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ORGANOSILICON COMPOUNDS CONTAINING PHOSPHORUS
(Kremiyorganicheskiye soedineniya, soderzhashcheye fosfor)

by

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Translated from
Plasticheskiye massy
No. 4, 1962.
pp. 16 - 19

by

Scripta Technica, Inc.
1000 Vermont Avenue, N.W.
Washington, D.C.

May 1963

BUREAU OF SHIPS - NAVY DEPARTMENT - WASHINGTON 25, D.C.
ORGANOSILICON COMPOUNDS CONTAINING PHOSPHORUS

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Silicon phosphororganic compounds have many valuable properties which attract the researcher's attention.

In recent years, this class of compounds has also become important in applied chemistry. Organo-silicon phosphates are being used as hydraulic liquids and lubricants, plasticizers, antifoaming agents and flame arresters.

The simplest way of introducing phosphorus into a molecule of polyorganosiloxane is by heating polysiloxane oil, obtained by hydrolysis of dimethyl- and diethyldichlorosilane in water\(^1\), with phosphorus pentoxide. Solid or oily products are thus obtained which are, in our opinion, silicon phosphoroorganic polymers containing the bond

\[
\begin{align*}
\text{P}_2\text{O}_5 + 4\text{HOSi} & \rightarrow \\
\text{SiO}_2 \text{P} & \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

Certain polymers resembling these have found practical applications. Articles made of them are very strong\(^2\).

The reaction of difunctional alkylalkoxysilanes with \(\text{P}_2\text{O}_5\) produces solid polymers, as follows\(^3\):\(^4\):

\[
3nR_2\text{Si(OR)}_2 + n\text{P}_2\text{O}_5 \rightarrow [\text{Si}_3\text{P}_2\text{O}_8\text{R}_2]_n + 3n\text{R}_2\text{O}
\]

(2)
Trifunctional alkylalkoxysilanes react with \( P_2O_5 \) as follows:

\[
2nRSi(O'R')_3 + nP_2O_5 \rightarrow [RSi(O'R')_3OP_2O_5OSi(O'R')_3]_n + R'O
\]

(3)

The corresponding polymers, which are solids, are separated.

The reaction of chloromethyldimethylethoxysilane or dichloromethyldimethylethoxysilane with phosphorus pentoxide at 200 - 210° gives rise to polymers corresponding to the structures:

\[
[(\text{CH}_3)_2\text{Si} - \text{O} - \text{P} - \text{O} - \text{P} - \text{O} - \text{Si} - (\text{CH}_3)_2\text{Si}]_n
\]

(4)

and

\[
[(\text{CH}_3)_2\text{ClSi} - \text{O} - \text{P} - \text{O} - \text{P} - \text{O} - \text{Si} - (\text{CH}_3)_2\text{ClSi}]_n
\]

(5)

By refluxing for two hours 0.1 mole of hexaalkyldisiloxane and 0.5 mole of phosphorus pentoxide, tris(trialkylsilyl) phosphates, which are viscous, colorless, sufficiently heat-stable liquids (when \( R = \text{CH}_3 \) and \( \text{C}_2\text{H}_5 \)) are obtained in 80% yield.

If hexaalkyldisiloxane and phosphorus pentoxide are taken in equimolar quantities, tris(trialkylsilyl) phosphate is obtained:

\[
P_2O_5 + 3R_2SiOSiR_3 \rightarrow 2[R_2SiO]_3PO
\]

(6)
If, however, excess phosphorus pentoxide is added, a solid polymer, trialkylsilylpyrophosphate, is chiefly obtained:

\[
nR_3SiOSiR_3 + nP_2O_5 \rightarrow 2[R_3Si(\equiv O\equiv O)_n]
\]  

(7)

On heating with hexaalkyldisiloxane, this metastable compound can be converted into tris(trialkysilyl) phosphate:

\[
[R_3SiP(\equiv O\equiv O)_n] + n[R_3SiO]_3PO \rightarrow n[R_3SiO]_3PO
\]  

(8)

It has also been found possible to obtain tris(trialkysilyl) phosphates by the reaction of trialkyalkoxy- or trialkylchlorosilane with phosphoric acid, and also with trialkyl phosphate\(^8\).

Chlorides of silicophosphoric acids, containing the \(-\text{Si}--\text{O}--\text{P}=\) bond, which can be used to prepare organosilicon polymers with phosphorus in the end groups, have also been described\(^9,10\). These compounds have proven unstable to hydrolysis\(^11\). In all cases, the hydrolysis takes place primarily at the \(-\text{Si}--\text{O}--\text{P}=\) bond, irrespective of whether monomeric silicophosphates or polymers are subjected to hydrolysis:

\[
R_3SiOP(\text{OR})_n + \text{HOH} \rightarrow R_3SiOH + \text{HO-}P' \text{OR}'
\]  

(9)

The stability to hydrolysis increases somewhat if the organic radical of the silicon atom is replaced by a trialkylsilyl group. But even these compounds can hydrolyze in several minutes\(^12\).

By reacting trialkylchlorosilane with sodium dialkyl phosphate,

\[
R_3SiCl + Na\equiv P(\text{OR})_n \rightarrow R_3Si\equiv P(\text{OR})_n + \text{NaCl}
\]  

(10)

several silicon phosphororganic compounds have been obtained\(^13,14\) which contain the
A study was made of the reaction of sodium or potassium hydrophosphide with trialkylfluorosilane with the aim of investigating the heteroorganic compounds in which silicon is linked directly to phosphorus:

\[
4(CH_3)SiF + 5KPH \rightarrow [(CH_3)_3Si]_2P + [(CH_3)_3Si]_2P + KF + 3PH_3
\]  

(11)

The structure of the substances obtained is confirmed by the formation of phosphine and hexamethyldisiloxane in hydrolysis with water or an aqueous solution of alkali, as in the equation:

\[
2(CH_3)_2SiP + H_2O \rightarrow 2PH_3 + 6(CH_3)_2SiOH \rightarrow 3(CH_3)_2SiOSi(CH_3)_3
\]  

(12)

As shown by the works cited above, the \(-\text{Si-P-}\) bond is still less stable to hydrolysis than the \(-\text{Si-O-P-}\) bond.

Thus, the alcoholysis of bis(\(n\)-butyl)trimethylsilyl phosphate occurs readily in the presence of alcohol or even phenol. This compound reacts rather easily with aniline and \(n\)-butylamine, and also with \(n\)-butyl mercaptan.

As we know, esters of thiophosphoric acid are much more stable to hydrolysis than those of phosphoric acid. In order to examine the effect of the introduction of sulfur on the stability to hydrolysis of compounds containing the \(-\text{Si-O-P-}\) bond, condensed sulfur-containing products with the structural units

\[
\text{\(-\text{Si-O-P-}, \quad \text{\(-\text{Si-S-P-}, \quad \text{\(-\text{Si-N-P-}\)}}
\]

(13)

were synthesized and their properties investigated.

All the prepared esters of silicothiophosphoric acid hydrolyze easily. Neither the introduction of a second sulfur atom nor the creation of the \(-\text{Si-P-}\) bond has shown any positive effect on the stability to hydrolysis.

A description has been given of the synthesis of organosilicon esters of dithiophosphoric acid, which were obtained by the reaction of vinylalkylsilanes and allylalkylsilanes with dialkylidithiophosphoric acids.
The most stable substances are organosilicon phosphates containing the \(-\text{Si}--\text{C}--\text{P}--\) bond. In most cases, such substances are obtained by Grignard reactions.

In the reaction of \(p\)-trimethylsilylphenylmagnesium bromide with phosphorus trichloride, \(p\)-trimethylsilylphenylphosphine and a certain amount of \(p\)-trimethylsilylphenylchlorophosphine were obtained. The same reaction with phosphoryl chloride leads to the formation of \(p\)-trimethylsilylphenylphosphine oxide. These substances are recommended as antifoaming agents, flame arresters, plasticizers, lubricating oils and as additives.

Solid phosphine oxides \([(\text{CH}_3)\text{SiCH}_2]\text{P=O}\) and \(\left[\text{I} \text{CIC(R)}\text{SiCH}_2\right]\text{P=O}\) are obtained from \((\text{CH}_3)\text{SiCH}_2\text{MgCl}\) and phosphoryl chloride in ether. The same reaction of phosphoryl chloride with \(\text{n-CIC(CH}_3)\text{SiCH}_2\text{MgCl}\) yields only bis(p-chlorophenyl(dimethyl)silyl) phosphonic acid.

Phosphorus-containing polysiloxanes are similarly obtained by the reaction of dialkyl- or diarylphosphorus chloride with a Grignard reagent prepared from a haloarylsiloxane.

A number of organosilicon phosphates have been synthesized by the action of dialkyl phosphates on substituted vinyl-, allyl- and cyclohexenylsilanes in the presence of organic peroxides acting as initiators.

\[
(\text{CH}_3)_2(\text{C}_4\text{H}_5\text{O})\text{SiCH} = \text{CH}_2 + \text{HP(OCH}_3\text{H})_3 \xrightarrow{\text{trot., } (\text{OC}_3\text{H}_5\text{O})_2} (\text{CH}_3)_2(\text{OC}_3\text{H}_5\text{H})\text{SiCH}_2\text{CH}_2\text{P(OCH}_3\text{H})_3
\]

Substances thus obtained are hydrolyzed at the \(-\text{Si}--\text{C}--\text{P}--\) bond only with hydrochloric acid, forming the corresponding phosphonic acid. No cleavage of the \(-\text{Si}--\text{C}--\text{P}--\) bond was observed when other acids or alkalis were used.

The organosilicon phosphates used as hydraulic fluids and lubricants have been obtained by the reaction of phenyl dichlorophosphine and hydroxyalkylsilane in the presence of an acceptor of hydrogen chloride such as pyridine.

Other methods of preparing silicon phosphororganic compounds containing the \(-\text{Si}--\text{C}--\text{P}--\) bond are also known.
The copolymerization of 1,3-diene hexaorganosiloxanes having the general formula

\[
\text{R} \quad \text{R} \\
\text{CH}_2\text{CR'}-(\text{CH}_2)_n-\text{Si}-\text{O}-\text{Si}-(\text{CH}_2)_n-\text{CR'}=\text{CH}_2
\]

(15)

with alkylphosphines in the presence of catalysts or ultraviolet light produces polymers containing phosphorus in the principal chain.\(^{24}\)

To prepare heat-stable polymers, attempts have been made to carry out the condensation of phosphonitrile chloride trimer with diphenyldi hydroxysilane as in the synthesis of organic esters. However, no reactions took place even on heating between 180 and 220\(^0\) for 3 to 5 hours: neither chlorine, nor water, nor hydrogen chloride was evolved.\(^{25}\)

Compounds containing boron and phosphorus in the chain, the dimethylphosphineborine cyclic polymers have been described as being stable at temperatures above 500\(^0\).\(^{26}\)

The object of this work was the preparation of silicon phosphororganic monomers and polymers containing the grouping \(\text{Si}-\text{C}-\text{O}-\text{P}\) \(\|$ \), and their condensation with \(\alpha, \omega\)-dichloropolydimethylsiloxanes.

The diethylthiophosphatometethylidimethylethoxysilane monomer was obtained by the reaction of chloromethylidimethylethoxysilane and sodium diethylthiophosphate according to the equation:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OSi(CH}_3)_2\text{CH}_2\text{Cl} + \text{NaOP(OC}_2\text{H}_5)_2 & \rightarrow \\
\text{S} & \rightarrow \text{C}_2\text{H}_5\text{OSi(CH}_3)_2\text{CH}_2\text{OP(OC}_2\text{H}_5)_2 \\
\end{align*}
\]

(16)

This reaction takes place readily in an alcohol medium with an appreciable yield of diethylthiophosphatometethylidimethylethoxysilane. The synthesized diethylthiophosphatometethylidimethylethoxysilane is a liquid which distills under vacuum without decomposing.

The condensation of diethylthiophosphatometethylidimethylethoxysilane with
α, ω-dichloropolydimethylsiloxanes takes place as follows:

\[
2(C_8H_{16})_n P(S)OCH_3Si(CH_3)_nOC_2H_5 + Cl[Si-O-]Cl \rightarrow \\
S_\text{CH}_3 \quad \text{CH}_3
\]

(17)

This reaction was also carried out for other α, ω-dichloropolydimethylsiloxanes with the degree of polymerization ω = 4, 5, 6 and 7.

Analysis for the carbon, phosphorus and silicon content of the products obtained was performed on a single sample, using a method due to B. M. Luskinina (method of wet combustion).

**EXPERIMENTAL**

1. **Preparation of Diethylthiophosphatomethyldimethylethoxysilane**

To a four-necked flask provided with a mechanical stirrer, a reflux condenser, a dropping funnel and a thermometer is added 24.6 g of diethylchlorothiophosphate and, on cooling (at 0⁰), an alcohol solution of an equimolar amount of sodium hydroxide is added dropwise. The mixture is brought to room temperature and stirred for half an hour. Two to three drops of pyridine are then added with 20.1 g of chloromethylidimethylethoxysilane, which is added dropwise, and the mixture is refluxed for three hours.

The precipitate of sodium chloride formed is filtered out, the alcohol is distilled from the filtrate, the residue is dried over calcium chloride and distilled under reduced pressure.

The yield of diethylthiophosphatomethyldimethylethoxysilane, a transparent, colorless liquid, was 19.5 g (52% of theoretical). B.P., 89–94⁰ (at 15 mm), \(d_4^2\), 1.0581; \(n_D^{25}\), 1.4450; molecular refraction: calculated, 71.60; found, 71.93.

For \(\text{C}_9\text{H}_2\text{O}_4\text{SiPS}\), we found, %: C—37.4; 37.8; Si—9.26; 9.05; P—10.7; 10.6.

Calculated, %: C—37.7; Si—9.8; P—10.8.
2. Condensation of Diethylthiophosphatomethyldimethylethoxysilane with \( \alpha, \omega \)-Dichloropolydimethylsiloxanes

A mixture of \( \alpha, \omega \)-dichloropolydimethylsiloxane (\( \omega = 4, 5, 6, 7, 8 \)) and diethylthiophosphatomethyldimethylethoxysilane, taken in the ratio of 1:2, is heated for three hours in the presence of 0.5% FeCl\(_3\), at an elevated temperature in a four-necked flask provided with a mechanical stirrer, a thermometer and an outlet for the ethyl chloride being formed. After the reaction mixture has cooled, it is distilled under vacuum. The \( \alpha, \omega \)-bis(diethylthiophosphatomethyl) polydimethylsiloxanes boil in the 130—165° range (at 1.5 mm).

For \( \text{C}_8 \text{H}_{24} \text{O}_3 \text{Si} \text{P} \text{S} \) we calculated, %: C—33.0; Si—25.73; P—5.67.

Found, %: C—33.4; 33.16; Si—26.14; 26.20; P—4.68; 4.59.

CONCLUSIONS

1. A new monomer, diethylthiophosphatomethyldimethylethoxysilane, was obtained.

2. The reaction of condensation of diethylthiophosphatomethyldimethylethoxysilane with \( \alpha, \omega \)-bis(dichloro) polydimethylsiloxanes was studied, and the possibility of synthesizing an oligomer of \( \alpha, \omega \)-bis(diethylthiophosphatomethyl) polydimethylsiloxanes was demonstrated.

REFERENCES

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