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(54) **PROCEDE POUR L'ALKYLATION DE PHOSPHORE ELEMENTAIRE**

(54) **METHOD FOR ALKYLATING ELEMENTAL PHOSPHOR**

(57) L'invention concerne un procédé pour la préparation de sels alcalins et/ou alcalino-terreux des acides alkylphosphoniques et des acides dialkylphosphiniques à partir de phosphore jaune élémentaire et d'halogénures d'alkyle, caractérisé en ce que la réaction s'effectue en présence d'hydroxyde alcalin ou alcalino-terreux aqueux ou de mélanges de ceux-ci. L'invention concerne également l'utilisation des composés préparés selon ce procédé pour la fabrication d'agents ignifuges, de produits d'extraction et de produits phytosanitaires.

(57) The invention relates to a method for producing alkali and/or alkaline-earth salts of alkylphosphonous acids and dialkylphosphinic acids from elemental yellow phosphor and alkyl halides, characterised in that the reaction takes place in the presence of aqueous alkali or alkaline-earth hydroxide or mixtures thereof. The invention also relates to the use of the compounds obtained according to the inventive method for producing flameproofing agents, extracting agents and plant protection agents.

Process for alkylating elemental phosphorus

Abstract

The invention relates to a process for preparing alkali metal salts and/or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids from elemental yellow phosphorus and alkyl halides, which comprises carrying out the reaction in the presence of aqueous alkali metal hydroxide or alkaline earth metal hydroxide or mixtures thereof.

The invention likewise relates to the use of the compounds prepared by the process of the invention to prepare flame retardants, extraction media and plant protection compositions.

Process for alkylating elemental phosphorus

The invention relates to a process for preparing alkali metal salts and/or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids from elemental yellow phosphorus and alkyl halides.

Organic phosphorus compounds are becoming of increasing industrial importance. They are principally used to prepare herbicides or as herbicide themselves, as extraction media and as flame retardants. The starting materials used are preferably PH_3 and phosphorus halides, which must in turn be prepared from yellow phosphorus.

To date, only a few processes are known by which organic phosphorus compounds having more than one phosphorus-carbon bond may be prepared from simple starting materials.

The reaction of red phosphorus in the superbasic medium dimethyl sulfoxide/potassium hydroxide (DMSO/KOH) with acetylenes or olefins as alkylating agents (Trofimov et al., Phosphorus, Sulfur and Silicon 55, 271, 1991) preferentially gives triorganylphosphines and triorganylphosphine oxides.

Alkylating red phosphorus with acrylonitrile predominantly leads, under the abovementioned

conditions with ultrasonic treatment of the reaction mixture, to secondary phosphine oxide. If 1,1-diphenylethylene is used, this produces tertiary phosphine oxide (30%), secondary phosphine oxide (10%) and phosphinic acid (35%) [D. Semenzin et al., Tetrahedron Letters 35, 3297, 1994].

An attempt has also been made (Trofimov et al., Main Group Chem. News 4, 18, 1996, Phosphorus, Sulfur and Silicon, 109/110, 601, 1996) to react elemental phosphorus, in its red modification, with alkyl halides in the presence of potassium hydroxide, water, dioxane and a phase-transfer catalyst. Tertiary phosphine oxides were found as main products (up to 75% with benzyl bromide, about 60-65% with butyl bromide). Secondary phosphine oxides and phosphinic esters were produced at 19% and 6%, respectively, as by-products, but the former only in the presence of zinc powder as reducing agent.

However, the abovementioned processes have the disadvantage that the red phosphorus or organophosphorus intermediates must be prepared first of all. These processes are highly complex industrially and thus are also not economical; the products produced must frequently be purified further, which is laborious. Just the specific preparation of certain compounds in a high yield is frequently particularly difficult.

Considerably more favorable, therefore, would be a synthesis which starts from elemental yellow phosphorus and which, using further, readily industrially available starting materials, would lead in a simple manner to the desired alkali metal salts or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids.

The object therefore underlying the invention is to provide a process for preparing alkali metal salts and/or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids which avoids the abovementioned disadvantages and by which the desired end products can be prepared without problem and in the appropriate mass ratios.

This object is achieved by a process of the type described at the outset, which comprises carrying out the reaction in the presence of aqueous alkali metal hydroxide or alkaline earth metal hydroxide or mixtures thereof.

Preferably, the reaction is carried out in a two-phase system of aqueous alkali metal hydroxide or alkaline earth metal hydroxide or mixtures thereof and an organic solvent.

Preferably, as alkyl halides, use is made of methyl chloride or methyl bromide.

Preferably, as organic solvents, use is made of unbranched or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible, or only partially water-miscible, alcohols or ethers, alone or in combination with one another.

Particularly preferably, as organic solvent, use is made of toluene, alone or in combination with alcohols.

Preferably, the reaction is carried out in the presence of a phase-transfer catalyst.

Preferably, the phase-transfer catalyst is tetraalkylphosphonium halides, triphenylalkylphosphonium halides or tetraorganylammonium halides.

Preferably, the temperature in the reaction is from -20 to +60°C.

Particularly preferably, the temperature is from 0 to 30°C.

Preferably, the reaction is carried out at a pressure of from 0 to 10 bar.

Preferably, the process according to the invention is carried out in such a manner that the yellow phosphorus is suspended in a solvent or a solvent mixture and then reacted with alkyl halide and a compound of the formula MOH or $M'(OH)_2$ or mixtures thereof, where M is an alkali metal and M' is an alkaline earth metal.

Preferably, the yellow phosphorus and the alkyl halide are reacted with one another in a molar ratio of from 1:1 to 1:3, the molar ratio of yellow phosphorus to the compound of the formula MOH or $M'(OH)_2$ being from 1:1 to 1:5.

Preferably, the two-phase system obtained after the reaction is separated and processed further as aqueous phase.

The invention also relates to the use of the alkali metal salts and/or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids prepared in accordance with the invention to prepare flame retardants, extraction media and plant protection compositions.

Surprisingly, it has been found that elemental yellow phosphorus, according to the process of the invention, may be reacted with alkyl halides in the two-phase system (organic solvent/aqueous alkali metal hydroxide) and with or without a (phase-transfer) catalyst, under

extremely mild conditions to form a product mixture which comprises, as main product, the salt of the corresponding alkylphosphonous acid RP(:O)HOH. Further technically useful phosphorus-containing products found are salts of hypophosphorous and phosphorous acid, in addition to the equally valuable salt of dialkylphosphinic acid $R_2P(:O)OH$.

Small amounts of trialkylphosphine oxide $R_3P(:O)$, dialkylphosphine oxide and unidentified phosphorus compounds can also be formed in conjunction which are removed from the product mixture in the conventional manner. In addition, as a by-product, hydrogen is formed, which can be separated off without problem from the reaction mixture.

Surprisingly, according to the process of the invention, neither phosphine (PH_3), nor alkylphosphines (RPH_2, R_2PH), are formed in significant amounts. By choosing suitable reaction conditions, such as adding small amounts of alcohols to the organic phase, the formation of all unidentified phosphorus-containing by-products is minimized to a surprisingly small extent of a few mol% of the yellow phosphorus used, to the benefit of the three main products, namely the salts of alkylphosphonous acid, hypophosphorous acid and phosphorous acid.

The process according to the invention can be carried out, for example, in such a manner that the solvent is introduced together with the phase-transfer catalyst and, if appropriate, heated above the melting point of the yellow phosphorus, then the elemental (yellow) phosphorus is added, the mixture is cooled with vigorous stirring to temperatures of, for example, from -10 to +30°C, and then the alkyl halide is added.

The reaction is started by adding alkali metal hydroxide solution. After completion of the reaction, the reaction system can be diluted, for example with water, and then the readily volatile components (H_2, PH_3, RPH_2, R_2PH and excess alkyl halide) are removed.

By this means an aqueous/organic two-phase system is produced, whose phases are separated. The constituents from the phases are determined by analysis.

The aqueous phase can be worked up by the known processes of the prior art to produce the pure acids, such as alkylphosphonous acid, for example (such as by ion exchange or distillation).

In the abovementioned reaction, mixtures of alkali metal hydroxides and alkaline earth metal hydroxides can also advantageously be used, in order to separate off phosphite formed in the reaction, as $Ca(HPO_3)$ for example.

The reaction partners can also be added in a different sequence, for example by introducing these continuously in the abovedefined molar ratio into a reactor (pressurized tube, pressurized reactor or cascade) and discharging them again from the reactor after residence times of from 0.5 to 2 h. The organic phase obtained after the phase separation, which still comprises the majority of any phase-transfer catalyst used, is expediently recycled.

Example 1

2 l of toluene and 25 g (0.05 mol) of tributylhexadecylphosphonium bromide were introduced into a 5-liter stainless steel pressurized reactor and heated to approximately 60°C. 62 g (2 mol) of molten yellow phosphorus were introduced into the reactor and then cooled with vigorous stirring to 0°C. 151 g (3 mol) of methyl chloride were then condensed in.

At 0°C, 600 g of a 56% strength KOH solution (6 mol KOH) were pumped in in the course of one hour. The heat of reaction was removed by cooling the reactor jacket and the temperature in the reactor interior during the addition time was kept to from 0 to +2°C. After a post-reaction time of one hour at 0°C, the mixture was warmed to room temperature and the entire batch diluted with 1 l of water.

The reactor was expanded via a combustion system, the resulting hydrogen, excess methyl chloride and traces of gaseous phosphines (PH_3, $MePH_2$) being burnt. The residue obtained was two homogeneous liquid phases which no longer contained any yellow phosphorus. The phases were drained off separately and analyzed by ^{31}P-NMR spectroscopy.

	aqueous phase mol% phosphorus
Trimethylphosphine oxide	2.3
Dimethylphosphinic acid potassium salt	0.5
Methylphosphonous acid potassium salt	64.2
Phosphorous acid potassium salt	15.8
Hypophosphorous acid potassium salt	14.2
Unidentified compounds	3.1

Example 2

The procedure of Example 1 was followed, but the reaction temperature was 25°C.

Analysis:

	aqueous phase mol% phosphorus
Trimethylphosphine oxide	2.5
Dimethylphosphinic acid potassium salt	18.0
Methylphosphonous acid potassium salt	54.4
Phosphorous acid potassium salt	13.3
Hypophosphorous acid potassium salt	6.0
Unidentified compounds	5.7

Example 3

500 ml of diethylene glycol diethyl ether, 13 g (0.026 mol) of tributylhexadecylphosphonium bromide and 93 g (1 mol) of n-butyl chloride were introduced into a 2 liter stirred flask. To this solution was added a solution of 150 g of NaOH (3.75 mol) in 150 g of water at room temperature.

15.5 g (0.5 mol) of molten yellow phosphorus were added dropwise in the course of 1 hour at 0°C to the vigorously stirred two-phase mixture. After a further reaction time of 3 h, the two clear phases were separated and the resulting reaction products were characterized by ^{31}P-NMR spectroscopy:

	aqueous phase mol% phosphorus
Butylphosphonous acid sodium salt	41
Hypophosphorous acid sodium salt	3
Phosphorous acid sodium salt	56
Unidentified compounds	< 0.5

Example 4

A 5 L stainless steel pressurized reactor was charged with a solution of 26.1 g (0.05 mol) of tributylhexadecylphosphonium bromide in 1000 mL of toluene and this initial charge was preheated to 60°C. Following the addition of 62 g (2 mol) of yellow phosphorus, the mixture was cooled to -10°C with thorough stirring and then 202 g (4 mol) of methyl chloride were condensed in. Subsequently, 400 g of 50% strength aqueous sodium hydroxide solution were metered in over the course of 2 hours, the temperature being held at -10°C. 400 g of water were added over the course of one hour, and then stirring was continued for an hour, the mixture was heated to room temperature and then the reactor was expanded via a combustion system. Two homogenous liquid phases were obtained, which were separated and analyzed.

The aqueous phase (weight: 920 g) contained 65.6 mol% of methylphosphonous acid, 14.9 mol% of phosphorous acid and 13.7 mol% of hypophosphorous acid, and

2.8 mol% of dimethylphosphinic acid in the form of their sodium salts.

Example 5

A 5 L stainless steel pressurized reactor was charged with a solution of 29 g (0.05 mol) of tetraoctyl-phosphonium bromide in 1000 mL of toluene and this initial charge was preheated to 60°C. Following the addition of 62 g (2 mol) of yellow phosphorus, the mixture was cooled to -10°C with thorough stirring and then 202 g (4 mol) of methyl chloride were condensed in. Subsequently, the mixture was warmed to 20°C and 400 g of 50% strength aqueous sodium hydroxide solution were metered in over the course of 2 hours, the temperature being held at 20°C. 400 g of water were added over the course of one hour, and then stirring was continued for an hour, the mixture was warmed to room temperature and then the reactor was expanded via a combustion system. Two homogenous liquid phases were obtained, which were separated and analyzed.

The aqueous phase (weight: 940 g) contained 51.2 mol% of methylphosphonous acid, 24.7 mol% of phosphorous acid and 18.5 mol% of hypophosphorous acid, and 2.6 mol% of dimethylphosphinic acid in the form of their sodium salts.

The acids may be prepared in a known manner, for example by ion exchange, from the salts prepared in Examples 1 to 5.

Process for alkylating elemental phosphorus

Patent Claims

1. A process for preparing alkali metal salts and/or alkaline earth metal salts of alkylphosphonous acids and dialkylphosphinic acids from elemental yellow phosphorus and alkyl halides, which comprises carrying out the reaction in the presence of aqueous alkali metal hydroxide or alkaline earth metal hydroxide or mixtures thereof.

2. The process as claimed in claim 1, wherein the reaction is carried out in a two-phase system of aqueous alkali metal hydroxide or alkaline earth metal hydroxide or mixtures thereof and an organic solvent.

3. The process as claimed in claim 1 or 2, wherein, as alkyl halides, use is made of methyl chloride or methyl bromide.

4. The process as claimed in one or more of claims 1 to 3, wherein, as organic solvents, use is made of unbranched or branched alkanes, alkyl-substituted aromatic solvents, water-immiscible, or only partially water-miscible, alcohols or ethers, alone or in combination with one another.

5. The process as claimed in one or more of claims 1 to 4, wherein, as organic solvent, use is made of toluene, alone or in combination with alcohols.

6. The process as claimed in one or more of claims 1 to 5, wherein the reaction is carried out in the presence of a phase-transfer catalyst.

7. The process as claimed in claim 6, wherein the phase-transfer catalyst is tetraalkylphosphonium halides, triphenylalkylphosphonium halides or tetraorganylammonium halides.

8. The process as claimed in one or more of claims 1 to 7, wherein the temperature in the reaction is from -20 to +60°C.

9. The process as claimed in one or more of claims 1 to 8, wherein the temperature is from 0 to 30°C.

10. The process as claimed in one or more of claims 1 to 9, wherein the reaction is carried out at a pressure of from 0 to 10 bar.

11. The process as claimed in one or more of claims 1 to 10, wherein the yellow phosphorus is suspended in a solvent or a solvent mixture and then reacted with an alkyl halide and a compound of the formula

MOH or $M'(OH)_2$ or mixtures thereof, where M is an alkali metal and M' is an alkaline earth metal.

12. The process as claimed in one or more of claims 1 to 11, wherein the yellow phosphorus and the alkyl halide are reacted with one another in a molar ratio of from 1:1 to 1:3, the molar ratio of yellow phosphorus to the compound of the formula MOH or $M'(OH)_2$ being from 1:1 to 1:5.

13. The process as claimed in one or more of claims 1 to 12, wherein the two-phase system obtained after the reaction is separated and processed further.