

## Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1996 American Chemical Society

J 2290-1

## Supporting Information for The Catalytic Shapiro Reaction

Keiji Maruoka,<sup>#</sup> Masataka Oishi, and Hisashi Yamamoto\*

School of Engineering, Nagoya University

Chikusa, Nagoya 464-01, Japan

**Preparation of 6-Undecanone Phenylaziridine Hydrazone.** To a stirred solution of 6-undecanone (8.2 mL, 40 mmol) in dichloromethane (40 mL) was added 1-amino-2-phenylaziridine (6.4 g, 48 mmol) at room temperature. The resulting solution was stirred for 5 h, after which it was diluted with dichloromethane (40 mL), and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated, and the crude residue was purified by column chromatography on silica gel (ether/hexane = 1:5 as eluent) to yield phenylaziridine hydrazone of 6-undecanone (10.0 g, 88% yield).

**Phenylaziridine Hydrazone of 6-Undecanone:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.23-7.34 (5H, m, Ph-H), 2.78 (1H, dd,  $J$  = 4.8, 7.5 Hz, Ph-CH), 2.41 (1H, d,  $J$  = 7.5 Hz, Ph-C-CHH), 2.35-2.56 (2H, m,  $\text{CH}_2\text{-C=N}$ ), 2.24 (1H, d,  $J$  = 4.8 Hz, Ph-C-CHH), 2.17 (2H, dd,  $J$  = 7.8, 8.1 Hz,  $\text{CH}_2\text{-C=N}$ ), 1.38-1.54 (4H, m, 2 $\text{CH}_2$ ), 1.24-1.36 (4H, m, 2 $\text{CH}_2$ ), 1.09-1.22 (4H, m, 2 $\text{CH}_2$ ), 0.89 (3H, t,  $J$  = 6.9 Hz,  $\text{CH}_3$ ), 0.79 (3H, t,  $J$  = 6.9 Hz,  $\text{CH}_3$ ).

Other phenylaziridine hydrazones were also prepared in a manner similar to that described above. The analytical data of these hydrazones are as follows.

**Phenylaziridine Hydrazone of Butyl Cyclohexyl Ketone:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.28-7.36 (5H, m, Ph-H), 2.74 (1H, dd,  $J$  = 4.6, 7.5 Hz, Ph-CH), 2.40 (1H, d,  $J$  = 7.5 Hz, Ph-C-CHH), 2.26-2.52 (2H, m,  $\text{CH}_2\text{-C=N}$ ), 2.23 (1H, d,  $J$  = 4.6 Hz, Ph-C-CHH), 2.05-2.19 (1H, m, CH-C=N), 1.62-1.86 (5H, m, CH, 2 $\text{CH}_2$ ), 1.06-1.56 (9H, m, CH, 4 $\text{CH}_2$ ), 0.74 (3H, t,  $J$  = 7.2 Hz,  $\text{CH}_3$ ).

**Phenylaziridine Hydrazone of (E)-3-Methyl-2-dodecen-4-one:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20-7.34 (5H, m, Ph-H), 6.00 (1H, q,  $J$  = 7.0,  $\text{CH}=\text{C}$ ), 2.79 (1H, dd,  $J$  = 4.5, 7.5 Hz, Ph-CH), 2.51-2.76 (2H, m,  $\text{CH}_2\text{-C=N}$ ), 2.51 (1H, d,  $J$  = 7.5 Hz, Ph-C-CHH), 2.31 (1H, d,  $J$  = 4.5 Hz, Ph-C-CHH), 1.80 (3H, s,  $\text{CH}_3\text{-C-C=N}$ ), 1.78 (3H, d,  $J$  = 6.9 Hz, CH<sub>3</sub>-C=), 0.98-1.50 (12H, m, 6 $\text{CH}_2$ ), 0.87 (3H, t,  $J$  = 6.9 Hz,  $\text{CH}_3$ ).

**Phenylaziridine (Z)-Hydrazone of 3-Undecanone:**  $R_f$  = 0.32 (ether/hexane = 1:5 as eluent); 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20-7.34 (5H, m, Ph-H), 2.78 (1H, dd,  $J$  = 4.5, 7.5 Hz, Ph-CH), 2.41 (1H, d,  $J$  = 7.5 Hz, Ph-C-CHH), 2.36-2.56 (2H, m, (Z)- $\text{CH}_2\text{-C=N}$ ), 2.24 (1H, d,  $J$  = 4.5 Hz, Ph-C-CHH), 2.21 (2H, q,  $J$  = 7.5 Hz, (E)- $\text{CH}_2\text{-C=N}$ ), 1.33-1.54 (2H, m,  $\text{CH}_2$ ),

J 2290-2

1.11-1.30 (10H, m, 5CH<sub>2</sub>), 1.07 (3H, t, *J* = 7.5 Hz, CH<sub>3</sub>), 0.87 (3H, t, *J* = 6.9 Hz, CH<sub>3</sub>); 75 MHz <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  174.88 (C=N), 139.51, 128.22, 126.91, 126.16 (ipso, meta, para, ortho), 49.90, 41.70 (Ph-CH-CH<sub>2</sub>), 31.82, 30.94, 29.96, 29.67, 29.22, 26.19 ((CH<sub>2</sub>)<sub>6</sub>-C(=N)-CH<sub>2</sub>), 22.61 (CH<sub>2</sub>-CH<sub>3</sub>), 14.07 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 11.19 (CH<sub>3</sub>).

**Phenylaziridine (*E*)-Hydrazone of 3-Undecanone:** R<sub>f</sub> = 0.40 (ether/hexane = 1:5 as eluent); 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.24-7.34 (5H, m, Ph-H), 2.80 (1H, dd, *J* = 4.5, 7.5 Hz, Ph-CH), 2.49 (2H, q, *J* = 7.8 Hz, (Z)-CH<sub>2</sub>-C=N), 2.39 (1H, d, *J* = 7.5 Hz, Ph-C-CHH), 2.25 (1H, d, *J* = 4.5 Hz, Ph-C-CHH), 2.18 (2H, dd, *J* = 7.5, 8.1 Hz, (*E*)-CH<sub>2</sub>-C=N), 1.42-1.56 (2H, m, CH<sub>2</sub>), 1.16-1.39 (10H, m, 5CH<sub>2</sub>), 1.04 (3H, t, *J* = 7.8 Hz, CH<sub>3</sub>-C-C=N), 0.88 (3H, dd, *J* = 6.5, 7.1 Hz, CH<sub>3</sub>); 75 MHz <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  174.88 (C=N), 139.51, 128.25, 126.91, 126.16 (ipso, meta, para, ortho), 43.87, 40.99 (Ph-CH-CH<sub>2</sub>), 36.09 (CH<sub>2</sub>-CH<sub>2</sub>-C=N), 31.84, 29.50, 29.40, 29.20, 26.83, 24.11, 22.64 ((CH<sub>2</sub>)<sub>5</sub>-CH<sub>2</sub>-C(=N)-CH<sub>2</sub>, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 14.07 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 10.61 (CH<sub>3</sub>).

The *E/Z* mixture was easily separated by column chromatography on silica gel (ether/hexane = 1:3 to 1:5 as eluents). The *E/Z* assignment of the phenylaziridine hydrazone of 3-undecanone was made by comparison of the <sup>13</sup>C NMR chemical shifts according to the literature procedure.<sup>1</sup>

**Preparation of (*R*)-1-Amino-2-Phenylaziridinium acetate.** The optically active hydrazine was prepared from (*S*)-phenyl ethylene glycol via the two-step sequences and purified by recrystallization of 1-amino-2-phenylaziridinium acetate from CH<sub>2</sub>Cl<sub>2</sub>/pentane according to the literature procedure.<sup>2</sup> The ee value was determined to be up to 99% by HPLC analysis after conversion into the 3-pantanone phenylaziridine hydrazone: m.p. 79-80°C;  $[\alpha]_D^{25}$  +160.8° (c 0.5 in CHCl<sub>3</sub>); 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.15-7.34 (5H, m, Ph-H), 2.66 (1H, dd, *J* = 4.8, 8.1 Hz), 2.09 (3H, s, CH<sub>3</sub>), 2.08 (1H, d, *J* = 4.8 Hz), 2.05 (1H, d, *J* = 8.1 Hz).

**(*R,R*)-Phenylaziridine Hydrazone (5) of 4-Methyl-4-*p*-tolyl cyclohexanone :** R<sub>f</sub> = 0.23 (ether/hexane = 1:2 as eluent); 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.22-7.36 (7H, m, Ar-H), 7.12-7.19 (2H, m, CH), 2.88-2.93 (1H, m, CHH), 2.86 (1H, dd, *J* = 4.8, 7.5 Hz, Ph-CH), 2.39-2.51 (2H, m, CH<sub>2</sub>), 2.33 (3H, s, Ar-CH<sub>3</sub>), 2.30 (1H, d, *J* = 7.5 Hz, Ph-C-CHH), 2.26 (1H, d, *J* = 4.8 Hz, Ph-C-CHH), 2.16-2.36 (3H, m, CH<sub>2</sub>, CHH), 1.64-1.84 (2H, m, CH<sub>2</sub>), 1.24 (3H, s, Ar-C-CH<sub>3</sub>).

**(*S,R*)-Phenylaziridine Hydrazone (6) of 4-Methyl-4-*p*-tolyl cyclohexanone :** R<sub>f</sub> = 0.15 (ether/hexane = 1:2 as eluent); 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.12-7.34 (9H, m, Ar-H), 2.94-3.05 (1H, m, CHH), 2.65 (1H, dd, *J* = 4.5, 7.5 Hz, Ph-CH), 2.44 (1H, d, *J* = 7.5 Hz, Ph-C-CHH), 2.33 (3H, s, Ar-CH<sub>3</sub>), 2.27 (1H, d, *J* = 4.5 Hz, Ph-C-CHH), 2.13-2.39 (5H, m, 2CH<sub>2</sub>, CHH), 1.64-1.82 (2H, m, CH<sub>2</sub>), 1.21 (3H, s, Ar-C-CH<sub>3</sub>).

The mixture of (*R, R*)- and (*S, R*)-phenylaziridine hydrazones was easily separated by column chromatography on silica gel (ether/hexane = 1:2 as eluent). The stereochemistry of these diastereotopic phenylaziridine hydrazones was estimated by that of optically active alkene products

J2290-3

7 and 8 yielded via the LDA-catalyzed regioselective decomposition of the phenylaziridine hydrazones 5 and 6 respectively.

**Preparation of Phenylaziridine (E)-Hydrazone (10) of 2-Hexanone.** The *E/Z* mixture of 2-hexanone phenylaziridine hydrazone (*E/Z* ratio = 9:1) was prepared in a manner similar to that of 6-undecanone phenylaziridine hydrazone and the major (*E*)-isomer 10 was easily separated by column chromatography on silica gel (ether/hexane = 1:5 as eluent): 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.24-7.34 (5H, m, Ph-H), 2.81 (1H, dd, *J* = 4.5, 7.5 Hz, Ph-CH), 2.39 (1H, d, *J* = 7.5 Hz, Ph-C-CHH), 2.28 (1H, d, *J* = 4.5 Hz, Ph-C-CHH), 2.19 (2H, dd, *J* = 7.5, 8.1 Hz, CH<sub>2</sub>-C=N), 1.97 (3H, s, CH<sub>3</sub>-C=N), 1.43-1.54 (2H, m, CH<sub>2</sub>), 1.25-1.39 (2H, m, CH<sub>2</sub>), 0.91 (3H, t, *J* = 7.5 Hz, CH<sub>3</sub>).

**Preparation of Phenylaziridine (Z)-Hydrazone (11) of 14-(*tert*-Butyldimethylsiloxy)-5-tetradecanone.** To a solution of lithium diisopropylamide (3.0 mmol) in THF/hexane (6.0 mL), which was prepared from diisopropylamine (3.0 mmol) and BuLi (3.0 mmol) at 0 °C for 20 min, was added at -78 °C phenylaziridine (*E*)-hydrazone 9 dropwise. The solution was stirred at -78 °C for 1 h and 8-(*tert*-butyldimethylsiloxy) octyl bromide (970 mg, 3.0 mmol) was added at this temperature. After stirring at -45 °C for 2 h, the resulting mixture was diluted with ether (6.0 mL) and transferred into separatory funnel containing water (50 mL). The aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were dried, concentrated under reduced pressure, and subjected to column chromatography on silica gel (ether/hexane = 1:5 as eluent) to furnish the desired hydrazone 11 (565 mg, 64 % yield) as yellowish oil: 300 MHz <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.20-7.34 (5H, m, Ph-H), 3.59 (2H, t, *J* = 6.6 Hz, CH<sub>2</sub>-O), 2.77 (1H, dd, *J* = 4.5, 7.5 Hz, Ph-CH), 2.40 (1H, d, *J* = 7.5 Hz, Ph-C-CHH), 2.34-2.56 (2H, m, CH<sub>2</sub>-C=N), 2.23 (1H, d, *J* = 4.5 Hz, Ph-C-CHH), 2.17 (2H, dd, *J* = 7.5, 8.1 Hz, CH<sub>2</sub>-C=N), 1.41-1.56 (4H, m, 2CH<sub>2</sub>), 1.10-1.40 (12H, m, 6CH<sub>2</sub>), 0.91 (3H, t, *J* = 7.2 Hz, CH<sub>3</sub>), 0.90 (9H, s, *t*-Bu), 0.05 (6H, s, Si(CH<sub>3</sub>)<sub>2</sub>).

**General Procedure for the Decomposition of Phenylaziridine Hydrazones.** To a solution of phenylaziridine hydrazone (1.0 mmol) in dry ether at 0 °C under argon atmosphere was added a solution of lithium diisopropylamide (0.5 M in ether/hexane, 0.1-0.6 mL), which was prepared from a solution of diisopropylamine in dry ether and a 1.6 M of hexane solution of BuLi at 0 °C for 0.5 h under argon atmosphere. Evolution of the nitrogen gas was observed and the mixture was stirred at -20~25 °C for several hours. This was diluted with ether (3.0 mL) and poured into separatory funnel containing 1N HCl or water (30 mL). The aqueous layer was extracted with ether (3 × 15mL). The organic layers were combined, washed with brine (30 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation of solvents and purification of the residue by column chromatography on silica gel (hexane) afforded the corresponding alkene in 82-98% yield.

The physical and analytical data of alkenes are as follows.

J2290-4

**(Z)-5-Undecene:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.33-5.37 (2H, m,  $\text{CH}=\text{CH}$ ), 2.00-2.03 (4H, m,  $\text{CH}_2\text{-C}=\text{C-CH}_2$ ), 1.26-1.36 (10H, m, 5 $\text{CH}_2$ ), 0.90 (3H, t,  $J$  = 6.9 Hz,  $\text{CH}_3$ ), 0.89 (3H, dd,  $J$  = 6.0, 6.9 Hz,  $\text{CH}_3$ ).

The *E/Z* assignment of the alkene was made by comparison with the spectral data of the known (*E*)-5-undecene.<sup>3</sup> The *E/Z* ratio of the alkene was determined by capillary GLC analysis after conversion to the corresponding epoxide with MCPBA.

**(Z)-1-Pentenylcyclohexane:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.15-5.33 (2H, m,  $\text{CH}=\text{CH}$ ), 2.16-2.34 (1H, m,  $\text{CH-C}=\text{C}$ ), 1.97-2.07 (2H, m,  $\text{CH}_2\text{-C}=\text{C}$ ), 1.52-1.80 (4H, m, 2 $\text{CH}_2$ ), 1.00 (10H, m, 5 $\text{CH}_2$ ), 0.91 (3H, t,  $J$  = 7.2 Hz,  $\text{CH}_3$ ).

The *E/Z* assignment of the alkene was made by comparison with the spectral data of the known (*Z*)-1-pentenylcyclohexane.<sup>4</sup> The *E/Z* ratio and the regioselectivity of the alkene product was determined by capillary GLC analysis.

**(*E, Z*)-3-Methyl-2,4-dodecadiene:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.79 (1H, d,  $J$  = 11.7 Hz,  $\text{CH}=\text{CH-CH}_2$ ), 5.42 (1H, q,  $J$  = 6.9 Hz,  $\text{CH}_3\text{-CH}=\text{C}$ ), 5.26 (1H, ddd,  $J$  = 7.2, 7.5, 11.7 Hz,  $\text{CH}=\text{CH-CH}_2$ ), 2.17-2.28 (2H, m,  $\text{CH}_2\text{-C}=\text{C}$ ), 1.77 (3H, s,  $\text{CH}_3\text{-C}=\text{CH}$ ), 1.67 (3H, d,  $J$  = 6.9 Hz,  $\text{CH}_3\text{-CH}=\text{C}$ ), 1.18-1.42 (10H, m, 5 $\text{CH}_2$ ), 0.88 (3H, t,  $J$  = 6.8 Hz,  $\text{CH}_3$ ).

**(*E, E*)-3-Methyl-2,4-dodecadiene:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.05 (1H, d,  $J$  = 15.6 Hz,  $\text{CH}=\text{CH-CH}_2$ ), 5.54 (1H, ddd,  $J$  = 6.9, 8.4, 15.6 Hz,  $\text{CH}=\text{CH-CH}_2$ ), 5.44 (1H, q,  $J$  = 6.9 Hz,  $\text{CH}_3\text{-CH}=\text{C}$ ), 2.01-2.12 (2H, m,  $\text{CH}_2\text{-CH}=\text{CH}$ ), 1.72 (3H, s,  $\text{CH}_3\text{-C}=\text{CH}$ ), 1.70 (3H, d,  $J$  = 6.9 Hz,  $\text{CH}_3\text{-CH}=\text{C}$ ), 1.16-1.40 (10H, m, 5 $\text{CH}_2$ ), 0.88 (3H, dd,  $J$  = 6.3, 6.9 Hz,  $\text{CH}_3$ ).

The *EE/EZ* assignment of these dienes was made by comparison with the  $^1\text{H}$  NMR coupling constants of C-4, C-5 double bonds of these isomers [ $J$  = 15.6 Hz ( $\text{CH}=\text{CH}$  of the (*E, E*)-isomer) > 11.7 Hz ( $\text{CH}=\text{CH}$  of the (*E, Z*)-isomer)]. The *EE/EZ* ratio was determined by capillary GLC analysis.

**(Z)-3-Undecene:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.27-5.42 (2H, m,  $\text{CH}=\text{CH}$ ), 1.99-2.11 (4H, m,  $\text{CH}_2\text{-C}=\text{C-CH}_2$ ), 1.18-1.41 (10H, m, 5 $\text{CH}_2$ ), 0.96 (3H, t,  $J$  = 7.5 Hz,  $\text{CH}_3$ ), 0.88 (3H, t,  $J$  = 6.8 Hz,  $\text{CH}_3$ ); 75 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  131.64 (C-3), 129.50 (C-4), 31.76, 29.66, 29.11, 29.11 (C-6, 7, 8, 9), 26.96 (C-5), 22.53 (C-10), 20.34 (C-2), 14.21 (C-11), 13.93 (C-1).

The *E/Z* assignment of 3-undecene was made by comparison with the  $^{13}\text{C}$  NMR chemical shift values of the literature data.<sup>5</sup> The *E/Z* ratio of the alkene was determined by capillary GLC analysis after conversion to the corresponding epoxide with MCPBA.

**(Z)-2-Undecene:** 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.32-5.50 (2H, m,  $\text{CH}=\text{CH}$ ), 1.94-2.08 (2H, m,  $\text{CH}_2\text{-C}=\text{C}$ ), 1.60 (3H, dd,  $J$  = 0.9, 4.8 Hz,  $\text{CH}_3\text{-C}=\text{C}$ ), 1.19-1.42 (12H, m, 6 $\text{CH}_2$ ), 0.88 (3H, t,  $J$  = 6.8 Hz,  $\text{CH}_3$ ); 75 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  131.06 (C-3), 123.70 (C-2), 31.79, 29.42, 29.20 (C-5, 6, 7, 8, 9), 26.70 (C-4), 22.54 (C-10), 13.93 (C-11), 12.54 (C-1)

J 2290-5

The *E/Z* assignment of 2-undecene was made by comparison with the  $^{13}\text{C}$  NMR chemical shift values of the literature data.<sup>5</sup> The *E/Z* ratio of the alkene was determined by capillary GLC analysis after conversion to the corresponding epoxide with MCPBA.

**(R)-4-Methyl-4-*p*-tolyl cyclohexene (7):**  $[\alpha]_D^{25} -41.4^\circ$  (c 1.0,  $\text{CHCl}_3$ ); 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26 (2H, d,  $J = 8.1$  Hz, Ar-H), 7.12 (2H, d,  $J = 8.1$  Hz), 5.71-5.79 (1H, m, C=CH), 5.59-5.67 (1H, m, C=CH), 2.42-2.53 (1H, m, CHH), 2.32 (3H, s, Ar-CH<sub>3</sub>), 1.68-2.16 (5H, m, 2H<sub>2</sub>, CHH), 1.25 (3H, s, Ar-C-CH<sub>3</sub>).

**(S)-4-Methyl-4-*p*-tolyl cyclohexene (8):**  $[\alpha]_D^{25} +40.4^\circ$  (c 1.1,  $\text{CHCl}_3$ ); 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26 (2H, d,  $J = 8.1$  Hz, Ar-H), 7.12 (2H, d,  $J = 8.1$  Hz), 5.71-5.79 (1H, m, C=CH), 5.59-5.67 (1H, m, C=CH), 2.42-2.53 (1H, m, CHH), 2.32 (3H, s, Ar-CH<sub>3</sub>), 1.68-2.16 (5H, m, 2H<sub>2</sub>, CHH), 1.25 (3H, s, Ar-C-CH<sub>3</sub>).

The absolute configurations of **7** and **8** were established by correlation to the optical rotation value of the known diester **9**.<sup>6</sup> The optical purity of **7** and **8** was determined by HPLC analysis based on separated 2 peaks using the chiral column, CHIRALCEL OJ:  $t_R(7) = 25.1$  min,  $t_R(8) = 27.1$  min (*i* PrOH-hexane = 1:200, flow rate 0.3 mL/min).

**(R)-3-Methyl-3-*p*-tolyl adipic acid dimethyl ester (9).** Ozonolysis of **7** in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  followed by PDC oxidation in dry DMF in the presence of MeOH gave the known diester **9**<sup>7,8</sup> (61% yield):  $[\alpha]_D^{23} -24.3^\circ$  (c 0.75,  $\text{CHCl}_3$ ); lit.<sup>6</sup>  $[\alpha]_D -20.0^\circ$  (c 1.3,  $\text{CHCl}_3$ ); 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.18 (2H, d,  $J = 8.4$  Hz, Ar-H), 7.12 (2H, d,  $J = 8.4$  Hz, Ar-H), 3.59 (3H, s, O-CH<sub>3</sub>), 3.54 (3H, s, O-CH<sub>3</sub>), 2.70 (1H, d,  $J = 14.0$  Hz, CHH), 2.60 (1H, d,  $J = 14.0$  Hz, CHH), 2.31 (3H, s, Ar-CH<sub>3</sub>), 1.98-2.19 (4H, m, CH<sub>2</sub>-CH<sub>2</sub>), 1.46 (3H, s, Ar-C-CH<sub>3</sub>).

**Synthesis of (Z)-9-Tetradecenyl Acetate (12).** To a solution of phenylaziridine (Z)-hydrazone **11** (446 mg, 1.0 mmol) in dry ether (1.0 mL) at 0°C under argon atmosphere was added a solution of lithium diisopropylamide (0.5 M in ether/hexane, 0.2 mL) prepared described above. The solution was stirred at 0°C for 1 h and then it was poured into a mixture of AcOH/THF/H<sub>2</sub>O (2:1:1, 40 mL). The mixture was stirred vigorously at room temperature for 3 h. Ether (50 mL) was added and the organic layer was washed with sat. aqueous NaHCO<sub>3</sub> followed by brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude alcohol was treated with Ac<sub>2</sub>O (142  $\mu\text{L}$ , 1.5 mmol) and pyridine (121  $\mu\text{L}$ , 1.5 mmol) in dichloromethane (3.0 mL) in the presence of catalytic DMAP at 25 °C for 1 h. A standard work-up and purification by column chromatography on silica gel (ether/hexane = 1:8 as eluent) afforded the title compound (201 mg, 79 % yield): 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.33-5.36 (2H, m, CH=CH), 4.05 (2H, t,  $J = 6.9$  Hz, CH<sub>2</sub>-O), 2.04 (3H, s, CH<sub>3</sub>-C=O), 1.96-2.07 (4H, m, 2H<sub>2</sub>-C=C), 1.52-1.68 (2H, m, CH<sub>2</sub>), 1.24-1.40 (14H, m, 7CH<sub>2</sub>), 0.90 (3H, dd,  $J = 6.0, 6.9$ , CH<sub>3</sub>).

The acetate **12** was identified by comparison with the spectral data of the literature<sup>9</sup> and the isomeric purity of **12** was determined by GLC analysis after conversion to the corresponding epoxide. The *cis/trans* mixtures of 9- and 10-tetradecenyl acetate were prepared from acetoxy aldehydes by Wittig reaction. The GLC retention times of each isomer using a capillary column of

J2290-6

PEG-HT at 140°C are as follows: 58.9 min (*trans*-9,10-epoxide), 59.8 min (*trans*-10,11-epoxide), 65.2 min (*cis*-9,10-epoxide), 67.4 min (*cis*-10,11-epoxide).

---

# Present address: Department Chemistry, Graduate School of Science, Hokkaido University.

## References

- (1) Bunnell, C. A.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2614.
- (2) Muller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Winter, C.; Eschenmoser, A. *Org. Synth. Coll. Vol. 6*, **1988**, 56.
- (3) Tanigawa, Y.; Ohta, H.; Sonoda, A.; Murahashi, S. *J. Am. Chem. Soc.* **1978**, *100*, 4610.
- (4) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 3806.
- (5) Katritzky, A. R.; El-Mowafy, A. M. *J. Org. Chem.* **1982**, *47*, 3506.
- (6) Honda, T.; Kimura, N.; Tsubuki, M. *Tetrahedron Asymmetry* **1993**, *4*, 21.
- (7) Claus, R. E.; Schreiber, S. L. *Org. Synth. Coll. Vol. 7*, **1990**, 168.
- (8) O'Connor, B.; Just, G. *Tetrahedron Lett.* **1987**, *28*, 3235.
- (9) Mitra, R. B.; Reddy, G. B. *Synthesis* **1989**, 694.