As has been shown [2,3], acetylenic alcohols can be used successfully for the synthesis of various \( \gamma \)-hydroxyacetylenic carboxylic acids, which are interesting starting materials for the production of a number of unsaturated oxygen-containing compounds. In order to find new routes for the synthesis of such systems, we have systematically studied the reaction of magnesium halide derivatives of a series of readily accessible acetylenic alcohols [4] and vinylacetylenes with carbon dioxide. It has been found that the reaction of Iotsich's complexes obtained from dimethyl, methyl ethyl, cyclopentyl, and cyclohexyl ethinyl carbinols, dehydrolinalool, isopropenylacetylene, and ethinylcyclohexene with \( \text{CO}_2 \) under pressure leads to good yields of the corresponding \( \gamma \)-hydroxyacetylenic carboxylic (I)-(V) and vinylacetylenecarboxylic (VI)-(VII) acids, esterification of which readily gives the methyl esters corresponding to them:

\[
R' \quad R \quad R'' \quad C \quad \equiv \quad \text{CMgX} \quad \rightarrow \quad \text{CO}_2 \quad R' \quad R \quad R'' \quad C \quad \equiv \quad \text{C} \quad \equiv \quad \text{COOH} \\
\text{(I)-(IV)} \\
\text{(V)} \\
\text{(VI)} \\
\text{(VII)}
\]

As has been shown earlier [5], the selective hydrogenation of \( \gamma \)-hydroxyacetylenic acids (as a result of the cis-addition of hydrogen) inevitably leads to unsaturated \( \gamma \)-lactones, which considerably narrows the synthetic possibilities of the initial acetylenic acids. In order to find routes for the synthesis of trans-addition products, we have made a detailed study of the reaction of esters of some \( \gamma \)-hydroxyacetylenic carboxylic acids with sodium phenoxide, which, in the case of \( \text{B}-(1 \text{-hydroxycyclohexyl}) \text{-propionic acid} \) leads to a mixture of cis- and trans-products of addition to the acetylenic bond [3]. We have found that the reaction of sodium phenoxide with the methyl esters of 4-methyl-4-hydroxypent-2-ynoic acid (VIII), 4-methyl-4-hydroxyhex-2-ynoic acid (IX), and \( \text{B}-(1 \text{-hydroxycyclopentyl}) \text{-propionic (X) acids gives a 70% yield of a mixture of reaction products, containing about 50% of the corresponding } \beta \text{-phenoxy derivatives of trans-acrylic esters (XI)-(XIII) and 15% of the phenoxy lactones (XIV)-(XVI) corresponding to cis-addition. Separation of this mixture can be accomplished relatively simply by crystallization and high-vacuum distillation.}

\[
R' \quad C \quad \equiv \quad \text{C} \quad \equiv \quad \text{COOH} \\
\text{(VIII-X)} \\
\text{(IX-X)} \\
\text{(X)} \\
\text{(XI-XIII)} \\
\text{(XIV-XVI)}
\]
The phenoxy group in the esters (XI)-(XIII) is fairly stable in an alkaline medium, and on saponification in aqueous-alcoholic alkali at room temperature the corresponding substituted trans-acrylic acids (XVII)-(XIX) have been obtained. However, acid hydrolysis readily leads to saponification of the phenoxy group and under these conditions the trans-acid (XVII) gives 5,5-dimethyltetronic acid (XX). The same acid is formed by saponification of the lactone (XIV), which is a direct proof of the structure of both series of compounds.

Dehydration of the ester of the trans-acid (XI) using phosphoryl chloride readily yields the ester of 3-methyl-2-phenoxybutadiene-1-carboxylic acid (XII) which is also formed by the direct addition of phenol to the ester of isopropenylpropionic acid (XXII). Alkaline saponification then gave a good yield of the 3-methyl-2-phenoxybutadiene-1-carboxylic acid (XXIII) itself. The presence of the diene system in the ester (XXI) was shown by the UV spectrum and the reaction with maleic anhydride, which forms the adduct (XXIV), which on saponification with water gives the corresponding acid (XXV).

The most highly selective trans-addition of phenol takes place in the case of the ester of cyclohexenylpropionic acid (XXVI), and the corresponding 5-phenoxydienic ester (XXVII) is formed with a yield of 85%; when it is saponified with aqueous-alcoholic alkali, the dienic acid (XXVIII) is readily formed, but this does not give an adduct with maleic anhydride.

The addition of water to the triple bond of the acetylenic acids was studied on the basis of the ester of β-(1-hydroxycyclohexyl)-propionic acid (XXIX). However, in this case, only the lactone (XXX) was formed, with a yield of 40%; this was also formed in an attempt to cyclize trans-β-phenoxy-β-(1-hydroxycyclohexyl)-acrylic acid (XXI) to form a chromanone system.