(s, 2 H), 3.37 (s, 3 H), 3.07-2.53 (m, 4 H). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.03; H, 7.39.

14: IR (neat) 1730, 1720 cm^{-1}; NMR ($CDCl_3$) δ 8.00 (d, J = 9 Hz, 2 H), 7.25 (d, J = 9 Hz, 2 H), 5.43-4.83 (m, 2 H), 3.00 (t, J = 7 Hz, 2 H), 2.60 (t, J = 7 Hz, 2 H), 1.37 (d, J = 7 Hz, 6 H), 1.20 (d, J = 7 Hz, 6 H). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.92; H, 8.00.

15: IR (neat) 1710 cm^{-1}; NMR ($CDCl_3$) δ 7.73 (d, J = 16.5 Hz, 1 H), 7.27-7.60 (m, 5 H), 6.42 (d, J = 16.5 Hz, 1 H), 5.13 (s, 2 H), 2.27 (s, 3 H).

16: IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 7.40-7.07 (m, 4 H), 7.60 (d, J = 16 Hz, 1 H), 6.30 (d, J = 16 Hz, 1 H), 5.13 (s, 2 H), 2.27 (s, 3 H).

17: mp 67-68 °C; IR (KBr) 1720 cm^{-1}; NMR ($CDCl_3$) δ 7.77-7.17 (m, 10 H), 7.27 (s, 5 H), 5.13 (s, 2 H), 2.70 (s, 1 H). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.93; H, 5.60.

18: IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 7.97-7.80 (m, 1 H), 7.57-7.20 (m, 8 H), 5.38 (s, 2 H). Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.49. Found: C, 68.01; H, 4.21.

19: IR (neat) 1720 cm^{-1}; NMR (CCl_4) δ 8.00 (d, J = 9 Hz, 2 H), 7.37 (d, J = 9 Hz, 2 H), 7.33 (s, 5 H), 5.27 (s, 2 H).

20: IR (neat) 1720 cm^{-1}; NMR (CCl_4) δ 8.00 (d, J = 9 Hz, 2 H), 7.47-7.03 (m, 5 H), 6.83 (d, J = 9 Hz, 2 H), 5.27 (s, 2 H), 3.80 (s, 3 H).

21: IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 6.87 (s, 2 H), 5.27 (m, 1 H), 2.33 (s, 9 H), 1.35 (d, J = 7 Hz, 6 H).

22: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 8.13-7.90 (m, 2 H), 7.53-7.17 (m, 3 H), 6.33-5.67 (m, 1 H), 5.50-5.07 (m, 2 H), 4.87-4.67 (m, 2 H).

23: IR (neat) 3350, 1740, 1710 cm^{-1}; NMR ($CDCl_3$) δ 7.53 (s, 5 H), 5.18 (s, 2 H), 3.76 (s, 3 H), 1.39 (d, J = 7 Hz, 3 H); $[\alpha]^{23}_D$ -34.8° (c 2.5, CH_3OH) [lit.[45] $[\alpha]^{23}_D$ -35°].

Synthesis of Macrolides 25, 27, 29, 31, 32, and 33. The preparation of **2a-c** in DMF was carried out under the same reaction conditions as described above. Into a DMF solution (500 mL) of an ω-bromo carboxylic acid (1 mmol), a solution of **2** (2 mmol) in 6 mL of DMF was added at -60 °C, and the reaction mixture was stirred for 24 h at room temperature. After the solvent was evaporated, the products were isolated through silica gel column with a mixed solvent of hexane and ethyl acetate (5:1). The ratios of macrolides **27** and **29** and diolides **28** and **30** were determined by the relative intensity of protons at the position α to oxygen by using 400-MHz ^1H NMR spectrometer.

25:[27] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.12517 (t, J = 5.6 Hz, 2 H), 2.32304 (t, J = 6.8 Hz, 2 H), 1.66930-1.26106 (m, 26 H); mass speectrum, m/e 254 (M^+).

27:[46] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.15632 (dd, J = 6.5, 5.3 Hz, 2 H), 2.37373-2.34289 (m, 2 H), 1.69190-1.34595 (m, 18 H); mass spectrum, m/e 198 (M^+).

28:[46] mp 80.5-82 °C; IR (neat) 1732 cm^{-1}; NMR ($CDCl_3$) δ 4.10440 (t, J = 5.9 Hz, 4 H), 2.31235 (t, J = 7 Hz, 4 H), 1.64976-1.27633 (m, 36 H); mass spectrum, m/e 396 (M^+).

29:[46] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.19891 (dd, J = 6.3, 5.3 Hz, 2 H), 2.38502-2.35327 (m, 2 H), 1.72762-1.36274 (m, 16 H); mass spectrum, m/e 184 (M^+).

30:[46] mp 72-73 °C; IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.10349 (t, J = 5.9 Hz, 4 H), 2.31816 (t, J = 6.8 Hz, 4 H), 1.65831-1.24213 (m, 32 H); mass spectrum, m/e 368 (M^+).

31:[29b] IR (neat) 1733 cm^{-1}; NMR ($CDCl_3$) δ 4.14746 (t, J = 5.4 Hz, 2 H), 2.39144-2.36029 (m, 2 H), 1.68701-1.26747 (m, 20 H); mass spectrum, m/e 212 (M^+).

32:[47] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.13769 (t, J = 5.4 Hz, 2 H), 2.36701-2.33556 (m, 2 H), 1.69343-1.32892 (m, 22 H); mass spectrum, m/e 226 (M^+).

33:[29b] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.13402 (t, J = 5.6 Hz, 2 H), 2.33006 (t, J = 6.0 Hz, 2 H), 1.67755-1.26381 (m, 24 H); mass spectrum, m/e 240 (M^+).

35:[48] IR (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 4.97951-4.91051 (m, 1 H), 2.49464-2.17587 (m, 2 H), 1.77373-0.85723 (m, 33 H); mass spectrum, m/e 282 (M^+).

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(47) Kruizinaga, W. H.; Kellog, R. M. *J. Chem. Soc., Chem. Commun.* **1979**, 286.
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Facile Preparation of Nitrones by Electrochemical Oxidation of *N*-Hydroxy Secondary Amines Using Halogen Ions as Mediators[1]

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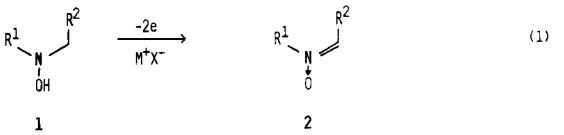
Nitrones **2** are versatile 1,3-dipoles useful for the construction of nitrogen heterocycles.[2] Synthesis of nitrones by oxidation[3] of *N*-hydroxy secondary amines **1** is not always convenient owing to the requisite of using an excess amount of the oxidizing agents and the resulting troublesome workup. In our continuing study on the anodic oxidation using mediators,[4] we have found a new electrooxidative method of synthesis of **2** from **1** (eq 1).



(1)

1 **2**

The procedure is simple and practical as exemplified by the oxidation of *N*-hydroxypiperidine (**1a**). Thus, nitrone **2a** was prepared by passing a constant current through a solution of **1a** in methanol containing sodium iodide as a supporting electrolyte (M^+X^-). The results obtained under several conditions are shown in Table I indicating that using even a catalytic amount of iodide as the supporting electrolyte gave satisfactory results (runs 1, 2, 4, and 5), whereas bromide and chloride (runs 6 and 7) gave poor results.

On the basis of these facts, the formation of **2a** can reasonably be explained by the working hypothesis in which I^- is anodically oxidized to the active species "I^+",[5,6] and the intermediate **3** formed from the reaction of **1a** with "I^+" yielded **2a** through elimination of HI catalyzed by a cathodically generated base[7] (Scheme I).

Since I^- regenerated is again reoxidized to "I^+", only a catalytic amount of NaI is enough to complete the oxidation of **1a** to **2a**. The formation of **2a** may be, however,

(1) Electroorganic Chemistry. 92. A part of this study has been presented: "Abstract of Papers", 49th Annual Meeting of the Chemical Society of Japan Tokyo, 1981: Chemical Society of Japan: Tokyo, 1984; p 848.
(2) For reviews of synthetic utilization of nitrones, see: (a) Black, D. St. C.; Crozier, R. J.; Davis, V. C. *Synthesis* **1975**, 205. (b) Harmer, J.; Macaluso, A. *Chem. Rev.* **1964**, 474. (c) Tufariello, J. J.; Tette, J. P. *J. Org. Chem.* **1975**, *40*, 3866. (d) Tufariello, J. J. *Acc. Chem. Res.* **1979**, *12*, 396.
(3) For examples, see: (a) Thesing, J.; Sirrenberg, W. *Chem. Ber.* **1959**, *92*, 1748. (b) Kropf, H.; Lambeck, R. *Justus Liebigs Ann. Chem.* **1966**, *700*, 18. (c) Thesing, J.; Mayer, H. *Ibid.* **1957**, *609*, 46. (d) Utzinger, G. E.; Regenass, F. A. *Helv. Chem. Acta* **1954**, *37*, 1982. (e) De La Mare, H. E.; Coppinger, G. M. *J. Org. Chem.* **1963**, *28*, 1068. (f) Murahashi, S.; Mitsui, H.; Watanabe, T.; Zenki, S. *Tetrahedron Lett.* **1983**, *24*, 1049.
(4) (a) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Tetrahedron Lett.* **1979**, 165; (b) **1979**, 3861.
(5) "I^+" denotes the positive iodine species anodically generated from iodide anion.
(6) The decrease in the yields of **2a** as a function of increasing iodide supports the formation of this intermediate.
(7) For example, see: (a) Baizer, M. M.; Chruma, J. L.; White, D. A. *Tetrahedron Lett.* **1973**, 5209. (b) Allen, P. M.; Hess, U.; Foote, C. S. *Synth. Commun.* **1982**, *12*, 123. (c) Iverson, P. E.; Lund, H. *Tetrahedron Lett.* **1969**, 3523. (d) Shono, T.; Kashimura, S.; Ishizaki, K.; Ishige, O. *Chem. Lett.* **1983**, 1311. (e) Shono, T.; Kashimura, S.; Nogusa, H. *J. Org. Chem.* **1984**, *49*, 2043.

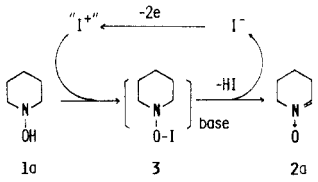
0022-3263/86/1951-0549$01.50/0

Table I. Electrooxidation of *N*-Hydroxypiperidine (1a)[a]

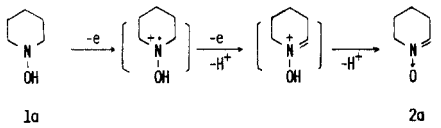
run	supporting electrolyte (equiv)	yield of nitrone **2a**,[b] %
1	NaI (0.2)	92 (85)[c]
2	(0.5)	90
3	(1.0)	89
4	KI (0.2)	83
5	Et_4NI (0.2)	80
6	NaBr (0.2)	54
7	NaCl (0.2)	16

[a] The amount of electricity passed was $2.5F$/mol. [b] Yield of **2a** was determined by NMR method using ethyl orthoformate as a standard compound. [c] Isolated yield.

Scheme I



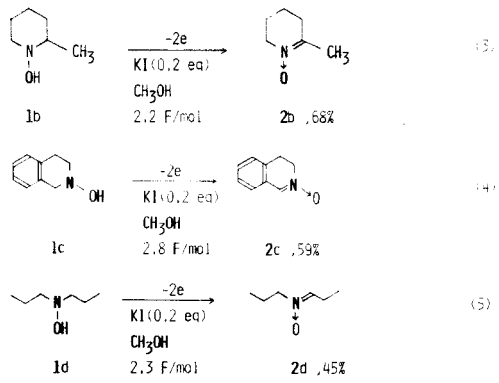
also explained by another route in which **1a** is oxidized by the direct oxidation mechanism (eq 2). However, this



(2)

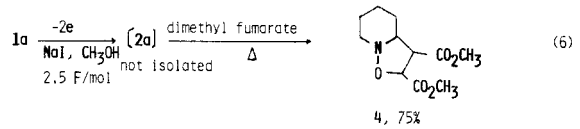
mechanism may be unlikely, since the oxidation potential of I^- is more cathodic than **1a**.[8] Also, the direct oxidation of **1a** in methanol containing Et_4NOTs gave **2a** in low yield (30–40%) at the stage where $3F$/mol of electricity was passed, and the yield was decreased when more electricity was passed.

Several other *N*-hydroxy secondary amines (**1b–d**) were similarly electrooxidized in methanol containing KI to the corresponding nitrones (eq 3–5).[9]

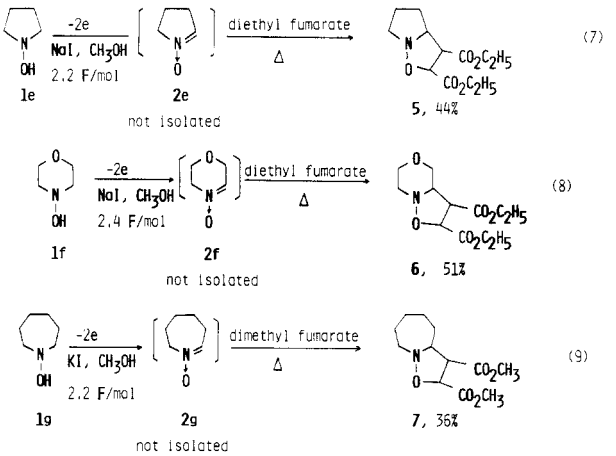


(3)
(4)
(5)

Isolation of nitrones is not always necessary for their utilization as 1,3-dipoles. In fact, the crude products **2** obtained from **1** yielded the corresponding 1,3-dipolar adducts **4–7** upon heating with dimethyl or diethyl fumarate (eq 6–9).[9]



(6)



Experimental Section

***N*-Hydroxy secondary amines 1b–g** were prepared according to the procedure of J. Thesing[10] through the oxidation of the secondary amines with 30% H_2O_2. *N*-Hydroxypiperidine (**1a**) was commercially available.

Electrooxidative Preparation of Nitrones. The general procedure is exemplified by the oxidation of *N*-hydroxypiperidine (**1a**). To an undivided cell equipped with a platinum anode and a carbon cathode was put a solution of **1a** (5 mmol) and NaI (1 mmol) in methanol (30 mL). A constant current (0.2 A) was passed through the cell with external cooling by ice–water. After $2.5F$/mol of electricity was passed, the solvent was evaporated in vacuo, and the residue was chromatographed on a column of silica gel (1:10 MeOH–AcOEt) to afford **2a** in 85% yield. The structure of **2a** was identified by comparison of its spectroscopic data with those described in the literature.[3f]

2b: IR (neat) 2950, 2860, 1620, 1450, 1200, 1170, 730 cm^{-1}; NMR ($CDCl_3$) δ 1.40–2.23 (m, 4 H), 2.18 (br s, 3 H), 2.30–2.73 (m, 2 H), 3.58–4.10 (m, 2 H); mass spectrum, m/e 113 (M^+), 55.

2c: IR (neat) 3075, 1600, 1570, 1500, 1460, 1340, 1320, 1300, 1275, 1215, 1190, 905, 765 cm^{-1}; NMR ($CDCl_3$) δ 3.23 (t, 2 H, J = 7 Hz), 4.20 (t, 2 H, J = 7 Hz), 7.00–7.57 (m, 3 H), 7.67–7.97 (m, 2 H); mass spectrum, m/e 147 (M^+). Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.29; H, 5.89; N, 9.22.

2d: IR (neat) 2980, 2895, 1600, 1470, 1425, 1195 cm^{-1}; NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7 Hz), 1.10 (t, 3 H, J = 7 Hz), 1.60–2.23 (m, 2 H), 2.23–2.90 (m, 2 H), 3.73 (t, 2 H, J = 6 Hz), 6.73 (t, 1 H, J = 6 Hz), 6.73 (t, 1 H, J = 6 Hz); mass spectrum, m/e 116 ($M^+ + 1$), 115 (M^+), 114 ($M^+ - 1$), 86 ($M^+ - CH_2CH_3$).

1,3-Cycloaddition Reaction. The general procedure is exemplified by the reaction of dimethyl fumarate with the crude oxidation product of **1a**. After a methanolic solution of **1a** (5 mmol) containing NaI (1 mmol) as a supporting electrolyte was electrolyzed according to the procedure described above, the solvent was evaporated, and a solution of dimethyl fumarate (5 mmol) in $CHCl_3$ (20 mL) was added to the residue. The resulting solution was heated to reflux for 1 h under a nitrogen atmosphere, and the solvent was evaporated under reduced pressure to give a residue, which was then subjected to silica gel column chromatography (1:10 AcOEt–hexane) to afford **4** in 75% yield: IR (neat) 2940, 2845, 1740, 1440, 1270, 1200, 1015, 795 cm^{-1}; NMR (CCl_4) δ 1.03–2.60 (m, 8 H), 3.20–3.62 (m, 2 H), 3.75 (s, 3 H), 3.77 (s, 3 H), 4.60 and 4.78 (2 d, 1 H, J = 4 Hz). Anal. Calcd for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.06; H, 7.11; N, 5.75.

5: The structure of **5** was identified by comparison of its spectroscopic data with those described in the literature.[3c]

6: IR (neat) 2995, 1740, 1375, 1195, 1120, 1030, 860, 790 cm^{-1}; NMR (CCl_4) δ 1.30 (t, 3 H, J = 5 Hz), 1.33 (t, 3 H, J = 5 Hz), 2.90–4.43 (m, 8 H), 4.22 (q, 4 H, J = 5 Hz), 4.60–5.15 (m, 1 H). Anal. Calcd for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.44; H, 7.22; N, 4.89.

7: IR (neat) 2930, 2710, 1740, 1440, 1210, 1030, 815, 730 cm^{-1}; NMR (CCl_4) δ 1.15–2.00 (m, 8 H), 2.37–3.10 (m, 2 H), 3.30–3.68

(8) Oxidation peak potential of I^- is more cathodic than that of **1a**. (E_p for Et_4NI (0.01 M) = 0.60 V vs. SCE, E_p for **1a** (0.01 M) = 0.68 V vs. SCE in CH_3OH–0.1 M $LiClO_4$–$3H_2O$, 100 mV/s).

(9) Yields were not optimized.

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(m, 2 H), 3.78 (s, 6 H), 4.45–4.92 (m, 1 H). Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.02; H, 7.44; N, 5.44. Found: C, 55.74; H, 7.52; N, 5.62.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid for Special Project Research (1) (No. 57118003, 58110003, and 59104003) (to T.S.) and for a Grant-in-Aid for Developmental Scientific Research (2) (No. 58850178) (to Y.M.).

Registry No. **1a**, 4801-58-5; **1b**, 99687-80-6; **1c**, 54105-63-4; **1d**, 7446-43-7; **1e**, 5904-62-1; **1f**, 5765-63-9; **1g**, 6763-87-7; **2a**, 34418-91-2; **2b**, 55386-67-9; **2c**, 24423-87-8; **2d**, 20135-16-4; **4**, 99687-81-7; **5**, 99745-91-2; **6**, 99687-82-8; **7**, 99687-83-9; NaI, 7681-82-5; KI, 7681-11-0; Et_4NI, 68-05-3; Pr_2NH, 142-84-7; 2-methylpiperidine, 109-05-7; 1,2,3,4-tetrahydroisoquinoline, 91-21-4; dimethyl fumarate, 624-49-7; diethyl fumarate, 623-91-6; pyrrolidine, 123-75-1; morpholine, 110-91-8; hexahydroazepine, 111-49-9.

Preparation of 8-Phenylmenthol and Its Diastereomer, 2-*epi*,*ent*-8-Phenylmenthol. A Caveat

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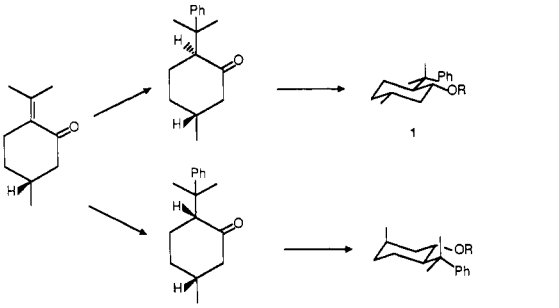
Received May 21, 1985

A number of publications[1] that detail the use of 8-phenylmenthol (phenmenthol, **1a**) as a chiral auxiliary for asymmetric induction followed initial publications in this area by Corey[2] and Oppolzer.[3] Our research[4-6] has produced the highest levels of induction with this auxiliary and the observation of diastereomeric excess (de) values of at least 99.9 to 0.1 in the ene reaction of the glyoxylate ester of **1** with hexene probably stands as an all time record in the area of asymmetric induction in carbon–carbon bond formation. The power of this chiral auxiliary as well as the interest demonstrated in its application to a variety of processes prompts us to detail here our experimental findings on its preparation. In particular, we draw attention to the fact that the sequence to be described starting from pulegone results inevitably in phenmenthol (**1a**) admixed with a diastereomer (**2a**) that is epimeric at both C-1 and C-2 (hence our trivial name of epientphenmenthol for **2a** since it is the enantiomer of 8-phenylmenthol save for being epimeric at C-5). Since it is these centers that appear to be solely responsible for the induction of asymmetry, it would be anticipated that this diastereomer would be equally as effective as phenmenthol as a chiral auxiliary in inducing the opposite sense of chirality.[7] We have been able to show that this is indeed the case.

Table I

reaction	auxiliary, de 1	2
1b/2b + $H_2C{=}CHC_4H_9$	99.8	99.8
1c/2c + C_5H_5	90	86
1d/2d + RMgBr	92	68

The procedure used for the synthesis of **1a** (and of **2a**) is that described by Corey[1,5] beginning with pulegone.



Since the degree of induction observed will depend on the purity of the starting material, we have examined the level of enantiomeric purity of **1a** derived from commercial pulegone (Givaudan) through analysis by our published procedure[8] involving the formation of the mandelic acid ester. Using this method, we are able to set a minimum level of enantiomeric excess for phenmenthol (and hence for the pulegone from which it is derived) of 99%. This result corresponds well with an independent analysis by Eliel of the methoxytrifluorophenylacetate ester of menthol prepared by reduction of pulegone.[9] It would thus appear that pulegone derived from natural sources can be considered to be enantiomerically pure.

The conversion of pulegone to **1a** and **2a** involves the copper-catalyzed addition of phenylmagnesium bromide followed by dissolving metal reduction of the derived ketone. The conjugate addition afforded a mixture of diastereomers epimeric at the newly formed stereocenter (C-2) where the ratio varied depending on the method of quenching of the reaction from 60:40 to near the equilibrium value of 85:15. However, since in the next step reduction of the carbonyl is slower than epimerization, the ratio of the epimeric ketones was not reflected in the ratio of phenmenthol to epientphenmenthol which invariably is 85:15. Indeed, we examined a range of reducing agents and reaction conditions in an attempt to improve the overall amount of epientphenmenthol produced. However, with all other reagents either the reduction proceeded to afford predominantly the axial alcohol or the chemical yield was significantly lower than that with the simple dissolving metal conditions.

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