REATIONS OF VINYL ETHERS

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It has already been noted in previous papers [1-3] that mixed acetals of the type CH₂CH undergo partial disproportionation when distilled:

\[
2\text{CH}_2\text{CH} \xrightarrow{\text{OR}} \text{CH}_2\text{CH(OR)}_2 + \text{CH}_2\text{CH(OR')}_2.
\]

Acetals of ethylene glycol are particularly susceptible to such changes. Attempts to prepare hydroxy acetals by direct addition of alcohols to 2-vinylxyethanol were not successful owing to the rapidity with which the vinyl ether undergoes cyclization, when heated, or in presence of acid catalyst.

Moreover, acetaldehyde ethyl 2-hydroxyethyl acetal, prepared by a different method [4], is also notable for its high instability, and shows a great tendency to react with formation of the same ethylene cyclic acetal (2-methyl-1,3-dioxolane):

\[
\text{heating} \quad \begin{array}{c}
\text{CH}_3\text{CH}
+ \text{HOCH}_2\text{CH}_2\text{OH} \\
+ \text{HOCH}_2\text{CH}_2\text{Cl} \\
+ \text{ROH} \\
+ \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\end{array} \rightarrow \text{CH}_3\text{CH}
\]

Even the diethyl ethylene diacetal (1,2-di(1-ethoxyethoxy)ethane), which has no free hydroxyl group, splits on being distilled at atmospheric pressure with formation of 2-methyl-1,3-dioxolane:

\[
\begin{array}{c}
\text{CH}_3\text{CH}
+ \text{C}_2\text{H}_5\text{OH}
+ \text{CH}_3\text{CH(OCH}_2\text{CH}_2\text{)}_2
\end{array} \rightarrow \begin{array}{c}
\text{CH}_3\text{CH}
+ \text{C}_2\text{H}_5\text{OH} + \text{HOCH}_2\text{CH}_2\text{OH}
+ \text{CH}_3\text{CH(OCH}_2\text{CH}_2\text{)}_2
\end{array}
\]
We have observed similar reactions when attempting to effect the synthesis of the cyclic diacetal (I) from ethylene glycol and the heterocyclic acetal (II) from diethylene glycol, in accordance with the following equations:

\[
\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_2\text{O}-\text{CH} = \text{CH}_2 + \text{H} \rightarrow \text{CH}_2\text{CH} \quad \text{(I)}
\]

However, in the first case, instead of the expected cyclic diacetal (I), the same 2-methyl-1,3-dioxolane was isolated in quantitative yield. The result obtained is to be explained by the decomposition, under the conditions of the reaction, of the 2-hydroxyethyl 2-vinylxyethyloxyethyl acetal formed, giving two molecules of 2-vinylxyethanol, which then undergoes cyclization:

\[
\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_2\text{OCH} = \text{CH}_2 + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH} \quad \rightarrow 2\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_2\text{OH} \rightarrow
\]

Similarly, in the second case (synthesis of the heterocyclic acetal (II)), we obtained completely unexpected results, a 90% yield of a dihydroxy polyacetal derived from diethylene glycol being obtained:

\[
\text{CH}_2=\text{CHOCH}_2\text{H} + \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH} \quad (\text{III})
\]

It is evident that here we have again encountered a series of readily occurring reactions, which, we think, may be schematically represented as follows:

\[
\text{CH}_2=\text{CHOCH}_2\text{H} + \text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{CH} \quad (\text{III})
\]