Chemistry

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Abstract

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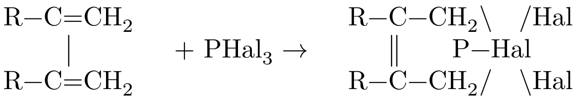
MONOMERIC TRIHALOPHOSPHORANES OF THE CYCLIC SERIES AND SOME OF THEIR TRANSFORMATIONS. SYNTHESES BASED ON PHOSPHORUS TRIBROMIDE

In recent years, following the work of McCormack (1), many investigators have studied the addition reaction of dienes to derivatives of trivalent phosphorus (2–7). Aryl- and alkyldichlorophosphines (1–3), aryl- and alkyldichlorophosphites (3), chloranhydrides of glycolphosphorous acids (4,5), mono- and dithioethylene glycolphosphorous acids (6), and also pyrocatecholphosphorous acids (7) have been used as the phosphorus component. As a rule, adducts of phosphorane structure were not isolated. In some cases this was due to isomerization or decomposition of the adducts according to the scheme of the second stage of the Arbuzov rearrangement (3–6), and in others to the difficulty of purifying the addition products because of their extreme hygroscopicity and strong resinification. Usually the products of further transformations were isolated and described. Only in one case (7) were adducts isolated in analytically pure form; these compounds contained one chlorine atom at the phosphorus atom. There had been no reports, up to November 1963, on the isolation of cyclic phosphoranes with a large number of halogen atoms at phosphorus, or on the interaction of phosphorus trihalides with dienes.

In studying the interaction of derivatives of trivalent phosphorus with diene systems, we found that not only halides of organic derivatives of trivalent phosphorus of varying complexity add to dienes, but also phosphorus trichloride and phosphorus tribromide (8). Phosphorus trihalides react with dienes considerably more vigorously than do organic derivatives and, in good yields, form adducts—representatives of a previously unknown class of organophosphorus compounds—trihalides of the cyclic series. In general form the reaction may be represented by the scheme:



$$\begin{array}{c} R{-}C{=}CH_2 \\ | \\ R{-}C{=}CH_2 \end{array} + PHal_3 \rightarrow \begin{array}{c} R{-}C{-}CH_2\backslash \quad /Hal \\ \| \qquad P{-}Hal \\ R{-}C{-}CH_2/ \quad \backslash Hal \end{array}$$

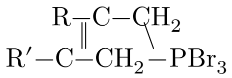
The discovered reaction makes trihalophosphoranes—compounds of great interest from the standpoint of reactivity—readily accessible and opens broad possibilities for obtaining various derivatives of phosphacyclopentene.

Experiments showed that phosphorus tribromide reacts with dienes more vigorously than phosphorus trichloride; tribromophosphoranes are formed in better yields and in a purer form than trichlorophosphoranes. Reactions with phosphorus trichloride, as a rule, are accompanied by strong resin formation.

The reaction was carried out by mixing equimolar amounts of the diene and the phosphorus trihalide in a reaction vessel well protected from moisture. Copper stearate served as the polymerization inhibitor. The temperature of the reaction mixture was maintained within the range 10–30°. The duration of the process depended on the nature of the diene and varied from several hours to a month. In the reaction of isoprene or 2,3-dimethylbutadiene-1,3 with phosphorus tribromide, toward the end of the reaction, when a large amount of adduct had accumulated and the reaction mixture had lost mobility, rapid self-heating and decomposition were often observed. To preserve the mobility of the reaction mass and to prevent local overheating, we developed a procedure for the gradual introduction of solvent (8). The use of solvents in the initial stages of the process greatly slows the reaction. The gradual-dilution procedure made it possible to obtain the adducts in pure form fairly rapidly and in acceptable yields. The phosphoranes formed were filtered off from the unreacted starting materials, washed with a dry inert solvent, and dried in vacuo at a temperature not above 50°. All the operations listed were carried out in a closed system in an atmosphere of solvent vapor or dry inert gas.

Table 1

Cyclic tribromophosphoranes of the general formula:



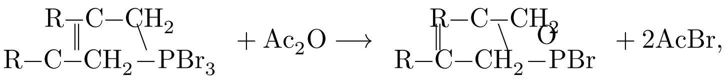
No.	R	R′	Yield, %	m.p., °C	Equiv. wt.*	P*, %	Br*, %
1	CH_3	CH_3	56	151–153	88.2688.22	8.808.78	67.9767.95
2	CH_3	H	49	114–117	83.5184.71	–	–
3	H	H	18	125–127	81.7081.20	10.099.54	–

* Upper figures are found values, lower figures are calculated.

Despite their extreme hygroscopicity (exceeding the hygroscopicity of phosphorus pentoxide), by observing the precautions described above we were able to isolate the tribromophosphoranes as snow-white, finely crystalline powders, determine their melting points (with decomposition), and carry out some analyses.

Nine months after our communication (^{8}), a paper by Hasserodt, Hunger, and Korte (^{9}) appeared; they also studied the interaction of phosphorus trihalides with dienes. They worked mainly with phosphorus trichloride, but also obtained adducts of phosphorus tribromide with 2,3-dimethylbutadiene-1,3 and isoprene. For the former they reported only the yield, and for the latter—the yield and the results of direct titration. All the trihalophosphoranes they obtained were apparently heavily contaminated with resin, since they were characterized as a “brown mass.” No other bromine-containing derivatives of phosphacyclopentene were described by Hasserodt, Hunger, and Korte.

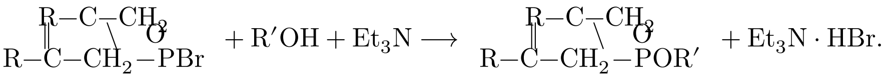
In studying the properties of tribromophosphoranes we found that they react smoothly with acetic anhydride according to the equation:



$$\begin{array}{l} R-C-CH_2 \\ \quad \| \qquad \backslash \\ R-C-CH_2-PBr_3 \end{array} + Ac_2O \longrightarrow \begin{array}{l} R-C-CH_2 \\ \quad \| \qquad \backslash \quad O \\ R-C-CH_2-PBr \end{array} + 2AcBr,$$

forming the bromanhydrides of cyclophosphinic acids. The yields of crude bromanhydrides are close to quantitative. On distillation the yields decrease sharply. Undistilled products are quite suitable for subsequent reactions.

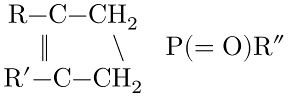
By the reaction of bromanhydrides of cyclophosphinic acids with alcohols in the presence of organic bases, we obtained the corresponding esters.



$$\begin{array}{l} R-C-CH_2 \\ \quad \| \qquad \backslash \quad O \\ R-C-CH_2-PBr \end{array} + R'OH + Et_3N \longrightarrow \begin{array}{l} R-C-CH_2 \\ \quad \| \qquad \backslash \quad O \\ R-C-CH_2-POR' \end{array} + Et_3N \cdot HBr.$$

Table 2

Derivatives of phosphacyclopentene-3 of the general formula



$$\begin{array}{l} R-C-CH_2 \\ \quad \| \qquad \backslash \\ R'-C-CH_2 \end{array} P(=O)R''$$

No.	R	R′	R″	Yield, %	M.p., °C	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D^*	P*, %	C*, %	H*, %
4	CH_3	CH_3	Br	72,7	85 – 87	102 – 104 (0,55)	–	–	–	14,83	14,81	–

No.	R	R′	R″	Yield, %	M.p., °C	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D^*	P*, %	C*, %	H*, %
5	CH_3	H	Br	32	–	123–125 (0,02)	1,5682	1,6216	39,36 39,52	15,25 15,88	–	–
6	H	H	Br	38	46–48	72–74 (0,53)	1,5593	1,7037	34,31 34,63	17,04 17,11	–	–
7	CH_3	CH_3	OCH_3	42	–	131 (10)	1,4892	1,1072	41,76 41,62	19,07 19,34	52,35 52,49	8,50 8,18
8	CH_3	CH_3	OC_2H_5	46	42–43	85–87 (0,20)	–	–	–	17,88 17,78	–	–
9	CH_3	CH_3	OC_3H_7-*n*	39	–	135–136 (9)	1,4778	1,0482	50,81 51,06	16,84 16,46	56,95 57,43	9,23 9,11
10	H	H	OC_2H_5	51	–	71–72 (0,52)	1,4801	1,1351	36,54 36,19	21,84 21,20	–	–

* Upper numbers are found values; lower numbers are calculated values.

The structure of the compounds obtained was confirmed by high-resolution NMR spectra. Compounds with a symmetrical molecular structure (compounds Nos. 4 and 7) were chosen as the objects. The spectrum of 1-oxo-1-bromo-3,4-dimethylphosphacyclopentene-3 has a doublet at $\tau = 7.02$ and 7.42 and a peak at $\tau = 8.35$ ppm, with an area ratio, expressed in protons, of 3.86 : 6.13 (for the protons of the methylene and methyl groups, respectively). The calculated proton ratio is 4 : 6. The spectrum of 1-oxo-1-methoxy-3,4-dimethylphosphacyclopentene-3 has a doublet at $\tau = 6.25$ and 6.66 (methoxy group), a doublet at $\tau = 7.46$ and 8.00 ppm (methylene groups), and a peak at $\tau = 8.35$ (methyl groups at the double bond), with an area ratio of 3.16 : 3.80 : 6.05. The calculated proton ratio in the compound is 3 : 4 : 6.

The compounds obtained and their properties are given in Tables 1 and 2.

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Note: Figure translations are in progress. See original paper for figures.

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