AUSTRALIA

672301

PAT/QUT 28/5/81
Section 29

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: HOECHST AKTIENGESELLSCHAFT

Address: D-65926 FRANKFURT AM MAIN, FEDERAL REPUBLIC OF GERMANY

[70] Nominated Person: HOECHST AKTIENGESELLSCHAFT

Address: D-65926 FRANKFURT AM MAIN, FEDERAL REPUBLIC OF GERMANY

[54] Invention Title: PROCESS FOR PREPARING SULFONATED ARYLPHOSPHINES

[72] Name(s) of actual inventor(s): HELMUT BAHRMANN, PETER LAPPE, WOLFGANG A. HERRMANN, RAINER MANETSBERGER, GUIDO ALBANESE and KLAUS BERGRATH

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of The Atrium, 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: **WM**

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P 43 21 512.2	GERMANY	DE	29TH JUNE, 1993
P 43 44 066.5	GERMANY	DE	23RD DECEMBER, 1993

Basic Applicant(s): HOECHST AKTIENGESELLSCHAFT

Drawing number recommended to accompany the abstract .....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....

Darryl B. Mischlewski

Registered Patent Attorney

DATED this 27th day of June, 1994

M057285 270694

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, HOECHST AKTIENGESELLSCHAFT, of D-65926 Frankfurt am Main, Germany, being the applicant in respect of Application No. 65981/94 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors: Bahrmann, Lappe and Bergrath by virtue of German inventorship law and from the inventors Herrmann, Manetsberger and Albanese by virtue of a contract dated September 15, 1986.

The Person nominated for the grant of the patent is the applicant of the basic applications listed on the patent request form.

The basic applications listed on the request form are the first applications made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

..... 5 August 1996

Karen J. Sinclair

Registered Patent Attorney

AU9465981

(12) PATENT ABRIDGMENT (11) Document No. AU-B-65981/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 672301

(54) Title
PROCESS FOR PREPARING SULFONATED ARYLPHOSPHINES

International Patent Classification(s)
(51)[5] C07F 009/50

(21) Application No. : 65981/94 (22) Application Date : 27.06.94

(30) Priority Data

(31) Number	(32) Date	(33) Country
4321512	29.06.93	DE GERMANY
4344066	23.12.93	DE GERMANY

(43) Publication Date : 12.01.95

(44) Publication Date of Accepted Application : 26.09.96

(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

(72) Inventor(s)
HELMUT BAHRMANN; PETER LAPPE; WOLFGANG A. HERRMANN; RAINER MANETSBERGER; GUIDO ALBANESE; KLAUS BERGRATH

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(57)

It has surprisingly been found that the addition of a Lewis acid to the sulfonation mixture effectively prevents the formation of phosphine oxides. The sulfonation can therefore be carried out at a higher temperature and/or over a longer period of time than without the addition with achievement of a higher degree of sulfonation. Furthermore, a selective removal of phosphine oxides contained in the reaction mixture becomes unnecessary in most cases.

CLAIM

1. A process for preparing sulfonated arylphosphines by sulfonation of aryl-containing mono-, di-, oligo- or polyphosphines with oleum, which comprises carrying out the sulfonation at temperatures between 0 and 80°C in the presence of Lewis acids.

P/00/011 2/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:
Lodged:

Invention Title: PROCESS FOR PREPARING SULFONATED ARYLPHOSPHINES

The following statement is a full description of this invention, including the best method of performing it known to us :-

Process for preparing sulfonated arylphosphines

The invention relates to a process for preparing sulfonated arylphosphines by reaction of arylphosphines with SO_3/H_2SO_4, i.e. a solution of sulfur trioxide in concentrated sulfuric acid (oleum). The novel process avoids side-reactions, in particular the formation of phosphine oxides.

Complex compounds which contain as central atom a metal of group VIII A of the Periodic Table (IUPAC version) and as ligands P(III) compounds such as phosphines and additionally, if desired, further groups capable of complex formation, have in recent years gained increasing importance as catalysts. Thus, the reaction of olefins with synthesis gas to give aldehydes (hydroformylation) which is practiced on a large scale in industry is carried out in the presence of catalysts which comprise cobalt and particularly rhodium and triphenylphosphine. In accordance with the solubility of these catalysts in organic media the reaction proceeds in a homogeneous phase.

Instead of in a homogeneous phase, this reaction, like other stoichiometric and catalytic reactions too, can be carried out in heterogeneous reaction systems. This original development is not limited to complex compounds of metals of group VIII A, but also includes complex compounds of groups VII A and I B of the Periodic Table (IUPAC version) as catalysts. The use of catalysts dissolved in water has the advantage that they can be separated from the water-insoluble reaction product simply and gently.

For example, the process described in DE-C-27 00 904 for the addition of hydrogen cyanide to an unsaturated organic compound having at least one ethylenic double bond is carried out according to this principle. Suitable catalysts for this reaction are nickel/TPPTS [TPPTS is tris(m-sulfophenyl)phosphine], palladium/TPPTS or

iron/TPPTS. According to the process of DE-C-26 27 354, aldehydes are prepared by reaction of olefins with carbon monoxide and hydrogen using rhodium in metallic form or in the form of one of its compounds together with a water-soluble phosphine, for example TPPTS, as catalyst. Further catalysts of the type mentioned and their use in various reactions such as hydrogenations, the allene/alkyne coupling and the amine addition to double bonds are, for example, the subject of EP-A-372 313.

Sulfonated phenylphosphines are obtained by a process described in J. Chem. Soc., 1958, pages 281, 282 by reacting triphenylphosphine with oleum, heating the reaction mixture on a water bath, diluting the reaction product with water and neutralizing with sodium hydroxide. The sodium salt of m-sulfophenyldiphenylphosphine crystallizes from the sulfonation mixture.

Similar processes are also used to obtain disodium salts of di(m-sulfophenyl)phenylphosphine and tri(m-sulfophenyl)phosphine. The starting material in both cases is again triphenylphosphine which is reacted with oleum at temperatures between 18 and 40°C for from 15 to 63 hours. The reaction product is again diluted with water and neutralized with sodium hydroxide, care having to be taken that during the addition of the sodium hydroxide temperatures in the mixture are maintained below 20°C (DE-C-26 27 354).

Apart from monophosphines, sulfonated di- and polyphosphines are also used as components of catalysts. Examples of the preparation thereof are given in DE-A-40 40 314.

A disadvantage of all known processes for obtaining sulfonated arylphosphines is the undesired formation of phosphorus/oxygen compounds, i.e. the oxidation of the trivalent phosphorus to pentavalent phosphorus by sulfur trioxide. The resulting phosphine oxides are not able to

form catalytically active complex compounds with metal ions, and are thus worthless as catalyst components. They are therefore customarily selectively removed from the mixture of the sulfonation products, so as not to excessively burden the catalyst solution with inert materials. To limit the oxidation the sulfonation is carried out at temperatures which are as low as possible. This measure leads to the formation of water-soluble phosphines in which the maximum possible degree of sulfonation and thus the highest achievable solubility in water, which is important for the retention of the metal component of the catalyst system in the water, are not achieved. A more extensive sulfonation by increasing the reaction time has the drawback that the oxidation simultaneously increases.

It is therefore an object of the invention to develop a process which suppresses the oxidation of the phosphines used which accompanies the sulfonation, thus allows higher reaction temperatures and longer reaction times and the use of more concentrated oleum and hence promotes the formation of highly sulfonated products.

The invention provides a process for preparing sulfonated arylphosphines by sulfonation of aryl-containing mono-, di-, oligo- or polyphosphines with oleum. It comprises carrying out the sulfonation at temperatures between 0 and 80°C in the presence of Lewis acids.

It has surprisingly been found that the addition of a Lewis acid to the sulfonation mixture effectively prevents the formation of phosphine oxides. The sulfonation can therefore be carried out at a higher temperature and/or over a longer period of time than without the addition with achievement of a higher degree of sulfonation. Furthermore, a selective removal of phosphine oxides contained in the reaction mixture becomes unnecessary in most cases.

Those skilled in the art are familiar with the term

"Lewis acids". These are molecules or ions which act as electron acceptors. For use in the process of the invention, the group of these is limited to those which are stable in the sulfonating agent and under the sulfonation conditions. Examples of Lewis acids are boron halides, boric acid, the halides of aluminum, phosphorus, antimony, arsenic, iron, zinc and tin. Compounds which have proven particularly suitable in the novel process are boron compounds, preferably boric acid as a readily available, cheap and nontoxic material.

The Lewis acid is used in about equimolar amounts based on the P(III) atoms contained in the phosphine to be sulfonated. A slightly lower amount does no harm, but an excess is preferred. When boric acid is used as Lewis acid it is particularly advantageous to dissolve it to saturation in the oleum. The Lewis acids can be used as a single compound or as a mixture of various compounds.

Starting compounds for the sulfonation are arylphosphines. This general designation comprehends mono-, di-, oligo- and polyphosphines which contain at least one aromatic radical capable of being sulfonated. The aromatic radical can comprise one or more benzene rings which, as in biphenyl, are connected by a single C-C bond or have a plurality of common carbon atoms in their carbon rings (condensed ring systems), as in the naphthyl group. The aromatic radicals can furthermore be singly or multiply substituted, for example by chloro, fluoro, alkyl, alkoxy and nitro groups. Examples of monophosphines which can be sulfonated according to the novel process are dimethylphenyl-, methyldiphenyl- and triphenylphosphine. Examples of the diphosphine group are 2,2'-bis(diphenylphosphinomethyl)biphenyl and 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl. For the purposes of the present invention, phosphines also include compounds of trivalent phosphorus in which the phosphorus atom is part of a ring system. Examples of these classes of compounds are phosphorin substituted by

aromatic radicals, also aryl- and/or alkyl-substituted phospholes and phosphanorbornadienes.

The sulfonation according to the process of the invention can be applied to arylphosphines in commercial form or in the form obtained by synthesis. Special purification is unnecessary unless the use of the sulfonated compounds as catalyst component requires it. The sulfonating agent used is oleum having an SO_3 concentration from 20 to 65% by weight, based on the solution, to which the Lewis acid has advantageously already been added before the introduction of the arylphosphine. The phosphine is added to the solution while maintaining a temperature from -5 to +50°C, preferably from 0 to +40°C, ensuring, for example by stirring, a rapid and uniform distribution of the phosphorus compound in the sulfonating agent to avoid local overheating. Instead of being added as such, the phosphine is preferably mixed with the oleum as a solution in concentrated sulfuric acid, advantageously by adding oleum in portions and while stirring to the solution which also contains the Lewis acid. The molar ratio of SO_3 to phosphine depends on the desired degree of sulfonation. The higher the amount of available SO_3 under otherwise identical reaction conditions, the more sulfonic acid groups are introduced into the phosphine molecule. The actual sulfonation reaction, which follows the dissolution of the phosphine in the oleum, is carried out at temperatures between 0 and 80°C, preferably between 10 and 50°C, likewise with continual stirring to maintain as uniform as possible a temperature in the reaction mixture. The reaction time can be limited to a few minutes, in general it is from a number of hours to a number of days, in special cases even a number of weeks. Raising the reaction temperature and lengthening the reaction time lead, for the same amount of available SO_3, to increased sulfonation of the aryl radicals of the phosphine molecule. It is worth emphasizing that addition of Lewis acids to the sulfonation mixture in accordance with the invention allows substantially free selection of

the decisive reaction parameters, in particular SO_3 concentration, temperature and reaction time, within the limits given above. This is because oxidation as undesired secondary reaction hardly occurs. In this context it has proven useful to monitor the progress of the sulfonation analytically to match the reaction parameters to one another for optimization of the reaction. A suitable sensitive and powerful method for this is ^{31}P-NMR spectroscopy which makes possible the easy differentiation of tertiary phosphines and the phosphine oxides derived therefrom in the reaction mixture.

As soon as the reaction is complete, the reaction mixture is diluted with water and worked up. There are various methods available for this purpose. According to one known procedure, the sulfuric acid solution is first neutralized. Both in the dilution and also in the neutralization care should be taken to ensure that the reaction mixture does not overheat; it has proven useful to maintain temperatures from 0 to 40°C, in particular from 0 to 20°C. The neutralization is carried out using the aqueous solution of an alkali metal hydroxide, preferably of sodium hydroxide. Alkali metal hydroxide concentrations of from 20 to 60% by weight, based on the solution, have proven useful. To achieve as complete as possible a removal of the alkali metal sulfate formed from sulfuric acid and alkali metal hydroxide, it is recommended that the dilution be not too great. Alkali metal sulfate separates out from the neutralized reaction mixture. It is filtered off and washed a number of times with a lower alcohol, preferably a C_1- to C_4-alcohol, in particular methanol. The sulfonated arylphosphine is isolated from the filtrate by removal of the water under gentle conditions, for example by distillation in an oil pump vacuum. For purification, the crystalline product obtained is redissolved in a little water, the solution is admixed with a lower alcohol, preferably a C_1- to C_4-alcohol, in particular methanol, and filtered and the solvent is again gently removed.

According to a preferred process, the acid, aqueous solution of the sulfonation product is extracted with the solution of a water-insoluble amine in a water-insoluble organic solvent. In this way there are obtained sulfonated arylphosphines which are substantially free of the Lewis acids added in the sulfonation step. This method has proven particularly useful when using boric acid as Lewis acid.

In detail, in this workup method the sulfonation mixture is admixed while maintaining the abovementioned temperatures with the amount of water required to dilute the sulfuric acid present to from 0.5 to 50% by weight, preferably from 25 to 35% by weight. To the diluted solution is added the water-insoluble amine dissolved in a water-insoluble organic solvent. The concentration of the amine solution is from 1.0 to 35% by weight, preferably from 10 to 30% by weight and in particular from 13 to 25% by weight of amine, in each case based on the solution.

From 0.5 to 3.0 mol, preferably from 0.5 to 2.5 mol, of amine are used per equivalent of sulfonic acid. The use of excess amine ensures that only small phosphine losses occur. An amine excess higher than that given above is possible, but does not lead to improvement in the result of the separation or purification operation or in the yield.

After intensive mixing, two phases are formed. The aqueous phase, which has a higher specific gravity, contains the sulfuric acid and almost all of the Lewis acid; the organic phase, which is low in sulfate and almost free of Lewis acid, contains the amine salt of the sulfonated phosphine dissolved in the organic solvent. The two phases are separated from one another. The organic phase is reacted with the solution of an inorganic base in water. The base is here used in an amount equivalent to the amount of dissolved amine salt. Excess

base is to be avoided because it contaminates the end product. In this way the aqueous solution of the sulfonated arylphosphine is obtained with recovery of the water-insoluble amine. The amine is available for further use.

The process described can be carried out either batchwise or continuously. The conventional material-separation equipment, such as countercurrent extraction units, is used.

Instead of adding the base dissolved in water all at once to the solution of the amine salt in the organic medium, the addition may, according to a preferred embodiment, be made in portions. This method is successfully used particularly when it is desired to separate a sulfonation mixture which contains products of various sulfonation stages.

Suitable water-insoluble amines used for carrying out the process are water-insoluble homo- and heterocyclic, aliphatic, aromatic, araliphatic and preferably open-chain, branched or unbranched aliphatic amines having from 10 to 60, preferably from 13 to 36, carbon atoms. Less well suited are amines whose salts with the sulfonic acids are insoluble or soluble only to a limited extent in the organic solvent. Examples of particularly useful amines are: tri-n-octylamine, triisooctylamine, tri-2-ethylhexylamine and tridodecylamine.

The amines are dissolved in a water-insoluble organic solvent. Suitable solvents are, in particular, aliphatic or aromatic hydrocarbons or hydrocarbon mixtures, for example toluene or kerosine, in addition also C_4- to C_{20}-alcohols, C_8- to C_{20}-ethers.

Suitable bases for transferring the sulfonated phosphines to the aqueous phase are the hydroxides of the alkali and alkaline earth metals, in particular alkali metal

hydroxide, ammonia, in addition also the alkali metal carbonates.

The workup is advantageously carried out in the range from room temperature to about 40°C. Higher temperatures give no advantages. The statements about the solubility of the amine and the organic solvent in water are here in each case based on the temperatures at which the process is carried out. The end product is either left in the aqueous solution or isolated in solid form by evaporation or by crystallization, decantation or filtration.

The novel process is illustrated in the following examples, but it is not limited to the embodiment described.

Example 1

Sulfonation of triphenylphosphine

5.0 g (81 mmol) of commercial boric acid are dissolved in 50 ml of concentrated sulfuric acid at room temperature in a two-neck flask fitted with dropping funnel. The mixture is stirred further for about 30 minutes in vacuo and argon gas is subsequently passed in. In this way oxidizing gases dissolved in the acid mixture are completely removed. The mixture is then cooled to 0°C, 15 g (57 mmol) of triphenylphosphine are added and the flask is again evacuated. After 15 minutes the phosphine has completely dissolved. Subsequently, under an argon atmosphere, 250 ml of oleum (65% by weight of SO_3) are added dropwise while maintaining a rate of about 6 ml/min and a temperature of the reaction mixture of at most 10°C. After the addition is complete, the mixture is allowed to slowly warm to room temperature and is stirred for a further 10 days. If the reaction mixture solidifies because of the high SO_3 content it can be heated for up to 2 days to at most 43°C.

For the workup, the reaction mixture is poured in an

argon atmosphere onto ice in a 3 l Büchner funnel (or a glass frit). A 10 l round-bottom flask serves as receiver. The whole apparatus is evacuated beforehand for 10 minutes and the ice is thereby degassed. To avoid overheating, care must be taken to ensure that the oleum always drops onto ice and not directly onto water. For this purpose, the level of the aqueous hydrolysate in the funnel (or in the frit) can be lowered at regular time intervals by creating a vacuum in the receiver flask. When the whole mixture is hydrolyzed, the funnel (or the frit) is washed through with 25% strength sodium hydroxide solution and the strongly acid solution in the receiver is neutralized with cooling and intensive stirring. The solution is then evaporated in vacuo on a water bath until considerable amounts of sodium sulfate precipitate. 2 l of methanol are added to this suspension while stirring intensively and the sodium sulfate precipitated in large amounts is subsequently filtered off. The filter residue is washed further three times with 150 ml of methanol each time and the combined filtrates are evaporated to dryness. The residue is then taken up in a minimum amount (about 30 ml) of water and the solution is syringed while stirring into 250 ml of methanol. Precipitated sodium sulfate is again filtered off and the solution is evaporated to dryness in vacuo.

The results of different experiments are summarized in Table I below; experiments 1 to 3 were carried out with addition of boric acid, experiments 4 to 6 without addition of boric acid.

Table I: Sulfonation of triphenylphosphine

Experiment No.	SO_3 in H_2SO_4 (% by wt.)	Temp.	Reaction time	Oxide formation	Proportion of tri-substituted phosphine (%)
1	42	RT*	72 h	none	50
2	42	RT	24 h	none	50
3	65	RT,48h:43°C	18 d	none	85
4	40	RT	42 h	considerable	<10
5	65	RT	18 h	moderate	ca. 20
6	65	RT	72 h	complete	<5

* RT = room temperature

The experiments show that in the presence of boric acid there is no formation of oxide at room temperature, 42% by weight of SO_3 in the oleum and 72 hours' reaction time (Experiment 1), while under similar conditions without addition of boric acid considerable amounts of oxide are formed after only 42 hours (Experiment 4). Even more drastic are the differences when using oleum containing 65% by weight of SO_3. Even after a reaction duration of 18 days, 2 days of which are at 43°C, there is no formation of oxide in the presence of boric acid (Experiment 3); in comparison, the starting material is completely oxidized after only 72 hours if no boric acid has been added.

Example 2

Sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene (NAPHOS)

5.0 g (81 mmol) of boric acid are dissolved in 50 ml of concentrated sulfuric acid at room temperature in a two-neck flask fitted with dropping funnel. The mixture is stirred further for about 30 minutes in vacuo and argon gas is subsequently passed in. In this way oxidizing gases dissolved in the acid mixture are completely removed. The mixture is then cooled to 0°C, 7.5 g of

NAPHOS (11.5 mmol) are added and the flask is again evacuated. After about 15 minutes the phosphine has completely dissolved. Subsequently, under an argon atmosphere, 150 ml of oleum (65% by weight of SO_3) are added dropwise while maintaining a rate of about 3 ml/min and a temperature of the reaction mixture of at most 10°C. After the addition is complete, the mixture is allowed to slowly warm to room temperature and is stirred for a further 60 hours. If the reaction mixture solidifies because of the high SO_3 content, the mixture can be heated for a short time to 35°C to ensure thorough mixing.

For the workup, the reaction mixture is poured in an argon atmosphere onto ice in a 3 l Büchner funnel (or a glass frit). A 10 l round-bottom flask serves as receiver. The whole apparatus is evacuated for 10 minutes and the ice is thereby degassed. To avoid overheating, care must be taken to ensure that the oleum always drops onto ice and not directly onto water. For this purpose, the level of the aqueous hydrolysate in the funnel (or on the frit) can be lowered at regular time intervals by creating a vacuum in the receiver flask. When the whole mixture is hydrolyzed, the funnel (or the frit) is washed through with 25% strength sodium hydroxide solution and the strongly acid solution in the receiver is neutralized with cooling and intensive stirring. The solution is then evaporated in vacuo on a water bath until considerable amounts of sodium sulfate precipitate. 1 l of methanol is added to this suspension while stirring intensively and the sodium sulfate precipitated in large amounts is subsequently filtered off. The filter residue is washed further three times with 75 ml of methanol each time and the combined filtrates are evaporated to dryness. The residue is then taken up in as small as possible an amount (about 15 ml) of water and the remaining sodium sulfate is removed by means of gel chromatography on Sephadex G-15.

The results are shown in Table II.

Table II: Sulfonation of NAPHOS

Experiment	SO_3 in H_2SO_4 (% by wt.)	Temp.	Reaction time (h)	Oxide formation	Degree of sulfonation
1	25	43°C	12	none	
2	25	70°C	24	complete	
3	60	RT*	60	5 %	>6
4	40	RT	96	5 %	
5	25	43°C	12	15 %	
6	25	43°C	48	25 %	

* RT = room temperature

Example 3

a) Sulfonation of NAPHOS

200 g of concentrated sulfuric acid are charged under a nitrogen atmosphere into a 1 l flask fitted with stirrer, thermometer, dropping funnel and condenser and admixed with 26.1 g (422.3 mmol) of boric acid. After complete dissolution of the solid, 27.7 g (42.6 mmol) of NAPHOS are added to the solution. The mixture is stirred for 1 hour at room temperature and subsequently 550.7 g (4474 mmol) of oleum (65% strength) are added dropwise over a period of 30 minutes. The homogeneous reaction mixture is then stirred for 72 hours at room temperature.

For the workup, the sulfonation mixture (804.5 g) is added under nitrogen protection to a 6 l flask containing 3195.1 g of water at about 10°C. During the addition the internal temperature is maintained between 15 and 25°C by intensive cooling.

The hydrolysis mixture (3999.6 g) containing 0.65% (= 420.7 mmol) of boric acid is subsequently extracted with different mixtures of triisooctylamine (TIOA) and toluene.

b) Extraction

950 g of the hydrolysis mixture containing 99.9 mmol of boric acid are extracted for 2 hours at room temperature with the amounts of TIOA/toluene described in Table III below.

Table III

Experiment	TIOA (g)	Toluene (g)	TIOA/toluene (parts by weight)	TIOA/NAPHOS* (mol)
3.1	53.6	536.0	1 : 10	15 : 1
3.2	53.6	375.2	1 : 7	15 : 1
3.3	53.6	214.4	1 : 4	15 : 1
3.4	35.7	357.0	1 : 10	10 : 1

* NAPHOS: Starting material for BINAS

The aqueous waste acid phases obtained after phase separation have the following boric acid contents (Table IV):

Table IV

Experiment	Waste acid (g)	Boric acid (mmol)	Boric acid (% of I*)
3.1	926.1	99.3	99.4
3.2	926.1	98.3	98.4
3.3	926.0	97.9	98.0
3.4	931.4	98.8	98.9

* I: amount of boric acid used

Example 4

In accordance with the method of Example 3, 10.1 g (15.5 mmol) of NAPHOS and 7.6 g (123 mmol) of boric acid are dissolved in 66.8 g of concentrated sulfuric acid and

subsequently admixed with 221.5 g (1800 mmol) of oleum (65% strength). After 2 hours' reaction time at room temperature, the sulfonation mixture (306.0 g) is hydrolyzed with 1300.0 g of water; the boric acid content of the hydrolysis mixture (1606.0 g) is 0.47% (= 122 mmol).

The hydrolysis mixture is extracted for 1 hour at room temperature with a solution of 82.1 g (233 mmol) of TIOA in 821.0 g of toluene. The waste acid phase obtained after phase separation contains 7.4 g (120 mmol) of boric acid.

The organic phase is gradually admixed with 1.5% strength sodium hydroxide solution while simultaneously measuring the pH with a commercial glass electrode. The aqueous sodium salt solution of the sulfonation mixture obtained in the pH range up to 3.5 is separated off and discarded.

The desired product fraction obtained in the pH range from 3.5 to 11.1 and containing 0.22 mmol of boric acid can be used without further purification as a component of a catalyst system for hydroformylation.

Example 5

Example 4 was repeated except that a reaction time of 6 hours was used, affording 1606.0 g of hydrolysis mixture containing 0.47% (= 122 mmol) of boric acid.

After working up as in Example 4, the waste acid phase contains 7.5 g (121 mmol) of boric acid. Just 0.14 mmol of boric acid are found in the desired product fraction (pH range from 3.5 to 11.1).

Example 6

a) Sulfonation of triphenylphosphine

1281.0 g (4.00 mol of SO_3) of oleum (25% strength) are charged under a nitrogen atmosphere into a 1 l flask

fitted with stirrer, thermometer, dropping funnel and condenser and admixed with 79.1 g (1.28 mol) of boric acid. After complete dissolution of the solid, 83.6 g (0.32 mol) of triphenylphosphine are added to the solution. The homogeneous reaction mixture is stirred for 48 hours at room temperature.

For the workup, the sulfonation mixture (1443.7 g) is added under nitrogen protection to a 6 l flask containing 2866.2 g of water at about 10°C. During the addition the internal temperature is maintained between 15 and 25°C by intensive cooling.

The hydrolysis mixture (4309.9 g) containing 1.8% (= 1276 mmol) of boric acid is subsequently extracted with different mixtures of TIOA and toluene.

b) Extraction

800 g of hydrolysis mixture containing 237 mmol of boric acid are extracted for 1 hour at 40°C with the amounts of TIOA/toluene described in Table V below.

Table V

Experiment	TIOA (g)	Toluene (g)	TIOA/toluene (parts by weight)	TIOA/TPP (mol)
6.1	75.8	303.4	1 : 4	1 : 3.6
6.2	94.8	379.2	1 : 4	1 : 4.5
6.3	75.8	530.6	1 : 7	1 : 3.6
6.4	75.8	758.0	1 : 10	1 : 3.6

The aqueous waste acid phases obtained after phase separation have the following boric acid contents (Table VI):

Experiment	Waste acid (g)	Boric acid (mmol)	Boric acid (% of I)
6.1	753.5	225	94.9
6.2	753.6	226	95.4
6.3	755.7	228	96.2
6.4	756.9	230	97.0

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing sulfonated arylphosphines by sulfonation of aryl-containing mono-, di-, oligo- or polyphosphines with oleum, which comprises carrying out the sulfonation at temperatures between 0 and 80°C in the presence of Lewis acids.

2. The process as claimed in claim 1, wherein the sulfonation of the arylphosphine is carried out at temperatures between 10 and 50°C.

3. The process as claimed in claim 1 or 2, wherein the sulfonation is carried out by adding oleum to a solution of arylphosphine and Lewis acid in concentrated sulfuric acid.

4. The process as claimed in any one of claims 1 to 3, wherein the Lewis acid is a boron compound.

5. The process as claimed in claim 4, wherein the boron compound is boric acid.

6. The process as claimed in any one of claims 1 to 5, wherein the Lewis acid is used in at least a molar amount based on the P(III) atoms contained in the arylphosphine to be sulfonated.

7. The process as claimed in any one of claims 1, 2, 3, 5 and 6, wherein sulfonation is carried out using a solution of arylphosphine in concentrated sulphuric acid saturated with boric acid.

8. The process as claimed in any one of claims 1 to 7, wherein the sulfonation mixture is diluted with water and the aqueous solution obtained is extracted with the solution of a water-insoluble amine in a water-insoluble organic solvent, using from 0.5 to 3 mol of the amine per chemical equivalent of

sulfonic acid, the organic phase is separated off and brought into intimate contact with the aqueous solution of a base, after which the aqueous phase is separated off and the sulfonated arylphosphine is isolated therefrom.

9. The process as claimed in claim 8, wherein the sulfonation mixture is, while maintaining a temperature between 0 and 40°C, in particular 0 and 20°C, admixed with the amount of water required to dilute the sulfuric acid present to from 0.5 to 50% by weight, preferably from 25 to 35% by weight.

10. The process as claimed in claim 8 or 9, wherein from 0.5 to 2.5 mol of amine are used per chemical equivalent of sulfonic acid.

11. The process as claimed in ~~one or more~~ any one of claims 8 to 10, wherein the concentration of the amine in the amine solution is from 1.0 to 35% by weight, preferably from 10 to 30% by weight and in particular from 13 to 25% by weight, in each case based on the solution.

12. The process as claimed in ~~one or more~~ any one of claims 8 to 11, wherein the water-insoluble amines are open-chain, branched or unbranched aliphatic amines having from 10 to 60, preferably from 13 to 36, carbon atoms.

13. The process as claimed in claim 12, wherein the amine is tri-n-octylamine, triisooctylamine, diisooctylamine, tri-2-ethylhexylamine or tri-dodecylamine.

14. The process as claimed in ~~one or more~~ any one of claims 8 to 13, wherein the water-insoluble organic solvent is an aliphatic or aromatic hydrocarbon or a hydrocarbon mixture.

15. The process as claimed in claim 14, wherein the solvent is toluene or kerosine.

DATED this 27th day of June 1994.

HOECHST AKTIENGESELLSCHAFT

WATERMARK PATENT & TRADEMARK ATTORNEYS
"THE ATRIUM"
290 BURWOOD ROAD
HAWTHORN. VIC. 3122.

Frankfurt, January 19, 1994
PAT/rcht-sei Hoe93/Y008K

Hoechst Aktiengesellschaft, 65926 Frankfurt

Abstract

The sulfonation of arylphosphines, i.e. mono-, di-, oligo- and polyphosphines which contain at least one aromatic radical capable of being sulfonated, is carried out according to the invention in the presence of a Lewis acid. The novel process avoids side-reactions, in particular the formation of phosphine oxides. In working up the sulfonation mixture the Lewis acid can be removed together with the sulfuric acid.