at room temperature overnight. Crystals of **4** were obtained (2.11 g, 89%), mp 250–252 °C (lit.[12] mp 250–251 °C).

It is not necessary to dry rigorously the diacid/anhydride prior to the recrystallization step. Repetition of the experiment, starting with 2.36 g of **3** and omitting the vacuum drying of the filtrand, gave 1.93 g (89%) of pure **4** as a single crop from acetic anhydride (washed with ether).

**Acknowledgment.** Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

**Registry No.** **1**, 75802-19-6; **3** (stereoisomer 1), 109428-59-3; **3** (stereoisomer 2), 114027-87-1; **4**, 716-39-2; maleic anhydride, 108-31-6; 1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylic acid anhydride, 29811-05-0.

## Diastereoselective Alkylation of 3-Acylimidazolidin-2-ones: Synthesis of (*R*)- and (*S*)-Lavandulol

Giuliana Cardillo,* Anna D'Amico, Mario Orena,* and Sergio Sandri

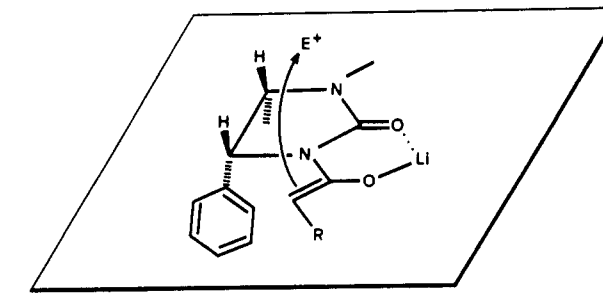
*Centro per lo Studio della Fisica delle Macromolecole del CNR, Dipartimento di Chimica "G. Ciamician", Via Selmi 2, 40126 Bologna, Italy*

*Received July 24, 1987*

In connection with our general interest in the search for new approaches to prenyl compounds,[1] we developed a procedure incorporating one prenyl unit at a time, through the alkylation of the Li dianion of 3-methyl-2-butenoic acid.[2] This methodology provides terpenes with the lavandulyl skeleton, since this dianion undergoes alkylation predominantly at C-2.[3,4] Owing to the increasing importance of optically active monoterpenes,[5] their asymmetric synthesis through chiral auxiliaries has attracted interest.[6]

Herein we report a new method for asymmetric alkylation that we believe has considerable potential in the synthesis of prenyl compounds. This process, outlined in Scheme I, appears to offer many advantages, including high efficiency, procedural simplicity, predictable configuration of the introduced stereogenic center, and mildness of the reaction conditions. The utility of chiral auxiliaries in the alkylation of carboxylic acid derivatives has been recently reported;[7] we now exploit the use of the readily accessible imidazolidin-2-ones 4*R*,5*S* **1a** and 4*S*,5*R* **1b**[8] (Figure 1).


**Figure 1.**




| Chiral auxiliary | Priority | Configuration of the new chiral center |
|---|---|---|
| **1a** (4R,5S) | E < R | R |
| | E > R | S |
| **1b** (4S,5R) | E < R | S |
| | E > R | R |

**Figure 2.**

In our approach to the enantiomerically pure lavandulol,[9] the lithium anion of **1a** is acylated with 3-methyl-2-butenoyl chloride, to obtain **2a** in high yield. After treatment of **2a** with an equimolar amount of LDA in THF at −78 °C, the alkylation is performed at the same temperature[10] with 1-bromo-3-methyl-2-butene, to afford **3a** in 83% yield.

The diastereoselection of the reaction can be determined by $^1$H NMR spectroscopy, by observing the doublet of the CHPh proton of the auxiliary moiety, which shows different chemical shifts in the two diastereomers. An asymmetric induction ≥95% can be assumed if only one diastereomer is recognizable in the $^1$H NMR spectrum.[11] A 96:4 diastereomeric ratio is determined from the $^{13}$C NMR spectrum[12] and successively confirmed by reduction of the alkylated product **3a** with lithium aluminum hydride (LAH) to afford (−)-lavandulol (**4a**), $[\alpha]_D$ −10.04°,[9a] a value corresponding to 92% ee. The synthetic sequence starting

(1) (a) Cainelli, G.; Cardillo, G.; Contento, M.; Trapani, G.; Umani Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 400. (b) Cainelli, G.; Cardillo, G.; Contento, M.; Grasselli, P.; Umani Ronchi, A. *Gazz. Chim. Ital.* **1973**, *103*, 117. (c) Cardillo, G.; Contento, M.; Sandri, S. *Tetrahedron Lett.* **1974**, 2215. (d) Cardillo, G.; Orena, M.; Sandri, S. *Tetrahedron* **1976**, *32*, 107. (e) Cainelli, G.; Cardillo, G.; Orena, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1597. (f) Cardillo, G.; Contento, M.; Sandri, S.; Panunzio, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1729.

(2) Cainelli, G.; Cardillo, G.; Contento, M.; Umani Ronchi, A. *Gazz. Chim. Ital.* **1974**, *104*, 625.

(3) Pitzele, B. S.; Baran, J. S.; Steinman, D. H. *Tetrahedron* **1976**, *32*, 1347.

(4) For recent approaches to the lavandulyl skeleton, see: (a) Bertrand, M.; Gil, G.; Viala, J. *Tetrahedron Lett.* **1977**, 1785. (b) Oakleaf, J. A.; Thomas, M. T.; Wu, A.; Snieckus, W. *Tetrahedron Lett.* **1978**, 1645. (c) Julia, M.; Perez, C.; Saussine, L. *J. Chem. Res., Synop.* **1978**, 311.

(5) (a) Mori, K.; Okada, K. *Tetrahedron* **1985**, *41*, 557. (b) Ruo, R. R.; Herz, W. *J. Org. Chem.* **1985**, *50*, 700. (c) Hedge, S. C.; Beckwith, D.; Doti, R.; Wolinsky, J. *J. Org. Chem.* **1985**, *50*, 894. (d) Hatakeyama, S.; Sajio, K.; Takano, S. *Tetrahedron Lett.* **1985**, *26*, 865. (e) Shastri, M. H.; Patil, D. G.; Patil, V. D.; Dev, S. *Tetrahedron* **1985**, *41*, 3083. (f) Mori, K.; Mori, H. *Tetrahedron* **1985**, *41*, 5487. (g) Hirama, M.; Noda, T.; Ito, S. *J. Org. Chem.* **1985**, *50*, 127. (h) Sato, T.; Funabora, M.; Watanabe, M.; Fujisawa, T. *Chem. Lett.* **1985**, 1391. (i) Ortuno, R. M.; Mercé, R.; Font, J. *Tetrahedron Lett.* **1986**, *27*, 2519. (j) Meyers, A. I.; Fleming, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 306. (k) Ikeda, N.; Arai, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1986**, *108*, 483. (l) Ohwa, M.; Kogure, T.; Eliel, E. *J. Org. Chem.* **1986**, *51*, 2599. (m) Lombardo, D. A.; Weedon, A. C. *Tetrahedron Lett.* **1986**, *27*, 5555.

(6) (a) Helmchen, G.; Schmierer, R. *Tetrahedron Lett.* **1983**, *24*, 1235. (b) Oppolzer, W.; Schneider, P. *Helv. Chim. Act* **1986**, *69*, 1817. (c) Matteson, D. S.; Sadhu, K. M.; Peterson, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 810.

(7) (a) Meyers, A. I. *Acc. Chem. Res.* **1979**, *11*, 375, and references therein cited. (b) Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, p 1 and references therein cited. (c) Helmchen, G.; Selim, A.; Dorsch, D.; Taufer, I. *Tetrahedron Lett.* **1983**, *24*, 3213. (d) Oppolzer, W.; Dudfield, P.; Stevenson, T.; Godel, T. *Helv. Chim. Acta* **1985**, *68*, 212.

(8) (a) Close, W. J. *J. Org. Chem.* **1950**, *15*, 1131. (b) Roder, H.; Helmchen, G.; Peters, E. M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 898.

(9) For enantioselective approaches to lavandulol, see: (a) Kramer, A.; Pfander, H. *Helv. Chim. Acta* **1982**, *65*, 293. (b) Takano, S.; Tanaka, M.; Seo, K.; Hirama, M.; Ogasawara, K. *J. Org. Chem.* **1985**, *50*, 931.

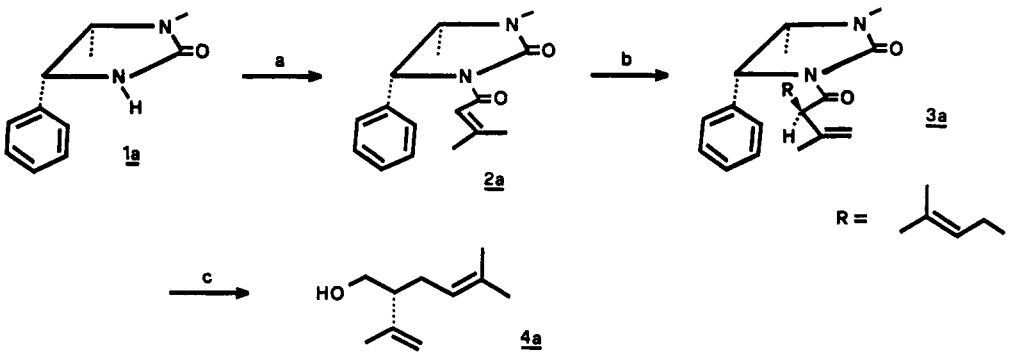
(10) The diastereoselection of the alkylation strongly depends on the temperature. In fact, the same reaction, carried out at −10 °C, affords a diastereomeric ratio 85:15.

(11) Schöllkopf, U.; Hausberg, H. H.; Hoppe, I.; Segal, M.; Reiter, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 117.

(12) The diastereomeric mixture cannot be separated by TLC nor by column chromatography.

0022-3263/88/1953-2354$01.50/0 

Scheme I[a]




[a] (a) *n*-BuLi, $Me_2C{=}CHCOCl$; (b) LDA, -78 °C, $Me_2C{=}CHCH_2Br$; (c) LAH, 0 °C.

from the (4*S*,5*R*)-imidazolidin-2-one **1b** gives (+)-lavandulol (**4b**) in the same ee. It is worth mentioning that, after the reductive cleavage, the chiral auxiliary is recovered unchanged in very good yield.

Since the absolute configuration of lavandulol is *R* for the (-) enantiomer **4a**, the (+) enantiomer **4b** obtained by starting from (4*S*,5*R*)-imidazolidin-2-one **1b** is assigned the *S* configuration.[9a] This is consistent with the mechanism of the alkylation,[13] and the observed diastereoselection can be ascribed to the planar anion, one diastereotopic side of which is strongly shielded by the large phenyl group (Figure 2).

It follows that a new stereogenic center in a definite configuration can be obtained by the proper choice of the chiral auxiliary **1a** or **1b** (Table I).

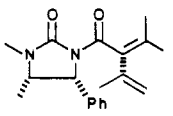
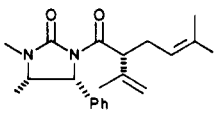
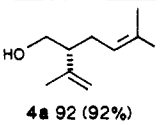
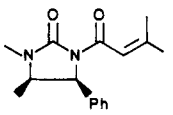
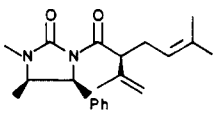
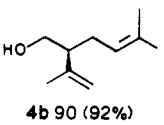
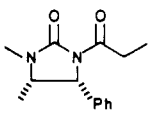
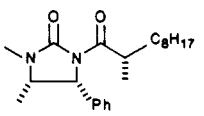
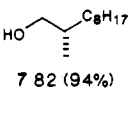
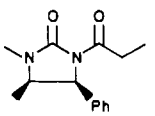
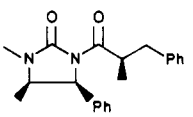
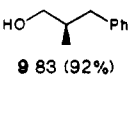
Further examples of this diastereoselective alkylation have been studied. Thus, with the aim to obtain (*S*)-2-methyldecanol (**7**),[14] the key intermediate in the synthesis of the pheromone of *Neodipirion sertifer*,[15] the (4*R*,5*S*)-3-propanoylimidazolidin-2-one **5a** is alkylated with 1-iodooctane, to give **6** in a 97:3 diastereomeric mixture, as determined from the $^{13}C$ NMR spectrum. After reductive cleavage of **6** with LAH, (*S*)-2-methyldecanol (**7**) is obtained in 82% yield and 94% ee.[13,14] The synthesis of (*R*)-3-phenyl-2-methylpropanol (**9**),[13] proceeding through the alkylation of (4*S*,5*R*)-3-propanoylimidazolidin-2-one **5b**, affords a diastereomeric mixture, 96:4, of the alkylated product **8**. Successive treatment of **8** with LAH gives the corresponding *R* alcohol **9**[13,16] in 83% yield and 92% ee.

In conclusion, the use of the imidazolidin-2-ones **1a** and **1b** as chiral auxiliaries can be useful for many applications in the field of natural compounds, and further applications will be reported.

## Experimental Section

**General.** Reactions involving carbanions were carried out under argon. Tetrahydrofuran (THF) was freshly distilled from LAH, and diisopropylamine was distilled from $CaH_2$. Butyllithium (2.5 M in hexanes) was purchased from Janssen and titrated against 2-propanol to the 1,10-phenanthroline end point. Melting points were taken on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 682 infrared spectrophotometer. $^1H$ NMR (90 MHz) spectra were recorded on a Varian EM 390 instrument, with $CDCl_3$ as solvent. $^{13}C$ NMR (20 MHz) spectra were recorded in $CDCl_3$ solution on a Varian FT 80 A Fourier transform spectrometer. Chemical shifts are given with respect to $Me_4Si$ used as internal standard. Mass spectra were taken with a Varian MAT 112 instrument (direct inlet, 70 eV). Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter.

**Table I. Diastereoselective Alkylation and Reductive Cleavage of 3-Acylimidazolidin-2-ones**

| starting material | alkylation prod yield, % (de)[a] | reductive cleavage prod yield, % (ee)[b] |
|---|---|---|
|  2a |  3a 83 (92%) |  4a 92 (92%) |
|  2b |  3b 80 (94%) |  4b 90 (92%) |
|  5a |  6 79 (94%) |  7 82 (94%) |
|  5b |  8 86 (92%) |  9 83 (92%) |

[a] Determined by $^{13}C$ NMR. [b] See Experimental Section.

**(4*R*,5*S*)-1,5-Dimethyl-4-phenylimidazolidin-2-one (1a).** This compound is prepared as described in the literature[8a] by starting from urea and (-)-ephedrine hydrochloride: mp 175 °C (lit.[8b] mp 177-179 °C); IR (Nujol) 3280, 1705, 1670 $cm^{-1}$; $^1H$ NMR δ 0.7 (d, 3 H, *J* = 6 Hz), 2.85 (s, 3 H), 3.85 (dq, *J* = 6, 7 Hz), 4.75 (d, 1 H, *J* = 7 Hz), 5.3 (br s, 1 H, NH), 7.3 (m, 5 Ar H); $^{13}C$ NMR δ 14.3, 28.2, 57.7, 58.2, 127.2, 128.0, 128.5, 137.0; $[\alpha]_D$ -43.2° (*c* 1, MeOH) (lit.[8b] $[\alpha]_D$ -44.5° (*c* 3, MeOH)); MS, *m/e* 190 ($M^+$), 175, 94. Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.55; H, 7.41; N, 14.70.

**(4*S*,5*R*)-1,5-Dimethyl-4-phenylimidazolidin-2-one (1b).** This compound is prepared as described in the literature[8a] by starting from urea and (+)-ephedrine: mp 176 °C (lit.[8b] mp for 4*R*,5*S* isomer 177-179 °C); $[\alpha]_D$ +43.7° (*c* 1, MeOH) (lit.[8b] $[\alpha]_D$ for 4*R*,5*S* isomer -44.5° (*c* 3, MeOH)). Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.51; H, 7.40; N, 14.71.

**General Procedure for Preparation of 3-Acylimidazolidin-2-ones 2a,b and 5a,b.** A solution of 9.5 g (50 mmol) of **1a** or **1b** in dry THF (100 mL) is treated with an equimolar amount of *n*-butyllithium at 0 °C. After the solids are dissolved, the clear solution is stirred for 0.5 h at 0 °C, then the appropriate acyl chloride (50 mmol) dissolved in THF (25 mL) is added, and

(13) Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737.
(14) Bystrom, S.; Hogberg, H. E.; Norin, T. *Tetrahedron* **1981**, *37*, 2249.
(15) Jewett, D. M.; Matsumura, F.; Coppel, H. C. *Science (Washington, D.C.)* **1976**, *51*, 192.
(16) Terashima, S.; Yamada, S.-I. *Chem. Pharm. Bull.* **1968**, *16*, 1953.

the mixture is stirred for 1 h at 0 °C. Workup with saturated ammonium chloride solution and $CH_2Cl_2$, followed by flash chromatography (cyclohexane/$CH_2Cl_2$, 4:6), affords the pure products **2a,b** and **5a,b**.

**(4*R*,5*S*)-1,5-Dimethyl-4-phenyl-3-(3'-methyl-2'-butenoyl)imidazolidin-2-one (2a).** Reaction from **1a** and 3-methyl-2-butenoyl chloride affords 12.8 g (94%) of **2a** as white crystals: mp 158 °C; IR (Nujol) 1715, 1660, 1630 $cm^{-1}$; $^1H$ NMR $\delta$ 0.8 (d, 3 H, $J$ = 6 Hz), 1.95 (s, 3 H), 2.09 (s, 3 H), 2.85 (s, 3 H), 3.9 (dq, 1 H, $J$ = 6, 7 Hz), 5.35 (d, 1 H, $J$ = 7 Hz), 7.1–7.4 (m, 6 H, vinyl + Ar H); $^{13}C$ NMR $\delta$ 15.0, 21.1, 27.9, 28.2, 54.0, 59.3, 117.3, 127.0, 127.9, 128.5, 137.1, 155.8; $[\alpha]_D$ -105.4° (*c* 1.2, $CH_2Cl_2$); MS, *m/e* 272 ($M^+$), 189, 176, 108, 57. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.44; H, 7.39; N, 10.31.

**(4*S*,5*R*)-1,5-Dimethyl-4-phenyl-3-(3'-methyl-2'-butenoyl)imidazolidin-2-one (2b).** Reaction from **1b** and 3-methyl-2-butenoyl chloride affords 12.5 g (92%) of **2b** as white crystals: mp 159 °C; $[\alpha]_D$ +106.1° (*c* 0.9, MeOH). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.49; H, 7.41; N, 10.26.

**(4*R*,5*S*)-1,5-Dimethyl-4-phenyl-3-propanoylimidazolidin-2-one (5a).** Reaction from **1a** and propanoyl chloride affords 11.3 g (92%) of **5a** as white crystals: mp 90 °C; IR (Nujol) 1765, 1740 $cm^{-1}$; $^1H$ NMR $\delta$ 0.8 (d, 3 H, $J$ = 6 Hz), 1.1 (t, 3 H, $J$ = 5 Hz), 2.85 (s, 3 H), 3.0 (q, 2 H, $J$ = 5 Hz), 3.9 (dq, 1 H, $J$ = 6, 7 Hz), 5.3 (d, 1 H, $J$ = 7 Hz), 7.0–7.4 (m, 5 Ar H); $^{13}C$ NMR $\delta$ 8.6, 14.9, 28.1, 29.3, 54.0, 59.3, 127.0, 128.0, 128.5, 136.9, 173.5; $[\alpha]_D$ -54.7° (*c* 1, $CH_2Cl_2$); MS, *m/e* 246 ($M^+$), 217, 189, 94. Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.19; H, 7.35; N, 11.40.

**(4*S*,5*R*)-1,5-Dimethyl-4-phenyl-3-propanoylimidazolidin-2-one (5b).** Reaction from **1b** and propanoyl chloride affords 11.4 g (93%) of **5b** as white crystals: mp 91 °C; $[\alpha]_D$ +54.2° (*c* 1, $CH_2Cl_2$). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.23; H, 7.36; N, 11.39.

**General Procedure for Alkylation of 3-Acylimidazolidin-2-ones 2a,b and 5a,b.** To a solution of the 3-acylimidazolidin-2-one **2a,b** or **5a,b** (30 mmol) in THF (40 mL) at -78 °C is added 30 mmol of lithium diisopropylamide (LDA) in THF (20 mL). After 1 h, a solution of the appropriate alkyl halide (30 mmol) in THF (20 mL) is slowly dropped and the mixture is allowed to warm to 0 °C in 12 h. Workup with 2 M HCl and $CH_2Cl_2$, followed by flash chromatography on silica gel (cyclohexane/$CH_2Cl_2$, 6:4), yields the products **3a,b** or **6** and **8** as diastereomeric mixtures, the ratios of which are determined on the basis of the $^{13}C$ NMR spectra.

**(4*R*,5*S*,2'*R*)-1,5-Dimethyl-4-phenyl-3-[2'-(1-propen-2-yl)-5'-methyl-4'-hexenoyl]imidazolidin-2-one (3a).** Reaction from **2a** and 1-bromo-3-methyl-2-butene affords 8.5 g (83%) of **3a** as white crystals: diastereomeric ratio 96:4; mp 71 °C; IR (Nujol) 1740, 1670, 900 $cm^{-1}$; $^1H$ NMR $\delta$ 0.75 (d, 3 H, $J$ = 6 Hz), 1.45 (s, 3 H), 1.6 (s, 3 H), 1.8 (s, 3 H), 2.0–2.6 (m, 3 H), 2.8 (s, 3 H), 3.8 (dq, 1 H, $J$ = 6, 7 Hz), 4.5–5.1 (m, 3 H), 5.25 (d, 1 H, $J$ = 7 Hz), 7.2 (m, 5 Ar H); $^{13}C$ NMR $\delta$ 15.0, 17.6, 21.2, 25.7, 28.2, 30.1, 50.3, 53.5, 59.7, 112.8, 121.8, 127.0, 128.3, 133.0, 137.0, 144.0, 172.9; $[\alpha]_D$ -88.8° (*c* 1, $CH_2Cl_2$); MS, *m/e* 340 ($M^+$), 272, 189, 108, 71. Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 74.18; H, 8.27; N, 8.21.

**(4*S*,5*R*,2'*S*)-1,5-Dimethyl-4-phenyl-3-[2'-(1-propen-2-yl)-5'-methyl-4'-hexenoyl]imidazolidin-2-one (3b).** Reaction from **2b** and 1-bromo-3-methyl-2-butene affords 8.2 g (80%) of **3b** as white crystals: diastereomeric ratio 97:3; mp 73 °C; $[\alpha]_D$ +90.1° (*c* 1.02, $CH_2Cl_2$). Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 74.13; H, 8.28; N, 8.24.

**(4*R*,5*S*,2'*S*)-1,5-Dimethyl-4-phenyl-3-(2'-methyldecanoyl)imidazolidin-2-one (6).** Reaction from **5a** and 1-iodooctane affords 8.4 g (79%) of **6** as a low-melting solid: diastereomeric ratio 97:3; IR (Nujol) 1730, 1680 $cm^{-1}$; $^1H$ NMR $\delta$ 0.8 (d, 3 H, $J$ = 6 Hz), 0.85 (t, 3 H, $J$ = 4 Hz), 1.1 (d, 3 H, $J$ = 6 Hz), 1.2 (m, 14 H), 1.4–1.8 (m, 1 H), 2.8 (s, 3 H), 3.9 (dq, 1 H, $J$ = 6, 7 Hz), 5.3 (d, 1 H, $J$ = 7 Hz), 7.3 (m, 5 Ar H); $^{13}C$ NMR $\delta$ 14.1, 15.0, 16.8, 22.7, 28.3, 29.3, 29.6, 31.9, 34.2, 37.5, 53.8, 59.4, 127.1, 128.0, 128.4, 137.0, 173.5; $[\alpha]_D$ -15.0° (*c* 1, $CH_2Cl_2$); MS, *m/e* 358 ($M^+$), 261, 248, 242, 189, 87, 85. Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.57; H, 9.57; N, 7.78.

**(4*S*,5*R*,2'*R*)-1,5-Dimethyl-4-phenyl-3-(2'-methyl-3'-phenylpropanoyl)imidazolidin-2-one (8).** Reaction from **5b** and benzyl bromide affords 8.7 g (86%) of **8** as white crystals: diastereomeric mixture 96:4; mp 88 °C; IR (Nujol) 1730, 1685 $cm^{-1}$; $^1H$ NMR $\delta$ 0.75 (d, 3 H, $J$ = 6 Hz), 1.05 (d, 3 H, $J$ = 6 Hz), 2.4 (dd, 1 H, $J$ = 9, 14 Hz), 2.8 (s, 3 H), 3.4 (dd, 1 H, $J$ = 6, 14 Hz), 3.8 (dq, 1 H, $J$ = 6, 7 Hz), 4.35 (m, 1 H, $J$ = 6, 9 Hz), 5.35 (d, 1 H, $J$ = 7 Hz), 6.9–7.4 (m, 5 Ar H); $^{13}C$ NMR $\delta$ 15.0, 16.3, 28.2, 39.5, 39.8, 53.7, 59.4, 125.9, 126.9, 127.8, 128.2, 128.4, 129.3, 136.7, 139.7, 176.0; $[\alpha]_D$ +11.7° (*c* 1, $CH_2Cl_2$); MS, *m/e* 336 ($M^+$), 223, 189, 94, 85. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.87; H, 7.18; N, 8.35.

**General Procedure for Reductive Cleavage of 3-Acylimidazolidin-2-ones 3a,b, 6, and 8.** A solution of the imidazolidin-2-one **3a,b**, **6**, or **8** (20 mmol) in THF (40 mL) is slowly added at 0 °C under inert atmosphere to a stirred suspension of 1.6 g (40 mmol) of LAH in THF (30 mL), and the mixture is stirred at 0 °C for 1 h. After the reaction is quenched by cautious addition of MeOH (3 mL), workup with 2 M HCl and ethyl acetate, followed by flash chromatography on silica gel (cyclohexane/ethyl acetate, 8:2), provides the alcohols **4a,b**, **7**, and **9**. Further elution with ethyl acetate gives the imidazolidin-2-ones **1a** or **1b** in 90–93% yield.

**(*R*)-2-(1-Propen-2-yl)-5-methyl-4-hexen-1-ol (Lavandulol) (4a).** Reductive cleavage of **3a** gives 2.8 g (92%) of **4a** as an oil: IR (neat) 3360, 895 $cm^{-1}$; $^1H$ NMR $\delta$ 1.65 (s, 3 H), 1.8 (s, 6 H), 1.9–2.4 (m, 3 H), 2.1 (br s, 1 H, OH), 3.45 (d, 2 H, $J$ = 4 Hz), 4.75 (s, 1 H), 4.85 (s, 1 H), 5.1 (t, 1 H, $J$ = 5 Hz); $^{13}C$ NMR $\delta$ 17.8, 19.6, 25.7, 28.5, 50.0, 63.8, 112.9, 122.2, 132.7, 145.6; $[\alpha]_D$ -10.04° (*c* 1, MeOH) (lit.[9a] $[\alpha]_D$ for *S* isomer +10.8° (*c* 0.94, MeOH)). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.97; H, 11.78.

**(*S*)-2-(1-Propen-2-yl)-5-methyl-4-hexen-1-ol (Lavandulol) (4b).** Reductive cleavage of **3b** gives 2.75 g (90%) of **4b** as an oil: $[\alpha]_D$ +9.94° (*c* 1, MeOH) (lit.[9a] $[\alpha]_D$ +10.8° (*c* 0.94, MeOH)). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.97; H, 11.77.

**(*S*)-2-Methyldecan-1-ol (7).** Reductive cleavage of **6** gives 2.8 g (82%) of **7** as an oil: IR (neat) 3400, 1460 $cm^{-1}$; $^1H$ NMR $\delta$ 0.95 (m, 6 H), 1.3 (m, 14 H), 2.3 (br s, 1 H, OH), 3.4 (m, 2 H); $^{13}C$ NMR $\delta$ 14.1, 16.6, 22.7, 27.0, 29.5, 29.6, 30.0, 31.9, 33.2, 35.7, 68.4; $[\alpha]_D$ -9.4° (*c* 1, $CH_2Cl_2$) (lit.[13,14] -10.0° (*c* 4.2, $CH_2Cl_2$)). Anal. Calcd for $C_{11}H_{24}O$: C, 76.68; H, 14.04. Found: C, 76.52; H, 14.06.

**(*R*)-2-Methyl-3-phenylpropan-1-ol (9).** Reductive cleavage of **8** gives 2.5 g (83%) of **9** as an oil: IR (neat) 3350 $cm^{-1}$; $^1H$ NMR $\delta$ 0.88 (d, 3 H, $J$ = 6 Hz), 1.55 (br s, 1 H, OH), 1.95 (m, 1 H), 2.45 (dd, 1 H, $J$ = 6, 13 Hz), 2.80 (dd, 1 H, $J$ = 5, 13 Hz), 3.5 (d, 2 H, $J$ = 5 Hz), 7.2 (m, 5 Ar H); $^{13}C$ NMR $\delta$ 16.5, 37.8, 39.7, 67.6, 125.9, 128.3, 129.2, 140.2; $[\alpha]_D$ +10.3° (*c* 1; $C_6H_6$) (lit.[13,16] $[\alpha]_D$ +11.0° (*c* 1, $C_6H_6$). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.87; H, 9.40.

**Acknowledgment.** We thank MPI (Rome) for a grant.

**Registry No.** **1a**, 92841-65-1; **1b**, 112791-04-5; **2a**, 112712-53-5; **2b**, 112791-05-6; **3a**, 112712-54-6; **3b**, 112791-06-7; **4a**, 498-16-8; **4b**, 50373-53-0; **5a**, 112712-55-7; **5b**, 112791-07-8; **6**, 112712-56-8; **7**, 79847-79-3; **8**, 112712-57-9; **9**, 77943-96-5; 3-methyl-2-butenoyl chloride, 3350-78-5; propanoyl chloride, 79-03-8; 1-bromo-3-methyl-2-butene, 870-63-3; 1-iodooctane, 629-27-6; benzyl bromide, 100-39-0.

---

## Type II Intramolecular [2 + 2] Cycloadditions of Alkenes with Alkylvinylketenes. Synthesis of Methyl Jasmonate

Susanna Y. Lee, Maho Niwa, and Barry B. Snider*

*Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254*

*Received July 27, 1987*

The cycloaddition of ketenes to alkenes provides an attractive route to cyclobutanones and a general method for functionalization of alkenes. We have recently initiated a program to develop the intramolecular version of this

0022-3263/88/1953-2356$01.50/0 