SUMMARY.

This thesis deals with the pyrolysis of 1-alkoxy-1-alkynes and ethoxyethynylcarbinols and with the reaction between 1-alkoxy-1-alkynes and ketene.

In chapter I, the pyrolysis of 1-alkoxy-1-alkynes and the reaction between these compounds and ketene are described.

The pyrolysis was performed with methoxy-, ethoxy-, propoxy-, isopropoxy-, butoxy-, sec. butoxy-, isobutoxy-, tert.butoxy-, n.pentoxy- and neopentoxy-1-alkynes. Except for the 1-methoxy- and the 1-neopentoxy-1-alkynes, all these compounds evolve on heating an alkene while in good yield a product, which is a dimer minus the alkene, is formed. This product is a cyclobutenone ether; hydrolysis gives a symmetrical ketone.

\[
\begin{align*}
2 \text{ R-CH}=\text{C}=\text{C}-\text{O-alkyl} & \xrightarrow{\text{alkene}} \text{ R-C-C=O} \quad \text{H} \\
\text{alkyl-O-C=C-R} & \xrightarrow{\text{H}_2\text{O}} \text{ O=C-C-R} \quad \text{H} \\
\text{R-CH}_2\text{-CO-CH}_2\text{-R} + \text{CO}_2
\end{align*}
\]

The thermal stability of the 1-alkoxy-1-alkynes decreases in the order: \( \text{C}_2\text{H}_8\text{O} > \text{i.C}_3\text{H}_7\text{O} > \text{t.C}_4\text{H}_9\text{O} \).

1-Neopentoxy-1-alkynes and 1-methoxy-1-alkynes polymerise on heating; this reaction has not been investigated. Thermal decomposition of ethynylethers gives varying results.

Very probably the pyrolysis of the ethers first yields aldo-ketenes, these react further with a second mole of ether.

\[
\begin{align*}
\text{R-CH}=\text{C}=\text{C}-\text{O} \xrightarrow{\text{C}_4\text{H}_4} \left[ \text{R-CH}=\text{C}=\text{O} \right] \xrightarrow{\text{R-CH}=\text{C}=\text{O-}\text{C}_2\text{H}_4} \text{ C}_4\text{H}_4\text{O-}\text{C}=\text{C-R}
\end{align*}
\]

This view is supported by the following facts:

i. the methoxy- and neopentoxy-1-alkynes do not undergo the reaction;

ii. the pyrolysis of 1-ethoxy-1-alkynes in the presence of aniline gives anilides in almost quantitative yields, the amount of ethene formed in the presence of aniline is approximately
twice as large as in the absence of aniline because now each mole of ethynylether gives a mole of ethene

\[ R\text{-}C\equiv\text{C}\text{-}O\text{-}C_2\text{H}_4 \rightarrow R\text{-}\text{CH}\equiv\text{C}\text{-}\text{O} \rightarrow R\text{-}\text{CH}_2\text{-CO-NH-C}_6\text{H}_4 \]

iii in a preliminary study of the kinetics of the decompositions of ethoxyheptyne and isopropoxyheptyne, it was found that the rate determining steps were monomolecular.

Furthermore we have demonstrated unambiguously the presence of a ketene intermediate in the case of 1-t.butoxy-1-propyne by carrying out the pyrolysis on a preparative gaschromatography column and studying the reaction products by means of infrared-spectroscopy immediately after they had left the column.

The reaction between 1-alkoxy-1-alkynes and ketene also yields cyclobutenone ethers; hydrolysis gives a ketone.

\[ R\text{-}C\equiv\text{C} \rightarrow O=C=CH_2 \]

In their infrared-absorption spectrum all the isolated cyclobutenone ethers show a very characteristic \( C=O \) band at about 1745–1770 cm\(^{-1}\).

In chapter II the preparation of ethoxyethynylcarbinols is described. These carbinols are formed by the action of a carbonyl compound on a metallated ethoxyethyne.

\[ \text{RM} + H\text{-}C\equiv\text{C} \rightarrow RH + M\text{-}C\equiv\text{C} \]

\( M = \text{Li, Na, MgBr, or } RM = \text{NaNH}_2 \)

\[ R_1\text{-}C=O + M\text{-}C\equiv\text{C} \rightarrow R_1\text{-}C\equiv\text{C} \rightarrow \text{NH}_4\text{Cl (M=MgBr)} \]

In our opinion the condensation of ethoxyethynylmagnesiumbromide with ketones should be performed at a low temperature (\(-20^\circ\text{C}\)). Boiling the ethereal solution is unnecessary and harmful; brown colours develop (aldol condensation) and the yields diminish. Because of the extreme sensitivity of the ethoxyethynylcarbinols to acids the reaction mixture must be worked up by pouring into a cold aqueous solution of ammonium chloride or,
if the lithium or sodium derivatives are used, in cold water. The carbinols should be distilled from alkaline glass-ware (rinsed with ammonia followed by drying) and the bath temperatures are not allowed to rise above 130—140 °C. Above these temperatures vigorous decompositions may occur. The Grignard derivatives of ethoxyethyne usually cannot be employed for the preparation of secondary carbinols from aldehydes. Aldehydes react further with the initially formed magnesium bromide carbinolates.

In chapter III the pyrolysis of ethoxyethynylcarbinols in boiling triethylamine is discussed. The carbinol (CH₃)₂C(OH)C≡CO₂H₅ upon heating gives a gas consisting of ethene, isobutene and carbon dioxide; while the reaction mixture contains among others β,β-dimethylacrylic acid and its ethyl ester. The formation of these compounds can be explained as follows.

\[ \text{(CH₃)₂C(OH)C≡C—O—C₂H₅} \xrightarrow{\text{thermal rearrangement}} \text{(CH₃)₂C=CH—COOC₂H₅} \]  
\[ \xrightarrow{\text{rearrangement}} \text{(CH₃)₂C=CH—CO₂H} \]  
\[ \text{(CH₃)₂C—CH₂—C=O} \xrightarrow{\text{heat}} \text{(CH₃)₂C=CH + CO₂} \]  

This pattern is a very general one; in the case of the secondary carbinols only the third reaction does not happen. An exception is the carbinol 1-ethoxy-3,3-diphenyl-1-propyn-3-ol; this gives only benzophenone and the ethyl ester of β,β-dimethylacrylic acid.

In chapter IV the pyrolysis of ethoxyethynylcarbinols in boiling benzene and carbon tetrachloride is described. The isomeric α,β-unsaturated esters are the main reaction products. In the case of the carbinol (CH₃)₂C(OH)C≡C—O—C₂H₅ we have also isolated a small amount of 1,3-bis-(isopropylidene)-cyclobutanedione-2,4, which may be a dehydrated dimer of the hydroxyketene (CH₃)₂C(OH)CH—C=O. The structure of this dione was unambiguously established. From the carbinol (C₄H₉)₂C(OH)C≡C—O—C₂H₅ a crystalline compound was also isolated, which presumably is 1,3-bis-(bisphenylmethylene)-cyclobutanedione-2,4.
Fig. 1. 1-methyl-2-tert.butoxycyclobut-2-een-4-on (in paraffineolie).

Fig. 2. 1-ethyl-2-methoxycyclobut-2-een-4-on.

Fig. 3. 1-ethylcyclobutaandion-2-4 (in paraffineolie).

Fig. 4. 1-ethoxy-1-propyn-3-ol.
Fig. 5. 1-ethoxy-3-ethyl-1-pentyn-3-ol.

Fig. 6. β-butyrolacton.

Fig. 7. 1,3-diisopropylideencyclobutaandion-2,4 (in tetrachloorkoolstofoplossing, oplosmiddelbanden gestippeld).

Fig. 8. 1,3-diisopropylcyclobutaandion-2,4 (in paraffineolie).