The synthesis and investigation of the properties of acetylenic glycols are of undoubted interest in view of their great reactivity. In previous communications [1, 2] methods were presented for synthesis of mono- and dialkyl acetics of acetylenic alcohols with the general formulas:

\[
\begin{align*}
\text{(I)} & \quad \text{R}_2\text{C} - \text{C}==\text{C} - \text{C(OH)}\text{R}_2 \\
\text{OCH} & - \text{CH}_3 \\
\text{OR'} & \\
\text{(II)} & \quad \text{R}_2\text{C} - \text{C}==\text{C} - \text{CR}_2 \\
\text{OCH} & - \text{CH}_3 \\
\text{OCH} & - \text{CH}_3 \\
\text{OR'} & - \text{OR'}
\end{align*}
\]

The new substances which have been synthesized and the methods for their synthesis are of interest for acetylene chemistry. As was previously observed [1, 2], the synthesis of diacetics of acetylenic glycols is always accompanied by formation of the corresponding monosubstituted acetics. For this reason we suggested that a stepwise reaction was involved, i.e., that the monoacetal formed in the first step may either be isolated or (if left in the reaction medium) may join on with another molecule of vinyl ether to form the diacetal in accordance with the following equations:

\[
\begin{align*}
\text{R}_2\text{C(OH)} - \text{C}==\text{C} - \text{C(OH)}\text{R}_2 + \text{CH}_2=\text{CH} - \text{OR'} & \rightarrow \\
\rightarrow \text{R}_2\text{C(OH)} - \text{C}==\text{C} - \text{CR}_2 \quad \text{CH}_2=\text{CH} - \text{OR'} & \rightarrow \text{R}_2\text{C} - \text{C}==\text{C} - \text{CR}_2 \\
\text{OCH} & - \text{CH}_3 \\
\text{OR'} & - \text{OR'} \\
\text{OCH} & - \text{CH}_3 \\
\text{OCH} & - \text{CH}_3 \\
\text{OR'} & - \text{OR'}
\end{align*}
\]

where \( R' \) and \( R'' = \text{C}_2\text{H}_5; \text{C}_4\text{H}_9; \text{C}_6\text{H}_{13} \).

The stepwise mechanism of the synthesis enables two series of derivatives of acetylenic glycols to be obtained: mono- and diacetics. Most of the known derivatives of acetylenic glycols are di-substituted compounds [3, 4]. Mono-substituted acetylenic derivatives reported in the literature are the partial ethyl and isoamyl ethers of tetramethylbutyrene which were prepared and examined by Zalkind [5]. It is interesting that the formation of monoacetics of the type of (I), as well as of mixed acetics, is only found possible for the acetylenic glycols series. In the case of saturated or of olefinic glycols, as well as of glycerol and other polyhydric alcohols, attempts to separate the mono- and diacetics have proved unsuccessful due to cyclization [6, 7, 8, 9].

In the case of glycerol [8] this process takes place according to the scheme:

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{CHOH} \quad \text{CH}_2\text{OH} \quad \text{CH}_2=\text{CH} - \text{OR} \quad \rightarrow \\
\rightarrow \quad \text{CH}_2\text{OH} & \quad \text{CHOH} \quad \text{CH}_2\text{OH} \quad \text{CH}_2=\text{CH} - \text{OR} \quad \rightarrow \\
\quad \quad \text{CH}_2\text{OH} & \quad \text{CHOH} \quad \text{CH}_2\text{OH} \quad \text{CH}_2=\text{CH} - \text{OR} \quad \rightarrow \\
\quad \quad \text{CH}_2\text{OH} & \quad \text{CHOH} \quad \text{CH}_2\text{OH} + 2\text{ROH}.
\end{align*}
\]

Reaction of ethyleneglycol with vinyl ethers usually leads to dicyclic acetics [9], and only the application of exceptional synthesis conditions (excess of vinyl ether, a strict temperature limit and absence of acid catalyst) enabled this author to partly avoid cyclization. The isolated ethylene glycol monoacetics, however, proved to be very
unstable and underwent cyclization on distillation:

\[
\text{OCH}_2 - \text{CH}_2 - \text{OCH} - \text{CH}_2 \rightarrow \text{CH}_2 - \text{CH} - \text{C(OH)} - \text{CH}_2 + \text{AlkOH}
\]

Dehydration of tetramethyl- and tetraphenylbutynediols [10, 11] was observed on their condensation with phenol; during this process the phenol added on to the triple bond of the glycol.

The literature also contains earlier reports of the hindering effect of the triple bond, for example during dehydration of acetylenic glycols [12]. In this case, instead of the cyclization which occurs with saturated pinacones, formation takes place of unsaturated hydrocarbons:

Similarly a study of the magnetic fields of acetylenic hydroxyl-containing compounds [13] revealed the screening effect of the triple bond.

Investigations by Favorsky and his school [14, 15, 16] demonstrated the possibility of existence of carbocyclic systems with a triple bond, starting only from an 8-membered ring. Cyclization of monoacetals of acetylenic glycols is also excluded by the circumstance that the triple bond creates a great strain in the hydrocarbon chain of the molecule, hindering the cyclization which might have led to formation of only a 7-membered ring.

In this communication experimental confirmation is given of the stepwise formation of diacetals of acetylenic glycols with reference to the diethyl, ethylbutyl and dioctyl acetals of butynediol.

Stepwise synthesis of the diacetals was realized by two methods: catalytic and thermal. By these methods the corresponding diacetals were isolated from the monoacetals in good yields. An attempt to obtain the mixed ethylbutyloctyl diacetals of butynediol led to isolation of the symmetrical diethyl acetal whose formation may be explained by the process of symmetrization of the mixed diacetal formed in the first step.

Symmetrization of the mixed ethylbutyloctyl acetal of acetaldehyde gives, in accordance with the following scheme, the acetaldehyde dioctyl acetal which we isolated:

It is interesting that symmetrization was observed mainly in the case of butynediol ethylbutyloctyl diacetal and to a lesser degree in that of butynediol ethylbutyloctyl diacetal. Such a difference in behavior is probably to be explained by the large difference in molecular weights of the alkoxy radicals simultaneously present in the molecule of the diacetal; the greater this difference the less stable is the molecule of mixed acetal and the greater the tendency to symmetrization.

**EXPERIMENTAL**

The starting vinyl ethers were purified by the previously described method [14] and had the constants set forth in Table 1. The butynediol had b.p. 142-143° (14 mm); b.p. 57-58°.

1. **Stepwise synthesis of the diethylacetal of butynediol** \( \text{C}_4\text{H}_8\text{O} - (\text{CH}_3)\text{CHO} - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_2 - \text{OCH}(\text{CH}_3) - \text{OC}_2\text{H}_5 \)

Preparation of butynediol monoethylacetal by the thermal method. Heating in an autoclave to 81-88° of a

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