alternate route to anisole. This process is analogous to one of the reactions invoked to explain the electrochemical behavior of decyl mercuric halides in dimethylformamide,[37] but this pathway to anisole is neither excluded nor required by any experimental finding in the present study. In addition, it is conceivable that the *p*-anisyl radical might abstract a hydrogen atom from the solvent to yield anisole. However, in two earlier papers from our laboratory, it was found that isobutane (obtained from *tert*-butyl radicals electrogenerated at mercury from *tert*-butyl bromide)[23] and that octane (derived from *sec*-octyl radicals electrogenerated at mercury from 2-iodooctane)[34] are both formed almost exclusively via radical disproportionation and not by abstraction of a hydrogen atom from dimethylformamide. We infer from these results that transfer of a hydrogen atom from dimethylformamide to a *p*-anisyl radical does not play a significant role in the electrochemical reduction of 4-haloanisoles.

Because reduction of 4-bromoanisole at mercury requires a potential 400–500 mV more negative than that needed to electrolyze 4-iodoanisole, the transient *p*-anisyl radical should immediately accept another electron, without the need for interaction with the surface of the mercury cathode, to give the *p*-anisyl carbanion, protonation of which affords anisole. Accordingly, we conclude that reactions 1 and 2, formulated above, account satisfactorily for the electrochemistry of 4-bromoanisole at mercury as well as for the electrochemical behavior of both of the 4-haloanisoles at carbon.

Registry No. 4-Iodoanisole, 696-62-8; 4-bromoanisole, 104-92-7.

Electrochemical Oxidation of Ketone Acylhydrazones and Their HCN Adducts in NaCN–MeOH. Transformation of Ketones to Nitriles

Mitsuhiro Okimoto and Toshiro Chiba*

Department of Applied Chemistry, Kitami Institute of Technology, Kitami, Japan 090

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A variety of aliphatic and alicyclic ketone acylhydrazones ($R_1R_2C{=}NNHCOR_3$) were subjected to electrolytic oxidation in methanol containing sodium cyanide by using a carbon anode at room temperature. The hydrazones underwent an addition of hydrogen cyanide, followed by anodic oxidation to give nitriles (R_1R_2CHCN) and methyl esters ($MeOCOR_3$), liberating N_2. This electrolytic reaction was developed into a practical procedure for the preparation of nitriles, which involves an in situ formation of HCN adducts of hydrazones ($R_1R_2C(CN)NHNHCOR_3$), prior to passing current. When the HCN adducts were prepared separately and electrooxidized under similar conditions, higher yields of nitriles could be obtained.

The electrooxidative behavior of hydrazine derivatives has been extensively studied, and it has been found that the 1,2-disubstituted hydrazines and hydrazones give the corresponding diazene or diazenium compounds in many cases, by a two-electron oxidation.[1] Several reports are available for the application of these reactive species generated anodically to organic syntheses,[2] but there are only a few reports for the synthetic application of the electrolytic oxidation of ketone acylhydrazones and related compounds.[3]

In our continued investigation of the electrochemical oxidation of nitrogen-containing compounds,[4] we were led to the oxidation of these compounds since they were expected to undergo nucleophilic reaction with anionic species at the carbon atom of the azomethine and/or the carbonyl group.

The present paper describes the results of the electrolytic oxidation of ketone acylhydrazones and their HCN adducts in methanol-containing sodium cyanide, which can

Table I. Electrolytic Oxidation of Ketone Acylhydrazones in NaCN–MeOH[a]

hydrazone	$E_{1/2}$, V vs SCE[b]	yield of nitrile,[c] %	yield of ester,[c] %
1a	0.78	70	62
1b	0.85	45	43
1c	0.85	44	45
1d	–	30	31
1e	0.86	61	64
1f	0.90	44	51
1g	0.90	27	28
2a	1.08–1.10[d]	68	
2b	1.08–1.10[d]	14	
2c	<1.10	27	
2d	–	27	
3a	0.97	61	52
3b	0.98–1.02[d]	6	
3c	<1.10	34	
3d	–	21	

[a] Anolyte: hydrazone (40 mmol) and NaCN (80 mmol) in MeOH (80 mL). Constant current: 0.5 A. Current passed: 2.2 F/mol. Temperature: ca. 17 °C. [b] Read from the current–potential curve. The measurements were carried out in 0.1 M NaCN–MeOH with Pt electrodes. The concentration of hydrazone was 2 mM and the scan rate was 0.1 V/s. [c] By GLC analysis. [d] Estimated value. The i–E curve did exhibit a well-defined S-shape, due to the closeness to that of the background.

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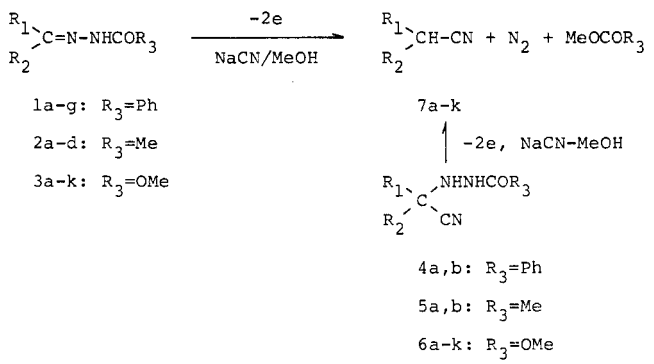
0022-3263/90/1955-1070$02.50/0

Scheme I



1-7	R_1	R_2
a	$-(CH_2)_5-$	
b	$-(CH_2)_4-$	
c	$n-C_3H_7-$	$n-C_3H_7-$
d	$iso-C_3H_7-$	$iso-C_3H_7-$
e	C_2H_5-	C_2H_5-
f	CH_3-	$n-C_6H_{13}-$
g	CH_3-	$iso-C_4H_9-$
h	$-(CH_2)_6-$	
i		
j		
k		

be utilized in the transformation of a carbonyl group of ketones into a cyanomethylene group (Scheme I).

Results and Discussion

In the present study, the benzoyl, acetyl, and carbomethoxyhydrazones which are readily available from ketones and the corresponding N-substituted hydrazines[5] were used. All of the preparative electrolyses were performed in a divided cell with a carbon rod anode under constant current conditions at room temperature.

Table I shows the results with the several hydrazones in NaCN–MeOH. During the electrolyses, an evolution of N_2 from the anolyte was always observed, and approximately equimolecular quantities of nitrile and methyl ester were formed simultaneously. The product yields differed markedly for the starting hydrazone, and they appeared to be governed by the structure of the parent ketone component (R_1 and R_2) rather than the substituent R_3 of the hydrazide moiety.

From voltammetric experiments in NaCN–MeOH with a platinum anode, it was found that the benzoylhydrazones employed are oxidized in a potential range from +0.8 to +0.9 V vs SCE, whereas acetyl- and carbomethoxyhydrazones are oxidized at about +1.1 and +1.0 V or with more anodic potentials, respectively. Thus, the oxidation potential difference seemed not to have much influence on the nitrile yields.

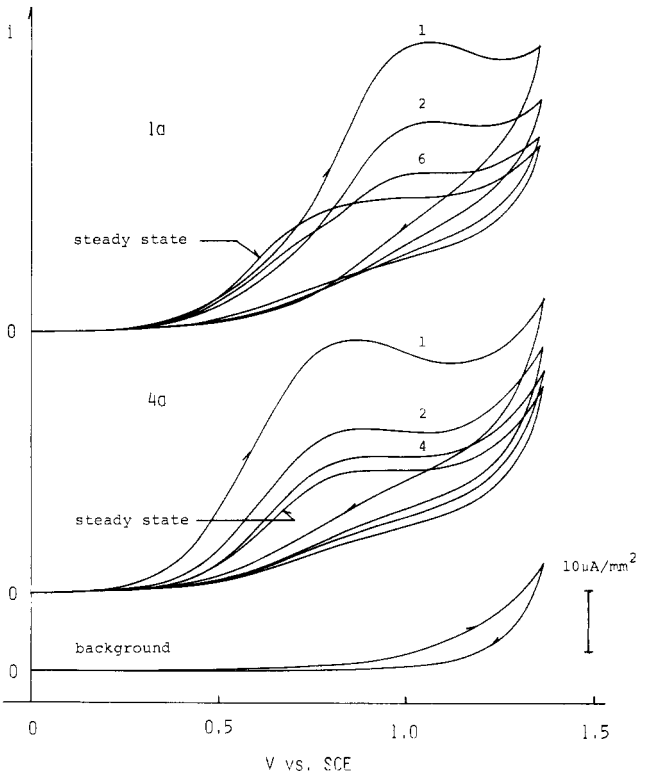


Figure 1. Cyclic voltammograms of **1a** and **4a** in NaCN–MeOH at platinum. Concentration of **1a** or **4a**: 2 mM in 0.1 M NaCN–MeOH. Scan rate: 0.1 V/s. Temperature: ca. 17 °C.

On the other hand, cyclic voltammetry of cyclohexanone benzoylhydrazone (**1a**) in NaCN–MeOH exhibited an oxidation peak at +1.05 V. When the scan was repeated beyond the peak, another wave appeared at a more cathodic potential, and the cyclic voltammogram of the stationary state was superposable on that of HCN adduct of the hydrazone (**4a**) (Figure 1).

In addition, in coulometric experiments with **1a** and **4a** at a constant potential of +0.8 V, ca. 2 F of current was counted for the formation of 1 mol of the nitrile (**7a**), respectively.[6] These results strongly suggested that the electrolytic oxidation of hydrazones to give nitriles proceeds through mainly their HCN adducts and that the addition of HCN to the hydrazone does not involve a direct electron transfer between the anode and the hydrazone.

The marked differences in nitrile yields depending upon the starting hydrazones would likely be attributed to the rate of the formation of the HCN adduct. In fact, when hydrazones were treated with HCN generated in situ from NaCN and acetic acid in MeOH (see Experimental Section), **1a** which afforded a good yield of the nitrile gave **4a** in a 90% yield within 1 day, in contrast to only about a 60% yield with **1b** even in a reaction for a week.

On the basis of the above observations, the present electrolysis was developed as a practical procedure for the preparation of nitriles. Hydrazones were electrolyzed by adding acetic acid to the anolyte system, followed by several days standing before the electrolysis, so as to allow the addition reaction of HCN to the hydrazones. Further, HCN adducts **4–6** were prepared separately and were electrooxidized in NaCN–MeOH. In these electrolyses, carbomethoxyhydrazone derivatives (**3**, **6**) were used mainly, because of the convenient isolation of nitriles by

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(6) Although the constant potential electrolyses were carried out in the same cell used for the preparative electrolyses equipped with a reference electrode, the exact control of the potential was difficult because of the evolution of N_2 near the anode surface.

Table II. Electrolytic Oxidation of Hydrazones in NaCN–MeOH after Several Days Standing[a]

hydrazone	yield of nitrile,[b] % 3 days	7 days
3a	77 [88]	82 [91]
3b	[37]	42 [46]
3c	71	77
3d	[43]	57
3e	73 [79]	
3f	62 [68]	72 [77]
3g	[53]	55 [59]
3h	[45]	59
3i	74 [88]	
3j	78 [83]	
3k	[29]	43

[a] Anolyte: hydrazone (20 mmol), NaCN (20 mmol + 40 mmol), and AcOH (25 mmol) in MeOH (80 mL). Constant current: 0.3 A. Current passed: 2.2–2.7 F/mol. Temperature: ca. 17 °C. [b] Isolated yield based on **3**. Values in brackets are GLC yield.

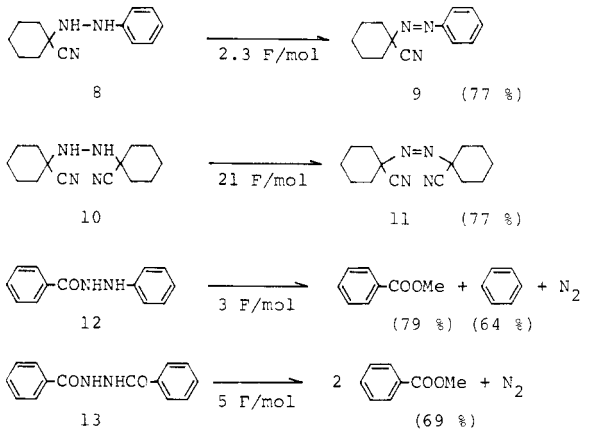
simple distillation. Although benzoylhydrazones (**1**) tended to favor the formation of nitriles in many cases, the simultaneously formed methyl benzoate has a boiling point close to those of the nitriles obtained.

As can be seen from Table II, the nitrile yields significantly increased on increasing the standing period. By this method, relatively good yields of nitriles could be obtained with hydrazones which are susceptible to an addition of HCN, whereas with hydrazones which are less reactive with HCN, such as sterically hindered ketone hydrazones and cyclopentanone hydrazone, the yields did not exceed 60%. In the electrolyses of HCN adducts themselves, however, satisfactory results were obtained in each case (Table III).

An attempted analogous electrolysis with HCN adduct of cyclohexanone phenylhydrazone (**8**) afforded phenyldiazenecyclohexylcarbonitrile (**9**), likewise 1,2-bis(1-cyanocyclohexyl)hydrazine (**10**) gave 1,1′-azobis(1-cyclohexanenitrile) (**11**)[7] as the main product, while the current efficiency was very low, presumably due to its poor solubility. In contrast, 2-substituted benzoylhydrazines such as 1-benzoyl-2-phenylhydrazine (**12**)[8] or 1,2-dibenzoylhydrazine (**13**)[9] produced methyl benzoate and benzene or methyl benzoate along with the evolution of N_2, respectively (Scheme II). Accordingly, it can be postulated that the electrolytic oxidation of HCN adduct of hydrazone (**4–6**) gives in the first step the diazene compound, which immediately undergoes cleavage to nitrile and methyl ester involving the liberation of N_2 by nucleophilic attack of methanol on the carbonyl group.[10]

The most likely reaction pathway may therefore be depicted as shown in Scheme III. Initially, the hydrazone (A) is oxidized through two electrons and one proton loss to give the cation (B), which can react with cyanide ion to form the diazene (C). As the electrolytic oxidation progresses, the local acidity near the anode surface would increase by the liberated proton, especially when the electrolysis is carried out in a divided cell. In this situation, hydrazone (A) undergoes the chemical addition reaction of HCN generated in situ. Since the HCN adduct (D) is more oxidizable than A, the oxidation of D predominantly proceeds at the anode to give C by a two-electron process. The generation of HCN may further be caused by the proton liberated in the anodic oxidation of D. The resulting C subsequently fragments to the nitrile, methyl ester, and N_2 as described above.

Scheme II



The transformation of the carbonyl group of ketones into a cyanomethylene group appears to be an attractive synthetic process. Several methods have been reported for the preparation of nitriles from ketones,[11] including the action of toluene-*p*-sulfonylmethyl isocyanate to ketones in the presence of base, and the multistep processes via addition of HCN to hydrazone derivatives. In the latter methods, the HCN adducts have subsequently been pyrolyzed[11c] or oxidized to the diazene derivatives which are readily decomposed to afford nitriles.[11a,b] Although the one-pot operation has been achieved by the use of toluene-*p*-sulfonylmethyl isocyanate[11e] or 2,4,6-triisopropylbenzenesulfonylhydrazine,[11f] these reagents are expensive and unaccessible. In contrast, the method using carbomethoxyhydrazones by Ziegler, while readily available materials are used, requires the processes no less than four steps; that is condensation of carbomethoxyhydrazine with ketone, addition of HCN, oxidation with bromine, followed by decomposition with base such as sodium methoxide.[11a,b]

The present process is related to the procedure of Ziegler; however, by the electrolytic method the desired nitriles could be obtained from the corresponding ketone in two or three steps under mild conditions without the use of oxidizing agent and special reagents. Also, the simultaneously formed methyl esters may be used again as the starting material for the acylhydrazines. But, this was not applicable for aldehyde hydrazones or unreactive hydrazones to HCN such as aromatic ketone hydrazones.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Hitachi 295 IR spectrophotometer, and the samples were analyzed as $CHCl_3$ solutions unless otherwise noted. ^1H NMR spectra were measured on a JEOL FX 200 spectrometer

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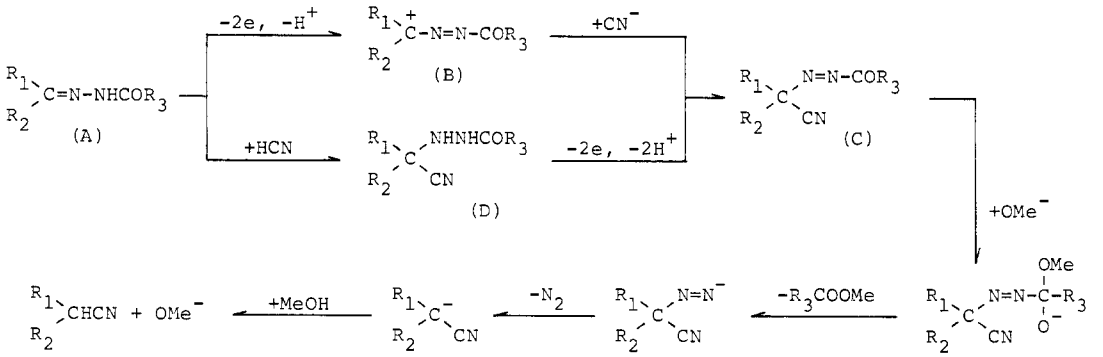
Table III. Electrolytic Oxidation of HCN Adducts of Hydrazones[a]

HCN adduct	current passed, F/mol	yield of 7,[b] %	bp, °C (mmHg)	lit. bp, °C (mmHg)	ref
4a	2.6	[83][c]			
5a	2.6	83	80–82 (22)	64–66 (12)	11 e
6a	2.6	86		61 (11)	11f
4b	2.3	[64]			
5b	2.3	65	160–165	101 (100)	11f
6b	2.5	71			
6c	2.3	79	67–69 (13)	64 (11), 63 (11)	11e, 11f
6e	2.1	70	144–146	141–143	12
6f	2.2	78	87–89 (14)	85–90[d]	13
6g	2.2	72	74–76 (52)	93 (99)	14
6h	2.2	84	90–91 (14)	85–86 (10)	11e
6i	2.6	83	79–82 (17)	79–81 (16)	15
6j	2.3	83	124–126 (17)	116–117 (8)	16
6k	2.6	86	89–90 (14)	73–75 (10)	17

[a] Anolyte: HCN adduct (40 mmol) and NaCN (80 mmol) in MeOH (80 mL). Constant current: 0.5 A. Temperature: ca. 17 °C. [b] Isolated yield based on HCN adduct. [c] GLC yield. [d] Water aspiration.

Scheme III



at 200 MHz in $CDCl_3$. Chemical shifts are reported in δ units relative to internal TMS. Gas–liquid chromatography (GLC) were performed on a Hitachi 163 gas chromatograph using a 2-m glass column packed with FFAP on Chromosorb W AW and a 1-m stainless steel column packed with Silicone SE-30 on Uniport B, or on a Shimadzu GC-14A gas chromatograph using a 30-m Shimadzu ULBON HR-20M glass capillary column (0.53 mm in diameter). The carrier gas for each was N_2, and the detector was FID. Mass spectra were obtained on a Hitachi M-52 spectrometer. Ionization potential was 70 eV. Elemental analyses were performed by Instrumental Analyses Laboratories, Hokkaido University, Sapporo.

Electrolysis apparatuses used were similar to those previously described.[4b] Voltammetric measurements were carried out in a divided H-type cell provided with a platinum disk electrode, a saturated calomel reference electrode, and a platinum wire as the counter electrode. The anolyte volume was ca. 25 mL. Preparative electrolyses were conducted in a 100-mL cylindrical flask equipped with a fine-frit glass cup as the cathode compartment, four carbon rods (8-mm diameter, 100-mm long) as the anode, and a platinum coil cathode.

Materials. Benzoyl-, acetyl-, and carbomethoxyhydrazine were prepared by the methods in the literature.[18–20] All of the hydrazones were prepared by refluxing a solution of the corresponding substituted hydrazine (0.2 mol) and commercially available ketone (0.2 mol) in MeOH (100 mL) containing a few drops of acetic acid for 6 h, except for diisopropyl ketone (3 days).[5] Approximately quantitative yields were obtained in most cases. The HCN adducts of hydrazones were prepared by treatment of hydrazone (0.1 mol) with NaCN (0.3 mol) in acetic acid–MeOH (60 mL/400 mL) at room temperature for several days according to the procedure of Cacchi,[11c] or by our convenient procedure using phase-transfer catalyst from hydrazone.[21] Compound **8** was prepared by mixing cyclohexanone (0.1 mol), phenylhydrazine hydrochloride (0.1 mol), and NaCN (0.1 mol) in H_2O (150 mL) at room temperature overnight.[22] The white solid thus obtained was recrystallized from MeOH to give **8** in a yield of 70%. Compounds **10**, **12**, and **13** were prepared by usual methods given in the literature.[7,8,23] Since many of the starting materials were not found in the literature, they were characterized with IR, ^1H NMR, and elemental analyses. Their physical and spectral data are shown afterward.

Preparative Electrolyses of 1–6. General Procedure. (A) Immediate Electrolyses of 1–3. An anolyte consisting of hydrazone (40 mmol) and NaCN (80 mmol) in MeOH (80 mL) was electrooxidized under a constant current of 0.5 A for 4.7 h. The amount of current passed was 2.2 F/mol. During the electrolysis, the anolyte was stirred by a magnetic stirring bar, and the cell was cooled with running water.

(B) Electrolyses of 1–3 after Standing of the Anolyte. The flask was charged with hydrazone (20 mmol), NaCN (20 mmol), and MeOH (80 mL), and then acetic acid (25 mmol) was added carefully with stirring. The flask was stoppered and allowed to stand in the dark for several days at room temperature. Before the beginning of the electrolysis, additional NaCN (40 mmol) was dissolved into the solution. Then the electrodes were placed, and a constant current of 0.3 A was passed through the cell.

(C) Electrolyses of 4–6. The HCN adduct of hydrazone (40 mmol) was electrooxidized in MeOH (80 mL) containing NaCN (80 mmol) under a constant current of 0.5 A until no further product formation was detected.

Posttreatment of the Electrolyses. After the electrolysis, the anolyte was analyzed by GLC, and the product yields that are indicated in the tables were determined by internal standard method. The conditions of the GLC analyses and the retention times of products were as follows [product: column, column

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temperature, flow rate of carrier gas, retention time of product, internal standard (retention time)]. **7a**: FFAP 2 m, 180 °C, 6 mL/min, 8.0 min, phenetole (5.6 min). **7b**: FFAP 2 m, 160 °C, 15 mL/min, 3.9 min, naphthalene (12.8 min). **7c**: FFAP 2 m, 140 °C, 5 mL/min, 11.7 min, phenetole (14.1 min). **7d**: SE-30 1 m, 115 °C, 6.5 mL/min, 2.9 min, tetralin (7.4 min). **7e**: FFAP 2 m, 140 °C, 11.5 mL/min, 3.5 min, phenetole (7.2 min). **7f**: FFAP 2 m, 170 °C, 10 mL/min, 5.6 min, phenetole (4.2 min). **7g**: FFAP 2 m, 150 °C, 5.5 mL/min, 6.6 min, phenetole (11.4 min). **7h**: FFAP 2 m, 170 °C, 10 mL/min, 10.4 min, phenetole (4.2 min). **7i**: FFAP 2 m, 180 °C, 6 mL/min, 8.5 min, phenetole (5.6 min). **7j**: FFAP 2 m, 180 °C, 11.5 mL/min, 12.0 and 13.9 min, naphthalene (10.8 min). **7k**: FFAP 2 m, 170 °C, 8 mL/min, 12.6 min, naphthalene (17.6 min). Methyl benzoate: FFAP 2 m, 160 °C, 15 mL/min, 8.1 min, naphthalene (12.8 min). Benzene: FFAP 2 m, 100 °C, 3 mL/min, 7.7 min, toluene (11.3 min).

For the isolation of the products, the solvent was removed under reduced pressure without heating, and the residue was treated with H_2O.[24] The oily layer was extracted into CH_2Cl_2, sufficiently washed with H_2O, dried with anhydrous sodium sulfate, and distilled. The isolated yields by distillation are given in Tables II and III. Analytical samples were obtained by redistillation.

Cyclohexanecarbonitrile (7a): bp 85 °C (22 mm) [lit.[11e] bp 64–66 °C (12 mm), lit.[11f] bp 61 °C (11 mm)]; IR (neat) ν 2240 cm^{-1} (CN); ^1H NMR δ 1.3–1.6 (m, 4 H), 1.6–2.0 (m, 6 H), 2.64 (m, 1 H); MS m/z (relative intensity) 110 ($M^+ + 1$, 5), 109 (M^+, 4), 108 ($M^+ - 1$, 22), 56 (100), 54 (76), 41 (73). Anal. Calcd for $C_7H_{11}N$: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.92; H, 10.20; N, 12.73.

Cyclopentanecarbonitrile (7b): bp 108–110 °C (108 mm) [lit.[11f] bp 101 °C (100 mm)]; IR (neat) ν 2240 cm^{-1} (CN); ^1H NMR δ 1.6–2.2 (m, 8 H), 2.76 (ca. pent, 1 H); MS m/z (relative intensity) 96 ($M^+ + 1$, 8), 56 (100), 42 (78). Although satisfactory combustion analysis was not obtained, the purity of the product was judged to be ≥97% by GLC analysis (FFAP 2 m), and IR and ^1H NMR data were identical with those reported in the literature.[11f]

2-*n*-Propylvaleronitrile (7c): bp 67–69 °C (13 mm) [lit.[11e] bp 64 °C (11 mm), lit.[11f] bp 63 °C (11 mm)]; IR (neat) ν 2240 cm^{-1} (CN); ^1H NMR δ 0.96 (t, 6 H), 1.4–1.7 (m, 8 H), 2.55 (br m, 1 H); MS m/z (relative intensity) 126 ($M^+ + 1$, 7), 96 (17), 83 (43), 54 (100), 43 (42). Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.41; H, 12.04; N, 11.28.

3-Methyl-2-isopropylbutyronitrile (7d): bp 86–87 °C (45 mm) (lit.[12] bp 169–170 °C); IR (neat) ν 2230 cm^{-1} (CN); ^1H NMR δ 1.05 (dd, J = 9.8, 6.8 Hz, 12 H), 1.93 (oct, 2 H), 2.14 (t, 1 H); MS m/z (relative intensity) 126 ($M^+ + 1$, 8), 83 (46), 66 (100). Satisfactory combustion analysis was not obtained. The purity of the product was judged to be ≥93% by GLC analysis (SE-30 1 m).

2-Ethylbutyronitrile (7e): bp 82–83 °C (102 mm) (lit.[12] bp 141–143 °C); IR (neat) ν 2230 cm^{-1} (CN); ^1H NMR δ 1.08 (t, 6 H), 1.64 (pent, 4 H), 2.42 (pent, 1 H); MS m/z (relative intensity) 98 ($M^+ + 1$, 4), 82 (39), 69 (30), 55 (100), 29 (23). Satisfactory combustion analysis was not obtained. The purity of the product was judged to be ≥98% by GLC analysis (FFAP 2 m).

2-Methyloctanenitrile (7f): bp 96–97 °C (18 mm) [lit.[13] bp 85–90 °C (water aspiration)]; IR (neat) ν 2240 cm^{-1} (CN); ^1H NMR δ 0.89 (distorted t, 3 H), 1.2–1.7, 1.31 (m, d, J = 7.3 Hz, total 13 H), 2.60 (ca, sext, 1 H); MS m/z (relative intensity) 140 ($M^+ + 1$, 6), 138 ($M^+ - 1$, 5), 110 (38), 97 (77), 96 (100), 82 (48), 68 (55), 55 (77), 43 (95). Anal. Calcd for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.52; H, 12.49; N, 10.05.

2,4-Dimethylvaleronitrile (7g): bp 80–81 °C (55 mm) [lit.[14] bp 93 °C (99 mm)]; IR (neat) ν 2230 cm^{-1} (CN); ^1H NMR δ 0.94 (dd, J = 6.8, 2.9 Hz, 6 H), 1.2–1.4, 1.31 (m, d, J = 6.8 Hz, total 4 H), 1.5–1.7 (m, 1 H), 1.7–1.95 (m, 1 H), 2.66 (m, 1 H); MS m/z (relative intensity) 112 ($M^+ + 1$, 6), 100 ($M^+ - 1$, 3), 69 (100), 57 (62), 55 (74), 54 (58), 46 (58), 41 (57). Anal. Calcd for $C_8H_{13}N$: C, 75.61; H, 11.79; N, 12.60. Found: C, 75.21; H, 11.70; N, 12.59.

Cycloheptanecarbonitrile (7h): bp 95 °C (13 mm) [lit.[11e] bp 85–86 °C (10 mm)]; IR (neat) ν 2230 cm^{-1} (CN); ^1H NMR δ 1.5–2.0 (m, 12 H), 2.79 (m, 1 H); MS m/z (relative intensity) 124 ($M^+ + 1$, 2), 123 (M^+, 3), 122 ($M^+ - 1$, 16), 94 (41), 81 (29), 55 (100), 42 (38). Anal. Calcd for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 78.06; H, 10.66; N, 11.23.

2-Methylcyclohexanecarbonitrile (7i): bp 92–94 °C (23 mm) [lit.[15] bp 79–81 °C (16 mm)]. GLC analysis (ULBON, HR-20M, 30 m, at 90 °C) revealed that the product consists of two stereoisomers with the retention times of 16.9 and 17.9 min. The area ratio was 46:54. This was characterized as a mixture: IR (neat) ν 2230 cm^{-1} (CN); ^1H NMR δ 1.08, 1.12 [d, d, J = 8.8 Hz each, total 3 H (45:55)], 1.2–1.4 (m, 2 H), 1.5–1.9 (m, 6 H), 1.9–2.2 (m, ca. 1.5 H), 2.83 (br pent, ca. 0.5 H); MS m/z (relative intensity) 124 ($M^+ + 1$, 4), 123 (M^+, 2), 122 ($M^+ - 1$, 5), 55 (100). Anal. Calcd for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 77.68; H, 10.81; N, 11.31.

4-*tert*-Butylcyclohexanecarbonitrile (7j): bp 126–127 °C (18 mm) [lit.[16] bp 116–117 °C (8 mm)]. GLC analysis (FFAP 2 m, at 180 °C) revealed that the product consists of two stereoisomers with the retention times of 12.0 and 13.9 min. The area ratio was 57:43. From the ^1H NMR data, the former was assumed to be the cis form and the later was trans. This was characterized as a mixture: IR (neat) ν 2240 cm^{-1} (CN); ^1H NMR δ 0.84, 0.87 [s, s, total 9 H (42:58)], 1.0 (m, 1 H), 1.2–1.95 (m complex, 5 H), 1.95–2.4 (m complex, ca. 2.4 H), 2.92 (br pent, ca. 0.6 H); MS m/z (relative intensity) 166 ($M^+ + 1$, 1), 165 (M^+, 0.7), 57 (100). Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48. Found: C, 79.66; H, 11.75; N, 8.42.

From the mixture, the cis isomer crystallized directly on standing in an ice box. The white crystals were collected by filtration and washed with small portions of Et_2O: mp 51–54 °C (lit.[16] mp 59.5–60 °C); ^1H NMR δ 0.87 (s, 9 H), 1.0 (m, 1 H), 1.2–1.6 (m, 4 H), 1.77 (br d, J = 12 Hz, 2 H), 2.04 (br d, J = 12 Hz, 2 H), 2.92 (br pent, 1 H).

2-Norbornanecarbonitrile (7k): bp 89–90 °C (14 mm), mp 42–46 °C [lit.[17] bp 73–75 °C (10 mm), mp 43–45 °C]. GLC analysis (ULBON, HR-20M, 30 m, at 110 °C) revealed that the product consists of two stereoisomers with the retention times of 16.3 and 17.7 min. The area ratio was 40:60. This was characterized as a mixture: IR ν 2220 cm^{-1} (CN); ^1H NMR δ 1.1–1.9 (m complex, ca. 7.5 H), 1.9–2.1 (ddt ?, ca. 0.6 H), 2.3–2.45 (m, ca. 1.4 H), 2.5 (br m, 0.6 H), 2.6 (br m, 0.4 H), 2.63–2.8 (m, ca. 0.6 H); MS m/z (relative intensity) 121 (M^+, 3), 120 ($M^+ - 1$, 6), 68 (100). Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.18; H, 8.96; N, 11.22.

Electrolysis of 8. A solution of 8 (40 mmol) in MeOH (80 mL) containing NaCN (80 mmol) was electrooxidized under a constant current of 0.5 A. The amount of current passed was 2.3 F/mol. After the usual workup, the crude product was recrystallized from hexane to give yellowish flakes of **9** in a yield of 77%. **9**: mp 55–56 °C; IR ν 2230 cm^{-1} (CN), no NH absorption; ^1H NMR δ 1.1–2.3 (m, 10 H), 7.48 (m, 3 H), 7.7 (m, 2 H). Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.42; H, 7.12; N, 19.70.

Electrolysis of 10. Finely powdered **10** (10 mmol) was suspended in MeOH (80 mL) containing NaCN (30 mmol) and electrooxidized under a constant current of 0.3 A until 12 F/mol of current was passed. From the anolyte, white solid of **11** was obtained in a yield of 77%. **11** had mp 112–115 °C (lit.[7] mp 113–116 °C). The mixed melting point with authentic sample was undepressed.

Electrolysis of 12 and 13. Analogously, the benzoylhydrazine (10 mmol) was electrooxidized in MeOH (80 mL) containing NaCN (30 mmol) under a constant current of 0.3 A. The resulting anolyte was analyzed by GLC (FFAP 2 m).

Characterization of Starting Materials. Cyclohexanone benzoylhydrazone (1a): needles from EtOH, mp 164–165 °C (lit.[25] mp 162–164 °C); IR ν 3380 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 1.7 (br m, 6 H), 2.4 (br m, 4 H), 7.4 (m, 3 H), 7.8 (m, 2 H), 8.6 (br s, 1 H). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.34; H, 7.67; N, 13.11.

Cyclopentanone benzoylhydrazone (1b): rodlike crystals from EtOH, mp 149–151 °C (lit.[25] mp 150–152 °C); IR ν 3360 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 1.7–2.0 (m, 4 H), 2.3–2.7 (m, 4 H), 7.4 (m, 3 H), 7.8 (m, 2 H), 8.6 (br s, 1 H). Anal. Calcd for

(24) In many cases, a small amount of dimethyl oxalimidate [mp 32–34 °C, bp 44 °C (15 mm)] was formed. Probably, the byproduct was derived from dicyan by methanolysis. See: Nef, J. U. *Justus Leibigs Ann. Chem.* **1895**, *287*, 265.

(25) Offe, H. A.; Siefken, W.; Domagk, G. *Z. Naturforsch.* **1952**, *7b*, 446.

$C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.18; H, 7.04; N, 13.80.

4-Heptanone benzoylhydrazone (1c): needles from cyclohexane, mp 106–108 °C; IR ν 3380 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 1.02 (distorted t, 6 H), 1.61 (distorted sext, 4 H), 2.32 (distorted q, 4 H), 7.44 (m, 3 H), 7.8 (m, 2 H), 8.85 (br s, 1 H). Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.40; H, 8.79; N, 11.95.

2,4-Dimethyl-3-pentanone benzoylhydrazone (1d): cottonlike crystals from benzene, mp 150–151 °C; IR ν 3450 (NH), 1675 cm^{-1} (CO); ^1H NMR δ 1.21 (br m, 12 H), 2.6–2.8 (br m, 1 H), 2.93 (m, 1 H), 7.43 (m, 3 H), 7.77 (m, 2 H), 8.85 (br s, 1 H). Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.43; H, 8.72; N, 11.96.

3-Pentanone benzoylhydrazone (1e): needles from MeOH–H_2O, mp 92–94 °C; IR ν 3380 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 1.17 (t, 6 H), 2.38 (distorted q, 4 H), 7.47 (m, 3 H), 7.81 (m, 2 H), 8.7 (br s, 1 H). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.45; H, 7.92; N, 13.70.

2-Octanone benzoylhydrazone (1f): cottonlike crystals from hexane, mp 79.5–81 °C; IR ν 3380 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 0.88 (distorted t, 3 H), 1.31 (br m, 6 H), 1.58 (br m, 2 H), 1.94, 2.13 (s, s, total 3 H), 2.30, 2.42 (t, t, total 2 H), 7.48 (m, 3 H), 7.81 (br m, 2 H), 8.6 (br s, 1 H). Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37. Found: C, 73.09; H, 9.06; N, 11.47.

4-Methyl-2-pentanone benzoylhydrazone (1g): leaflets from cyclohexane, mp 111–112 °C; IR ν 3390 (NH), 1680 cm^{-1} (CO); ^1H NMR δ 0.96, 1.00 (d, d, J = 6.6 and 5.8 Hz, total 6 H), 1.94, 2.10 (s, s, total 3 H), 2.0–2.4 (m, 3 H), 7.45 (m, 3 H), 7.80 (m, 2 H), 8.8 (br s, 1 H). Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31; N, 12.83. Found: C, 71.58; H, 8.38; N, 12.94.

Cyclohexanone acetylhydrazone (2a): leaflets from cyclohexane, mp 126.5–127.5 °C; IR ν 3350 (NH), 1660 cm^{-1} (CO); ^1H NMR δ 1.7 (br m, 6 H), 2.25, 2.3 (s, br m, total 7 H), 9.05 (br s, 1 H). Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.39; H, 9.32; N, 18.18.

Cyclopentanone acetylhydrazone (2b): needles from cyclohexane, mp 124–125 °C; IR ν 3350 (NH), 1660 cm^{-1} (CO); ^1H NMR δ 1.7–2.0 (m, 4 H), 2.24, 2.26 (s, t, total 5 H), 2.40 (t, 2 H), 8.7 (br s, 1 H). Anal. Calcd for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.99. Found: C, 60.06; H, 8.58; N, 19.92.

4-Heptanone acetylhydrazone (2c): rodlike crystals from hexane, mp 39–40 °C; IR ν 3340 (NH), 1660 cm^{-1} (CO); ^1H NMR δ 0.96 (dt, J = 7.3, 6.6 Hz, 6 H), 1.4–1.7 (m, 4 H), 2.1–2.2 (m, 4 H), 2.26 (s, 3 H), 8.7 (br s, 1 H). Anal. Calcd for $C_9H_{18}N_2O$: C, 63.49; H, 10.66; N, 16.46. Found: C, 63.40; H, 10.63; N, 16.54.

2,4-Dimethyl-3-pentanone acetylhydrazone (2d): leaflets from cyclohexane, mp 93–94.5 °C; IR ν 3350 (NH), 1660 cm^{-1} (CO); ^1H NMR δ 1.10 (dd, J = 7.3, 5.8 Hz, 12 H), 2.26 (s, 3 H), 2.62, 2.81 (hept, hept, 1 H, 1 H), 8.7 (br s, 1 H). Anal. Calcd for $C_9H_{18}N_2O$: C, 63.49; H, 10.66; N, 16.46. Found: C, 63.47; H, 10.63; N, 16.47.

Cyclohexanone carbomethoxyhydrazone (3a): viscous oil[5c] (this could not be purified and was used in the next step as such); IR ν 3380 (NH), 1740 cm^{-1} (OCO); ^1H NMR δ 1.7 (br m, 6 H), 2.2–2.5 (m, 4 H), 3.82 (s, 3 H), 8.2 (br s, 1 H).

Cyclopentanone carbomethoxyhydrazone (3b): rodlike crystals from cyclohexane, mp 77–79 °C (lit.[5c] mp 78–79 °C); IR ν 3380 (NH), 1740 cm^{-1} (OCO); ^1H NMR δ 1.7–2.0 (m, 4 H), 2.22 (t, 2 H), 2.47 (t, 2 H), 3.82 (s, 3 H), 7.7 (br s, 1 H). Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.78; H, 7.82; N, 18.03.

4-Heptanone carbomethoxyhydrazone (3c): needles from hexane, mp 88.5–90.5 °C; IR ν 3380 (NH), 1740, 1710 cm^{-1} (OCO); ^1H NMR δ 0.96 (dt, J = 7.3, 11.7 Hz, 6 H), 1.4–1.7 (m, 4 H), 2.1–2.3 (m, 4 H), 3.82 (s, 3 H), 8.0 (br s, 1 H). Anal. Calcd for $C_9H_{18}N_2O_2$: C, 58.03; H, 9.47; N, 15.04. Found: C, 57.87; H, 9.69; N, 15.14.

2,4-Dimethyl-3-pentanone carbomethoxyhydrazone (3d): cottonlike crystals from cyclohexane, mp 131–132 °C; IR ν 3380 (NH), 1740, 1710 cm^{-1} (OCO); ^1H NMR δ 1.14 (dd, J = 6.6, 5.8 Hz, 12 H), 2.65 (hept, 1 H), 2.80 (hept, 1 H), 7.8 (br s, 1 H). Anal. Calcd for $C_9H_{18}N_2O_2$: C, 58.03; H, 9.74; N, 15.04. Found: C, 58.07; H, 9.72; N, 15.10.

3-Pentanone carbomethoxyhydrazone (3e): needles from cyclohexane, mp 72–73 °C (lit.[5c] mp 65–66 °C); IR ν 3380 (NH), 1745 cm^{-1} (OCO); ^1H NMR δ 1.11 (dt, J = 8.0, 3.7 Hz, 6 H), 2.2–2.4 (m, 4 H), 3.83 (s, 3 H), 7.7 (br s, 1 H). Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.22; H, 8.93; N, 17.68.

2-Octanone carbomethoxyhydrazone (3f): needles from hexane, mp 59–61 °C; IR ν 3370 (NH), 1740 cm^{-1} (OCO); ^1H NMR δ 0.87 (distorted t, 3 H), 1.1–1.6 (br m, 8 H), 1.82, 2.01 (s, s, total 3 H), 2.18, 2.30 (t, t, total 2 H), 3.82 (s, 3 H), 7.75 (br s, 1 H). Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 59.97; H, 10.07; N, 13.99. Found: C, 60.03; H, 10.15; N, 14.06.

4-Methyl-2-pentanone carbomethoxyhydrazone (3g): cottonlike crystals from cyclohexane, mp 75.5–76.5 °C; IR ν 3380 (NH), 1750, 1715 cm^{-1} (OCO); ^1H NMR δ 0.92, 0.97 (d, d, J = 6.6 and 5.9 Hz, total 6 H), 1.81, 2.02 (s, s, total 3 H), 2.09, 2.21 (d, d, J = 9.5 and 7.3 Hz, total 2 H), 1.9 (m, 1 H), 3.82 (s, 3 H), 7.7 (br s, 1 H). Anal. Calcd for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27. Found: C, 55.67; H, 9.43; N, 16.38.

Cycloheptanone carbomethoxyhydrazone (3h): needles from cyclohexane, mp 78.5–79.5°C; IR ν 3380 (NH), 1750, 1720 cm^{-1} (OCO); ^1H NMR δ 1.60 (br m, 8 H), 2.30 (m, 2 H), 2.50 (m, 2 H), 3.82 (s, 3 H), 7.8 (br s, 1 H). Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.68; H, 8.79; N, 15.28.

2-Methylcyclohexanone carbomethoxyhydrazone (3i): prisms from cyclohexane, mp 82–83 °C; IR ν 3380 (NH), 1750, 1715 cm^{-1} (OCO); ^1H NMR δ 1.15, 1.17 (d, d, J = 7.3 Hz each, total 3 H), 1.3–1.9 (m, 6 H), 2.0–2.2 (m, ca. 0.7 H), 2.2–2.6 (m, 2 H), 2.92 (br m, ca. 0.3 H), 3.82, 3.84 (s, s, total 3 H), 7.9 (br s, 1 H). Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.21. Found: C, 58.65; H, 8.82; N, 15.29.

4-*tert*-Butylcyclohexanone carbomethoxyhydrazone (3j): viscous oil (this could not be purified and was used in the next step as such); IR ν 3380 (NH), 1745, 1715 cm^{-1} (OCO); ^1H NMR δ 0.88 (s, 9 H), 1.27 (m, 3 H), 1.7–2.4 (m complex, 4 H), 2.5–2.8 (m, 2 H), 3.83 (s, 3 H), 8.0 (br s, 1 H).

2-Norbornanone carbomethoxyhydrazone (3k): needles from cyclohexane, mp 95.5–97 °C; IR ν 3375 (NH), 1745, 1720 cm^{-1} (OCO); ^1H NMR δ 1.2–1.75 (m, complex, 6 H), 1.84 (dd, J = 16.8, 2.9 Hz, 1 H), 2.11 (ddd, J = 16.1, 4.4, 1.5 Hz, 1 H), 2.61 (br s, 1 H), 2.98 (br s, 1 H), 3.82 (s, 3 H), 7.42 (s, 1 H). Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.39; H, 7.70; N, 15.45.

1-(1-Cyanocyclohexyl)-2-benzoylhydrazine (4a): rodlike crystals from MeOH–H_2O, mp 133–134 °C (lit.[22] mp 131–132.5 °C); IR ν 3400, 3250 (NH), 2220 vw (CN), 1660 cm^{-1} (CO); ^1H NMR δ 1.1–2.3 (m, 10 H), 4.1 (br s, 1 H), 7.4 (m, 3 H), 7.8 (m, 3 H). Anal. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.21. Found: C, 69.10; H, 7.07; N, 17.33.

1-(1-Cyanocyclopentyl)-2-benzoylhydrazine (4b): needles from MeOH–H_2O, mp 127–128 °C; IR ν 3340, 3230 (NH), 2210 (CN), 1655 cm^{-1} (CO); ^1H NMR δ 1.7–2.3 (m, 8 H), 4.3 (br s, 1 H), 7.5 (m, 3 H), 7.8 (m, 3 H). Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.29; H, 6.66; N, 18.33.

1-(1-Cyanocyclohexyl)-2-acetylhydrazine (5a): rodlike crystals from MeOH–H_2O, mp 106–107.5 °C (lit.[22] mp 101.5–103 °C); IR ν 3410, 3270 (NH), 2220 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 1.1–1.9 (m, 8 H), 2.04 (s, 3 H), 2.1–2.2 (m, 2 H), 3.8 (br s, 1 H), 7.1 (br s, 1 H). Anal. Calcd for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.77; H, 8.32; N, 23.22.

1-(1-Cyanocyclopentyl)-2-acetylhydrazine (5b): needles from benzene, mp 106–107.5 °C; IR ν 3420, 3180 (NH), 2230 (CN), 1695 cm^{-1} (CO); ^1H NMR δ 1.7–2.2, 2.03 (m, s, total 11 H), 4.8 (br s, 1 H), 7.7 (br s, 1 H). Anal. Calcd for $C_8H_{13}N_3O$: C, 57.46; H, 7.84; N, 25.13. Found: C, 57.32; H, 7.61; N, 25.02.

1-(1-Cyanocyclohexyl)-2-carbomethoxyhydrazine (6a): needles from MeOH–H_2O, mp 133–134 °C (lit.[11b] mp 135–136 °C); IR ν 3400 (NH), 2210 vw (CN), 1740 cm^{-1} (OCO); ^1H NMR δ 1.1–2.2 (m, 10 H), 3.77 (s, 3 H), 4.34 (s, 1 H), 6.55 (s, 1 H). Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.80; H, 7.67; N, 21.31. Found: C, 54.72; H, 7.66; N, 21.34.

1-(1-Cyanocyclopentyl)-2-carbomethoxyhydrazine (6b): needles from cyclohexane, mp 92.5–94 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 1.7–2.2 (m, 8 H), 3.76 (s, 3 H), 4.10 (s, 1 H), 6.59 (s, 1 H). Anal. Calcd for $C_8H_{13}N_3O_2$: C, 52.44; H, 7.15; N, 22.94. Found: C, 52.59; H, 7.30; N, 23.08.

1-[4-(4-Cyanoheptyl)]-2-carbomethoxyhydrazine (6c): needles from cyclohexane, mp 51–53 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^1H NMR δ 0.98 (t, 6 H), 1.4–1.8 (m, 8 H), 3.78 (s, 3 H), 4.36 (s, 1 H), 6.43 (s, 1 H). Anal. Calcd for

$C_{10}H_{19}N_3O_2$: C, 56.31; H, 8.96; N, 19.70. Found: C, 56.43; H, 9.17; N, 19.60.

1-[3-(3-Cyanopentyl)]-2-carbomethoxyhydrazine (6e): needles from cyclohexane, mp 89–91.5 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.05 (t, 6 H), 1.74 (q, 4 H), 3.75 (s, 3 H), 4.02 (s, 1 H), 6.35 (s, 1 H). Anal. Calcd for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.69. Found: C, 51.98; H, 8.11; N, 22.75.

1-[2-(2-Cyanooctyl)]-2-carbomethoxyhydrazine (6f): leaflets from hexane, mp 45.5–47 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 0.89 (distorted t, 3 H), 1.1–1.9, 1.44 (m, s, total 13 H), 3.76 (s, 3 H), 4.0 (br s, 1 H), 6.4 (s, 1 H). Anal. Calcd for $C_{11}H_{21}N_3O_2$: C, 58.12; H, 9.31; N, 18.49. Found: C, 58.06; H, 9.37; N, 18.61.

1-[2-(4-Methyl-2-cyanopentyl)]-2-carbomethoxyhydrazine (6g): cottonlike crystals from cyclohexane: mp 96–97 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.06 (dd, J = 6.6, 2.9 Hz, 6 H), 1.47 (s, 3 H), 1.66 (dd, J = 8.8, 6.6 Hz, 2 H), 1.9 (m, 1 H), 3.77 (s, 3 H), 4.19 (s, 1 H), 6.48 (s, 1 H). Anal. Calcd for $C_9H_{17}N_3O_2$: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.30; H, 8.68; N, 21.20.

1-(1-Cyanocycloheptyl)-2-carbomethoxyhydrazine (6h): needles from MeOH–H_2O, mp 117–119 °C; IR ν 3410 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.4–2.2 (m, 12 H), 3.7 (s, 4 H), 6.41 (s, 1 H). Anal. Calcd for $C_{10}H_{17}N_3O_2$: C, 56.85; H, 8.11; N, 19.89. Found: C, 56.78; H, 8.11; N, 19.86.

1-(1-Cyano-2-methylcyclohexyl)-2-carbomethoxyhydrazine (6i): rodlike crystals from MeOH–H_2O, mp 139–140 °C (lit.[11b] mp 138 °C); IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.14 (d, J = 5.9 Hz, 3 H), 1.2–1.9 (m complex, 8 H), 2.20 (dd, J = 9.5, 2.9 Hz, 1 H), 3.76 (s, 3 H), 4.0 (br s, 1 H), 6.25 (br s, 1 H). Anal. Calcd for $C_{10}H_{17}N_3O_2$: C, 56.85; H, 8.11; N, 19.89. Found: C, 56.85; H, 8.12; N, 19.73.

1-(1-Cyano-4-*tert*-butylcyclohexyl)-2-carbomethoxyhydrazine (6j): needles from MeOH–H_2O, mp 137–138 °C (lit.[11b] mp 132–133.5 °C); IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 0.88 (s, 9 H), 0.9–1.1 (m, 1 H), 1.42 (m, 4 H), 1.86 (br d, J = 13 Hz, 2 H), 2.16 (br d, J = 13 Hz, 2 H), 3.77 (s, 3 H), 3.8 (br s, 1 H), 6.3 (br s, 1 H). Anal. Calcd for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59. Found: C, 61.49; H, 9.25; N, 16.57.

1-[2-(2-Cyanonorbornyl)]-2-carbomethoxyhydrazine (6k): cubes from benzene, mp 125–126 °C; IR ν 3400 (NH), 2210 (CN), 1740 cm^{-1} (OCO); ^{1}H NMR δ 1.2–1.7 (m complex, 5 H), 1.84 (d?, J = 11 Hz, 1 H), 1.9–2.2 (m complex, 2 H), 2.36 (br m, 1 H), 2.59 (br m, 1 H), 3.76 (s, 3 H), 4.28 (br s, 1 H), 6.35 (br s, 1 H). Anal. Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.57; H, 7.25; N, 20.08.

1-(1-Cyanohexyl)-2-phenylhydrazine (8): rhombs from MeOH, mp 101–103 °C; IR ν 3300 (NH), 2220 (CN), 1600 cm^{-1}; ^{1}H NMR δ 1.2–2.2 (m, 10 H), 4.5 (br s, 2 H), 6.8 (m, 3 H), 7.2 (m, 2 H). Anal. Calcd for $C_{13}H_{17}N_3$: C, 72.52; H, 7.96; N, 19.52. Found: C, 72.70; H, 7.92; N, 19.48.

Registry No. **1a**, 24214-79-7; **1b**, 24214-78-6; **1c**, 124243-15-8; **1d**, 124243-16-9; **1e**, 14850-77-2; **1f**, 124243-17-0; **1g**, 124243-18-1; **2a**, 28766-50-9; **2b**, 28766-48-5; **2c**, 124243-19-2; **2d**, 14849-39-9; **3a**, 14702-42-2; **3b**, 14702-41-1; **3c**, 14978-96-2; **3d**, 124243-20-5; **3e**, 68180-96-1; **3f**, 124243-21-6; **3g**, 124243-22-7; **3h**, 88693-07-6; **3i**, 124243-23-8; **3j**, 83859-38-5; **3k**, 124243-24-9; **4a**, 27702-93-8; **4b**, 41857-46-9; **5a**, 27702-91-6; **5b**, 28766-49-6; **6a**, 61827-29-0; **6b**, 124266-40-6; **6c**, 124243-25-0; **6e**, 124243-26-1; **6f**, 124243-27-2; **6g**, 124243-28-3; **6h**, 124243-29-4; **6i**, 61827-30-3; **6j**, 61827-31-4; **6k**, 124243-30-7; **7a**, 766-05-2; **7b**, 4254-02-8; **7c**, 13310-75-3; **7d**, 62391-96-2; **7e**, 617-80-1; **7f**, 2570-96-9; **7g**, 69975-94-6; **7h**, 32730-85-1; *cis*-**7i**, 25144-00-7; *trans*-**7i**, 10479-61-5; *trans*-**7j**, 15619-18-8; *cis*-**7j**, 15619-18-8; *exo*-**7k**, 3211-90-3; *endo*-**7k**, 3211-87-8; **8**, 17643-00-4; **9**, 124243-31-8; **10**, 17643-01-5; **11**, 2094-98-6; **12**, 532-96-7; **13**, 787-84-8; $PhNHNH_2$·HCl, 59-88-1; $PhCONHNH_2$, 613-94-5; $AcNHNH_2$, 1068-57-1; MeO_2CNHNH_2, 6294-89-9; Pr_2CO, 123-19-3; i-Pr_2CO, 565-80-0; Et_2CO, 96-22-0; $MeCO(CH_2)_5CH_3$, 111-13-7; $MeCOCH_2CH(CH_3)CH_3$, 108-10-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; bicyclo[2.2.1]heptan-2-one, 497-38-1.

Novel Reactions of 1-Triptycylcarbinols with Thionyl Chloride–Dimethylformamide

David S. Crumrine,* Michael L. Curtin, and Hiizu Iwamura*,†

Chemistry Department, Loyola University of Chicago, Chicago, Illinois 60626, and The Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

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Reactions of thionyl chloride–dimethylformamide reagent at 58 °C in deuteriochloroform with 1-triptycylcarbinol and ditriptycylcarbinol produced the sulfite ester and the interesting rearranged compound 1-chloro-2-(1-triptycyl)tribenzobicyclo[3.2.2]nonatriene (a triptycyl-substituted homotriptycene), respectively. The mechanistic differences that occur after initial formation of chlorosulfite intermediates are discussed. Molecular mechanics calculations were used to explore the exothermicity of this and related rearrangements.

We wish to report some interesting products from reactions of 1-triptycylcarbinol (**1**) and ditriptycylcarbinol (**2**) with thionyl chloride–dimethylformamide reagent at 58 °C. Ditriptycyl compounds have been studied recently because of interest in "geared" systems,[1] and the rotational barriers for various triptycyl derivatives have been measured and calculated.[2] There have been several attempts to ring expand triptycylmethyl compounds[3] to homotriptycene derivatives. The use of very reactive intermediates in these studies confirmed that bridgehead benzobicyclic carbinyl compounds were very resistant to solvolytic reactions.[4]

Results and Discussion

Our work began with an attempt to prepare ditriptycylmethyl chloride (**3**) from the known[5] **2**. Initial

† Chemistry Department, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113 Japan.

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