Chemistry

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1964

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Abstract

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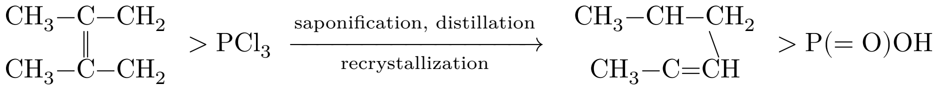
PHOSPHACYCLOPENTENE DERIVATIVES. SYNTHESIS AND STRUCTURE OF ISOMERS

In a previous paper (^{1}) the addition reaction of phosphorus trihalides to dienes was described. It was shown that this reaction makes it possible readily to obtain cyclic trihalophosphoranes, and also opens broad possibilities for the synthesis of various phosphacyclopentene derivatives.

The present communication is devoted to possibilities for obtaining phosphacyclopentene derivatives with different positions of the double bond in the ring. As our experiments have shown, the double bond may occupy different positions depending on which phosphorus trihalide is used in the reaction—chloride or bromide. Another factor capable of affecting the position of the double bond in the ring proved to be the route of synthesis. When bromides are used, any method leads to products with a symmetrical arrangement of the double bond with respect to the phosphorus atom. When chlorides are used, depending on the route of synthesis, compounds may be obtained with either a symmetrical or an unsymmetrical arrangement of the double bond.

The lability of the double bond and the tendency toward prototropic isomerization are apparently a specific property of 1,1,1-trichlorophosphacyclopentene and determine both the formation of isomers and the strong resinification that always accompanies the reactions of phosphorus trichloride with dienes.

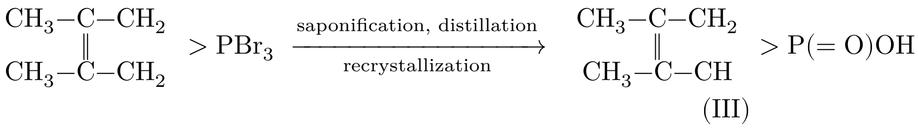
The influence of the nature of the halogen on the structure of the product obtained is well illustrated by the following reactions:



$$\begin{matrix} CH_3-C-CH_2 \\ \| \\ CH_3-C-CH_2 \end{matrix} > PCl_3 \xrightarrow[\text{recrystallization}]{\text{saponification, distillation}} \begin{matrix} CH_3-CH-CH_2 \\ \quad\backslash \\ CH_3-C=CH \end{matrix} > P(=O)OH \qquad (1)$$

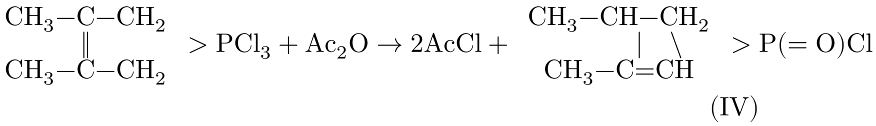
(I) (II)

\end{equation}

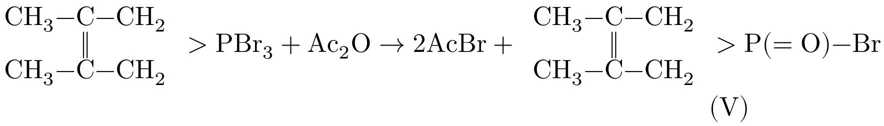


$$\begin{matrix}CH_3{-}C{-}CH_2\\ \|\\ CH_3{-}C{-}CH_2\end{matrix} > PBr_3 \xrightarrow[\text{recrystallization}]{\text{saponification, distillation}} \underset{\text{(III)}}{\begin{matrix}CH_3{-}C{-}CH_2\\ \|\\ CH_3{-}C{-}CH\end{matrix}} > P(=O)OH \tag{2}$$

\end{equation}



$$\begin{matrix}CH_3{-}C{-}CH_2\\ \|\\ CH_3{-}C{-}CH_2\end{matrix} > PCl_3 + Ac_2O \to 2AcCl + \underset{\text{(IV)}}{\begin{matrix}CH_3{-}CH{-}CH_2\\ |\quad\backslash\\ CH_3{-}C{=}CH\end{matrix}} > P(=O)Cl \tag{3}$$



$$\begin{matrix}CH_3{-}C{-}CH_2\\ \|\\ CH_3{-}C{-}CH_2\end{matrix} > PBr_3 + Ac_2O \to 2AcBr + \underset{\text{(V)}}{\begin{matrix}CH_3{-}C{-}CH_2\\ \|\\ CH_3{-}C{-}CH_2\end{matrix}} > P(=O){-}Br \tag{4}$$

To elucidate the structure of the compounds obtained, high-resolution NMR spectroscopy was used. All the compounds studied were synthesized from 2,3-dimethylbutadiene-1,3 and had substituents in the ring in positions 3 and 4. This structure provided the easiest interpretation of the spectra, since the position of the double bond is un—

is largely determined by the presence or absence of the ethylenic proton (a doublet in the interval τ 3.5–4.9 ppm). The spectra were recorded on a YaMR-KGU-1 NMR spectrometer at a frequency of 24.342 MHz (^{2}). Figure 1 shows the spectra of the isomeric acids. The symmetrical acid contains two types of protons: methylene and methyl. They correspond to three peaks: a doublet at $\tau = 7.4$ and 7.9 ppm (methylene protons; the splitting is caused by spin-spin interaction with the neighboring phosphorus atom) and a peak at $\tau = 8.4$ (protons of two methyl groups). The unsymmetrical acid II has a more complex spectrum. A doublet appears at $\tau = 3.8$ and 4.8 ppm, corresponding to the ethylenic proton. The splitting is due to the proximity of the phosphorus atom. A doublet at $\tau = 7.4$ and 7.9 ppm and a peak at $\tau = 8.2$, as in the preceding case, correspond to the protons of the methylene group and the methyl group located at the double bond. The doublet at $\tau = 8.8$ and 9.1 is due to the protons of the methyl located at the tertiary carbon atom. The hydroxyl-group proton has a considerably smaller τ value and does not fall within this region of the spectrum. The spectra of the isomeric bromo anhydride V and chloro anhydride IV (Fig. 2) repeat the same pattern.

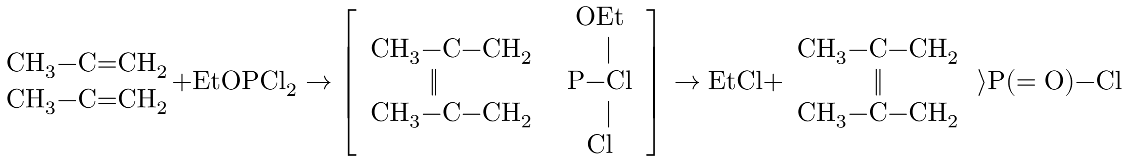
NMR spectra of 1-oxo-1-hydroxy-3,4-dimethylphosphacyclopentene-3 (III) and 1-oxo-1-hydroxy-3,4-dimethylphosphacyclopentene-2 (II)

Fig. 1. NMR spectra of 1-oxo-1-hydroxy-3,4-dimethylphosphacyclopentene-3 (III) and 1-oxo-1-hydroxy-3,4-dimethylphosphacyclopentene-2 (II)

NMR spectra of 1-oxo-1-bromo-3,4-dimethylphosphacyclopentene-3 (V) and 1-oxo-1-chloro-2,3-dimethylphosphacyclopentene-2 (IV)

Fig. 2. NMR spectra of 1-oxo-1-bromo-3,4-dimethylphosphacyclopentene-3 (V) and 1-oxo-1-chloro-2,3-dimethylphosphacyclopentene-2 (IV)

The dependence of the product structure on the method of its preparation is revealed by comparing chloro anhydride IV, obtained by reaction (3), with the isomeric chloro anhydride VI, formed by the interaction of Menshutkin' s chloro anhydride with 2,3-dimethylbutadiene-1,3 according to the previously described (^{3}) reaction (5).



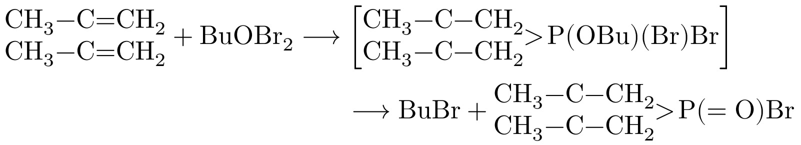
$$\begin{matrix}CH_3-C=CH_2\\CH_3-C=CH_2\end{matrix}+EtOPCl_2\rightarrow\left[\begin{array}{cc} & OEt\\ CH_3-C-CH_2 & |\\ \| & P-Cl\\ CH_3-C-CH_2 & |\\ & Cl\end{array}\right]\rightarrow EtCl+\begin{matrix}CH_3-C-CH_2\\ \|\\ CH_3-C-CH_2\end{matrix}\rangle P(=O)-Cl$$

(5)

(VI)

On saponification, chloro anhydride VI is converted into acid III with a melting point of 122° (^{3}), which makes it possible to assign to it a symmetrical structure.

Alkyl dibromophosphites behave analogously in a reaction of this type. The products formed also have a symmetrical structure. The bromoanhydride obtained according to scheme (6) (yield 38.6%),



$$\begin{matrix}CH_3-C=CH_2\\CH_3-C=CH_2\end{matrix}+BuOBr_2\longrightarrow\left[\begin{matrix}CH_3-C-CH_2\\CH_3-C-CH_2\end{matrix}>P(OBu)(Br)Br\right]\longrightarrow BuBr+\begin{matrix}CH_3-C-CH_2\\CH_3-C-CH_2\end{matrix}>P(=O)Br$$

(6)

(V)

does not differ in any way from bromoanhydride V obtained by reaction (4). A mixed sample of these products causes no depression of the melting point.

NMR spectra of VII and VIII

Fig. 3. NMR spectra of 1-oxo-1-methoxy-3,4-dimethylphosphacyclopentene-3 (**VII**) and 1-oxo-1-methoxy-3,4-dimethylphosphacyclopentene-2 (**VIII**)

Saponification of the symmetrical bromoanhydride, as well as of the chloroanhydride, is not accompanied by migration of the double bond. Acid III is formed in 92.7% yield.

The examples given show that, on the basis of trivalent phosphorus chlorides, by varying the methods of synthesis, one can obtain one or another isomer of phosphacyclopentene. However, it cannot be said that route (3) leads exclusively to the unsymmetrical form. In one of the experiments carried out according to scheme (3), it was possible to isolate a small amount (9%) of crystalline chloroanhydride with m.p. 85°. In a mixed sample with the symmetrical product VI, no depression of the melting point was observed. Evidently, reaction (3) leads to the formation of a mixture of isomers with predominance of the unsymmetrical chloroanhydride IV.

Hasserodt, Hunger, and Korte (^{4}), who also obtained some of the compounds considered in the present communication (Nos. I, II, IV, and VIII), isolated and described only liquid 1-oxo-1-chloro-3,4-dimethylphosphacyclopentene-2. The constants given by them agree well with the constants recorded by us for the unsymmetrical chloroanhydride IV.

The established dependence of the structure of phosphacyclopentenes on the nature of the phosphorus halide introduced into the reaction makes it possible to synthesize esters of cyclophosphinic acids with a specified position of the double bond in the ring. Thus, by the interaction of methyl alcohol in the presence of triethylamine with bromoanhydride V and with trichlorophosphorane I, the isomeric esters VII and VIII were obtained, the structure of which is un-

Spatial representation of phosphacyclopentene derivatives

Fig. 4. Spatial representation of phosphacyclopentene derivatives with different positions of the double bond in the ring.
A –VI, R=Cl, m.p. 85°; III, R=OH, m.p. 122°.
B –IV, R=Cl, liquid; II, R=OH, m.p. 70°.

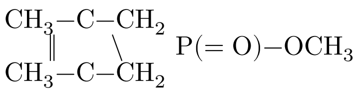
Table 1

No.	Compound	Yield, %	m.p., °C	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D^*	P*, %	C*, %	H*, %
I	CH_2-C-CH_2 ‖ \ PCl_3 CH_3-C-CH_2	53	108– 10	–	–	–	–	13.0214.10	–	–
II	$CH_2-CH-CH_2$ | \ P(=O)OH $CH_3-C=CH$	32.4	65– 70	1950.03	1.5115	–	–	21.1421.49	49.6049.35	7.587.56
III	CH_3-C-CH_2 ‖ \ P(=O)OH CH_3-C-CH_2	27.4	122– 3	168– 90.05	–	–	–	21.3521.20	–	–

No.	Compound	Yield, %	m.p., °C	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D^*	P*, %	C*, %	H*, %
IV	$CH_3{-}CH{-}CH_2$ $CH_3{-}C{=}CH$ P(= O)Cl	33		94 60.05	1.5134	1.2074	40.9940.58	9018.83	–	–
V	$CH_3{-}C{-}CH_2$ $CH_3{-}C{-}CH_2$ P(= O)Br	72.7	85–87	102 40.55	–	–	–	14.831431	1234537	64.83
VI	$CH_3{-}C{-}CH_2$ $CH_3{-}C{-}CH_2$ P(= O)Cl	62	83–86	132–10	–	–	–	19.0418.83	–	–
VII	$CH_3{-}C{-}CH_2$ $CH_3{-}C{-}CH_2$ P(= O)–OCH$_3$	42		131–10	1.4892	1.1072	41.7641.16	9026195	3459528	5088.18
VIII	$CH_3{-}CH{-}CH_2$ $CH_3{-}C{=}CH$ P(= O)–OCH$_3$	15		134 510	1.4882	1.1062	41.7241.16	9037195	3436528	5408.18

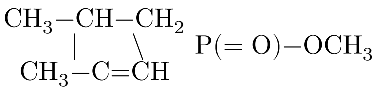
* Upper figures are found values; lower figures are calculated.

is unambiguously determined by the NMR spectra shown in Fig. 3.



$$\begin{matrix} CH_3{-}C{-}CH_2 \\ \| \quad\quad \backslash \\ CH_3{-}C{-}CH_2 \end{matrix}\ P(=O){-}OCH_3$$

(VII)



$$\begin{matrix} CH_3{-}CH{-}CH_2 \\ | \quad\quad \backslash \\ CH_3{-}C{=}CH \end{matrix}\ P(=O){-}OCH_3$$

(VIII)

These spectra are analogous to those considered earlier, but in them a new doublet appears at $\tau = 6.3$ and 6.7 ppm, corresponding to the protons of the methoxy group.

The melting points of the isomers also provide information on the structure of the molecules. In Fig. 4 it is shown that, when the double bond is shifted from position 3–4 to position 2–3, one of the methyl groups leaves the plane of the ring. At the same time, carbon atom 4 becomes asymmetric. In the general case, the phosphorus atom also becomes asymmetric. The loss of symmetry, disruption of coplanarity, and the possible formation of a mixture of diastereomers and optical antipodes must markedly lower the melting point. This agrees well with the observed facts. In those cases where the symmetrical product is a crystalline substance, its unsymmetrical isomer has a lower melting point or does not crystallize at all.

The products obtained and their properties are given in Table 1.

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Received
22 VI 1964

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