INVESTIGATION IN THE FIELD OF UNSATURATED PHOSPHINIC ACIDS

PART 22. ADDITION OF PHOSPHORUS PENTACHLORIDE TO ISOPROPENYLACETYLENE

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The present investigation reports results obtained by us in an investigation of the interaction between phosphorus pentachloride and isopropenylacetylene. It is known from data published in the literature [2-3] that phosphorus pentachloride adds to unsymmetric unsaturated compounds, forming crystalline products. These have been formulated as complexes with the structure $R-CHC_1-CHzPCl_4-P_2Cl_6$.

It has been established [4-5] that phosphorus pentachloride in the crystalline state has the structure of the complex $[PCl_4]^+ \cdot [PCl_6]^-$, where $[PCl_4]^+$ has the structure $P^+Cl_4$, while $[PCl_6]^-$ has the structure $Cl_6^-$. We carried out the reaction in a benzene solution, i.e., in a solvent in which phosphorus pentachloride is soluble to only a slight extent, so that one may assume that the reaction proceeded heterolytically. It would therefore be more accurate to formulate the addition product as a complex of the structure $RCHCl-CH_2P^+Cl_4 \cdot P_2Cl_6$, especially in view of the fact that complexes which contain cations of this type have already been described [6-7]: $RP^+Cl_4$, $Fe^+Cl_4$, $RP^+Cl_4 \cdot Al^+Cl_4$.

As a result of the interaction of one mole of isopropenylacetonitrile with two moles of phosphorus pentachloride in pure benzene there was formation of a crystalline addition product. Because of its great hygroscopicity, it could not be separated from the reaction mixture. The reaction products were treated by passing a stream of $SO_2$ through them. After this treatment we succeeded in isolating two fractions in a pure state. The reaction which took place can be described by the following scheme:

$$
\begin{align*}
CH_2=C-C\equiv CH + 2 PCl_5 \rightarrow & CH_3Cl-CCl-CCl=CHCl + SO_2 \\
& CH_3Cl-CCl-CCl=CHCl \\
& CH_3Cl-CCl-CCl=CHCl \\
& CH_3Cl-CCl-CCl=CHCl \\
& CH_3Cl-CCl-CCl=CHCl \\
& CH_3Cl-CCl-CCl=CHCl \\
CH_3Cl-CCl-CCl=CHCl \\
& CH_3Cl-CCl=CHPOCl_2 + PCl_3 + 2 SOCl_2 + HCl
\end{align*}
$$

The physical constants of the compounds which formed are listed in Table 1.

1,2,3,4-Tetrachloro-3-methylbutene-1 is a colorless liquid which dissolves in all organic solvents and de-colorizes bromine water. Investigation of the properties of the chloride of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid showed that it reacts readily with alcohols. This made it possible to prepare neutral esters of the acid by applying the reaction described by Milobendzki and Sachnovski [8]:

*After our investigation had been completed, a brief communication was published in regard to the reaction of addition of $PCl_5$ to isopropenylacetylene [1].
\[
\begin{align*}
\text{CH}_2\text{C} & \equiv \text{C} - \text{CCl} = \text{CHPOCl}_2 + 2\text{ROH} + 2\text{C}_6\text{H}_5\text{N} \\
& \equiv \text{CH}_2\text{Cl} \\
\text{CH}_2\text{C} & \equiv \text{C} - \text{CCl} = \text{CHPO(OR)}_2 + 2\text{C}_6\text{H}_5\text{N} \cdot \text{HCl} \\
& \equiv \text{CH}_2\text{Cl}
\end{align*}
\]

By employing this reaction, the dimethyl, diethyl, and di-n-propyl esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid were prepared. Their physical constants are listed in Table 2.

**TABLE 1**

<table>
<thead>
<tr>
<th>Formula</th>
<th>B.p., °C (pressure in mm Hg)</th>
<th>( \delta^D )</th>
<th>( \delta^A )</th>
<th>Yield, %</th>
<th>MR found</th>
<th>MR calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CH}_2\text{Cl} - \text{CCl} - \text{CCl} - \text{CHCl}</td>
<td>60 (3)</td>
<td>1,5192</td>
<td>1,4304</td>
<td>16.7</td>
<td>44.22</td>
<td>44.29</td>
</tr>
<tr>
<td>\text{CH}_2\text{Cl} - \text{C} - \text{CCl} - \text{CHPOCl}_2</td>
<td>121 (3)</td>
<td>1,5405</td>
<td>1,5400</td>
<td>50</td>
<td>51.75</td>
<td>52.14</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Formula</th>
<th>B.p., °C (pressure in mm Hg)</th>
<th>( \delta^D )</th>
<th>( \delta^A )</th>
<th>Yield, %</th>
<th>MR found</th>
<th>MR calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CH}_2\text{Cl} - \text{CCl} - \text{CHPO(OCH}_3\text{)}_2</td>
<td>136 (3)</td>
<td>1,4957</td>
<td>1,3155</td>
<td>69</td>
<td>54.36</td>
<td>54.17</td>
</tr>
<tr>
<td>\text{CH}_2\text{Cl} - \text{C} - \text{CCl} - \text{CHPO(OCH}_3\text{)}_2</td>
<td>142.5 (2)</td>
<td>1,4838</td>
<td>1,2305</td>
<td>73</td>
<td>63.15</td>
<td>63.41</td>
</tr>
<tr>
<td>\text{CH}_2\text{Cl} - \text{C} - \text{CCl} - \text{CHPO(OCH}_3\text{)}_2</td>
<td>158 (2)</td>
<td>1,4805</td>
<td>1,1749</td>
<td>67</td>
<td>72.78</td>
<td>72.66</td>
</tr>
</tbody>
</table>

The esters of (2-chloromethyl-3-chlorobutadiene-1,3)-4-phosphinic acid are colorless, mobile liquids which give a positive reaction for chlorine, decolorize bromine water, and dissolve in ordinary organic solvents. They polymerize readily when stored.

To establish the structure of the reaction products, we used infrared spectroscopy. The infrared spectra of the compounds were determined on a D-209 Hilger spectrometer with a sodium chloride prism in the 700-2000 cm\(^{-1}\) range and an IKS-1 spectrometer with a lithium fluoride prism in the 2500-3600 cm\(^{-1}\) range. Analysis of the infrared spectrum of the first reaction product indicated that the constitution of the compound which had been synthesized most likely corresponded to the formula \text{CHCl} - \text{CCl} - \text{CCl} - \text{CH}_2\text{Cl}. The results of the elementary analysis and the chemical properties of the compound confirmed this. In spectra of compounds of the type \text{CH}_2 = \text{CH}_2 or \text{CH}_2 = \text{C} < the absorption bands of the double bond \text{C} = \text{C} are situated in the 1640-1650 cm\(^{-1}\) region [9], whereas in the spectrum of the tetrachloromethylbutene prepared by us the band in question is in the vicinity of 1612 cm\(^{-1}\) (Fig. 1). Lowering the frequency of the vibration of the double bond in nonchlorinated olefins takes place because of the influence of the adjacent chlorine atoms; the same lowering of the double bond frequency is observed in spectra of other compounds which have chlorine atoms next to the double bond [10, 11].

In the compound investigated by us the chlorine atoms at the double bond are in a cis-configuration. This follows from a comparison of the spectrum of this compound with the spectrum of 1,2-dichloro-1-propene \text{CCl} - \text{CHCl} with \text{CH}_2.

[4] Just like the spectrum of the cis-isomer of dichloropropene, the spectrum of the tetrachloromethylbutene has strong absorption bands at 1612 and 1010 cm\(^{-1}\), whereas the spectrum of the trans-isomer of dichloropropene has an absorption band of low intensity in the region of 1612 cm\(^{-1}\), and instead of the strong band at 1010 cm\(^{-1}\), which is characteristic for the cis-isomer, shows a strong absorption band at 950-990 cm\(^{-1}\).