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Abstract

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OXYMETHYLATION OF PHOSPHINE AND ITS DERIVATIVES

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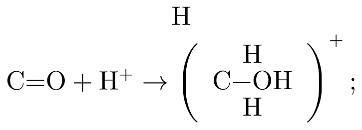
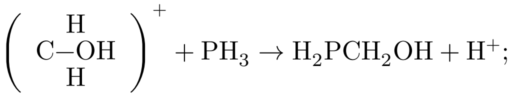
Until now it has been known that phosphorous hydrogen, as well as alkyl- and arylphosphines, are capable of reacting with formaldehyde only in the presence of hydrochloric acid or certain salts, the products of these reactions being phosphonium compounds, for example tetra-(oxymethyl)-phosphonium chloride ($(HOCH_2)_4PCl$), obtained as a result of the interaction of phosphine with an aqueous solution of formaldehyde and hydrochloric acid ($^{1-5}$).

For this reaction a mechanism was previously proposed (^{6}), according to which the process proceeds through the intermediate formation of a formaldehyde cation (I), reacting with a molecule of phosphorous hydrogen with elimination of a proton and conversion first into the mono-oxymethyl derivative (II), and then into di- and tri-(oxymethyl)-phosphines and further into tetraoxymethylphosphonium chloride

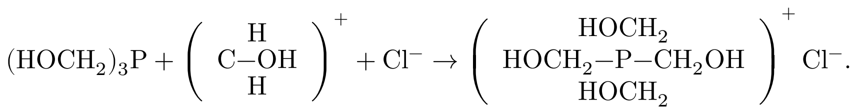


$$\mathrm{C{=}O + H^+ \rightarrow \overset{H}{\left(\begin{array}{c} H \\ C{-}OH \\ H \end{array}\right)^+}};$$

(I)



$$\left(\begin{array}{c} \mathrm{H} \\ \mathrm{C{-}OH} \\ \mathrm{H} \end{array}\right)^+ + \mathrm{PH_3 \rightarrow H_2PCH_2OH + H^+};$$



$$\mathrm{(HOCH_2)_3P} + \left(\begin{array}{c} \mathrm{H} \\ \mathrm{C{-}OH} \\ \mathrm{H} \end{array}\right)^+ + \mathrm{Cl^-} \rightarrow \left(\begin{array}{c} \mathrm{HOCH_2} \\ \mathrm{HOCH_2{-}P{-}CH_2OH} \\ \mathrm{HOCH_2} \end{array}\right)^+ \mathrm{Cl^-}.$$

We have found that the reaction of formaldehyde with phosphines can be carried out by another mechanism, with the formation of the corresponding derivatives of trivalent phosphorus. Thus, paraformaldehyde at 80—100° reacts with phosphorous hydrogen (at molar ratios of 3 : 1), forming tri-(oxymethyl)-phosphine in good yield according to the equation:

$$3\,CH_2O + PH_3 \rightarrow (HOCH_2)_3P.$$

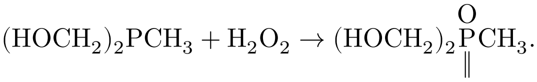
On oxidation of the resulting tri-(oxymethyl)-phosphine with a dilute solution of hydrogen peroxide, tri-(oxymethyl)-phosphine oxide was obtained:

$$(HOCH_2)_3P + H_2O_2 \rightarrow (HOCH_2)_3P{=}O + H_2O.$$

Methylphosphine, as experiments showed, enters into reaction with paraformaldehyde more readily (at a lower temperature and with a shorter duration of the process) than phosphorous hydrogen, giving the undescribed di-(oxymethyl)-methylphosphine—a liquid boiling at 90°/3 mm.

$$CH_3{-}PH_2 + 2CH_2O \rightarrow (HOCH_2)_2PCH_3.$$

Di(hydroxymethyl)methylphosphine is oxidized by hydrogen peroxide with the formation of an oxide hitherto unknown:



$$(HOCH_2)_2PCH_3 + H_2O_2 \rightarrow (HOCH_2)_2\overset{O}{\underset{\|}{P}}CH_3.$$

Dimethylphosphine reacts still more readily with paraformaldehyde, forming dimethylhydroxymethylphosphine:

$$(CH_3)_2PH + CH_2O \rightarrow (CH_3)_2PCH_2OH.$$

It should be noted that the latter compound belongs to a previously undescribed type of monohydric alcohols containing, at the carbon atom bonded to the hydroxyl group, an organophosphorus residue.

The fact that, in our experiments, phosphine and organic phosphines react with formaldehyde under conditions in which there is no source of protons necessary for the formation of formaldehyde cations gives grounds to suppose that this reaction proceeds through electrophilic attack by the carbon atom of the carbonyl group on the phosphorus atom of the phosphine molecule, leading to the formation of hydroxymethylphosphine.

The latter is then converted into the corresponding di- and tri(hydroxymethyl) derivatives. This supposition is in good agreement with the observation noted above that methyl- and dimethylphosphine enter into reaction with paraformaldehyde more readily than phosphine. This is due to the strengthening of the electron-donor properties of phosphorus in the series

$$PH_3 < CH_3PH_2 < (CH_3)_2PH\ (7).$$

By the method described, various hydroxyalkyl-substituted phosphines can be obtained by using all possible alkyl- and arylphosphines and carbonyl compounds.

Experimental Part

1. Preparation of di(hydroxymethyl)methylphosphine. Into a stainless-steel cylinder of 150 cm^3 capacity, equipped with a pressure gauge and a valve, were placed 17.7 g of paraformaldehyde * (16.8 g; 0.56 mole, calculated as 100% CH_2O) and 10.1 g of methylphosphine (0.21 mole). After charging the reaction components, the cylinder was heated with shaking for 40 min at 82–85°. The maximum pressure in the cylinder reached 6 atm at 73° and after only 3 min decreased to 0 atm. A total of 26.9 g of reaction product was obtained in the form of a syrupy liquid possessing the odor of phosphines.

On distillation of the reaction product in vacuum, pure di(hydroxymethyl)methylphosphine was isolated, b.p. 89–91°/3 mm (the bulk of the product passed over at 90°). Yield 18.9 g, or 83% of theory, calculated on methylphosphine. Di(hydroxymethyl)methylphosphine is a viscous, colorless, transparent liquid, which does not crystallize on cooling. n_D^{20} 1.5325; d_4^{20} 1.157; MR found 28.95; calculated 29.34.

Found, %:	C 33.48; H 8.59; P 28.43
$C_3H_9O_2P$. Calculated, %:	C 33.34; H 8.34; P 28.70

The substance is readily soluble in water and alcohol and poorly soluble in nonpolar solvents. The aqueous solution shows an alkaline reaction.

2. Preparation of di(hydroxymethyl)methylphosphine oxide. To 26.4 ml of a 6% aqueous solution of hydrogen peroxide, cooled with ice, with continuous stirring, there was gradually added a solution of 4.9 g of "crude" di(hydroxymethyl)methylphosphine (containing about 81% $CH_3P(CH_2OH)_2$ in 10 ml of water. From the aqueous solution obtained after the reaction had ended, after filtration and evaporation in vacuo to constant weight, 4.65 g (98.5%) of di-(hydroxymethyl)-methylphosphine oxide was obtained as a very viscous, syrupy liquid, which on cooling and rubbing crystallized completely in the form of needle-shaped colorless crystals that deliquesce in air.

The substance obtained does not distill in vacuo on heating to 200° and does not decompose under these conditions. The product is soluble in water and alcohol, but insoluble in nonpolar liquids (benzene, ether).

Found, %: C 29.24; H 7.25; P 24.10
$C_3H_9O_3P$. Calculated, %: C 29.03; H 7.26; P 25.00

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* For this and the other reactions with phosphines described in the present work, paraformaldehyde containing 95% formaldehyde (in polymeric form) was used.

3. **Preparation of hydroxymethyl-dimethylphosphine.** Into the same reaction vessel as in experiment 1 were placed 4.84 g of paraformaldehyde (4.6 g, or 0.153 mole, calculated as 100% CH_2O), and, after evacuation, 10.1 g (0.163 mole) of dimethylphosphine. The cylinder with the reaction mixture was heated with shaking for 1 hour at 65-67°. 14.2 g of reaction product was obtained; on distillation in vacuo a fraction with b.p. 50-51°/10 mm was collected, which was pure hydroxymethyl-dimethylphosphine. Yield 12.1 g, or 80.7% of theoretical (calculated on dimethylphosphine). A colorless, transparent, mobile liquid, b.p. 70°/30 mm, n_D^{20} 1.5011; d_4^{20} 0.9931. *MR* found 27.29; calculated 27.83.

Found, %: C 39.17; H 9.78; P 34.1
C_3H_9OP. Calculated, %: C 39.13; H 9.89; P 33.7

4. **Preparation of tri-(hydroxymethyl)-phosphine.** For the reaction, which was carried out in the same reaction vessel as in experiments 1 and 3, 26.0 g of paraformaldehyde (0.821 mole, calculated as 100% CH_2O) and 9.77 g (0.286 mole) of phosphine were taken. The cylinder was heated (with shaking) at 100° for about 2 hours. The maximum pressure reached 35-40 atm and, as the phosphine entered into the reaction, gradually decreased. After the reaction had ended, unreacted phosphine (0.26 g) was removed from the cylinder. 34.25 g of crude reaction product was obtained in the form of a slightly colored syrupy liquid with a characteristic phosphine odor, gradually crystallizing into almost colorless hygroscopic needles with m.p. 51-53°.

Yield about 94% based on the phosphine that entered into the reaction.

Found, %: C 29.26; H 7.57; P 24.2
$C_3H_9O_3P$. Calculated, %: C 29.0; H 7.26; P 25.0

The substance distills in vacuo with noticeable decomposition (b.p. 111-113°/2.5 mm Hg), is readily soluble in water and alcohol, and insoluble in nonpolar organic solvents. Its aqueous solution is neutral. On storage the product gradually decomposes (an orange coloration and acidic impurities appear).

5. **Preparation of tri-(hydroxymethyl)-phosphine oxide.** To 27 ml of a 7% aqueous solution of hydrogen peroxide (0.054 mole H_2O_2), cooled with ice, 6.45 g (0.053 mole) of tri-(hydroxymethyl)-phosphine was gradually added with continuous stirring.* The aqueous solution obtained after completion of the reaction, after filtration, was evaporated in vacuo to constant weight. As a result, 6.92 g (yield 95.0%) of tri-(hydroxymethyl)-phosphine oxide was obtained in the form of a transparent, colorless, thick syrup, which crystallized completely on cooling in the form of colorless, very hygroscopic crystals, which after recrystallization from ethyl alcohol melt—

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* It is also possible to add a solution of tri-(hydroxymethyl)-phosphine in water or alcohol to the calculated amount of hydrogen peroxide solution, or vice versa.

crystallized at 56–58°. The substance is insoluble in benzene and ether. The product contains no trivalent phosphorus and, unlike tri-(hydroxymethyl)-phosphine, does not decompose on storage.

$C_3H_9O_4P$.	Found, %:	C 25.88; H 6.28; P 21.60
	Calculated, %:	C 25.71; H 6.43; P 22.15

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