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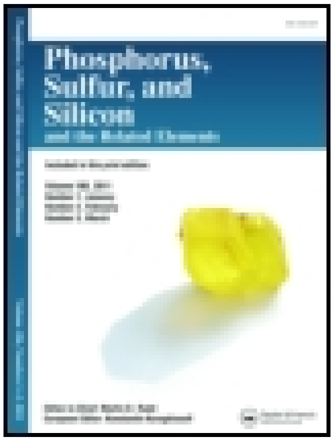

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Formation of Methylphosphonous Acid by Alkylation of Yellow Phosphorus

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FORMATION OF METHYLPHOSPHONOUS ACID BY ALKYLATION OF YELLOW PHOSPHORUS

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Methylphosphonous acid is a key intermediate in the synthesis of phosphinic acid salts, a new class of halogen-free flame retardants. This paper describes a novel and simple synthesis of this synthon: By alkylation of elemental yellow phosphorus with methyl chloride under phase-transfer conditions, methylphosphonous acid alkali salt is formed as the main product. Most of the by-products were identified. The mechanism of the reaction is discussed.

Keywords: Alkylation; phase-transfer catalysis; two-phase system; yellow phosphorus

In 1979 Sandler[1] reported for the first time the flame-retarding effect of salts of the dialkylphosphinic acid for technical thermoplastics like polyesters and polyamides. However, only a few years ago Kleiner[2] discovered that the aluminum salt of methyl-ethylphosphinic acid showed excellent flame retardancy in these polymers. Trying to find an economically feasible route of synthesis for salts of methyl-ethylphosphinic acid, a process was developed that started from methyldichlorophosphine, which is commercially available.[3] Since it was necessary to find an even less expensive process for this class of compounds, a route of synthesis was developed that was based on methylphosphonous acid as a key substance. The subsequent synthetic steps, like the addition of ethylene and precipitation of aluminum salt, are also innovative, but are not treated here.[4]

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ALKYLATION OF P_4 UNDER PHASE-TRANSFER CONDITIONS

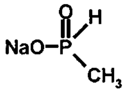
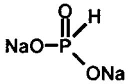
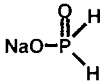
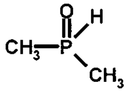
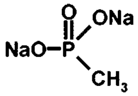
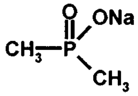
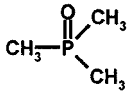
In 1991 Trofimov et al.[5,6] described the alkylation of red phosphorus under phase-transfer (PT) conditions [KOH, water, dioxane, PT catalyst (PTC)] with alkyl- and benzylhalogenides, which resulted in a yield of 65–72% of the corresponding trialkylphosphinoxides. However, when we reacted yellow phosphorus with alkylhalogenides in a two-phase system (aqueous alkali, organic solvent/PTC) we obtained the corresponding alkylphosphonous acids and their sodium salts respectively at yields of 65–75% based on the amount of phosphorus. The qualitative and quantitative result of the reaction is mostly independent of the base used (NaOH, KOH), on the akylation reagent (alkylchloride, -bromide, dialkylsulfate), and the PTC (phosphonium-, ammonium-quat). Catalysts with relatively long alkyl chains generally produce better yields from alkylphosphonous acids than catalysts with short-chain quats. Over a temperature range of -10°C to more than $+30^\circ$C the reaction progression is mostly independent of temperature. With increasing temperature, higher concentrations of di- and trialkylated products are found. The proportion of oxidated products and unidentified side-products increases as well.

We now focus on the reaction of methyl chloride under PTC conditions, because this reaction allows a simple and inexpensive route to methyl phosphonous acid from which mentioned salts of methyl phosphonous acid can be obtained in turn.

This reaction requires intensive dispersion and mixing of the reaction components, because there is a multiphase reaction system (solid, liquid organic, aqueous liquid, gas). Otherwise, exchange processes at phase boundaries would become limiting for the reaction rate. First yellow phosphorus is added to the reactor, with the aprotic nonpolar solvent containing the PTC. The yellow phosphorus is heated above its melting point and subsequently finely dispersed by cooling to the desired process temperature. This will also lead to a partial dissolution of the yellow phosphorus in the organic solvent. Next, an amount of methyl chloride equivalent to the amount of phosphorus is added under pressure. Further addition of an aqueous alkali hydroxide solution starts an exothermic reaction. Even though methyl chloride is consumed in the reaction, the overall pressure increases because of the released hydrogen.

Table I shows the molar ratios of phosphorus-containing reaction products in the aqueous phase (average values of a series of experiments). Besides the added catalyst, the organic phase contains only minor amounts of phosphines [mainly CH_3PH_2, some $(CH_3)_2PH$, no PH_3].

TABLE I Products of the PT-Catalyzed Alkylation of Yellow Phosphorus (Aqueous Phase)

Product	Formular	Yield (%)	Oxidation state
Methylphosphonous acid (sodium salt)	 **1**	72	+1
Phosphorous acid (disodium salt)	 **2**	8	+3
Hypophosphorous acid (sodium salt)	 **3**	7.5	+1
Dimethylphosphine oxide	 **4**	5	−1
Methylphosphonic acid (disodium salt)	 **5**	3.5	+3
Dimethylphosphinic acid (sodium salt)	 **6**	0.5	+1
Trimethylphosphine oxide	 **7**	1	−1
Unknown compounds and diphosphorus compound **8**		2.5	

The formation of most of the products can be explained by known mechanisms in a straightforward manner. With the help of the PTC, hydroxide ions are transported to the yellow phosphorus, which is dissolved in the organic phase. These hydroxide ions undertake a nucleophilic attack, resulting in the formation of phosphide ions, which renders the deeply red color of the reaction mixture. The phosphide ions can now react either with methyl chloride to form a P—C bond or with water to form a P—H bond and another hydroxide ion (see Figure 1).

On the one hand, oxidation products like methylphosphonate and sodium phosphite can be formed via this successive degradation of the P_4 tetrahedrons. On the other hand, they can be formed from the sodium salt of methylphosphonous acid, respectively the hypophosphite, by

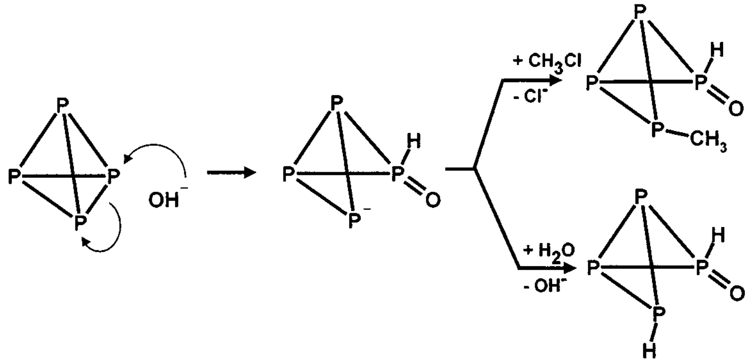
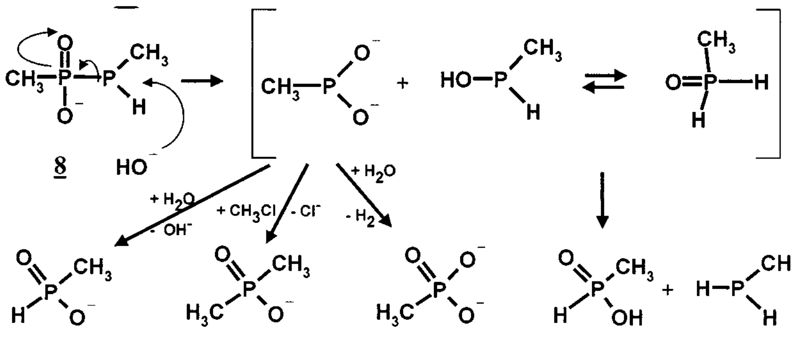


FIGURE 1 First steps of P_4 cleavage reaction in the presence of methyl chloride.

base-catalyzed oxidation of P—H compounds[7] accompanied by release of hydrogen. The formation of trimethylphosphine oxide **7** might be the successor of the intermediate $(CH_3)_2P{-}O^-$, which reacts with methyl chloride by loss of chloride to phosphinic acid methyl ester. This in turn rearranges to the more stable tertiary phosphine oxide. The analogous reaction with water would lead to dimethylphosphine oxide, which is also observed.

Despite major analytical efforts, for the time being only one product with a P—P bond could be detected during the reaction: $CH_3PH{-}P({:}O)(OH)CH_3$ **8**, as its sodium salt. The cleavage of the P—P bond in **8** by hydroxide ions is assumed to proceed as depicted in Figure 2.

The phosphine part of **8** (δ_P: -109.7, ${}^1J_{PP} = 129.6$ Hz, ${}^1J_{PH} = 209.3$ Hz) reacts to the stable end products methylphosphine and



1 **6** **5** **1**

FIGURE 2 Suggested process for the cleavage of **8**.

methylphosphonic acid via the fairly instable primary phosphine oxide $CH_3P(:O)H_2$. The sodium salt of methylphosphonous acid **1** is a result of the reaction of the oxidized part (δ_P: +51.4, $^1J_{PP} = 129.6$ Hz) with water. Oxidation by release of hydrogen will produce **5**, whereas a methylation after rearrangement will yield the dimethylphosphinate **6**.

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