We here report an investigation of the acid hydrolysis of the previously synthesized \[1\] products of the condensation of \(\beta\)- and \(\alpha\)-ionone diethyl dithioacetals with ethyl vinyl ether. It is known that acetals \[2\] and monothioacetals \[3\] of alkylthio aldehydes are converted into unsaturated aldehydes when boiled with glacial acetic acid. By the use of this method we proposed to prepare 3-methyl-5-(2,6,6-trimethyl-1- and -2-cyclohexen-1-yl)-2,4-pentadienals by the following scheme:

\[
\begin{align*}
\text{CH}_3 & \quad \text{OC}_3\text{H}_5 \\
/ & \quad \text{I} \\
\text{SC}_2\text{H}_5 & \quad \text{SC}_2\text{H}_5 \\
\text{OHaCOOH} & \\
\text{CH}_8 & \quad \text{OC}_2\text{H}_5 \\
\text{HgCl}_2 & \quad \text{=~} \\
\text{I} & \quad \text{/} \\
--&---\text{RCH=CH--C--CH}--\text{CH} & \quad \text{CH}_3 & \quad \text{OC}_3\text{H}_5 \\
\text{C=H,OH} & \quad \text{I} \\
\text{0C}_2\text{H}_5 & \quad \text{0C}_3\text{H}_5 \\
\text{CH}_8 & \quad \text{I} \\
\text{-~} & \quad \text{RCH=CH--C=CH--CHO,} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

However, on detailed investigation of these transformations it was found that in the case of \(\beta\)-ionone (1-cyclohexen-1-yl) derivatives the reaction did not go in the way to be expected on analogy with the reactions of previously studied compounds.

It was found that in the reaction of mercuric chloride and ethanol with 3-(ethylthio)-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-4-pentenal diethyl monothioacetal \(I\) the product was not 3-ethoxy-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-4-pentenal diethyl acetal, but 5-ethoxy-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-pentenal diethyl acetal \(II\).
The formation of the acetal (II) from the monothioacetal (I) can be explained by the occurrence of allyl rearrangement during the reaction, which is often observed in nucleophilic substitution in compounds with an allyl system of bonds.

The chemical properties of the acetal obtained and, particularly, its behavior toward acids, indicate that the compound is a 1,1,5-triethoxy derivative. Thus, when it was heated with glacial acetic acid, instead of 3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal which should be formed from the normal product (the 3-ethoxy acetal), we obtained the aldehyde (III), which differed greatly in refractive index ($n_D^{20}$ 1.5220) from trans-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-4-pentenal ($n_D^{20}$ 1.5765) and from its cis isomer ($n_D^{20}$ 1.5662) [4]. Increase in the time of heating from three to eight hours had little effect on the physical properties of the aldehyde formed.

To elucidate the nature of the aldehyde (III) we prepared its 2,4-dinitrophenylhydrazone and semicarbazone. In the reaction of (III) with an alcoholic solution of 2,4-dinitrophenylhydrazine hydrochloride we isolated two 2,4-dinitrophenylhydrazones of the same elemental composition as the 2,4-dinitrophenylhydrazone of 3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal. One of the 2,4-dinitrophenylhydrazones obtained (IV), which was formed in much the greater amount, formed large bright-orange crystals, m. p. 186-188°, and the second (V) formed small yellowish-orange needles, m. p. 180-181.5°. Both these isomers differed from the 2,4-dinitrophenylhydrazones of cis- and trans-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienals, which form dark-red crystals of m. p. 193° [5] and 198-199° [5, 6], respectively. It is known that, in the dehydration of various intermediate products in the synthesis of vitamin A [7, 8], "retroionylidene rearrangements" often occur. It is probable that, in the reactions that we have investigated, the compound (II) undergoes "retroionylidene rearrangement" of the ethoxy group into the ring of the ionone residue. When the ethoxy compound so formed is heated with acetic acid the elimination of alcohol occurs with formation of two stereoisomers ([III], cis and trans) of 3-methyl-5-(2,6,6-trimethyl-2-cyclohexen-1-ylidene)-3-pentenal, which give the 2,4-dinitrophenylhydrazones (IV) and (V).

This view is supported by the ultraviolet absorption spectra of (IV) ($\lambda_{\text{max}}$ 378 m$\mu$, $\varepsilon$ 32,000) and (V) ($\lambda_{\text{max}}$ 373 m$\mu$, $\varepsilon$ 31,000), which are shifted toward the shorter waves in comparison with the absorption spectra of the 2,4-dinitrophenylhydrazones of the cis ($\lambda_{\text{max}}$ 400 m$\mu$, $\varepsilon$ 33,800) and trans ($\lambda_{\text{max}}$ 408 m$\mu$, $\varepsilon$ 37,000) isomers of 3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal [5]. A shift in the absorption maximum toward the shorter waves was observed earlier for trans-3-methyl-5-(2,6,6-trimethyl-2-cyclohexen-1-ylidene)-3-pentenoic acid when compared with 3-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienoic acids [9]. In view of the fact that (V) is converted into (IV) when heated with concentrated hydrochloric acid, it may be supposed that (IV) is the hydrazone of the trans aldehyde and (V) is the hydrazone of the cis aldehyde. This view is supported by the somewhat higher melting point of (IV).

In the preparation of (III) by boiling the triethoxy compound (II) with acetic acid we were unable to isolate the separate isomers, and we therefore attempted to obtain one of them by decomposing its 2,4-dinitrophenylhydrazone. For this purpose the 2,4-dinitrophenylhydrazone (IV) was heated with levulinic acid by a known procedure [10], and we obtained an aldehyde with $n_D^{20}$ 1.5390, which in accordance with the above consideration was probably trans-3-methyl-5-(2,6,6-trimethyl-2-cyclohexen-1-ylidene)-3-pentenal [trans-(III)]. The behavior of the aldehyde (III) when treated with semicarbazide was unusual; instead of the expected semicarbazone we obtained the disemicarbazone (VI) in the form of colorless gleaming crystals, m. p. 197-198° ($\lambda_{\text{max}}$ 228 m$\mu$, $\varepsilon$ 18,800).