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TRANSFORMATION OF N-TOSYL-2-(1,3-BUTADIENYL)AZIRIDINE INTO N-TOSYL-2-ETHENYL-3-PYRROLINE

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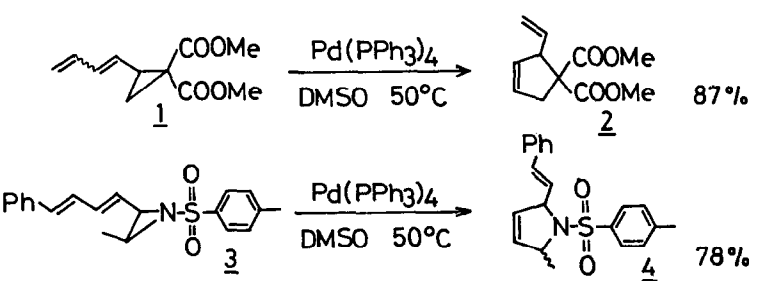
Abstract: 1,3-Butadienylaziridines or 1,3-butadienylazetidines activated by N-tosyl group smoothly rearrange to vinylpyrroline derivatives or vinylpiperidines in the presence of a catalytic amount of $Pd(PPh_3)_4$. Triphenyltin radical induced rearrangement of title compounds is also described.

The vinylcyclopropane-cyclopentene rearrangement has attracted much interest from the mechanistic point of view.[2] The synthetic application, however, has been limited[3] because the reaction normally proceeds at high temperature (300-500 °C).[4] Previously we have reported that 1,3-butadienylcyclopropanes activated by two electron-withdrawing groups smoothly rearranged to vinylcyclopentene derivatives in the presence of a Pd(0) catalyst under mild conditions.[5] For instance, dimethyl 1,3-butadienylcyclopropane-1,1-dicarboxylate (**1**) reacted with 3 mol% $Pd(PPh_3)_4$ in DMSO at 50°C for 30 min to provide dimethyl 2-ethenyl-3-cyclopentene-1,1-dicarboxylate (**2**) in 87% yield. Here we wish to describe further extension of this reaction to 3-pyrroline synthesis. Palladium(0) promoted isomerization of 1,3-butadienylaziridines **3** having $>N\text{-}SO_2Ar$ group provides 3-pyrrolines **4** carrying $ArSO_2$ group on nitrogen.[6]

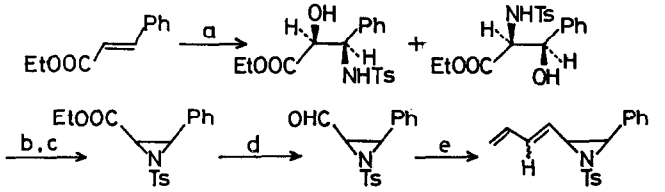


1 2 3 4

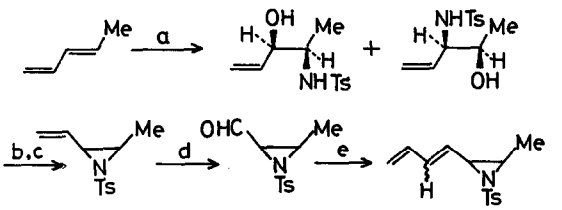
The required aziridines and azetidines were prepared as follows (Scheme 1 and 2). Oxyamination[7] of ethyl cinnamate gave a regioisomeric mixture of hydroxyamide. Mesylation followed by the intramolecular displacement of the methanesulfonyl group resulted in the stereoselective formation of cis-N-tosylaziridine. The ethyl ester moiety was converted into aldehyde group,[8] which was

treated with a phosphorane such as $Ph_3P{=}CHCH{=}CH_2$ to give dienylaziridines. Alternatively, 2-formyl-3-methyl-1-tosylaziridine was prepared from 1,3-pentadiene according to the following sequences: (1) oxyamination, (2) mesylation, (3) aziridine ring formation, and (4) formylation.

Scheme 1



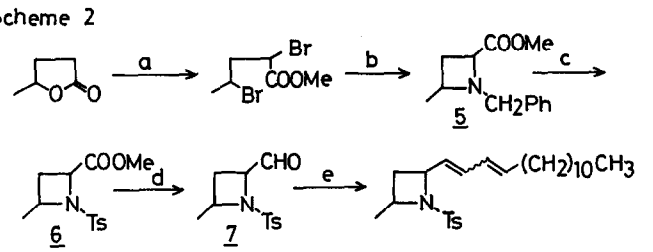
a: TsN(Cl)Na, cat OsO_4 b: CH_3SO_2Cl-Et_3N c: K_2CO_3/MeOH
d: $^iBu_2AlH$ e: $Ph_3P{=}CH{-}CH{=}CH_2$



a: TsN(Cl)Na, cat OsO_4 b: CH_3SO_2Cl-Et_3N c: K_2CO_3/MeOH
d: $NaIO_4$, cat OsO_4 e: $Ph_3P{=}CH{-}CH{=}CH_2$

Azetidine carboxylic acid ester **5** was easily derived from γ-butyrolactone according to the reported procedure.[9] Hydrogenolysis of the benzyl derivative followed by treatment with tosyl chloride-pyridine provided N-tosyl azetidine **6**. The ester **6** was converted to aldehyde **7** and then transformed to dienylazetidine by Wittig reaction.

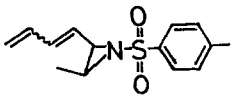
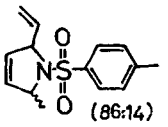
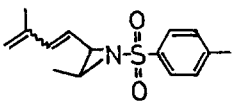
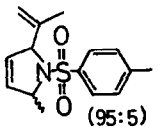
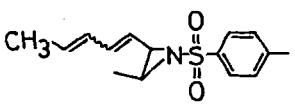
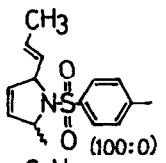
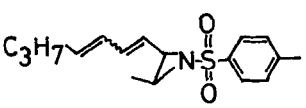
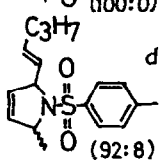
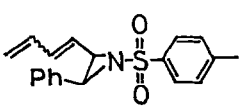
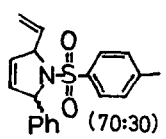
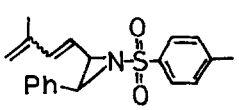
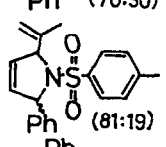
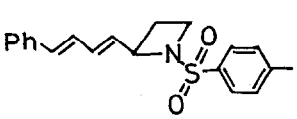
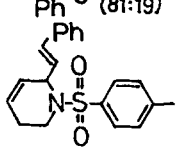
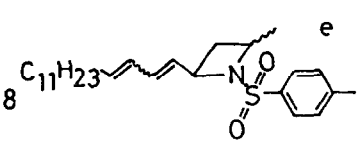
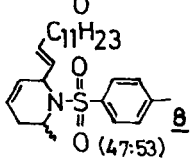
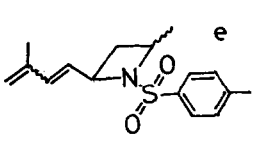
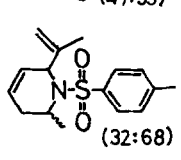
Scheme 2



a: 1) PBr_3-Br_2 2) HCl/MeOH b: $PhCH_2NH_2$ c: 1) H_2/Pd-C
2) TsCl/py d: $^iBu_2AlH$ e: $Ph_3P{=}CH{-}CH{=}CH{-}(CH_2)_{10}CH_3$

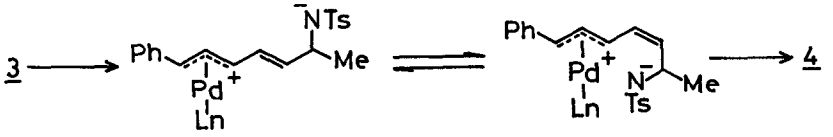
Dienylaziridine **3** was treated with 3 mol% of $Pd(PPh_3)_4$ in DMSO at 50°C for 30 min to give 1-tosyl-2-styryl-3-pyrroline **4** in 78% yield. The generality of the rearrangement was explored with the examples shown in Table 1. The reaction of 1-tosyl-2-vinylaziridine yielded complex mixture and no trace of pyrroline derivatives were detected. Thus, the presence of N-tosyl group and dienic moiety is essential for the rearrangement. The rearrangement might proceed through nucleophilic attack of Pd(0) on the dienic group to form a zwitterion consisting of alkenyl π-allylpalladium[10] and stabilized tosylamide anion

Table 1. Pd(0) Catalyzed Rearrangement of Dienylaziridines[a]

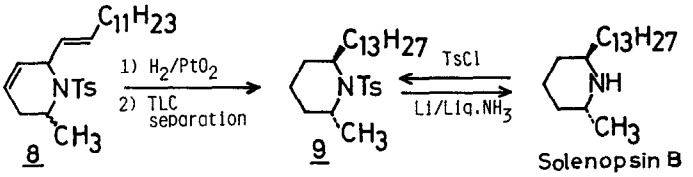
Entry	Substrate	Temp (°C)	Time (h)	Yield[b] (%)	Product (cis:trans)[c]
1		50	0.2	82	 (86:14)
2		50	0.4	98	 (95:5)
3		50	1.0	73	 (100:0)
4		50	1.2	81	 d (92:8)
5		50	0.3	76	 (70:30)
6		50	0.5	53	 (81:19)
7		25	12	80	
8	 e	25 50	10 0.4	86 91	 8 (47:53)
9	 e	25	12	85	 (32:68)

a) Reactions were performed on a 1-2 mmol scale with 3 mol% of $Pd(PPh_3)_4$. b) Isolated yields. c) Determined by the examination of the NMR spectra. See experimental part. d) See ref 11. e) Isomeric ratios (cis:trans) could not be determined.

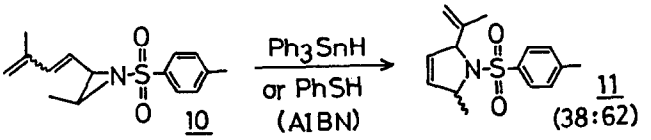
moieties under aziridine ring cleavage. The intermediate collapses to form five-membered ring and not a seven-membered one. The attack of Pd(0) on C-NTs bond may be another possible route to the zwitterion.



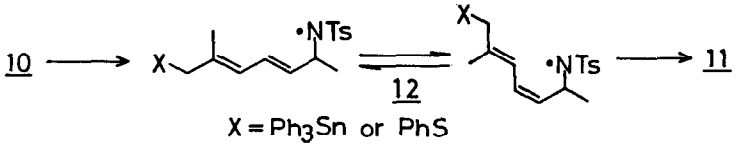
The reaction was successfully applied to the transformation of 1-tosyl-2-(1,3-butadienyl)azetidines into vinylpiperidine derivatives and a couple of examples are also shown in Table 1. The product **8** (Entry 8 in Table 1) was easily transformed into Solenopsin B[12] which was isolated from the red form of the fire ant, Solenopsis saevissima.[13]



Free radical reactions have been used increasingly in recent years for the synthesis of organic molecules.[14] The cis-trans isomerization of olefins by the addition-elimination sequence of PhS radical[15] or Ph_3Ge radical[16] has been reported. This methodology has been applied to the title rearrangement reaction.[17] Heating a solution of triphenyltin hydride, the aziridine **10**, and azobisisobutyronitrile (AIBN) in benzene at 80°C for 4 h gave the corresponding pyrroline **11** in 76% yield. The use of benzenethiol instead of Ph_3SnH also provided a satisfactory result and gave **11** in 64% yield. In the case of benzenethiol, the reaction proceeded in the absence of AIBN.



The rearrangement is ascribed to the attack of Ph_3Sn radical on the dienic group to form a radical **12** which has a dienylstannyl group (or dienylsulfide group). This collapses to form the respective pyrroline derivative with new C-N bond formation exclusively producing a five-membered ring.



EXPERIMENTAL

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by an airbath temperature without correction. All melting points were obtained on a Yanaco MP-50929 melting point apparatus and are uncorrected, too. ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl.

Synthesis of Aziridine Carboxylates. Preparation of methyl cis-3-phenyl-1-tosylaziridine-2-carboxylate is representative. To a solution of methyl cinnamate (5.0 g, 31 mmol) in t-butyl alcohol (200 ml) was added powdered silver nitrate (6.5 g, 38 mmol) and chloramine T (10.8 g, 38 mmol) at room temperature under an argon atmosphere. An olefin free hexane solution of osmium tetroxide (7.9×10^{-2} mol dm^{-3}, 5 ml, 0.4 mmol) was added to the resulting white suspension and the reaction mixture immediately turned yellow. Then the mixture was heated at 60 °C over night and the purple gray precipitate thus produced was filtered off. The filtrate was cocentrated in vacuo to afford 8.1 g of brown crystals. This crude product was dissolved in THF (120 ml) under an argon atmosphere. The solution was cooled to 0 °C, then triethylamine (5.1 ml, 36 mmol) and methanesulfonyl chloride were added dropwise. The mixture was warmed to room temperature and stirred for 90 min. Yellow deposit was filtered off and the mother liquid was washed with brine (100 ml). Solvent was evaporated and the dark brown residue was resolved in methanol (40 ml) and treated with potassium carbonate (6.3 g, 45 mmol) at room temperature for 30 min. Then the muddy reaction mixture was poured into water and extracted twice with dichloromethane. Solvent was evaporated in vacuo and purification of the residue by silica-gel column chromatography gave methyl cis-3-phenyl-1-tosylaziridine-2-carboxylate (5.5 g) in 54% overall yield: mp 69.5°C ($CHCl_3$); IR (neat) 3030, 2950, 1756, 1598, 1497, 1440, 1332, 1208, 1160, 1092, 1048, 909, 815, 780, 697, 682, 595, 553 cm^{-1}; ^{1}H-NMR δ 2.44 (s, 3H), 3.49 (s, 3H), 3.72 (d, J = 7.6 Hz, 1H), 4.13 (d, J = 7.6 Hz, 1H), 7.2-7.4 (m, 5H), 7.36 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H); ^{13}C-NMR δ 21.6, 43.2, 45.2, 52.3, 127.3, 128.0, 128.2, 128.5, 129.8, 131.0, 133.9, 145.1, 164.8. Found: C, 61.37; H, 5.14; N, 4.17%. Calcd for $C_{17}H_{17}NO_4S$: C, 61.62; H, 5.17; N, 4.23%.

Preparation of Methyl 1-Tosylazetidine-2-carboxylates. These compounds were synthesizded partially according to a reported procedure.[9] Typical procedure is as follows. Bromine (15 ml) was added to a heated mixture of phosphorus tribromide (0.5 ml) and γ-butyrolactone (25 g, 0.29 mol) at such a rate as to maintain a temperature of 100-115 °C. After completion of the addition, dark brown mixture was heated for an additional 30 min. Then the mixture was cooled with an ice-water bath, methanol (50 ml) was added carefully, and HCl gas was bubbled in. The resulting orange coloured solution was heated at 50 °C for 48 h. Evaporation of volatile component provided a residual oil which was diluted with ether and washed twice with 3% aqueous sodium bicarbonate and then with brine. The washings were extracted with ether and the combined organic layers were concentrated in vacuo. Distillation under reduced pressure (0.2 Torr) afforded methyl 2,4-dibromobutyrate (62.5 g, 83% yield) as a colourless liquid. Benzylamine (16 ml, 146 mmol) was added to an acetonitrile solution (40 ml) of dibromoester (10.9 g, 42 mmol). Upon heating at 60 °C, white precipitates came out. Within half an hour, dibromoester has been consumed and the precipitated solid was filtered off. The filtrate was poured into aqueous ammonium chloride and extracted twice with dichloromethane. The organic layers were combined, dried (Na_2SO_4), and concentrated, and the residue was purified by column chromatography on silica-gel to give methyl 1-benzylazetidine-2-carboxylate (6.0 g, 55% yield). Then, N-benzyl group was replaced by tosyl group. To a methanol solution of N-benzyl derivative (1.1 g, 5.0 mmol) was added 10% palladium on

charcoal (0.6 g, 0.56 mmol) and the mixture was stirred at room temperature for 22 h under a hydrogen atmosphere. Palladium charcoal was filtered off and the solvent was carefully removed under reduced pressure to give approximately 1 ml of yellow oil. The oil was dissolved in pyridine (8 ml) and tosyl chloride (1.4 g, 7.3 mmol) was added portionwise at 0 °C. After an additional stirring for 2 h at room temperature, the reaction mixture was poured into aqueous ammonium chloride, extracted with dichloromethane. The combined extracts were evaporated in vacuo and purification by silica-gel column chromatography gave methyl 1-tosylazetidine-2-carboxylate (0.94 g, 66% yield) whose spectral data were identical with those in the literature.[18]

Preparation of 2-Formylaziridine Derivatives and 2-Formylazetidines from the Corresponding 2-Carbomethoxy Derivatives. Synthesis of cis-2-formyl-3-phenyl-1-tosylaziridine is representative. A hexane solution of diisobutylaluminum hydride (1.0 mol dm^{-3}, 3.0 ml, 3.0 mmol) was added to a dichloromethane solution (10 ml) of methyl cis-3-phenyl-1-tosylaziridine-2-carboxylate (0.92 g, 2.8 mmol) at -78 °C under an argon atmosphere.[8] After the completion of the addition, the mixture was stirred for another 15 min and sodium fluoride (1.3 g) and water (0.9 ml) was added. Then, the reaction mixture was warmed slowly to room temperature and white solid thus formed was filtered off. The filtrate was concentrated and the residual oil was submitted to silica-gel column chromatography to afford cis-2-formyl-3-phenyl-1-tosylaziridine (0.69 g, 2.2 mmol) in 79% yield: bp 180 °C/0.1 Torr; IR (neat) 3070, 3030, 1727, 1598, 1496, 1452, 1328, 1243, 1155, 1090, 883, 767, 698, 674 cm^{-1}; ^{1}H-NMR δ 2.43 (s, 3H), 3.47 (dd, J = 7.7, 5.8 Hz, 1H), 4.21 (d, J = 7.7 Hz, 1H), 7.2-7.4 (m, 5H), 7.38 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 8.89 (d, J = 5.8 Hz, 1H); ^{13}C-NMR δ 21.5, 45.5, 47.3, 127.1, 128.1, 128.7, 129.7, 130.0, 130.7, 133.6, 145.5, 195.3.

Preparation of cis-2-Formyl-3-methyl-1-tosylaziridine. An olefin free hexane solution of osmium tetroxide (7.9×10^{-2} mol dm^{-3}, 0.35 ml, 2.8×10^{-2} mmol) was added to a solution of 2-ethenyl-3-methyl-1-tosylaziridine (0.30 g, 1.25 mmol) in THF (6.6 ml) and water (2.2 ml).[19] The reaction mixture turned dark within 5 min. Then sodium metaperiodate (0.66 g, 3.1 mmol) was added at room temperature under an argon atmosphere and the resulting white suspension was stirred over night. The reaction mixture was poured into an aqueous sodium thiosulfate and extracted with dichloromethane. The combined organic layers were dried, and concentrated in vacuo and the residue was submitted to silica-gel column chromatography to give the title compound (0.26 g) in 87% yield. Spectral and analytical data have been given in a preceding paper.[10]

General Procedure for the Preparation of Dienylaziridine and Dienylazetidine. To a suspension of 2-methyl-2-propenyltriphenylphosphonium bromide (1.2 g, 3.0 mmol) in diethyl ether (15 ml) was added a powdered potassium *t*-butoxide (0.22 g, 2.0 mmol) at 0 °C under an argon atmosphere. The resulting red suspension was stirred for 10 min, then allowed to stand still, and the red supernatant was sucked up with a syringe and added to an ether solution of cis-2-formyl-3-methyl-1-tosylaziridine (0.36 g, 1.5 mmol). After stirring for 1 h, twenty drops of saturated aqueous ammonium chloride was added to this pale orange reaction mixture. The reaction mixture was stirred for an additional 5 min and the precipitates were filtered off. The filtrate was washed with saturated aqueous ammonium chloride, solvent was removed in vacuo and the residue was submitted to silica-gel column chromatography to afford cis-3-methyl-2-(3-methyl-1,3-butadienyl)-1-tosylaziridine (**10**) (0.23 g, E:Z = 22:78) in 54% yield: bp 120 °C/0.2 Torr; ^{1}H-NMR δ 1.20 (d, J = 5.9 Hz, 0.66H), 1.22 (d, J = 5.9 Hz, 2.34H), 1.80 (t, J = 1.0 Hz, 0.66H), 1.90 (s, 2.34H), 2.44 (s, 3H), 2.9-3.2 (m, 1H), 3.42 (ddd, J = 7.9, 7.9, 0.6 Hz, 0.22H), 3.79 (ddd, J = 8.3, 7.4, 1.2 Hz, 0.78H), 4.96 (brs, 0.78H), 5.00 (brs, 0.44H), 5.08 (dd, J = 2.2, 1.5 Hz, 0.78H), 5.15 (dd, J = 11.8, 8.3 Hz, 0.78H), 5.37 (dd, J = 15.8, 7.6 Hz, 0.22H), 6.14 (d, J = 11.8 Hz, 0.78H), 6.46 (d, J = 15.8 Hz, 0.22H), 7.34 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 1.56H), 7.83 (d, J = 8.4 Hz, 0.44H); ^{13}C-NMR

(parentheses indicate chemical shifts of the peak belonging to E-isomer) δ (12.3), 12.7, (18.3), 21.6, 22.8, (41.2), 41.4, 42.7, (45.7), 117.7, (117.9), (120.6), 122.2, 127.6, 129.6, (135.4), 135.5, 137.7, (139.0), 140.5, (140.8), 144.3. Found: C, 65.06; H, 7.01; N, 4.80%. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05%.

cis-2-(1,3-Butadienyl)-3-methyl-1-tosylaziridine and cis-3-Methyl-2-(4-phenyl-1,3-butadienyl)-1-tosylaziridine. These compounds were prepared by the reported procedure.[10]

cis-2-(1,3-Heptadienyl)-3-methyl-1-tosylaziridine (E:Z = 15:85): bp 140 °C/0.2 Torr; ^{1}H-NMR δ 0.90 (t, J = 6.0 Hz, 3H), 1.1-1.6 (m, 5H, including d, J = 6.1 Hz at 1.16 ppm), 1.8-2.2 (m, 2H), 2.35 (s, 3H), 2.8-3.1 (m, 1H), 3.33 (dd, J = 7.7, 7.3 Hz, 0.15H), 3.62 (dd, J = 8.0, 7.0 Hz, 0.85H), 4.8-6.6 (m, 4H), 7.30 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H).

cis-3-(1,3-Butadienyl)-2-phenyl-1-tosylaziridine (E:Z = 17:83): bp 206 °C/2 Torr; IR (neat) 3030, 2922, 1735, 1597, 1450, 1375, 1328, 1242, 1161, 1092, 997, 919, 893, 812, 767, 732, 698, 571 cm^{-1}; ^{1}H-NMR δ 2.43 (s, 3H), 3.67 (dd, J = 8.6, 7.3 Hz, 0.17H), 3.96 (ddd, J = 8.7, 7.3, 1.0 Hz, 0.83H), 4.08 (d, J = 7.3 Hz, 0.17H), 4.12 (d, J = 7.3 Hz, 0.83H), 4.85 (ddddd, J = 11.0, 8.7, 1.2, 1.1, 0.9 Hz, 0.83H), 5.10 (ddm, J = 15.2, 8.6 Hz, 0.17H), 5.2-5.3 (m, 2H), 6.14 (dddm, J = 11.2, 11.0, 1.0 Hz, 0.83H), 6.41 (ddd, J = 15.2, 10.5, 0.6 Hz, 0.17H), 6.74 (dddd, J = 17.2, 11.2, 9.7, 1.0 Hz, 0.83H), 6.7-6.9 (m, 0.17H), 7.2-7.4 (m, 7H), 7.90 (d, J = 8.3 Hz, 2H); ^{13}C-NMR δ 21.6, 42.7, 46.4, 103.2, 120.9, 122.0, 127.4, 127.8, 127.9, 128.2, 129.7, 131.0, 132.4, 135.0, 136.0, 144.6.

cis-3-(3-Methyl-1,3-butadienyl)-2-phenyl-1-tosylaziridine (E:Z = 9:91): bp 133 °C/0.2 Torr; IR (neat) 3028, 2974, 2920, 1735, 1598, 1497, 1452, 1375, 1329, 1242, 1161, 1091, 1019, 1000, 904, 846, 813, 766, 698, 673, 574 cm^{-1}; ^{1}H-NMR δ 1.88 (s, 3H), 2.44 (s, 3H), 4.0-4.2 (m, 2H), 4.8-5.1 (m, 3H, including dd, J = 11.7, 8.0 Hz at 4.89 ppm, and two broad singlets at 4.99 and 5.10 ppm), 6.02 (d, J = 11.7 Hz, 0.91H), 6.49 (d, J = 15.5 Hz, 0.09H), 7.2-7.4 (m, 5H), 7.34 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H); ^{13}C-NMR δ 21.7, 22.8, 43.9, 47.0, 117.7, 122.0, 127.4, 127.9, 127.9, 128.3, 132.7, 135.1, 138.2, 140.5, 144.6.

2-((3E)-4-Phenyl-1,3-butadienyl)-1-tosylazetidine (1E:1Z = 65:35): bp 130 °C/0.2 Torr (dec.); ^{1}H-NMR δ 2.0-2.3 (m, 2H), 2.44 (s, 3H), 3.5-3.8 (m, 2H), 4.42 (ddd, J = 7.9, 7.0, 7.0 Hz, 0.65H), 4.88 (ddd, J = 8.0, 7.0, 7.0 Hz, 0.35H), 5.67 (dd, J = 8.0, 10.5 Hz, 0.35H), 5.89 (dd, J = 15.1, 7.1 Hz, 0.65H), 6.19 (dd, J = 10.5, 10.0 Hz, 0.35H), 6.37 (ddd, J = 15.1, 10.0, 0.9 Hz, 0.65H), 6.55 (d, J = 15.5 Hz, 0.65H), 6.58 (d, J = 15.6 Hz, 0.35H), 6.73 (dd, J = 15.5, 10.0 Hz, 0.65H), 6.90 (ddd, J = 15.6, 10.0, 1.0 Hz, 0.35H), 7.2-7.5 (m, 7H), 7.73 (d, J = 8.5 Hz, 0.70H), 7.74 (d, J = 8.4 Hz, 1.30H); ^{13}C-NMR δ 21.4, 24.3, 29.6, 38.5, 54.8, 125.6, 125.7, 125.8, 126.0, 126.5, 126.8, 126.9, 127.2, 127.7, 128.0, 128.4, 128.7, 129.2, 129.4, 129.7, 132.3, 136.4, 138.1, 138.1, 142.9.

4-Methyl-2-(1,3-pentadecadienyl)-1-tosylazetidine (cis:trans = 60:40): bp 145 °C/0.2 Torr; IR (neat) 2890, 2827, 1463, 1375, 1340, 1156, 1088, 988, 813, 670 cm^{-1}; ^{1}H-NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.1-1.6 (m, 21H), 2.0-2.3 (m, 4H), 2.43 (s, 3H), 4.2-4.5 (m, 1H), 4.6-4.8 (m, 0.6H), 5.0-6.5 (m, 4.4H), 7.2-7.7 (m, 4H).

General Procedure for the Palladium Mediated Rearrangement of Dienylaziridines to Vinylpyrrolines. Tetrakis(triphenylphosphine)palladium(0) (3 mol%) was added to a solution of dienylaziridines in dimethyl sulfoxide at room temperature under an argon atmosphere. The reaction mixture was stirred at 50 °C or 25 °C (see Table 1) until the starting material was completely consumed. The resulting solution was diluted with ether and washed with aqueous ammonium

chloride. After ether extraction, the combined organic layers were dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was submitted to preparative thin layer chromatography on silica-gel to give vinylpyrrolines.

2-Ethenyl-5-methyl-1-tosyl-3-pyrroline and 1-Tosyl-2-(E)-2-styryl-5-methyl-3-pyrroline. The physical data of the title compounds were given in the previous report.[10]

cis-2-Isopropenyl-5-methyl-1-tosyl-3-pyrroline (11): mp 97 °C ($CHCl_3$); IR (neat) 2922, 2854, 1649, 1453, 1341, 1163, 1132, 1094, 902, 815, 667, 600 cm^{-1}; ^{1}H-NMR δ 1.44 (d, J = 6.5 Hz, 3H), 1.70 (dd, J = 1.4, 0.9 Hz, 3H), 2.42 (s, 3H), 4.56 (ddq, J = 6.5, 4.2, 2.2 Hz, 1H), 4.84 (dd, J = 3.9, 0.9 Hz, 1H), 4.90 (dq, J = 3.9, 1.4 Hz, 1H), 5.06 (m, 1H), 5.40 (ddd, J = 6.15, 2.1, 2.0 Hz, 1H), 5.58 (ddd, J = 6.15, 2.2, 2.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H); ^{13}C-NMR δ 17.9, 21.5, 23.1, 63.8, 73.2, 112.9, 127.5, 127.6, 129.5, 131.0, 135.2, 143.3, 144.0. Found: C, 64.78; H, 6.96; N, 4.85%. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05%.

cis-5-Methyl-2-(1-propenyl)-1-tosyl-3-pyrroline: bp 125 °C/0.2 Torr; ^{1}H-NMR δ 1.35 (d, J = 6.3 Hz, 3H), 1.63 (dd, J = 5.1, 2.0 Hz, 3H), 2.35 (s, 3H), 4.35 (qm, J = 6.3 Hz, 1H), 4.75 (dm, J = 6.0 Hz, 1H), 5.1-5.9 (m, 4H), 7.22 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H).

5-Methyl-2-(1-pentenyl)-1-tosyl-3-pyrroline (cis:trans = 92:8): bp 150 °C/0.2 Torr; IR (neat) 2980, 1723, 1584, 1485, 1443, 1334, 1153, 1086, 1035, 1009, 961, 808, 757, 698 cm^{-1}; ^{1}H-NMR δ 0.88 (t, J = 7.3 Hz, 3H), 1.2-1.5 (m, 5H, including d, J = 6.5 Hz at 1.37 ppm), 2.00 (dt, J = 6.6, 6.3 Hz, 2H), 2.41 (s, 2.76H), 2.43 (s, 0.24H), 4.51 (ddq, J = 6.5, 1.8, 1.5 Hz, 0.92H), 4.5-4.8 (m, 0.08H), 4.69 (dm, J = 6.9 Hz, 0.92H), 4.9-5.1 (m, 0.08H), 5.3-5.8 (m, 4H), 7.28 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H).

2-Methyl-5-pentylpyrrolidine. A solution of 5-methyl-2-(1-pentenyl)-1-tosyl-3-pyrroline (50 mg) in ethyl acetate (3 ml) was stirred for 30 min under a hydrogen atmosphere in the presence of platinum dioxide (ca. 2 mg). Filtration of the catalyst followed by purification by preparative thin layer chromatography gave 2-methyl-5-pentylpyrrolidine quantitatively. The authentic sample of pyrrolidine (cis:trans = 85:15) was prepared from 2,5-decadione according to the reported procedure.[11]

5-Ethenyl-2-phenyl-1-tosyl-3-pyrroline (cis:trans = 70:30): mp 75-80 °C ($CHCl_3$); IR (neat) 3030, 2925, 1735, 1598, 1494, 1455, 1349, 1164, 1095, 1048, 923, 814, 762, 697, 666 cm^{-1}; ^{1}H-NMR δ 2.32 (s, 0.9H), 2.36 (s, 2.1H), 4.9-5.2 (m, 1H), 5.17 (dm, J = 10.1 Hz, 1H), 5.31 (dm, J = 17.1 Hz, 1H), 5.5-5.8 (m, 3H), 5.86 (ddd, J = 17.1, 10.1, 7.1 Hz, 0.7H), 5.8-5.9 (m, 0.3H), 6.9-7.3 (m, 7H), 7.52 (d, J = 8.4 Hz, 2H); ^{13}C-NMR (parenthesis means peaks assigned to minor isomer) δ 21.4, 69.3, (69.7), 70.8, (70.9), (115.8), 116.9, 126.9, 127.4, 127.7, (127.8), 128.1, 128.3, 128.7, 129.3, 129.8, (130.2), 136.0, 137.8, (138.3), (140.3), (142.2), 143.1. Found: C, 70.38; H, 5.77; N, 4.30%. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30%.

5-Isopropenyl-2-phenyl-1-tosyl-3-pyrroline (cis:trans = 81:19): bp 193 °C/0.2 Torr; ^{1}H-NMR δ 1.58 (s, 0.57H), 1.70 (s, 2.43H), 2.40 (s, 2.43H), 2.46 (s, 0.57H), 3.73 (dd, J = 8.0, 8.0 Hz, 0.19H), 4.0-4.2 (m, 0.81H), 4.8-5.2 (m, 3H), 5.6-5.8 (m, 2H), 7.0-7.5 (m, 7H), 7.57 (d, J = 8.2 Hz, 2H).

2-(E-2-Phenylethenyl)-1-tosyl-3,4-dehydropiperidine: bp 190 °C/0.2 Torr; ^{1}H-NMR δ 1.90 (dm, J = 17.7 Hz, 1H), 2.0-2.3 (m, 1H), 2.36 (s, 3H), 3.08 (ddd, J = 13.5, 11.3, 4.5 Hz, 1H), 3.85 (dd, J = 13.5, 5.8 Hz, 1H), 4.99 (br.s, 1H), 5.67 (dm, J = 10.2 Hz, 1H), 5.83 (dm, J = 10.2 Hz, 1H), 6.00 (dd, J = 16.0, 6.4 Hz, 1H), 6.48 (dd, J = 16.0, 0.9 Hz, 1H), 7.1-7.3 (m, 7H), 7.70 (d, J = 8.4 Hz,

2H); ^{13}C-NMR δ 24.0, 26.9, 41.1, 57.5, 128.5, 128.5, 128.7, 129.1, 129.2, 129.8, 130.4, 131.1, 132.1, 135.0, 142.0, 145.6.

6-Methyl-2-(1-tridecenyl)-1-tosyl-3,4-dehydropiperidine (cis:trans = 47:53): IR (neat) 2990, 2885, 1587, 1460, 1320, 1160, 1085, 975, 810 cm^{-1}; ^{1}H-NMR δ 0.88 (t, J = 6.5 Hz, 3H), 1.14 (d, J = 7.0 Hz, 1.41H), 1.2-1.3 (m, 18H), 1.32 (d, J = 7.0 Hz, 1.59H), 1.7-2.3 (m, 4H), 2.40 (s, 3H), 4.09 (ddq, J = 7.0, 7.0, 4.8 Hz, 0.53H), 4.28 (dq, J = 7.0, 7.0 Hz, 0.47H), 4.86 (t, J = 7.0 Hz, 0.53H), 5.17 (dddd, J = 15.2, 7.2, 1.2, 1.2 Hz, 0.47H), 5.5-5.9 (m, 4H), 7.2-7.7 (m, 4H).

N-Tosyl Derivative of Solenopsin B and its cis Isomer. A stereoisomeric mixture of 6-methyl-2-(1-tridecenyl)-1-tosyl-3,4-dehydropiperidine (0.3 g, 0.7 mmol) was dissolved in ethanol (3 ml) and platinum(IV) oxide (22 mg, 0.1 mmol) was added to the solution at room temperature. The resulting black suspension was vigorously stirred for 30 min under a hydrogen atmosphere. Then the reaction mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by preparative thin layer chromatography on silica-gel gave two stereoisomeric products. The comparison with authentic samples synthesized independently from Solenopsin B and its stereoisomer,[12] showed that the more polar component (122 mg, 40% yield) was identical with N-tosyl derivative of Solenopsin B, and the less polar one (110 mg, 36% yield) was its cis isomer. N-Tosyl derivative of Solenopsin B: mp 66 °C ($CHCl_3$); IR (nujor) 1737, 1656, 1333, 1167, 1157, 11095, 996, 972, 908, 872, 811 cm^{-1}; ^{1}H-NMR δ 0.88 (t, J = 7.0 Hz, 3H), 1.2-1.9 (m, 33H, including d, J = 7.0 Hz, 3H at 1.30 ppm), 2.43 (s, 3H), 3.9-4.2 (m, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H); ^{13}C-NMR δ 13.7, 14.1, 21.5, 22.7, 27.3, 27.4, 29.4, 29.6, 29.7, 31.9, 35.5, 47.9, 52.7, 106.8, 126.7, 129.5, 139.1. Cis isomer: mp 51 °C; IR (neat) 2922, 2850, 1726, 1654, 1599, 1492, 1459, 1318, 1153, 1089, 990, 811, 709, 684 cm^{-1}; ^{1}H-NMR δ 0.88 (t, J = 7.0 Hz, 3H), 1.2-1.9 (m, 33H), 2.41 (s, 3H), 3.5-3.8 (m, 1H), 4.1-4.3 (m, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H); ^{13}C-NMR δ 14.1, 19.3, 20.2, 22.7, 26.9, 28.0, 29.4, 29.5, 29.6, 29.7, 31.0, 31.9, 32.8, 50.5, 55.5, 126.9, 129.3, 141.7, 142.3. Elemental analysis of the stereoisomeric mixture gave a satisfactory result. Found: C, 71.86; H, 10.66; N, 3.43%. Calcd for $C_{26}H_{45}NO_2S$: C, 71.67; H, 10.41; N, 3.21%.

Radical Induced Rearrangement of N-Tosylaziridine to N-Tosylvinylpyrroline. Triphenyltin hydride (0.14 g, 0.4 mmol) was added to a solution of cis-2-(3-methyl-1,3-butadienyl)-3-methyl-1-tosylaziridine (**10**) (0.27 g, 1.0 mmol) and AIBN (66 mg, 0.4 mmol) in benzene (20 ml) under an argon atmosphere. The mixture was heated at 80 °C for 4 h. The resulting mixture was concentrated and the residual oil was submitted to silica-gel column chromatography to give 5-methyl-2-isopropenyl-1-tosyl-3-pyrroline (**11**) (0.21 g) in 76% yield. In the case of benzenethiol, a solution of **10** (1.0 mmol) and benzenethiol (0.4 mmol) in benzene was heated for 4 h without AIBN to give **11** in 64% yield after similar workup followed by purification.

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