J. Chem. Chem. Eng. 15 (2021) 22-23
doi: 10.17265/1934-7375/2021.01.004

New RedOx Multicomponent Reactions Phosphine, Phosphorous, Phosphide and Hypophosphite

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Abstract: We have discovered new RedOx multicomponent reactions phosphine, phosphorous, phosphide and hypophosphite. These new RedOx multicomponent reactions can be used for arsenic, antimony and bismuth. We have performed quantum-chemical calculations of new multicomponent reactions of phosphorus and arsine.

Key words: RedOx multicomponent reactions, phosphine, phosphorous, phosphide, hypophosphite.

1. Introduction

Multicompounts reactions (MCRs) are of interest from both a fundamental and a practical point of view. They have been successfully applied to the synthesis of complex polyfunctional compounds. The creation of new synthetic methodologies that allow the synthesis of target compounds at lower costs and faster is an important task of modern organic chemistry. One of the most effective methods for solving this problem is the development of new cascade and multicomponent reactions with the participation of phosphine and arsine.

This work is devoted to the creation and development of the newest direction in organic chemistry—cascade and multicomponent reactions of phosphorus, arsenic, antimony and bismuth.

2. Theory

Yerkin and Kenzhaliev [1] found that, when a PH_3-Ar gas mixture is passed through an alcoholic solution of Na_2PtCl_6 (at 25-150 °C), trialkyl phosphites (at 25-70 °C), trialkyl phosphates and tertiary phosphine oxides (at 90-150 °C) are formed:

$$PH_3 + 3ROH + 3Na_2PtCl_6 \rightarrow P(RO)_3 + 6HCl + 3Na_2PtCl_4 \quad (1)$$

$$PH_3 + 3RCH_2OH + 1.5Na_2PtCl_6 \rightarrow (RCH_2)(RCHOH)_2PO + 1.5Pt + 3NaCl + 6HCl \quad (2)$$

$$PH_3 + 4RCH_2OH + 2Na_2PtCl_6 \rightarrow (RCH_2O)_3PO + 2Pt + 4NaCl + RCH_2Cl + 7HCl \quad (3)$$

New RedOx multicomponent reactions come very quickly. During the absorption of PH_3, the RedOx potential of the Pt(IV)/Pt(II) pair shifts to the cathode side.

3. Results and Discussion

We have systematically investigated new RedOx multicomponent reactions for phosphine, phosphorous, phosphide and hypophosphite, as well as for arsenic.

For various oxidation states of phosphorus (-3; -1; 0; +1; +3) new RedOx multicomponent reactions will be as follows:

$$P_4 + 12ROH + 5O_2 \rightarrow 4(RO)_3PO + 6H_2O \quad (4)$$

$$PH_3 + 3ROH + 2O_2 \rightarrow (RO)_3PO + 3H_2O \quad (5)$$

$$Zn_3P_2 + 6ROH + 4O_2 \rightarrow 2(RO)_3PO + 3Zn(OH)_2 \quad (6)$$

$$Na(PH_2O_2) + 7ROH + O_2 \rightarrow (RO)_2HPO + (RO)_3PO + (RO)_2(HO)PO \quad (7)$$

In the first reaction, a 5-electron transition occurs: phosphorus (0) is oxidized to P (+5), in the second reaction, an 8-electron transition: P (-3) is oxidized to

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P (+5), in the third reaction, a 2-electron transition: P (+3) is oxidized to phosphate (+5), in the fourth reaction, 4-electron transition: P (+1) is oxidized to P (+5).

Similarly for arsine:

$$AsH_3 + 2ROH + RCHO + RNH2 \rightarrow (RO)_2As(O)C(R)(R1)NHR \quad (8)$$

We have proposed a general scheme for new RedOx multicomponent reactions:

$$E\ (-1) - 6e \rightarrow E\ (+5) \quad (9)$$

where E = P, As, Sb, Bi.

$$E\ (0) - 5e \rightarrow E\ (+5) \quad (10)$$

$$E\ (+1) - 4e \rightarrow E\ (+5\ ) \quad (11)$$

$$E\ (+3) - 2e \rightarrow E\ (+5\ ) \quad (12)$$

Thus, these new RedOx multicomponent reactions can be applied to other elements: B, Si, S, Se, Te and others.

4. Conclusion

As a result of the research carried out, the following results were achieved: for the first time, an original method for creating new tandem reactions was developed, based on simultaneous temperature variation in already known reactions of this type; discovered four new groups of reactions of phosphines, phosphorus, phosphide and hypophosphites with alcohols, amines, mercaptans, which significantly expands the existing understanding of the reactivity of the phosphorus group; found a new general method for increasing the selectivity of tandem reactions of phosphine, phosphorous, phosphide and hypophosphite; similarly for arsenic derivatives (arsine, arsenide, hypoarsenite), antimony and bismuth.

The results considered in this work are fundamentally new. For the first time, a method for the synthesis of phosphorus- and arsenic-containing compounds, which can be potentially anticancer agents, has been proposed.

New RedOx multicomponent reactions of phosphorus and arsenic have been studied in detail for the first time. On their basis, an effective method for the synthesis of P- and As-containing compounds has been developed.

Thus, we have proposed a new theory of RedOx multicomponent reactions using a method for controlling their selectivity, including varying the nature of the catalytic system, the temperature regime, the type of activation, the structure of the reactants, and other reaction parameters, which open up wide possibilities for effective synthesis and increasing diversity organic compounds.

References

[1] Yerkin, A., and Kenzhaliev, B. 2014. *The New Reactions in Organometallic Chemistry of Arsenic, Antimony*. GmbH, Germany: Lambert Academic Publishing.