Title: Studies on Acetylene and its Derivatives. (XIII) Preparation of Caprolactam from Propargyl Alcohol.

Author(s): Kunichika, Sango; Oka, Shinzaburo; Yoshikawa, Tomikazu

Citation: Bulletin of the Institute for Chemical Research, Kyoto University (1954), 32(2): 101-101

Issue Date: 1954-03-31

URL: http://hdl.handle.net/2433/75416

Type: Departmental Bulletin Paper

Textversion: publisher
19. Studies on Acetylene and its Derivatives. (XIII)

Preparation of Caprolactam from Propargyl Alcohol. (1)

Sango KUNICHIKA, Shinzaburo OKA and Tomikazu YOSHIKAWA
(Nodzu Laboratory)

According to the following scheme, we have been trying the preparation of caprolactam.

\[
\begin{align*}
2\text{CH} \equiv \text{C} \cdot \text{CH}_2\text{OH} + \frac{1}{2} \text{O}_2 & \xrightarrow{\text{CuCl}_2 / \text{NH}_3\text{Cl}} \text{HOCH}_2 \equiv \text{C} \equiv \text{C} \equiv \text{C} \cdot \text{CH}_2\text{OH} \\
\text{Raney Ni} & \xrightarrow{+4\text{H}_2} \text{HO}(\text{CH}_2)_2\text{OH} \xrightarrow{\text{Cu}, \text{Cr}} \text{CH}_2 \xrightarrow{-2\text{H}_2} \text{CH}_2 \xrightarrow{\text{H}_2\text{H}} \text{C} \equiv \text{O} \xrightarrow{\text{NH}_3} \text{CH}_2 \xrightarrow{\text{H}_2\text{H}} \text{C} \equiv \text{N}
\end{align*}
\]

In this paper, the oxidative coupling of propargyl alcohol to hexadiynediol, using air or oxygen and a cuprous salt as catalyst, and its hydrogenation to hexanediol are described.

A shaking stainless steel autoclave of 300 c.c. capacity was filled with a mixture of 60g. \(\text{H}_2\text{O}\), 19g. \(\text{NH}_3\text{Cl}\), 6g. \(\text{CuCl}_2\) and pure propargyl alcohol. Air or oxygen was pressed to 10~20 atm. After the reaction was over, the contents of the autoclave were filtered, the solid washed with a possible minimum amount of water and dissolved in 10 times methanol. Removing the insoluble materials, the methanol solution of hexadiynediol was hydrogenated with 40 atm. hydrogen at 10~20°, in the presence of Ranney nickel catalyst. The anti-catalytic action of copper ions could be eliminated by addition of a small amount of zinc dust.

The yields of hexanediol boiling at 110°/4mm., melting at 40~41° were 50~60% of the theoretical amounts based on the propargyl alcohol used. Using pure hexadiynediol melting at 112° which was recrystallized from methanol or water, 94% yield of hexanediol was obtained.

20. On the Action of Papain Enzyme. (VII)

Masashichi YOSHIOKA
(Ogiu Laboratory)

It was formerly reported that Rongalite makes papain enzyme active in protein decomposition.