The Search for New Methods of Synthesis Possible of Organometallic Compounds of P, As, Sb, Bi

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Abstract: The authors spent the search for new methods of synthesis possible of organometallic compounds of phosphorus, arsenic, antimony, bismuth. For modifications classical reactions the N (nitrogen) atoms have been replaced on atoms of P (phosphorus), As (arsenic), Sb (antimony) and Bi (bismuth). The authors have proposed a new mechanism for the possible reactions.

Key words: Organometallic chemistry, P, As, Sb, Bi.

1. Introduction

In recent years, many chemists are actively investigated nucleophilic organohalogenids phosphine with electrophilic heterarylkenes, allowing to obtain primary, secondary, tertiary and quaternary phosphines, selectively and in high yield [1-4].

Although the chemistry of organophosphorus compounds has devoted a considerable amount of books, but the reaction of organic compounds of arsenic, antimony and bismuth are very limited.

Currently, much attention to the search of new metal-organic compounds had potential biological activity.

The purpose of this paper is to search the new methods of synthesis possible of organometallic compounds of boron, Al (aluminum), Ga (gallium), In (indium), Tl (thallium), P (phosphorus), As (arsenic), Sb (antimony), Bi (bismuth).

2. Theory

It is known that N (nitrogen) forms several compounds with H (hydrogen), such as hydroxylamine and hydrazine.

Hydrazine (diamide) H₂N-NH₂ a colorless, highly hygroscopic liquid with an unpleasant odor. N₂H₄ molecule consists of two groups of NH₂, the rotated relative to each other, which causes the polarity of the molecule of hydrazine, μ = 0.62 × 10⁻⁹ C/m (Coulomb/m), hydrazine and its derivatives are most toxic.

Hydrazine is much less thermodynamically stable than ammonia as N-N bond is not very strong: the decomposition of hydrazine-exothermic reaction in the absence of catalysts at 200-300 °C:

$$3N_2H_4 \rightarrow 4NH_3 + N_2$$

The transition metals (Co (carbon monoxide), Ni (nickel), Cu (copper), Ag (silver)) catalyze the decomposition of hydrazine, catalysed by platinum, rhodium and palladium are the main decomposition products N and H:

$$N_2H_4 \rightarrow N_2 + 2H_2$$

Due to the presence of two unshared electron pairs on the nitrogen atoms, hydrazine able to join one or two h ions. When you join one proton obtained hydrazine compound with a charge of 1⁺, two protons-hydrazone charge 2⁺ ions containing respectively N₂H₃⁺ and N₂H₆²⁺. Aqueous solutions of hydrazine have basic properties, but significantly less basicity than ammonia:

$$N_2H_4 + H_2O \rightarrow [N_2H_3]^+ + OH^-, K_b = 3.0 \times 10^{-6}$$

(for ammonia $K_b = 1.78 \times 10^{-5}$)
Protonation second pair of electrons proceed more difficultly:
\[ \text{[N}_2\text{H}_5\text{]}^+ + \text{H}_2\text{O} \rightarrow \text{[N}_2\text{H}_6\text{]}^{2+} + \text{OH}^-; K_b = 8.4 \times 10^{-16} \]

Hydrazine-energetic reducing agent. The hydrazine solution also typically is oxidized to N:
\[ 4\text{KMnO}_4 + 5\text{N}_2\text{H}_4 + 6\text{H}_2\text{SO}_4 \rightarrow 5\text{N}_2 + 4\text{MnSO}_4 + 2\text{K}_2\text{SO}_4 + 16\text{H}_2\text{O} \]

Recover hydrazine to ammonia can only strong reducing agents, such as Sn\(^{2+}\), Ti\(^{3+}\), nascent H (Zn + HCl):
\[ \text{N}_2\text{H}_4 + \text{Zn} + 4\text{HCl} \rightarrow 2\text{NH}_4\text{Cl} + \text{ZnCl}_2 \]

Hydrazine is produced by oxidation of ammonia NH\(_3\) or urea CO(NH\(_2\))\(_2\), sodium hypochlorite NaClO (method Raschig):
\[ \text{NH}_3 + \text{NaOCl} \rightarrow \text{NH}_2\text{Cl} + \text{NaOH} \]
\[ \text{NH}_2\text{Cl} + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4\text{-HCl} \]
the reaction is performed at a temperature of 160 °C and a pressure of 2.5-3.0 MPa.

The synthesis of hydrazine hypochlorite oxidation of urea by the mechanism is similar to the synthesis of amides, amines Hofmann:
\[ (\text{NH}_2\text{)}_2\text{CO} + \text{NaOCl} + 2\text{NaOH} \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O} + \text{NaCl} + \text{Na}_2\text{CO}_3 \]
the reaction is conducted at a temperature of about 100 °C and atmospheric pressure.

Bayer method:
\[ 2\text{NH}_3 + \text{H}_2\text{O}_2 \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O} \]

Hydroxylamine NH\(_2\text{OH}\) – colorless crystals, readily soluble in water to form a hydrate NH\(_2\text{OH}\)·H\(_2\text{O}\). The aqueous solution is dissociated by basic type, being a weak base:
\[ \text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow [\text{NH}_3\text{OH}]^- + \text{OH}^-; K_a = 2 \times 10^{-8} \]

It may also be dissociated and the acid type with a pKa = 14.02:
\[ \text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{O}^- + \text{H}_3\text{O}^+ \]

Hydroxylamine exhibits the properties of a reducing agent, under the action of oxidants allocated N\(_2\) or N\(_2\)O:
\[ 2\text{NH}_2\text{OH} + \text{J}_2 + 2\text{KOH} \rightarrow \text{N}_2 + 2\text{KJ} + 4\text{H}_2\text{O} \]

In some reactions occur NH\(_2\text{OH}\) oxidizing properties, while it is reduced to NH\(_3\) or NH\(_4^+\):
\[ \text{NH}_2\text{OH} + \text{H}_2\text{S} \rightarrow \text{NH}_3 + \text{S} + \text{H}_2\text{O} \]

Hydroxylamine interacting with aldehydes and ketones, form oximes: R-CH=NOH and R=C=NOH.

Hydrazoic acid azoimid (azidovodorod), N\(_3\)-acid compound of N with H. A colorless, volatile, highly explosive (explode when heated, impact or friction) liquid with a pungent odor. This compound is very toxic.

Dilute aqueous solutions are not explosive, but upon standing HN\(_3\) solution slowly decomposes to N and hydroxylamine:
\[ \text{HN}_3 + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{NH}_3\text{OH} \]

In aqueous solution HN\(_3\) exhibits properties of a weak acid (pKa = 4.59). By strength is close to acetic acid. In solutions of hydrazoic acid dissociates into ions:
\[ \text{HN}_3 \leftrightarrow \text{H}^+ + \text{N}_3^- \]

The acid HN\(_3\) is an oxidant. With metals forming a metal salt, ammonia and N:
\[ \text{Cu} + 3\text{HN}_3 \rightarrow \text{Cu(N}_3\text{)}_2 + \text{N}_2 + \text{NH}_3 \]

HN\(_3\) prepared by the action of phosphoric acid on sodium azide NaN\(_3\), which was synthesized from sodium amide:
\[ 2\text{NaN}_3 + \text{H}_3\text{PO}_4 \rightarrow 3\text{HN}_3 + \text{Na}_3\text{PO}_4 \]

3. Results and Discussions

The authors propose to expand and replace the nitrogen atoms into atoms of P, As, Sb, Bi and receive P, As, Sb, Bi oxidation of hydrazine derivatives of phosphine, arsine, stibine and bismuthine EH\(_3\) or urea CO(NH\(_2\))\(_2\) sodium hypochlorite NaClO (Raschig method):
\[ \text{EH}_3 + \text{NaOCl} \rightarrow \text{EH}_2\text{Cl} + \text{NaOH} \]
\[ \text{EH}_2\text{Cl} + \text{EH}_3 \rightarrow \text{E}_2\text{H}_4\text{HCl} \]
where, E = N, P, As, Sb, Bi.

Synthesis hydrozine urea oxidation of hypochlorite by a mechanism similar to the amine from amides Hofmann:
\[ (\text{EH}_2\text{)}_2\text{CO} + \text{NaOCl} + 2\text{NaOH} \rightarrow \text{E}_2\text{H}_4 + \text{H}_2\text{O} + \text{NaCl} + \text{Na}_2\text{CO}_3 \]
The authors propose to expand and replace the nitrogen atoms on the P atoms, As, Sb and Bi and receive P, As, Sb, Bi derivatives of HE₃ prepared by the action of phosphoric acid (P-, As-, Sb-, Bi) azide, sodium NaE₃, which is synthesized from NaEH₃:

$$2\text{NaEH}_3 + \text{E}_2\text{O} \rightarrow \text{NaE}_3 + \text{NaOH} + \text{EH}_3$$

$$3\text{NaE}_3 + \text{H}_3\text{PO}_4 \rightarrow 3\text{HE}_3 + 3\text{Na}_3\text{PO}_4$$

where, E = N, P, As, Sb, Bi.

Comparison of organic nitrogen compounds with organic As, Sb, Bi showed that they all substitution reactions of amines with a variety of organic compounds having a labile hydrogen atom.

Thus, the authors first proposed to expand and replace atoms and N atoms of P, As, Sb, Bi, and receive new methods of synthesis possible of organometallic compounds of phosphorus, arsenic, antimony, bismuth. The authors have proposed a new mechanism for the possible reactions.

4. Conclusions

The authors have for the first time provided novel methods for the synthesis of possible organometallic compounds of boron, aluminum, gallium, indium, thallium, phosphorus, arsenic, antimony, bismuth.

The authors propose a mechanism of these reactions, which can be used in the synthesis of new organometallic compounds of boron, aluminum, gallium, indium, thallium, phosphorus, arsenic, antimony, bismuth.

The proposed new methods of synthesis potential of organometallic compounds of boron, aluminum, gallium, indium, thallium, phosphorus, arsenic, antimony, bismuth open new horizons to expand the potential application of biologically active substances, catalysts, pharmaceuticals preparations.

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References


