Electrolytic Oxidation of Ketones in Ammoniacal Methanol in the Presence of Catalytic Amounts of KI

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Received May 1, 1995[⊗]

The indirect electrooxidation of ketones in ammoniacal methanol using iodide ion as a mediator afforded 2,2-dialkyl-2,5-dihydro-1*H*-imidazoles **3** via an oxidative cyclocoupling of ketimine intermediates formed from ketones and ammonia. The treatment of **3** with dilute HCl gave α-amino ketone hydrochlorides **4** and the parent ketones in good yields. A similar electrooxidation of **3** resulted in the formation of the corresponding 2*H*-imidazoles **6**, which were hydrolyzed to α-diketones and the parent ketones. The same products **6** could also conveniently be obtained by chemical oxidation of **3** with aqueous NaOCl.

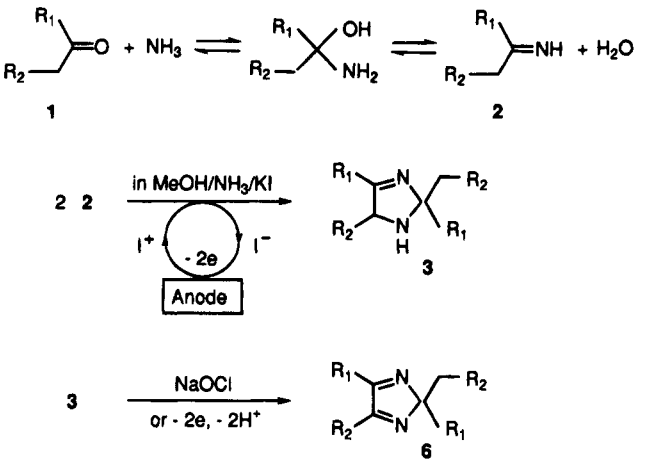
Introduction

Aldehydes and ketones undergo a reversible condensation reaction with ammonia to give imines and water.[1,2] In most cases, such imines cannot be isolated due to their instability and subsequent condensations with the carbonyl compounds. However, the intermediate imines that are generated in situ are often employed for organic synthesis.[3]

Previously, we reported that the electrolytic oxidation of aldehydes in the NH_3–NaOMe–MeOH–KI electrolyte system yields nitriles, resulting from dehydration of aldimines formed as intermediates.[4] In an attempt to extend this reaction, we found that a similar electrolysis of aliphatic and alicyclic ketones exclusively affords 2,5-dihydro-1*H*-imidazoles **3**, resulting from oxidative cyclocoupling of ketimines **2**, and that the further oxidation of **3** yields the corresponding 2*H*-imidazoles **6** (Scheme 1).

Analogous electrolysis in aqueous media has been studied by Wilen and Levine.[5] According to their report, electrolytic oxidation of simple ketones, such as acetone or cyclohexanone, in aqueous ammonia containing potassium iodide, produces the corresponding pyrazines via 2,5-dihydropyrazines in low yields. To elucidate why the different products were formed depending upon the solvent used, we investigated the indirect electrochemical oxidation using various ketones and examined the chemical properties of the resulting products in detail, because very few examples of **3** have been reported in the literature.[6]

Scheme 1



Results and Discussion

Preparative electrolyses were performed in a divided cell using a platinum anode. The anolyte, consisting of ketone, excess ammonia, and a catalytic amount of KI in methanol, was electrolyzed at a constant current under a gentle stream of dry ammonia at room temperature. The results are summarized in Table 1.

The structures of compounds **3a-g** were confirmed by elemental analysis or HR-MS, IR, NMR, and MS. The IR spectra of **3** showed bands in the ranges of ν 3280–3325, 1647–1663, and 1441–1467 cm^{-1} arising from the N–H and the C=N stretching frequencies. Apparently, the obtained products are neither 2,5-dihydropyrazines nor pyrazines. In the ^{13}C NMR spectra, the imino carbon signal appeared in the range from δ 164 to 178 and the sp^3-hybridized C-2 from δ 90 to 98, which indicated that alternative structures bearing two alkyl groups on an azomethinyl carbon can be ruled out. The mass spectra of all compounds, except for **1a**, did not exhibit molecular ions, but a prominent $M^+ - R_1$ ion peak was present. The

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

(1) (a) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*, 2nd ed; Academic: Orlando, 1986; Vol. 2, Chapter 12. (b) Sollenberger, P. Y., Martin, R. B. *The Chemistry of the Amino Group*; Patai, S., Ed; Interscience: London, 1968; p 350. (c) Layer, W. R. *Chem. Rev.* **1963**, *63*, 489. (d) Dayagi, S.; Dagani, V. *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; p 61.

(2) For preparation of imines, see: (a) Pickerd, P. L.; Tolbert, T. L. *J. Org. Chem.* **1961**, *26*, 4886. (b) Pickerd, P. L.; Tolbert, T. L. *Org. Synth.* **1973**, *5*, 520. (c) Middleton, W. J.; Carlson, H. D. *Org. Synth.* **1988**, *6*, 664. (d) Verardo, G.; Giumanini, A. G.; Strazzolini, P.; Poiana, M. *Synth. Commun.* **1988**, *18*, 1501. (e) Findeisen, K.; Heitzer, H. *Synthesis* **1981**, 702. (f) Schönberg, A.; Junghans, K. *Chem. Ber.* **1966**, *99*, 1015. (g) Appel, R.; Hauss, A. *Chem. Ber.* **1960**, *93*, 405.

(3) (a) Emerson, W. S. *Organic Reactions*; Wiley: New York, 1948; Vol. 4, p 174. (b) Weygand/Hilgetag. *Preparative Organic Chemistry*, 4th ed; Hilgetag, G., Martini, A., Eds.; Wiley: New York, 1972; p 520.

(4) Okimoto, M.; Chiba, T. *J. Org. Chem.* **1988**, *53*, 218. See also: Okimoto, M.; Chiba, T. *J. Org. Chem.* **1993**, *58*, 6194.

(5) Wilen, S. H.; Levine, A. W. *Chem. Ind. (London)* **1969**, 237.

(6) (a) Sammes, M. P., Katritzky, A. R. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1984; Vol. 35, p 375. (b) Grimmett, M. R. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1980; Vol. 27, p 241. (c) Grimmett, M. R. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1970; Vol. 12, p 103. (d) Loudon, J. D. *Chemistry of carbon compounds*; Rodd, E. H., Ed.; Elsevier: London, 1957; Vol. 4A, p 244.

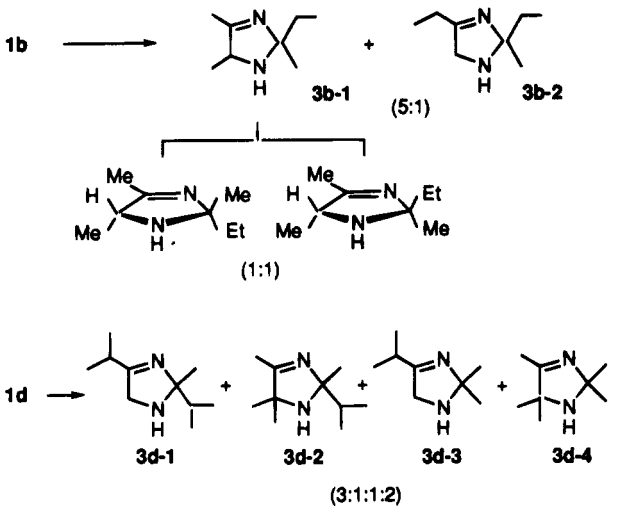
0022-3263/95/1960-6764$09.00/0

Table 1. Electrolytic Oxidation of Ketones in NH_3/MeOH in the Presence of a Catalytic Amount of KI[a]

	starting ketone 1		current passed, F/mol	2,5-dihydro-1*H*-imidazole **3** (yield, %)[b]	current efficiency, %
	R_1	R_2			
1a	Me	H	1.01	**3a** (75)	74
1b	Me	Me	0.82	**3b** (69)[c]	84
1c	Et	Me	0.73	**3c** (60)	82
			0.84	(66)	79
			1.10	(68)	62
1d	*i*-Pr	H	1.93	**3d** (<68)[d]	<35
1e	*t*-Bu	H	0.56[e]	**3e** (37)	68
			0.85[f]	(48)	56
			0.87[g]	(50)	57
1f	*n*-Pr	Et	0.93	**3f** (55)	59
1g	$-(CH_2)_4-$		1.03	**3g** (76)	74

[a] Anolyte: ketone **1** (50 mmol) and KI (10 mmol) in 8 M NH_3–MeOH (80 mL). Strength of constant current: 0.5 A. [b] Isolated yield. [c] A mixture of **3b**–**1** and **3b**–**2**. [d] A mixture of **3d**–**1**, **3d**–**2**, **3d**–**3**, and **3d**–**4**. [e] Prior to the current being passed, the anolyte was allowed to stand for 9 days. [f] The anolyte was allowed to stand for 12 days. [g] NH_4I (0.5 mmol) was added to the anolyte and was allowed to stand for 6 days.

Scheme 2



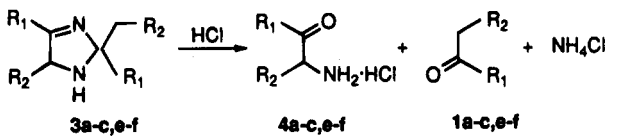
assignment of dihydroimidazole structures was further supported by their reactions.

The electrolysis of unsymmetric ketones, such as 2-butanone (**1b**) or 3-methyl-2-butanone (**1d**), led to the formation of isomers (Scheme 2). For example, **1b** gave 2-ethyl-2,4,5-trimethyl-2,5-dihydro-1*H*-imidazole (**3b-1**) along with the structural isomer 2,4-diethyl-2-methyl-2,5-dihydro-1*H*-imidazole (**3b-2**) in a ratio of 5:1. Furthermore, ^1H and ^{13}C NMR suggested that **3b-1** is a mixture of two stereoisomers, present in a ratio of 1:1. The reaction of **1d** was complicated. Excess electricity was required to complete the reaction, and mainly four compounds formed, **3d-1**, **3d-2**, **3d-3**, and **3d-4**, in a ratio of ca. 3:1:1:2. In this case, ring cleavage of **3d-2** may occur to form acetone imine.

2,5-Dihydro-1*H*-imidazoles of type **3**, which are unsubstituted on the nitrogen, are rare compounds. Asinger and his co-workers have described the preparation of 2,2,4,5-tetraalkyl-2,5-dihydro-1*H*-imidazoles by cyclization of α-bromo ketone with ammonia and a second ketone.[7] No spectral data on such compounds have been available, whereas chemical confirmation of the assignment structures has been provided, namely, the oxidation

(7) Asinger, F.; Thiel, M.; Sowada, R. *Monatsh. Chem.* **1959**, *90*, 402.

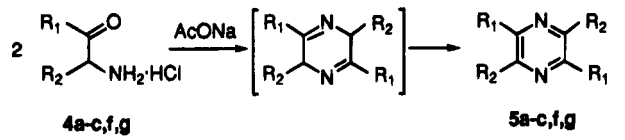
Scheme 3



1, 3, 4

a: R_1 = Me, R_2 = H	**4a** (55%)	
b: R_1 = Me, R_2 = Me	**4b** (70%)	
c: R_1 = Et, R_2 = Me	**4c** (85%)	**1c** (89%)
e: R_1 = t-Bu, R_2 = H	**4e** (80%)	**1e** (66%)
f: R_1 = n-Pr, R_2 = Et	**4f** (77%)	**1f** (85%)
g: R_1, R_2 = $-(CH_2)_4-$	**4g** (79%)	**1g** (90%)

Scheme 4



4, 5

a: R_1 = Me, R_2 = H	**5a** (30%)
b: R_1 = Me, R_2 = Me	**5b** (73%)
c: R_1 = Et, R_2 = Me	**5c** (66%)
f: R_1 = n-Pr, R_2 = Et	**5f** (67%)
g: R_1, R_2 = $-(CH_2)_4-$	**5g** (65%)

of **3** with sulfur affords the corresponding 2*H*-imidazoles (**6**) and acid-catalyzed hydrolysis followed by treatment with alkaline solution yields the parent ketone and 2,5-dihydropyrazine which is rationalized as arising from self-condensation of the α-amino ketone.

We also observed that **3** readily underwent hydrolysis with hydrochloric acid to afford the corresponding α-amino ketone hydrochloride **4** and the parent ketone in good yields as is shown in Scheme 3. Likewise, a comparable yield of **4** could be obtained when Et_2O extracts of the electrolysis products were directly treated with dilute HCl. Although α-amino ketones are versatile synthetic intermediates for a wide variety of heterocyclic compounds, the methods for their synthesis are surprisingly difficult and the yields are not always satisfactory.[8] The present method may be promising for the transformation of simple ketones into α-amino ketones, because the operation is simple and the reagents used are quite readily available. Also, the simultaneously formed ketones may be reused.

Furthermore, the preparation of pyrazines from **4** was attempted according to the literature method with minor modifications.[9] By heating **4** with sodium acetate in methanol in contact with air, the corresponding pyrazines **5** were obtained in reasonable yields (Scheme 4). It is possible that the pyrazines which had been isolated by Wilen and Levine were derived from the α-amino ketone resulting from hydrolysis of **3**. Indeed, the isolation of

(8) (a) Mayer, D. In *Houben-Weyl Methoden der Organishen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 7/2c, p 2251. (b) Baumgarten, H. E.; Petersen, J. M. *Org. Synth.* **1973**, *5*, 909. (c) Farnum, D. G.; Carlson, G. R. *Synthesis* **1972**, 191.

(9) (a) Iida, H.; Hayashi, K.; Yamada, M.; Takahashi, K.; Yamada, K. *Synth. Commun.* **1973**, *3*, 225. (b) Pratt, Y. T. *Heterocyclic Compounds*; Elderfield, R. C., Ed.; Wiley: New York, 1957; Vol. 6, p 385.

(10) Fellman, J. H.; Wilen, S. H.; VanderWerf, C. A. *J. Org. Chem.* **1956**, *21*, 713.

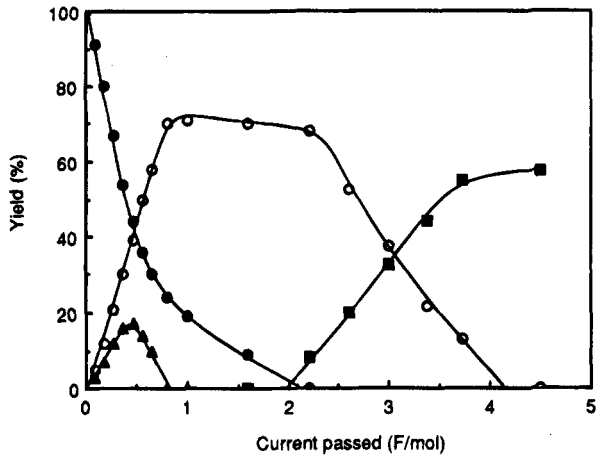


Figure 1. Relationships between the product yields and consumed current in the electrolysis of 3-pentanone **1c** (50 mmol) in 8 M NH_3–MeOH (80 mL) in the presence of KI (10 mmol): (●) 3-pentanone; (▲) 3-pentanimine; (○) dihydro-1*H*-imidazole **3c**; (■) 2*H*-imidazole **6c**.

the product has been carried out by steam distillation after the reaction mixture was allowed to stand overnight in aqueous media.[5,10]

For the formation of **3**, the occurrence of ketimine **2** seems to be essential, and the yield of **3** would primarily be governed by the amount of **2** being formed in the anolyte, which may be attributed to both the rate and equilibrium constants for the condensation reaction of the ketone with ammonia.

Kinetic measurement for the formation of ketimine using 3-pentanone (**1c**) in saturated ammoniacal methanol indicated that at least 12 h of reaction time were required to reach equilibrium under the conditions employed for the present electrolysis, where approximately 40% of **1c** was converted into the ketimine **2c**.[11] In spite of the sluggish equilibration, the formation of **3c** in the present electrolysis was completed within 2.5 h. Probably electrogenerated positive iodide species catalyzed the ketimine formation. In fact, the ketimine **2c** was formed immediately when current was passed through the ammoniacal solution of **1c** in the presence of KI. In the case of pinacolone (**1e**) bearing a bulky alkyl group around the carbonyl group, the rate of ketimine formation was extremely slow, and therefore only a trace amount of **3e** was formed in the usual way. The transformation of **1e** into **3e** was successfully performed in such a way that the anolyte was allowed to stand for a long time prior to the current being passed, followed by electrolysis. Addition of an acid catalyst, such as NH_4I, brought about a considerable reduction in the time required for the equilibration, but it did not contribute to increasing the yield of **3e** in the subsequent electrolysis.

The result of a coulometric experiment with **1c** is illustrated in Figure 1, which indicates that the yield of **3c** almost linearly increases on increasing the applied electricity by the time 0.8 F/mol of electricity has passed through the anolyte and then it remains constant al-

(11) To quantify the occurrence of the ketimine, the reaction progress of ketones in saturated ammoniacal methanol was monitored as a function of time by GLC. For this purpose, 3-pentanone was chosen as the starting ketone, because 3-pentanimine is one of a few aliphatic ketimines which has heretofore been isolated and characterized. It was prepared by Grignard reaction between propionitrile and ethylmagnesium bromide according to the procedure of Pickard.[2a]

Table 2. Oxidation of 2,5-Dihydro-1*H*-imidazoles into 2*H*-Imidazoles

	starting dihydro-1*H*-imidazole **3**		by electrolytic oxidation[a] current passed, F/mol	by oxidation with NaOCl[b] molar ratio, NaOCl/**3**	2*H*-imidazole **6** (yield, %)[c]
	R_1	R_2			
3a	Me	H	4.2		**6a** (13)
				1.2	(53)
3b	Me	Me	3.7		**6b** (53)
				1.1	(63)
3c	Et	Me	3.5		**6c** (73)
				1.1	(83)
3d	*i*-Pr	H		1.4	**6d** (50)[d]
3e	*t*-Bu	H	3.4		**6e** (83)
				4.3	(38)
3f	*n*-Pr	Et	3.1		**6f** (88)
				1.3	(80)
3g	$-(CH_2)_4-$		4.4		**6g** (43)
				1.2	(88)

[a] Anolyte: 2,5-dihydro-1*H*-imidazole (**3**) (25 mmol) and KI (10 mmol) in 8 M NH_3–MeOH (80 mL). Strength of constant current: 0.5 A. [b] Approximately 0.8 M NaOCl was added to a solution of 2,5-dihydro-1*H*-imidazole (**3**) (20 mmol) in MeOH (50 mL) at rt. [c] Isolated yield. [d] A mixture of **6d**–**1** and **6d**–**3**.

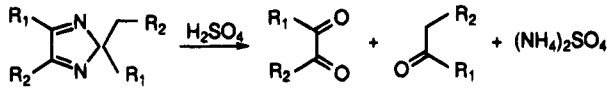
though a considerable amount of ketone still remains. The increase of water content in the anolyte may depress the dehydration of carbinolamine intermediate to the ketimine, as the reaction proceeds. At that moment, the ketimine disappeared and GLC analysis of the anolyte showed that **3c** was formed in a yield of 70% and ketone was recovered in a yield of 24%. Thus, the selectivity and the current efficiency for the formation of **3c** were calculated to be 92% and 88% (assuming a 2e process), respectively. When the electrolysis was allowed to continue by the passage of excess current, further oxidation of **3c** took place, affording 2*H*-imidazoles **6c**, after the starting ketone was completely consumed. This suggests that the order of ease of oxidation in this system is ketimine > ketone > dihydro-1*H*-imidazole > 2*H*-imidazole.

The electrolytic oxidation of **3** was next attempted under conditions similar to those applied for the formation of **3**. As can be seen from Table 2, the yield of **6** varied from 13 to 88% depending upon the structure of **3**. Although the reason is not clear, **3a** was exceptionally resistant to the oxidation, and a considerable amount of **3a** remained unchanged even after passage of electricity of over 4 F/mol. On the other hand, chemical oxidation of **3** by sodium hypochlorite was found to be much more efficient for the formation of **6** than the electrolytic oxidation. The conversion of **3** into **6** could be accomplished by addition of only slightly excess amounts of sodium hypochlorite to the methanolic solution of **3** at room temperature. The low yield of **6e** may be due to poor solubility of **3e** in the aqueous methanol.

Although a large number of 1*H*-imidazoles are known, 2*H*-imidazoles **6**, like 2,5-dihydro-1*H*-imidazoles **3**, have not been mentioned very often in the literature and methods for their synthesis are few.[6] Weiss first succeeded in preparing a series of 4,5-diphenyl-2*H*-imidazoles from benzil, a ketone, and ammonium acetate in 1952.[12] Further examples from benzil have been reported; however, this method is less convenient for aliphatic diketones.[13] Asinger and his co-workers have

(12) Weiss, M. *J. Am. Chem. Soc.* **1952**, *74*, 5193.
(13) (a) Hill, J. H. M.; Fogg, T. R.; Guttmann, H. *J. Org. Chem.* **1975**, *40*, 2562. (b) Katritzky, A. R.; Borja, S. B.; Marquet, J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2065.

Scheme 5



6c,f,g 7c,f,g 1c,f,g

1, 6, 7

c: R_1 = Et, R_2 = Me	7c (80% GLC yield)	1c (55% GLC yield)
f: R_1 = n-Pr, R_2 = Et	7f (78% GLC yield)	1f (83% GLC yield)
g: R_1, R_2 = -$(CH_2)_4$-	7g (55% GLC yield)	1g (90% GLC yield)

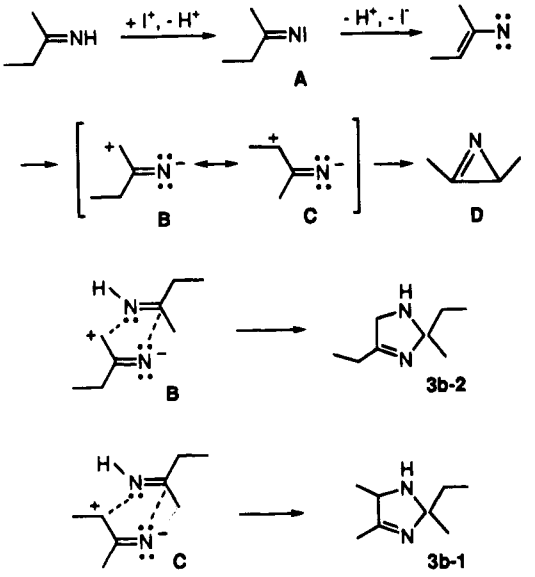
described the preparation of 2,2,4,5-tetraalkyl-2*H*-imidazoles by the joint action of sulfur and ammonia upon ketones,[14] or by oxidation of **3** with sulfur.[7] Photochemical cycloaddition of 2,2-dimethyl-3-phenyl-2*H*-azirine with nitriles to the 2*H*-imidazole derivatives has also been reported.[15]

The structures of **6** were confirmed by elemental analysis or HR-MS, IR, NMR, and MS as in the case of **3**. Some, especially lower alkyl substituted 2*H*-imidazoles **6**, were strongly hygroscopic, and hence the analytical samples were always contaminated with a very small amount of water. Consequently, combustion analysis gave unsatisfactory results for C and H. Unlike **3**, 2*H*-imidazoles formed picrates in benzene, and their analytical data were in satisfactory agreement with the calculated values. In the IR spectra of **6**, the absorption due to the NH present in the IR spectra of **3** disappeared, and a characteristic absorption arising from C=N bonds was observed near 1550 cm^{-1}.[16] Although no ^{13}C NMR spectral data are available for tetraalkyl-2*H*-imidazoles, each signal for the ring carbon atoms appeared at a position comparable to that reported for several aryl-2*H*-imidazoles.[15,17] The mass spectra of all compounds, except for **6g**, exhibited the intense $M^+ - R_1CN$ and $M^+ - R_2CN$ fragment peaks, which are frequently observed with 2,2-dimethyl-5-phenyl-2*H*-imidazoles and 2,2-diphenyl-2*H*-imidazoles.[15,18]

Compared to **3**, the imidazoles **6**, which can be regarded as cyclic diimines, were relatively stable in aqueous acid; however, they underwent ring cleavage by refluxing with 20% sulfuric acid, affording the corresponding α-diketone **7** and the parent ketone in reasonable yields (by GLC) (Scheme 5). The isolation of α-diketones from the reaction mixture by distillation was unsuccessful, because the simultaneously formed parent ketones have boiling points close to those of the α-diketones.

Although we have no reliable evidence for the mechanism of the electrooxidative cyclocoupling of ketimine described here, *N*-iodo imine (**A**) may be produced by reaction of ketimine with positive iodide species generated at the anode,[19] followed by elimination of HI to afford the nitrenium ion (**B** or **C**) or azirine (**D**), which have been represented to be more plausible intermediates in the formation of α-amino ketones from *N,N*-dichloroamines or ketoxime tosylate (the Neber rearrangement),[20,21] as well as in the pyrolysis or photolysis of vinyl azides[22,23] (Scheme 6). In the absence of a strong nucleophile such as methoxide ion, such intermediates would cycloadd to the azomethinyl linkage of ketimine to give **3** due to their 1,3 dipolar character.[24]

Scheme 6



Experimental Section

General. Melting and boiling points are uncorrected. The ^1H NMR and ^{13}C NMR spectra were measured at 200 and 22.4 MHz, respectively, in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. GC-MS analyses were performed using a 30-m capillary column (0.32 mm in diameter: liquid phase, SBP-1). High-resolution mass spectra (HR-MS) were obtained at an ionization potential of 70 eV. GLC analyses were performed using a glass column (1-m, 3.2 mm in diameter) packed with 20% Apiezon grease L and 10% KOH on Chromosorb W AW with N_2 as the carrier gas and an FID detector. The same packing was employed for preparative GLC using a glass column (1-m, 1/8 in. in diameter). He served as the carrier gas.

All reagents and solvents from commercial sources were used without purification or drying.

Electrolysis Apparatus. All electrolyses were performed in a 100-mL divided cell. A fine-frit glass cup served as the cathode compartment. The anode compartment was provided with a cylindrical platinum net as the anode, a gas bubbler, and a gas outlet tube. The cathode compartment was provided with a platinum coil as the cathode and a gas outlet tube that connected to the outlet tube from the anode compartment to equalize the pressure in the two compartments.

General Procedure for the Electrolysis of Ketones 1a-g. A solution of ketone (50 mmol) and KI (10 mmol) in saturated NH_3–MeOH (80 mL) was electrooxidized at a constant current of 0.5 A. Throughout the electrolysis, a gentle

(14) Asinger, F.; Leuchtenberger, W. *Justus Liebigs Ann. Chem.* **1974**, 1183.
(15) Stegmann, W.; Gilgen, P. G.; Heimgartner, H.; Schmid, S. H. *Helv. Chim. Acta* **1976**, *59*, 1081.
(16) White, D. M.; Sonnenberg, J. *J. Org. Chem.* **1964**, *29*, 1926.
(17) Domany, G.; Nyitrai, J.; Lempert, K.; Voelter, W.; Horn, H. *Chem. Ber.* **1978**, *111*, 1464. See also: Graziano, L. G.; Iesce, M. R.; Scarpati, R. *J. Chem. Soc., Chem. Commun.* **1979**, 7.
(18) Hortmann, A. G.; Koo, J.-Y.; Yu, C.-C. *J. Org. Chem.* **1978**, *43*, 2289.
(19) If α-iodo imine is generated the mechanism for the formation of **3** may be almost same as that proposed by Asinger and his co-workers.[7] In the present electrolysis, however, the ring formation reaction seems to proceed via *N*-iodo imine rather than α-iodo imine, because imines are halogenated with HOCl or *t*-BuOCl to give *N*-chloro imines.[20c,d]
(20) (a) Baumgarten, H. E.; Bower, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 4561. (b) Baumgarten, H. E.; Petersen, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 459. (c) Baumgarten, H. E.; Petersen, J. M.; Wolf, D. C. *J. Org. Chem.* **1963**, *28*, 2369. (d) Baumgarten, H. E.; Dirks, J. E.; Petersen, J. M.; Wolf, D. C. *J. Am. Chem. Soc.* **1960**, *82*, 4422.
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stream of dry ammonia was passed through the anolyte, and the cell was cooled with running water. The progress of the reaction was monitored by GLC. After the electrolysis was stopped the anolyte was evaporated *in vacuo* at rt. Ether (20 mL) was added to the residue, and the precipitated KI was removed by filtration and washed with a small portion of ether. The filtrates and washing fluid were combined, dried with anhydrous K_2CO_3, and distilled *in vacuo* under dry nitrogen. The isolated yields of **3** are given in Table 1. Analytical samples were obtained by redistillation or preparative GLC.

2,2,4-Trimethyl-2,5-dihydro-1*H*-imidazole (3a): bp 51−52 °C (16 mm); IR (neat) 3281, 1655, 1441 cm^{-1}; ^1H NMR δ 1.36 (s, 6H), 2.03 (s, 3H), 2.52 (br s, 1H), 3.73 (s, 2H); ^{13}C NMR δ 17.3 (CH_3), 28.1 (CH_3), 58.0 (CH_2), 90.4 (C), 163.9 (C); MS *m/z* (relative intensity) 112 (M^+, trace), 97 (M^+ − Me, 100), 56 ($^1/_2M^+$, 41); HR-MS calcd for $C_6H_{12}N_2$ 112.1000, found 112.0976.

Electrolysis Products from 1b. The distillation of the crude product gave 2.15 g of colorless liquid at bp 60−65 °C (12 mm). GLC analysis (column temperature, 120 °C; flow rate, 40 mL/min) revealed that the fraction consists of two structural isomers (**3b-1** and **3b-2**) with retention times of 5.3 and 6.8 min. The area ratio was 85:15. The main product **3b-1** was isolated by fractional distillation. The minor product **3b-2** was purified by preparative GLC, and its structure was inferred from the spectral data. From the NMR spectral data, **3b-1** was assumed to be a mixture of geometric isomers.

2-Ethyl-2,4,5-trimethyl-2,5-dihydro-1*H*-imidazole (3b-1) (mixture of geometrical isomers): bp 67−68 °C (16 mm) [lit.[7] bp 54 °C (11 mm); IR (neat) 3308, 1655, 1456 cm^{-1}; ^1H NMR δ 0.88 and 0.92 (t, t, J = 7.3 Hz each, total 3H), 1.24 (s, 1.5H), 1.29 (d, J = 6.6 Hz, 3H), 1.38 (s, 1.5H), 1.5−1.75 (m, 2H), 1.81 (br s, 1H), 1.98 and 1.99 (s, s, total 3H), 3.87 and 3.91 (q, q, total 1H); ^{13}C NMR δ 8.6 (CH_3), 15.8 (CH_3), 15.9 (CH_3), 19.1 (CH_3), 20.0 (CH_3), 28.5 (CH_3), 34.4 (CH_2), 34.6 (CH_2), 63.8 (CH), 65.0 (CH), 90.7 (C), 91.0 (C), 172.2 (C); MS *m/z* (relative intensity) 125 (M^+ − Me, 49), 111 (M^+ − Et, 100), 70 ($^1/_2M^+$, 99). Anal. Calcd for $C_8H_{16}N_2$: N, 19.98. Found: N, 19.68.

2,4-Diethyl-2-methyl-2,5-dihydro-1*H*-imidazole (3b-2) (isolated by preparative GLC): IR (neat) 3292, 1652, 1460 cm^{-1}; ^1H NMR δ 0.89 (t, J = 7.3 Hz, 3H), 1.17 (t, J = 7.7 Hz, 3H), 1.32 (s, 3H), 1.67 (q, J = 7.7 Hz, 2H), 3.73 (br s, 2H); ^{13}C NMR δ 8.4 (CH_3), 10.9 (CH_3), 24.7 (CH_2), 26.5 (CH_3), 34.0 (CH_2), 56.9 (CH_2), 93.0 (C), 174.0 (C); MS *m/z* (relative intensity) 125 (M^+ − Me, 12), 111 (M^+ − Et, 100), 70 ($^1/_2M^+$, 11).

5-Methyl-2,2,4-triethyl-2,5-dihydro-1*H*-imidazole (3c): bp 50−51 °C (2 mm) [lit.[7] bp 78 °C (11 mm)]; IR (neat) 3325, 1655, 1460 cm^{-1}; ^1H NMR δ 0.83, 0.86 (t, t, J = 7.3 Hz each, total 6H), 1.18 (t, J = 7.3 Hz, 3H), 1.27 (d, J = 7.3 Hz, 3H), 1.5−1.9 (br s, m, total 5H), 2.1−2.4 (m, 2H), 3.92 (q, 1H); ^{13}C NMR δ 8.0 (CH_3), 8.2 (CH_3), 11.0 (CH_3), 19.6 (CH_3), 23.1 (CH_2), 32.7 (CH_2), 33.2 (CH_2), 63.9 (CH), 93.4 (C), 176.9 (C); MS *m/z* (relative intensity) 139 (M^+ − Et, 100), 84 ($^1/_2M^+$, 30). Anal. Calcd for $C_{10}H_{20}N_2$: C, 71.37; H, 11.98; N, 16.65. Found: C, 70.99; H, 12.21; N, 16.36. **Picrate of 3c**: mp 128.5 °C dec (plates from methanol). Anal. Calcd for $C_{16}H_{23}N_5O_7$: C, 48.36; H, 5.83; N, 17.63. Found: C, 48.32; H, 5.77; N, 17.55.

Electrolysis Products from 1d. GLC analysis (column temperature, 140 °C; flow rate, 40 mL/min) indicated that the crude product contains at least four compounds (**3d-1**, **3d-2**, **3d-3**, and **3d-4**) with retention times of 7.2, 5.2, 2.6, and 1.9 min. The area ratio was 44:15:14:25. The most abundant **3d-1** was isolated by fractional distillation and purified by preparative GLC. The latter three were isolated by preparative GLC, and their structures were inferred from their spectral data.

2,4-Bis(methylethyl)-2-methyl-2,5-dihydro-1*H*-imidazole (3d-1): bp 48−49 °C (2 mm); IR (neat) 3319, 1651, 1467 cm^{-1}; ^1H NMR δ 0.86 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 7.1 Hz, 6H), 1.28 (s, 3H), 1.3−2.1 (br s, m, total 2H), 2.67 (m, 1H), 3.75 (d, J = 3.5 Hz, 2H); ^{13}C NMR δ 17.3 (CH_3), 17.6 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 24.7 (CH_3), 30.9 (CH), 37.5 (CH), 55.0 (CH_2), 95.2 (C), 176.8 (C); MS *m/z* (relative intensity) 125 (M^+ − *i*-Pr, 100), 83 (66). Anal. Calcd for $C_{10}H_{20}N_2$: C, 71.37; H, 11.98; N, 16.65. Found: C, 70.98; H, 12.03; N, 16.36.

2-(Methylethyl)-2,4,5-tetramethyl-2,5-dihydro-1*H*-imidazole (3d-2): IR (neat) 3300, 1657, 1464 cm^{-1}; ^1H NMR δ 0.88, 0.97 (d, d, J = 6.8 Hz each, total 6H), 1.28, 1.30 (s, s, br s, total 10H), 1.6−1.9 (m, 1H), 1.96 (s, 3H); ^{13}C NMR δ 14.5 (CH_3), 17.7 (CH_3), 18.0 (CH_3), 26.4 (CH_3), 27.4 (CH_3), 28.6 (CH_3), 37.9 (CH), 68.9 (C), 91.9 (C), 173.8 (C=N); MS *m/z* (relative intensity) 125 (M^+ − *i*-Pr, 100), 84 ($^1/_2M^+$, 70).

2,2-Dimethyl-4-(methylethyl)-2,5-dihydro-1*H*-imidazole (3d-3): IR (neat) 3279, 1647, 1466 cm^{-1}; ^1H NMR δ 1.17 (d, J = 6.8 Hz, 6H), 1.6 (s, 6H), 2.40 (br s, 1H), 2.63 (m, 1H), 3.77 (s, 2H); ^{13}C NMR δ 20.1 (CH_3), 28.0 (CH_3), 30.7 (CH), 54.4 (CH_2), 90.1 (C), 177.3 (C=N); MS *m/z* (relative intensity) 140 (M^+, 5), 125 (M^+ − Me, 63), 83 (74), 71 (100); HR-MS calcd for $C_8H_{16}N_2$ 140.1313, found 140.1338.

2,2,4,5-Pentamethyl-2,5-dihydro-1*H*-imidazole (3d-4): IR (neat) 3302, 1652, 1464 cm^{-1}; ^1H NMR δ 1.30 (s, 6H), 1.38 (s, 6H), 1.9−2.2 (s, br s, total 4H); ^{13}C NMR δ 1.46 (CH_3), 28.0 (CH_3), 30.6 (CH_3), 69.6 (C), 86.9 (C), 174.2 (C=N); MS *m/z* (relative intensity) 140 (M^+, 2), 125 (M^+ − Me, 70), 84 (100); HR-MS, calcd for $C_8H_{16}N_2$ 140.1313, found 140.1275.

2,4-Bis(dimethylethyl)-2-methyl-2,5-dihydro-1*H*-imidazole (3e): bp 52−53 °C (2 mm); IR (neat) 3335, 1647, 1479 cm^{-1}; ^1H NMR δ 0.94 (s, 9H), 1.17 (s, 9H), 1.27 (s, 3H), 1.75 (br s, 1H), 3.70 and 3.89 (d, d, J = 16.1 Hz each, total 2H); ^{13}C NMR δ 23.2 (CH_3), 25.4 (CH_3), 28.3 (CH_3), 34.7 (C), 38.9 (C), 54.4 (CH_2), 97.7 (C), 178.2 (C); MS *m/z* (relative intensity) 139 (M^+ − *t*-Bu, 26), 83 (100). Anal. Calcd for $C_{12}H_{24}N_2$: C, 73.41; H, 12.32; N, 14.27. Found: C, 73.24; H, 12.51; N, 14.17.

5-Ethyl-2,2,4-tripropyl-2,5-dihydro-1*H*-imidazole (3f): bp 89−91 °C (2 mm); IR (neat) 3325, 1651, 1464 cm^{-1}; ^1H NMR δ 0.8−1.0 (m complex, 12H), 1.1−1.4 (m, 6H), 1.5−2.0 (m, 7H), 2.2−2.4 (m, 2H), 3.76 and 3.80 (d, d, J = 3.7 Hz each, total 1H); ^{13}C NMR δ 11.0 (CH_3), 14.1 (CH_3), 14.5 (CH_3), 17.0 (CH_2), 17.3 (CH_2), 20.0 (CH_2), 26.6 (CH_2), 32.3 (CH_2), 43.4 (CH_2), 43.5 (CH_2), 69.8 (CH), 92.9 (C), 174.6 (C); MS *m/z* (relative intensity) 139 (M^+ − Et, 100), 84 ($^1/_2M^+$, 30). Anal. Calcd for $C_{14}H_{28}N_2$: C, 74.94; H, 12.58; N, 12.49. Found: C, 74.84; H, 12.51; N, 12.33.

2,4,5,6,7,7a-Hexahydro-1*H*-benzimidazole-2-spiro-1′-cyclohexane (3g): bp 78−82 °C (0.20 mm); IR (neat) 3298, 1663, 1448 cm^{-1}; ^1H NMR δ 1.0−2.8 (br m, 19H), 3.63 and 3.75 (d, d, J = 6.2 and 6.6 Hz, total 1H); ^{13}C NMR δ 23.5 (CH_2), 23.9 (CH_2), 25.5 (CH_2), 26.8 (CH_2), 30.6 (CH_2), 36.7 (CH_2), 37.5 (CH_2), 40.0 (CH_2), 65.2 (CH), 90.8 (C), 173.7 (C); MS *m/z* (relative intensity) 192 (M^+, 12), 149 (100); HR-MS calcd for $C_{12}H_{20}N_2$ 192.1626, found 192.1604. Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.61; H, 10.70; N, 14.24.

Typical Procedure for the Acid-Catalyzed Hydrolysis of 3c. Dihydroimidazole **3c** (4.60 g, 27.4 mmol) was dissolved in 3 N HCl (40 mL) and warmed to 40 °C in a water bath for 30 min with stirring. After being cooled to rt, the organic oily layer that was liberated was extracted into ether (20 mL × 3), from which almost pure 3-pentanone was obtained (2.10 g, 24.4 mmol). The water layer was evaporated to dryness at a temperature not greater than 40 °C. To the residue was added a 20 mL of hot *n*-propanol. The mixture was heated to boiling, and insoluble materials were removed by hot filtration. The filter cake was washed with a small portion of hot *n*-propanol. The combined filtrates and washing fluid were cooled at rt, and a small amount of precipitate was filtered off. The evaporation of the filtrates yielded a nearly colorless solid. It was then suspended in a small amount of acetone, collected by filtration, and washed with small portions of acetone. The crude product was recrystallized from acetonitrile to give pure **4c** (3.2 g, 85%).

Simplified Method for the Preparation of 4c. Electrolysis of **1c** (50 mmol) was repeated by passage of a current of 46 mF. The resulting ether extract from the anolyte was shaken with 3 N HCl (20 mL). The heterogeneous solution was warmed to 40 °C in a water bath and stirred for 1 h. After being cooled, the water layer was separated from the ether layer, washed with ether (20 mL × 3), and worked up in a manner similar to that described above. Almost pure **4c** was obtained in 60% yield (2.1 g).

1-Amino-2-propanone hydrochloride (4a): mp 75.5−77 °C in a sealed tube very hygroscopic crystals from *n*-PrOH

(lit.[25] mp 75 °C); ^{1}H NMR (CD_3OD) δ 2.27 (s, 3H), 4.02 (s, 2H), 4.81 (s, 3H); ^{13}C NMR (CD_3OD) δ 27.2 (CH_3), 48.7 (CH_2), 201.9 (C=O).

2-Amino-3-butanone hydrochloride (4b): mp 107–110 °C in a sealed tube hygroscopic crystals from EtOH–Et_2O (lit.[26] mp 110 °C); ^{1}H NMR (CD_3OD) δ 1.56 (d, J = 7.3 Hz, 3H), 2.30 (s, 3H), 4.22 (q, 2H), 4.82 (s, 3H); ^{13}C NMR (CD_3OD) δ 15.6 (CH_3), 26.1 (CH_3), 56.3 (CH), 205.1 (C=O).

2-Amino-3-pentanone hydrochloride (4c): mp 130–131 °C (from MeCN) (lit.[27] mp 128 °C); ^{1}H NMR (CD_3OD) δ 1.09 (t, J = 7.3 Hz, 3H), 1.52 (d, J = 7.3 Hz, 3H), 2.65 (dq, J = 7.3 and 2 Hz, 2H), 4.12 (q, J = 7.3 Hz, 1H), 4.87 (s, 3H); ^{13}C NMR (CD_3OD) δ 7.5 (CH_3), 15.8 (CH_3), 32.5 (CH_2), 55.6 (CH), 207.5 (C=O).

1-Amino-3,3-dimethyl-2-butanone hydrochloride (4e): mp 199–200 °C dec (from MeCN); ^{1}H NMR (CD_3OD) δ 1.22 (s, 9H), 4.16 (s, 2H), 4.82 (broad s, 3H); ^{13}C NMR (CD_3OD) δ 26.3 (CH_3), 44.8 (CH_2), 156.5 (C), 209.4 (C=O). Anal. Calcd for $C_6H_{14}ClNO$: C, 47.52; H, 9.31; Cl, 23.38; N, 9.24. Found: C, 47.21; H, 9.22; Cl, 23.52; N, 9.40.

3-Amino-4-heptanone hydrochloride (4f): mp 130–131 °C (from MeCN); ^{1}H NMR (CD_3OD) δ 0.95, 1.01 (t, t, J = 7.3 Hz each, total 6H), 1.65 (q, J = 7.3 Hz, 2H), 1.8–2.2 (m, 2H), 2.59 (dt, J = 7.3 and 2.2 Hz, 2H), 4.11 (dd, J = 7.3 and 4.4 Hz, 1H), 4.87 (s, 3H); ^{13}C NMR (CD_3OD) δ 9.2 (CH_3), 13.8 (CH_3), 17.6 (CH_2), 23.9 (CH_2), 41.7 (CH_2), 60.9 (CH), 206.9 (C=O). Anal. Calcd for $C_7H_{16}ClNO$: C, 50.75; H, 9.74; Cl, 21.40; N, 8.46. Found: C, 50.48; H, 9.65; Cl, 21.45; N, 8.49.

2-Aminocyclohexanone hydrochloride (4g): mp 157–158 °C dec (from MeCN) (lit.[8b] mp 156 °C); ^{1}H NMR (DMSO-d_6) δ 1.4–1.9 (m, 4H), 1.9–2.7 (m, 4H), 4.0–4.4 (br m, 1H), 8.50 (br s, 3H); ^{13}C NMR (DMSO-d_6) δ 22.7 (CH_2), 26.6 (CH_2), 31.6 (CH_2), 39.8 (CH_2), 56.6 (CH), 205.3 (C=O).

Typical Procedure for the Preparation of 5c. A mixture of α-amino ketone **4c** (1.38 g, 10 mmol) and anhydrous NaOAc (1.00 g, 12.2 mmol) in 25 mL of methanol was heated to 60 °C for 1 h with stirring. Throughout the reaction, air was bubbled through the solution. The solution changed from light yellow to red near the end of the reaction. The solvent was removed by evaporation, and water was added to the residue. The organic layer that was liberated was extracted into ether (15 mL × 3), dried with anhydrous sodium sulfate, and concentrated in vacuo. From the residue, **5c** was isolated by column chromatography on silica gel, eluting with a mixture of cyclohexane–ether (1:1) (0.69 g, 66% yield).

2,5-Dimethylpyrazine (5a):[7] isolated by column chromatography on silica gel eluting with ether; ^{1}H NMR δ 2.56 (s, 6H), 3.36 (s, 2H); ^{13}C NMR δ 20.8 (CH_3), 143.4 (CH), 150.6 (C); MS *m/z* (relative intensity) 108 (M^+, 82), 42 (100); HR-MS calcd for $C_6H_8N_2$ 108.0687, found 108.0692.

2,3,5,6-Tetramethylpyrazine (5b): mp 87–88 °C (from cyclohexane) (lit.[28] mp 85 °C); ^{1}H NMR δ 2.45 (s, 12H); ^{13}C NMR δ 21.3 (CH_3), 148.1 (C); MS *m/z* (relative intensity) 136 (M^+, 100); HR-MS calcd for $C_8H_{12}N_2$ 136,1000, found 136.1008.

2,5-Diethyl-3,6-dimethylpyrazine (5c): bp 100–101 °C (15 mm) [lit.[7] bp 65 °C (2 mm)]; ^{1}H NMR δ 1.26 (t, J = 7.3 Hz, 6H), 2.50 (s, 6H), 2.76 (q, 4H); ^{13}C NMR δ 12.7 (CH_3), 20.9 (CH_3), 27.8 (CH_2), 147.6 (C), 152.6 (C); MS *m/z* (relative intensity) 164 (M^+, 69), 149 (M^+ – Me, 100); HR-MS calcd for $C_{10}H_{16}N_2$ 164.1313, found 164.1323.

2,5-Diethyl-3,6-dipropylpyrazine (5f): isolated by column chromatography on silica gel eluting with a mixture of cyclohexane–ether (1:1); ^{1}H NMR δ 1.00 (t, J = 7.3 Hz, 6H), 1.26 (t, J = 7.3 Hz, 6H), 1.72 (q, 4H), 2.69–2.84 (m, 8H); ^{13}C NMR δ 13.5 (CH_3), 14.2 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 36.1 (CH_2), 151.1 (C), 152.3 (C); MS *m/z* (relative intensity) 220 (M^+, 36), 205 (M^+ – 15, 34), 192 (100); HR-MS calcd for $C_{14}H_{24}N_2$ 220.1939, found 220.1943.

Octahydrophenazine (5g): mp 110–111.5 °C (from hexane) (lit.[19a] mp 109.6–110.6 °C); ^{1}H NMR δ 1.7–2.2 (br m, 8H), 2.7–3.2 (br m, 8H); ^{13}C NMR δ 22.8 (CH_2), 31.6 (CH_2), 149.2 (C); MS *m/z* (relative intensity). Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.70; H, 8.60; N, 14.77.

General Procedure for the Electrolysis of Dihydro-1*H*-imidazoles 3a-g. A solution of dihydroimidazole **3** (25 mmol) and KI (10 mmol) in 8 M NH_3–MeOH (80 mL) was electrooxidized at a constant current of 0.5 A. After the usual workup, the ether extract was shaken with a small portion of saturated $Na_2S_2O_3$ solution, washed with brine, dried with anhydrous K_2CO_3, and distilled *in vacuo* under dry nitrogen. If the starting **3** still remained, the ether extract was treated with a dilute HCl to quench **3** by hydrolysis. The aqueous layer was made alkaline, and the liberated **6** was extracted with ether. The isolated yields of **6** are given in Table 2.

General Procedure for the Oxidation of 3 with Aqueous Sodium Hypochlorite Solution. Into a solution of **3** (20 mmol) in methanol (50 mL) was added 0.8 M NaOCl aqueous solution (30 mL, 24 mmol) dropwise with stirring at rt over 1 h. The stirring was continued for 30 min and then concentrated to two-thirds volume *in vacuo* at rt. Sodium chloride was added to the solution, and the oily material that was liberated by salting out was extracted into ether (20 mL × 3). The ether extracts were dried with anhydrous K_2CO_3 and distilled. In the case of **3a**, water was used as the solvent instead of methanol, and the product **6a** was isolated by continuous extraction with ether. The isolated yields of **6** are given in Table 2. Analytical samples were obtained by redistillation or preparative GLC.

2,2,4-Trimethyl-2*H*-imidazole (6a): bp 34–36 °C (16 mm); IR (neat) 1541, 1381 cm^{-1}; ^{1}H NMR δ 1.44 (s, 6H), 2.31 (s, 3H), 7.75 (s, 1H); ^{13}C NMR δ 15.6 (CH_3), 23.4 (CH_3), 104.7 (C), 156.8 (CH), 163.5 (C); MS *m/z* (relative intensity) 110 (M^+, trace), 83 (M^+ – HCN, 67), 69 (M^+ – MeCN, 76), 42 (100); HR-MS calcd for $C_6H_{10}N_2$ 110.0844, found 110.0832.

2-Ethyl-2,4,5-trimethyl-2*H*-imidazole (6b): bp 61–63 °C (16 mm) [lit.[14] bp 47 °C (7 mm)]; IR (neat) 1574, 1447 cm^{-1}; ^{1}H NMR δ 0.70 (t, J = 7.3 Hz, 3H), 1.38 (s, 3H), 1.87 (q, J = 7.3 Hz, 2H), 2.27 (s, 6H); ^{13}C NMR δ 8.3 (CH_3), 15.1 (CH_3), 22.2 (CH_3), 103.1 (C), 164.7 (C); MS *m/z* (relative intensity) 138 (M^+, trace), 97 (M^+ – MeCN, 100); HR-MS calcd for $C_8H_{14}N_2$ 138.1157, found 138.1127. Anal. Calcd for $C_8H_{14}N_2$: N, 20.27. Found: N, 19.91. **Picrate of 6b:** mp 157–158 °C dec (from benzene–cyclohexane). Anal. Calcd for $C_{14}H_{17}N_5O_7$: C, 45.77; H, 4.67; N, 19.07. Found: C, 45.82; H, 4.64; N, 19.16.

5-Methyl-2,2,4-triethyl-2*H*-imidazole (6c): bp 48–49 °C (2 mm) [lit.[14] bp 68–69 °C (9 mm); IR (neat) 1574, 1458 cm^{-1}; ^{1}H NMR δ 0.60 (t, J = 7.3 Hz, 6H), 1.28 (t, J = 7.3 Hz, 3H), 1.96 (q, 4H), 2.29 (s, 3H), 2.60 (q, 2H); ^{13}C NMR δ 7.7 (CH_3), 11.3 (CH_3), 15.1 (CH_3), 22.5 (CH_2), 29.0 (CH_2), 105.3 (C), 165.0 (C), 169.8 (C); MS *m/z* (relative intensity) 166 (M^+, trace), 125 (M^+ – MeCN, 91), 111 (M^+ – EtCN, 100); HR-MS calcd for $C_{10}H_{18}N_2$ 166.1470, found 166.1475. Anal. Calcd for $C_{10}H_{18}N_2$: N, 16.85. Found: N, 16.64. **Picrate of 6c:** mp 139–140 °C (from benzene–cyclohexane). Anal. Calcd for $C_{16}H_{21}N_5O_7$: C, 48.60; H, 5.35; N, 17.72. Found: C, 48.71; H, 5.35; N, 17.79.

Oxidation Products from a Mixture of 3d. GLC analysis (column temperature, 140 °C; flow rate, 40 mL/min) indicated that the crude product contains two compounds (**6d-1** and **6d-3**) with retention times of 4.5 and 1.7 min. The area ratio was 10:3. The main product **6d-1** was isolated by fractional distillation. The minor product **6d-3** was purified by preparative GLC, and its structure was inferred from the spectral data.

2,4-Bis(methylethyl)-2-methyl-2*H*-imidazole (6d-1): bp 78–79 °C (16 mm); IR (neat) 1541, 1463 cm^{-1}; ^{1}H NMR δ 0.82 (d, J = 7.3 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H), 1.29 (d, J = 6.6 Hz, 6H), 1.39 (s, 3H), 2.19 (hept, 1H), 2.95 (hept, 1H), 7.92 (s, 1H); ^{13}C NMR δ 17.6 (CH_3), 18.1 (CH_3), 20.2 (CH_3), 20.5 (CH_3), 29.4 (CH), 34.7 (CH), 109.0 (C), 155.8 (CH), 172.3 (C); MS *m/z* (relative intensity) 166 (M^+, 2), 139 (M^+ – HCN, 69), 125 (100), 97 (M^+ – *i*-PrCN, 63), 84 (100); HR-MS calcd for $C_{10}H_{18}N_2$ 166.1470, found 166.1451.

2,2-Dimethyl-4-(methylethyl)-2*H*-imidazole (6d-3): IR (neat) 1541, 1464 cm^{-1}; ^{1}H NMR δ 1.29 (d, J = 6.8 Hz, 6H),

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1.45 (s, 6H), 2.92 (sept, 1H), 7.86 (s, 1H); ^{13}C NMR δ 20.0 (CH_3), 23.5 (CH_3), 29.2 (CH), 104.2 (C), 155.3 (C=N), 171.9 (C=N); MS *m/z* (relative intensity) 138 (M^+, 2), 111 (M^+ − HCN, 76), 69 (M^+ − *i*-PrCN, 100); HR-MS calcd for $C_8H_{14}N_2$ 138.1157, found 138.1157.

2,4-Bis(dimethylethyl)-2-methyl-2*H*-imidazole (6e): bp 47 °C (2 mm); IR (neat) 1541, 1466 cm^{-1}; ^{1}H NMR δ 0.97 (s, 9H), 1.30 (s, 9H), 1.35 (s, 3H), 8.00 (s, 1H); ^{13}C NMR δ 18.7 (CH_3), 26.2 (CH_3), 28.1 (CH_3), 33.5 (C), 36.6 (C), 111.0 (C), 154.7 (CH), 174.3 (C); MS *m/z* (relative intensity) 194 (M^+, trace), 167 (M^+ − HCN, 72), 123 (100), 111 (M^+ − *t*-BuCN, 65); HR-MS calcd for $C_{12}H_{22}N_2$ 194.1783, found 194.1832. Anal. Calcd for $C_{12}H_{22}N_2$: N, 14.42. Found: N, 14.13. **Picrate of 6e:** mp 98−95.8 °C dec (from cyclohexane). Anal. Calcd for $C_{18}H_{25}N_5O_7$: C, 51.06; H, 5.95; N, 16.54. Found: C, 50.73; H, 5.86; N, 16.70.

5-Ethyl-2,2,4-tripropyl-2*H*-imidazole (6f): bp 88−89 °C (2 mm); IR (neat) 1568, 1464 cm^{-1}; ^{1}H NMR δ 0.7−0.9 (m, 10H), 1.01 (t, J = 7.3 Hz, 3H), 1.27 (t, J = 7.3 Hz, 3H), 1.74 (m, 2H), 1.9−2.0 (m, 4H), 2.53 and 2.57 (t, q, total 4H); ^{13}C NMR δ 11.3 (CH_3), 14.0 (CH_3), 14.3 (CH_3), 16.4 (CH_2), 20.5 (CH_2), 22.5 (CH_2), 31.1 (CH_2), 38.8 (CH_2), 105.2 (C), 168.2 (C), 169.5 (C); MS *m/z* (relative intensity) 222 (M^+, 3), 167 (M^+ − EtCN, 66), 153 (M^+ − PrCN, 88) 138 (100), 124 (91); HR-MS calcd for $C_{14}H_{26}N_2$ 222.2096, found 222.2091. Anal. Calcd for $C_{14}H_{26}N_2$: C, 75.61; H, 11.79; N, 12.60. Found: C, 75.25; H, 11.84; N, 12.53. **Picrate of 6f:** mp 117−118 °C (from benzene−cyclohexane). Anal. Calcd for $C_{20}H_{29}N_5O_7$: C, 53.20; H, 6.47; N, 15.51. Found: C, 53.33; H, 6.53; N, 15.55.

4,5,6,7-Tetrahydro-2*H*-benzimidazole-2-spiro-1′-cyclohexane (6g): bp 74−75 °C (0.12 mm) [lit.[14] bp 97 °C (0.9 mm)]; IR (neat) 1570, 1447 cm^{-1}; ^{1}H NMR δ 1.2−2.2 (br m, 14H), 2.6−3.0 (br m, 4H); ^{13}C NMR δ 22.0 (CH_2), 23.2 (CH_2), 24.6 (CH_2), 26.6 (CH_2), 33.3 (CH_2), 103.6 (C), 163.8 (C); MS *m/z* (relative intensity) 190 (M^+, 100), 123 (56); HR-MS calcd for $C_{12}H_{18}N_2$ 190.1470, found 190.1455. Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.45; H, 9.71; N, 14.48. **Picrate of 6g:** mp 133−134 °C dec (from benzene−cyclohexane). Anal. Calcd for $C_{18}H_{21}N_5O_7$: C, 51.55; H, 5.05; N, 16.70. Found: C, 51.63; H, 5.09; N, 16.78.

Typical Precedure for the Acid-Catalyzed Hydrolysis of 6g. A solution of 2*H*-imidazole **6g** (3.00 g, 15.8 mmol) in 3 N H_2SO_4 (45 mL) was refluxed for 2 h. After being cooled, the liberated oil was extracted with ether (15 mL × 3), washed with brine, dried with anhydrous Na_2SO_4, and analyzed by GLC (FFAP 2-m, column temperature, 130 °C; flow rate, 40 mL/min). The yields of cyclohexanone and 1,2-cyclohexanedione were estimated by the internal standard method to be 90 and 55%, respectively. The identity of each was established by comparison of its GC mass spectrum with that of an authentic sample and by conversion to the oxime.

To a solution of hydroxylamine hydrochloride (3.75 g, 54 mmol) dissolved in 10 mL of water was added NaOH (2.16 g, 54 mmol) in 10 mL of water, and then the crude reaction mixture described above (2.41 g) was added with vigorous stirring at ice bath temperature. After 4 h, the solid separated was collected by suction and washed with water. Each oxime was isolated by Kugelrohr distillation. Pure cyclohexanone oxime was obtained as a fraction at 100 °C (15 mm) which solidified at rt (yield, 1.21 g, 68% based on **6g**); mp 89−90 °C [lit.[29] bp 100−105 °C (10−12 mm), mp 87−88 °C]. The residue (0.83 g) was recrystallized from water using activated charcoal to give the dioxime of 1,2-cyclohexanedione (yield, 0.6 g, 27% based on **6g**); mp 190−192 °C (lit.[30] mp 186−188 °C). The mixed melting point with an authentic sample was undepressed.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from The Japanese Ministry of Education, Science and Culture.

JO950812R

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