Facile Access to 6-Methoxy-1,2,3,6-tetrahydro- and 4-Hydroxy-1,2,3,4-tetrahydropyridines by Electrochemical Haloalkoxylation-Dehydrohalogenation Sequence as a Key Operation

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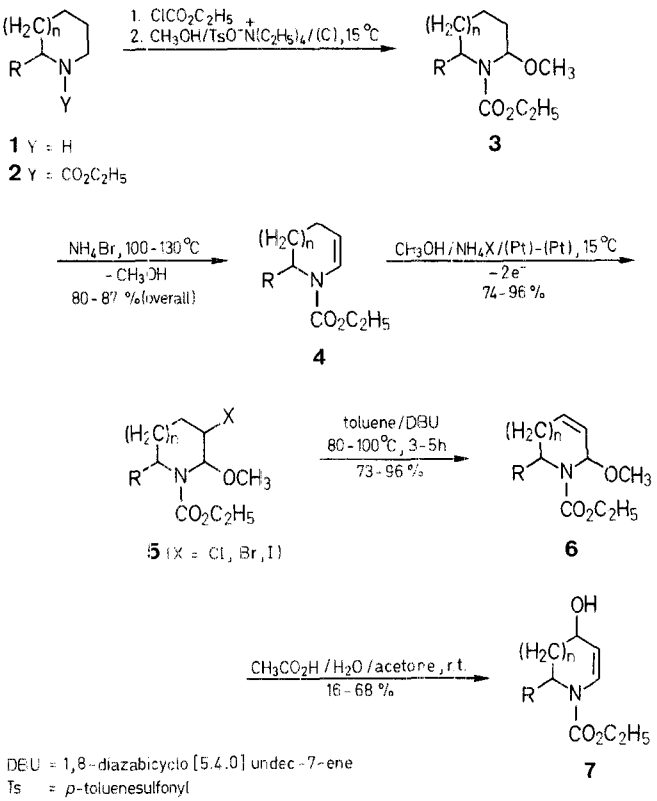
A facile procedure for the synthesis of *N*-ethoxycarbonyl-6-methoxy-1,2,3,6-tetrahydropyridines **6** and *N*-ethoxycarbonyl-4-hydroxy-1,2,3,4-tetrahydropyridines **7** from piperidines **1** is described. The electrochemical halomethoxylation of *N*-ethoxycarbonyl-1,2,3,4-tetrahydropyridines **4** (easily accessible from **1** by ethoxycarbonylation followed by electrooxidative methoxylation and acid-catalyzed elimination of methanol) in a CH_3OH–NR_4X (X = Cl, Br, I)-(Pt)-(Pt) system provides *N*-ethoxycarbonyl-3-halo-2-methoxypiperidines **5** in 74–90% yields. Dehydrohalogenation of iodides **5** (X = I) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene gave the desired olefin **6**, which was isomerized in aqueous acetic acid to afford the alcohol **7** in 34–55% yields (from **5**). The procedure is also applicable to the synthesis of seven membered derivatives **6f** and **7f** from **1f**.



Oxygenated tetrahydropyridines are important building block in the synthesis of numerous heterocyclic compounds,[1-3] including alkaloids, agricultural materials, and medicinal chemicals. Thus, there is a continuous interest in the development of new synthetic methods for the preparation of these compounds. Although a variety of procedures have been reported for the synthesis of 2,3-dihydro-4(1H)-pyridinones (4-oxo-1,2,3,4-tetrahydropyridines) from acyclic 1,3-dicarbonyl compounds[4-11] and from δ-amino-α, β-acetylenic aldehydes,[12] as well as for the synthesis of six-membered ring heterocycles such as 4(1H)-pyridinones,[13-19] 4-piperidinones,[20] and 2,3-dihydro-4-pyrones,[21] little attention has been paid to the preparation and utilization of their reduced derivatives, e.g., 4-hydroxy-1,2,3,4-tetrahydropyridines **7** and 6-alkoxy-1,2,3,6-tetrahydropyridines **6**. To our knowledge, only two publications deal with the preparation of derivatives of **7** from 2,3-dihydro-4(1H)-pyridinones,[22] one by the reduction with sodium borohydride/cerium(III) trichloride and the other by hydrolysis of 4-chloro-1,2,3,4-tetrahydropyridines.[12] The synthesis of these compounds *via* functionalization of piperidines, however, seems to be a promising strategy in terms of easy availability of the precursors. In this paper, we report a facile access to **6** and **7** from simple piperidines derivatives **1**.

1–7	n	R
a	1	H
b	1	CH_3
c	1	C_2H_5
d	1	OCH_3
e	1	OH
f	2	H

The carbamates **2**, prepared in the normal manner from the corresponding piperidines **1**, underwent smooth electrochemical methoxylation at the α-position to afford **3**.[23,24] Treatment of **3** with ammonium bromide[25] caused the elimination of methanol to give the enamines **4**. In analogy to our reported procedure,[26] the electrochemical haloalkoxylation of **4** was carried out using ammonium halides such as NH_4Cl, NH_4Br, NH_4I, or $(C_2H_5)_4NI$ as the electrolyte and source of halogen. The results are listed in Table 1. Thus, passage of 2.5–3.0 Faraday/mol of electricity (a constant voltage of 3 V with a current density of 5–7 mA/cm²) through a methanol solution of **4b** containing an appropriate ammonium halide provided **5b** in 68–96% yields. The 3-bromo derivative **5b** (X = Br) was obtained in higher yield (96%) than either the chloride **5b** (X = Cl, 68%) or the iodide **5b** (X = I, 86%). It is interesting to note that iodination of **4d** and **4e** with $(C_2H_5)_4NI$ required 12.6–17.5 F/mol of electricity while halogenation of **4a–4c** with NH_4I could be achieved with 2.4–4.6 F/mol of electricity.

Dehydrohalogenation of **5** to **6** was effected with 1.5–2.0 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[27] in toluene at 80–100 °C (see Table 1). 3-Iodo-2-methoxypiperidine

Table 1. Results of Electrochemical Halomethoxylation of **4** to **5**, Dehydrohalogenation of **5** to **6**, and Acid-catalyzed Rearrangement of **6** to **7**

Compound	4 ⟶ 5			5 ⟶ 6		6 ⟶ 7
	Method[a]	F/mol[b]	Yield[c] (%) of **5** (X)	Temp./(°C)/(h)	Yield[c] (%) of **6**	Yield[c] (%) of **7**
a	C	2.4	90 (I)	95/3	88	58
b	A	2.7	68 (Cl)	100/5	–[d]	
b	B	2.5	96 (Br)	80/3	53	
b	C	3.0	86 (I)	80/4	81	68 (*cis*/*trans*, 2:3)
c	C	4.6	74 (I)	85/3.5	96	53 (*cis*/*trans*, 2:3)
d	D	17.5	90 (I)	90/4	93	16 (+53)[e]
f	D	12.6	80 (I)	80/5	73	46

[a] Electrolyte in CH_3OH–(Pt) system: NH_4Cl (Method A), NH_4Br (Method B), NH_4I (Method C), and Et_4NI (Method D).
[b] Electricity consumed for complete conversion of the substrate **4**.
[c] Yield based on isolated products.
[d] **5b** recovered.
[e] In addition to **7d**, *N*-ethoxycarbonyl-2,4-dihydroxy-1,2,3,4-tetrahydropyridine **7e** (yield 53%) is produced during hydrolysis.

5b (X = I) has been converted into the alkene **6b** in 81% yield, whereas the corresponding bromides **5b** (X = Br) afforded **6b** in only 53% yield under identical conditions. Under the same conditions the chloride **5b** (X = Cl) was recovered unchanged. The physical properties and spectral data for tetrahydropyridines **6** obtained by this method are listed in Table 2.

Acid-catalyzed rearrangement of **6** to 4-hydroxy-1,2,3,4-tetrahydropyridines **7** could be achieved under mild conditions. Thus, treatment of **6b** with aqueous 5% acetic acid in acetone at room temperature resulted in the migration of C-C double bond and hydrolysis to give **7b** in 68% yield. Identification of both the *cis* and the *trans* isomers of **7b**, separated by column chromatography in a 2 : 3 ratio, was carried out by comparison of ^{13}C-NMR spectral data. N-ethoxycarbonyl-2,4-dihydroxy-1,2,3,4-tetrahydropyridine (**7e**) was formed in 53% yield along with a small amount of **7d** by aqueous acidic treatment of **6d**.

The procedure described here is also applicable for the synthesis of *N*-ethoxycarbonyl-4-hydroxy-1-azacyclohept-2-ene **7f** from azacycloheptane **1f** (see Table 1). Unfortunately, our attempts to prepare acyclic δ-hydroxy-*N*-ethoxycarbonylenamines from aliphatic primary amines were unsuccessful due to the difficulty of isolating the reactive *N*-protected enamines.

Table 2. Physical Properties and Spectral Data for Compounds **5**, **6**, **7** Prepared

Compound	b.p. (°C)/torr	Molecular Formula[a]	IR (Film)[b] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS_{int})[c] δ (ppm)
5a (X = I)[d]	94–97/1.5	$C_9H_{16}UNO_3$ (313.1)	1705	1.27 (t, 3H, J = 7 Hz, CH_3); 1.15–2.40 (m, 4H, CH_2); 2.65–3.20 (m, 1H, CH_2N); 3.33 (s, 3H, OCH_3); 3.70–4.60 (m, 2H, CH_2N, CHI); 4.16 (q, 2H, J = 7 Hz, CH_2O); 5.43 (br s, 1H, CHO)
5b (X = Cl)	96–98/1.5	$C_{10}H_{18}ClNO_3$ (235.7)	1710	1.26 (d, 3H, J = 7 Hz, CH_3); 1.29 (t, 3H, J = 7 Hz, CH_3); 1.70–2.40 (m, 4H, CH_2); 3.32 (s, 3H, OCH_3); 4.22 (q, 2H, J = 7 Hz, CH_2O); 4.00–4.60 (m, 2H, CHN, CHCl); 5.45 (d, 1H, J = 3 Hz, CHO)
5b (X = Br)	98–100/3.0	$C_{10}H_{18}BrNO_3$ (280.2)	1710	1.24 (d, 3H, J = 7 Hz, CH_3); 1.27 (t, 3H, J = 7 Hz, CH_3); 1.40–2.70 (m, 4H, CH_2); 3.30 (s, 3H, OCH_3); 3.90–4.60 (m, 2H, CHN, CHBr); 4.20 (q, 2H, J = 7 Hz, CH_2O); 5.30–5.70 (m, 1H, CHO)
5b (X = I)[d]	105–108/1.5	$C_{10}H_{18}INO_3$ (327.2)	1710	1.26 (d, 3H, J = 7 Hz, CH_3); 1.29 (t, 3H, J = 7 Hz, CH_3); 1.30–2.40 (m, 4H, CH_2); 3.27 (s, 3H, OCH_3); 4.10–4.40 (m, 1H, CHN); 4.17 (q, 2H, J = 7 Hz, CH_2O); 4.25–4.67 (m, 1H, CHI); 5.55 (br s, 1H, CHO)
5c (X = I)	118–120/5.0	$C_{11}H_{20}INO_3$ (341.2)	1705	0.89 (t, 3H, J = 7 Hz, CH_3); 1.28 (t, 3H, J = 7 Hz, CH_3); 1.40–2.25 (m, 6H, CH_2); 3.30 (s, 3H, OCH_3); 3.80–4.60 (m, 2H, CHN, CHI); 4.18 (q, 2H, J = 7 Hz, CH_2O); 5.53 (br s, 1H, CHO)
5d (X = I)	115–117/1.5	$C_{10}H_{18}INO_4$ (343.2)	1705	1.31 (t, 3H, J = 7 Hz, CH_3); 1.50–2.45 (m, 4H, CH_2); 3.32 (s, 3H, OCH_3); 3.39 (s, 3H, OCH_3); 4.22 (q, 2H, J = 7 Hz, CH_2O); 4.35–4.65 (m, 1H, CHI); 5.20–5.70 (m, 2H, CHO)
5f (X = I)	125–128/1.5	$C_{10}H_{18}INO_3$ (327.2)	1703	1.31 (t, 3H, J = 7 Hz, CH_3); 1.30–3.90 (m, 8H, CH_2); 3.27 (s, 3H, OCH_3); 3.90–4.20 (m, 1H, CHI); 4.21 (q, 2H, J = 7 Hz, CH_2O); 5.35–5.75 (m, 1H, CHO)
6a[d]	57–59/1.5	$C_9H_{15}NO_3$ (185.2)	3030, 1705, 1655	1.27 (t, 3H, J = 7 Hz, CH_3); 1.60–2.60 (m, 2H, CH_2); 2.83–3.40 (m, 1H, CH_2N); 3.31 (s, 3H, OCH_3); 3.38–4.25 (m, 1H, CH_2N); 4.15 (q, 2H, J = 7 Hz, CH_2O); 5.30–6.10 (m, 3H, CH=CH, CHO)
6b[d]	62–64/1.5	$C_{10}H_{17}NO_3$ (199.3)	3030, 1705, 1655	1.26 (d, 3H, J = 7 Hz, CH_3); 1.28 (t, 3H, J = 7 Hz, CH_3); 1.50–2.65 (m, 2H, CH_2); 3.37 (s, 3H, CH_2); 3.37 (s, 3H, OCH_3); 4.16 (q, 2H, J = 7 Hz, CH_2O); 4.58 (t, 1H, J = 7 Hz, CHN); 5.30–6.05 (m, 3H, CH=CH, CHO)
6c	82–84/5.0	$C_{11}H_{19}NO_3$ (213.3)	3030, 1705, 1660	0.89 (t, 3H, J = 7 Hz, CH_3); 1.29 (t, 3H, J = 7 Hz, CH_3); 1.40–2.60 (m, 4H, CH_2); 3.31 (s, 3H, OCH_3); 4.05–4.60 (m, 1H, CHN); 4.18 (q, 2H, J = 7 Hz, CH_2O); 5.30–5.95 (m, 3H, CH=CH, CHO)
6d	88–92/3.0	$C_{10}H_{17}NO_4$ (215.2)	3030, 1705, 1670	1.31 (t, 3H, J = 7 Hz, CH_3); 2.10–2.60 (m, 2H, CH_2); 3.30 (s, 3H, OCH_3); 3.47 (s, 3H, OCH_3); 4.23 (q, 2H, J = 7 Hz, CH_2O); 5.20–6.05 (m, 4H, CH=CH, CHO)
6f	68–71/1.5	$C_{10}H_{17}NO_3$ (199.3)	3030, 1706, 1652	1.29 (t, 3H, J = 7 Hz, CH_3); 1.45–2.60 (m, 4H, CH_2); 3.26 (s, 3H, OCH_3); 2.90–3.95 (m, 2H, CH_2N); 4.19 (q, 2H, J = 7 Hz, CH_2O); 5.37–6.03 (m, 3H, CH=CH, CHO)
7a[d]	75–78/2.5	$C_8H_{13}NO_3$ (171.2)	3400, 1710, 1690, 1650	1.27 (t, 3H, J = 7 Hz, CH_3); 1.60–2.10 (m, 2H, CH_2); 2.96 (br s, 1H, OH); 3.15–4.30 (m, 3H, CH_2N, CHO); 4.16 (q, 2H, J = 7 Hz, CH_2O); 4.97 (dd, 1H, J = 9 Hz, 5 Hz, NC=CH); 6.83 (d, 1H, J = 9 Hz, NCH=)
trans-**7b**[d]	75–77/1.5	$C_9H_{15}NO_3$ (185.2)	3410, 1710, 1690, 1650	1.31 (t, 3H, J = 7 Hz, CH_3); 1.36 (d, 3H, J = 7 Hz, CH_3); 1.98 (t, 2H, J = 4 Hz, CH_2); 2.58 (br s, 1H, OH); 4.10–4.65 (m, 2H, CHN, CHO); 4.23 (q, 2H, J = 7 Hz, CH_2O); 5.10 (dd, 1H, J = 9 Hz, 5Hz, NC=CH); 6.87 (d, 1H, J = 9 Hz, NCH=)
cis-**7b**[d]			3390, 1710, 1690, 1650	1.17 (d, 3H, J = 7 Hz, CH_3); 1.30 (t, 3H, J = 7 Hz, CH_3); 1.60–2.65 (m, 3H, CH_2, OH); 3.90–4.60 (m, 2H, CHN, CHO); 4.20 (q, 2H, J = 7 Hz, CH_2O); 4.88 (d, t, 1H, J = 9 Hz, 1.5 Hz, NC=CH); 6.75 (d, 1H, J = 9 Hz, NCH=C)

Table 2. (Continued)

Compound	b.p. (°C)/torr	Molecular Formula[a]	IR (Film)[b] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS_{int})[c] δ (ppm)
trans-**7c**	83–85/1.5	$C_{10}H_{17}NO_3$ (199.3)	3440, 1705, 1642	0.89 (t, 3H, J = 7 Hz, CH_3); 1.26 (t, 3H, J = 7 Hz, CH_3); 1.48–2.38 (m, 4H, CH_2); 3.78 (br s, 1H, OH); 3.70–4.62 (m, 2H, CHN, CHO); 4.14 (q, 2H, J = 7 Hz, CH_2O); 5.03 (dd, 1H, J = 9 Hz, 6 Hz, NC=CH); 6.78 (d, 1H, J = 9 Hz, NCH=)
cis-**7c**			3390, 1708, 1656	0.91 (t, 3H, J = 7 Hz, CH_3); 1.28 (t, 3H, J = 7 Hz, CH_3); 1.46–2.68 (m, 4H, CH_2); 3.74 (br s, 1H, OH); 3.70–4.62 (m, 2H, CHN, CHO); 4.16 (q, 2H, J = 7 Hz, CH_2O); 4.86 (d, t, 1H, J = 9 Hz, 1.5 Hz, NC=CH); 6.68 (d, 1H, J = 9 Hz, NCH=)
7d	97–99/1.5	$C_9H_{15}NO_4$ (201.2)	3500, 1720, 1650	1.31 (t, 3H, J = 7 Hz, CH_3); 1.60–2.65 (m, 2H, CH_2); 3.27 (s, 3H, OCH_3); 3.70–4.35 (m, 2H, OH, CHO); 4.18 (q, 2H, J = 7 Hz, CH_2O); 5.00–5.35 (m, 1H, NC=CH); 5.57 (br s, 1H, NCHO); 6.70 (d, 1H, J = 9 Hz, NCH=)
7e	88–90/1.5	$C_8H_{13}NO_4$ (187.2)	3390, 1705, 1645	1.31 (t, 3H, J = 7 Hz, CH_3); 1.60–2.65 (m, 2H, CH_2); 3.45 (br s, 1H, OH); 3.90–4.45 (m, 1H, CHO); 4.22 (q, 2H, J = 7 Hz, CH_2O); 4.85 (br s, 1H, OH); 5.00–5.35 (m, 1H, NC=CH); 5.78 (br s, 1H, CHO); 6.78 (d, 1H, J = 9 Hz, NCH=)
7f	75–77/2.5	$C_9H_{15}NO_3$ (185.2)	3390, 1707, 1642	1.29 (t, 3H, J = 7 Hz, CH_3); 1.55–2.65 (m, 4H, CH_2); 3.05–4.62 (m, 4H, CH_2N, OH, CHO); 4.20 (q, 2H, J = 7 Hz, CH_2O); 5.05 (dd, 1H, J = 9 Hz, 5 Hz, NC=CH); 6.59 (d, 1H, J = 9 Hz, NCH=)

[a] Satisfactory microanalyses obtained: C ±0.29, H ±0.29.
[b] Recorded on a JASCO IR-1 grating spectrometer.
[c] Measured at 60 MHz using a Hitachi R-24 spectrometer.
[d] ^{13}C-NMR ($CDCl_3$/TMS_{int}): δ (ppm) measured at 25.05 MHz using a JEOL FX-100 spectrometer are as follows.
5a: 14.7 (q), 21.1 (t), 28.1 (t), 29.5 (d), 38.1 (t), 54.9 (q), 61.7 (t), 86.0 (d), 156.0 (s)
6a: 14.6 (q), 24.7 (t), 28.6 (t), 61.7 (t), 62.0 (q), 72.5 (d), 125.8 (d), 129.4 (d), 165.1 (s)
6b: 14.6 (q), 20.0 (q), 36.1 (t), 43.3 (d), 55.9 (q), 61.6 (t), 79.6 (d), 124.1 (d), 126.0 (d), 156.1 (s)
7a: 14.5 (q), 30.5 (t), 37.7 (t), 60.7 (d), 62.2 (t), 107.6 (d), 127.5 (d), 153.4 (s)
trans-**7b**: 14.5 (q), 17.4 (q), 36.5 (t), 47.3 (d), 61.6 (d), 61.9 (t), 109.0 (d), 124.4 (d), 153.1 (s)
cis-**7b**: 14.5 (q), 17.9 (q), 35.5 (t), 45.4 (d), 60.6 (d), 62.0 (t), 106.7 (d), 125.7 (d), 153.2 (s)

Electrolysis Apparatus:
An undivided cell is equipped with a gas inlet tube, a stirring bar, and a thermometer; two carbon plate electrodes (5 cm^2) or two platinum foil electrodes (3 cm^2) are placed parallel to each other 5 mm apart. The vessel is immersed in a water bath externally cooled to 10–15 °C.

***N*-Ethoxycarbonyl-1,2,3,4-tetrahydropyridine (4a); Typical Procedure:**
N-ethoxycarbonyl-2-methoxypiperidine (**3a**): A solution of *N*-ethoxycarbonylpiperidine (**2a**; 3.14 g, 20 mmol) in methanol (30 ml) containing tetraethylammonium tosylate (250 mg) as a supporting electrolyte is electrolyzed with carbon electrodes under a constant current of 200 mA (terminal voltage: 8–15 V) at 15 °C. After passage of 2.4–7.0 F/mol of electricity, the mixture is concentrated *in vacuo* and the residue was taken up in benzeneethyl acetate (1 : 1, 20 ml). The resultant solution is washed with brine (15 ml), dried with sodium sulfate, and concentrated on a rotary evaporator. The crude product is purified by column chromatography (silica gel, hexane/ethyl acetate, 3 : 1) to give **3a**; yield: 3.37 g (90%) *N-ethoxycarbonyl-1,2,3,4-tetrahydropyridine* (**4a**): A mixture of **3a** (561 mg, 3 mmol) and ammonium bromide (353 mg, 3.6 mmol) is heated at 100–130 °C over a period of 2 h in Kugelrohr column. The residue is purified by column chromatography (silica gel, hexane/ethyl acetate 3 : 1) to give **4a**; yield: 428 mg (92%).

The overall yields of **4a–4e** from **2a–2e** are 80–87%.

***N*-Ethoxycarbonyl-3-iodo-2-methoxy-6-methylpiperidine (5b); Typical Procedure:**
A solution of *N*-ethoxycarbonyl-2-methyl-1,2,3,4-tetrahydropyridine (**4b**; 338 mg, 2 mmol) in methanol (10 ml) containing tetraethylammonium iodide (617 mg, 2.4 mmol) as an electrolyte is electrolyzed with platinum electrodes under a constant applied voltage of 2 V (current density: 5–7 mA/cm^2) at 15 °C. After passage of 3.0 F/mol of electricity, the mixture is concentrated *in vacuo*, and the residue is taken up in benzene-ethyl acetate (1 : 1, 15 ml). The resultant solution is washed with brine (15 ml), dried with sodium sulfate, and concentrated on a rotary evaporator. The crude product is purified by column chromatography (silica gel, hexane/ethyl acetate 3 : 1) to give **5b** (X = I); yield: 562 mg (86%).

Spectral and physical data of **5** are given in Table 2.

***N*-Ethoxycarbonyl-6-methoxy-1,2,3,6-tetrahydropyridine (6a); Typical Procedure:**
To a stirred solution of *N*-ethoxycarbonyl-3-iodo-2-methoxypiperidine (**5a**, X = I; 313 mg, 1 mmol) in toluene (0.5 ml) is added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 228 mg, 1.5 mmol). The mixture is heated at about 100 °C for 3 h. After cooling, the mixture is poured into cold (0 °C) aqueous 5% hydrochloric acid (10 ml) and extracted with benzene-ethyl acetate (1 : 1, 2 × 10 ml). The combined extracts are washed with brine (15 ml), dried with sodium sulfate, and concentrated on a rotary evaporator. The residue is purified by fractional distillation *in vacuo* to give a fraction containing **6a**; yield: 172 mg (88%); b.p. 57–59 °C/1.5 torr.

The yields of **6** are shown in Table 1; the physical properties along with spectral data for **6** are shown in Table 2.

***N*-Ethoxycarbonyl-4-hydroxy-2-methyl-1,2,3,4-tetrahydropyridine (7b); Typical Procedure:**
To a stirred solution of *N*-ethoxycarbonyl-6-methoxy-2-methyl-1,2,3,6-tetrahydropyridine (**6b**; 185 mg, 1 mmol) in water (1.5 ml) and acetone (0.5 ml) is added acetic acid (0.07 ml, 1.22 mmol) over a 1 h period. After the addition is complete, the reaction mixture is allowed to stir for 10 min at room temperature. The mixture is concentrated, and the residue is purified by column chromatography (silica gel, hexane/ethyl acetate, 1 : 1) to give 30 mg (27%) of *cis*-**7b** and 46 mg (41%) of *trans*-**7b** (*cis*: *trans* = 2 : 3).

Yields of **7** are shown in Table 1; the physical properties as well as spectral data of **7** are shown in Table 2.

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