A New Modification Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker and Raymond Reactions with Organic Compounds Arsenic, Antimony and Bismuth

Aibassov Erkin Zhakenovich*, Kenzhaliev Bagdaulet Kenzhalievich, Berkinbaeva Ainura, Chukmanova Marzhan and Iskhakova Renata

Kazakh-British Technical University, Almaty 050000, Kazakhstan

Received: October 25, 2013 / Accepted: November 10, 2013 / Published: March 25, 2014.

Abstract: In this work study, we investigated possibility of modifying the new Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker, Raymond reactions with organic compounds of arsenic, antimony and bismuth is discovered. A new mechanism for possible reactions has been proposed.

Key words: Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker, Raymond reactions, organic compounds of arsenic, antimony, bismuth.

1. Introduction

In recent years, as effective catalysts and reagents in organic synthesis is increasingly used organometallic compounds of arsenic, antimony and bismuth provides enhanced selectivity, high speed and mild process conditions. Expanding the range of organometallic compounds of As, Sb and Bi, used for this purpose, of course, is an important task. In this regard, one of the fundamental problems of chemistry is the synthesis of stable organic compounds, arsenic, antimony, bismuth, and the study of their capabilities in this aspect. As-, Sb-, Bi-organic compounds are not only practical interest. The large size of the bismuth atom and features of its electronic structure produces a greater possibility of its coordination sphere. The purpose was to search for new methods of synthesis of As-, Sb-, Bi-organic compounds based on the

Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker, Raymond reactions.

2. Theory

Known reaction Michaelis-Arbuzov rearrangement trialkyl phosphonates in the reaction with alkyl halides:

where, X = Cl, Br, J.

Reacting a halogenated variety: primary alkyl halides, CCl₄, α-halo ethers, esters, halides. The easiest way to react AlkX and Ar₃CX. Reactivity of RX decreases in the ranges: J, Br, Cl, as well as with increasing chain length carbon radicals of R.

By a similar rearrangement is also capable of other compounds containing the group = POR', e.g., R'P(OR')₂ and R'₂POR', and also with a group of thio derivatives = PSR', except for P(SR')₃ reacting P(OR')₃ with α-haloketones flows abnormally (see

*Corresponding author: Aibassov Erkin Zhakenovich, Professor, research fields: metallorganic chemistry of arsenic, antimony and bismuth. E-mail: erkin53@mail.ru.

Perkova reaction).

The rearrangement is general in nature and can be defined as the transformation of phosphorous acid esters in the pentavalent phosphorus derivatives that occur under the influence of electrophilic reagents and accompanied by the formation of a new connection P-E (E = C, N, O, S, Si, etc.), for example:

Reactions are widely used for the preparation of insecticides, medicinal substances, and other physiologically active organophosphorus compounds.

Allen is known for reaction to form phosphorylated oxime reacting phosphorous acid esters with α -galogennitro or α -galogennitroso-compounds:

where X = O, S, Se, Te; R'—Alk, Ar, OAlk, NAlk₂, NHalk, F, Cl, Br, J; R''—H, Alk, F, Cl, Br, J; R'''—Alk, COOAlk, F, Cl, Br, J; Hal—Cl, Br, J.

The reaction is carried out in an organic solvent or without at temperatures of -40-50 °C. Nitroso compounds usually have a higher reactivity than nitro. Reaction rate increases with increasing the mobility of atoms and Hal atom with increasing nucleophilicity P; yield 10%-80%.

Byproducts—fosforil soedineniya ROP(O)R'₂ (in reactions with nitro derivatives), compounds resulting from Arbuzov rearrangement (RHal by reacting the starting compounds with P(III)), as well as high molecular compound (with involvement of the reaction of cyclic esters).

It is believed that the initial reaction act -P attack atom per atom Hal to give intermediates I or II, when cleaved RHal converted to the final product.

Similarly, the reaction proceeds trialkyl, and dialkylgalogen alkildigalogenfosfitov with α -galogennitrozoalkanami:

where R, R' = OC₂H₅; Cl; R'' = CF₃, CF₂NO₂; R''' = CF₃, F, Cl.

The advantage of the nitroso compounds is the lack of a side reaction of oxidation.

The resulting phosphorylated oximes are nitrogenous analogues enolfosfatov—Perkova reaction products.

Allen's reaction was used in the laboratory. It is opened by J. Allen in 1957.

Known reaction Milobendzki-Szulgin conversion in trialkyl O,O-diarilmetilfosfonaty when heated to 215 and a pressure operating with methanol:

where, Ar = C₆H₅, C₆H₄CH₃.

Similarly react trialkyl phosphites:

When using ethanol yield decreases phosphonates:

In the case of higher alcohols, the main reaction is a transesterification:

Know the reaction Michaelis-Becker for the synthesis of organophosphorus compounds by alkylation or arylation of compounds hydrophosphoryl neutral salts (phosphites, phosphonites and phosphinites of alkali metals) by reacting an alkyl or aryl halides or other alkylating or arylating agents:

where, M = Li, Na, K; R = Alk, Ar; Y, Z = Alk, Ar, AlkO, ArO, Alk₂N, AlkS.

Reactivity AlkHal decreases from secondary to secondary to tertiary, and further, and with increasing molecular weight alkyl radical.

Michaelis-Becker reaction used to prepare many organophosphorus-pesticides, medicines and other extractants.

Reaction opened A. Michaelis and T. Becker in

1897.

Know the reaction of alkyl halides Rydon getting action on alcohol with alkyltriphenoxiphosphonihalogenides:

where, R = Alk; R' = Alk; X = Cl, Br, J.

Reacting a well alicyclic, allene and acetylenic alcohols, glycols, steroid alcohols.

The reaction can be carried out without prior conversion into phosphonium triphenyl phosphite compound:

Unsaturated alcohols very smoothly converted to the bromide by the action of $(\text{C}_6\text{H}_5\text{O})_3\text{P}$ with Br_2 in pyridine.

Method Forsman-Lipkin—converting alcohols to iodides difenil hlorfosfitom reaction with a pyridine or fenilen hlorfosfitom followed by treatment with iodine:

3. Results and Discussion

The authors have studied the possibility of extending the scope of this reaction by incorporating atoms of arsenic, antimony, bismuth, and substituted derivatives.

Comparison Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker and Raymond reactions with organic compounds arsenic, antimony and bismuth showed that they all substitution reactions of amines with a variety of organic compounds which have a labile hydrogen atom.

The authors have proposed a general view of the proposed new reaction Michaelis-Arbuzov, Allen,

Milobendzky-Shulgin, Michaelis-Becker and Raymond reactions of amines on the replacement of an atom of arsenic, antimony and bismuth.

The authors propose a general Michaelis-Arbuzov rearrangement of trialkyl-(arsine, stibine, bismuth) itov in phosphine (arsine, stibine, bismuth) aty by reaction with alkyl halides:

where, E = P, As, Sb, Bi; X = Cl, Br, J.

The authors propose to expand the Allen reaktsiyu obtain phosphorus (arsenic, antimony, bismuth) pegylated oxime acid esters by reaction of trivalent phosphorus, arsenic, antimony and bismuth galogennitro- α or α -galogennitroso compounds:

where, E = P, As, Sb, Bi; X = O, S, Se, Te; R' = Alk, Ar, OAlk, NAlk₂, NHAlk, F, Cl, Br, J; R'' = H, Alk, F, Cl, Br, J; R''' = Alk, COOAlk, F, Cl, Br, J; Hal—Cl, Br, J.

The authors propose expanding region Milobendzky-Shulgin reaction conversion trialkyl (arsine, stibolyl, bismuth) to itov O,O-diarilmetilfosf (arsine, stibolyl, bismuth) on at when heated to 215 °C and the operating pressure with methanol:

where, E = P, As, Sb, Bi; Ar = C_6H_5 , $\text{C}_6\text{H}_4\text{CH}_3$.

The authors propose to expand and modify the Michaelis-Becker reaction-synthesis of phosphorus (arsenic, antimony, bismuth) organic compounds, alkylation or arylation gidrofosfor neutral salts (arsine, stibine, bismuthine) yl compounds (phosphites, phosphonites and phosphinites of alkali metals), by reacting alkyl or aryl halides or other alkylating or arylating agents:

where, E = P, As, Sb, Bi; M = Li, Na, K; R = Alk, Ar; Y, Z = Alk, Ar, AlkO, ArO, Alk₂N, AlkS.

The authors propose to expand and modify the

reaction of alkyl halides Rydon for action on alcohol alkyltrifenoxysifosfony (arsonium, stibonium, vismutony) halides:

where, E = As, Sb, Bi; R = Alk; R' = Alk; X = Cl, Br, J.

Thus, the theoretical concept allows research to predict new reactions in organometallic chemistry.

4. Conclusions

The authors discovered the possibility of modifying the new Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker, Raymond reactions with organic compounds of arsenic, antimony and bismuth. The authors have proposed a new mechanism for possible reactions. New proposed Michaelis-Arbuzov, Allen, Milobendzky-Shulgin, Michaelis-Becker, Raymond reactions are will used for the synthesis of new catalysts, bioactive substances, drugs.

The authors hope that this material will further expand the research in the chemistry of arsenic, antimony, bismuth, and the development of new reactions based on their synthesis of various organometallic compounds.

Acknowledgments

The authors would like to thank Ruben M. Savizky (Columbia University, New York) and Chistopher L. Cahill (George Washington University) for discussion of the results.

References

[1] Michaelis, A.; Kaehne, R. *Ber.* **1898**, *31*, 1048.

- [2] Arbuzov, A. E. *Journal Russian Physico-Chem. Soc.* **1906**, *38*, 687.
- [3] Burt, D. W.; Simpson, P. J. *Chem. Soc.* **1969**, 2273.
- [4] Rafikov, S. R.; Chelnova, G. N.; Dzhilkibaeva, G. M. *Proceed of the Institute of Chemical Sciences of the Kazakh SSR* **23**, 80.
- [5] Arbuzov, B. A. Z. *Chem.* **1974**, *14*, 41-49.
- [6] Kirby, A.; Warren, C. *The Organic Chemistry of Phosphorus*; Pudovik, A. N., Ed.; Wiley: New York, 1971; p 44.
- [7] Pudela, D.; Valchanov, R. Chemistry of Organic Phosphorus Compounds. In *Trans. from Rum*; Kabachnil, M. I., Ed.; Chemistry: Moscow, 1972; p 382.
- [8] Organic Reaction. In *Trans. From English*; Kocheshkov, K. A., Ed.; Moscow, 1948; p 276.
- [9] Reactions and Methods of Organic Reactions. Rodionov, V. M., Ed., Chemistry: Moscow, 3, p 7.
- [10] Allen, J. F. *J. Am. Chem. Soc.* **1957**, *79*(12), 3071-3073.
- [11] Martynov, I. V.; Kruglyak, J. L.; Pereverntseva, N. F. *J. Org. Chem.* **1967**, *37*, 1125-1132.
- [12] Malekin, S. I.; Yakutin, V. I.; Sokolsky, M. A. *J. Org. Chem.* **1972**, *42*, 807.
- [13] Pudela, D.; Valchanov, R. Chemistry of Organic Phosphorus Compounds. In *Lane from Rum*; Kabachnil, M. I., Ed., Chemistry: Moscow, 1972; p 390.
- [14] Milobendzki, T.; Szulgin, K. *Chem. Polski* **1917**, *15*, 66.
- [15] Cason, J.; Baxter, W. N. *J. Org. Chem.* **1958**, *23*, 1302.
- [16] Pudela, D.; Valchanov, R. Chemistry of Organic Phosphorus Compounds. In *Lane from Rum*; Kabachnil, M. I., Ed.; Chemistry: Moscow, 1972; p 387.
- [17] Michaelis, A.; Becker, T. *Ber.* **1897**, *30*(1), 1003.
- [18] Shieybert, A. I.; Wise, L. M.; Wise, F. W. *J. Org. Chem.* **1969**, *39*, 1416.
- [19] Vilceanu, R. *Neamtia J. Rev. Chim.* **1973**, *24*(3), 153.
- [20] Landauer, S. R.; Rydon, H. N. *J. Chem. Soc.* **1953**, 2224.
- [21] Forsman, J. P.; Lipkin, D. *J. Am. Chem. Soc.* **1953**, *75*, 3145.
- [22] Fieser, L.; Fieser, M. *Reagents for Organic Synthesis*. John Wiley, 1970; Vol. 3, p 416.