Oxidation of Benzoins with Pyridine N-oxide – SbCl₅ (1 : 1) Complexes

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Abstract: When a mixture of a few benzoins and a pyridine N-oxide – SbCl₅ (1 : 1) complex (Complex A) was boiled in nitromethane, the corresponding benzils were obtained in various yields dependent upon the kinds of substituents in each reactant. The yield of benzil becomes higher by adding some tertiary amines. In this reaction, tribenzylamine is a good accelerator to promote it.

When Complex A, 4-picoline N-oxide – SbCl₅ (1 : 1) complex (Complex B) and 4-nitro-pyridine-SbCl₅ (1 : 1) complex (Complex C) were used as the oxidant of benzoin, the order of the reaction rate was as follows: Complex C > Complex A > Complex B

The oxidation of benzoin with these pyridine N-oxide – SbCl₅ (1 : 1) complexes seems to proceed according to the following three processes: i) the oxidation by pyridine oxide – SbCl₅ (1 : 1) complexes themselves ii) the oxidation by α–OSbCl₄ pyridines and iii) the oxidation by the mixture of pyridine N-oxides and antimony (V) chloride.

Key words: oxidation, pyridine N-oxide – SbCl₅ (1 : 1) complexes, benzoins

1 Introduction

We have already obtained a 84.5% yield of benzil by treating a mixture of pyridine N-oxide – SbCl₅ (1 : 1) complex (Complex A) and benzoin in a molar ratio (Complex A : benzoin=1.0 : 2.1) in nitromethane for 5 h at 40°C.

For further development in this area, the oxidation of a few benzoins using Complex A, 4-picoline-N-oxide – SbCl₅ (1 : 1) complex (Complex B) and 4-nitropyridine – SbCl₅ (1 : 1) complex (Complex C) was studied in detail.

The reaction of 4,4’-dimethylbenzoin and 4,4’-dichlorobenzoin with Complex A were attempted to find Complex A able to oxidize other benzoins. Among three Sb-complexes, Complex C seems to be most efficient reagent for these benzoins. Tribenzylamine is a good promoter for the oxidation of benzoin. Finally, this reaction pathway was estimated through the reaction of benzoin with Complex A.

2 Experimental

2.1 Preparation of pyridine N-oxide – SbCl₅ (1 : 1) complex (Complex A)

Upon mixing equimolar carbon tetrachloride solutions of pyridine N-oxide and antimony (V) chloride, Complex A was deposited in almost quantitative yield. Complex B and Complex C were prepared by the same procedure.

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2.2 Preparation of 4,4'-dimethylbenzoin

4,4'-Dimethylbenzoin was prepared by mixing an ethanol solution of p-tolylaldehyde and a water solution of potassium cyanide, mp 92.0~93.0°C (Lit3), 88.0~89.0°C). 4,4'-Dichlorobenzoin was also prepared by the same procedure, mp 88.0~89.0°C (Lit4), 88.0°C).

2.3 Oxidation of benzoin with pyridine N-oxide-SbCl5 (1 : 1) complex (Complex A)

A mixture of benzoin 1.0 g (4.7 mmol) and Complex A 0.5 g (1.3 mmol) was boiled in nitromethane (10 mL) for 7 h. The reaction mixture was poured into cold water and then filtered. The filtrate was extracted with benzene and the benzene solution was dried. After the benzene was distilled off, benzil 0.43 g (45%) mp 97.0°C (Lit5), 95.0°C) and benzoin 0.47 g (47%) were separated from each other by TLC (Silicagel-benzene). The reaction of benzoins with other Sb-complexes was performed using the same procedure, 4,4'-dimethylbenzil mp 102.0~104.0°C (Lit6), 104.0~105.0°C), 4,4'-dichlorobenzil mp 194.5~195.5°C (Lit7). 195.0~196.0°C).

2.4 Reaction of benzoin with a-OSbCl4 pyridine

Complex A 0.5 g (1.3 mmol) was boiled in nitromethane (10 mL) for 5 h, and then benzoin 1.0 g (4.7 mmol) was added. The reaction mixture was boiled again for 5 h. Benzil 0.38 g (39%), 2-pyridone 0.012 g (10%) and benzoin 0.52 g (52%) were separated from each other by the same procedure as stated in 2.3.

2.5 The reaction of benzoin with a equimolar mixture of 2-pyridone and antimony (V) chloride (SbCl5)

After mixing 2-pyridone 0.14 g (13 mmol) and SbCl5 0.5 g (13 mmol) in nitromethane (10 mL), benzoin 1.0 g (4.7 mmol) was added to the solution and the total reaction mixture was boiled for 5 h. After work up, benzil 0.42 g (43%), benzoin 0.53 g (53%) and 2-pyridone 0.043 g (31%) were obtained from the reaction mixture, respectively.

3 Results

When a mixture of benzoin and Complex A in a molar ratio (3.1 : 1.0) was boiled in nitromethane, the yield of benzil increased and the recovery of benzoin decreased with reaction time, respectively. After 9 h, 57% of benzil was obtained with 34% of benzoin (Fig. 1).

Using Complexes A, B and C in the oxidation of benzoin under the same reaction conditions, the activity of three Sb-complexes is shown in following order (Table 1).

<table>
<thead>
<tr>
<th>Sb-complexes</th>
<th>Yield of benzil (%)</th>
<th>Recovery of benzoin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\text{SbCl}_5</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td>\text{CH}_3</td>
<td>38</td>
<td>55</td>
</tr>
<tr>
<td>O\text{SbCl}_5</td>
<td>95</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

A mixture of benzoin (4.7 mmol) and Sb-complexes (1.3 mmol) was boiled in nitromethane (100 mL) foe 7 h.
In order to compare in detail the reaction rate in the oxidation of benzoin using complex A and Complex C, the time dependence in the yield of benzil using Complex C is given in Fig. 2. Since the reaction goes essentially to completion at 1.5 h, Complex C must be more efficient than Complex A in the oxidation of benzoin (Fig. 1, Fig. 2). When Complex C was used as an oxidant in the oxidation of 4,4'-dimethylbenzoin and 4,4'-dichlorobenzoin, higher yields of the corresponding benzils were obtained in comparison with the case which Complex A was used (Table 2).

Air oxidation of benzoin in solvent and atmosphere may be negligible (Entry 1, Table 3). Very low yields of benzil were obtained in the reaction of benzoin with Complex A in boiling dichloromethane (Entry 2, Table 3). Some tertiary amines were added to a mixture of Complex A and benzoin to find whether the reaction could be accelerated. Tribenzylamine is a more effective accelerator in comparison to pyridine and α-picoline (Entries 3, 4, 5, Table 3). Understandably, when benzoin was also treated with Complex A under various conditions, the reaction was promoted by adding tribenzylamine (Entries 6, 7, 8, 9, 10, Table 3).

4 Discussion

In the oxidation of benzoin with Complex A, addition of some tertiary amines promoted the reaction rate. This seems to be due to the elimination of hydrogen chloride generated during the reaction (Table 3). Complex C is the most effective reagent for oxidation of benzoin among three Sb-complexes (Table 1). This potency may be due to the fact that chlorine atoms on Complex C can be liberated easily because of the strong electron drawing character of the nitro group.

We have already reported on the thermolysis of Complex A, Complex B and Complex C in nitromethane to give the corresponding 2-pyridones via α-OSbCl₅-pyridine². The rearrangement product 2-pyridone was also obtained by boiling dichloromethane so-
Fig. 2 Oxidation of Benzoin with 4-Nitropyridine N-oxide-SbCl₅ (1:1) Complex (Complex C). The reaction was carried out in a molar ratio (Complex C : benzoin = 1.0 : 3.6) in nitromethane at reflux temperature. ●: Benzil ○: Benzoin

### Table 2 Oxidation of Benzoin with Pyridine N-oxide-SbCl₅ (1:1) Complex and 4-Nitropyridine N-oxide-SbCl₅ (1:1) Complex.

<table>
<thead>
<tr>
<th>Benzoins</th>
<th>X</th>
<th>Yield of benzils (%)</th>
<th>Recovery of benzoins (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Benzoin Structure" /></td>
<td>H</td>
<td>27</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>88</td>
<td>4</td>
</tr>
<tr>
<td><img src="image" alt="Benzoin Structure" /></td>
<td>H</td>
<td>34</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>79</td>
<td>7</td>
</tr>
<tr>
<td><img src="image" alt="Benzoin Structure" /></td>
<td>H</td>
<td>33</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>NO₂</td>
<td>55</td>
<td>31</td>
</tr>
</tbody>
</table>

Benzoins (4.7 mmol) were boiled with pyridine N-oxide-SbCl₅ (1:1) complex or 4-nitropyridine N-oxide-SbCl₅ (1:1) complex (1.3 mmol) in nitromethane (100 mL) for 2 h.
Table 3 Oxidation of Benzoin with Pyridine N-oxide-SbCl₅ (1 : 1) Complex (Complex A) in the Presence of Tertiary Amines.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amines</th>
<th>Solvent</th>
<th>Reaction temp. (°C)</th>
<th>Reaction time (h)</th>
<th>Yield of benzil (%)</th>
<th>Recovery of benzoin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a)</td>
<td>CH₃NO₂</td>
<td>reflux</td>
<td>5</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>b)</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Pyridine</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>28</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>α-Pycoline</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>23</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>(C₆H₅CH₂)₃N</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>1</td>
<td>49</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>none</td>
<td>CH₃NO₂</td>
<td>reflux</td>
<td>16</td>
<td>24</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>(C₆H₅CH₂)₃N</td>
<td>CH₃NO₂</td>
<td>room temp.</td>
<td>16</td>
<td>29</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>none</td>
<td>CH₂Cl₂</td>
<td>room temp.</td>
<td>16</td>
<td>16</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>(C₆H₅CH₂)₃N</td>
<td>CH₂Cl₂</td>
<td>room temp.</td>
<td>16</td>
<td>22</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>(C₆H₅CH₂)₃N</td>
<td>CH₃NO₂</td>
<td>reflux</td>
<td>1</td>
<td>43</td>
<td>51</td>
</tr>
</tbody>
</table>

a) Benzoin (1.0 g, 4.7 mmol) was boiled in nitromethane in the absence of Complex A and amine.
b) Benzoin (1.0 g, 4.7 mmol) and Complex A (0.5 g, 1.3 mmol) were used as the starting materials in the absence of amine.

![Diagram]

α-SbCl₅, pyridine

Table 4 Thermal Reaction of Benzoin and Pyridine N-oxide-SbCl₅ (1 : 1) Complex (Complex A).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent (mL)</th>
<th>Pyridone (%)</th>
<th>Benzil (%)</th>
<th>Recovery of benzoin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂Cl₂(100)²a</td>
<td>24</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>CH₃NO₂(10)²a</td>
<td>81</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂(100)²b</td>
<td>10</td>
<td>39</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>CH₃NO₂(10)²b</td>
<td>24</td>
<td>45</td>
<td>47</td>
</tr>
<tr>
<td>5</td>
<td>CH₂Cl₂(100)²c</td>
<td>17</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>CH₃NO₂(10)²c</td>
<td>26</td>
<td>40</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>CH₃NO₂(10)²d</td>
<td>31</td>
<td>42</td>
<td>53</td>
</tr>
</tbody>
</table>

a) Complex A (1.0 g, 4.7 mmol) was boiled for 5 h. b) A mixture of benzoin (1.0 g, 4.7 mmol) and Complex A (0.5 g, 1.3 mmol) was boiled for 5 h. c) After Complex A (0.5 g, 1.3 mmol) was boiled for 5 h, benzoin (1.0 g, 4.7 mmol) was added in this and was boiled again for 5 h. d) After 2-pyridone (0.34 g, 1.3 mmol) and SbCl₅ (0.34 g, 1.3 mmol) were mixed, benzoin (1.5 g, 4.7 mmol) was added in this and was boiled for 5 h.
applied in the oxidation of benzoin. The product benzil was also obtained in the same yield as the yield shown in Entry 4 (Entry 7, Table 4). Since hydrogen chloride were generated as soon as two nitromethane solutions of 2-pyridone and SbCl₅ were mixed, chemical species α-OSbCl₄ pyridine should be produced very rapidly in the reaction mixture. Therefore, benzoin seems to be also oxidized by α-OSbCl₄ pyridine which is formed on the thermolysis of Complex A.

\[
\text{N}^\circ\text{O} + \text{SbCl}_3 \rightarrow \text{N}^\circ \text{OSbCl}_4 + \text{HCl}
\]

Air and antimony (III) chloride (SbCl₃) itself was not affected at all in the oxidation of benzoin (Entries 1, 2, Table 5). Pyridine N-oxide is not a good reagent for oxidation of benzoin (Entry 3, Table 5). When the mixture of SbCl₃ and three kinds of pyridine N-oxides was heated in nitromethane, respectively, the substituent effect was observed in the yield of benzil (Entries 4, 5, 6, Table 5). The oxidation of benzoin may also take place by the interaction between SbCl₃ and pyridine N-oxides.

From these results, the oxidation of benzoin with Complex A seems to proceed according to the following three processes:

i) The oxidation of benzoin by Complex A itself (Eq. 1)

\[
\text{N}^\circ\text{O} + 2\text{Ph-C} = \text{CH-Ph} \rightarrow \text{N} + 2\text{Ph-C} = \text{C-Ph} + \text{SbCl}_3 + 2\text{HCl} \quad (1)
\]

ii) The oxidation of benzoin by α-OSbCl₄ pyridine derived from Complex A (Eq. 2)

\[
\text{N}^\circ\text{O} + \text{Ph-C} = \text{CH-Ph} \rightarrow \text{N} + \text{Ph-C} = \text{C-Ph} + \text{SbHCl}_2 + \text{HCl} \quad (2)
\]
iii) The oxidation of benzoin by the interaction with pyridine N-oxide and SbCl₃ (Eq. 3)

\[
2 \text{Ph-C} = \text{CH-Ph} + 2 \text{SbCl}_3 \xrightarrow{\text{pyridine N-oxide}} 2 \text{Ph-C} = \text{C-Ph} + 2 \text{SbCl}_3 + 2 \text{H}_2
\]  (3)

5 Conclusion

Among complex A, Complex B and Complex C, Complex C is most effective in the oxidation of benzoin. When some tertiary amines were added to obtain benzil in a high yield, it was found that tribenzilamine is the best promoter among them in this reaction.

The oxidation of benzoin with Complex A seems to proceed in the following three pathways: (i) the oxidation by Complex A itself (ii) the oxidation by \(\alpha\)-OSbCl₄ pyridine and (iii) the oxidation by interaction between pyridine N-oxide and SbCl₃.

\[
\begin{align*}
\text{SbCl}_3 + \text{Benzoin} & \quad \text{Pyridine N-oxide} \\
\text{Benzoin} + \text{Complex A} & \rightarrow \text{Benzil} \quad \alpha\text{-OSbCl}_4 \text{pyridine} + \text{Benzoin}
\end{align*}
\]

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References

【報文】 セトウチャマイマイのスフィンゴ脂質（第3報）
内臓部のセラミド

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近畿大学理工学部化学教室（〒577 大阪市小倉北区）

有肺類のセトウチャマイマイ（Euhadra hichonis）の内臓部より単離された2つのセラミド（セラミド-Ⅰとセラミド-Ⅱ）について，FAB/MS，GC，GC/MS そして化学的な方法を用いて構造研究を行った。

セラミド-Ⅰの主な脂肪酸はヘキサデカン酸（19.6%）と2-ヒドロキシヘキサデカン酸（14.3%），セラミド-Ⅱは2-ヒドロキシヘキサデカン酸（39.5%）であった。

セラミド-Ⅰの主な長鎖塩基は2-アミノ-16-メチルオクタデセン-1,3-ジオール（39.8%），セラミド-Ⅱは2-アミノ-16-メチルオクタデセン-1,3,4-トリオール（47.2%）であった。その結果，セラミド-Ⅰの主な分子種の構造はN-ヘキサデカノイル-2-アミノ-16-メチルオクタデセン-1,3-ジオールとN-2-ヒドロキシヘキサデカノイル-2-ア