<table>
<thead>
<tr>
<th>Title</th>
<th>Reaction of Ketene with Ethyl Acetoacetate in the Presence of Pyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Isoshima, Toshizo</td>
</tr>
<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1954), 32(3): 140-142</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1954-05-31</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/75439">http://hdl.handle.net/2433/75439</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
</tbody>
</table>
NOTES

derivatives were produced.

(3) In the reactions with their sodium salts, O-acetyl derivatives were produced, containing a small amount of C-acetyl derivatives.

Some experimental results were cited in Tables 1 and 2.

Table 2. Some physical constants of O-acetyl derivatives obtained from phenol, resorcin, phloroglucine and dímédone.

<table>
<thead>
<tr>
<th>O-acetyl derivative</th>
<th>Physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m.p. (°C)</td>
</tr>
<tr>
<td>OAc</td>
<td>—</td>
</tr>
<tr>
<td>Ac</td>
<td>—</td>
</tr>
<tr>
<td>OH</td>
<td>—</td>
</tr>
<tr>
<td>OAc</td>
<td>—</td>
</tr>
<tr>
<td>AcO</td>
<td>105-7</td>
</tr>
<tr>
<td>AcO</td>
<td>—</td>
</tr>
</tbody>
</table>

Reaction of Ketene with Ethyl Acetoacetate
in the Presence of Pyridine

Toshizo Isosima*
(Nodzu Laboratory)
Received June 25, 1954

In the presence of a very small amount of pyridine, ketene was reacted with ethyl acetoacetate above -20°C, and a reaction product rich in O-acetyl- (II), poor in C-acetyl ethyl acetoacetate (I), was obtained.

* 磐島敏三
NOTES

On the other hand, when an equimolar amount of pyridine was used above -40°C, O-acetyl derivative was a sole product, no C-acetyl derivative being formed.

A mechanism of the formation of C-acetyl derivative in the reaction of ketene with sodium salt of ethyl acetoacetate is probably as follows:

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{CH} \cdots \text{COOEt} \\
\text{O} & \quad \text{Na} \cdots \text{O}^– \\
\text{H}^+ & \quad \Rightarrow \\
\text{HO} \cdots \text{C} & \equiv \text{CH}_2 \\
\text{O} & \quad \text{O} \\
\text{r}e\text{arr} & \text{angement}
\end{align*}
\]

(I)

The formation of O-acetyl derivative in the presence of pyridine may occur through following mechanism.

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{CH} \cdots \text{COOEt} \\
\text{O} & \quad \text{CH}_2\text{C} \equiv \text{OH} \\
\text{H} & \quad \text{N} \\
\text{r}e\text{arr} & \text{angement}
\end{align*}
\]

(II)

The author anticipates the presence of H-bonding (III) or (IV) between ethyl acetoacetate and pyridine. The H-bonding (III), however, was denied by Le Fèvre.

\[
\begin{align*}
\text{CH}_3\text{C} & \equiv \text{CH} \cdots \text{COOEt} \\
\text{O} & \quad \text{Cl} \\
\text{H} & \quad \text{N} \\
(\text{III})
\end{align*}
\]

and in

\[
\begin{align*}
\text{Cl} & \quad \text{O} \cdots \text{H} \\
\text{Cl} & \quad \text{N} \\
(\text{IV})
\end{align*}
\]

Though the presence of H-bonding (IV) has not yet been confirmed, it is quite probable, taking into account that the H-bonding in

\[
\begin{align*}
\text{Cl} & \quad \text{C} \equiv \text{H} \cdots \text{N} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

was already proved, and \(pK_a\) values of O-chlorophenol (\(pK_a=10-11\)) and ethyl acetoacetate (\(pK_a=10.7\)) are almost equal.

REFERENCES

NOTES

(4) L.V. Lemmerman et al., ibid., 68, 1361 (1946).