ALKENYL DERIVATIVES OF ARSENIC

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The present work forms a continuation of an investigation of unsaturated organometallic compounds of the ethylene series. The preceding communications were devoted to the investigation of alkenyl compounds of ter- and quinque-covalent antimony [1-4] and of tervalent phosphorus [5]. We are now able to report on the synthesis and some properties of propenyl and isopropenyl compounds of arsenic.

By the action of cis- and trans-propenyllithiums on arsenic trichloride we obtained the corresponding stereoisomeric tri-cis- and tri-trans-propenylarsines, and by the reaction of arsenic trichloride with isopropenyllithium we obtained triisopropenylarsine:

$$3RLi + AsCl_3 \rightarrow R_3As + 3LiCl$$

$$R = \text{cis- and trans-CH}_3\text{CH} = \text{CH} - \text{and } \text{CH}_3 = \text{C}$$

These isomeric compounds are clear liquids of good solubility in ether, alcohol, acetone, and benzene; they readily combine with halogens with formation of halo alkenyl quinquevalent arsenic compounds:

$$R_3As + 2\text{Hal} \rightarrow R_3\text{AsHal}_2.$$ 

In this way we prepared tri-cis-propenylarsine dibromide, tri-trans-propenylarsine dibromide, and triisopropenylarsine dibromide.

Propenyl and isopropenyl compounds of arsenic react with methyl iodide with varying ease with formation of the corresponding arsonium iodides $R_3As \cdot CH_3I$, and with mercuric chloride they give the corresponding complex compounds:

$$\left( \begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array} \right) \text{C = C} \left( \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \right) \text{As} \cdot \text{HgCl}_3; \quad \left( \begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array} \right) \text{C = C} \left( \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \right) \text{As} \cdot \text{HgCl}_3; \quad \left( \begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array} \right) \text{C = C} \left( \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \right) \text{As} \cdot \text{HgCl}_3.$$

The configurations of the alkenylarsenic compounds obtained were determined on the basis of their infrared absorption spectra. As in the case of propenylantimony compounds [4], there is a fairly characteristic difference between the cis and trans isomers of tripropenylarsine in the infrared absorption spectra (see table). Trans configurations are assigned to compounds having intense absorption frequencies due to nonplanar vibrations of the CH group at an olefinic carbon atom in the range 950-960 cm$^{-1}$ and higher frequencies due to the C=C bond in the region of 1620 cm$^{-1}$, but cis compounds have the absorption frequencies of the same CH vibrations at 925 cm$^{-1}$ and lower C=C vibration frequencies at 1610 cm$^{-1}$.

Our attempts to synthesize propenyl compounds of arsenic of the type $R_6As$, on analogy with quinquevalent antimony compounds [4], were not successful, although pentaphenylarsenic [6, 7] and pentamethylarsenic [8] have been described. By the reaction of triisopropenylarsine dibromide with isopropenyllithium we could isolate only a
Characteristic Vibration Frequencies (cm⁻¹) in the Infrared Absorption Spectra of Propenylarsines

<table>
<thead>
<tr>
<th>Formula of compound</th>
<th>Trans</th>
<th>Cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3\text{CH}=\text{CH})_3\text{As})</td>
<td>700 m, 960 s, 1070 w, 1220 m, 1310 w, 1620 s, 1660 w, 1215 m, 1620 s, 680 s, 925 m, 960 w, 1040 m, 1200 m, 1610 s, 1180 s, 1425 s, 1610 s</td>
<td>720-740 s, 955 s, 1075 m, 1615 s, 680 s, 710 s, 878 s, 925 m, 955 w, 1042 w, 1610 s, 680 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
</tr>
<tr>
<td>((\text{CH}_3\text{CH}=\text{CH})_3\text{AsBr}_2)</td>
<td>750 s, 950 s, 1075 m, 1215 m, 1620 s, 680 s, 755 s, 925 s, 1180 s, 1425 s, 1610 s</td>
<td>720-740 s, 955 s, 1075 m, 1615 s, 680 s, 710 s, 878 s, 925 m, 955 w, 1042 w, 1610 s, 680 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
</tr>
<tr>
<td>((\text{CH}_3\text{CH}=\text{CH})_3\text{AsCH}_3)</td>
<td>690 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
<td>690 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
</tr>
<tr>
<td>((\text{CH}_3\text{CH}=\text{CH})_3\text{As} \cdot \text{HgCl}_2)</td>
<td>690 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
<td>690 s, 715-735 s, 955 s, 1075 s, 1220 s, 1610 s, 1680 w, 1610 s</td>
</tr>
</tbody>
</table>

Note. s = strong; m = medium strength; w = weak.

substance that was close in constants and analysis to triisopropenylarsine, and from the products of the reaction of triisopropenylarsine, and from the products of the reaction of triisopropenylarsine dibromide with phenyllithium, we isolated triisopropenylarsine, which was characterized in the form of the complex \((\text{CH}_3\text{CH}=\text{CH})_3\text{As} \cdot \text{HgCl}_2\), and biphenyl. The course of this process can be represented as follows:

\[
\begin{align*}
\text{R}_3\text{AsBr}_2 + 2\text{RLi} \rightarrow [\text{R}_3\text{As}] + 2\text{LBr} \\
[\text{R}_3\text{As}] \rightarrow \text{R}_3\text{As} + 2\text{R}_1 \\
2\text{R}_1 \rightarrow \text{R} + \text{R}_1
\end{align*}
\]

The quinquevalent arsenic compound formed is unstable and decomposes with formation of a tervalent arsenic compound and two radicals, which in the first case form 2,3-dimethyl-1,3-butadiene and in the second case biphenyl.

EXPERIMENTAL

Triisopropenylarsine. A solution of 6.7 g of arsenic trichloride in 30 ml of dry ether was added dropwise to a stirred cooled ethereal solution of isopropenyllithium, prepared from 2.2 g of lithium, 20 g of isopropenyl bromide, and 250 ml of dry ether. The reaction mixture was heated for three hours in a water bath, cooled, and decomposed with 35 ml of water, slightly acidified with HCl. The ether layer was separated and dried over CaCl₂. Ether was distilled off, and the residue was vacuum-fractionated. We obtained 5.17 g (70.6%) of a clear colorless substance, b.p. 66-67.5 °C (15 mm); nᵣ 1.5143; d₄ 1.0751. Found: C 54.86, 54.15; H 7.65, 7.68%. i-C₅H₁₃As. Calculated: C 54.55; H 7.63%.

Tri-cis-propenylarsine. This compound was synthesized under conditions analogous to those for the preparation of triisopropenylarsine by the reaction of 6.7 g of AsCl₃ with an ethereal solution of cis-propenyllithium prepared from 2.2 g of lithium, 20 g of cis-propenyl bromide, and 250 ml of dry ether. We obtained 5.25 g (71.2%) of a clear colorless substance, b.p. 87-88 °C (18 mm); nᵣ 1.5257; d₄ 1.0942. Found: C 54.15, 54.17; H 7.40, 7.48%. cis-C₅H₁₃As. Calculated: C 54.55; H 7.63%.

Tri-trans-propenylarsine. This compound was synthesized under conditions analogous to those for the preparation of triisopropenylarsine by the reaction of 6.7 g of AsCl₃ with an ethereal solution of cis-propenyllithium prepared from 2.2 g of lithium, 20 g of trans-propenyl bromide, and 250 ml of dry ether. We obtained 5.98 g (81%) of product, b.p. 71-72 °C (6 mm); nᵣ 1.5209; d₄ 1.0717. Found: C 54.57, 54.86; H 7.54, 7.63%. trans-C₅H₁₃As. Calculated: C 54.55; H 7.63%.

Triisopropenylarsine Dibromide. A solution of 2.45 g of bromine in 5 ml of dry chloroform was added dropwise to a solution of 3 g of triisopropenylarsine in 30 ml of dry ether cooled to -30 °C. The white crystalline precipitate that formed was washed several times with dry ether and vacuum-dried. We obtained 4.13 g (76.1%) of product, m.p. 157 °C. Found: C 30.56, 30.82; H 4.29, 4.24%. i-C₅H₁₃AsBr₂. Calculated: C 30.19; H 4.22%.