A Facile Method for Preparing Aminobicyclo[n.1.0]alkane Derivatives

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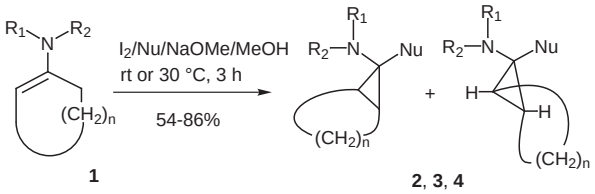
Abstract: The action of iodine on enamine (**1**) in the presence of anions, such as methoxide, cyanide, or succinimide ion, in methanol brings about an intramolecular cyclization and simultaneous substitution with these anions to give the corresponding aminobicyclo[n.1.0]alkane derivatives (**2–4**) in good yields.

Key words: enamine, iodine, intramolecular cyclization, cyclopropanone *N,O*-acetal, bicyclic iminium cation

The title compounds **2–4**, particularly **2**, can be regarded as ring-fused cyclopropanone equivalents, and generate the iminium cation **5**, which can be readily trapped by various nucleophiles.[1] The most practical method for preparing bicyclic compounds like **2–4** appears to be that of Vilsmaier and his co-workers; chlorination of enamines with *N*-chlorosuccinimide and subsequent cyclopropanation with sodium methoxide in methanol or with aqueous sodium cyanide under phase-transfer conditions.[2] *N,O*-Acetals **2** have also been prepared by alcoholysis of *gem*-diaminobicyclo[n.1.0]alkanes **6**,[1b] which are obtained by reacting 2-chlorocycloalkanones with *sec*-amines.[3] In this report, we present a very simple method for preparing aminobicyclo[n.1.0]alkane derivatives from enamines under mild conditions without using special reagents.

Cyclopropanation was achieved by adding an equimolar amount of iodine to a solution of the enamine in methanol containing sodium methoxide, sodium cyanide, or succinimide, with stirring at ambient temperature. The reaction proceeded stereoselectively with enamines derived from cyclohexanone, cycloheptanone, or cyclooctanone (n = 3, 4, 5), and resulted in the exclusive formation of *endo*-amino derivatives, whereas larger ring ketone enamines, such as cyclodecanone or cyclododecanone enamines (n = 7, 9), gave a mixture of *cis* and *trans* isomers of the bicyclic compounds. Using the present method, *N,O*-acetals **2** were obtained from various alicyclic ketone enamines in yields of 54–83%. Replacement of iodine by bromine gave **2** in lower yields. For the formation of cyclopropane aminonitrile (**3**), the presence of an equimolecular amount of sodium methoxide for the enamine was required to obtain satisfactory yields of **3**. In the absence of a strong base, little or no **3** was formed, whereas excess amounts of sodium methoxide resulted in the formation of *N,O*-acetals **2**. Unlike acetal formation, this reaction was limited to pyrrolidinoenamines. With morpholino and piperidinoenamines, cyclopropanation did not take place. In a similar manner, cyclopropane succinimides **4** could be obtained in yields of 67–86% when 2 equivalents of sodium methoxide and succimide were used for **1**.



1 **2**, **3**, **4**

1-4	R_1	R_2	n
a	Et	Et	3
b	Me	Ph	3
c		-$(CH_2)_4$-	3
d		-$(CH_2)_5$-	3
e		-$(CH_2)_2$-O-$(CH_2)_2$-	3
f		-$(CH_2)_4$-	4
g		-$(CH_2)_2$-O-$(CH_2)_2$-	4
h		-$(CH_2)_4$-	5
i		-$(CH_2)_2$-O-$(CH_2)_2$-	5
j		-$(CH_2)_4$-	7
k		-$(CH_2)_2$-O-$(CH_2)_2$-	7
l		-$(CH_2)_4$-	9
m		-$(CH_2)_2$-O-$(CH_2)_2$-	9

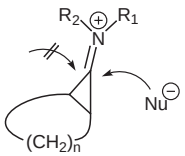
2, Nu = OMe

3, Nu = CN

4, Nu =

Scheme

The structures of the products were established by comparing the spectral data with those reported in the literature and those of authentic samples which had been prepared by our electrochemical method.[4] In the ^{1}H NMR spectra of morpholinobicyclohexane and bicycloheptane



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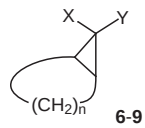
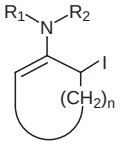


6-9

6: X = Y = R_2N
7: X = R_2N, Y = H
8: X = OH, Y = R_2N
9: X = OH, Y = H, n = 4



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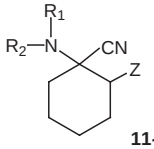

11-14

11: R_1, R_2 = -$(CH_2)_4$-, Z = I
12: R_1, R_2 = -$(CH_2)_4$-, Z = H
13: R_1, R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-, Z = I
14: R_1, R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-, Z = H

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Table 1 Aminobicyclo[n.1.0]alkanes **2**, **3**, **4** Prepared

Product	Yield[a] (%)	mp (°C) or bp (°C)/Torr[b]		Molecular Formula[c]	IR[d] ν (cm^{-1})
		Found (solvent)	Reported		
2a	69	54–55/2		$C_{11}H_{21}N_1O_1$	1458, 1263, 1097 (OMe)
2b	77	105–106/2		$C_{14}H_{19}N_1O_1$	1599, 1500, 1331, 1101 (OMe)
2c	68	57–60/2		$C_{11}H_{19}N_1O_1$	1406, 1312, 1082 (OMe)
2d	80	66–70/2		$C_{12}H_{21}N_1O_1$	1442, 1333, 1248, 1105, 1080 (OMe)
2e	81	77–79/2	77–79/0.04[2e]		1456, 1248, 1117 (OMe)
2f	62	79–82/3		$C_{12}H_{21}N_1O_1$	1458, 1342, 1319, 1080 (OMe)
2g	78	54–55 (pentane, –50 °C) 94–97/2	49[2c] 57–62/0.007[2c]		1456, 1264, 1117 (OMe)
2h	54	65/0.1		$C_{13}H_{23}N_1O_1$	1317, 1097 (OMe)
2k	83[e, f] (*cis/trans* = 10:7)[g]			$C_{15}H_{27}N_1O_2$	1452, 1265, 1117 (OMe)
2m	70[e, f] (*cis/trans* = 10:5)[g]			$C_{17}H_{31}N_1O_2$	1474, 1263, 1117 (OMe)
3c	63	88–92/4		$C_{11}H_{16}N_2$	2218 (CN), 1444, 1307, 1137
3f	64	50–51 (cyclohexane, –20 °C) 94–96/3	44[2c] 80–85/0.05[2c]		2216 (CN), 1439, 1323, 1144
3h	63	98–100 (hexane, –20 °C)		$C_{13}H_{20}N_2$	2216 (CN), 1466, 1312, 1223
3j	72[e] (*cis/trans* = 69:31)[h]	85–86 (*cis*) (hexane, –50 °C) 125/3 (*trans*)		$C_{15}H_{24}N_2$ $C_{15}H_{24}N_2$	2212 (CN), 1475, 1311, 1248 2214 (CN), 1460, 1278
3l	78[e] (*cis/trans* = 67:33)[h]	109–112 (*cis*) (hexane, –50 °C) 150/3 (*trans*)		$C_{17}H_{28}N_2$ $C_{17}H_{28}N_2$	2214 (CN), 1477, 1315, 1136 2216 (CN), 1467, 1356, 1248, 1142
4d	86	152–154 (MeCN)		$C_{15}H_{22}N_2O_2$	1707 (CO), 1364, 1346, 1205
4e	81	192–193 (MeCN)	191[2d]		1707 (CO), 1350, 1115
4f	74	172–173 (MeCN)	160[2c]		1707 (CO), 1364, 1346, 1193
4g	83	199–200 (MeCN)	184[2d]		1710 (CO), 1350, 1115
4i	67	188–191 (MeCN)	193[2d]		1707 (CO), 1359, 1265, 1115
4k	83[e] (*cis/trans* = 58:42)[i]	192–195 (*cis*) (MeCN) 134–137 (*trans*) (MeCN)	159[2d] 137[2d]		1707 (CO), 1355, 1265, 1115 1709 (CO), 1350, 1269, 1115
4m	80[e] (*cis/trans* = 54:46)[i]	189–194 (*cis*) (MeCN) 155–158 (*trans*) (MeCN)	170[2d] 153[2d]		1707 (CO), 1377, 1228,1115 1709 (CO), 1350, 1230, 1115

[a] Yield of isolated product based on **1**.
[b] Uncorrected. Melting points are given for recrystallized samples.
[c] Satisfactory analyses obtained: C ± 0.26, H ± 0.21, N ± 0.23%; except for **2k** (C – 0.49).
[d] IR spectra were recorded on a Shimadzu FT-IR 8200 spectrophotometer. Compounds **2**, **3c**, and **3f** were measured as liquid films; and compounds **3h**, **3j**, **3l**, and **4** were measured in $CHCl_3$.
[e] Yield of isomer mixture.
[f] Characterized as a mixture.
[g] Estimated by integration of the methoxy proton absorptions in the ^1H NMR spectrum.
[h] Estimated by GLC analysis (Silicone SE–30, 2 m, at 210 °C).
[i] Estimated by HLPC analysis [Shim-pack CLC-ODS, 4.6 x 150 mm, CH_3CN/H_2O (65:35)].

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Table 2 ^{1}H and ^{13}C NMR Spectral Data of Compounds **2**, **3**, and **4**

Compound	^{1}H NMR (90 MHz, $CDCl_3$, TMS)[a] δ, *J* (Hz)	^{13}C NMR (22.4 MHz, $CDCl_3$, TMS)[a] δ					
		Amino moiety	Bicyclic system				Others
			quat. C	CH	CH_2		
2a	1.08 (t, 6H, *J* = 7.2), 1.4–1.9 (m, 8H), 2.96 (q, 4H, *J* = 7.2), 3.27 (s, 3H)	14.0 (CH_3), 45.6 (CH_2)	84.6	33.5	25.5 26.8		55.0 (CH_3)
2b	0.7–2.1 (m, 8H), 3.10 (s, 3H), 3.23 (s, 3H), 6.6–7.4 (m, 5H)	38.6 (CH_3), 113.3 (CH), 117.7 (CH), 128.7 (CH), 147.2 (C)	80.3	30.6 34.7	23.5	26.4 27.0	53.6 (CH_3)
2c	1.4–2.0 (m, 12H), 2.9–3.2 (m, 4H), 3.30 (s, 3H)	25.4 (CH_2), 47.8 (CH_2)	79.4	32.3	25.8	26.6	55.4 (CH_3)
2d	1.2–1.8 (m, 14H), 2.6–3.4 (m, 4H), 3.35 (s, 3H)	25.3 (CH_2), 26.6 (CH_2), 51.0 (CH_2)	83.9	32.9	25.3	26.8	56.3 (CH_3)
2e[b]	1.4–2.0 (m, 8H), 2.74 (H_A, 2H), 3.08 (H_B, 2H), 3.37 (s, 3H), 3.42 (H_X, 2H), 3.75 (H_Y, 2H) (ABXY system)	50.0 (CH_2), 67.6 (CH_2)	83.3	32.6	26.5		56.5 (CH_3)
2f[c]	0.8–1.4 (m, 6H), 1.4–2.0 (m, 8H), 2.8–3.2 (m, 4H), 3.31 (s, 3H)	25.0 (CH_2), 47.8 (CH_2)	79.5	22.1	19.9	21.7	55.7 (CH_3)
2g[d]	0.9–2.0 (m, 10H), 2.78 (H_A, 2H), 3.08 (H_B, 2H), 3.38 (s, 3H), 3.56 (H_X, 2H), 3.80 (H_Y, 2H) (ABXY system)	49.9 (CH_2), 67.6 (CH_2)	82.2	21.8	19.5	21.5	56.6 (CH_3)
2h	1.0–1.4 (m, 6H), 1.4–2.2 (m, 10H), 2.8–3.1 (m, 4H), 3.33 (s, 3H)	24.8 (CH_2), 48.0 (CH_2)	82.5	31.1	26.0	29.9 32.9	56.4 (CH_3)
2k[e]	0.6–2.2 (m, 16H), 2.7–3.1 (m, 4H), 3.37, 3.41 (s, s, total 3H), 3.5–3.8 (m, 4H)	50.4 (CH_2), 67.7 (CH_2)	81.0	30.5	22.4 26.3	23.1 24.0	56.6 (CH_3)
		50.0 (CH_2), 67.7 (CH_2)	82.1	34.5 35.0	26.0 28.1	26.7 27.9 30.9	57.9 (CH_3)
2m[e]	0.9–1.2 (m, 2H), 1.2–1.9 (m, 18H), 2.7–3.0 (m, 4H), 3.36, 3.39 (s, s, total 3H), 3.5–3.8 (m, 4H)	50.2 (CH_2), 67.6 (CH_2),	82.8	29.8	22.2 26.1	23.0 26.6 23.4	56.5 (CH_3)
		49.8 (CH_2), 67.6 (CH_2)	84.3	32.9 33.5	25.3	27.2 27.4	57.8 (CH_3)
3c	1.6–2.0 (m, 12H), 2.3–3.0 (br s, 4H)	24.4 (CH_2), 50.8 (CH_2)	40.3	34.0	26.4	26.4	119.4 (CN)
3f[d]	1.1–1.4 (m, 4H), 1.4–1.6 (m, 2H), 1.6–2.1 (m, 8H), 2.4–3.3 (br s, 4H)	24.0 (CH_2), 50.3 (CH_2)	38.6	23.4	18.9	21.5	120.6 (CN)
3h	1.0–1.6 (m, 6H), 1.6–2.2 (m, 10H) 2.4–2.9 (m, 4H)	24.0 (CH_2), 50.6 (CH_2)	40.8	31.2	23.4	28.6 32.4	120.0 (CN)
cis-**3j**	1.4–2.3 (m, 20H), 2.6–3.0 (m, 4H)	24.1 (CH_2), 51.1 (CH_2)	37.5	31.8	21.0 25.6	23.9 25.3	120.8 (CN)
trans-**3j**	0.8–2.4 (m, 20H), 2.5–3.0 (m, 4H)	23.9 (CH_2), 50.7 (CH_2)	39.3	34.6 37.0	23.0 26.6	23.1 26.3 29.5 30.4	118.6 (CN)
cis-**3l**	1.2–1.7 (m, 20H), 1.7–2.0 (m, 4H), 2.6–2.9 (m, 4H)	24.1 (CH_2), 51.0 (CH_2)	39.4	31.0	20.9 25.7	23.3 23.6 26.4	120.8 (CN)
trans-**3l**	0.8–2.4 (m, 24H), 2.6–3.0 (m, 4H)	23.9 (CH_2), 50.7 (CH_2)	41.9	32.9 36.1	23.0 25.7 26.4	24.8 25.5 25.9 25.9 26.8 28.6	118.6 (CN)
4d	1.0–2.3 (m, 16H), 2.64 (mc, 4H), 2.9–3.2 (m, 2H)	24.8 (CH_2), 26.3 (CH_2), 51.7 (CH_2)	58.6	32.5	26.8	28.0	178.0 (CO)

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Table 2 (continued[b])

Compound	^{1}H NMR (90 MHz, $CDCl_3$, TMS)[a] δ, *J* (Hz)	^{13}C NMR (22.4 MHz, $CDCl_3$, TMS)[a] δ					
		Amino moiety	Bicyclic system				Others
			quat. C	CH		CH_2	
4e[f]	1.6–2.1 (m, 8H), 2.66 (mc, 4H), 2.41 (H_A, 2H), 2.84 (H_B, 2H), 3.46 (H_Y, 2H), 3.73 (H_X, 2H) (ABXY system)[g]	50.7 (CH_2), 67.2 (CH_2)	57.5	32.4	26.2	26.8 28.0	177.9 (CO)
4f[d]	1.1–1.45 (m, 6H), 1.45–1.75 (m, 4H), 1.75–2.0 (m, 4H), 2.2–2.6 (br m, 2H), 2.62 (mc, 4H), 2.7–3.2 (br, 2H)	23.7 (CH_2), 48.5 (CH_2)	53.8	22.0	19.5	21.7 28.1	178.3 (CO)
4g[f]	1.1–1.7 (m, 6H), 1.7–2.1 (m, 10H), 2.40 (H_A, 2H), 2.63 (H_B, 2H), 2.84(mc, 4H), 3.53 (H_Y, 2H), 3.72 (H_X, 2H) (ABXY system)[g]	50.8 (CH_2), 67.2 (CH_2)	56.0	21.7	19.2	21.7 28.0	178.1 (CO)
4i[f]	1.1–1.7 (m, 8H), 1.7–2.0 (m, 2H), 2.0–2.8 (m, 10H), 3.3–3.9 (m, 4H)	50.7 (CH_2), 67.1 (CH_2)	59.5	29.9	24.9 32.7	28.0 29.2	179.9 (CO)
cis-**4k**[f]	0.9–1.2 (m, 2H), 1.2–1.9 (m, 12H) 1.9–3.0 (m, 10H), 3.4–3.8 (m, 4H)	51.1 (CH_2), 67.1 (CH_2)	54.9	30.2	21.7 25.8	23.9 25.6 28.1	178.1 (CO)
trans-**4k**[f]	0.3–0.7 (m, 1H), 0.7–2.1 (m, 15H) 2.1–2.5 (m, 2H), 2.5–2.9 (m, 6H), 3.4–3.7 (m, 4H)	50.6 (CH_2), 67.2 (CH_2)	56.6	32.9 34.8	22.7 26.5 28.5	23.1 26.2 27.3 27.9 29.6 30.8	178.3 (CO) 178.4 (CO)
cis-**4m**[f]	1.0–1.7 (m, 18H), 1.7–2.1 (m, 2H) 2.3–3.0 (m, 8H), 3.5–3.8 (m, 4H)	50.9 (CH_2), 67.1 (CH_2)	56.7	29.5	21.6 25.7	23.2 23.5 26.6 28.0	177.9 (CO)
trans-**4m**[f]	0.2–0.7 (m, 1H), 0.8–1.8 (m, 17H) 1.9–2.3 (m, 2H), 2.5–2.8 (m, 8H), 3.4–3.7 (m, 4H)	50.6 (CH_2), 67.2 (CH_2)	59.1	31.6 33.7	22.5 26.5 28.5	25.6 26.1 27.7 28.1	178.2 (CO) 178.5 (CO)

[a] Recorded on a JEOL JNM-EX 90A spectrometer.
[b] The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[2e]
[c] The ^{1}H NMR spectrum agreed with that reported in the literature.[1b]
[d] The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[2c]
[e] Characterized as a mixture of *cis* and *trans* isomers.
[f] The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[2d]
[g] *J* (Hz): $J_{AB} \approx 12$, $J_{XY} \approx 11$, $J_{AY} \approx 11$, $J_{AX} \approx 3$, $J_{BY} \approx 1.5$.

derivatives, the methylene signals of the amino moiety displayed an ABXY pattern, which supports the *endo*-morpholino configuration.[5] We also observed that the reduction of **2c–g** with $LiAlH_4$ provides the corresponding *endo*-aminobicyclo[n.1.0]alkane **7**[6] in a yield of 80% or more. Furthermore, acid-catalyzed hydrolysis of **2f** to the *N,O*-semiaminal **8**, followed by reduction with $NaBH_4$, gave *endo*-norcanol (**9**)[3] in an overall yield of 64%.

The present reaction most likely involves the formation of iodoenamine **10**. As in the cyclopropanation of chloroenamines,[7] the resulting iodoenamine **10** undergoes the elimination of iodide anion to give bicyclic iminium cation **5**, which is then attacked by a nucleophile from the less hindered *exo* direction. In the aminonitrile formation, ICN adduct of enamines may form initially, followed by dehydrocyanation by strong base to give **10**,[8] because the action of iodine on sodium cyanide induces the immediate formation of cyanogen iodide (ICN)[9] which can readily add to enamines.[10] In fact, upon adding iodine to a solution of pyrrolidino or morpholinoenamine (**1c** or **1e**) in methanol containing sodium cyanide at 0 °C, the ICN adduct (**11**, **13**) was formed along with the HCN adduct (**12**, **14**), respectively. Treatment of the ICN adduct **11** with an equimolar amount of sodium methoxide in methanol at 30 °C provided the corresponding aminonitrile **3c** in a yield of 71%, whereas with excess amounts of sodium methoxide, *N,O*-acetal **2c** was obtained instead of **3c** in comparable yield. However, such reactions did not occur with the ICN adduct **13** under these conditions, although the prolonged heating gave *N,O*-acetal **2e**. On the other hand, the HCN adduct **12** readily underwent dehydrocyanation at room temperature with methanolic sodium methoxide to give enamine **1c**, whereas the HCN adduct **14** was quite resistant to the strong base under similar conditions. Consequently, the different reactivities between pyrrolidino and morpholino or piperidinoenamines for the cyclopropanation in the presence of cyanide ion may be attributed to the ease with which iodoenamine **10** is formed by elimination of HCN from the ICN adduct.

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Enamines **1a–g**[11] and succinimide[12] were prepared by methods published in the literature.

Cyclopropane *N,O*-Acetals 2; General Procedure

To a stirred solution of enamine **1** (30 mmol) in MeOH (60 mL) containing NaOMe (60 mmol) was added iodine (30 mmol) portionwise at r.t. over 2 h. The stirring was continued for 30 min, and the mixture was evaporated in vacuo. H_2O (20 mL) was added to the residue, and the organic layer was extracted with Et_2O (3 x 20 mL). The combined Et_2O extracts were washed with brine (20 mL), dried (Na_2SO_4), and distilled in vacuo. The products **2k** and **2m** were isolated as a mixture of cis and trans isomers by column chromatography on aluminium oxide using Et_2O/hexane (1:1) as the eluent.

Cyclopropane Aminonitrile 3; General Procedure

To a stirred solution of enamine **1** (20 mmol) in MeOH (40 mL) containing NaOMe (20 mmol) and NaCN (40 mmol) was added iodine (20 mmol) portionwise at 30 °C over 1 h. For **1h**, iodine (30 mmol), and for **1l**, MeOH (80 mL) was used. After workup as described above, the combined Et_2O extracts were washed with dil. HCl (10 mL), washed with brine (20 mL), dried (Na_2SO_4), and distilled in vacuo. The products **3j** and **3l** were isolated as a mixture of the cis and trans isomers by column chromatography on silica gel using Et_2O/hexane (1:1) as the eluent. Separation of the two isomers was achieved by cooling a solution of the mixture in hexane at -50°C. The crystallized cis isomer was collected by filtration, and rinsed with small portions of cold hexane. The trans isomer was obtained from the mother liquid by Kugelrohr distillation.

Cyclopropane Succinimide 4; General Procedure

Enamine **1** (10 mmol) was dissolved in a solution of succinimide (20 mmol) in MeOH (20 mL) containing NaOMe (20 mmol). Iodine (10 mmol) was then added to the solution at r.t. over 1 h. Stirring was continued for an additional 1 h, and the mixture was evaporated in vacuo. The residue was treated with H_2O (20 mL), and the solid was collected by filtration, washed with dil. NaOH (10 mL), washed with H_2O (10 mL), and rinsed with pentane (10 mL). In the case of **4k** and **4m**, each isomer was separated by fractional recrystallization from MeCN.

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