Tetrahedron Letters,Vol.26,No.7,pp 857-860,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

Pd(0) PROMOTED TRANSFORMATION OF N-TOSYL-2-(1,3-BUTADIENYL)-AZIRIDINE INTO N-TOSYL-2-VINYL-3-PYRROLINE

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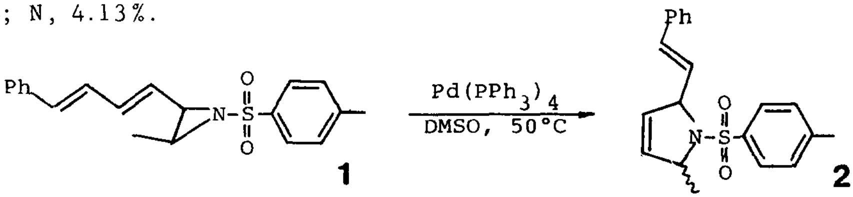
Abstract: 1,3-Butadienylaziridines activated by N-tosyl group smoothly rearrange to vinylpyrrolidine derivatives in the presence of a catalytic amount of $Pd(PPh_3)_4$. Transformation of dienylazetidines into vinylpiperidine derivatives is also described.

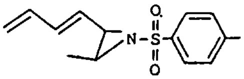
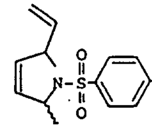
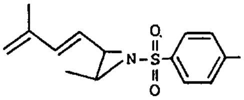
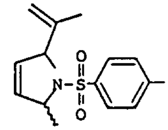
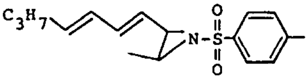
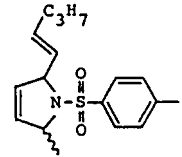
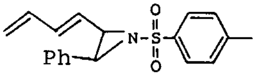
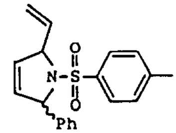
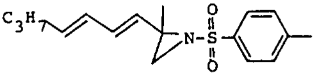
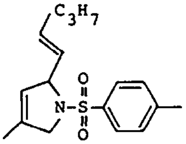
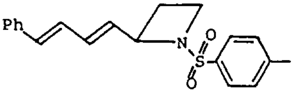
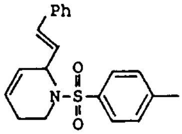
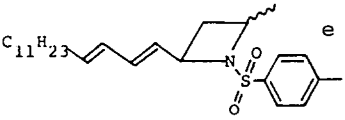
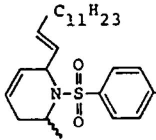
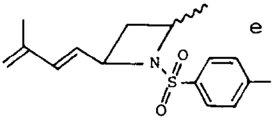
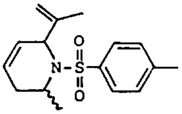
Previously reported reaction of 1,1-dialkoxycarbonyl-2-(1,3-butadienyl)cyclopropanes affords 2-ethenyl-3-cyclopentenes as a result of vinylcyclopropane-cyclopentene rearrangement in the presence of a catalytic amount of $Pd(PPh_3)_4$.[1] Here we wish to describe further extension of this reaction to 3-pyrroline synthesis. Pd(0) promoted isomerization of 1,3-butadienylaziridines having $>N-SO_2Ar$ group provides 3-pyrrolines carrying $ArSO_2$ group on nitrogen.

To a solution of dienylaziridine **1** (0.17 g, 0.49 mmol) (vide infra) in DMSO (2 ml), $Pd(PPh_3)_4$ (5.5 mg, 5×10^{-3} mmol) was added under an argon atmosphere. The mixture was heated at 50°C for 30 min. The resulting dark yellow solution was diluted wih ether (10 ml) and poured into water. After ether extraction, the combined organic solution was dried (Na_2SO_4) and concentrated. Purification of the residue by silica gel thin layer chromatography gave vinylpyrroline **2** (0.13 g, 78% yield, cis:trans = 82:18) as a semi-solid: IR (neat) 3000, 2930, 1722, 1587, 1488, 1441, 1325, 1150, 658 cm^{-1}; ^1H-NMR ($CDCl_3$) δ1.42 (d, J = 6.5 Hz, 2.46H), 1.55 (d, J = 6.3 Hz, 0.54H), 2.33 (s, 0.54H), 2.37 (s, 2.46H), 4.58 (ddq, J = 6.5, 3.7, 2.0 Hz, 0.82H), 4.64-4.76 (m, 0.18H), 5.05 (ddd, J = 7.0, 1.7, 0.85 Hz, 0.82H), 5.11-5.22 (m, 0.18H), 5.4-5.8 (m, 2H), 6.07 (dd, J = 15.9, 7.0 Hz, 1H), 6.50 (d, J = 15.9 Hz, 0.18H), 6.55 (dd, J = 15.9, 0.85 Hz, 0.82H), 7.2-7.8 (m, 9H). Found: C, 70.70; H, 6.29; N, 3.88%. Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13%.



1 **2**

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	 **3** (86:14)[d]
2		50	0.4	98	 (95: 5)
3		50	1.2	81	 (92: 8)
4		50	0.3	76	 (70:30)
5		50	1.0	44	
6		25	12	80	
7	 [e]	25 50	10 0.4	86 91	 **4** (47:53)[f]
8	 [e]	25	12	85	 (32:68)

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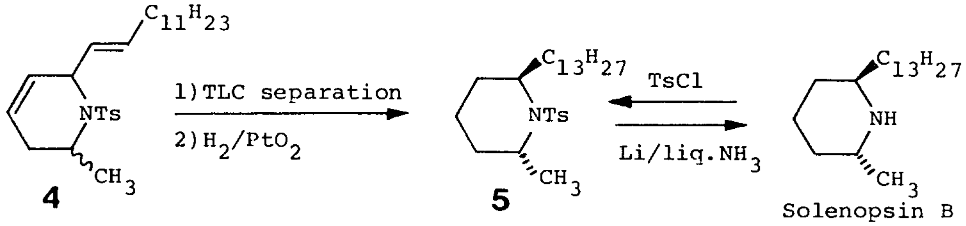
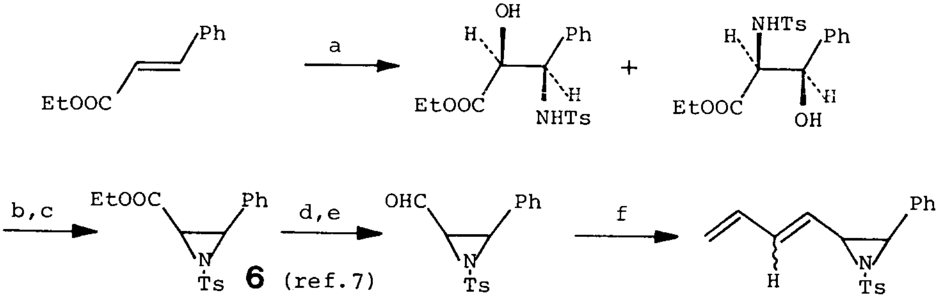
[a] Reactions were performed on a 1-2mmol scale with 5 mol% $Pd(PPh_3)_4$.
[b] Isolated yields. [c] Determined by the examination of the NMR spectra.
[d] See ref. 2. [e] Isomeric ratios (cis:trans) could not be determined.
[f] See ref. 3.

The generality of this rearrangement was explored with the examples shown in Table 1. The reaction of N-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.[4]

The reaction was successfully applied to the transformation of N-tosyl-2-(1,3-butadienyl)azetidines into vinylpiperidine derivatives and a couple of examples are also shown in Table 1. The product **4** (Entry 7 in Table 1) was easily transformed into Solenopsin B[5] which was isolated from the red form of the fire ant, Solenopsis saevissima.[6]

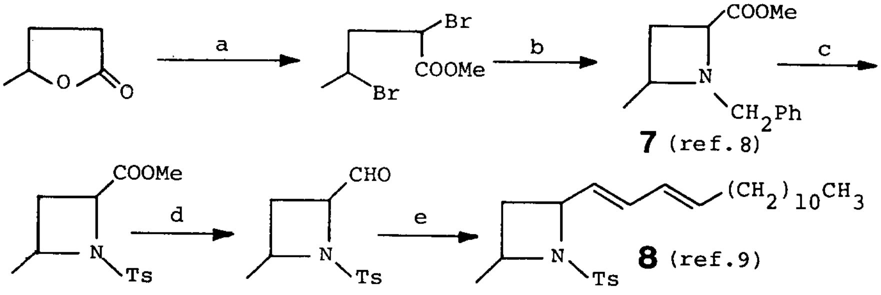


The required aziridines and azetidines were prepared as follows.[10]



a: $TsN<^{Cl}_{Na}$, cat. OsO_4 b: $CH_3SO_2Cl-Et_3N$ c: $K_2CO_3/MeOH$

d: $^iBu_2AlH$ e: PCC   f: $Ph_3P=CH-CH=CH_2$



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

References and Notes

1. Y, Morizawa, K. Oshima, and H. Nozaki, Tetrahedron Lett., 23, 2871 (1982); idem, Israel Journal of Chemistry, **24**, 149 (1984).

2. A mixture of cis and trans-2-ethyl-5-methylpyrrolidine (cis:trans = 85:15) was prepared independently according to the reported procedure (T. H. Jones, M. S. Blum, and H. M. Fales, Tetrahedron Lett., **1979**, 1031). Tosylation gave a mixture of cis and trans-N-tosyl-2-ethyl-5-methylpyrrolidine which was identical with a sample obtained by hydrogenation (PtO_2, H_2) of the compound **3**.

3. **4**: IR (neat) 2990, 2885, 2820, 1587, 1460, 1320, 1160, 1085, 975, 810, 705 cm^{-1}; NMR ($CDCl_3$) δ0.88 (t, J = 6.5 Hz, 3H), 1.14 (d, J = 7.0 Hz, 1.41H), 1.20-1.30 (m, 18H), 1.32 (d, J = 7.0 Hz, 1.59H), 1.70-2.30 (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), 5.50-5.85 (m, 4H), 7.23-7.69 (m, 4H).

4. The rearrangement might proceed through nucleophilic attack of Pd(0) on the dienic group to form a zwitterion consisting of π-pentadienylpalladium and stabilized tosylamide anion 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.

5. K. Maruoka, T. Miyazaki, M. Ando, Y. Matsumura, S. Sakane, K. Hattori, and H. Yamamoto, J. Am. Chem. Soc., **105**, 2831 (1983) and references cited therein. The compound **5** was identical with the sample prepared by tosylation of Solenopsin B. We are grateful to Prof. H. Yamamoto at Nagoya University for a gift of Solenopsin B and its cis isomer.

6. J. G. MacConnell, M. S. Blum, and H. M. Fales, Tetrahedron, **27**, 1129 (1971).

7. J.-E. Bäckvall, K. Oshima, R. E. Palermo, and K. B. Sharpless, J. Org. Chem., **44**, 1953 (1979). Alternatively, N-tosyl-1-formyl-2-methylaziridine was prepared from 1,3-pentadiene according to the following sequences: (1) oxyamination (TsN(Cl)Na, OsO_4), (2) mesylation of alcohol ($MeSO_2Cl$, Et_3N), (3) aziridine ring formation (K_2CO_3, MeOH), and (4) formylation ($NaIO_4$, OsO_4).

8. H. H. Wasserman, B. H. Lipshutz, A. W. Tremper, J. S. Wu, J. Org. Chem., **46**, 2991 (1981); D. S. Soriano, K. F. Podraza, N. H. Cromwell, J. Heterocycl. Chem., **17**, 623 (1980).

8: a mixture of cis and trans isomer (cis/trans = 3/2). IR (neat) 2890, 2827, 1463, 1375, 1340, 1156, 1088, 988, 813, 670 cm^{-1}; NMR ($CDCl_3$) δ0.88 (t, J = 6.5 Hz, 3H), 1.15-1.57 (m, 21H), 2.00-2.25 (m, 4H), 2.43 (s, 3H), 4.25-4.45 (m, 1H), 4.60-4.80 (m, 0.6H), 5.05-6.50 (m, 4.4H), 7.20-7.70 (m, 4H).

0. Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research No. 59104005) is acknowledged.

(Received in Japan 13 November 1984)