Polymerisation of Phenyl Glycidyl Ether and Thioepichlorohydrin

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Citation
京都大学化学研究所報告 (1952), 30: 50-52

Issue Date
1952-09-30

URL
http://hdl.handle.net/2433/74453

Type
Departmental Bulletin Paper

Textversion
publisher
Among these, the condensation product with mono-\textit{t}-butyl-\textit{p}-cresol showed the highest activity, which was superior to commercial 2,6-di-\textit{t}-butyl-\textit{p}-cresol. The condensation products with mono-\textit{t}-butyl-\textit{o}-cresol and mono-\textit{t}-butyl-\textit{m}-cresol, respectively, showed some activities, but other products did not show high activities.

Some of the polynuclear alkylphenols previously reported, that is condensation products of dimethylol-\textit{p}-cresol with \textit{o}-cresol (C-3), thymol (C-5), eugenol (C-6), \textit{p}-hydroxyanisole (C-7), respectively, as well as the condensation product of eugenol and formaldehyde (E-2) were divided into three or four portions with different molecular weights by fractional precipitation with the aid of acetic acid and water. In the case of (C-3), (C-5), (C-6), (C-7), a portion with molecular weight of 300-500 were most effective. An anomaly was observed in the case of (E-2), that is, the monomethylolated product of eugenol, i.e., eugenotine alcohol, m. p. 38°C, was the highest in the activity.

The effects of these compounds to the stability of vitamin A were investigated by G. Katui in the Laboratory of Prof. R. Takata. The results, which coincided with our ones, will be published elsewhere.

16. Polymerisation of Phenyl Glycide Ether and Thioepichlorohydrin

Kiyohisa Furukawa and Ryohei Oda

(Oda Laboratory)

A. Phenyl Glycide Ether (P.G.E.)

1) Synthesis

P.G.E. was prepared by the method of Boyd and Marle (J. Chem. Soc., 93, 838, (1908)) according to the following reaction:

\[
\begin{align*}
\text{O} & \quad \text{Cl-CH}_2\text{CH-CH}_2 \quad \text{\underline{NaOH}} \quad \text{OCH}_2\text{CH-CH}_2
\end{align*}
\]

2) Polymerisation

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Polym. temp. (°C)</th>
<th>Polym. time (hr)</th>
<th>Catalyst</th>
<th>Mol. wt. (Cryoscopic method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120-130</td>
<td>18</td>
<td>NaOH (5)</td>
<td>1357</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>79\frac{1}{2}</td>
<td>(5)</td>
<td>1844</td>
</tr>
<tr>
<td>3</td>
<td>80-90</td>
<td>18\frac{1}{2}</td>
<td>(1)</td>
<td>1816</td>
</tr>
<tr>
<td>4</td>
<td>120-130</td>
<td>47\frac{1}{2}</td>
<td>(1)</td>
<td>1279</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>24\frac{1}{2}</td>
<td>KOH (5)</td>
<td>1531</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>14</td>
<td>(1)</td>
<td>1120</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>65</td>
<td>(1)</td>
<td>923</td>
</tr>
</tbody>
</table>

A brown, soft polymer was obtained, when the monomer was treated with molten and powdered KOH or NaOH as catalyst in a sealed tube. It is im-
important that the polymerisation must be carried out in the dry state. The polymerisation may be assumed to proceed as follows:

\[ \text{O-CH}_2\text{-CH-CH}_2 \xrightarrow{\text{Alkali}} \text{CH}_2\text{-CH-O-CH-CH}_2\text{-O-CH-CH}_2\text{-} \]

3) **Application**

As the end group of P.G.E. polymer is thought to be OH-group, we tried to prepare a non-ionic surfactant by reacting ethylene oxide upon the polymer.

The surface tension of this product was as follows:

<table>
<thead>
<tr>
<th>1%</th>
<th>0.5</th>
<th>0.2</th>
<th>0.1</th>
<th>0.05</th>
<th>0.02</th>
<th>0.01</th>
<th>pure water (16°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dyne/cm</td>
<td>51.6</td>
<td>51.9</td>
<td>52.3</td>
<td>53.2</td>
<td>53.9</td>
<td>55.9</td>
<td>58.7</td>
</tr>
</tbody>
</table>

**B. Thioepichlorohydrin (T.E.C.)**

1) **Synthesis**

\[ \text{Cl-CH}_2\text{-CH-CH}_2 + \text{NH}_2\text{CSNH}_2 \rightarrow \text{Cl-CH}_2\text{-CH-CH}_2 \]

According to the above course, T.E.C. was prepared by the aid of Davies' report (J. Chem. Soc., 1050, (1946)).

2) **Polymerisation**

Contrary to the ordinary ethylene sulfi de derivatives, T.E.C. was not polymerized by alkali catalysts. We have succeeded in its polymerisation by adding a few drops of H_2SO_4 as catalyst at ordinary temperature.

The polymerisation can be considered to proceed as follows:

\[ \text{Cl-CH}_2\text{-CH-CH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{S-CH}_2\text{-CH}_2 \xrightarrow{\text{Cl}} \text{S-CH}_2\text{-CH}_2 \xrightarrow{\text{Cl}} \]

When 5g. of T.E.C. was warmed with a drop of H_2SO_4, polymerisation occurred spontaneously and a dark brown slightly mobile resinous product was obtained.

On the other hand, gradual polymerisation at ordinary temperature resulted a colourless, transparent, soft resin.

The former is soluble in benzene and the molecular weight is about 1000 (by cryoscopic method). The latter is soluble only in CHCl_3 and so we cannot determine the molecular weight. Quantitative analysis of Cl of the colourless resin is as follows:

Calcd. 32.72%; Found 32.68%

3) **The reaction between T.E.C. resin and aniline,**
Resin Aniline CHCl₃ React. React. Product
2.7g. 11g. 20g. 2½ hr. b. p. of 3.6g. CHCl₃

According to the above details, light yellow and brittle resin was formed. Theoretical value of N contents calculated from the weight which increased in the product was 6.11%, and analytical value was 6.14%. From this result, it is apparent that 63% of Cl was replaced by aniline.

17. Studies on Cobalt Metabolism of *Bacillus subtilis* by Using Co⁶⁰

Shozo Tanaka, Yasuo Sawada and Takuro Yamamoto
(K. Kimura Laboratory)

Among many microbes, *Streptomyces griseus* and *Bacillus subtilis* are reported to be the good producers of vitamin B₁₂. Microorganisms are expected that they absorb cobaltous ion from the culture media and synthesize this vitamin. These investigations were undertaken with the intention of explaining physiological functions of vitamin B₁₂ and other cobalt containing substances for microorganisms.

![Fig. 1. Absorption of Co⁶⁰ by bacillus subtilis (in 250 ml. medium).](image-url)

The chemical constituents of *bacillus subtilis*, grown on Waksman's media containing 2 p.p.m. radioactive Co⁶⁰, and of the remaining media were precisely analysed during the growth. Total cobalt content in the unit weight of bacterial cells was found to increase with the growth. Co⁶⁰ in the 75% alcoholic extract, however, showed the maximum after 48 hr. of inoculation. The amount of vitamin B₁₂ in bacterial cells and remaining media were also estimated by means of colorimetric determination of cyanide in cyanoco-