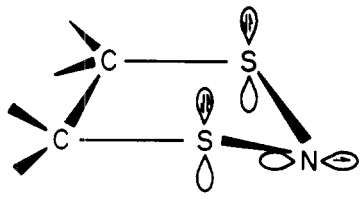

7

conjugative electron delocalization from N to S will be disfavored. The cyclic dithioamino radicals will therefore have smaller g values and smaller hyperfine splittings by ^{33}S than the acyclic dithioamino radicals (as is observed; see Table II). In addition, because the cyclic radical is less stabilized than the acyclic radical by conjugative electron delocalization, it is more reactive. This provides a simple explanation as to why **3** reacts with oxygen but **5** does not.

The 1,3,2-dithiazolidine ring is almost unknown.[44] Since radicals analogous to **3** can be produced from sulfur nitrides and a variety of strained[46] olefins,[12,13] styrene,[43] and certain acetylenes[47] (see Table II), it seems not unlikely that **1** and related compounds could serve as the starting point for the synthesis of compounds containing this unexplored heterocyclic ring system.[48]

Acknowledgment. L.H.S. thanks Miss S. A. Fairhurst for technical assistance and Professor A. P. Marchand (Oklahoma) for the dideuterionorbornene.

Registry No. **1**, 61501-72-2; **3**, 71042-46-1; **5**, 41601-45-0; **6**, 71042-47-2; S_4N_4, 28950-34-7; norbornene, 498-66-8; *exo,exo*-5,6-dideuterio-1,2-norbornyl-1′,3′,2′-dithiazolidin-2′-yl, 71042-48-3; 5,8-dimethoxy-4,9-methanonaphtho[2,3-*d*][1,3,2]dithiazol-2-yl, 71042-49-4; 4-phenyl-1,3,2-dithiazolidin-2-yl, 71042-50-7; 4-phenyl-1,3,2-dithiazol-2-yl, 71042-51-8; 4,5-diphenyl-1,3,2-dithiazol-2-yl, 71042-52-9; 4,5-bis(trifluoromethyl)-1,3,2-dithiazol-2-yl, 71042-53-0.

(44) The only example we could discover in the literature[45] was $SCH_2CH_2SNCH_3$.

(45) Mueller, W. H.; Dines, M. *J. Heterocycl. Chem.* **1969**, *6*, 627.

(46) We failed to obtain radicals with the following olefins: ethylene, tetramethylethylene, bromotrifluoroethylene, cyclopentene, 3-ethylcyclopentene, cyclohexene, 3,3,4,4-tetrafluorocyclobutene, tetramethylallene, citraconic anhydride, maleic anhydride, *N*-vinylimidazole, methyl methacrylate, stilbene, and thiophene.

(47) We failed to obtain radicals with 1-pentyne, 3,3-dimethyl-1-butyne, and 2-butyne.

(48) The S_4N_4 adduct with *trans*-cyclooctene has been reduced to the dithiol with zinc and HCl.[11]

Electrochemical Oxidation of Enamines in the Presence of Organic Anions

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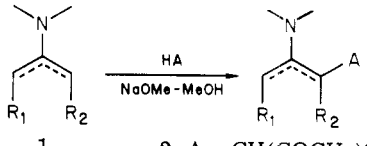
Received April 18, 1979

Anodic oxidations of enamines were examined in the presence of organic anions derived from methyl acetoacetate, acetylacetone, and dimethyl malonate. Enamines are very readily oxidized at a platinum anode and are substituted by the anionic substrates. The produced enamine intermediates are hydrolyzed with dilute hydrochloric acid to the corresponding α-substituted ketones. By treatment with more concentrated hydrochloric acid, some of them are converted to furan derivatives involving an intramolecular condensation.

Enamines are very useful intermediates for the formation of ketone derivatives, and the chemical reaction of enamines has been extensively studied by various investigators.[1] Although the anodic behavior of diaminoalkenes has been examined by cyclic polarographic and ESR spectroscopic methods,[2] only a few reports seem to be available on the electrochemical oxidation of enamines from a synthetic point of view. Recently, Shono and his co-workers showed that the anodic oxidation of enamines in methanol containing sodium methoxide gives rise to methoxylation at the β-carbon atom to the nitrogen.[3] On the other hand, the most common organic anions derived from β-dicarbonyl compounds are well-known to readily undergo electrochemical oxidation to form radicals which can add to the double bond of olefins.[4] In our laboratory, the electrochemical reaction of enamines with these anions

Scheme I



1

2, A = $CH(COCH_3)COOCH_3$
3, A = $CH(COCH_3)_2$
4, A = $CH(COOCH_3)_2$

	N	R_1, R_2
a	morpholino	$(CH_2)_3$
b	morpholino	CH_3, CH_3
c	morpholino	$(CH_2)_2$
d	piperidino	$(CH_2)_3$
e	piperidino	$(CH_2)_2$
f	pyrrolidino	$(CH_2)_3$
g	pyrrolidino	$(CH_2)_2$

was attempted at a platinum anode, and the synthetic application of this reaction was examined.

Results

Prior to the preparative studies, current–potential measurements were carried out in methanol containing sodium methoxide in the presence and absence of enamines at a platinum anode.

(1) See, for example, G. Stork, A. Brizzolara, H. Landesman, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); A. G. Cook, Ed., "Enamines", Marcel Dekker, New York, N.Y., 1969.

(2) J. M. Fritsch, H. Weingarten, and J. D. Wilson, *J. Am. Chem. Soc.*, **92**, 4038 (1970); J. M. Fritsch and H. Weingarten, *ibid.*, **90**, 793 (1968); K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

(3) T. Shono, Y. Matsumura, H. Hamaguchi, T. Imanishi, and K. Yoshida, *Bull. Chem. Soc. Jpn.*, **51**, 2179 (1978).

(4) H. Schäfer, *Chem.-Ing.-Tech.*, **42**, 164 (1970); H. Schäfer, *Angew. Chem.*, **82**, 134 (1970); H. Schäfer and A. Alazrak, *ibid.*, **80**, 485 (1968).

0022-3263/79/1944-3519$01.00/0

Table I. Anodic Oxidation of Enamines in the Presence of Organic Anions[a]

expt	starting materials: anion source	starting materials: enamine	discharged[b] pot, V vs. SCE	anode pot, V vs. SCE	product[c]	material[d] yield, %
I	MA[h]	1a	0.43	0.4-0.9	2a	67
II		1b	0.42	0.4-0.8	2b	68
III		1c	0.32	0.3-0.6	2c	59
IV		1d	0.38	0.3-0.9	2d	48
V		1e	0.29	0.3-0.6	2e	29
VI		1f	0.22	0.2-0.8	2f	*e*, *f*
VII		1g	0.18	0.2-0.5	2g	12[f]
VIII	AA[i]	1a	0.43	0.4-0.9	3a	60
IX		1b	0.42	0.4-0.9	3b	51[g]
X		1c	0.32	0.3-0.6	3c	43
XI	DM[j]	1a	0.43	0.4-0.6	4a	61
XII		1b	0.42	0.4-0.6	4b	29

[a] Anolyte: enamine (50 mmol) and β-dicarbonyl compound (70 mmol) in 75 mL of MeOH containing 50 mmol of NaOMe. Constant 0.5-A current. Consumed current 0.114 faraday. Temperature 15 °C. [b] Read from the current-potential curve. [c] Products were isolated by distillation and were identified by elemental analyses and by IR, NMR, and mass spectra. [d] Based on enamine consumed. [e] Not isolated (see expt VII' in Table II). [f] A considerable quantity of the pyrrolidine enamine of methyl acetoacetate was obtained. [g] Isolated by column chromatography (Al_2O_3, $CHCl_3$). [h] Methyl acetoacetate. [i] Acetylacetone. [j] Dimethyl malonate.

A 0.2 M NaOMe–MeOH solution without enamines was only slightly discharged up to 1.0 V (SCE), whereas all of the enamines employed in the present experiment were significantly oxidized at potentials more cathodic than 0.5 V (see Table I). Generally, enamines derived from cyclopentanone were more easily oxidized than the corresponding enamines from cyclohexanone, and pyrrolidine enamines were oxidizable at more cathodic potentials than those of the corresponding piperidine or morpholine enamines. In similar measurements for NaOMe–MeOH solutions of β-dicarbonyl compounds, dimethyl malonate (DM), methyl acetoacetate (MA), and acetylacetone (AA) showed oxidation peaks at 0.56, 0.65, and 0.68 V, respectively.

Next, in order to find favorable conditions for macroscale electrolyses, we conducted a series of preliminary experiments by using a system consisting of the morpholine enamine of cyclohexanone (**1a**), MA, and NaOMe–MeOH. The following became apparent from the results: (a) an approximately 40% excess of MA to enamine should be used to avoid a methoxylation reaction; (b) when an excess of more than 1 equiv of sodium to the enamine is added, the yield of the product **2a** is decreased; (c) at potentials where the enamine is predominantly oxidized (0.3–0.5 V), the current efficiency for the formation of **2a** goes up to 70% (assuming a 2e process). On the basis of the above observations, a practical condition for macroscale electrolyses was determined (Table I, footnote a).

Table I shows representative results of the macroscale electrolyses of enamines in the presence of organic anions derived from MA, AA, and DM.

In each case, the enamine was substituted by these anions at the β-carbon atom to the nitrogen. The product yields were more or less dependent on the oxidation potential of the starting enamines; namely, the yield decreased with increasing ease of the electrolytic oxidation. For example, in a series of electrolyses using MA as an anion source, enamine **1a** discharged at a more anodic potential and gave **2a** in a yield of 67%, whereas with the pyrrolidine enamine of cyclopentanone (**1g**), which was the most easily oxidized of all of the employed enamines, the yield of **2g** was less than 15%. The lower yield of the desired products in this series tended to involve formation of byproducts such as tarry materials and saturated amines which seemed to be produced from the imminium cations at the cathode. In addition, one of the major reasons for the very poor yields in experiment VI or VII was due to a side reaction of the enamine with MA. Only when pyrrolidine enamines **1f,g** were used for the electrolyses was a considerable quantity of the pyrrolidine enamine of MA isolated. This interchange of the ketone component of the enamines was recognized to be caused by a chemical reaction (not an electrochemical reaction). In electrolysis using either AA or DM, **1a** gave the substituted product in a relatively high yield; however, the cyclopentanone enamine combined with DM was hardly obtainable, and a large amount of tarry material was formed, which was difficult to separate in a usual way. Therefore, the present reaction may be affected by the basicity of the enamines, the nucleophilic ability of the organic anions, and the stability of the products for the anodic oxidation.

The resulting enamine intermediates **2–4** could be transformed to several compounds by treatment with acid,

Scheme II

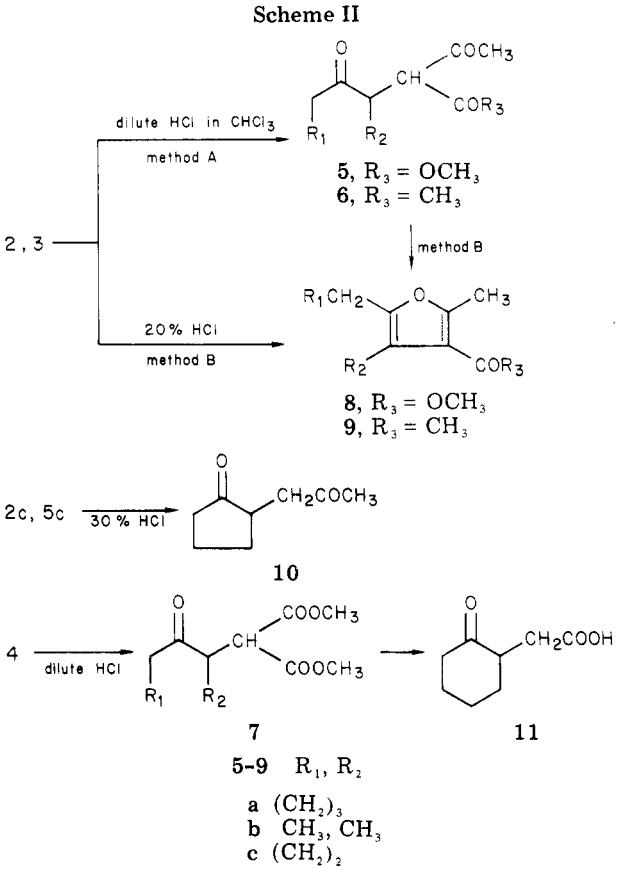


Table II. Hydrolysis Products of Enamine Intermediates

expt[a]	product[b] by method A[c]	yield, %	product[b] by method B[d]	yield, %
I′	5a	57[e] (72)[f]	8a	64[e] (77)[g]
II′	5b	68 (68)	8b	61 (84)
III′	5c	54 (82)	10	51 (82)
IV′	5a	35		
V′	5c	20		
VI′	5a	16		
VII′	5c	15		
VIII′	6a	61 (76)	9a	42 (83)
IX′	6b	51	9b	47 (77)
X′	6c	41 (69)		
XI′	7a	54 (74)	11	(70)[h]
XII′	7b	37 (67)		

[a] Corresponds to experiment number in Table I. [b] Products were isolated by distillation. [c] Treated with a 7% HCl aqueous solution in $CHCl_3$ (see Experimental Section). [d] Treated with a 20% HCl aqueous solution. [e] Based on the starting enamine employed for the electrolyses. [f] Based on the substituted enamine intermediate. [g] Based on α-substituted ketone. [h] According to a malonic ester synthesis.

especially some of the enamines which were substituted by MA or AA (**2a–c** or **3a,b** gave two distinct products, depending on the hydrolysis conditions (Table II)).

When a mixture of intermediates **2–4** and an equimolar quantity of a dilute hydrochloric acid solution was refluxed for 1 h in chloroform, they underwent a hydrolytic cleavage of the C–N bond to give α-substituted ketones **5–7**, whereas when the electrolysis product from cyclohexanone enamine and MA or AA (**2a** or **3a**) was heated in 20% hydrochloric acid without solvent, each of them was converted to a tetrahydrobenzofuran derivative **8a** or **9a**, involving an intramolecular condensation. Analogous enamine intermediates from 3-pentanone (**2b**, **3b**) also led to the furan derivatives **8b** and **9b** by the same treatment. However, no condensed-ring compounds were obtainable from cyclopentanone enamine intermediates **2c** or **3c**. For **2c**, hydrolysis of the ester group and a simultaneous decarboxylation occurred by heating with more concentrated acid, and γ-diketone **10** was preferentially formed. An attempt to prepare the analogous diketone from **2a** by an acetoacetic ester synthesis was unsuccessful, while the enamine combined with DM (**4a**) was further hydrolyzed in alkaline solution, followed by decarboxylation to lead to γ-keto acid **11** in a reasonable yield.

Moreover, it was confirmed that although α-substituted ketones such as **5a,b** or **6a,b** were converted to the furan derivatives **8a,b** or **9a,b** by treatment with 20% hydrochloric acid, the intramolecular condensation was not achieved with the cyclopentanone derivative **5c** or **6c** under the same conditions.

Discussion

Although the present reaction seems to proceed by a scheme similar to that of anodic methoxylation of enamines,[3] methoxide ion would scarcely participate in this reaction when the amount of sodium methoxide was less than that of MA, AA, or DM, because the C–H acidity of the β-dicarbonyl compounds is moderately higher than the O–H acidity of methanol,[5] therefore the resulting carbanions were more readily oxidized than methoxide ion.[6] When the applied potential is sufficient for the oxidation of the carbanions, there is a possibility that the free radicals produced from these anions give rise to a coupling reaction;[7] however, no dimers could be isolated in our experiments.

On the other hand, we believe that a part of the enamine is protonated by the excess β-dicarbonyl compound to form the imminium cation. Particularly, pyrrolidine enamines must prefer the formation of the imminium ion, since they favor the increase of the electron density on the C–N bond because of the exo double-bond character which is maintained.[8] The saturated amines produced from such enamines would probably be formed by cathodic reduction of the imminium cations.

As for the reaction forming furan derivatives **8** and **9** by acid, it proceeded advantageously in ketones or enamines combined with either MA or AA which favor an enolic form. (In such compounds, the considerable intensity of the enol resonance peaks was confirmed by NMR.[9]) For example, cyclohexanone combined with MA (**5a**) gave the furan **8a** in a yield of 77%, whereas in a similar reaction of 2-(2-ketopropyl)cyclohexanone, the yield of furan was very low. Although, in the case of **5a**, the condensed-ring reaction occurred in preference to a hydrolysis of its ester group, cyclopentanone combined with MA (**5c**) forced hydrolysis of the ester group and a simultaneous decarboxylation to lead to γ-diketone **10**. For these reasons, it is thought that the five-membered-ring ketone derivatives would be unfavorable for the formation of the double bond in themselves, because it will bring about an appreciable strain in the ring system compared with that in a six-membered ring.

By application of this electrolytic reaction to enamines with different ketone components, preparation of several kinds of the corresponding α-substituted ketones or furan derivatives can be expected.

Experimental Section[10]

Reagents. Enamines of cyclic ketones were prepared by the usual methods.[1,11] The morpholine enamine of 3-pentanone was synthesized according to the procedure of Stork,[1] using molecular sieves as the dehydrating agent. Reagent grade dimethyl malonate, methyl acetoacetate, and acetylacetone were used without purification.

Analytical Methods. Gas chromatographic analyses were conducted with a Hitachi 163 gas chromatograph. The low-boiling components were measured on a 1.5-m glass column packed with 10% FFAP on Uniport B. For the high-boiling components, a 1-m stainless steel column packed with 5% SE-30 was used. The carrier gas for each was nitrogen. IR, NMR, and mass spectra were recorded on Hitachi EPI-G2, 20-A, and M-52 spectrometers, respectively. Elemental analyses were determined with a Yanagimoto MU-2 C,H elemental analyzer.

Electrolysis Apparatus. Controlled-potential electrolyses were performed with a Nichia HP-E500H type potentiostat which was connected with a Nichia S-5A potentio programer. The relationships between current and potential were recorded on a Yokogawa 3077 X–Y recorder. Consumed current was integrated with a Yanagimoto CC-2 coulometer. For constant-current electrolyses, a Torio Model PR-654 dc power supply was used, and the potential of the working electrode was measured by a Takeda-Riken TR-6355 electrometer. The electrolysis cells and the electrodes were similar to those previously described.[12]

Current–Anode Potential Relationships. Current–potential measurements were made in a two-compartment cell, using a

(5) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).
(6) Methoxylated products were rarely obtained under these conditions.
(7) T. D. Binns, R. Brettle, and J. G. Parkin, *Chem. Commun.*, 409 (1965); T. D. Binns and R. Brettle, *J. Chem. Soc. C*, 336 (1966).
(8) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).
(9) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).
(10) All boiling and melting points are uncorrected, and chemical shifts in NMR spectra are given in parts per million from Me_4Si (δ 0).
(11) S. Hünig, E. Lücke, and W. Breninger, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1972, p 808.
(12) T. Chiba and Y. Takata, *J. Org. Chem.*, **42**, 2973 (1977).

Pt-plate anode, a saturated calomel electrode, and a Pt-wire cathode. A 20-mL, 0.2 M NaOMe–MeOH solution containing 5 mmol of reactant was placed in the cell, and the anode potential was set at a point where the current was zero. Then the potential was swept at the rate of 55 mV/s until the electrolytic current was limited.

Electrolyses for Preparative Studies. The general procedure was as follows. A mixture of 50 mmol of enamine, 70 mmol of β-dicarbonyl compound, and 75 mL of methanol containing 50 mmol of sodium methoxide was electrolyzed under a constant current at 0.5 A for 6 h. The total consumed current was 112 mF. After completion of the reaction, methanol was removed under reduced pressure. The residue was shaken with water and extracted three times with 30-mL portions of chloroform. The combined extracts were dried over calcium chloride and distilled under reduced pressure. Analytical samples were obtained by redistillation. The results of the distillations of the anolytes are given in Table III.

Morpholine Enamine of Cyclohexanone with MA (2a): bp 144–146 °C (1.5 mm); IR (neat) ν 1700, 1630, 1115 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.2–2.0 (m, CH_2CH_2, $CH_2C{=}CH_2$), 2.14 and 2.16 (s, keto–enol $COCH_3$), 2.5–2.7 (m, NCH_2), 3.02 (m, COCHCO), 3.4–3.7 (t?, OCH_2), 3.59 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 281 (M^+, 34), 238 ($M^+ - 43$, 65), 166 ($M^+ - 115$, 100). Anal. Calcd for $C_{15}H_{23}N_1O_4$: C, 64.03; H, 8.24. Found: C, 63.99; H, 8.24.

Morpholine Enamine of 3-Pentanone with MA (2b): bp 134 °C (1.5 mm); IR (neat) ν 1700, 1640, 1115 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 0.7–1.3 (m, CH_3CH_2, CH_3CH), 1.86 (ca. q, CH_3CH_2), 2.10 and 2.13 (s, keto–enol $COCH_3$), 2.58 (m, NCH_2), 2.8–3.4 (m, COCHCO), 3.61 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 269 (M^+, 22), 226 ($M^+ - 43$, 89), 154 ($M^+ - 115$, 100). Anal. Calcd for $C_{14}H_{23}N_1O_4$: C, 62.43; H, 8.61. Found: C, 62.62; H, 8.77.

Morpholine Enamine of Cyclopentanone with MA (2c): bp 138 °C (1.5 mm); IR (neat) ν 1700, 1635 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.64 (m, $CH_2CH_2CH_2$), 2.14 and 2.16 (s, keto–enol $COCH_3$), 2.5–2.8 (m, NCH_2), 3.26 (m, COCHCO), 3.4–3.7 (m, OCH_2), 3.59 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 267 (M^+, 31), 152 ($M^+ - 115$, 100). Anal. Calcd for $C_{14}H_{21}N_1O_4$: C, 62.90; H, 7.92. Found: C, 62.92; H, 7.99.

Piperidine Enamine of Cyclohexanone with MA (2d): bp 137–140 °C (2 mm); IR (neat) ν 1700, 1625 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.47 (m, $CH_2CH_2CH_2$), 2.15 and 2.18 (s, keto–enol $COCH_3$), 2.64 (m, NCH_2), 3.05 (m, COCHCO), 3.63 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 279 (M^+, 11), 236 ($M^+ - 43$, 71), 164 ($M^+ - 115$, 100). Anal. Calcd for $C_{16}H_{25}N_1O_3$: C, 68.78; H, 9.02. Found: C, 68.76; H, 9.08.

Piperidine Enamine of Cyclopentanone with MA (2e): bp 119–120 °C (2 mm); IR (neat) ν 1700, 1630 cm^{-1}; NMR (CCl_4) δ 1.44 (m, $CH_2CH_2CH_2$), 2.08 and 2.10 (s, keto–enol $COCH_3$), 2.60 (broad, NCH_2), 3.0–3.3 (broad, COCHCO), 3.54 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 265 (M^+, 20), 222 ($M^+ - 43$, 13), 162 ($M^+ - 103$, 19), 150 ($M^+ - 115$, 100). Anal. Calcd for $C_{15}H_{23}N_1O_3$: C, 67.89; H, 8.74. Found: C, 68.00; H, 8.73.

Pyrrolidine Enamine of Cyclohexanone with MA (2f): bp 137 °C (2 mm); IR (neat) ν 1700, 1635 cm^{-1}; NMR (CCl_4) δ 1.67 (m, CH_2CH_2, $CH_2CH_2CH_2$), 2.08 and 2.10 (s, keto–enol $COCH_3$), 2.70 (m, NCH_2), 3.53 (s, $COOCH_3$), 3.67 (d?); mass spectrum m/e (relative intensity) 265 (M^+, 22), 222 ($M^+ - 43$, 23), 150 ($M^+ - 115$, 100), 84 (29). Anal. Calcd for $C_{15}H_{23}N_1O_3$: C, 67.89; H, 8.74. Found: C, 67.90; H, 8.67.

Pyrrolidine Enamine of Cyclopentanone with MA (2g): bp 123–124 °C (2 mm); IR (neat) ν 1700, 1630 cm^{-1}; NMR (CCl_4) δ 1.67 (m, CH_2CH_2), 2.08 and 2.10 (s, keto–enol $COCH_3$), 2.67 (m, NCH_2), 3.21 (m, COCHCO), 3.51 (s, $COOCH_3$); mass spectrum m/e (relative intensity) 251 (M^+, 30), 208 ($M^+ - 43$, 20), 148 ($M^+ - 103$, 29), 136 ($M^+ - 115$, 100). Anal. Calcd for $C_{14}H_{21}N_1O_3$: C, 66.90; H, 8.42. Found: C, 66.88; H, 8.61.

Morpholine Enamine of Cyclohexanone with AA (3a): bp 147 °C (1.5 mm); IR (neat) ν 1665, 1605, 1380, 1115 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.2–2.0 (m, CH_2CH_2, $CH_2C{=}CCH_2$), 2.15 and 2.20 (s, keto–enol $COCH_3$), 2.61 (m, NCH_2), 3.10 (m, COCHCO), 3.59 (t, OCH_2); mass spectrum m/e (relative intensity) 265 (M^+, 38), 222 ($M^+ - 43$, 91), 166 ($M^+ - 99$, 100). Anal. Calcd for $C_{15}H_{23}N_1O_3$: C, 67.89; H, 8.74. Found: C, 68.04; H, 8.79.

Table III. Fractions Obtained from Anolytes[a]

expt	collected range (bp °C (mm)), amt (g), principal constituent
I	−55 (21), 0.9, cyclohexanone + morpholine (ca. 9:1); 145–148 (1.5), 9.4, **2a**
II	139–140 (2), 9.2, **2b**
III	136–141 (2), 7.9, **2c**
IV	130–138 (2), 6.7, **2d**
V	−91 (16), 0.9, *N*-cyclopentylpiperidine (90%);[b,c,f] 134–135 (4), 3.8, **2e**; tarry residue, 3.2
VI	−95 (17), 1.4, cyclohexanone + *N*-cyclohexylpyrrolidine;[e,f] 80–108 (3), 3.5, pyrrolidine enamine of MA[g] + **2f**;[h] tarry residue, 3.6
VII	−92 (15), 0.9, *N*-cyclopentylpyrrolidine;[b,d,f] 80–108 (1.5), 4.5, pyrrolidine enamine of MA + **2g** (64:36);[i] tarry residue, 2.5
VIII	−53 (20), 0.8, cyclohexanone + morpholine (ca. 4:1); 85–130 (2), 1.3, *N*-cyclohexylmorpholine[e,f] + cyclohexanone; 145 (1.5), 8.0, **3a**
IX	5.4, **3b**[j]
X	143–147 (2), 5.9, **3c**
XI	−56 (16), 0.5, cyclohexanone + morpholine (ca. 9:1); 150–154 (2), 9.1, **4a**
XII	−71 (17), 0.5, morpholine; 80–100 (2), 0.4, **7b**; 130–135 (2), 4.1, **4b**

[a] Most of the produced enamine intermediates were highly viscous oils and were somewhat less stable to prolong heating. [b] The crude amine obtained from three such electrolyses was combined and redistilled. [c] Bp 89–91 °C (14 mm). [d] Bp 73–74 °C (12 mm). [e] Isolated by preparative GLC. [f] Identified with an authentic sample prepared by the Leukart–Wallach reaction[13] (IR, NMR, and mass spectra). [g] The enamine was precipitated on addition of *n*-hexane to this fraction; 2.5 g, mp 70–70.5 °C, leaflets from *n*-hexane–diethyl ether. It was identical with an authentic sample prepared from pyrrolidine and methyl acetoacetate by the usual manner[1,11] (determination of mixture melting point, IR, and mass spectra). [h] Could not be isolated. It was very readily obtainable from **5a** and pyrrolidine by the usual manner.[11] [i] The enamine of methyl acetoacetate was separated in the same manner as described in *g*; 2.4 g yield. The filtrate was cooled to −30 °C and the additional precipitate was filtered off, and then the *n*-hexane solution was distilled. A total of 1.5 g of **2g** was obtained. [j] Isolated by column chromatography on active alumina (3.0 × 80 cm), using chloroform as the eluent. This product was easily converted to the other compound by heating. For example, the vacuum distillation of the crude product gave a fraction with a boiling point of 146–150 °C (2 mm); however, the NMR spectrum of this fraction was different from that of **3b** isolated by the above column chromatography. When this fraction was poured into diethyl ether, a yellowish precipitate was deposited, mp 91–94 °C. From the analytical data, this compound was presumed to be a dehydrated-ring product of **3a**.

Morpholine Enamine of 3-Pentanone with AA (3b): obtained as a brownish oil; IR (neat) ν 1665, 1610, 1580, 1110 cm^{-1}; NMR (CCl_4) δ 0.6–1.3 (m, CH_3CH_2, CH_3CH–), 1.83 (ca. q, CH_3CH_2), 2.07 and 2.11 (s, keto–enol $COCH_3$), 2.51 (m, NCH_2), 2.7–3.3 (m, COCHCO), 3.47 (t, OCH_2); mass spectrum m/e (relative intensity) 253 (M^+, 64), 210 ($M^+ - 43$, 100), 154 ($M^+ - 99$, 71), 43 (48). Anal. Calcd for $C_{14}H_{23}N_1O_3$: C, 66.37; H, 9.15. Found: C, 66.14; H, 9.00.

Morpholine Enamine of Cyclopentanone with AA (3c): bp 144–147 °C (2 mm); IR (neat) ν 1665, 1605, 1580, 1110 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.66 (m, $CH_2CH_2CH_2$), 2.10 (s, $COCH_3$), 2.17 and 2.19 (s, keto–enol $COCH_3$), 2.5–2.8 (m, NCH_2), 3.2–3.4 (broad, COCHCO), 3.57 (ca. t, OCH_2); mass spectrum m/e (relative intensity) 251 (M^+, 47), 208 ($M^+ - 43$, 33), 152 ($M^+ - 99$, 100). Anal. Calcd for $C_{14}H_{21}N_1O_3$: C, 66.90; H, 8.42. Found: C, 66.96; H, 8.49.

Morpholine Enamine of Cyclohexanone with DM (4a): bp 151–152 °C (1.5 mm); IR (neat) ν 1740, 1430, 1110 cm^{-1}; NMR (CCl_4) δ 1.58 (broad, CH_2CH_2), 2.05 (broad, $CH_2C{=}CCH_2$), 2.49 (m, NCH_2), 2.7–3.3 (m), 3.3–3.7 (m, OCH_2), 3.57 (s, $COOCH_3$),

4.86 (t), 5.13 (s); mass spectrum *m/e* (relative intensity) 297 (M^+, 32), 238 (M^+ - 59, 33), 166 (M^+ - 131, 100). Anal. Calcd for $C_{15}H_{23}N_1O_5$: C, 60.59; H, 7.80. Found: C, 60.41; H, 7.82.

Morpholine Enamine of 3-Pentanone with DM (4b): bp 132–135 °C (2 mm); IR (neat) ν 1740, 1428, 1110 cm^{-1}; NMR (CCl_4) δ 0.8–1.2 (m, CH_3CH_2), 1.5–1.8 (m, CH_3CH), 1.9–3.0 (m, CH_3CH, NCH_2), 3.3–3.7 (complex, OCH_2, $COOCH_3$), 4.76 (q), 5.25 (s); mass spectrum *m/e* (relative intensity) 285 (M^+, 19), 226 (M^+ - 59, 100), 154 (M^+ - 131, 49). Anal. Calcd for $C_{14}H_{23}N_1O_5$: C, 58.93; H, 8.13. Found: C, 58.90; H, 8.07.

Hydrolyses to Ketones (Method A). To the chloroform extracts obtained from the anolyte (or to a solution of 50 mmol of the enamine intermediate dissolved in 100 mL of chloroform) was added 30 mL of 7% hydrochloric acid solution. The heterogeneous solution was heated under reflux for 30–60 min with stirring. After the solution had cooled, the aqueous layer was separated and extracted with chloroform. The combined chloroform layers were washed with a small portion of water, dried over calcium chloride, and distilled.

Methyl α-(2-Oxocyclohexyl)acetoacetate (5a):[14] bp 165–169 °C (14 mm); IR (neat) ν 1745, 1715 cm^{-1}; NMR (CCl_4) δ 1.2–2.0 (m, $CH_2CH_2CH_2$), 2.16 and 2.21 (s, keto–enol $COCH_3$), 2.0–2.6 (m, $COCH_2$), 2.8–3.5 (m), 3.60 (s, $COOCH_3$), 3.74 (d?); mass spectrum *m/e* (relative intensity) 212 (M^+, 5), 152 (M^+ - 60, 49), 138 (M^+ - 74, 100), 97 (M^+ - 115, 56), 43 (44). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.41; H, 7.66.

Methyl α-(1-Methyl-2-oxobutyl)acetoacetate (5b): bp 127–128 °C (14 mm); IR (neat) ν 1745, 1720 cm^{-1}; NMR (CCl_4) δ 0.94 (ca. t, CH_3CH_2, CH_3CH), 2.11 and 2.19 (s, keto–enol $COCH_3$), 2.51 (q, CH_3CH_2), 3.0–3.5 (m), 3.58 and 3.64 (s, $COOCH_3$), 3.78 (d?); mass spectrum *m/e* (relative intensity) 200 (M^+, trace), 143 (M^+ - 57, 30), 101 (62), 57 (100), 43 (39). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.99; H, 8.18.

Methyl α-(2-Oxocyclopentyl)acetoacetate (5c): bp 149–152 °C (14 mm); IR (neat) ν 1740, 1720 cm^{-1}; NMR (CCl_4) δ 1.4–2.3 (m, CH_2CH_2, $COCH_2$), 2.10 and 2.19 (s, keto–enol $COCH_3$), 2.4–2.9 (m, COCH), 3.58 and 3.64 (s, $COOCH_3$), 3.77 (d?); mass spectrum *m/e* (relative intensity) 198 (M^+, 5), 156 (M^+ - 42, 90), 124 (M^+ - 74, 100), 100 (M^+ - 98, 96), 43 (61). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.57; H, 7.17.

3-(2-Oxocyclohexyl)-2,4-pentanedione (6a): bp 156–160 °C (13 mm); IR (neat) ν 1710, 1352 cm^{-1}; NMR (CCl_4) δ 1.2–2.0 (m, $CH_2CH_2CH_2$), 2.04 and 2.14 (s, keto–enol $COCH_3$), 2.0–2.6 (m, $COCH_2$), 2.8–3.5 (m), 3.81 (d, COCHCO); mass spectrum *m/e* (relative intensity) 196 (M^+, trace), 178 (M^+ - 18, 25), 153 (M^+ - 43, 30), 111 (97), 97 (100), 43 (86). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.44; H, 8.26.

3-(1-Methyl-2-oxobutyl)-2,4-pentanedione (6b): bp 124–127 °C (13 mm); IR (neat) ν 1705, 1352 cm^{-1}; NMR (CCl_4) δ 0.94 and 0.98 (t, d?, CH_3CH_2, CH_3CH), 2.10 and 2.16 (s, keto–enol $COCH_3$), 2.51 (q, CH_3CH_2), 3.0–3.6 (m), 4.01 (d, COCHCO); mass spectrum *m/e* (relative intensity) 141 (M^+ - 43, 31), 85 (M^+ - 99, 100), 57 (72), 43 (41). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.03; H, 8.66.

3-(2-Oxocyclopentyl)-2,4-pentanedione (6c): bp 153–154 °C (13 mm); IR (neat) ν 1740, 1705, 1352 cm^{-1}; NMR (CCl_4) δ 1.3–2.3 (m, CH_2CH_2), 2.05 and 2.18 (s, keto–enol $COCH_3$), 2.4–3.3 (m, COCH), 3.96 (d, COCHCO); mass spectrum *m/e* (relative intensity) 140 (M^+ - 42, 40), 122 (M^+ - 60, 68), 97 (M^+ - 85, 100), 84 (88), 43 (70). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.96; H, 7.61.

Dimethyl α-(2-Oxocyclohexyl)malonate (7a): bp 166–169 °C (14 mm); IR (neat) ν 1755, 1715, 1428 cm^{-1}; NMR (CCl_4–$CDCl_3$) δ 1.81 (m, $CH_2CH_2CH_2$), 2.33 (ca. t, $COCH_2$), 2.8–3.5 (m), 3.64 (s, $COOCH_3$), 3.92 (d, COCHCO); mass spectrum *m/e* (relative intensity) 228 (M^+, 8), 169 (M^+ - 59, 44), 132 (67), 97 (100). Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.59; H, 6.93.

Dimethyl α-(1-Methyl-2-oxobutyl)malonate (7b): bp 138–139 °C (19 mm); IR (neat) ν 1740, 1720, 1430 cm^{-1}; NMR (CCl_4) δ 0.96 (t, CH_3CH_2, CH_3CH), 2.54 (q, CH_3CH_2CO), 2.9–3.4 (m), 3.57 and 3.64 (s, $COOCH_3$), 3.68 (d?); mass spectrum *m/e* (relative intensity) 216 (M^+, trace), 187 (M^+ - 29, 23), 185 (M^+ - 31, 21), 161 (M^+ - 55, 34), 159 (M^+ - 57, 35), 127 (M^+ - 89, 36), 57 (100). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.43; H, 7.50.

Hydrolyses to Furan Derivatives (Method B). The residue obtained by evaporation of the chloroform extracts of the anolyte (or 50 mmol of ketone combined with β-keto ester or β-diketone) was dissolved in a 40 mL of 20% hydrochloric acid and was heated on a water bath for 30–60 min. A liberated oil was extracted with chloroform, washed with water, and distilled after drying.

2-Methyl-3-(methoxycarbonyl)-4,5,6,7-tetrahydrobenzo[*b*]furan (8a):[14] bp 136–138 °C (14 mm); IR (neat) ν 1720, 1580, 1435, 1270, 1085 cm^{-1}; NMR (CCl_4) ν 1.6–2.0 (ca. sextet, CH_2CH_2), 2.43 (s, $=CO(CH_3)$), 2.3–2.8 (m, $CH_2C{=}CCH_2$), 3.68 (s, $COOCH_3$); mass spectrum *m/e* (relative intensity) 194 (M^+, 100), 179 (M^+ - 15, 35), 166 (M^+ - 28, 90). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.18; H, 7.35.

2,4-Dimethyl-3-(methoxycarbonyl)-5-ethylfuran (8b): bp 103 °C (13 mm); IR (neat) ν 1720, 1580, 1435, 1280, 1085 cm^{-1}; NMR (CCl_4) δ 1.00 (t, CH_3CH_2), 1.87 (s, $CH_3C{=}$), 2.28 (s, $=CO(CH_3)$), 3.56 (s, $COOCH_3$); mass spectrum *m/e* (relative intensity) 182 (M^+, 70), 167 (M^+ - 15, 100), 151 (M^+ - 31, 18), 135 (M^+ - 47, 46). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.80; H, 7.93.

2-Methyl-3-acetyl-4,5,6,7-tetrahydrobenzo[*b*]furan (9a): bp 138–140 °C (14 mm); IR (neat) ν 1675, 1555, 1350, 1270 cm^{-1}; NMR (CCl_4) δ 1.76 (ca. sextet, CH_2CH_2), 2.20 (s, $COCH_3$), 2.43 (s, $=CO(CH_3)$), 2.3–2.8 (broad, $CH_2C{=}CCH_2$); mass spectrum *m/e* (relative intensity) 178 (M^+, 100), 163 (M^+ - 15, 79), 150 (M^+ - 28, 43), 135 (M^+ - 43, 29). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.07; H, 8.02.

2,4-Dimethyl-3-acetyl-5-ethylfuran (9b): bp 109–110 °C (16 mm); IR (neat) ν 1670, 1555, 1280 cm^{-1}; NMR (CCl_4) δ 1.10 (t, CH_3CH_2), 1.97 (s, $CH_3C{=}$), 2.23 (s, $COCH_3$), 2.39 (s, $=CO(CH_3)$), 2.48 (q?, $=CO(CH_2CH_3)$); mass spectrum *m/e* (relative intensity) 166 (M^+, 60), 151 (M^+ - 15, 100), 43 (18). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.15; H, 8.46.

2-(2-Oxopropyl)-1-cyclopentanone (10): The treatment of **5c** with acid was carried out in a more concentrated hydrochloric acid solution than that described in the method B, because the β-keto ester was relatively stable to the acid. A 60-mL portion of 30% hydrochloric acid was added to 6.0 g of **5c**. Stirring and refluxing was continued for 5 h to ensure a complete reaction. After cooling, the mixture was worked up in the usual manner. The distillation of the crude product gave 3.5 g of **10**: bp 112–113 °C (14 mm); IR (neat) ν 1743, 1720 cm^{-1}; NMR (CCl_4) δ 1.3–2.4 (m, CH_2CH_2, $COCH_2$), 2.03 (s, $COCH_3$), 2.58 (t?), $COCH_2$); mass spectrum *m/e* (relative intensity) 140 (M^+, 46), 98 (M^+ - 42, 63), 97 (M^+ - 43, 100), 83 (M^+ - 57, 98), 43 (76). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.45; H, 8.65.

α-(2-Oxocyclohexyl)acetic Acid (11): According to a malonic ester synthesis,[15] **7a** was converted to **11**.. A 9.5-g amount of **7a** was hydrolyzed in an aqueous ethanol solution of potassium hydroxide to 2-(2-oxocyclohexyl)malonic acid (mp 155–157 °C dec) and the dicarboxylic acid was decarboxylated by heating to 180 °C for 10 min. A white precipitate was obtained in a yield of 70% based on **7a**, mp 74 °C (from *n*-hexane–diethyl ether). A mixture melting point determination with an authentic sample prepared by the procedure of Baumgarten[16] showed no depression.

Registry No. **1a**, 670-80-4; **1b**, 13654-48-3; **1c**, 936-52-7; **1d**, 2981-10-4; **1e**, 1614-92-2; **1f**, 1125-99-1; **1g**, 7148-07-4; **2a**, 71040-62-5; **2b**, 71040-64-7; **2c**, 71040-66-9; **2d**, 71060-29-2; **2e**, 71040-68-1; **2f**, 71040-70-5; **2g**, 71040-72-7; **3a**, 71040-74-9; **3b**, 71040-76-1; **3c**, 71040-78-3; **4a**, 71040-80-7; **4b**, 71040-82-9; **5a**, 71041-26-4; **5b**, 71041-27-5; **5c**, 71041-28-6; **6a**, 71041-29-7; **6b**, 71041-30-0; **6c**, 71041-31-1; **7a**, 63965-89-9; **7b**, 37069-22-0; **8a**, 63965-82-2; **8b**, 71041-32-2; **9a**, 71041-33-3; **9b**, 71041-34-4; **10**, 60415-94-3; **11**, 1438-96-6; cyclohexanone, 108-94-1; morpholine, 110-91-8; *N*-cyclopentylpiperidine, 7335-04-8; *N*-cyclohexylpyrrolidine, 7731-02-4; pyrrolidine enamine of MA, 71040-83-0; *N*-cyclopentylpyrrolidine, 18707-33-0; *N*-cyclohexylmorpholine, 6425-41-8; MA, 105-45-3; AA, 123-54-6; DM, 108-59-8.

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