese bromide.

The molecular oxygen is preferably introduced into the liquid phase of the reactor in the form of dry air. The process is advantageously carried out under an oxygen partial pressure of 1.5 to 8, preferably 2.4 to 7 and in particular 2.8 to 6 bar. The reaction temperature is advantageously in the range from 120 to 220°C, preferably from 130 to 180°C and in particular from 135 to 160°C.

For complete and rapid oxidation of the alkyl group on the benzene ring it is especially advantageous to carry out the reaction at a catalyst concentration of 0.04 to 0.08 mol of metal ions per l of liquid phase and to apply a high oxygen partial pressure of at least 2.4 or 2.5 bar at the entry point into the liquid phase. The combination of these two measures enables the reaction temperature required to be kept low. If extremely strict conditions are not combined, the alkanesulfonyl group is attacked only insignificantly by oxidation.

The alkanesulfonyl acids crystallize out of the reaction solution on cooling, according to their concentration, and can be separated off by filtration. However, the filtrate contains often considerable amounts of dissolved product and all the catalyst. An advantageous embodiment of the process thus comprises separating off the water formed during the reaction from the filtrate, for example on a column, and re-using this mother liquor as the reaction medium for the next oxidation. Catalyst is saved in this way, and the yield isolated from the subsequent batch is higher.

In the following examples, "OAc" represents acetate.

Examples

1) A mixture of 245.6 g of 2-chloro-4-methanesulfonyltoluene, 12.0 g of $Co(OAc)_2 \cdot 4H_2O$, 16.2 g of a 10 % strength hydrogen bromide solution in glacial acetic acid and 440 g of glacial acetic acid was heated to 150°C

under 16 bar of nitrogen in a 1 l autoclave of high-grade steel fitted with a thermometer, stirrer, reflux condenser and pressure retention valve. Air (16 bar) was then passed into the liquid phase via an immersed tube. The exothermic reaction started immediately and the temperature was kept at 155 to 160°C by cooling. The oxygen content in the waste gas was kept at 5 to 6 % by volume by regulating the air supply. At the end of the exothermic reaction, the hot reaction solution was removed and cooled to 20°C while stirring. The crystals which had precipitated were filtered off with suction, washed five times with 30 ml of glacial acetic acid each time and dried at 80°C under 65 mbar in a weak stream of air.

Yield: 243.6 g (86.5 % of theory) of 2-chloro-4-(methanesulfonyl)-benzoic acid; melting point 193 to 194°C

2) A mixture of 221.3 g of 3-(methanesulfonyl)-toluene, 7.5 g of $Co(OAc)_2 \cdot 4H_2O$, 2.45 g of $Mn(OAc)_2 \cdot 4H_2O$, 16.2 g of a 10 % strength hydrogen bromide solution in glacial acetic acid and 470 g of glacial acetic acid was oxidized with air at 150 to 155°C under 15 bar in the autoclave described in Example 1. At the end of the uptake of oxygen, 200 g of water were added to the hot reaction solution, which had a temperature of 100°C, for the purpose of precipitating the reaction product, and the mixture was cooled to 20°C. The crystals were filtered off with suction, washed five times with 30 ml of 70 % strength aqueous acetic acid each time and dried at 80°C under 65 mbar in a weak stream of air.

Yield: 236.7 g (91 % of theory) of 3-(methanesulfonyl)-benzoic acid; melting point 236 to 237°C.

3) A mixture of 221.1 g of 4-(methanesulfonyl)-1-ethylbenzene, 5.0 g of $Co(OAc)_2 \cdot 4H_2O$, 4.9 g of $Mn(OAc)_2 \cdot 4H_2O$, 12.2 g of a 10 % strength hydrogen bromide solution in glacial acetic acid and 480 g of glacial acetic acid was oxidized with air at 145 to 150°C under 16 bar in the autoclave described in Example 1. At

the end of the uptake of oxygen, the mixture was cooled to 20°C while stirring. The crystals were filtered off under a high suction, washed five times with 30 ml of glacial acetic acid each time and dried at 100°C under 65 mbar in a weak stream of air.

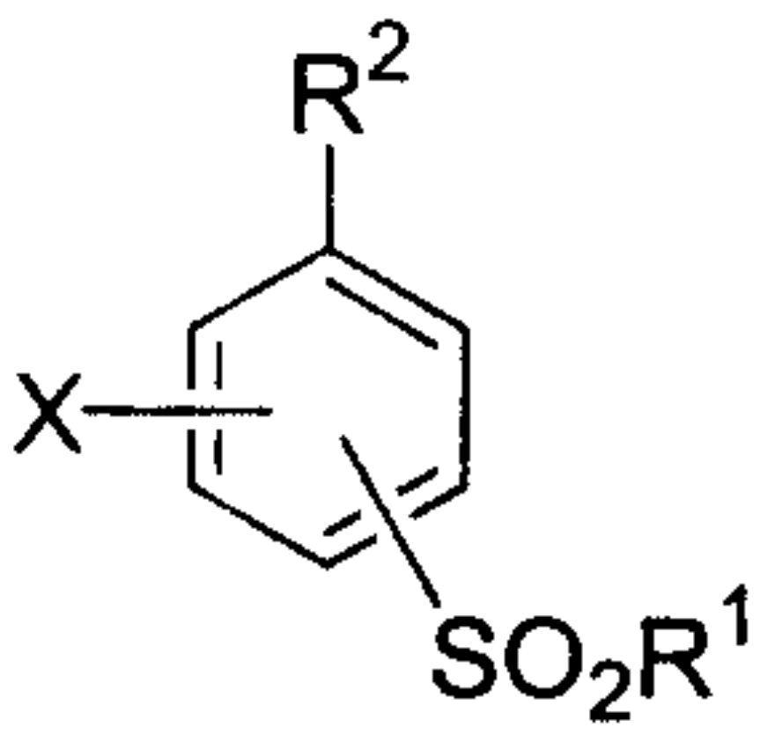
Yield: 223.9 g (93.2 % of theory) of 4-methanesulfonylbenzoic acid; melting point 273 to 274°C.

4) A mixture of 198.3 g (1.0 mol) of 1-propyl-4-tolylsulfone, 7.5 g of $Co(OAc)_2 \cdot 4H_2O$, 2.45 g of $Mn(OAc)_2 \cdot 4H_2O$, 8.1 g of a 10 % strength hydrogen bromide solution in glacial acetic acid and 500 g of glacial acetic acid was oxidized with air at 145 to 150°C under 20 bar in the autoclave described in Example 1. At the end of the uptake of oxygen, 200 g of water were added at 100°C and the mixture was cooled to 20°C while stirring. The crystals were filtered off under a high suction, washed five times with 30 ml of 70 % strength aqueous acetic acid each time and dried at 80°C under 65 mbar in a weak stream of air.

Yield: 189.0 g (82.8 % of theory) of 4-(propane-1-sulfonyl)-benzoic acid; melting point 196 to 198°C.

CLAIMS:

1. A process for the preparation of alkanesulfonylbenzoic acids, comprising oxidising alkanesulfonyl-alkylbenzenes of the formula



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in which R^1 and R^2 are identical or different and are alkyl having 1 to 4 carbon atoms, but R^2 has a meaning other than t-butyl, and X represents H, F, Cl, Br or NO_2, under increased pressure at temperatures above 120°C with molecular oxygen in acetic and/or propionic acid in the presence of a catalyst soluble therein, which contains cobalt ions and bromine ions and, if R^2 has a meaning other than methyl, also manganese ions.

2. A process according to claim 1, wherein the reaction system contains not more than 15% by weight of water.

3. A process according to claim 2, wherein the reaction system contains not more than 5% by weight of water.

4. A process according to any one of claims 1 to 3, wherein acetic acid is used.

5. A process according to claim 4, wherein the acetic acid is in anhydrous form.

6. A process according to any one of claims 1 to 5, wherein cobalt ions and manganese ions are used in a concentration ratio of 1:(0.2 to 3).

7. A process according to claim 6 wherein cobalt ions and manganese ions are used in a concentration ratio of 1:(0.3 to 1.2).

8. A process according to any one of claims 1 to 7 wherein the ratio of the sum of the concentrations of cobalt ions and manganese ions and the concentration of bromine ions is 1:(0.01 to 2).

9. A process according to claim 8, wherein the ratio of the sum of the concentrations of cobalt ions and manganese ions and the concentration of bromine ions is 1:(0.1 to 1).

10. A process according to claim 9, wherein the ratio of the sum of the concentrations of cobalt ions and manganese ions and the concentration of bromine ions is 1:(0.2 to 0.7).

11. A process according to any one of claims 1 to 10, wherein the sum of the concentrations of the two metal ions is 0.01 to 0.2 mol of metal ions per l of liquid phase.

12. A process according to claim 11 wherein the sum of the concentrations of the two metal ions is 0.02 to 0.1 mol of metal ions per l of liquid phase.

13. A process according to claim 12 wherein the sum of the concentrations of the two metal ions is 0.04 to 0.08 mol of metal ions per l of liquid phase.

14. A process according to any one of claims 1 to 13, wherein the oxygen partial pressure is 1.5 to 8 bar.

15. A process according to claim 14, wherein the oxygen partial pressure is 2.4 to 7 bar.

16. A process according to claim 15, wherein the oxygen partial pressure is 2.8 to 6 bar.

17. A process according to any one of claims 1 to 16, wherein the reaction temperature is 120 to 220°C.

18. A process according to claim 17, wherein the reaction temperature is 130 to 180°C.

19. A process according to claim 18, wherein the reaction temperature is 135 to 160°C.

20. A process acccording to any one of claims 1 to 19 further comprising steps wherein a crystalline product which has precipitated is separated off, water formed during the reaction is removed and the remaining mother liquor is reused as the reaction medium.

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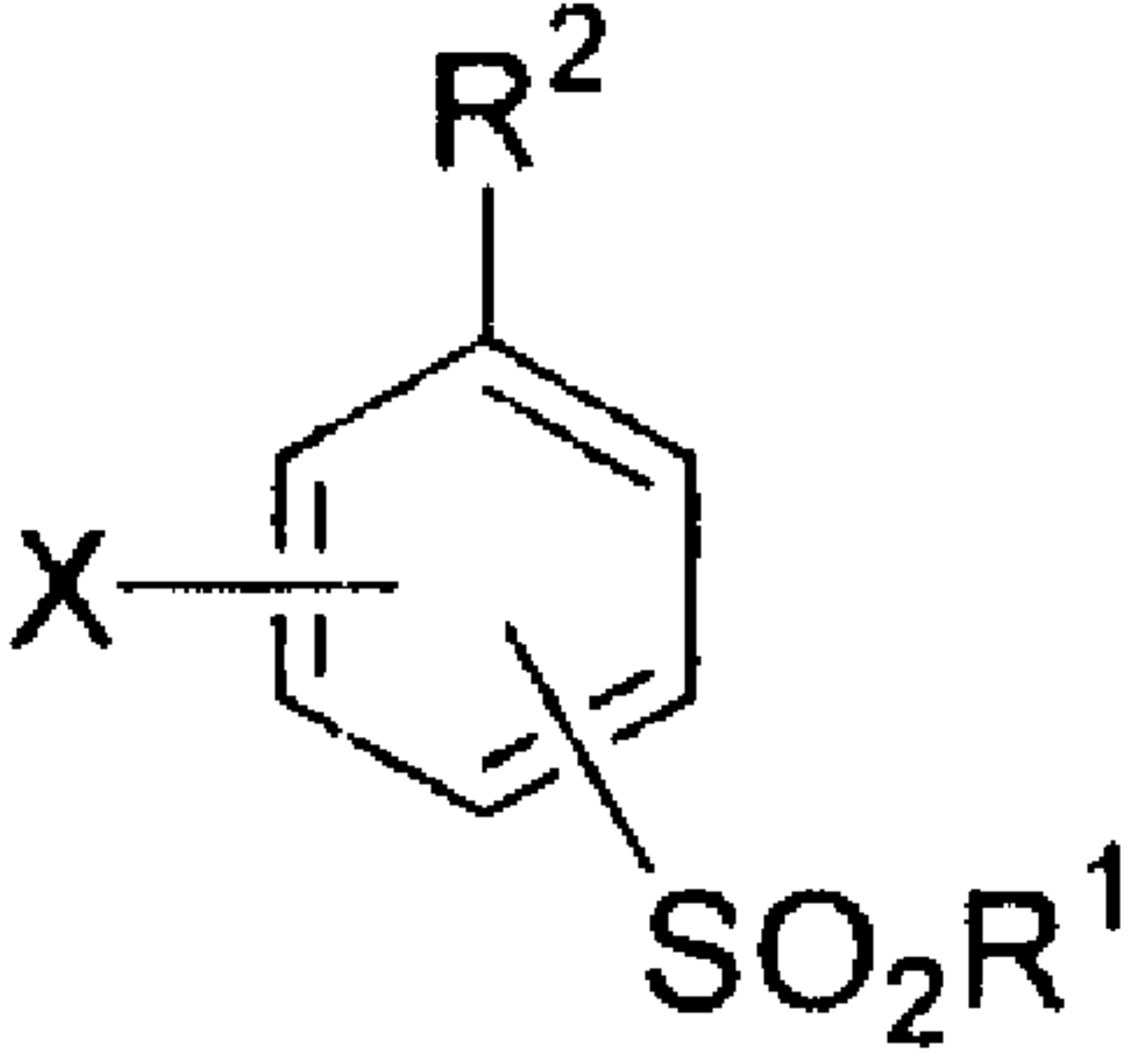
PATENT AGENTS



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