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Electroorganic Chemistry 139. Electroreductive Decyanation of Nitriles and Its Application to Synthesis of α-Alkylamines

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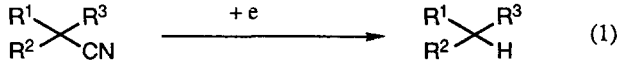
Abstract: Electroreduction of nitriles gave the corresponding decyanated products when Zn was used as the material of cathode in aprotic solvent (DMF or MeCN) containing Et_4NOTs as a supporting electrolyte. Alkylation of amines at the α-position was effectively achieved by cyanation of amines at the α-position, and α-alkylation of the resultant α-amino nitriles followed by the electroreductive decyanation.

Decyanation of nitriles seems to be one of the useful methods in organic synthesis since aliphatic nitriles are generally synthesized without any special difficulty and alkylation at their α-carbon is also rather easy due to the effect of a cyano group.[1] The hitherto known methods of decyanation, however, seem still inconvenient and exploitation of a new efficient method is strongly desired. Although the Birch reduction and its modified method are effective for decyanation,[2,3] their reaction conditions, that is, the use of alkali metal and liquid ammonia are not always convenient for practical application. On the other hand, electrochemical reduction has been known to be a promising alternative of the Birch reduction, though, so far, only one electroreductive decyanation of simple aliphatic nitriles carried out under conditions similar to the Birch reduction has been reported.[4] It has been found in the present study that the electroreductive decyanation is effectively achievable with Zn cathode in aprotic solvents such as DMF (eq 1) and it is a useful tool for α-alkylation of amines (eq 3).



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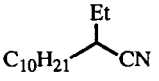
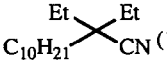
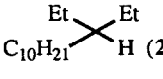
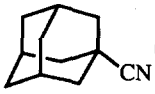
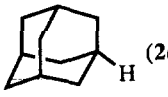
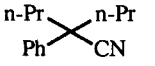
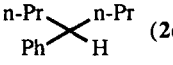
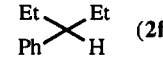
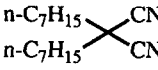
1 2

Electroreductive Decyanation

Electrochemical reduction of nitriles 1 with Zn cathode in DMF containing Et_4NOTs as a supporting electrolyte gave the corresponding decyanated products 2 in satisfactory yields. The reduction was highly influenced by supporting electrolytes, electrode materials and solvents as shown in Table 1. The fact that the use of Li^+ instead of Et_4N^+ resulted in recovery of the starting material (run 2) and deposition of Li metal on the cathode indicates that this electroreduction is not the same as the Birch type reduction promoted by Li metal which is deposited on the cathode. Zn gave the best result among the cathode materials examined (see runs 1, 3 and 4).[5]

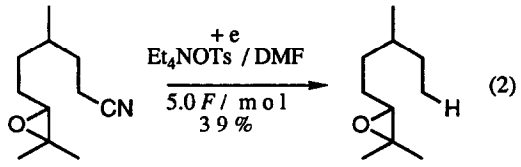
Table 1. Electroreductive Decyanation of Nitriles.

run	Substrate 1	Cathode material	Solvent	Supporting electrolyte	Electricity (*F*/mol)	Product 2 (yield %)[a]
1	n-$C_{11}H_{23}CN$ (**1a**)	Zn	DMF	Et_4NOTs	6.0	n-$C_{11}H_{24}$ (**2a**) (50)
2	**1a**	Zn	DMF	$LiClO_4$	4.4	**2a** (0)[b]
3	**1a**	Pb	DMF	Et_4NOTs	6.0	**2a** (9)
4	**1a**	Pt	DMF	Et_4NOTs	6.0	**2a** (15)
5	**1a**	Zn	THF	Bu_4NBF_4	9.3	**2a** (36)
6	**1a**	Zn	MeCN	Et_4NOTs	2.5	**2a** (0)[b]
7	 (**1b**)	Zn	DMF	Et_4NOTs	5.6	n-$C_{13}H_{28}$ (**2b**) (74)
8	 (**1c**)	Zn	DMF	Et_4NOTs	5.4	 (**2c**) (80)[c]
9	 (**1d**)	Zn	DMF	Et_4NOTs	6.0	 (**2d**) (73)
10	 (**1e**)	Zn	DMF	Et_4NOTs	2.5	 (**2e**) (85)[c]
11	**1e**	Zn	MeCN	Et_4NOTs	4.0	**2e** (79)
12	 (**1f**)	Zn	DMF	Et_4NOTs	4.0	 (**2f**) (74)[c]
13	 (**1g**)	Zn	DMF	Et_4NOTs	15	n-$C_{15}H_{32}$ (**2g**) (35)
14	 (**1h**)	Zn	DMF	Et_4NOTs	5.0	 (**2h**) (72)

[a] Yields were determined by glc unless otherwise stated. [b] Starting material was recovered.
[c] Isolated yield.

Use of THF as a solvent gave low yield and current efficiency (run 5). Acetonitrile was not effective as solvent (run 6) presumably due to cathodic limit of acetonitrile,[6] though it was effective for the reduction of a benzyl type cyanide **1e** (run 11) owing to the reason that reduction potential of benzyl type cyanide was more positive[7] than cathodic limit of acetonitrile.

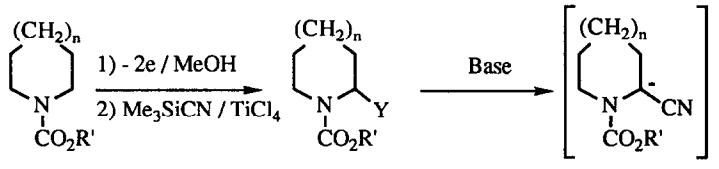
The reaction conditions, that is, using DMF in the absence of alkali metal also made it possible to achieve the selective decyanation[8] of an epoxy nitrile **3**, in which the epoxy group was remained unchanged (eq 2).



3 4

α-Alkylation of Amines

Alkylation at the position α to the nitrogen atom of amines has recently attracted much interest since it is often essential in the synthesis of alkaloids.[10] One of the methods is the generation of α-carbanion of amine followed by its trapping with alkyl halides, though the direct generation of such α-carbanion has been reported to require a strong base such as *sec*- or *tert*-butyllithium.[11] As a convenient method to introduce a cyano group into the α-position of amines has already been reported in our previous study,[12] the present decyanation was applied to removal of the cyano function after cyano carbamates were alkylated at the α-position. Eq 3 shows the strategy which consists of anodic methoxylation at the α-position of α-unsubstituted N-methoxycarbonylamines **5-7**, substitution of the methoxy group by a cyano group, generation of α-carbanions **14-16** from nitriles **11-13**, trapping of **14-16** with alkyl halides (R-X) to give α-cyano-α-alkylamines **17-19**, and electroreductive decyanation of **17-19**.



5-7

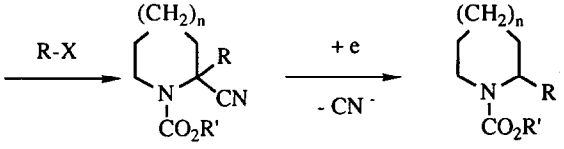
5: n= 0, R'= Me
6: n= 0, R'= t-Bu
7: n= 1, R'= Me

8-13

8: n= 0, R'= Me, Y=OMe
9: n= 0, R'= t-Bu, Y=OMe
10: n= 1, R'= Me, Y=OMe
11: n= 0, R'= Me, Y= CN
12: n= 0, R'= t-Bu, Y= CN
13: n= 1, R'= Me, Y= CN

14-16

14: n= 0, R'= Me
15: n= 0, R'= t-Bu
16: n= 1, R'= Me



(3)

17-19

17a: n= 0, R'= Me
18a,b,e: n= 0, R'= t-Bu
19a-e: n= 1, R'= Me

20-22

20a: n= 0, R'= Me
21a,b,e: n= 0, R'= t-Bu
22a-e: n= 1, R'= Me

a ; R= $PhCH_2$
b ; R= Me
c ; R= Et
d ; R= n-C_8H_{17}
e ; R= $CH_2CH{=}CH_2$

According to our previously reported method, the key intermediates **11-13** were easily synthesized by electrochemical oxidation of **5-7** in methanol followed by treatment of the products **8-10** with trimethylsilyl cyanide.[12] The subsequent α-alkylation of **13** was achieved satisfactorily by treatment of **13** with LDA followed by addition of alkyl halides (runs 6-10 in Table 2). In the case of a five membered cyclic amine **11**,

however, generation of α-carbanion by its treatment with LDA followed by addition of R-X resulted in a low yield (20%) (run 1 in Table 2) presumably because of the self-condensation of the anion. This self-condensation was, however, diminished by addition of a mixture of **11** and R-X into a solution of LDA in THF (the yield 57%, run 2 in Table 2). The self-condensation was also avoided by using a bulky *N*-protecting group. Namely, in the case of *N*-*t*-butoxycarbonyl derivative **12**, the yields of alkylation with R-X in the presence of $NaNH_2$ were satisfactory (runs 3, 4 and 5 in Table 2).[13] The yields of **8-13** and **17-19** are summarized in Table 2.

Table 2. Formation of α-Alkylated α-Cyano Amine Derivatives **17-19** from Amine Derivatives **5-7.**

run	Substrate **5-7**	Yield (%) of **8-10**	Yield (%) of **11-13**	RX	Base	Yield (%) of **17-19**
1	**5**	**8** (83)	**11** (92)	$PhCH_2Br$	LDA	**17a** (20)
2			**11**	$PhCH_2Br$	LDA	**17a** (57)*
3	**6**	**9** (74)	**12** (74)	$PhCH_2Br$	$NaNH_2$	**18a** (91)
4			**12**	Me I	$NaNH_2$	**18b** (62)
5			**12**		$NaNH_2$	**18e** (74)
6	**7**	**10** (86)	**13** (81)	$PhCH_2Br$	LDA	**19a** (90)
7			**13**	MeI	LDA	**19b** (87)
8			**13**	EtI	LDA	**19c** (76)
9			**13**	$n\text{-}C_8H_{17}I$	LDA	**19d** (83)
10			**13**		LDA	**19e** (86)

* A mixture of **11** and RX was added into a solution of LDA in THF.

The electroreduction of **11**, **13**, **17**, **18** and **19** under conditions shown in the first part of this report gave decyanated products **5**, **7**, **20**, **21** and **22** in yields shown in Table 3. Solvent used in this electroreductive decyanation was DMF or acetonitrile.

α-Alkylation of piperidine ring was also achieved through α,β-unsaturated α-cyanopiperidine **25**, which could be prepared from **10** according to the method shown in eq 4. Electrochemical reduction of α-ethylated piperidine **26** gave β,γ-unsaturated piperidine derivative **27** together with α,β–unsaturated isomer **27'** (eq 4).

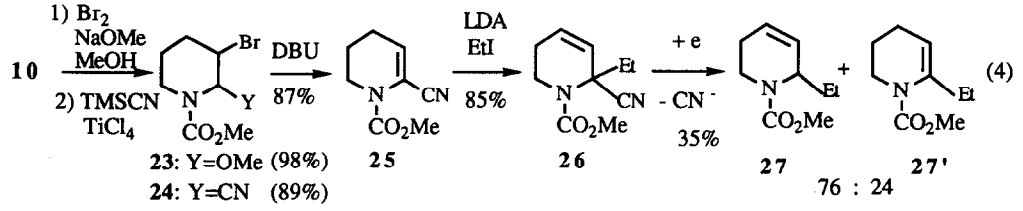
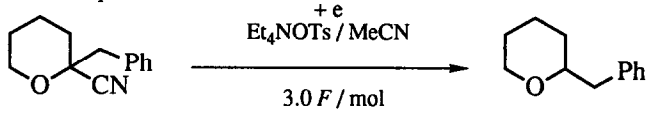


Table 3. Electroreductive Decyanation of α-Alkylated α-Cyano Amine Derivatives **11, 13** and **17-19.**

run	Substrate	Solvent	Electricity (F/mol)	Product	Yield (%)
1	**11**	DMF	3.0	**5**	75 *
2	**17a**	DMF	3.8	**20a**	41
3	**17a**	MeCN	4.5	**20a**	74
4	**18a**	MeCN	3.7	**21a**	85
5	**18b**	MeCN	8.1	**21b**	69
6	**18e**	MeCN	8.0	**21e**	62
7	**13**	DMF	3.0	**7**	89 *
8	**13**	MeCN	3.0	**7**	58 *
9	**19a**	DMF	3.0	**22a**	66
10	**19a**	MeCN	5.2	**22a**	80
11	**19b**	DMF	4.0	**22b**	100 *
12	**19b**	MeCN	10.0	**22b**	69 *
13	**19c**	DMF	3.0	**22c**	100 *
14	**19d**	DMF	4.2	**22d**	55
15	**19d**	MeCN	4.5	**22d**	78
16	**19e**	MeCN	6.0	**22e**	59

* GLC yield.

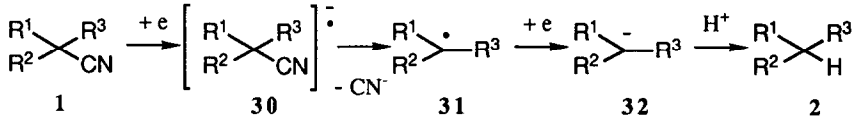
Furthermore, it was also found that the electrochemical method was applicable to the decyanation of α-alkoxy nitrile **28** as shown in eq 5.



28 **29** 57 % (5)

The fact that both α-amino and α-alkoxy nitriles were decyanated in acetonitrile suggests that these nitriles were reduced at more positive potential than reduction of simple aliphatic nitriles, though any reduction wave of these nitriles was not found at the potential more positive than -3.0 V vs SCE.

Although there are no clear evidences, it seems reasonable that a radical intermediate **31** is formed by one electron reduction of **1** in the first step of this electroreductive decyanation. The ease of reduction of benzyl, α-amino and α-alkoxy nitriles is explained in terms of stabilization of the radical intermediate **31** by the adjacent phenyl, alkoxy or amino group.[14] Further reduction of **31** and subsequent protonation of the resultant anion **32** give the product **2** (eq 5).[2]



1 **30** **31** **32** **2** (6)

EXPERIMENTAL

General. IR spectra were recorded on a Hitachi 260-10 spectrometer. ^{1}HNMR spectra were measured on a Varian Gemini 200 spectrometer with TMS as an internal standard. Mass spectra were obtained on a JEOL IMS-DX 300 instrument. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Electrochemical reactions were carried out by using DC Power Supply (GP 050-2) of Takasago Seisakusho, Ltd.

Materials. DMF and MeCN were distilled over CaH_2 before use. THF was dried by Na. Nitriles **1a, d, h** are commercially available. Nitriles **1e**,[15] **f**[15] and carbamates **5**,[10a] **6**,[16] **7**[10a] were known compounds. Nitriles **1b**,[17] **c**,[17] **g**,[18] **3**,[19] and **28**[17,20] were prepared according to the reported methods of nitriles synthesis and purified by column chromatography.

2-Ethyldodecanenitrile (1b); 93%; IR (neat) 2930, 2850, 2240, 1460 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.88 (t, 3H, J=7Hz), 1.08 (t, 3H, J=7Hz), 1.27 (br s, 16H), 1.39-1.71 (m, 5H), 2.38-2.54 (m, 1H); Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.26; H, 13.27; N, 6.51.

2,2-Diethyldodecanenitrile (1c); 90%; IR (neat) 2940, 2860, 2240, 1460, 1380 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.88 (t, 3H, J=7Hz), 0.99 (t, 6H, J=7Hz), 1.23 (br s, 14H), 1.36-1.56 (m, 4H), 1.60 (q, 4H, J=7Hz); exact mass calcd for $C_{16}H_{31}N$ 237.24583, found 237.24610.

Diheptylmalononitrile (1g); 86%; IR (neat) 2940, 2860, 1480 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.89 (m, 6H), 1.29 (br s, 20H), 1.56-1.76 (m, 2H), 1.82-1.99 (m, 2H); exact mass calcd for $C_{17}H_{23}N_2$ 262.24110, found 262.24111.

4,8-Dimethyl-7,8-epoxynonanenitrile (3) was prepared by epoxidation of 4,8-dimethyl-7-nonenenitrile[19] with *m*-chloroperbenzoic acid in CH_2Cl_2 at 0°C (99% yield); IR (neat) 2960, 2250, 1460, 1380, 1020 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.95 (d, 3H, J=7Hz), 1.27 (s, 3H), 1.32 (s, 3H), 1.35-1.83 (m, 7H), 2.38 (dt, 2H, J=7, 2Hz), 2.71 (t, 1H); Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.57; N, 7.73. Found: C, 73.05; H, 10.82; N, 7.71.

β-Bromo-α-methoxy-*N*-methoxycarbonylpiperidine (23) was prepared by adding bromine (90 mmol) into a solution of **10** (60 mmol) in methanol (50 ml) containing NaOMe (90 mmol) followed by refluxing the solution for 30 min. After the solution was added into saturated aqueous $NaHCO_3$ and washed with aqueous sodium thiosulfate, the organic portion was extracted with CH_2Cl_2 and dried on $MgSO_4$. **23** was isolated by column chromatography on silica gel (98% yield); IR (neat) 2952, 1712, 1448, 1272, 1160, 1082, 968, 952, 778 cm^{-1}; ^{1}HNMR(CCl_4) δ 1.29-2.45 (m, 4H), 2.95 (t, 1H, J=12Hz), 3.27 and 3.36 (2 s, 5/2H and 1/2H), 3.63-4.63 (m, 2H), 3.74 (s, 3H), 5.44 (br s, 1H); exact mass calcd for $C_{13}H_{14}NO_3Br$ 251.01575, found 251.01466.

β-Bromo-α-cyano-*N*-methoxycarbonylpiperidine (24): To a solution of **23** (20 mmol) and trimethylsilyl cyanide (40 mmol) in CH_2CH_2 (50 mL) was dropwise added a solution of $TiCl_4$ (20 mmol) in CH_2Cl_2 (25 mL) at -78°C, the resulting solution was stirred for 3h at 0°C. After the solution was added into saturated aqueous $NaHCO_3$, the organic portion was extracted with CH_2Cl_2 and dried on $MgSO_4$. **24** was isolated by column chromatography on silica gel (89% yield); IR (neat) 2950, 2850, 1695, 1435, 1390, 1250, 1195, 1140, 1110, 1020, 980, 950, 870, 760 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.65-2.38 (m, 4H), 3.06 (t, 1H, J=12Hz), 3.78 (s, 3H), 4.10-4.54 (m, 2H), 5.35-5.60 (br s, 1H); exact mass calcd for $C_8H_{11}N_2O_2Br$ 246.00044, found 246.00219.

α,β-Unsaturated α-cyano-*N*-methoxycarbonylpiperidine (25): A solution of 24 (20 mmol) and DBU (40 mmol) in DMF (25 mL) was heated at 80°C for 30 min, and the solution was added into water and the organic portion was extracted with ether. **25** was isoalted by column chromatography on silica gel (87% yield); mp 57°C; IR (neat) 2900, 2230, 1710, 1630, 1440, 1400, 1345, 1260, 1190, 1130, 1100, 1060, 980, 860, 880, 800, 760 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.87 (m, 2H), 2.27 (m, 2H), 3.67 (m, 2H), 3.84 (s, 3H), 6.05 (t, 1H, J=5Hz); exact mass calcd for $C_8H_{10}N_2O_2$ 166.07422, found 166.07470.

β,γ-Unsaturated α-cyano-α-ethyl-*N*-methoxycarbonylpiperidine (26): To a solution of LDA (5.7 mmol) in THF (5 mL) were added a solution of **25** in THF (8 mL) at -78°C and then a solution of ethyl iodide (5.7 mmol) in THF (10 mL), and the resulting solution was stirred at the temperature for 1 h. After the solution was added into saturated aqueous NH_4Cl, the organic portion was extracted with CH_2Cl_2 and dried on $MgSO_4$. **26** was isolated by column chromatography on silica gel (85% yield); IR (neat) 2950, 2880, 1705, 1440, 1365, 1255, 1210, 1100, 1065, 985, 950, 770, 720 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.95 (t, 3H, J=8Hz), 2.00 (m,1H), 2.2.0 (m,2H), 2.48 (m, 1H), 3.37 (m, 1H), 3.80 (s, 3H), 3.74-3.90 (m, 1H), 5.65 (m, 1H), 6.20 (m,1H); exact mass calcd for $C_{10}H_{14}N_2O_2$ 194.10552, found 194.10445.

2-Benzyl-2-cyano-3,4,5,6-tetrahydro-2H-pyran (28) was prepared by the reaction of 2-cyanotetrahydropyran[20] with LDA in tetrahydrofuran followed by adding benzyl bromide.[17] (90% yield); IR (neat) 2950, 2870, 1460, 1090,1050 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.47-1.88 (m, 6H), 3.04 (AB q, 2H, J=14Hz, Δν=30Hz), 3.73-4.04 (m, 2H), 7.32 (s, 5H); exact mass calcd for $C_{13}H_{15}NO$ 201.11545, found 201.11766.

α-Alkylation of amine derivatives

Anodic oxidation of *N*-alkoxycarbonylamine: Anodic oxidation of *N*-alkoxycarbonylamines was carried out according to the reported method.[10a] The yields of anodic oxidation, α-cyantion and α-alkylation are summarized in Table 2. The data of new compound **9** is as follows:

***N-tert*-Butoxycarbonyl-α-methoxypyrrolidine (9)**; IR (neat) 2990, 1710, 1390, 1170, 1090 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.41 (s, 9H), 1.67-2.16 (m, 4H), 3.19-3.51 (m, 2H), 3.35 (br s, 3H), 5.13 (br d, 1H, J=22Hz); Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.67; H, 9.52; N, 6.96. Found: C, 59.52; H, 9.71; N, 6.84.

α-Cyanation of *N*-Alkoxycarbonyl Amines. A solution of 2-methoxy-*N*-methoxycarbonylamine **8-10** (5 mmol) in CH_2Cl_2 was added into a solution of $TiCl_4$ (5 mmol) at 0°C, and subsequently a solution of trimethylsilyl cyanide (10 mmol) was added to the solution. After stirring the reaction mixture for 1h at 0°C, 20 mL of water was added to the solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic solution was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. After careful removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give α–amino cyanides **11-13**. Product **11** was a known compound.[12] The data of new compounds are as follows:

***N-tert*-Butoxycarbonyl-α-cyanopyrrolidine (12)**; IR (neat) 2980, 2245, 1700, 1385, 1160 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.51 (s, 9H), 1.93-2.34 (m, 4H), 3.25-3.61 (m, 2H), 4.41-4.61 (m, 1H); Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.28. Found: C, 60.97; H, 8.16; N, 14.07.

α-Cyano-*N*-methoxycarbonylpiperidine (13); IR (neat) 2980, 2890, 2260, 1720, 1455, 1270, 1180 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.16-2.23 (m, 6H), 3.01 (br t, 1H, J=12Hz), 3.74 (s, 3H), 4.11 (br d, 1H, J=16Hz), 5.14 (br s, 1H); Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.12; H, 7.19; N, 16.66. Found: C, 57.40; H, 7.47; N, 16.65.

Alkylation of α-Cyano-*N*-methoxycarbonylamines: To a solution of LDA (6 mmol) in THF, a solution of 2-cyano-*N*-alkoxycarbonylamine **11** or **13** (5 mmol) in THF was added at -78°C, and subsequently a solution of an alkyl halide (7.5 mmol) was added to the solution. After stirring the solution at -78°C for 1h, saturated aqueous NH_4Cl was added to the solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (30 mL x 2). The combined organic solution was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. After careful removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to give 2-alkylated products **17-19**.

α-Benzyl-α-cyano-*N*-methoxycarbonylpyrrolidine (17a); IR (neat) 2970, 2890, 2250, 1715, 1455, 1395, 1280, 775, 710 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.57-2.07 (m, 6H), 2.67-3.10 (m, 1H), 3.36 (s, 2H), 3.60-4.06 (m, 1H), 3.79 (s, 3H), 7.30 (br s, 5H); Anal. Calcd. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.56; H, 6.98; N, 10.70.

α-Benzyl-*N*-*tert*-butoxycarbonyl-α-cyanopyrrolidine (18a); IR (neat) 2990, 1710, 1390, 1165, 765, 710 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.30-2.33 (m, 4H), 1.57 (s, 9H), 2.89-3.75 (m, 2H), 3.27 (s, 2H), 7.06-7.44 (m, 5H); Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.31; H, 7.76; N, 9.53.

***N*-*tert*-Butoxycarbonyl-α-cyano-α-methylpyrrolidine (18b)**; IR (neat) 2980, 2250, 1700, 1380, 1165 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.52 (s, 9H), 1.71 (s, 3H), 1.81-2.16 (m, 3H), 2.42-2.59 (m, 1H), 3.34-3.69 (m, 2H); Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.33. Found: C, 63.07; H, 8.61; N, 13.14.

α-Allyl-*N*-*tert*-butoxycarbonyl-α-cyanopyrrolidine (18e); IR (neat) 2990, 1710, 1390, 1165 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.53 (s, 9H) 1.74-2.43 (m, 4H), 2.50-3.12 (m, 2H), 3.12-3.86 (m, 2H), 5.19 (d, 1H, J=17Hz), 5.24 (d, 1H, J=10Hz), 5.51-6.04 (m, 1H); Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53; N, 11.86. Found: C, 66.03; H, 8.53; N, 11.60.

α-Benzyl-α-cyano-*N*-methoxycarbonylpiperidine (19a); IR (neat) 2970, 2890, 2250, 1715, 1455, 1395, 1280, 775, 710 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.57-2.07 (m, 6H), 2.67-3.10 (m, 1H), 3.36 (s, 2H), 3.60-4.06 (m, 1H), 3.79 (s, 3H), 7.30 (br s, 5H); Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.56; H, 6.98; N, 10.70.

α-Cyano-*N*-methoxycarbonyl-α-methylpiperidine (19b); IR (neat) 2970, 2250, 1720, 1450, 1280 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.43-2.34 (m, 6H), 1.81 (s, 3H), 3.23-3.67 (m, 2H), 3.87 (s, 3H); Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.38. Found: C, 59.07; H, 7.83; N, 15.20.

α-Cyano-α-ethyl-*N*-methoxycarbonylpiperidine (19c); IR (neat) 2960, 2250, 1720, 1440, 1270 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.02 (t, 3H, J=7Hz), 1.34-2.38 (m,8H), 3.07-3.48 (m, 1H), 3.49-3.86 (m, 1H), 3.72 (s, 3H); Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.28. Found: C, 61.05; H, 8.35; N, 14.31.

α-Cyano-N-methoxycarbonyl-α-octylpiperidine (19d); IR (neat) 2940, 2855, 2245, 1715, 1440, 1380, 1270 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.90 (t, 3H, J=7Hz), 1.31 (br s, 14H), 1.51-2.23 (m, 6H), 3.14-3.93 (m, 2H), 3.77 (s, 3H); Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.07; N, 9.99. Found: C, 68.56; H, 10.32; N, 10.02.

α-Allyl-α-cyano-*N*-methoxycarbonylpiperidine (19e); IR (neat) 2955, 2250, 1710, 1445, 1380, 1265, 1200 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.59-1.84 (m, 4H), 1.87-2.13 (m, 2H), 2.83 (d, 2H, J=7Hz), 3.07-3.25 (m, 1H), 3.73-3.83 (m, 1H), 3.76 (s, 3H), 5.22 (d, 1H, J=17Hz), 5.24 (d, 1H, J=10Hz), 5.70-5.93 (m, 1H); Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.33; H, 7.88; N, 13.15.

Electroreductive Decyanation: A typical electrochemical reduction was carried out as follows: Into a divided cell equipped with a zinc cathode (1 x 2 cm^2), a carbon rod anode (8 mmϕ), and a ceramic diaphragm was

added a solution of nitrile **1** (2.0 mmol) in dry DMF (15 mL) containing tetraethylammonium *p*-toluenesulfonate (0.50 g, 1.7 mmol) as a supporting electrolyte. After the necessary amount of electricity shown in Table 1 was passed, the catholyte was poured into water and the organic portion was extracted with ether (3 x 50 mL). The combined ethereal solution was dried over magnesium sulfate and the solvent was carefully distilled off. The yields of **20a**, **21a**, **b**, **e**, **22a**, **d**, and **22e**, **4**, **27**, **27'** and **29** were determined after purification by distillation or by column chromatography. The yields of **5**, **7**, **22b**, and **22c** were measured by glc method after extraction of catholyte with ether. Products **2a**, **b**, **d**, **g**, **h** were commercially available, products **2c**,[21] **e**,[22] **f**,[23] **4**,[24] **22b**[10a] and **c**,[25] **29**,[26] were known compounds. The data of new compounds are shown as follows. The yields are summarized in Tables 1, 3 and eqs 2, 4 and 5.

α-Benzyl-*N*-methoxycarbonylpyrrolidine (20a); IR (neat) 2960, 1710, 1455, 1380, 1200, 1125, 780, 710 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.49-1.95 (m, 4H), 2.56 (dd, 1H, J=10,13Hz), 2.91-3.52 (m, 3H), 3.73 (s, 3H), 3.91-4.24 (m, 1H), 7.32 (s, 5H); Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20 H, 7.81; N, 6.39. Found: C, 70.93; H, 7.95; N, 6.36.

α-Benzyl-*N*-tert-butoxycarbonylpyrrolidine (21a); IR (neat) 2995, 1700, 1400, 1180 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.48 (ms, 9H), 1.60-1.84 (m, 4H), 2.50 (dd, 1H, J=10, 13Hz), 2.89-3.47 (m, 3H), 3.76-4.13(m, 1H), 7.19 (s, 5H); Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.52; H, 8.88; N, 5.36. Found: C, 73.38; H, 8.93; N, 5.47.

***N*-*tert*-Butoxycarbonyl-α-methylpyrrolidine (21b)**; IR (neat) 2980, 1695, 1400, 1175 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.15 (d, 3H, J=6Hz), 1.48 (s, 9H), 1.49-2.09 (m, 4H), 3.35 (br s, 2H), 3.86 (br s, 1H); Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.74; H, 10.63; N, 7.56.

α-Allyl-*N*-tert-butoxycarbonylpyrrolidine (21e); IR (neat) 2960, 1685, 1390, 1160, 1105 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.47 (s, 9H), 1.62-1.96 (m, 4H), 2.02-2.21 (m, 1H), 2.47 (br s, 1H), 3.23-3.45(m, 2H), 3.80 (br s, 1H), 5.04 (d, 1H, J=10Hz), 5.06 (d, 1H, J=18Hz), 5.64-5.88 (m, 1H); Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.51; H, 10.23; N, 6.58.

α-Benzyl-*N*-methoxycarbonylpiperidine (22a); IR (neat) 2950, 1700, 1455, 1270, 710 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.09-2.01 (m, 6H), 2.67-3.16(m, 1H), 2.80 (d, 2H, J=7Hz), 3.36 (s, 3H), 4.01 (br d, 1H, J=17Hz), 4.18-4.55 (m, 1H), 7.19 (s, 5H); Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 72.27; H, 8.21; N, 6.01.

***N*-Methoxycarbonyl-α-octylpiperidine (22d)**; IR (neat) 2950, 2870, 1710, 1455, 1270, 775 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.87 (t, 3H, J=7Hz), 1.29 (br s, 14H), 1.56 (br s, 6H), 2.58-2.97 (m, 1H), 3.69 (s, 3H), 3.86-4.40 (m, 2H); Anal. Calcd for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.45; N, 5.49. Found: C, 70.75; H, 11.57; N, 5.68.

α-Allyl-*N*-methoxycarbonylpiperidine (22e); IR (neat) 2945, 1705, 1648, 1456, 1415, 1367, 1264, 1185, 1158, 1100, 920, 780 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.30-1.83 (m, 6H), 2.13-2.43 (m, 2H), 2.63-3.00 (m, 1H), 3.61 (s, 3H), 3.80-4.40 (m, 2H), 4.83-5.17 (m, 2H), 5.45-6.00 (m, 1H); Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.65. Found: C, 65.54; H, 9.47; N, 7.87.

β,γ-Unsaturated α-ethyl-*N*-methoxycarbonylpiperidine (27); IR (neat) 2960, 2920, 1705, 1650, 1455, 1410, 1255, 1200, 1110, 1090, 770, 705 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.94 (t, 3H, J=7Hz), 1.85-2.33 (m, 2H), 2.90 (t, 1H, J=12Hz), 3.57 (q, 2H, J=7Hz), 3.72 (s, 3H), 3.95-4.45 (br s, 2H), 5.63-5.88 (m, 2H); exact mass calcd for $C_9H_{15}NO_2$ 169.11027, found 169.11017.

α,β-Unsaturated α-ethyl-*N*-methoxycarbonylpiperidine (**27'**); IR (neat) 2950, 2900, 1705, 1660, 1440, 1365, 1255, 1195, 1105, 1095, 1050, 970, 770 cm^{-1}; ^{1}HNMR($CDCl_3$) δ 0.93 (t, 3H, J=7Hz), 1.72 (m, 2H), 2.02 (m, 2H), 2.43 (q, 2H, J=7Hz), 3.53 (m, 2H), 3.68 (s, 3H), 4.96 (m, 1H); exact mass calcd for $C_9H_{15}NO_2$ 169.11027, found 169.11073.

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