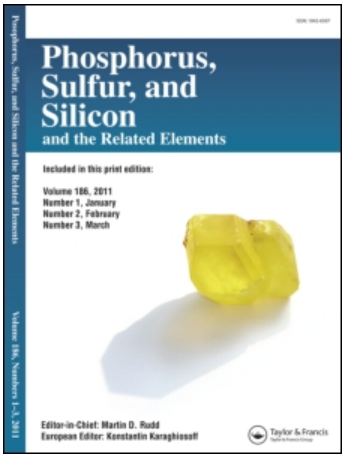

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Methyldichlorophosphine, a Versatile Starting Material for Flame Retardants and Performance Chemicals

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A status report on the chemistry of methyldichlorophosphine derivatives is given with regard to their technical and semi-technical production and application. New applications for oxaphospholane as a flame retardant are shown. The synthesis as well as the flame retardant properties of the aluminium salt of methylethyl-phosphinic acid are described.

Keywords: Methylphosphonous dichloride; flame retardant; phosphinic acid derivatives

INTRODUCTION

As one of the simplest organophosphorus compounds, methyl dichlorophosphine (methylphosphonous dichloride, MPC) has attracted the interest of many scientists in the field of phosphorus chemistry, both academic or industrial. A comprehensive review was published by Weissermel et al.[1]. A status report regarding the technology of synthesis of MPC and its chemistry as well as some derivatives is given by Cornils[2].
It is the aim of this paper to report the current status of MPC-derivatives, that are of technical interest, and to introduce promising new developments in this field; many of them are related to non-halogenated flame retardants as ecologically friendly alternatives to existing halogen based products.

2-METHYL-2,5-DIOXO-1-OXA-2-PHOSPHOLANE (OXAPHOSPHOLANE)

MPC was commercialised by Hoechst AG in 1986, based on a process described by Pianfetti and Quin[3]. The plant is now operated by the Hoechst affiliate AgrEvo. The majority of MPC is converted to the herbicide BASTA®, but a significant amount is used for the production of oxaphospholane, that was brought to technical maturity at the end of the 80s, and is now operated by Clariant. The synthesis of oxaphospholane is achieved by the following steps[4] (see Fig. 1):

- reaction of MPC **1** with acrylic acid and formation of the intermediate chloroformyl-ethyl-methylphosphinic acid chloride
- cyclisation with acetic acid anhydride with formation of two equivalents of acetyl chloride and oxaphospholane
- two-step purification by means of vacuum-stripping and rectification of the crude oxaphospholane

- solvolysis of purified oxaphospholane by adding ethylene glycole in a ratio 1:1 by weight, leading to a mixture of carboxyethyl phosphinic acid esters

The resulting product is mainly used by reactive incorporation into the polymerization process of PET-polyester to achieve a product, that is inherently flame retarded after being processed to fibres (e.g. Trevira®CS).

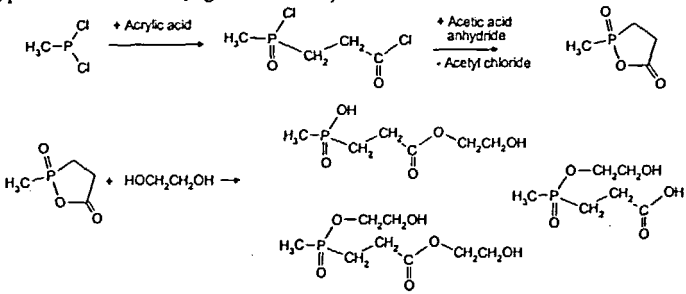


FIGURE 1: Process for the production of Oxaphospholane FR

OTHER FLAME RETARDANT APPLICATIONS OF OXAPHOSPHOLANE

Oxaphospholane can be used to achieve flame retardancy for unsaturated polyester and epoxy resins[5]. In the case of polyester resins, a polymer is made from maleic anhydride, phthalic acid, oxaphospholane and 1,2 propanediol (see Fig. 2). The incorporation of phosphorus gives inherent flame-retardant materials, which can be used in transport applications like the interior of waggons or trams.

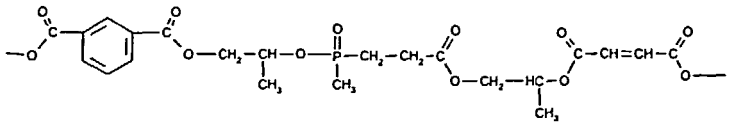


FIGURE 2: Structure of phosphorus modified unsaturated polyester resins

In epoxy resins, oxaphospholane is incorporated into a low molecular weight epoxy resin by reacting some of the epoxy groups with the acid groups of the phospholane (Fig. 3). To make printed circuit boards, the phosphorus modified epoxy resin is dissolved in methylethylketone and cured by catalysts like dicyandiamide. The flame retardancy specification UL 94 V-0 is passed at a phosphorus content of 3%. Then resins show a good long-term stability and a sufficient glass transition temperature.

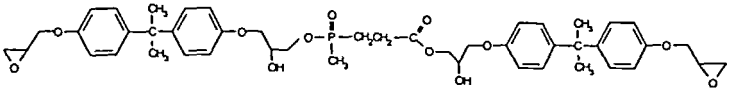


FIGURE 3: Structure of phosphorus modified epoxy resins

MPC AS A STARTING MATERIAL FOR PERFORMANCE CHEMICALS

Meanwhile, there are some derivatives of MPC, that are available in semi-technical scale, especially compounds 3, 4, and 5 (see Fig. 4):

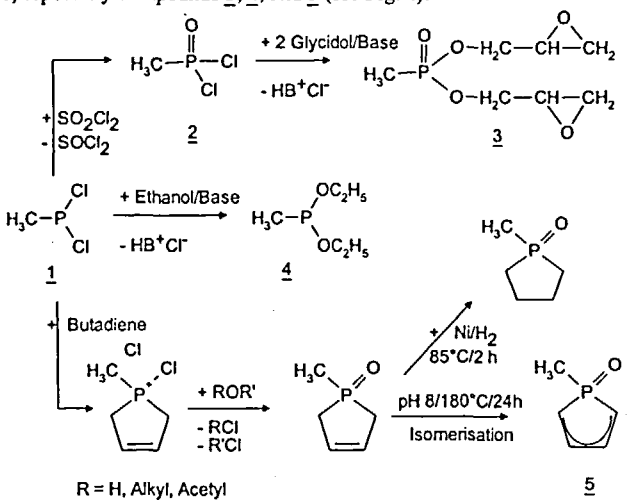


FIGURE 4: Some derivatives of methyldichlorophosphine

Among the various possibilities to oxidize MPC to methylphosphonic acid dichloride 2, the use of sulfuryl chloride has the advantage to furnish the desired product in good yields by a safe, easily controllable process. Thionyl chloride is readily distilled off with other light ends. 2 is reacted with glycidol to methylphosphonic acid bis-(glycidyl)ester 3, which is applied again as a reactive flame retardant for epoxy resins.

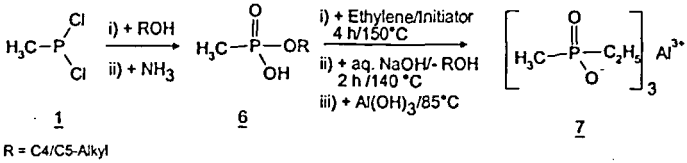
The esterification of MPC with ethanol leads to the appropriate methylphosphonous acid ester 4, that is of special interest as an intermediate for pharmaceuticals.

The reaction of MPC with dienes is well known (McCormack-reaction[6]). Thus, with butadiene an intermediate chlorophospholenium chloride is formed, that is further reacted with oxygen-releasing compounds like water, alcohols or anhydrides to form methyl-1-oxophospholene-3, which can be isomerised thermally to a liquid mixture of phospholene oxides 5. This product is a highly effective catalyst for the manufacture of carbodiimides, that are used for the production of thermoplastic polyurethanes and polyester fibres. If applied in di-isocyanates and in more than catalytic amounts, polycarbodiimide resins that are inherently flame retardent can be obtained.

Hydrogenation of 5 by means of Ni/H_2 leads to the saturated phospholane oxide in clean reaction. One of the exciting properties of this compound is the surprisingly high dielectricity constant of 53, which makes it of interest as a polar aprotic solvent.

MPC: STARTING MATERIAL FOR A NOVEL FLAME RETARDANT

By alcoholysis of 1, the monoalkylphosphinic acid ester 6 is readily available. This product, which is also a precursor for the production of BASTA®, can be converted to the dialkylphosphinic acid ester by reaction with ethylene under radical initiation conditions[7]. After hydrolysis of the ester, the aluminium salt of methyl-ethylphosphinic acid 7 (MEPAL) is precipitated by adding aluminium hydroxide or aluminium salts like $AlCl_3$ or $Al_2(SO_4)_3$ to the reaction mixture (Fig. 5):



1 6 7

R = C4/C5-Alkyl

FIGURE 5: Synthesis of MEPAL

In polyesters, especially glass fibre reinforced polybutylene terephthalate (PBT), MEPAL serves as an effective flame retardant. Thus, MEPAL is the only non-halogenated alternative to brominated flame retardants, known so far, to fulfill the requirements of UL94 test (V-0)[8]. Table 1 shows some data, that prove the superior properties of MEPAL in PBT:

Polymer	MEPAL [% by wt.]	FR 1025 [% by wt.]	UL 94 (0,8 mm)	LOI [%]
Celanex 2300 GV1/30			n.c.[1)]	21
Celanex 2300 GV1/30	20		V-0	49
Celanex 2360 GV1/30 FL[2)]		>15	V-0	30

TABLE 1: PBT-compounds containing 30 % glas fibers.
1) not classified; 2) brominated flame retardant + Sb_2O_3

Acknowledgements
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