Acta Chemica Scandinavica B 37 (1983) 491–498

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

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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,[1] 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 [2] of amides *1* to carbamates *2*, and to the oxidation [3] of secondary alcohols *3* to ketones *4* and primary alcohols *5* to esters *6*.

$$\underset{1}{RCONH_2} \xrightarrow[KBr\text{–}CH_3OH]{-e} \underset{2}{RNHCO_2CH_3} \quad (1)$$

$$\underset{3}{\begin{matrix}R\\R'\end{matrix}\!\!>\!CHOH} \xrightarrow[KI]{-e} \underset{4}{\begin{matrix}R\\R'\end{matrix}\!\!>\!C{=}O} \quad (2)$$

$$\underset{5}{2\,RCH_2OH} \xrightarrow[KI]{-e} \underset{6}{RCO_2CH_2R} \quad (3)$$

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]

$$\underset{7}{CH_2(NR'_2)_2} \qquad \underset{8}{RCH{=}CHNR'_2}$$

7 R′: alkyl group *8* R,R′: alkyl groups

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′*-tetramethylmethanediamine (*9*) containing one-fifth equivalent of KI gave *N,N*-dimethylformamide (DMF) in 75 % yield at the time when 4 F/mol of electricity was passed (eqn. (4)).

$$\underset{9}{(CH_3)_2NCH_2N(CH_3)_2} \xrightarrow[KI]{-e,\ 4\ F/mol} \underset{75\ \%}{DMF} \quad (4)$$

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)).

0302-4369/83 $02.50

Table 1. Electrochemical synthesis of *N,N*-dimethylformamide.[a]

Run	Mediator (mmol)	[Aldehyde]/ [Mediator]	Yield (%)[b]
1	KI (1.7)	30	76
2	(5)	10	91
3	(10)	5	95>
4	(10)	5	95>[c]
5	KBr (10)	5	25
6	KCl (10)	5	15
7	NaI (10)	5	95>
8	NaBr (10)	5	30
9	Et_4NI (10)	5	59
10	KOH (10)	5	15

[a] HCHO: 50 mol, Me_2NH: 55 mol. Anode, Pt; cathode, carbon. [b] Yields based on aldehyde were obtained by GLC method. [c] Carbon rods were used as cathode and anode.

$$9 + CH_2O \xrightarrow[\text{KI}]{-e} \underset{176\ \%}{\text{DMF}} \qquad (5)$$
$$4\ \text{F/mol}$$

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 $I^- \gg Br^- > Cl^- \sim OH^-$. A carbon rod instead of platinum was usable as an anode.

Although DMF has been prepared by several methods using formic acid,[6] carbon monoxide,[7] methyl formate [8] or hydrogen cyanide [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).

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

$$\underset{10}{RCH_2CHO} + \underset{11}{R'_2NH} \xrightarrow[\text{KI, } H_2O\text{–}t\text{-BuOH}]{-e} \underset{12}{RCCH_2N(R')_2} \qquad (6)$$

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

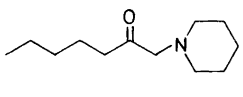
* The evolution of heat observed in the procedure indicates the formation of *9* in the solution. In fact, the ethereal extract of this solution gave *9* (Synthesis of *9*, see Ref. 5).

Table 2. Electrochemical synthesis of *N*-alkyl- and *N,N*-Dialkylformamides.[a]

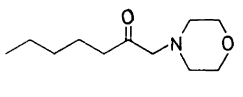
Run	Amine	Amide	F/mol	Yield (%)[b]
1	Et_2NH	Et_2NCHO	4.9	85
2	$(n\text{-Bu})_2NH$	$(n\text{-Bu})_2NCHO$	4.5	57
3	Morpholine	Morpholinecarboxaldehyde	4.2	83
4	Piperidine	1-Piperidinecarboxaldehyde	4.5	93
5	Pyrrolidine	1-Pyrrolidinecarboxaldehyde	4.8	75
6	$n\text{-BuNH}_2$	n-BuNHCHO	4.3	75

[a] HCHO: 20 mmol, amine: 20 mmol, KI: 10 mmol. [b] Isolated yields based on amines.

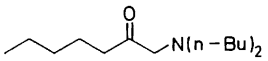
Table 3. Electrochemical synthesis of β-ketoamines.



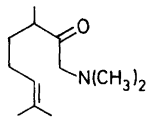
16c



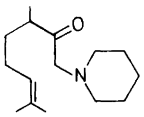
16d



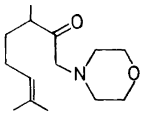
16e



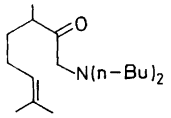
17a



17c



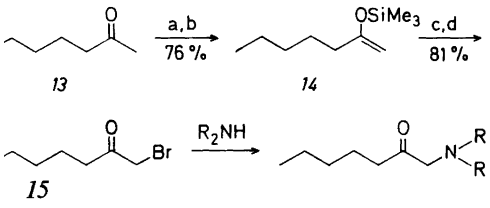
17d



17e

Amine	Product	Yield (%)[a,b,c]
Aldehyde: heptanal		
$(CH_3)_2NH$	*16a*	56
Pyrrolidine	*16b*	17
Piperidine	*16c*	41
Morpholine	*16d*	39
n-Bu_2NH	*16e*	48
Aldehyde: citronellal		
$(CH_3)_2NH$	*17a*	31
Pyrrolidine	*17b*	53 (39)[d]
Piperidine	*17c*	55 (33)[d]
Morpholine	*17d*	50 (35)[d]
n-Bu_2NH	*17e*	60 (35)[d]

[a] Determined by GLC method. [b] Electricity: 4 F/mol. [c] Based on aldehyde. [d] Isolated yield.

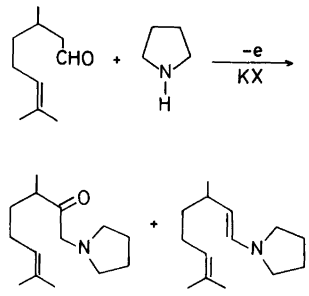


(7)

16a, R=CH_3, 60 %
16b, R=$-(CH_2)_4-$, 79 %

(a) LDA, THF; (b) TMSCl; (c) Br_2,CCl_4; (d) H_2O

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



(8)

17b *18*

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

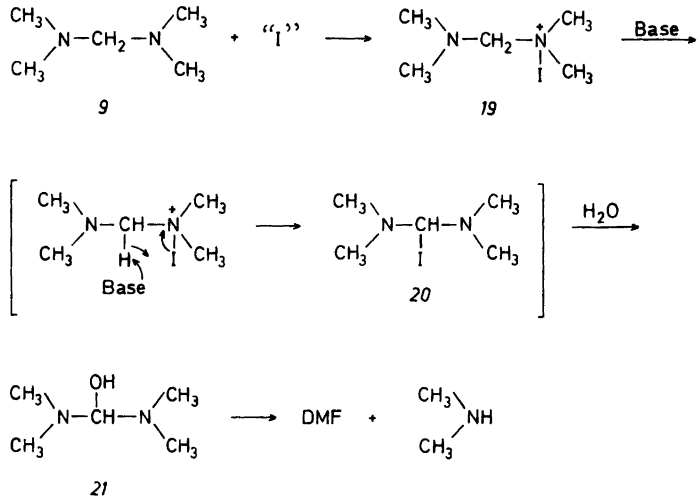
Reaction mechanism of formation of DMF. In the mediatory system using KI, the oxidation of I^- to active species tentatively denoted as "I" (eqn. (9))* is the initiation step. The fact that the yield of DMF obtained at a controlled potential (0.6 V *vs.* SCE) was reasonable (~60 %) also supports the oxidation of I^- in the initiation step, since the oxidation waves of *9*, dimethylamine and formaldehyde in aqueous solution containing Et_4NOTs were not observed at lower potential than 1.0 V *vs.* SCE.

$$I^- \xrightarrow{-2e} \text{"I"} \qquad (9)$$

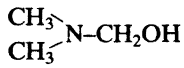
Thus, the attack of "I" on *9* followed by a base-catalyzed conversion of an intermediate *19* to *21* through *20* (Scheme 1) would reasonably explain the formation of DMF,** though the

* 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.



Scheme 1.



22

mechanism involving the attack of "I" on an *N*-hemiacetal *22*[11,**] 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 it has not been established that reduction of water in the presence of 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 K^+ or Na^+ plays an important role in this oxidation.

** *N*-Hydroxymethylnortropane has been postulated as an intermediate in the electrochemical oxidation of tropane to *N*-formylnortropane.[12]

* Although the electrochemical oxidation of DMBA has been extensively studied,[13] indirect oxidation of DMBA using mediators is not known so far.

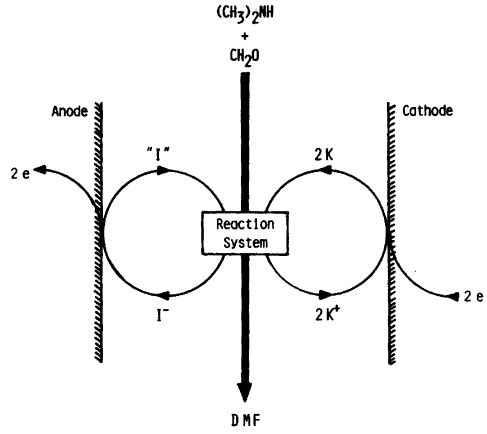
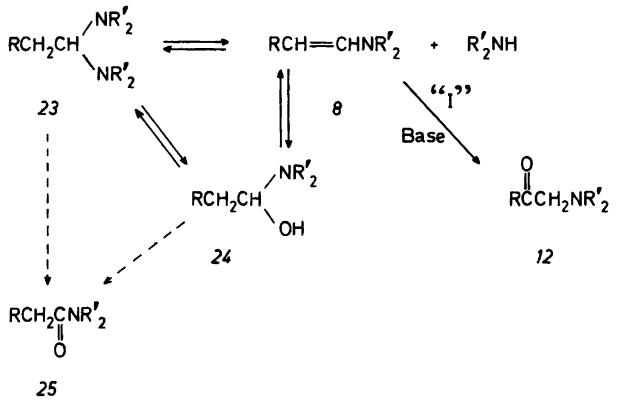


Fig. 1. Schematic representation of electrochemical preparation of DMF using KI as a mediator.

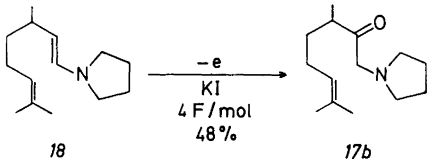


Scheme 2.

"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.[14] 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.

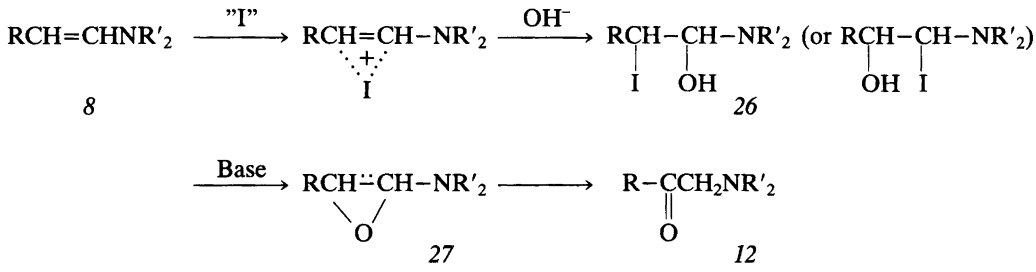


18 *17b* (10)

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 [15] (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 [16] 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".

* Although the direct oxidation of enamines in methanol has been known,[17] it would not take place in this mediatory system using two-phases since enamines with high molecular weights may be present in an organic phase.



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 potentiostat 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), succesively, 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 missible 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_2NCHO). The electrolysis of *9* [5] (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 electricity shown in Table 2 was passed with a constant current (0.5 A), the reaction mixture was extracted with CH_2Cl_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-morpholinecarboxaldehyde,[19,20] 1-piperidinecarboxaldehyde,[20] 1-pyrrolidinecarboxaldehyde,[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_2Cl_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 ($^+CH_2N(CH_2)_4$).

16c. B.p. 70 °C (0.7 mmHg); IR (neat) 2920, 2845, 2780, 1700, 1440, 1298, 1275, 1252, 1205, 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 ($^+CH_2N(CH_2)_5$).

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 ($^+CH_2N(C_2H_4)_2O$).

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 ($^+CH_2N(C_4H_9)_2$).

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 ($^+CH_2N(CH_3)_2$).

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, 930, 880, 828, 800 cm^{-1}; NMR (CCl_4) δ 1.04 (3H, d, 6.6 Hz), 1.00–2.20 (8H, m), 1.57 (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 ($^+CH_2N(CH_2)_4$).

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 (CCl_4) 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 ($^+CH_2N(CH_2)_5$).

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 (CCl_4) 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 ($^+CH_2N(C_2H_4)_2O$).

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 (CCl_4) 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 ($^+CH_2N(C_4H_9)_2$).

Using KBr as a mediator, the ratio of *17b* to enamine *18* was obtained by GLC method. When KCl was a mediator, enamine *18* was isolated by distillation from the ethereal extract of the reaction mixture. Enamine *18* was also prepared by the method of Mannich.[21]

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 (CCl_4) δ 0.95 (3H, d, 6.4 Hz), 1.00–2.35 (11H, m), 1.58 (3H, s), 1.66 (3 H, 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 $C_{14}H_{25}N$: 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-heptenone.* Trimethyl[(1-pentylvinyl)oxy]silane (*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 CCl_4 (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 ethereal extract was dried over $MgSO_4$, 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) (lit.[23] 96 °C (14 mmHg)); IR (neat) 2920, 2860, 1703, 1455, 1395, 1175, 1120, 1048 cm^{-1}; NMR (CCl_4) 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 ethereal extract: 36 % yield. The synthesis of *16b* from 1-bromo-2-heptanone and pyrrolidine 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, 0.5 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 mmol) and a solution of DMBA (1.35 g, 10 mmol) in CH_2Cl_2 (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 CH_2Cl_2. 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.

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Received September 24, 1982.