

Carboxylation of Organic Compounds with Metal Alkyl Carbonates (Review)

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Received July 16, 2008

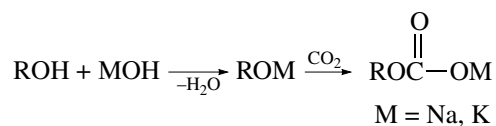
Abstract—Published data on the carboxylation of organic compounds with salts of alkyl carbonic acids (metal alkyl carbonates) are surveyed.

DOI: 10.1134/S096554410904001X

The use of carbon dioxide as a carbon source for organic synthesis is an important problem of modern organic chemistry and petroleum chemistry. The utilization of carbon dioxide in chemical synthesis is also of great environmental importance, because it is one of the ways to reduce atmospheric emission of CO₂, the main component of greenhouse gases [1–4].

So far, only two processes based on CO₂ have been implemented on the industrial scale, the synthesis of urea (carbamide) and that of salicylic acid. The carbon dioxide molecule has a low reactivity; so, the overwhelming majority of its reactions proceed only under special conditions: upon the activation with metal complexes, with the use of catalysts, under severe conditions of the process, etc. [3–9]. At the same time, some simplest derivatives of carbon dioxide are quite active.

In particular, syntheses based on metal salts of monoalkyl carbonic acids, metal alkyl carbonates, are of interest. The latter are easily obtained by the interaction of CO₂ with metal alkoxides [10–13]. Salts of esters of carbonic acid with alkali metals can also be synthesized by the interaction of CO₂ with alcohols and alkali metal halides in the presence of organic bases [14]. A simple, convenient, and economical synthetic procedure for the preparation of sodium or potassium ethoxide by the interaction of ethanol with sodium or potassium hydroxide has been developed [15–17]. Subsequently, the ethoxides can be used for the synthesis of sodium and potassium ethyl carbonates [16, 17]:

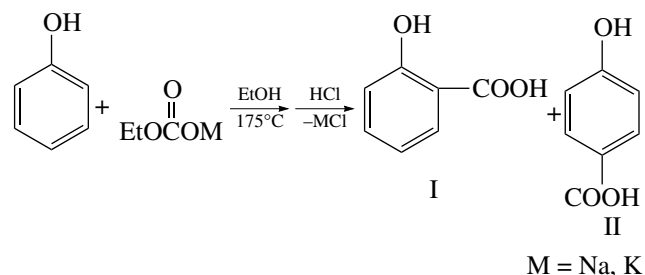


Hydroxyaromatic acids, which can be synthesized from alkali metal salts of alkyl carbonic acids and phenols or phenoxides, have a wide practical application.

Salicylic acid and its derivatives are used as pharmaceuticals [18, 19], *p*-hydroxybenzoic acid is used to manufacture polymer materials and liquid crystal polyesters [20], and arylamides of 2-hydroxy-3-naphthoic acid are the base for preparing cold-dyeing fiber dye-stuffs [21].

CARBOXYLATION OF SODIUM (POTASSIUM) PHENOXIDES WITH ALKALI METAL SALTS OF ALKYL CARBONIC ACIDS

The possibility of the use of alkali metal salts of alkyl carbonic acids as a carboxylating agent in the carboxylation reaction of hydroxyarenes was reported in 1958 [22]. Salicylic acid (I) was obtained with a yield of ~50% under slow heating to 175°C of a mixture of phenol with a suspension of sodium ethyl carbonate in ethanol and the simultaneous distilling off of the solvent and a portion of the unreacted phenol. A mixture of salicylic acid and *p*-hydroxybenzoic acid (II) was obtained using potassium ethyl carbonate:



Later, several papers of a Japanese group on the use of alkali metal salts of alkyl carbonic acids for the carboxylation of hydroxyarenes were published [23–26]. The influence of the conditions of the carboxylation of Na and K phenoxides with alkali metal salts of alkyl