Electroorganic Chemistry. 66. Electrochemical Oxidation of Aminals and Enamines Using a Mediatory System

TATSUYA SHONO, YOSHIHIRO MATSUMURA, JUE HAYASHI, MIKIKO USUI, SHIN-ICHIRO YAMANE and KENJI INOUE

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606, Japan

Electrochemical oxidation of aminals and enamines smoothly proceeded under the conditions using potassium iodide as a mediator to afford formamides and β-ketoamines, respectively. The reaction mechanisms of the formation of these products are discussed.

Electrochemical oxidation of organic compounds using mediators has been attracting much attention, since (i) the oxidation of substrates with this system proceeds at lower potentials than those required for the direct anodic oxidation of the substrates, and (ii) the oxidation is efficiently achievable under mild conditions. Accordingly, it is important to exploit new mediatory systems being effective to organic synthesis.

We have already found some mediatory systems which are applicable to the Hofmann rearrangement of amides 1 to carbamates 2, and to the oxidation of secondary alcohols 3 to ketones 4 and primary alcohols 5 to esters 6.

\[
\begin{align*}
\text{RCONH}_2 & \xrightarrow{-e} \text{KBr-CH}_3\text{OH} \rightarrow \text{RNHCO}_2\text{CH}_3 \quad (1) \\
\text{R}^\prime\text{CHOH} & \xrightarrow{-e} \text{KI} \rightarrow \text{R}^\prime\text{C}=\text{O} \quad (2) \\
2 \text{RCH}_2\text{OH} & \xrightarrow{-e} \text{KI} \rightarrow \text{RCO}_2\text{CH}_2\text{R} \quad (3)
\end{align*}
\]

In this report, we describe the electrochemical oxidation of aminals 7 and enamines 8 using potassium iodide (KI) as a mediator. The electrochemical oxidation of hexahydro-1,3,5-triazines to triazines has been reported.\(^4\)

\[
\begin{align*}
\text{CH}_2\text{NR}_2^\prime & \quad \text{RCH=CHNR}_2^\prime \\
7 \text{ R}^\prime: \text{alkyl group} & \quad 8 \text{ R,R}^\prime: \text{alkyl groups}
\end{align*}
\]

The oxidation of 7 leads to a convenient synthesis of \(n,n\)-dialkylformamides, while the latter compounds are oxidatively transformed to β-ketoamines.

RESULTS

Preparation of \(N,N\)-dialkylformamides. Constant current electrolysis of an aqueous solution of \(N,N,N',N'\text{-tetramethylmethanediame} \) (9) containing one-fifth equivalent of KI gave \(N,N\text{-dimethylformamide} \) (DMF) in 75 % yield at the time when 4 F/mol of electricity was passed (eqn. (4)).

\[
\begin{align*}
\text{CH}_3\text{NCH}_2\text{NCH}_3 \xrightarrow{-e} \text{KI} \rightarrow \text{DMF} \quad (4) \\
\text{CH}_3 & \quad 4 \text{ F/mol} \quad 75 \%
\end{align*}
\]

Also, the electrolysis of an aqueous solution containing equimolar amounts of 9 and formaldehyde resulted in the formation of DMF in 176 % yield based on 9 (eqn. (5)).
Table 1. Electrochemical synthesis of N,N-dimethylformamide.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Mediator (mmol)</th>
<th>([\text{Aldehyde}]/[\text{Mediator}])</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KI (1.7)</td>
<td>30</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>KI (5)</td>
<td>10</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>KI (10)</td>
<td>5</td>
<td>95&gt;</td>
</tr>
<tr>
<td>4</td>
<td>KI (10)</td>
<td>5</td>
<td>95&gt;</td>
</tr>
<tr>
<td>5</td>
<td>KBr (10)</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>KCl (10)</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>NaI (10)</td>
<td>5</td>
<td>95&gt;</td>
</tr>
<tr>
<td>8</td>
<td>NaBr (10)</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>Et\textsubscript{2}NI (10)</td>
<td>5</td>
<td>59</td>
</tr>
<tr>
<td>10</td>
<td>KOH (10)</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

\textsuperscript{a} HCHO: 50 mol, Me\textsubscript{2}NH: 55 mol. Anode, Pt; cathode, carbon. \textsuperscript{b} Yields based on aldehyde were obtained by GLC method. \textsuperscript{c} Carbon rods were used as cathode and anode.

\[ 9 + \text{CH}_2\text{O} \xrightarrow{-\text{e}} \text{KI} \xrightarrow{4 \ \text{F/mol}} \text{DMF} \ (5) \text{ 176%} \]

The latter result implies that it is not necessary to isolate 9 as the starting material for the synthesis of DMF from dimethylamine and formaldehyde. In fact, the preparation of DMF was satisfactorily achieved by passing electricity through an aqueous solution* of dimethylamine (1 equiv.) and formaldehyde (1 equiv.) containing KI (0.2 equiv.) (run 3 in Table 1). The effects of the amount of KI (runs 1–3), the type of mediators (runs 5–10) and anode materials (run 4) on the yields of DMF were also examined. The results are summarized in Table 1 showing that less than one-tenth equivalent of KI is sufficient for almost perfect oxidation, and that the yields of DMF increased in the order of $\Gamma^+ > \text{Br}^+ > \text{Cl}^+ > \text{OH}^−$. A carbon rod instead of platinum was usable as an anode.

Although DMF has been prepared by several methods using formic acid,\textsuperscript{6} carbon monoxide,\textsuperscript{7} methyl formate \textsuperscript{8} or hydrogen cyanide\textsuperscript{9} as the precursor of the formyl moiety, our mediatory method utilizing formaldehyde provides a new facile route for the production of DMF.

Formamides of primary and secondary amines other than dimethylamine were similarly synthesized using potassium iodide as a mediator (Table 2).

\textit{Preparation of \(\beta\)-ketoamines.} In contrast to the reaction of formaldehyde, the electrolysis of a solution containing higher aldehydes \textsuperscript{10} and amines \textsuperscript{11} did not give the corresponding amides but yielded \(\beta\)-ketoamines \textsuperscript{12} as main products together with some unidentified products. Results of the synthesis of \(\beta\)-ketoamines from heptaldehyde and citronellal are shown in Table 3.

\[ \text{RCH}_2\text{CHO} + \text{R}'\text{NH} \xrightarrow{-\text{e}} \text{KI, H}_2\text{O-t-BuOH}} \text{RCCH}_2\text{N}^\cdot\text{R'} \ (10) \text{ 11} \]

The structures of \(\beta\)-ketoamines were identified by IR, NMR and MS data. Some of the \(\beta\)-ketoamines were also identified by comparison with authentic samples independently prepared as follows.

Table 2. Electrochemical synthesis of \(N\)-alkyl- and \(N, N\)-Dialkylformamides.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Amine</th>
<th>Amide</th>
<th>F/mol</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et\textsubscript{2}NH</td>
<td>Et\textsubscript{2}NCHO</td>
<td>4.9</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>(n-Bu)\textsubscript{2}NH</td>
<td>(n-Bu)\textsubscript{2}NCHO</td>
<td>4.5</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>Morpholine</td>
<td>Morpholinocarboxaldehyde</td>
<td>4.2</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>Piperidine</td>
<td>1-Piperidinocarboxaldehyde</td>
<td>4.5</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>Pyrrolidine</td>
<td>1-Pyrrolidinocarboxaldehyde</td>
<td>4.8</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>n-BuNH\textsubscript{2}</td>
<td>n-BuNHCHO</td>
<td>4.3</td>
<td>75</td>
</tr>
</tbody>
</table>

\textsuperscript{a} HCHO: 20 mmol, amine: 20 mmol, KI: 10 mmol. \textsuperscript{b} Isolated yields based on amines.

\textsuperscript{5} The evolution of heat observed in the procedure indicates the formation of 9 in the solution. In fact, the ethereal extract of this solution gave 9 (Synthesis of 9, see Ref. 5).

Table 3. Electrochemical synthesis of \( \beta \)-ketoamines.

<table>
<thead>
<tr>
<th>Amine</th>
<th>Product</th>
<th>Yield (%)(^{a,b,c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehyde: heptanal</td>
<td>16a</td>
<td>56</td>
</tr>
<tr>
<td>(CH(_3)_2NH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrolidine</td>
<td>16b</td>
<td>17</td>
</tr>
<tr>
<td>Piperidine</td>
<td>16c</td>
<td>41</td>
</tr>
<tr>
<td>Morpholine</td>
<td>16d</td>
<td>39</td>
</tr>
<tr>
<td>n-Bu(_2)NH</td>
<td>16e</td>
<td>48</td>
</tr>
<tr>
<td>Aldehyde: citronellal</td>
<td>17a</td>
<td>31</td>
</tr>
<tr>
<td>(CH(_3)_2NH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrolidine</td>
<td>17b</td>
<td>53 (39)(^d)</td>
</tr>
<tr>
<td>Piperidine</td>
<td>17c</td>
<td>55 (33)(^d)</td>
</tr>
<tr>
<td>Morpholine</td>
<td>17d</td>
<td>50 (35)(^d)</td>
</tr>
<tr>
<td>n-Bu(_2)NH</td>
<td>17e</td>
<td>60 (35)(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Determined by GLC method. \(^b\) Electricity: 4 F/mol. \(^c\) Based on aldehyde. \(^d\) Isolated yield.

The effect of mediators on the yields of \( \beta \)-ketoamines was examined in the reaction of citronellal with pyrrolidine (eqn. (8)).

\[
\text{CHO} + \begin{array}{c}
\text{H} \\
\text{KX}
\end{array} \rightarrow \begin{array}{c}
\text{17a} \\
\text{18}
\end{array}
\]

KX
KI (53 %) 100: 0
KBr (40 %) 79: 21
KCl (61 %) 0:100

Although KI gave 17b exclusively, the formation of 18 and a mixture of 17b and 18 was observed in the reaction using KCl and KBr, respectively.

DISCUSSION

Reaction mechanism of formation of DMF. In the mediatory system using KI, the oxidation of \( \Gamma \) to active species tentatively denoted as “I” (eqn. (9))\(^*\) is the initiation step. The fact that the yield of DMF obtained at a controlled potential (0.6 V vs. SCE) was reasonable (~60 %) also supports the oxidation of \( \Gamma \) in the initiation step, since the oxidation waves of 9, dimethylamine and formaldehyde in aqueous solution containing Et\(_4\)N OTs were not observed at lower potential than 1.0 V vs. SCE.

\[
\Gamma \rightarrow \begin{array}{c}
-2e \\
\rightarrow \text{“I”}
\end{array}
\]

Thus, the attack of “I” on 9 followed by a base-catalyzed conversion of an intermediate 19 to 21 through 20 (Scheme 1) would reasonably explain the formation of DMF,\(^**\) though the

\(^*\) What “I” consists of is unknown.
\(^**\) The mechanism shown in Scheme 1 is a working hypothesis which may be depicted in different patterns. The mechanism proposed in oxidative fragmentation of trimethylenediamine with chlorine dioxide\(^10\) is, for instance, similar to Scheme 1.

\(16a, \text{R=CH}_3, 60\%\)

16b, \(\text{R=-(CH}_2)_4-\), 79 %

(a) LDA, THF; (b) TMSCl; (c) Br\(_2\), CCl\(_4\); (d) H\(_2\)O

mechanism involving the attack of "I" on an N-hemiacetal \(22\)\(^{11,12}\) is not necessarily ruled out if \(22\) exists in the system in equilibrium with \(9\). When the reaction is carried out in the presence of formaldehyde, dimethylamine formed in Scheme 1 gives \(9\) again, so that all the dimethylamine is transformed to DMF.

The base which catalyses the conversion of \(19\) to \(20\) can be generated by the reaction of water with potassium which is generated from potassium cation on the cathode.\(^*\) Accordingly, the overall process of this mediatory system can be schematically represented as Fig. 1 in which the reaction system involves the reactions described in Scheme 1.

In connection with this mechanism, it is interesting to examine whether simple tertiary amines can be oxidized in this mediatory system according to the mechanism similar to that described in Scheme 1. Preliminary experiments carried out for \(N\),\(N\)-dimethylbenzylamine (DMBA) using a two-phase system indicated the possibility that such mediatory oxidation of DMBA took place, since \(N\)-benzyl-\(N\)-methylformamide was obtained in 23 % yield.\(^*\)

In the system using mediators other than KI, the yield of DMF was low probably due to the difference of reactivity of active halonium ion.

\* Although the electrochemical oxidation of DMBA has been extensively studied,\(^*\) indirect oxidation of DMBA using mediators is not known so far.

---

\(\text{CH}_3\text{N-CH}_2\text{OH}\)

\(\text{CH}_3\text{N-CH}_2\text{N-CH}_3\)

\(22\)

---

\* Although it has not been established that reduction of water in the presence of \(\text{K}^+\) proceeds through the reductive formation of alkali metal, the result that using tetraethylammonium iodide instead of KI or NaI brought about a decrease in yield (59 %, run 9, Table 1) suggests that \(\text{K}^+\) or \(\text{Na}^+\) plays an important role in this oxidation.

\*\* \(N\)-Hydroxymethylmorpholine has been postulated as an intermediate in the electrochemical oxidation of tropine to \(\text{N-formylmorpholine}.\)\(^{12}\)

---

**Fig. 1.** Schematic representation of electrochemical preparation of DMF using KI as a mediator.
Scheme 2.

"X", and also the direct oxidation of 9 may contribute to a certain extent to the formation of DMF.

Reaction of mechanism of formation of β-ketoamines. It has been shown that equilibrated mixtures of enamines 8, aminals 23, and N-hemiacetals 24 form when aliphatic aldehydes and amines are allowed to react in solvents. Although these three types of compounds have the possibility to be oxidized by "I" in our mediatory system, 8 is the most plausible precursor of 12, because the oxidation of 23 or 24 must yield amides 25 through a similar mechanism to the formation of DMF from 9 (Scheme 2).

In fact, the electrochemical oxidation of an independently prepared enamine 18, using KI as a mediator, gave 17b (eqn. (10)), but 25 was not observed in the products.

These results suggest that the addition of "I" to 8 is much faster than that to 23 or 24 (Scheme 2). The oxidation of 8 to 12 is reasonably explained as follows: Thus, "I" adds to the double bond of 8 to yield an iodohydrine 26 which is converted by base to α-aminoepoxide 27. The conversion of α-aminoepoxides to β-ketoamines has been known (Scheme 3).

The formation of β-ketoamines in the mediatory system using KBr is also explicable by a similar mechanism to that described in Scheme 3. Using KCl as a mediator, it is assumed that the anode potential was not enough to oxidize Cl⁻ or that an active species generated by the oxidation of Cl⁻ did not work as an oxidant like "I".

Scheme 3.

EXPERIMENTAL

$^1$H NMR spectra were recorded on a Varian Associates EM-390 or EM-360 using tetramethylsilane as an internal standard. IR spectra were taken with a Hitachi 215 spectrometer. Mass spectra were recorded on a JEOL IMS-DX300 mass spectrometer. Elemental analysis was determined by the Center for Instrumental Analysis of Kyoto University. Constant current electrolyses were carried out using DC Power Supply (GPO 50–2) of Takasago Seisakusho, Ltd. A potentialstat HA-104 of Hokuto Denko, Ltd. was used for a controlled potential electrolysis. Gas chromatographic analyses were performed on a Yanaco GCG-550T gas chromatograph. Chemicals other than those described were commercially available and used without purification.

Preparation of N,N-dimethylformamide. General. Into a cell equipped with carbon rod cathode (8 mmφ) and platinum anode (2 cm×2 cm) were added potassium iodide (1.66 g, 10 mmol), a 37% aqueous solution of formaldehyde (4.05 g, 50 mmol) and a 50% aqueous solution of dimethylamine (4.9 g, 55 mmol), successively, without cooling. At that time, considerable exothermic reaction took place. After the solution was cooled to room temperature, water (2 ml) was added, and a constant current electrolysis (0.5 A, 0.24 A/cm$^2$) was carried out. After 2 F/mol of electricity was passed, DMF$^{18}$ was isolated by distillation in vacuo from the reaction mixture, and identified by spectroscopic method. Since DMF is miscible with water, the isolated yield was low (~50%). The yields shown in Table 1 were obtained by GLC method (Si DC550; 120°C, internal standard, Et$_2$NCHO). The electrolysis of 9$^3$ (1.02 g, 10 mmol) in water (5 ml) containing KI (0.332 g, 2 mmol) or a mixture of 9 (1.02 g, 10 mmol) and formaldehyde (10 mmol) in water (5 ml) containing KI (0.332 g, 2 mmol) was carried out in a similar way as above. Also, this method was similarly applied to mediators other than KI.

Preparation of N,N-dialkylformamides. N,N-Dialkylformamides shown in Table 2 were prepared by a similar method to the synthesis of DMF except for the following points. A 37% aqueous solution of formaldehyde (1.62 g, 20 mmol), amines (20 mmol), KI (1.66 g, 10 mmol) and water (8 ml) were added into the cell. After the electrolysis shown in Table 2 was passed with a constant current (0.5 A), the reaction mixture was extracted with CH$_2$Cl$_2$, and the extract was washed with an aqueous solution of sodium thiosulfate and dried over MgSO$_4$. Products, N,N-diethylformamide,$^{18}$ N,N-dibutylformamide,$^{18}$ 4-morpholinocarboxaldehyde,$^{19,20}$ 1-piperidinecarboxaldehyde,$^{20}$ 1-pyrolidine-carboxaldehyde,$^{20}$ and N-butylformamide$^{20}$ were isolated by distillation and identified by comparison of their spectroscopic data with those of authentic samples.

Electrochemical synthesis of β-ketoamines (16 and 17). Into a cell equipped with carbon rod cathode (8 mmφ), platinum anode (2 cm×2 cm), and a dropping funnel was placed a solution of secondary amines (40 mmol) and KI (1.66 g, 10 mmol) in water (10 ml). A solution of aldehydes (20 mmol) in tert-butanol (5 ml) was added dropwise into the cell over a period when 2 F/mol of electricity was passed, the reaction mixture was poured into a solution of saturated sodium thiosulfate, extracted with CH$_2$Cl$_2$ and dried over MgSO$_4$. Products (16 and 17) were isolated by distillation or by GLC after crude distillation and identified by IR, NMR and MS data.

Products 16a and 16b were identified by comparison of their spectra with those of independently prepared samples.

16a. B.p. 100°C (0.5 mmHg); IR (neat) 2920, 2855, 2820, 2770, 1705, 1640, 1450, 1400, 1350, 1265, 1150, 1130, 1040 cm$^{-1}$; NMR (CCl$_4$; δ 0.89 (3H, br t, 6 Hz), 1.00–1.90 (6H, m), 2.00–2.55 (2H, m), 2.23 (6H, s), 2.96 (2H, s); mass spectrum, m/e 157 (M$^+$).

16b. B.p. 50–55°C (0.5 mmHg); IR (neat) 2920, 2860, 2780, 1705, 1460, 1410, 1378, 1350, 1313, 1293, 1262, 1205, 1150, 1128, 1092, 1053, 903, 880, 722 cm$^{-1}$; NMR (CCl$_4$; δ 0.91 (3H, t, 6 Hz), 1.10–1.60 (4H, m), 1.60–2.00 (4H, m), 2.20–2.74 (6H, m), 3.18 (2H, s); mass spectrum, m/e 183 (M$^+$), 84 ($^4$CH$_3$N(CH$_3$)$_2$).

16c. B.p. 70°C (0.7 mmHg); IR (neat) 2920, 2845, 2780, 1700, 1440, 1298, 1275, 1252, 1208, 1155, 1120, 1038, 995, 860 cm$^{-1}$; NMR (CCl$_4$; δ 0.90 (3H, br t, 6 Hz), 1.05–1.90 (12H, m), 2.00–2.60 (6H, m), 2.92 (2H, s); mass spectrum, m/e 197 (M$^+$), 196 (M$^+$–1), 98 ($^4$CH$_3$N(CH$_3$)$_2$).

16d. B.p. 64–65°C (0.5 mmHg); IR (neat) 2840, 2800, 1695, 1442, 1375, 1290, 1270, 1240, 1210, 1110, 1065, 1033, 1005, 897, 862, 795, 715 cm$^{-1}$; NMR (CCl$_4$; δ 0.90 (3H, br t, 6 Hz), 1.06–1.90 (6H, m), 2.25–2.60 (6H, m), 3.00 (2H, s), 3.40–3.77 (4H, m); mass spectrum, m/e 199 (M$^+$), 100 ($^4$CH$_3$N(C$_2$H$_5$)$_2$O).

16e. B.p. 120°C (0.8 mmHg); IR (neat) 2950, 2920, 2855, 2800, 1705, 1455, 1350, 1300, 1260, 1150, 1121, 1081 cm$^{-1}$; NMR (CCl$_4$; δ 0.90 (9H, br t, 6 Hz), 1.05–1.90 (14H, m), 2.20–2.60 (6H, m), 3.02 (2H, s); mass spectrum, m/e 241 (M$^+$), 240 (M$^+$–1), 142 ($^4$CH$_3$N(C$_2$H$_5$)$_2$).

17a. B.p. 86–88°C (0.4 mmHg); IR (neat) 2920, 2865, 2820, 2770, 1703, 1443, 1375, 1270, 1150, 1095, 1040, 1008, 855, 825 cm$^{-1}$; NMR (CCl$_4$; δ 1.04 (3H, d, 7.2 Hz), 1.20–2.20 (4H, m),
1.57 (3H, s), 1.62 (3H, s), 2.20 (6H, s), 2.50 (1H, m), 2.98 (2H, s), 5.00 (1H, m); mass spectrum, m/e 197 (M⁺), 58 (CH₃N(CH₂)₃).

17b. B. p. 72–75 °C (0.9 mmHg); IR (neat) 2960, 2920, 2870, 2780, 1718, 1708, 1450, 1410, 1375, 1348, 1310, 1290, 1260, 1200, 1122, 1043, 1022, 980, 890, 808, 828, 800 cm⁻¹; NMR (CCL₄) δ 1.04 (3H, d, 6.6 Hz), 1.00–2.20 (8H, m), 1.67 (3H, s), 1.67 (3H, s), 2.20–3.90 (5H, m), 3.22 (2H, s), 5.03 (1H, m); mass spectrum, m/e 223 (M⁺), 84 (CH₃N(CH₂)₃).

17c. B. p. 83–86 °C (2.5 mmHg); IR (neat) 2920, 2850, 1703, 1443, 1375, 1300, 1278, 1255, 1155, 1110, 1038, 985, 893, 860, 792 cm⁻¹; NMR (CCL₄) δ 1.02 (3H, d, 6.8 Hz), 1.59 (3H, s), 1.67 (3H, s), 1.00–1.20 (10H, m), 2.20–2.70 (4H, m), 2.40–3.10 (1H, m), 3.00 (2H, s), 5.03 (1H, m); mass spectrum, m/e 237 (M⁺), 98 (CH₃N(CH₂)₃).

17d. B. p. 97–100 °C (0.9 mmHg); IR (neat) 2955, 2920, 2850, 2805, 1702, 1448, 1378, 1290, 1270, 1115, 1070, 1000, 865 cm⁻¹; NMR (CCL₄) δ 1.02 (3H, d, 6.8 Hz), 1.00–2.20 (4H, m), 1.60 (3H, s), 1.69 (3H, s), 2.44 (4H, m), 2.65 (1H, m), 3.06 (2H, s), 3.58 (4H, m), 5.02 (1H, m); mass spectrum, m/e 239 (M⁺), 100 (CH₃N(CH₂)₃O).

17e. B. p. 96–103 °C (2 mmHg); IR (neat) 2960, 2930, 2880, 2815, 1708, 1455, 1380, 1308, 1250, 1160, 1090, 1030, 943, 825, 730 cm⁻¹; NMR (CCL₄) δ 0.98 (3H, d, 6.6 Hz), 0.65–2.20 (18H, m), 1.57 (3H, s), 1.65 (3H, s), 2.40 (4H, m), 2.50–3.00 (1H, m), 3.09 (2H, s), 4.99 (1H, m); mass spectrum, m/e 281 (M⁺), 142 (CH₃N(CH₂)₂O).

Using KBr as a mediator, the ratio of 17b to enamine was obtained by GLC method. When KCl was a mediator, enamine 18 was isolated by distillation from the etheral extract of the reaction mixture. Enamine 18 was also prepared by the method of Mannich.¹⁻²

18. 61 % yield; B. p. 96–98 °C (0.6 mmHg); IR (neat) 2960, 1640, 1440, 1362, 1298, 1125, 1030, 930, 880, 823, 778, 738 cm⁻¹; NMR (CCL₄) δ 0.95 (3H, d, 6.4 Hz), 1.00–2.35 (11H, m), 1.58 (3H, s), 1.66 (3H, s), 2.93 (4H, m), 3.82 (1H, d, d, 8.0 and 13.6 Hz), 5.04 (1H, m), 5.96 (1H, d, 13.6 Hz). Anal. calc. for C₁₄H₂₅N: C, 81.09; H, 12.15; N, 6.76. Found: C, 81.03; H, 12.23; N, 6.52.

Synthesis of β-ketoamines (16a and 16b) from 1-bromo-2-heptanone. Trichloromethylvinyl(vinyl)oxysilane (14) was prepared from 2-heptanone (13) by the method of H. O. House.²² Into a solution of 14 (2.2 g, 11.8 mol) in CCL₄ (3 mol) was added slowly bromine (1.9 g, 11.8 mmol) at −10 °C. After the solution was stirred for 1 h, ice-water was added to the solution, and the organic portion was extracted with ether. The etheral extract was dried over MgSO₄, and subsequent evaporation of the extract in vacuo followed by distillation gave 1-bromo-2-heptanone (15) in 81 % yield.

15. B. p. 98–100 °C (20 mmHg); IR (neat) 2920, 2860, 1703, 1455, 1395, 1175, 1120, 1048 cm⁻¹; NMR (CCL₄) δ 0.92 (3H, br t, 5 Hz), 1.05–2.10 (6H, m), 2.63 (2H, t, 7.2 Hz), 3.74 (2H, s).

Into an aqueous solution of dimethylamine (40 %, 1.68 g, 9.6 mmol) was added 1-bromo-2-heptanone (15) (0.5 g, 2.59 mmol). After the solution was stirred at room temperature for 1.5 h, the organic portion was extracted with ether. Product 16a was isolated by distillation from the etheral extract; 36 % yield. The synthesis of 16b from 1-bromo-2-heptanone and pyrrolidone was also achieved: 60 % yield. The NMR and IR spectra of these products were identical with those of electrochemically prepared 16a and 16b.

Electrolysis of enamine 18. A solution of KI (0.83 g, 5.5 mmol) in water (5 ml) was placed into a cell similar to that used in the preparation of β-ketoamines. Into this cell was added dropwise a solution of 18 (2.07 g, 10 mmol) in t-butanol (2 ml) over the period that 2 F/mol of electricity was passed. After 4 F/mol of electricity was passed, the working up similar to the electrochemical oxidation of a mixture of aldehydes and amines gave 17b in 48 % yield.

Electrochemical oxidation of N,N-dimethylbenzylamine (DMBA). Into a cell equipped with a platinum anode (2 cm×2 cm) and a carbon rod cathode (8 mmφ) were placed water (30 ml) containing KI (0.83 g, 5.5 mmol) and a solution of DMBA (1.35 g, 10 mmol) in CH₂Cl₂ (10 ml). The solution was stirred and cooled with ice-water. After 5 F/mol of electricity was passed (0.5 A), the organic portion was separated, and the aqueous solution was extracted with CH₂Cl₂. After the combined extract was dried, the evaporation of the solvent followed by distillation of the residue gave N-benzyl-N-methylformamide (24) (23 %) together with DMBA (29 %). Those yields were determined by GLC method.

Acknowledgement. One of the authors (Y.M.) wishes to thank the Kurata Foundation for the Kurata Research Grant.

REFERENCES

18. Commercially available.

Received September 24, 1982.