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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 heterylalkens, 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) $H_2N\text{-}NH_2$- a colorless, highly hygroscopic liquid with an unpleasant odor. N_2H_4

molecule consists of two groups of NH_2, the rotated relative to each other, which causes the polarity of the molecule of hydrazine, $\mu = 0.62 \times 10^{-29}$ 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 $N_2H_5^+$ and $N_2H_6^{2+}$. Aqueous solutions of hydrazine have basic properties, but significantly less basicity than ammonia:

$$N_2H_4 + H_2O \rightarrow [N_2H_5]^+ + OH^-, K_b = 3.0 \times 10^{-6}$$

(for ammonia $K_b = 1.78 \times 10^{-5}$)

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Protonation second pair of electrons proceed more difficultly:

$$[N_2H_5]^+ + H_2O \rightarrow [N_2H_6]^{+2} + OH^-, K_b = 8.4 \times 10^{-16}$$

Hydrazine-energetic reducing agent. The hydrazine solution also typically is oxidized to N:

$$4KMnO_4 + 5N_2H_4 + 6H_2SO_4 \rightarrow$$
$$5N_2 + 4MnSO_4 + 2K_2SO_4 + 16H_2O$$

Recover hydrazine to ammonia can only strong reducing agents, such as Sn^{2+}, Ti^{3+}, nascent H (Zn + HCl):

$$N_2H_4 + Zn + 4HCl \rightarrow 2NH_4Cl + ZnCl_2$$

Hydrazine is produced by oxidation of ammonia NH_3 or urea $CO(NH_2)_2$, sodium hypochlorite NaClO (method Raschig):

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$
$$NH_2Cl + NH_3 \rightarrow N_2H_4 \cdot HCl$$

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:

$$(NH_2)_2CO + NaOCl + 2NaOH \rightarrow$$
$$N_2H_4 + H_2O + NaCl + Na_2CO_3$$

the reaction is conducted at a temperature of about 100 °C and atmospheric pressure.

Bayer method:

$$2NH_3 + H_2O_2 \rightarrow N_2H_4 + H_2O$$

Hydroxylamine NH_2OH—colorless crystals, readily soluble in water to form a hydrate $NH_2OH \cdot H_2O$. The aqueous solution is dissociated by basic type, being a weak base:

$$NH_2OH + H_2O \rightarrow [NH_3OH]^+ + OH^-, K_o = 2 \times 10^{-8}.$$

It may also be dissociated and the acid type with a pKa = 14.02:

$$NH_2OH + H_2O \rightarrow NH_2O^- + H_3O^+$$

Hydroxylamine exhibits the properties of a reducing agent, under the action of oxidants allocated N_2 or N_2O:

$$2NH_2OH + J_2 + 2KOH \rightarrow N_2 + 2KJ + 4H_2O$$

In some reactions occur NH_2OH oxidizing properties, while it is reduced to NH_3 or NH_4^+:

$$NH_2OH + H_2S \rightarrow NH_3 + S + H_2O$$

Hydroxylamine interacting with aldehydes and ketones, form oximes: R-CH=NOH and R_2-C=NOH.

Hydrazoic acid azoimid (azidovodorod), HN_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:

$$HN_3 + H_2O \rightarrow N_2 + NH_2OH$$

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:

$$HN_3 \leftrightarrow H^+ + N_3^-$$

The acid HN_3 is an oxidant. With metals forming a metal salt, ammonia and N:

$$Cu + 3HN_3 \rightarrow Cu(N_3)_2 + N_2 + NH_3$$

HN_3 prepared by the action of phosphoric acid on sodium azide NaN_3, which was synthesized from sodium amide:

$$2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$
$$3NaN_3 + H_3PO_4 \rightarrow 3HN_3 + Na_3PO_4$$

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):

$$EH_3 + NaOCl \rightarrow EH_2Cl + NaOH$$
$$EH_2Cl + EH_3 \rightarrow E_2H_4.HCl$$

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

Synthesis hydrozine urea oxidation of hypochlorite by a mechanism similar to the amines from amides Hofmann:

$$(EH_2)_2CO + NaOCl + 2NaOH \rightarrow$$
$$E_2H_4 + H_2O + NaCl + Na_2CO_3$$

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

Metod Bayer:

$$2EH_3 + H_2O_2 \rightarrow E_2H_4 + H_2O$$

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

Hydroxyl (phosph-, ars-, stib-, bismuth) ine, interacting with aldehydes and ketones, oximes forms: $R\text{-}CH = E\text{-}OH$ and $R_2\text{-}C = E\text{-}OH$

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

For example:

$$2\ (CH_3)_2CO + N_2H_4 \rightarrow 2\ H_2O + [(CH_3)_2C{=}N]_2$$

$$[(CH_3)_2C{=}N]_2 + N_2H_4 \rightarrow 2\ (CH_3)_2C{=}NNH_2$$

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

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 HE_3 prepared by the action of phosphoric acid (P-, As-, Sb-, Bi) azide, sodium NaE_3, which is synthesized from $NaEH_2$:

$$2NaEH_2 + E_2O \rightarrow NaE_3 + NaOH + EH_3$$

$$3NaE_3 + H_3PO_4 \rightarrow 3HE_3 + Na_3PO_4$$

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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