

industrial fine organic synthesis to meet the needs of the population and the national economy in such useful organic products as medicines, food preservatives, detergents, etc.

Oxybenzoic acids are widely used o-hydroxybenzoic acid (salicylic acid) and its derivatives exhibit biological activity and are used as pharmaceuticals (aspirin, p-aminosalicylic acid, etc.) [8,9]. o-Oxybenzoic acid is used to obtain polymeric materials and liquid crystal polyesters with high heat resistance [10,11].

The most common industrial method for the synthesis of hydroxybenzoic acids is carboxylation of phenol with carbon dioxide under pressure (Kolbe – Schmidt reaction) [7,12,13]. One of the big disadvantages of this method is the need for preliminary synthesis of dry sodium (potassium) phenolates, which is associated with great experimental difficulties: distillation of water in a vacuum and the extreme hygroscopicity of dry alkali metal phenolates [14-16]. In connection with the foregoing, it is of interest to synthesize oxybenzoic acids that exclude the use of alkali metal phenolates. One of these methods is the carboxylation of phenol with alkaline salts of alkyl carbonic acids.

It is known that in the Kolbe – Schmidt reaction, the use of potassium phenolate promotes the formation of p-hydroxybenzoic acid [17-18]. In order to verify the effect of the nature of the alkaline metal in the starting salts of carbonic esters on the direction of carboxylation, the phenol carboxylation reaction with potassium ethyl carbonate was studied [19-20].

**Experimental part.** The reagents used were dry sodium and potassium carbonates, reactive phenol by Sigma Aldrich. The experiments were carried out without the use of solvents in gaseous carbon dioxide. The individuality of the synthesized products was determined by physicochemical constants (mp), the study of mixed samples (absence of melting temperature depression) with pure reactive samples of the reaction products, as well as according to IR and PMR spectroscopy. IR spectra were recorded on a Nicolet 5700 single-beam infrared spectrometer of Thermo Electron Corporation (USA) in the region of 400–4000  $\text{cm}^{-1}$ . NMR1H spectra were recorded on a Bruker DPX 400 instrument, operating frequency 300 MHz. Tetramethylsilane was used as the standard. The chemical used were dry potassium ethyl carbonate, synthesized by reacting carbon dioxide with potassium ethyl carbonate as described in [20], and phenol. The experiments were conducted in the solvent free mode in a medium of gaseous  $\text{CO}_2$ . The IR spectra were recorded on a Mattson SatelliteFTIR Fouriertransform IR spectrometer in the frequency range of 4000–400  $\text{cm}^{-1}$  and the NMR spectra were recorded on a Bruker DPX 400 instrument operating at a frequency of 300 MHz.

**Synthesis of salicylic acid.** A glass reactor placed into a steel autoclave and equipped with a stirrer, electric heating, and carbon dioxide gas inlet (outlet) fittings, was loaded with 2,3 g (0,025 mol) of phenol and 3,46 g (0,027 mol) of potassium ethyl carbonate (reactants ratios was [phenol] : [potassium ethyl carbonate] = 1 : 1,1); the autoclave was pressurized; purged twice with  $\text{CO}_2$  to remove air and filled with  $\text{CO}_2$  to a pressure of 10 atm; after which stirring and heating were switched on. The reaction mixture was heated to 215°C over 6 h (at a heating rate of 40°C/h) and held at this temperature and a  $\text{CO}_2$  pressure of 10 atm for 5 h. After that, stirring and heating were stopped and the autoclave was cooled down to room temperature. The reaction mixture was treated with water. The obtained aqueous solution was extracted with ether to separate unreacted phenol. Unreacted phenol was recovered from the ether phase. The product (p-hydroxybenzoic acid) was isolated by acidifying the aqueous phase with hydrochloric acid to afford 2,46 g (71,0%) of p-hydroxybenzoic acid; melting temperature 203-205°C ; after recrystallization (water) at melting point 214-216°C.

*Synthesis of salicylic acid 7.05 g (0.075 mol) of phenol and 2.8 g (0.025 mol) of sodium ethyl carbonate are charged into a glass liner placed in a steel autoclave equipped with a stirrer, electric heating and the inlet (outlet) of carbon dioxide gas. The autoclave is sealed, flushed twice with carbon dioxide to remove air, and then filled with carbon dioxide to a pressure of 10 atm, include stirring and heating. The temperature of the reaction mixture is raised to 160 ° C over 4 hours, and at this temperature and a carbon dioxide pressure of 10 atm, it is held for 1 hour. After this, stirring and heating are stopped, the autoclave is cooled to room temperature. The reaction mixture is treated with water. The aqueous phase is extracted with toluene to separate unreacted phenol. The reaction product (salicylic acid) is isolated by acidification of the aqueous phase with hydrochloric acid. 3 g (86.0%) of salicylic acid are obtained; so pl. 154-155°C.*

It should be noted that at present the properties of alkaline salts of alkyl carbonic acids have been studied very little. They are difficult to clean white crystalline substances, extremely poorly soluble in many organic solvents (ether, ethanol, acetone, benzene, etc.); they do not have a clear melting point: when heated to 380-400°C, they slowly decompose without melting with the release of gaseous products.