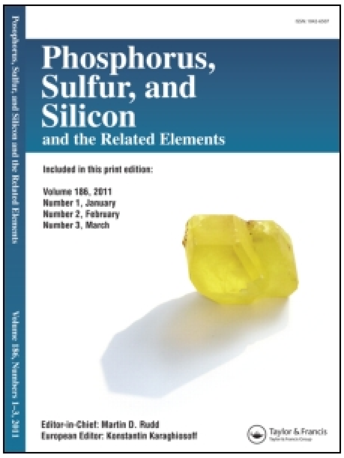

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PRODUCTION OF ORGANOPHOSPHORUS COMPOUNDS FROM HYDROGEN PHOSPHIDE

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Abstract Technical processes for the production of PH_3 and for its radical induced addition to nonactivated olefins are detailed. The influence of the reaction conditions chosen on the selectivity of the PH_3/Olefin-reaction is discussed.

HYDROGEN PHOSPHIDE AS A REAGENT

As a reactive molecule, PH_3 is able to add to a variety of double bonds.[1,2] In the following, only one special case shall be picked out: The addition of PH_3 to nonactivated carbon-carbon double bonds. It has been discovered already in the fifties, that PH_3 adds by a radical mechanism to olefins in the style of an anti-Markownikow-reaction. Meanwhile, azo-initiators, especially azobisisobutyronitrile, have 'become accepted generally for radical generation.

TECHNICAL PROCESS FOR THE PRODUCTION OF PH_3

With regard to the development of an industrial chemistry of PH_3 derivatives, it was of decisive importance to find appropriate processes for the production of PH_3 in sufficiant quantities and quality. Two methods, the so called acid and the alkaline disproportionation of elementary phosphorus have prevailed. The chemistry of the Hoechst process[3] which is used on an industrial scale since the end of the seventies, is described approximately by equation (1):

$$5\ PH_3 + 18\ NaOH + 15\ H_2O \xrightarrow{\text{Alcohol}} 5\ PH_3 + 3\ H_2 + 12\ NaH_2PO_2 + 3\ Na_2HPO_2 \quad (1)$$

By a skillful control of the reaction PH_3 and H_2 are not formed simultaneously, but largely in two separate reactors. According to Hoechst process, PH_3 is obtained continuously with a purity of at least 95 % by volume.

INDUSTRIAL CHEMISTRY OF HYDROGEN PHOSPHIDE

Apart from the production of Tetrakis-(hydroxymethyl-)-phosphonium salts by the addition of PH_3 to formaldehyde in acid aqueous solutions, there are, as far as we know, only radical initiated addition reactions of PH_3 with olefinic double bonds that are carried out on an industrial scale:

$$PH_3 + R^1R^2C{=}CR^3R^4 \xrightarrow[\text{pressure}]{I^\bullet} H_nP(CR^1R^2{-}CR^3R^4H)_{3-n} \quad (2)$$

$$n = 0,1,2$$

As indicated in eq. (2) the formation of primary, secondary, and tertiary phosphines may take place. Whether one, two or three bonds linking P to C are formed depends primarily on the nature of the olefin used, in particular to the steric space requirement of the alkyl group attached to the phosphorus atom. The selectivity of the reaction can be influenced to a lesser extend by the choice of appropriate reaction conditions.

Tertiary Phosphines

It is well known, that linear α-Olefins react with PH_3 in a stoichiometric ratio >3 and under pressure to form trialkylphosphines in very good yields.[2] Triethyl-, tributyl-, and trioctylphosphine are products which are obtained in technical quantities by this route. The process is carried out continously in stainless steel pressure-reactors of appropriate volume to ensure a sufficient residence time of the reactants. The conversion rate of PH_3 to trialkylphosphines is excellent (>96 %).

Primary and Secondary Phosphines from PH_3

Even with a high stoichiometric excess of PH_3 the reaction with linear α-Olefins in a pressure vessel furnishes a mixture of prim., sec. and tert. phosphines (figure (1)). However, if the reaction is carried out in a pressure pipe maintaining short residence times, high temperatures and high pressures, the formation of tert. and sec. phosphines is repressed in favour of a higher amount of prim. phosphine (fig. (1), dotted line).

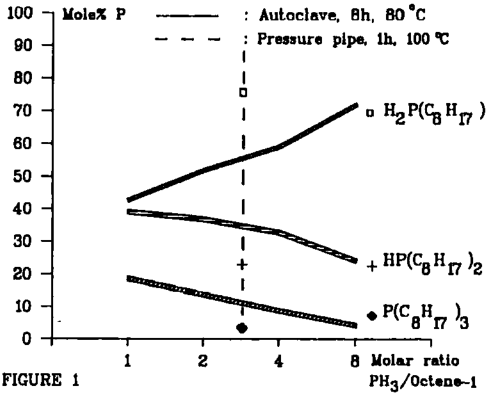

FIGURE 1

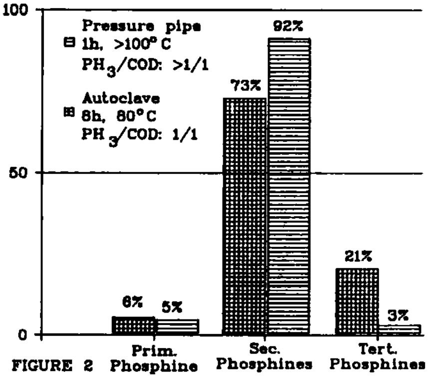

FIGURE 2

Reacting PH_3 with cyclic, branched or β-olefins, tertiary phosphines are formed to a minor extent, in special cases not at all. Addition of PH_3 to cyclohexene (excess), dicyclopentadiene and 1,5-cyclooctadiene (COD) furnishes sec. phosphines in high yield.[4,5] The reaction of PH_3 with COD leads to the formation of the isomeric products 9H-9phosphabicyclo[3.3.1]-resp.[4.2.1]-

nonane. The latter reaction is carried out in a pressure pipe with excess PH_3, which is recycled, short residence times, under a pressure of more than 100 bars and at high temperatures. In figure (2) the resulting product distribution is compared with that of a batch process in an autoclave, where the content of desired sec. phosphine is much lower.

Only a few prim. phosphines can be prepared selectively by synthesis from PH_3/olefin. Two of these exceptions are sec.-butylphosphine and monocyclohexylphosphine. The latter is produced with a high degree of selectivity by reacting an excess of PH_3 with cyclohexene in a pressure pipe.[5] In this case, too, it is advantageous to apply short reaction times, high pressures and temperatures.

OUTLOOK

The availability of organophosphorus products in commercial quantities opens up a large field for the synthesis of interesting compounds. In the already existing application areas for phosphororganics (e.g. ligands in catalysts, extraction agents, flame retardants, phase-transfer-catalysts) new and more powerful products can be manufactured (e.g. by addition of prim. or sec. phosphines to olefins containing functional groups). Chances are, that in the course of this development new application areas will be discovered.

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