α -naphthol and sodium ethyl carbonate has been carried out for a comparative evaluation of carboxylating activity [31]. It was shown that the yields of 1-hydroxy-2-naphthoic acid upon carboxylation of α -naphthol with sodium methyl carbonate and sodium propyl carbonate were 73.3% and 2.0%, respectively. Thus, as in the case of phenol carboxylation, the size of the alkyl radical in the reactant sodium salts of alkyl carbonic acids affects the carboxylating activity of the latter. Sodium salts of methyl and ethyl carbonic acids have approximately equal carboxylating activity, but a further increase in the size of the radical by one methylene group (sodium propyl carbonate) sharply reduces the carboxylating activity.

CARBOXYLATION WITH METHOXYMAGNESIUM METHYL CARBONATE

A promising method was reported in [35] for the synthesis of carboxylic acids by the carboxylation of organic compounds possessing labile hydrogen atoms with metoxymagnesium methyl carbonate (MMC), obtained via the reaction of magnesium methoxide with carbon dioxide in dimethylformamide (DMF):

CH₃O-Mg-OCH₃+ CO₂
$$\longrightarrow$$
 CH₃O-C-OMg-OCH₃
MMC

$$\begin{array}{c} O \\ \parallel \\ R - C - CH_2 - R^1 + MMC \longrightarrow \begin{array}{c} R \\ - C \\ O \\ Mg \end{array} \begin{array}{c} R \\ - C \\ - C \\ Mg \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg \\ - Mg \\ O \end{array} \begin{array}{c} O \\ - Mg \\ - Mg$$

ы

It is supposed that the formation of enolate carbanion and the carboxylation of the latter with MMC occur simultaneously during the reaction. The reverse reaction is prevented by the formation of a chelate intermediate with the participation of carbonyl group, enolate, and magnesium. The reaction can be used for the carboxylation of many substrates with active methylene groups. Some examples are given in Table 6.

Substrate	Reaction conditions	Product	Yield, wt %
$C_{6}H_{5} - C - CH_{3}$	MMC, DMF	О С ₆ H ₅ —С—СН ₂ СООН	68
	MMC, DMF, 130°C, 2 h	ОСООН	44
H ₃ CO	2MMC, DMF, 2h	H ₃ CO HOOC COOH	44
$C_4H_9 \longrightarrow 0$	MMC, DMF	COOH C ₄ H ₉ O	98
D ₂ NCH ₃ D ₂ N–CH ₂ CH ₂ CH ₃	MMC, DMF MMC, CH ₂ N ₂ , DMF	O ₂ N-CH ₂ COOH O ₂ N-CH-COOCH ₃ CH ₂ CH ₃	63 44

Table 6. Carboxylation of compounds having labile hydrogen atoms with the use of metoxymagnesium methyl carbonate [35]