

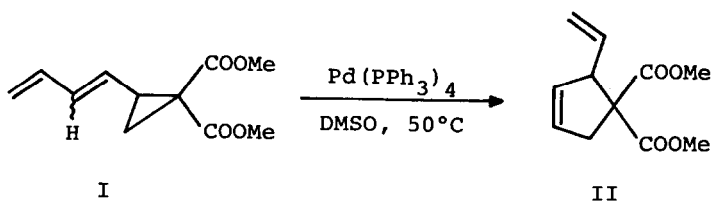
Pd(0) PROMOTED REARRANGEMENT OF 2-(1,3-BUTADIENYL)CYCLOPROPANE-  
1,1-DICARBOXYLATE ESTERS TO 2-ALKENYL-3-CYCLOPENTENE-1,1-DICARBOXYLATE ESTERS

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Abstract: The title dienylcyclopropanes smoothly rearrange to five-membered rings in the presence of a Pd(0) catalyst under mild conditions.

Although the vinylcyclopropane-cyclopentene rearrangement<sup>1</sup> has attracted mechanistic interest, the synthetic application has been limited because of the high temperature (300-500°C) required.<sup>2</sup> Here we wish to describe that dienylcyclopropanes activated by two electron-withdrawing groups easily rearrange to vinylcyclopentene derivatives in the presence of a catalytic amount of Pd(0) at 25-60°C.

To a solution of dienylcyclopropane I (0.24 g, 1.1 mmol) in DMSO<sup>3</sup> (3.0 ml), Pd(PPh<sub>3</sub>)<sub>4</sub><sup>4</sup> (30 mg, 0.03 mmol) was added under argon atmosphere. The mixture was heated at 50°C for 15 min. The resulting yellow solution was diluted with ether (5.0 ml) and washed with brine. After ether extraction (5 mlx2), the combined organic solution was dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated, and the residue purified by silica gel column chromatography (hexane-ethyl acetate = 10:1) to give vinylcyclopentene II (0.21 g, 87% yield) as a colorless oil.<sup>5</sup>



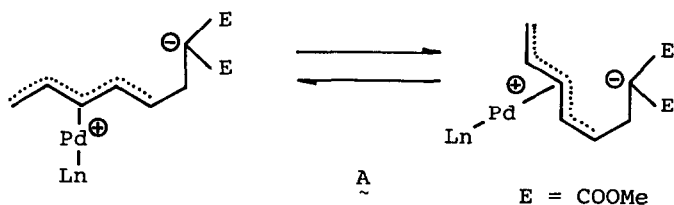
The generality of this rearrangement was explored with the examples shown in Table 1. Several aspects are quite noteworthy. Exposure of ethyl 3-(1,3-butadienyl)-2,2-dimethylcyclopropanecarboxylate derived from ethyl chrysanthemate to the reaction resulted in the recovery of the starting cyclopropane after prolonged heating (5 h) at 60°C. Moreover, the reaction of 2-vinylcyclopropane-1,1-dicarboxylate diethyl ester yielded complex mixture containing isomeric mixture of ethyl 2-carboethoxyhexadienoate, no trace of cyclopentene derivatives being detected. Thus, the presence of two electron-withdrawing groups and dienic moiety is essential for the rearrangement. The stereochemistry of both types of substituents on the cyclopropane ring did not affect the reaction pathway (Entry 2, 3, 4, 5, and 6).

Table 1. Pd(0) Catalyzed Rearrangement of Dienylcyclopropanes<sup>a</sup>

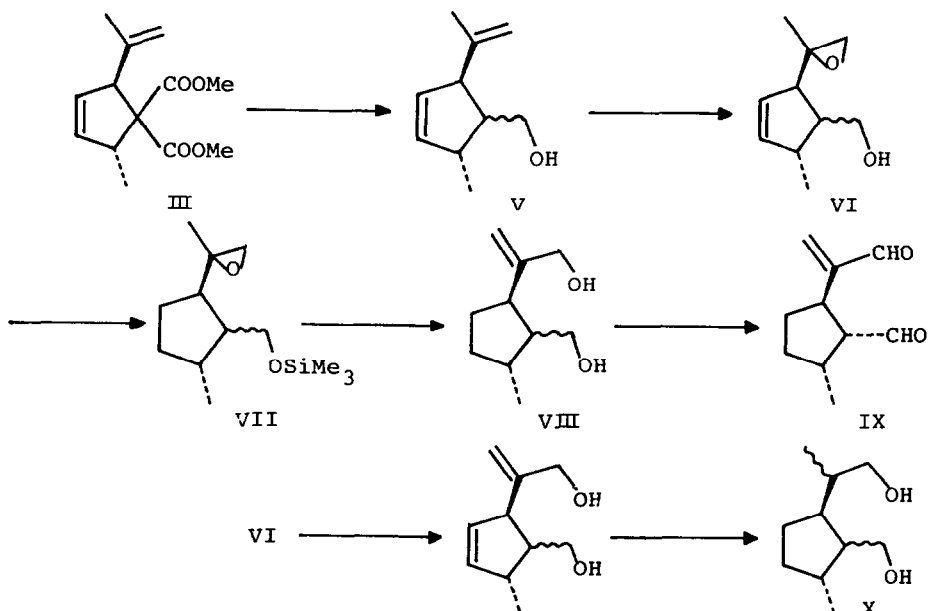
Entry	Substrate <sup>b</sup>	Temp(°C)	Yield(%) <sup>c</sup>	Product (Isomer Ratio) <sup>d</sup>
1		60	86 <sup>e</sup>	 III <sup>f</sup> (3:1) IV <sup>f</sup>
2		60	84	(3 : 1)
3	<i>E</i> : <i>Z</i> = 7 : 3 <sup>g</sup>	60	85	(3 : 1)
4	<i>Z</i>	60	70	(3 : 1)
5		60	96	(1 : 1)
6	(1 <i>R</i> *,2 <i>S</i> *) <sup>h</sup> (1 <i>S</i> *,2 <i>S</i> *)	60	88	(1 : 1)
7		25	82	 (1 : 1)
8		25	89	 (1:1)
9		60	81	

<sup>a</sup>Reactions were performed on a 1-2 mmol scale with 3 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> unless otherwise stated. Rearrangements were completed within 1 h. <sup>b</sup>Dienylcyclopropanes were prepared in 40-70% yields by Wittig reaction of the corresponding 2-formylcyclopropane-1,1-dicarboxylate esters or relative compounds with phosphorane such as Ph<sub>3</sub>P=CHCH=CH<sub>2</sub>. 2-Formylcyclopropane-1,1-dicarboxylate ester derivatives were prepared by the ozonolysis of 2-vinylcyclopropane-1,1-dicarboxylate<sup>6</sup> or directly by the reaction between  $\alpha,\beta$ -unsaturated aldehydes and bromomalonate diester.<sup>7</sup> <sup>c</sup>Isolated yields. <sup>d</sup>Determined by the examination of the NMR spectra. <sup>e</sup>Reaction was performed on 30 mmol scale. See ref. 10. <sup>f</sup>III and IV: IR (neat) 1740, 1652, 1262, 900 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  0.91 (d,  $J$  = 7.5 Hz, 0.75H, for IV), 1.28 (d,  $J$  = 7.5 Hz, 2.25H, for III) 1.69 (br s, 0.75H, for IV), 1.74 (br s, 2.25H, for III), 2.9-3.2 (m, 1H), 3.51 (s, 3H), 3.75 (s, 3H), 4.0-4.2 (m, 1H), 4.6-4.9 (m, 2H), 5.3-5.6 (m, 2H). Structure III and IV were easily assigned from the examination of the <sup>1</sup>H NMR spectra since 5-methyl groups are shielded by the *cis* substituents and absorb at  $\delta$  1.28 and 0.91, respectively. B. B. Snider, J. V. Dunčič, *J. Org. Chem.*, **45**, 3461 (1980); F. J. McQuillin, D. G. Parker, *J. Chem. Soc. Perkin I*, 1974, 809. <sup>g</sup>Pure *E* and *Z* isomers were prepared by glpc separation (3% Silicone OV-17 on Unipor HP, 2 m, 150°C). <sup>h</sup>Isomers were separated by preparative tlc. Assignment of the stereochemistry was based on the reported data. H. M. Hutton, T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962).

The rearrangement might proceed through nucleophilic attack of Pd(0) to the dienic group to form a zwitterion A consisting of  $\pi$ -pentadienylpalladium<sup>8</sup> and stabilized anion moieties under cyclopropane cleavage. The intermediate collapses to form cyclopentene derivative and the new C-C bond formation exclusively produces a five-membered ring and not a seven-membered one.<sup>9</sup> The regioselectivity is ascribed to the preferred W type conformation of the pentadienyl group.



The present new method has provided us with a simple route to terpenic cyclopentanoids as exemplified by the syntheses of dolichodial and iridodiol. Decarbalkoxylation of *gem*-diester III<sup>10</sup> (NaI/wet HMPA, 110°C, 20 min<sup>11</sup>) followed by reduction with LAH gave alcohol V<sup>12</sup> in 77% yield. Selective epoxidation to the key intermediate VI was realized with reasonable regioselectivity<sup>13</sup> by MCPBA at 0°C in dichloromethane (88%). Hydrogenation (PtO<sub>2</sub>, 1 atm of H<sub>2</sub>) and trimethylsilylation produced VII. Reaction of VII with diethylaluminum 2,2,6,6-tetramethylpiperidide (DATMP)<sup>14</sup> in benzene at 25°C for 4 h produced, after desilylation with 1*N* HCl, diol VIII in 54% overall yield from VI. Finally with PCC,<sup>15</sup> diol was transformed into dolichodial IX<sup>16</sup> in 60% yield. Treatment of VI-trimethylsilyl ether with DATMP *prior to* hydrogenation provided iridodiol X<sup>17</sup> in 60% overall yield from VI.<sup>18</sup>



## References and Notes

1. M. P. Doyle and D. V. Leusen, *J. Am. Chem. Soc.*, **103**, 5917 (1981) and references cited therein.
2. One exceptional rearrangement proceeding at 25°C has been recently reported. R. L. Danheiser, C. Martinez-Davila, R. J. Auchus, and J. T. Kadonaga, *J. Am. Chem. Soc.*, **103**, 2443 (1981).
3. Acetonitrile is as effective as DMSO. In THF, benzene, or dichloromethane, the reaction did not take place.
4. Pyrolysis at 250°C gave a complex mixture containing no cyclopentene II.
5. Bp 84°C (bath temp)/1.0 Torr; IR (neat) 1738, 1638, 974, 923  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  2.62 (br d,  $J = 17.0$  Hz, 1H), 3.1-3.4 (m, 1H), 3.60 (s, 3H), 3.67 (s, 3H), 3.9-4.2 (m, 1H), 4.8-5.2 (m, 2H), 5.3-5.7 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  39.9 (t), 52.3 (q), 52.8 (q), 54.7 (d), 64.0 (s), 117.3 (t), 128.4 (d), 131.4 (d), 135.8 (d), 170.2 (s), 172.3 (s). Found: C, 62.74; H, 6.73. Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : C, 62.85; H, 6.71.
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7. G. Bonavent, M. Causse, M. Guitard, and R. F-Jullien, *Bull. Soc. Chem. Fr.*, **1964**, 2462.
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9. Similar high regioselectivity has been reported. B. M. Trost, T. A. Runge, and L. N. Jungheim, *J. Am. Chem. Soc.*, **102**, 2840 (1980); J. Tsuji, Y. Kobayashi, H. Kataoka, and T. Takahashi, *Tetrahedron Lett.*, **21**, 1475 (1980).
10. Treatment of the dienylcyclopropane (7.1 g, 30 mmol) with  $\text{Pd}(\text{PPh}_3)_4$  (0.17 g, 0.15 mmol) in DMSO (20 ml) at 60°C for 20 min provided a mixture of III and IV (6.2 g, 86%, III/IV = 3:1). Pure III (>95%) was obtained by preparative tlc separation (hexane-ether = 10:1, three times developments).
11. T. Takahashi, K. Kasuga, M. Takahashi, J. Tsuji, *J. Am. Chem. Soc.*, **101**, 5072 (1979).
12. Ca. 2:1 mixture of two isomers. IR (neat) 3370, 1642, 890  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  1.00 (d,  $J = 6.6$  Hz,  $\text{CH}_3$ , 1H for minor isomer), 1.09 (d,  $J = 6.6$  Hz,  $\text{CH}_3$ , 2H, major isomer), 1.69 (br s,  $=\text{CCH}_3$ , 2H, major isomer), 1.75 (br s,  $=\text{CCH}_3$ , 1H, minor isomer), 2.3-3.6 (m, 6H), 4.6-4.9 (m, 2H), 5.3-5.8 (m, 2H).
13. The ratio of VI and its regioisomer derived from epoxidation of the double bond in the five-membered ring was 8:1.
14. A. Yasuda, S. Tanaka, H. Yamamoto, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **52**, 1752 (1979).
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16. C. Beaupin, J. C. Rossi, J. P. Vidal, J. P. Girard, and J. Passet, *Phytochemistry*, **19**, 1541 (1980).
17. Synthetic iridodiol X consists of 4 isomers ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -isomers). T. Sakai, K. Nakajima, and T. Sakan, *Bull. Chem. Soc. Jpn.*, **53**, 3683 (1980); J. Wolinsky, T. Gibson, D. Chan, and H. Wolf, *Tetrahedron*, **21**, 1247 (1965); K. Sisido, S. Kurozumi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966).
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