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ORGANOHALOPHOSPHANES AND THEIR DERIVATIVES - STATE OF CHEMISTRY AND TECHNOLOGY

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INTRODUCTION

Organohalophosphanes of the formula RPX_2 or R_2PX are valuable intermediates for a variety of downstream organophosphorous compounds. The most important RPX_2 -representatives are

- methyldichlorophosphane, CH_3PCl_2 ,
- phenyldichlorophosphane, $C_6H_5PCl_2$

both of which are commercially available.

METHYLDICHLOROPHOSPHANE

is readily available from methane and phosphorus trichloride by homogeneously catalysed gas phase reaction.



Hoechst AG has developed and brought to technical maturity and reliability a process for the manufacture of methyldichlorophosphane which is operated in a plant with a capacity of 2000 metric tons per annum.

According to the scheme to be discussed, phosphorous trichloride, methane and carbon tetrachloride are reacted at temperatures above 500°C and under pressure. The residence time is very short. To increase the selectivity of the reaction and to minimize the formation of by-products, methane is introduced in excess and the partial conversion of PCl_3 is limited to approximately 20%.

The reaction mixture is quenched with liquid reaction product and cooled by multi-step condensation down to minus temperatures. This separates lower boiling components, e.g. unreacted methane and hydrogen chloride, from the higher boiling ingredients such as methyldichlorophosphane, unconverted PCl_3 , and residues. The gaseous reactants are cleaned, dried and recycled after addition of fresh methane.

The higher boiling part of the reaction product is separated by distillation into residues - to be burned - and a liquid fraction. This liquid is separated into its components in a highly efficient tray-column. After replacement of the PCl_3 and CCl_4 portions consumed, the phosphorous trichloride is recycled to the PCl_3 -evaporator whilst methyldichlorophosphane with a purity of 98.7% is obtained as overhead-product of a second column. The yield of MePCl_2 is approximately 90%.

All liquid streams have a more or less pronounced tendency to deposit solid matter. This problem has been overcome by using special additives which allow the operation of evaporators, columns and condensers over service periods of years.

PHENYLDICHLOROPHOSPHANE

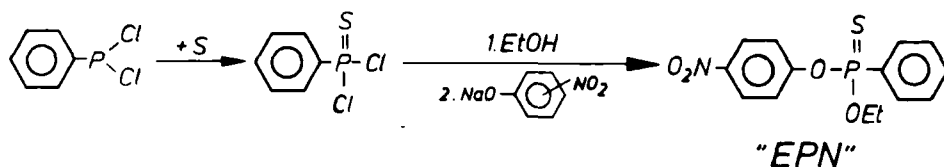
is produced by Stauffer Corp. using a gas phase process starting with benzene and phosphorous trichloride.

The capacity of Stauffer's plant is said to be 2500 tons per year. The possibility of PCB-formation in the course of this process may cause problems.

An alternative route used by Eastman and Ferro Corporation uses the Friedel-Crafts type reaction between benzene and PCl_3 , in the presence of AlCl_3 .

Methyldichlorophosphane is a colourless liquid which may be distilled without decomposition but which is extremely sensitive to moisture. As a highly reactive intermediate it has been used as a building block for a series of different reactions, several of which have technical importance. Hoechst AG developed two commercial processes using methyldichlorophosphane as an access to flame-retardant compounds or to herbicides, respectively. The chemical background and the processes for the production of phospholane - to be used in the production of flame-retardant polyesters, Trevira CS[®] and to methanephosphonous acid esters - to be used for the synthesis of herbicides, BASTA[®] - will be discussed in detail.

Phenyldichlorophosphane has been used for the production of the insecticide "EPN" (ethyl-p-nitrophenyl phenyl phosphonothionate) by Stauffer.



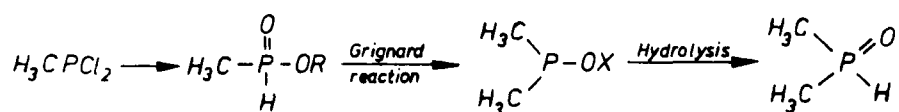
Today approximately 450 tons per year of benzenephosphonous acid are produced by hydrolysis of the appropriate dichloride. Benzenephosphonous acid is used as a condensation catalyst, stabiliser and as a dyeing aid for Nylon 66.

The compounds of the Type R_2PX are not so easily accessible as the derivatives RPX_2 . The preparation of dimethylchlorophosphane $(CH_3)_2PCl$, which is obtained along with methyldichlorophosphane on reacting vaporised phosphorous with methyl chloride in the presence of activated carbon, has not yet been commercialised.

The disproportionation of methyldichlorophosphane at higher temperatures also fails to yield dimethylchloro-

phosphane. Although the literature claims the alkylation of PCl_3 with lead tetraalkyls or alkyl aluminium compounds, no commercial application of this reaction exists so far.

Therefore, derivatives of $(\text{CH}_3)_2\text{PCl}$ have to be manufactured by indirect methods. Dimethylphosphane oxide, a well suited access to these indirect methods, is obtained in accordance with the following reaction sequence:



Methane phosphonous acid esters have become commercially available products; different derivatives are interesting intermediates, e.g. for the preparation of agrochemicals. Diphenylchlorophosphane is used as an intermediate for UV-stabilisers, polymerisation catalysts and other specialities. Derivatives of diphenylchlorophosphane are e.g. diphenylalkoxy phosphanes - prepared by reacting diphenylchlorophosphane with alkali metal alcoholates. They are used for the manufacture of photo initiators.