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CARBOXYLATION OF HYDROXYARENES WITH POTASSIUM ETHYL CARBONATE

Abstract. The influence of the conditions for carrying out the carboxylation reaction of phenol and its derivatives (petrochemical products) with alkaline salts of alkylcarbonic acids (potassium ethyl carbonate), easily synthesized from carbon dioxide, alcohols and alkaline metal hydroxides, was studied in order to develop new, effective methods for producing practically valuable p-hydroxybenzoic acid and other hydroxybenzoic acids (a class of compounds having a wide range of biologically active properties and other beneficial properties) is relevant and timely. A new simple and convenient method for the synthesis of p-hydroxybenzoic acid by the reaction of phenol carboxylation with potassium ethyl carbonate has been developed, which allows one to obtain the target product without impurity of o-hydroxybenzoic acid. For the first time, optimal conditions were found for the regioselective p-carboxylation of phenol (pressure of carbon dioxide, temperature and duration of the process) under which the yield of p-hydroxybenzoic acid is 71,0%, and the effect of various substituents in the aromatic ring on the yield of the target products of the carboxylation of phenol derivatives is determined sodium and potassium carbonates. The influence of the nature of the alkyl groups of potassium alkyl carbonates on the carboxylation activity of the latter in the phenol carboxylation reaction was determined. We have studied that temperature has a strong influence on the direction of phenol carboxylation. When carrying out the reaction below 200°C, carboxylation proceeds to the o- and p-positions with the formation of o-hydroxybenzoic and p- hydroxybenzoic acids; the o-isomer predominates (44,9-66,7%). When carrying out the reaction above 200°C, only p-hydroxybenzoic acid is formed without an impurity of o-hydroxybenzoic acid.

Key words: carboxylation, hydroxyarenes, hydroxybenzoic acid, carbon dioxide, potassium ethyl carbonate, p-hydroxybenzoic acid.

Introduction. Carbon dioxide in the future may become one of the most important sources of carbon raw materials for chemical synthesis [1,3]. Oil and coal reserves are gradually being depleted. After oil and coal natural gas reserves will also run out. Carbon dioxide reserves are almost inexhaustible. The most promising sources of CO_2, as carbon raw materials can be waste gases of chemical industry enterprises and power plants, as well as natural gas deposits, in some of the which the CO_2 content reaches 30%. Carbon dioxide recovery in chemical synthesis is also of great environmental significance, since it is one of the ways to reduce CO_2 emissions, the main component greenhouse gases into the atmosphere [2].

Use of carbon dioxide as a carbon source in organic synthesis is an urgent problem of modern organic chemistry. The huge interest in this problem is evidenced by the ever-accelerating growth of scientific publications on this subject. Analysis of the available data shows that carbon dioxide, contrary to popular beliefs, is able to enter into various reactions. At the same time, a small number of CO_2 based reactions have been implemented on an industrial scale, which is primarily due to the insufficient development of carbon dioxide chemistry at the moment [4-6].

In the Republic of Kazakhstan, the development of petrochemistry is very acute. All three oil refineries existing in the republic do not have the so-called petrochemical wing-petrochemical plants based on petroleum hydrocarbons and carbon oxides. The country also has an acute issue of developing