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<th>三硫化物の硫酸基触媒による還元過程における化合物、化合物、化合物の生成についての検討</th>
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<td>Author(s)</td>
<td>伊藤 清司</td>
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<td>Editor(s)</td>
<td>未定</td>
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<tr>
<td>Citation</td>
<td>大阪府立工業高等専門学校研究紀要, 1992, 26, p.37-41</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1992-10-30</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://repository.osakafu-u.ac.jp/dspace/">http://repository.osakafu-u.ac.jp/dspace/</a></td>
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Reduction of Sulfur Compounds with Fe₃(CO)₁₂–H₂O–Pyridine System

Keiji Itô

ABSTRACT

Sulfur Compounds such as thiols and dithioacetals were reduced with Fe₃(CO)₁₂–H₂O–Pyridine System. The products were mainly alkanes and small amounts of sulfides and disulfides. In these reactions, hydrogen source is water and the reactive species is hydride polynuclear ferrates such as [HFeₘ(CO)ₙ]⁺ (m=2,3,4, n=8,11,14).

Key Words: Iron Carbonyl, Reduction, Sulfur compounds

Introduction

Iron carbonyl complexes have been shown to be useful reagents for organic synthesis.¹ They can be used as reagents for deoxygenation of certain oxygen-containing compounds and desulfurization of sulfur compounds. Otsuka and coworkers reported the formation of azobenzene in low yield from the reaction of the corresponding sulfur diimide with Fe₃(CO)₁₂.² A potentially useful reaction, desulfurization of thiranes is synthesis of alkenes.³,⁴ Recently the author reported that the deoxygenative ability of iron carbonyl complexes is applied to the synthesis of heterocyclic compounds such as pyroles and pyridines,⁵ and also reduction of nitro compounds into aniline and α, β-unsaturated carbonyl compounds into saturated carbonyl compounds with Fe₃(CO)₁₂–H₂O–Pyridine System.⁶

In the reduction of ketones to alkanes, Clemmensen reduction and Wolf-Kishner reduction have been employed as convenient methods, both of which are performed under relatively harsh conditions. In the former reaction, zinc amalgam is used, but mercury is a hazard agent and dirty environment. In the later reaction, hydrogen and nickel catalyst are used, but hydrogen is dangerous because the explosive property. H. Alper reported that reduction of thioketones to the corresponding hydrocarbons has been found to occur on treatment with Na[HFe(CO)₄].⁷ The author has been interested in the development of a new reduction method of ketones to alkanes with iron carbonyl and water instead of the use of hydrogen and heavy metals.

\[
\text{PhCH}_2\text{SH} \xrightarrow{\text{Fe}_3(\text{CO})_{12}–\text{H}_2\text{O}–\text{pyridine}} 80^\circ \text{C}, 20 \text{h} \rightarrow \text{PhCH}_3 + (\text{PhCH}_2)_2\text{S} + (\text{PhCH}_2)_2\text{S} \quad (\text{eq} 1)
\]

Table 1. Reduction of Benzyl thiol with Fe₃(CO)₁₂–H₂O–Pyridine System.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Benzyl thiol (mmol)</th>
<th>Fe₃(CO)₁₂ (mmol)</th>
<th>H₂O (mmol)</th>
<th>Temp (°C)</th>
<th>Toluene</th>
<th>Sulfide</th>
<th>Disulfide</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>2.0</td>
<td>20</td>
<td>80</td>
<td>98 (490)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>2.0</td>
<td>0</td>
<td>80</td>
<td>32 (160)</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1.0</td>
<td>40</td>
<td>110</td>
<td>28 (560)</td>
<td>3</td>
<td>4</td>
</tr>
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</table>

Pyridine: 10 cm³  a) Isolated yields based on benzyl thiol used and those in parentheses based on iron carbonyl used.

Received April 10, 1992

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Bul. of Osaka Pref. Col. of Tech. Vol. 26 — 37 —
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hydrogen and heavy metals such as mercury. In this paper, the author reports that iron carbonyl complex reduces sulfur compounds such as thiols and dithioacetals to give the corresponding alkanes in good yields.

Results and Discussions

Reduction of thiols

A solution of Fe$_3$(CO)$_{12}$ in pyridine was heated at 80°C for 1.5 h under argon atmosphere. To the mixture, benzyl thiol and water were added and the resulting mixture was heated at same temperature for 20 h. The results are shown in Table 1. The reaction is illustrated in equation 1.

In this reduction reaction, toluene was obtained as a main product, and dibenzyl sulfide and dibenzyl disulfide were obtained as by-products. In run 1, toluene was given in good yield, 98% based on benzyl thiol and 490% based on iron carbonyl. In the absence of water in run 2, toluene was a main product but the yield was lower than that in the presence of water in run 1. In run 1, the result suggests that water is used as a source of hydrogen. But, in the absence of water in run 2, toluene was also obtained. The result suggests that thiol is used as a source of hydrogen. In run 2, the relative yields of by-products was increased in comparison with that in run 1. These results suggest that the dibenzyl sulfide and dibenzyl disulfide are reaction intermediates, and are reduced into toluene in the presence of water. In run 3, the maximum yield of toluene based on iron carbonyl was 560%. Reaction path way is shown in Scheme 1.

Table 2. Reduction of n-Decyl thiol with Fe$_3$(CO)$_{12}$-H$_2$O-Pyridine System.

<table>
<thead>
<tr>
<th>Run No</th>
<th>n-decyl thiol (mmol)</th>
<th>water (mmol)</th>
<th>Temp (°C)</th>
<th>Yield of n-decane/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>10</td>
<td>20</td>
<td>80</td>
<td>18 (90)</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>30</td>
<td>90</td>
<td>35 (175)</td>
</tr>
</tbody>
</table>

Fe$_3$(CO)$_{12}$: 2 mmol, Pyridine: 10 cm$^3$, Reaction time: 3 h. a) Yields based on n-decyl thiol used and those in parentheses based on Fe$_3$(CO)$_{12}$ used.

n-Decyl thiol was reduced to n-decane with Fe$_3$(CO)$_{12}$-H$_2$O-Pyridine system. In these reactions, the corresponding sulfide and disulfide were obtained only as trace products. The yield of alkane was increased with high temperature and more quantity of water added, and the maximum yield was 175% based on iron carbonyl used. These results suggest that Fe$_3$(CO)$_{12}$-H$_2$O-pyridine System is able to reduce aliphatic thiols to alkanes. But the yield is less than that in benzyl thiol reduction. This result suggests that reactivities of aliphatic thiols are less than that of benzyl thiol with Fe$_3$(CO)$_{12}$-H$_2$O-Pyridine

Reduction of Dithioacetals

Dithioacetals are used as protecting group of ketones and are conveniently prepared from reactions of ketones with 1, 2-ethane dithiol (equation 3). Dithioacetals are applied as a substrates in reduction method of ketones to alkanes (equation 4).

$\text{CH}_3(\text{CH}_2)_9\text{SH} + \text{Fe}_3(\text{CO})_{12} \to \text{CH}_3(\text{CH}_2)_9\text{CH}_3$ (eq 2)
Reduction of Sulfur Compounds

Reduction of Dithioacetals to Alkanes

<table>
<thead>
<tr>
<th>Run No</th>
<th>Dithioacetal (mmol)</th>
<th>Time (h)</th>
<th>Product Yield/% a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>5a (10)</td>
<td>6</td>
<td>7 (70)</td>
</tr>
<tr>
<td>7</td>
<td>5a (10)</td>
<td>17</td>
<td>18 (90)</td>
</tr>
<tr>
<td>8</td>
<td>5b (10)</td>
<td>20</td>
<td>14 (70)</td>
</tr>
</tbody>
</table>

Fe₃(CO)₁₂: 2 mmol, water: 40 mmol, Pyridine: 10 cm³, Reaction temperature: 95°C,

a) Yields based on dithioacetal used and those in parentheses based on iron carbonyls used.

Acetophenone dithioacetal was reduced to ethylbenzene. The yield of alkane was increased with reaction time and the maximum yield was given when the reaction time is 17–20 h (Run 6, 7). 2-Octanone dithioacetal was also reduced to the corresponding alkane at the same conditions (Run 8). In this method, the reaction condition is milder than that in Wolf Kishner reduction method and so that, the hydrogen source is water instead of hydrogen. It may be noted that the overall result is equivalent to Wolff-Kishner or Clemmensen reduction.

Isolation of Reactive Species in This Reaction System.

Fe₃(CO)₁₂ (2 mmol) in pyridine (10 cm³) was heated at 80°C for 1.5 h, and then, to the mixture water (10 mmol) was added. The resulting mixture was heated at 80°C for 1.5 h. After cooling the mixture, a solution of bis(triphenylphosphine)iminium chloride [(Ph₃P)₂N]Cl (PPNCI, 2 mmol) in dichloromethane (10 cm³) was added, and then the mixture stirred at room temperature for 1 h. After treatment of the reaction mixture, PPN[Fe₂(CO)₈]⁺ was isolated. In the previous paper, the author isolated [PPN][Fe₂(CO)₈] from reaction of Fe₃(CO)₁₂ in pyridine. Now in the presence of water, he has been found that [Fe₂(CO)₈]²⁻ reacts with water to give [HFe₂(CO)₈]⁻. S. R. Su and A. Wojcicki reported that the hydride carbonyl ferrate complex can catalyze water gas shift reaction, (eq 7). These results suggest that [HFe₂(CO)₈]⁻ is an active species in this reduction reaction.

From the results in the above sections, author proposes the following reaction scheme in the reduction of dithioacetals with Fe₃(CO)₁₂–H₂O–Pyridine System (Scheme 3).

Scheme 3
Experimental

General Data

All reactions were carried out under argon atmosphere. IR spectra were recorded on a Shimadzu IR 24 spectrometer. NMR spectra were recorded on a Hitachi NMR R 24A spectrometer. Gas chromatographic (GC) analyses were performed on a Shimadzu GC 4CPF using a 100 cm × 3.5 mm glass column packed with SE 30 (10%) chromosorb. Pyridine as a solvent were purified as follows; KOH pellet was added to pyridine, and the mixture was standing overnight. The mixture was filtrated and the filtrate was distilled with anhydrous CaH2 under argon atmosphere. Benzyl thiol, n-decyl thiol, acetophenone, 2-octanone and ethane 1,2-dithiol were commercial products. Before using, the reagents were distilled under argon atmosphere. Fe3(CO)12 was prepared from Fe(CO)5 described in the literature.11

Preparation of acetophenone dithioacetal

In a 500 cm³ three necked flask, 300 cm³ of anhydrous benzene and 38 g of anhydrous granular ZnCl2 were placed, and the mixture was vigorously stirred. To this mixture, 12 cm³ of acetophenone and 25 cm³ of ethane 1,2-dithiol were added. To the resulting mixture, HCl gas was passed through with a inlet tube for 3h. The mixture was washed with dil NaOH soln and then with water. The organic products were extracted with benzene and the extract was dried with anhydrous Na2SO4. The solvent was evaporated under reduced pressure. The residue was distilled under reduced pressure. Bp. 138°C/5 mmHg.

Reduction of sulfur compounds

A solution of Fe3(CO)12 (1–2 mmol) in pyridine (10 cm³) was heated at 80°C for 1.5 h and then, to the mixture, water (10 mmol) was added. The resulting mixture was heated at 80–95°C for 3–24 h. The products were extracted with ether from the reaction mixtures, chromatographed on silica gel with hexane. The structures were determined with the spectral analysis and the physical properties. The yields of products were determined with GC analysis using an internal standard method. The standard material was n-dodecane.

toluene: bp. 110°C; IR(CHCl3) 2958, 1488, 725, 690 cm⁻¹; NMR(CDC13) δ=2.10 (s, 3H), 7.12 (m, 5H).
dibenzyl sulfide: mp. 48°C; IR(KBr) 3045, 2910, 1490, 770, 700 cm⁻¹; NMR(CDC13) δ=3.46 (s, 4H), 7.17 (m, 10H).
dibenzyl disulfide: mp. 68°C; IR(KBr) 3050, 2910, 1640, 1500, 1465, 1230, 1200, 1070, 1030, 765, 680 cm⁻¹; NMR(CDC13) δ=3.57 (s, 4H), 7.20 (m, 10H).
n-decane: mp. 30 °C; IR(neat) 2920, 2850, 1460, 1380, 720 cm⁻¹; NMR(CDC13) δ=0.88 (t, J=7.0 Hz, 6H), 1.20–1.30 (m, 16H).
ethylbenzene: bp. 136°C; IR(CHCl3) 3030, 2930, 1495, 745, 695 cm⁻¹; NMR(CDC13) δ=1.20 (t, J=7.0 Hz, 3H), 2.60 (q, J=7.0 Hz, 2H), 7.10 (m, 5H). n-octane: bp. 126°C; IR(CHCl3) 2920, 2850, 1460, 1380, 720 cm⁻¹; NMR(CDC13) δ=0.88 (t, J=7.0 Hz, 6H), 1.20–1.30 (m, 12H).

Isolation of PPN[Fe2(CO)8]

A solution of Fe3(CO)12 (2 mmol) in pyridine (10 cm³) was heated at 80°C for 1.5 h, and then, to the mixture, water (10 mmol) was added. The resulting mixture was heated at 80°C for 1.5 h. After cooling the mixture, a solution of bis(triphenylphosphine)iminium chloride [(Ph3P)2N]Cl (PPNCl, 2 mmol) in dichloromethane (10 cm³) was added, and then the mixture stirred at room temperature for 1 h. The mixture was washed with water. The organic layer was separated, and dried over dry sodium sulfate. Ether was added to the organic solution, and the crystallized product was separate. The product was identified as PPN[Fe2(CO)8] with IR, CHN analysis. The
spectral data of this complex agreed with that of authentic sample.8)

The following analytical and spectral data were obtained for [PPN][HFe₂(CO)₉]

yellow brown crystal; IR(KBr) 1987, 1940, 1880, 1850, 1770 cm⁻¹; Found: C, 60.68; H, 3.46; N, 1.78%; Fe, 12.50%. Calcd for C₄₆H₃₁NO₅Fe₂P₂: C, 60.37; H, 3.57; N, 1.60; Fe, 12.76%.

References