is 33.8°. The configurations around atom C3 and C4 are such that C3–H3 and C4–H4 bonds are approximately perpendicular to the plane, and the C3–Cl1 and C4–H4 bonds are approximately parallel to the plane. The torsional angles for N1–C2–C3–C4 and N1–C5–C4–C3 are −17.0° and −33.9°, respectively. The corresponding torsional angles for unsubstituted pyrrolidinone were reported[13] to be −6.1° and −6.5°. The substituents at C3 and C4 in **1a** significantly amplify the distortion of the pyrrolidinone ring.

Conclusion

The major product **1a** is a trans isomer, and the minor product **1b** is a cis isomer. The distortion of the pyrrolidinone ring in **1a** causes H3 and H4 to be oriented at a dihedral angle such that the trans coupling constant becomes larger than the cis coupling constant. The low torsional angle for Cl1–C3–C4–C6 (−77.8°) in **1a** can be used to explain why the γ-compression shift between **1a** and **1b** is lower than that between *cis*- and *trans*-1,2-dimethylcyclopentane. This study points out that configurational assignments based solely on proton NMR coupling constants may lead to erroneous results.

Experimental Section

Fluorochloridone was prepared as described in the literature.[1] The major isomer was isolated by bulb to bulb distillation of the crude product [bp 180 °C (0.4 mmHg)] followed by recrystallization in MeOH to give colorless plates, mp 80–81 °C. Anal. Calcd for $C_{12}H_{10}Cl_2F_3NO$: C, 46.17; H, 3.23; N, 4.49. Found: C, 46.07; H, 3.23; N, 4.36. The minor isomer was isolated from the mother liquor by recrystallization from CS_2 to give very small white crystals, mp 54–55 °C.

Proton and carbon-13 NMR spectra were obtained on a Varian T60A spectrometer and a Varian CFT-20 NMR spectrometer, respectively. All spectra were measured in $CDCl_3$ with tetramethylsilane as an internal reference.

X-ray analysis was carried out on an Enraf-Nonius CAD-4 automated diffractometer. Crystals were thin transparent colorless plates. A crystal of **1a** grown from methanol (size 0.15 × 0.28 × 0.36 mm) was mounted on glass fibers in air by using cyanoacrylate cement. The crystal was triclinic, space group $P\bar{1}$ with cell parameters as follows: a = 6.7569 (9) Å; b = 8.8525 (14) Å; c = 11.7367 (17) Å; α = 78.638 (13)°; β = 73.121 (12)°; γ = 75.870 (12)°; V = 645.4 (2) Å^3; Z = 2; d(calcd) = 1.606 g/cm^3; μ(calcd) = 5.28 cm^{-1}.

The structure was solved by using the MULTAN 79 direct methods program package.[11] Standard least-squares refinement and Fourier techniques revealed the positions of the hydrogen atoms and the disordered configuration of the trifluoromethyl group. The hydrogen atoms were included in structure factor calculations at their idealized positions (C–H distance = 0.95 Å) with isotropic thermal parameters set to 5.0 Å. The disordered fluorine atoms, F1′, F2′, and F3′, were given an occupancy of 0.25 based on the height of the peaks in the difference Fourier map. The initially discovered fluorine atoms, F1, F2, and F3, were assigned an occupancy of 0.75. All nonhydrogen atoms were then allowed to refine in the least-squares analysis. All atoms except the low-occupancy fluorine atoms were given anisotropic thermal parameters. In the final cycles of the least-squares analysis a secondary extinction parameter[12] was allowed to refine.

The structure was determined by using 1700 reflections, and the R value for all 1700 data was 5.12%.

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Registry No. **1a**, 61213-60-3; **1b**, 61213-59-0; **2**, 4641-57-0.

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Supplementary Material Available: Listings of intramolecular angles and distances, selected torsional angles, general temperature factor expressions, root-mean-squares amplitudes of thermal vibration, positional and thermal parameters, and a unit cell crystal structure diagram (8 pages). Ordering information is given on any current masthead page.

Efficient Method for a One-Carbon Homologation of Aldehydes and Benzophenone to Carboxylic Acids

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We report here an efficient sequence for the one-carbon homologation of aldehydes and benzophenone to carboxylic acids (Scheme I). The present method for the homologation has been established by employing reactions of α-(*N*-methylanilino)acetonitrile with aldehydes or benzophenone to form α-cyano enamines, which could be easily converted into the corresponding carboxylic acids by acid hydrolysis in high yields.

Available methodology for the transformation of carbonyl compounds to carboxylic acids has relied on the intermediacy of (a) α-acetoxyacrylonitriles,[1] (b) cyanohydrins,[2] (c) nitriles,[3] (d) ketene thioacetal,[4] (e) α,β-unsaturated sulfones,[5] (f) α,β-unsaturated phosphonates,[6] (g) enol ethers,[7] (h) thioenol ethers,[8] (i) enamines,[9] (j) epoxides,[10] or (k) glycidic ethers[11] to introduce the requisite one-carbon unit. Most of these approaches involve production of an intermediate aldehyde which is subsequently oxidized to the carboxylic acid. Many of these methods, however, lack effective procedures for hydrolysis of the intermediates in each step or require starting materials which are difficulty to synthesize.

The α-cyano enamine synthon is known to be synthetically equivalent to an acyl cyanide in which the carbonyl group is masked as an enamine.[12] There is, however, no information about a general synthesis of α-cyano enamines

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Table I. Syntheses of α-Cyano Enamines 3

entry	carbonyl compd	method	base	conditions	yield of 3,[a] %
1	n-C_3H_7CHO	B	LDA[c]	room temp (14 h)	58 (69)[b]
2	n-C_3H_7CHO	B	KH	room temp (15 h)	56 (65)[b]
3	n-$C_5H_{11}CHO$	B	KH	room temp (17 h) and 50 °C (3 h)	53 (69)[b]
4	$Ph_2C=O$	B	KH	room temp (3 h) and reflux (2 h)	68
5	PhCHO	B	KH	room temp (2 h) and reflux (15 h)	100
6	PhCHO	A	KH	room temp (2 h)	80
7	2-thiophenecarbaldehyde	A	KH	room temp (4 h)	68 (76)[b]
8	p-$(CH_3O)C_6H_4CHO$	A	KH	room temp (5 h)	89
9	1-naphthalenecarbaldehyde	A	KH	room temp (3 h)	85

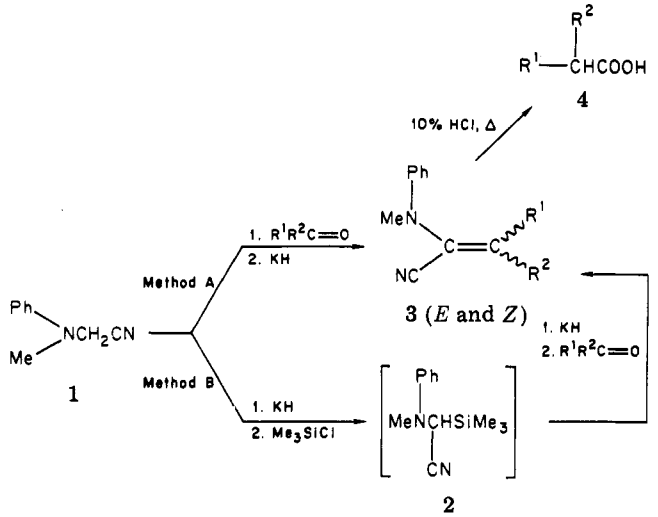
[a] α-Cyano enamines 3 were obtained as a mixture of E and Z isomers. [b] Conversion yield. [c] LDA stands for lithium diisopropylamide.

Table II. Conversion of α-Cyano Enamines 3 to Carboxylic Acids 4

enamine	for 3 R^1	for 3 R^2	conditions	yield of 4, %
3a	n-C_3H_7	H	30% $(COOH)_2$(aq)/THF, reflux (11 h)	36
3a	n-C_3H_7	H	10% HCl(aq)/THF, reflux (6 h)	76
3b	n-C_5H_{11}	H	10% HCl(aq)/THF, reflux (8 h)	78
3c	Ph	Ph	10% HCl(aq)/THF, reflux (27 h)	56
3d	Ph	H	30% $(COOH)_2$(aq)/THF, reflux (70 h)	24
3d	Ph	H	10% HCl(aq)/THF, reflux (3 h)	80 (98)[a]
3e	p-$CH_3OC_6H_4$	H	10% HCl(aq)/THF, reflux (8 h)	89
3f	2-thienyl	H	10% HCl(aq)/THF, reflux (10 h)	83
3g	1-naphthyl	H	10% HCl(aq)/THF, reflux (3 h)	96

[a] Conversion yield.

Scheme I



by reaction of α-aminoacetonitriles with carbonyl compounds except a single report of reaction of α-(N-methylanilino)-α-(trimethylsilyl)acetonitrile with formaldehyde.[13] Accordingly, this work was undertaken to investigate the reactions of α-aminoacetonitriles with carbonyl compounds to introduce the requisite one-carbon unit. We were, however, frustrated in efforts to synthesize the α-cyano enamines. For example, the synthesis of the α-cyano enamines was sensitive to the kind of amino group involved in the α-aminoacetonitrile. The choice of the amino group was critical: when dimethyl- and diethylamines and pyrolidine were employed as the amino group of the α-aminoacetonitrile, the reaction gave the corresponding α-cyano enamine in low yields or failed completely. On the other hand, when α-(N-methylanilino)-acetonitrile was used, the reaction with certain aromatic and heterocyclic aldehydes proceeded smoothly to afford the corresponding α-cyano enamines in high yields (see Table I). In the case of the N-methylanilino group, whose basicity is lower than that of other amines used in this work, contribution of the capto-dative substitution effect[14] was presumed to be smaller than that of the other α-aminoacetonitriles. In other words, the carbanion derived from α-(N-methylanilino)acetonitrile appears to be more stable than the carbanions derived from other α-aminoacetonitriles studied. On the other hand, a similar reaction of α-(N-methylanilino)acetonitrile with aliphatic aldehydes failed to afford the corresponding α-cyano enamines. An efficient solution to this problem was developed by using α-(N-methylanilino)-α-(trimethylsilyl)acetonitrile instead of α-(N-methylanilino)acetonitrile. The desired α-cyano enamines were then produced in good yields. As with aromatic aldehydes, the α-cyano enamines were obtained by a one-pot procedure: the α-(N-methylanilino)-α-(trimethylsilyl)acetonitrile was easily prepared by silylation of α-(N-methylanilino)acetonitrile and was not isolated but could be used for the subsequent reaction with aliphatic aldehydes in the same vessel. The problem of converting the α-cyano enamine to the corresponding carboxylic acid was easily solved: all α-cyano enamines obtained in this work were easily hydrolyzed in an aqueous solution of 10% hydrochloric acid by utilizing tetrahydrofuran (THF) as a cosolvent and led to the corresponding carboxylic acids in high yields. When 30% oxalic acid was used instead of 10% hydrochloric acid, the conversion was less successful (see Table II).

Thus, this reaction has the advantage of simplicity for one-carbon homologation of carbonyl compounds to carboxylic acids and ready availability of α-aminoacetonitriles as masked acyl anion equivalents. Work is in progress to extend the synthetic scope of this reaction for formation of C–C bonds.

Experimental Section

α-Aminoacetonitriles used as the starting materials in this work were prepared according to the procedure described in the lit-

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erature.[15] Their physical properties agreed with those in the literature: α-(*N*-Methylanilino)acetonitrile, bp 111 °C (2 mmHg) [lit.[16] bp 105–110 °C (2 mmHg)]; α-pyrolidinoacetonitrile, bp 78–81 °C (20 mmHg) [lit.[17] bp 84–85 °C (17 mmHg)]; α-(dimethylamino)acetonitrile, bp 79 °C (127 mmHg) [lit.[17] bp 138 °C (760 mmHg)]; α-(diethylamino)acetonitrile, 60–62 °C (15 mmHg) [lit.[17] bp 64 °C (15 mmHg)]. All α-cyano enamines obtained in this work are new compounds.

I. Reactions of α-(*N*-Methylanilino)acetonitrile with Aromatic Aldehydes (Method A). Typical Procedure: Preparation of α-(*N*-Methylanilino)cinnamonitrile (3d). To a mixture of α-(*N*-methylanilino)acetonitrile (0.599 g, 4.1 mmol) and benzaldehyde (0.542 g, 5.11 mmol) dissolved in dry tetrahydrofuran (THF, 12 mL) was added 0.178 g (4.44 mmol) of potassium hydride (KH) mixed with dry THF (8 mL) under a dry nitrogen atmosphere at room temperature. The reaction mixture was stirred for 2 h, poured into a mixture of ice and water, and extracted with diethyl ether (2 × 50 mL). The combined ether layers were washed with brine, and dried with anhydrous sodium sulfate. After the ether was distilled off, the residue was purified by means of column chromatography. Thus, α-(*N*-methylanilino)cinnamonitrile (**3d**) was obtained in 80% yield (0.771 g, 3.29 mmol) as a mixture of *E* and *Z* isomers: yellow oil; IR (liquid film, lf) ν_{CN} 2225 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 3.06 (s, NCH_3 of *E*), 3.24 (s, NCH_3 of *Z*), 6.57 (s, C=CH of *Z*), 6.84 (s, C=CH of *E*), 6.5–7.8 (m, phenyl H); mass spectrum (70 eV), *m/e* (relative intensity) 234 (M^+·, 38), 218 (37), 167 (100), 77 (50). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.84; H, 6.09; N, 11.84.

α-(*N*-Methylanilino)-*p*-methoxycinnamonitrile (3e). By use of the same procedure (method A), the reaction of α-(*N*-methylanilino)acetonitrile (0.468 g, 3.2 mmol) with *p*-anisaldehyde (0.507 g, 3.72 mmol) was carried out to give 0.756 g (2.86 mmol, 89%) of **3e** as a mixture of *E* and *Z* isomers: yellow oil; IR (lf) ν_{CN} 2210 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 3.10 (s, NCH_3 of *E*), 3.25 (s, NCH_3 of *Z*), 3.80 (s, OCH_3 of *E*), 3.84 (s, OCH_3 of *Z*), 6.6–7.8 (m, C=CH of *E* and *Z* isomers, and aromatic H of anilino and phenyl); mass spectrum (70 eV), *m/e* (relative intensity) 264 (M^+·, 100), 249 (26), 77 (21). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.15; H, 6.14; N, 10.50.

α-(*N*-Methylanilino)-β-(2-thienyl)acrylonitrile (3f). By use of the same procedure (method A), the reaction of α-(*N*-methylanilino)acetonitrile (0.525 g, 3.59 mmol) with 2-thiophenecarbaldehyde (0.514 g, 4.59 mmol) was carried out to give 0.583 g (2.43 mmol, 68%) of **3f** as a mixture of *E* and *Z* isomers: yellow oil; IR (lf) ν_{CN} 2200 cm^{-1}; NMR ($CDCl_3/Me_4Si$) 3.13 (s, NCH_3 of *E*), 3.28 (s, NCH_3 of *Z*), 6.74 (s, C=CH of *Z*), 6.98 (s, C=CH of *E*), 6.7–7.6 (m, aromatic H of thienyl and phenyl); mass spectrum (70 eV), *m/e* (relative intensity) 240 (M^+·, 40), 173 (100), 77 (54). Anal. Calcd for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66. Found: C, 70.05; H, 5.13; N, 11.62.

α-(*N*-Methylanilino)-β-(1-naphthyl)acrylonitrile (3g). By use of the same procedure (method A), the reaction of α-(*N*-methylanilino)acetonitrile (0.669 g, 4.58 mmol) with 1-naphthalenecarbaldehyde (0.852 g, 5.46 mmol) was carried out to give 1.105 g (3.89 mmol) of **3g** in 85% yield as a mixture of *E* and *Z* isomers: yellow crystal; mp 145–147 °C (*E*), 128–129 °C (*Z*); IR (KBr) ν_{CN} 2210 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 2.91 (s, NCH_3 of *E*), 3.32 (s, NCH_3 of *Z*), 6.7–8.4 (m, C=CH and aromatic H of phenyl and naphthyl groups of *E* and *Z* isomers); mass spectrum (70 eV), *m/e* (relative intensity) 284 (M^+·, 100), 217 (19), 141 (19), 77 (13). Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.53; H, 5.72; N, 9.72.

II. Reactions of α-(*N*-Methylanilino)acetonitrile with Aliphatic Aldehydes or Benzophenone (Method B). Typical Procedure: Preparation of 2-(*N*-Methylanilino)-2-hexenenitrile (3a). Under a dry nitrogen atmosphere, α-(*N*-methylanilino)acetonitrile (0.61 g, 4.2 mmol) dissolved in dry THF (4 mL) was added at 0 °C to a mixture of KH (0.21 g, 5.2 mmol) and dry THF (6.5 mL). The reaction mixture was stirred for 40 min and then added dropwise at 0 °C to a solution of THF (4 mL) and trimethylsilyl chloride (0.68 g, 6.3 mmol). After the reaction mixture was stirred for 30 min at 0 °C, 0.17 g (4.2 mmol) of KH and 0.53 g (7.3 mmol) of butyraldehyde were added successively. The reaction mixture was then stirred at room temperature for 15 h and was then poured into a mixture of ice and water. The subsequent procedure is similar to that described in method A. Thus, **3a** was obtained in 56% yield (0.47 g, 2.35 mmol) as a mixture of *E* and *Z* isomers: yellow oil; IR (lf) ν_{CN} 2220 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 0.5–1.8 (m, CH_3CH_2), 1.8–2.7 (m, C=$CHCH_2$), 3.02 (s, NCH_3 of *E*), 3.05 (s, NCH_3 of *Z*), 5.85 (t, *J* = 8 Hz, C=CH of *Z*), 6.20 (t, *J* = 8 Hz, C=CH of *E*), 6.5–7.7 (m, phenyl H); mass spectrum (70 eV), *m/e* (relative intensity): 200 (M^+·, 23), 171 (100), 154 (19), 141 (20), 77 (30). Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.80; H, 8.03; N, 13.99.

2-(*N*-Methylanilino)-2-octenenitrile (3b). By use of the same procedure (method B), the reaction of α-(*N*-methylanilino)acetonitrile (1.2 g, 8.2 mmol) with hexanal (1.28 g, 11.2 mmol) was carried out to give 0.99 g (4.34 mmol, 53%) of **3b** as a mixture of *E* and *Z* isomers: yellow oil; IR (lf) ν_{CN} 2225 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 0.5–1.8 (m, $CH_3(CH_2)_3$), 1.8–2.9 (m, C=$CHCH_2$), 3.08 (s, NCH_3 of *E*), 3.11 (s, NCH_3 of *Z*), 5.93 (t, *J* = 8 Hz, C=C*H* of *Z*), 6.28 (t, *J* = 8 Hz, C=CH of *E*), 6.5–7.7 (m, phenyl H); mass spectrum (70 eV), *m/e* (relative intensity) 228 (M^+·, 29), 171 (100), 156 (11), 144 (10), 91 (9), 77 (12). Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.67; H, 8.89; N, 12.35.

α-(*N*-Methylanilino)-β-phenylcinnamonitrile (3c). By use of the same procedure (method B), the reaction of α-(*N*-methylanilino)acetonitrile (0.772 g, 5.28 mmol) with benzophenone (1.498 g, 8.22 mmol) was carried out to give 1.115 g (3.59 mmol, 68%) of **3c**: mp 161–162 °C; IR (KBr) ν_{CN} 2210 cm^{-1}; NMR ($CDCl_3/Me_4Si$) δ 2.94 (s, 3 H, NCH_3), 6.6–7.7 (m, 15 H, phenyl H); mass spectrum (70 eV), *m/e* (relative intensity) 310 (M^+·, 100), 233 (29), 218 (29), 165 (27), 77 (16). Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.84; N, 9.03. Found: C, 85.38; H, 5.94; N, 8.99.

III. Preparation of Carboxylic Acids by Hydrolysis. The typical procedure of the hydrolysis is as follows. A mixture of **3a** (355 mg, 1.775 mmol) and 15 mL each of THF and 10% hydrochloric acid was gently refluxed for 6 h, poured into 10 mL of water, and then extracted with diethyl ether (2 × 50 mL). The combined ether layers were washed with aqueous sodium carbonate. The aqueous layer was slightly acidified with dilute hydrochloric acid, and valeric acid was extracted from the aqueous mixture with diethyl ether (2 × 150 mL). The combined ether layers were dried with anhydrous magnesium sulfate. After the magnesium sulfate was filtered off and the ether distilled off, valeric acid (**4a**) was obtained in 76% yield (138 mg, 1.35 mmol) as a colorless oil. Valeric acid was identified by comparison with an authentic sample, and NMR spectral data agreed with those in the literature:[18] NMR ($CDCl_3/Me_4Si$) δ 0.94 (t, 3 H, *J* = 5 Hz, CH_3), 1.1–1.9 (m, 4 H, $(CH_2)_2$), 2.39 (t, 2 H, *J* = 5 Hz, CH_2COOH), 10.50 (s, 1 H, COOH).

Heptanoic Acid (4b). By use of the same procedure, the hydrolysis of **3b** (586 mg, 2.567 mmol) was carried out to give 262 mg (78 yield) of **4b** as a colorless oil. Heptanoic acid was identified by comparison with an authentic sample, and NMR spectral data agreed with those in the literature:[18] NMR ($CDCl_3/Me_4Si$) δ 0.90 (t, 3 H, *J* = 3 Hz, CH_3), 1.1–1.9 (br s, 8 H, $(CH_2)_4$, 2.40 (t, 2 H, *J* = 3 Hz, CH_2COOH), 11.36 (s, 1 H, COOH).

Diphenylacetic Acid (4c). By use of the same procedure, the hydrolysis of **3c** (587 mg, 1.89 mmol) was carried out to give **4c**: 225 mg (56% yield); mp 147 °C (lit.[19] mp 146 °C).

Phenylacetic Acid (4d). By use of the same procedure, the hydrolysis of **3d** (515 mg, 2.20 mmol) was carried out to give **4d**: 240 mg (80% yield, conversion yield of 98%); mp 77 °C (lit.[20] mp 77 °C).

***p*-Methoxyphenylacetic Acid (4e).** By use of the same procedure, the hydrolysis of **3e** (693 mg, 2.62 mmol) was carried

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out to give **4e**: 389 mg (89% yield); mp 85 °C (lit.[21] mp 85–86 °C).

2-Thienylacetic Acid (4f). By use of the same procedure, the hydrolysis of **3f** (666 mg, 2.77 mmol) was carried out to give **4f**: 326 mg (83% yield); mp 74–75 °C (lit.[22] mp 76 °C).

1-Naphthylacetic Acid (4g). By use of the same procedure, the hydrolysis of **3g** (506 mg, 1.779 mmol) was carried out to give **4g**: 317 mg (96% yield); mp 131–132.5 °C (lit.[23] mp 131 °C).

Registry No. 1, 36602-08-1; (*E*)-**3a**, 86803-42-1; (*Z*)-**3a**, 86803-49-8; (*E*)-**3b**, 86803-43-2; (*Z*)-**3b**, 86803-50-1; **3c**, 86803-44-3; (*E*)-**3d**, 86803-45-4; (*Z*)-**3d**, 86803-51-2; (*E*)-**3e**, 86803-47-6; (*Z*)-**3e**, 86803-53-4; (*E*)-**3f**, 86803-46-5; (*Z*)-**3f**, 86803-52-3; (*E*)-**3g**, 86803-48-7; (*Z*)-**3g**, 86803-54-5; **4a**, 109-52-4; **4b**, 111-14-8; **4c**, 117-34-0; **4d**, 103-82-2; **4e**, 104-01-8; **4f**, 1918-77-0; **4g**, 86-87-3; *n*-C_3H_7CHO, 123-72-8; *n*-$C_5H_{11}CHO$, 66-25-1; $Ph_2C{=}O$, 119-61-9; PhCHO, 100-52-7; *p*-$(CH_3O)C_6H_4CHO$, 123-11-5; 2-thiophenecarboxaldehyde, 98-03-3; 1-naphthalenecarboxaldehyde, 66-77-3.

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Reactions of 2-*anti*-Hydroxy-4-aza-5-homoadamantan-5-one

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In a previous publication[1] we reported on rearrangement reactions of three different kinds of oxahomoadamantanes (**1–3**, Chart I). We had found that each derivative followed a different reaction pathway when exposed to concentrated mineral acids (H_2SO_4, HCl or HBr) and postulated a common epoxonium ion, **4**, as intermediate. In concentrated hydriodic acid, however, the oxahomoadamantanes **1–3** were reduced, and only iodoadamantanes could be isolated.[1]

In continuation of this work we performed analogous reactions using 2-*anti*-hydroxy-4-aza-5-homoadamantan-5-one (**5**) as the starting material.[2] Our purpose was to determine whether products were formed which indicate that an aziridinium ion, **6**, may have been formed during the reaction in analogy to the lactone.

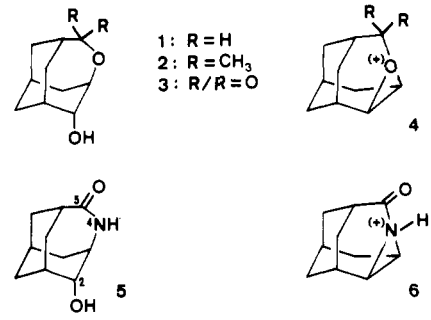
Results and Discussion

The hydroxy lactam **5** was refluxed in 36% hydrochloric, 48% hydrobromic, and 57% hydriodic acid, respectively, for 18 h, and the products isolated, after the workup and chromatographic separation, are listed in Chart II (the values in parentheses indicate the yields of isolated material).

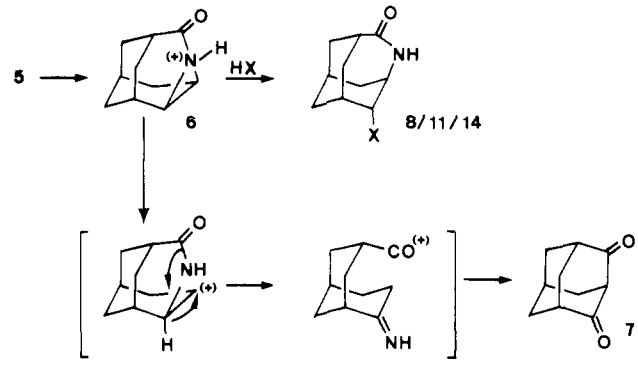
A variety of compounds were produced in contrast to the corresponding reactions[1] of the lactone **3** which furnished the diketone **7** as the sole isolable product in H_2SO_4 and HBr and a mixture of **15** and **16** in HI. In each case with **5**, small but detectable amounts of **7** were found as well as the halo lactams **8**, **11**, and **14** which were generated in increasing yields when going from Cl to Br and I. A comparison of these findings with the results of the lactone reactions (cf. Schemes IV and III in ref. 1) strongly suggests that the aziridinium ion **6** is involved as an intermediate which is either attacked regio and stereoselectively (probably due to steric reasons; cf. ref 1) by an halide anion to form **8**, **11**, or **14**, respectively, or undergoes a rearrangement[1,3] to **7** via an easily hydrolizable imine (Scheme I).

The reduction to iodoadamantanes (cf. Scheme VI in ref 1) is now retarded considerably. This is explicable on the basis of the reduction mechanism proposed for **3**[1] (Scheme II).

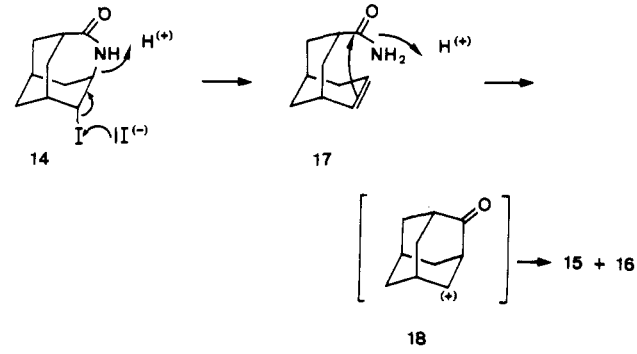
Chart I



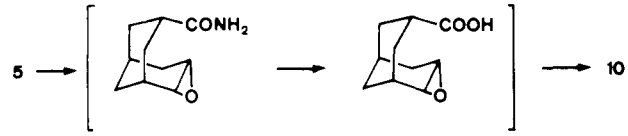
Scheme I



Scheme II



Scheme III



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