# Homodienyl [1,5]-Hydrogen Shift of *cis*- and *trans*-*N*-Acyl-2-alkylcyclopropylimines

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In 1964, Ellis and Frey investigated the thermal rearrangement of *cis*- and *trans*-1-methyl-2-vinylcyclopropanes to yield *cis*-1,4-hexadiene.[1] The *cis* configuration of the product from the *cis*-cyclopropane coupled with the low activation energy ($E_a = 31.2$ kcal/mol) suggested that this hydrogen rearrangement proceeds by a suprafacial, concerted homodienyl [1,5]-hydrogen shift. Alternatively, it can be described as a retro-ene reaction. In contrast, the higher activation energy ($E_a = 48.6$ kcal/mol) and the failure to detect any *trans*-1,4-hexadiene product from the *trans*-cyclopropane led to the postulation that this reaction proceeds by a diradical intermediate (Scheme 1). The intermediate can then proceed to the product by a radical hydrogen abstraction or by cyclization to the *cis*-cyclopropane, which undergoes a rapid homodienyl [1,5]-hydrogen shift. This rearrangement has received considerable attention with respect to its mechanism,[2] site selectivity,[3] and synthetic applications.[4]

Our recent work described the ring expansion of *N*-(methoxycarbonyl)cyclopropylimines **1** with phenyl and acyl substituents at C-1 or C-2 to *N*-(methoxycarbonyl)-2-pyrrolines **2** by flash vacuum thermolysis (FVT) (Scheme 2). However, compounds with methyl substituents at these positions did not lead to the desired pyrrolines.[5]

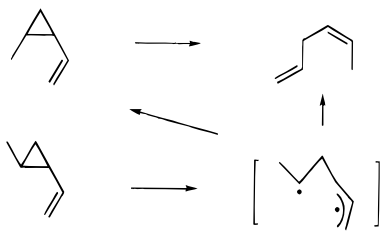
Continuing our interest in the thermal reactions of 2-methylcyclopropylimines (**1**, $R_1 = H$, $R_2 = CH_3$), in this work, we investigate the FVT of a series of 2-alkylcyclopropylimines **8** that were derived from their thermal precursors, *cis*- and *trans*-*N*,*O*-bis(methoxycarbonyl)-*N*-(cyclopropylmethyl)hydroxylamines **7** by elimination of $CO_2$ and MeOH.

The general cyclopropanation procedure[6] employs an appropriate alkene (allyl bromide, allyltrimethylsilane, or allylbenzene) and ethyl diazoacetate in the presence of catalytic rhodium(II) diacetate. This procedure produced esters **3a**−**c** and the *cis* and *trans* isomers were separated by careful silica gel chromatography using EtOAc/hexane (1:20) as eluent. A [2,3]-sigmatropic rearranged product, ethyl 2-bromo-4-pentenoate, accompanied the synthesis of **3a**.[6b,7] Treating the bromoester **3a** with methoxide, followed by acid workup and evaporation at 50 °C, produced the methoxy acid **3d**. The cyano ester, **3e**, was obtained by reacting **3a** with potassium cyanide. Reduction with lithium aluminum hydride (which also reduced the bromine of **3a**) furnished the alcohols **4a**−**d**. Lithium borohydride was used to selectively reduce the ester of **3e** to **4e**.[8] Oxidation of the alcohols **4** to aldehydes **5**, followed by oxiimination to oximes **6**, reduction again, and acylation, yielded diacylated hydroxylamine **7** (Scheme 3). Moreover, the *cis* and *trans* isomers were identified by the presence or lack of NOE between the two methylene signals in alcohols **4** or diacylated hydroxylamines **7**.

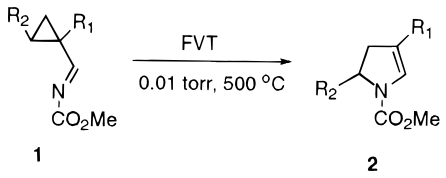
As previously shown, *N*,*O*-diacylated hydroxylamines **7** readily produced the *N*-acylimines **8** under thermal conditions.[9] Therefore, flash vacuum thermolysis of either *cis*-**7** or *trans*-**7** at 450°C and 0.01 Torr resulted in formation of 1-*cis*-1,4-pentadienylcarbamates **9**, the product of homodienyl [1,5]-hydrogen shift from **8** (Scheme 4). The *cis* configuration of the 1,2-double bond in **9** was established by the 7.4−7.6 Hz of coupling constant between H-1 and H-2 together with the presence of NOE between the same protons. The 4,5-double bond geometry tended to be the more stable *trans* configuration; however, **9b** and **9e** were a mixture of 4-*cis* and 4-*trans*.

The significantly higher yield of the rearranged product from the *cis*-**7** series over that of the *trans*-**7** series suggested that *cis*-**8** undergoes the symmetry-allowed, concerted homodienyl [1,5]-hydrogen shift. The direct transfer of hydrogen is precluded on geometric grounds for *trans*-**8**. Such a reaction likely involves cleavage of the three-membered ring forming a diradical intermediate followed by rotation around single bonds to attain

**Scheme 1**



**Scheme 2**




**1** **2**

(1) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578.
(2) (a) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 1650. (b) Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 2089. (c) Pegg, G. G.; Meehan, G. V. *Aust. J. Chem.* **1990**, *43*, 1071. (d) Pegg, G. G.; Meehan, G. V. *Aust. J. Chem.* **1990**, *43*, 1357. (e) Piers, E.; Maxwell, A. R. *Can. J. Chem.* **1984**, *62*, 2392. (f) Piers, E.; Nagakura, I.; Shaw, J. E. *J. Org Chem.* **1978**, *43*, 3431. (g) Somfai, P.; Ahman, J. *Tetrahedron Lett.* **1995**, *36*, 1953. (h) Ahman, J.; Somfai, P.; Tanner, D. *J. Chem. Soc., Chem. Commun.* **1994**, 2785. (i) Trost, B. M.; Ornstein, P. L. *J. Org. Chem.* **1982**, *47*, 748. (j) Pattenden, G.; Whybrow, D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3147. (k) Naf, F.; Decorzant, R. *Helv. Chim. Acta* **1978**, *61*, 2524. (l) Watson, J. M.; Irvine, J. L.; Roberts, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3348. (m) Klumpp, G. W.; Schakel, M. *Tetrahedron Lett.* **1983**, *24*, 4595. (n) Mazzocchi, P. H.; Tamburin, H. *J. Am. Chem. Soc.* **1975**, *97*, 555. (o) Jorgenson, M. J.; Thacher, A. F. *Tetrahedron Lett.* **1969**, 4651. (p) Frey, H. M.; Solly, R. K. *Int. J. Chem. Kinet.* **1969**, *1*, 473.
(3) (a) Piers, E.; Maxwell, A. R.; Moss, N. *Can. J. Chem.* **1985**, *63*, 555. (b) Ohloff, G. *Tetrahedron Lett.* **1965**, 3795.
(4) (a) Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* **1988**, *53*, 4682. (b) Corey, E. J.; Yamamoto, H.; Herron, D. K.; Achiwa, K. *J. Am. Chem. Soc.* **1970**, *92*, 6635. (c) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020. (d) Corey, E. J.; Herron, D. K. *Tetrahedron Lett.* **1971**, 1641.
(5) Wu, P. L.; Wang, W. S. *J. Org. Chem.* **1994**, *59*, 622.
(6) (a) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssie, P. *J. Org. Chem.* **1980**, *45*, 695. (b) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094. (c) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726.
(7) Doyle, M. P.; Griffin, J. H.; Chinn, M. S.; van Leusen, D. *J. Org. Chem.* **1984**, *49*, 1917.
(8) Brown, H. C.; Narasimhan, S.; Choi, Y. M. *J. Org. Chem.* **1982**, *47*, 4702.
(9) See ref 5 and: (a) Wu, P. L.; Chu, M.; Fowler, F. W. *J. Org. Chem.* **1988**, *53*, 963. (b) Lin, J. M.; Koch, K.; Fowler, F. W. *J. Org. Chem.* **1986**, *51*, 161. (c) Cheng, Y. S.; Lupo, A.; Fowler, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7696.

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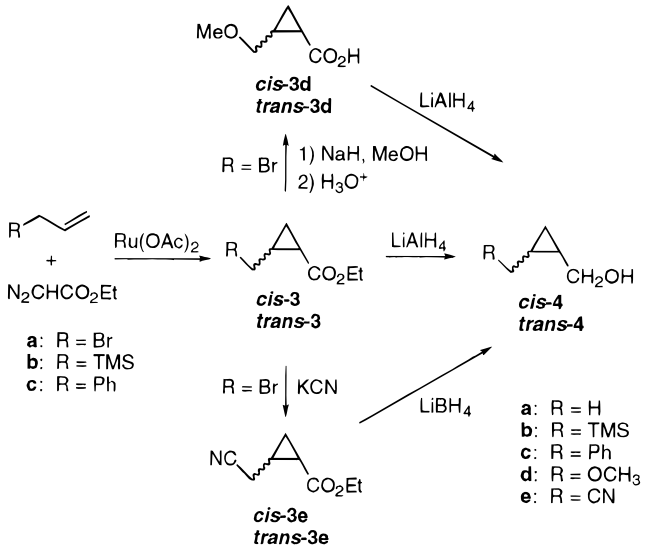
**Scheme 3**

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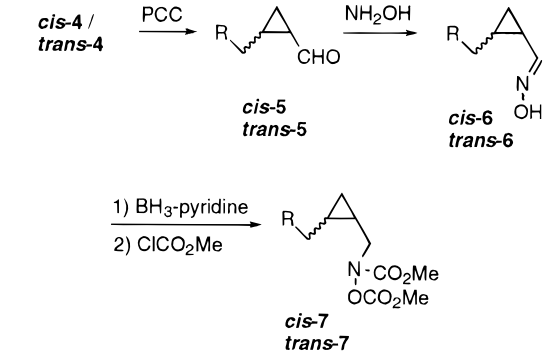


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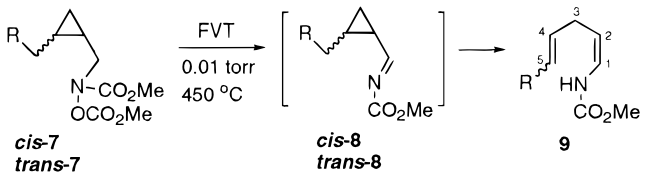


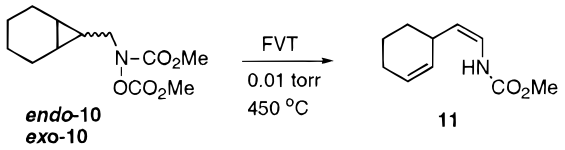

| | yield of **9** from *cis*-**7** | yield of **9** from *trans*-**7** |
|---|---|---|
| **a**: R = H | 60% | 15% |
| **b**: R = TMS | 66% | 28% |
| **c**: R = Ph | 53% | 9% |
| **d**: R = $OCH_3$ | 49% | 11% |
| **e**: R = CN | 68% | 9% |

the geometry required for the hydrogen abstraction. The low yields of the rearranged products in the *trans*-**7** series might be due to fragmentation and polymerization.

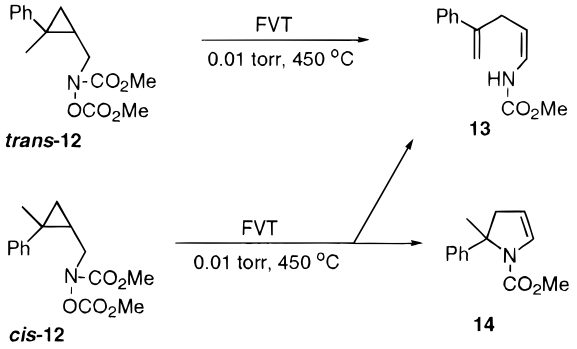
To examine the potential of this reaction in organic synthesis, we investigated the homodienyl [1,5]-hydrogen shift in a bicyclic ring system. The requisite diacylated hydroxylamines *endo*-**10** and *exo*-**10** were readily prepared from cyclohexene according to the procedure described above. Flash vacuum thermolysis of *endo*-**10** and *exo*-**10** provided the *cis*-enylcarbamate **11** in 75% and 29% yield, respectively (Scheme 5). Thus, incorporating the cyclopropyl imine into the more strained bicyclo[4.1.0]-heptane framework appeared to further accelerate the homodienyl [1,5]-hydrogen shift.

Finally, we explored the possibility of competition between the homodienyl [1,5]-hydrogen shift leading to

**Scheme 5**




**Scheme 6**




a dienylcarbamate versus ring expansion to a pyrroline. Accordingly, compounds *cis*-**12** and *trans*-**12** were prepared from α-methylstyrene. Thermolysis of *trans*-**12** (methyl *cis* to methylene) furnished a 61% yield of homodienyl [1,5]-hydrogen-rearranged product **13**, exclusively (Scheme 6). Interestingly, this is the same yield obtained on rearrangement of the compound *cis*-**7a**, lacking the phenyl group. On the other hand, evaporation of *cis*-**12** (methyl *trans* to methylene) *via* oven heating furnished 43% of hydrogen-rearranged product **13** and 7% of ring expanded pyrroline **14**. Here, we have been unable to obtain clear $^1$H and $^{13}$C NMR spectra for **14** due to the existence of rotamers that are afforded by the hindered rotation of amide group and the bulky phenyl group at C-5. The absence of an NH absorption in the IR spectrum and the molecular ion at *m*/*z* 217 in the GC−MS spectra can confirm the presence of **14**. Formation of **13** from *cis*-**12** can apparently account for the isomerization of *cis*-**12** to *trans*-**12** under FVT conditions.[10] The absence of **14** after reaction of *trans*-**12**, and any other pyrrolines from the other class described above reveals that the homodienyl [1,5]-hydrogen shift processes a markedly lower activation energy than that of the ring-expansion reaction.

This paper describes, to our knowledge, the first observation of the homodienyl [1,5]-hydrogen shift of *cis*- and *trans*-*N*-acylcyclopropylimines, which were generated by thermally eliminating diacylated hydroxylamines. The geometry required for 1,5-hydrogen shift produces the product's *cis* configuration in a 1,2-double bond. The symmetry-allowed homodienyl [1,5]-hydrogen shift appears to be preferred over ring expansion in the *N*-acyl-2-methyl-2-phenylcyclopropyl imine.

## Experimental Section

**General Methods.** Cyclopropanation of allyl bromide, allyltrimethylsilane, or allyl benzene with ethyl diazoacetate in the presence of catalytic rhodium(II) diacetate yielded *cis*- and *trans*-cyclopropyl esters **3a**,[6b] **3b**,[4a] and **3c**[6c] after chromatography over silica gel eluting with EtOAc/hexane (1:20). Functionality transformation from *cis*- or *trans*-**3a** to *cis*- or *trans*-**3d** and **3e** was achieved by reacting **3a** and sodium methoxide[11] followed

(10) (a) Schlag, E. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 5996. (b) Elliote, C. S.; Frey, H. M. *J. Chem. Soc.* **1964**, 900. (c) Willcott, M. R.; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723.

by acid workup and evaporation at 50 °C and the reaction between **3a** and potassium cyanide,[12] respectively. Reduction with lithium aluminum hydride[13] would produce *cis*- or *trans*-**4a**−**4d**; otherwise, reduction with lithium borohydride[8] would yield *cis*- or *trans*-**4e**. PCC oxidation produced aldehydes *cis*- or *trans*-**5a**−**5e**.[14] Then, oximes **6** were obtained by the reaction of aldehydes **5** and hydroxylamine.[15]

**General Procedure for Preparation of Diacylated Hydroxylamines**. A mixture of oxime **6** (5 mmol) and pyridine−borane (0.93 g, 10 mmol) in 8 mL of 95% ethanol was maintained at 0 °C. Then, 7.5 mL of 10% HCl solution was added over a 20 min period with vigorous mixing, and the mixture was stirred for 20 min at rt. Next, the solution was cooled to 0 °C, and NaOH pellets were carefully added until the pH ranged between 8−10. The mixture was extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to a volume of 50 mL. Triethylamine (1.01 g, 10 mmol) and then methyl chloroformate (0.95 g, 10 mmol) were added dropwise to the ether solution at 0 °C. After being stirred at rt for 2 h, the solution was acidified with 10% HCl solution. The ether layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The product was purified by column chromatography, eluting with EtOAc/hexane (1:8) to yield diacylated hydroxylamine *cis*- and *trans*-**7a**,**b**−**e** as a colorless liquid.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-methylcyclopropyl)methyl]hydroxylamine (*cis*-7a)**: yield 59%; IR (film) 1796, 1728 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ - 0.2−0.0 (m, 2H), 0.7−1.1 (m, 2H), 1.04 (d, 3H, $J$ = 5.8 Hz), 3.5−3.8 (m, 2H), 3.78 (s, 3H), 3.90 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.6, 10.6, 12.9, 13.1, 50.2, 53.5, 56.0, 154.9, 156.1; MS *m*/*z* (rel intensity) 217 (9, $M^+$), 69 (100), 59 (86). Anal. Calcd for $C_9H_{15}NO_5$: C, 49.79; H, 6.96; N, 6.45. Found: C, 49.95; H, 7.05; N, 6.53.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[(2-[(trimethylsilyl)-methyl]cyclopropyl]methyl]hydroxylamine (*cis*-7b)**: yield 75%; IR (film) 1796, 1727 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.02 (s, 9H), −0.2−0.2 (m 2H), 0.7−1.1 (m, 4H), 3.6−3.7 (m, 2H), 3.78 (s, 3H), 3.90 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ −1.7, 11.0, 11.1, 12.9, 15.0, 50.4, 53.4, 55.8, 154.8, 156.1; MS *m*/*z* (rel intensity) 289 (3, $M^+$), 73 (100), 59 (45). Anal. Calcd for $C_{12}H_{23}NO_5Si$: C, 49.85; H, 8.02; N, 4.84. Found: C, 49.79; H, 8.05; N, 4.82.

***trans*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[2-[(trimethylsilyl)-methyl]cyclopropyl]methyl]hydroxylamine (*trans*-7b)**: yield 62%; IR (film) 1797, 1728 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.01 (s, 9H), 0.2−0.8 (m, 6H), 3.4−3.6 (m, 2H), 3.78 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ −1.7, 12.1, 12.9, 17.4, 21.0, 53.4, 54.7, 55.8, 154.7, 156.0; MS *m*/*z* (rel intensity) 289 (4, $M^+$), 73 (100), 59 (49). Anal. Calcd for $C_{12}H_{23}NO_5Si$: C, 49.85; H, 8.02; N, 4.84. Found: C, 49.84; H, 8.02; N, 4.82.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-benzylcyclopropyl)methyl]hydroxylamine (*cis*-7c)**: yield 85%; IR (film) 1794, 1724 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.2−0.3 (m, 1H), 0.8−0.9 (m, 1H), 1.1−1.3 (m, 2H), 2.51 (dd, 1H, $J$ = 15.0, 8.0 Hz), 2.83 (dd, 1H, $J$ = 15.0, 5.0 Hz), 3.6−3.8 (m, 2H), 3.76 (s, 3H), 3.91 (s, 3H), 7.2−7.4 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 10.2, 13.4, 16.4, 50.6, 53.5, 56.0, 125.8, 128.0, 128.2, 141.5, 154.8, 156.1; MS *m*/*z* (rel intensity) 293 (1, $M^+$), 91 (100), 59 (23). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.46; H, 6.53; N, 4.78. Found: C, 61.34; H, 6.55; N, 4.75.

***trans*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-benzylcyclopropyl)methyl]hydroxylamine (*trans*-7c)**: yield 77%; IR (film) 1794, 1725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.4−0.5 (m, 2H), 0.9−1.1 (m, 2H), 2.47 (dd, 1H, $J$ = 14.6, 6.8 Hz), 2.70 (dd, 1H, $J$ = 14.6, 5.8 Hz), 3.5−3.6 (m, 2H), 3.75 (s, 3H), 3.91 (s, 3H), 7.2−7.4 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 10.3, 15.8, 18.3, 38.9, 53.5, 54.6, 56.0, 125.9, 128.2, 141.1, 154.8, 156.1; MS *m*/*z* (rel intensity) 293 (2, $M^+$), 91 (100), 59 (26). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.46; H, 6.53; N, 4.78. Found: C, 61.39; H, 6.62; N, 4.70.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[2-methoxymethyl)cyclopropyl]methyl]hydroxylamine (*cis*-7d)**: yield 73%; IR (film) 1795, 1729 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.2−0.3 (m, 1H), 0.7−0.9 (m, 1H), 1.1−1.3 (m, 2H), 3.1−4.0 (m, 4H), 3.33 (s, 3H), 3.77 (s, 3H), 3.89 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 8.5, 13.1, 15.0, 50.4, 53.6, 56.0, 58.3, 72.2, 154.9, 156.1; MS *m*/*z* (rel intensity) 247 (0.5, $M^+$), 67 (100), 59 (76). Anal. Calcd for $C_{10}H_{17}NO_6$: C, 48.61; H, 6.93; N, 5.67. Found: C, 48.41; H, 7.02; N, 5.63.

***trans*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[2-(methoxymethyl)cyclopropyl]methyl]hydroxylamine (*trans*-7d)**: yield 73%; IR (film) 1797, 1728 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.4−0.6, 0.9−1.1 (m, 4H), 3.1−3.3 (m, 2H), 3.32 (s, 3H), 3.5−3.6 (m, 2H), 3.78 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 8.5, 14.2, 16.8, 53.5, 54.1, 56.0, 58.1, 75.4, 154.7, 156.1; MS *m*/*z* (rel intensity) 247 (1, $M^+$), 67 (100), 59 (72); HRMS calcd for $C_{10}H_{17}NO_6$ [$M^+$] 247.1056, found 247.1055.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[2-(cyanomethyl)cyclopropyl]methyl]hydroxylamine (*cis*-7e)**: yield 40%; IR (film) 2250, 1792, 1730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.2−0.3 (m, 1H), 0.9−1.0 (m, 1H), 1.2−1.4 (m, 2H), 2.31 (dd, 1H, $J$ = 17.5, 7.6 Hz), 2.58 (dd, 1H, $J$ = 17.5, 6.2 Hz), 3.57 (dd, 1H, $J$ = 15.3, 8.0 Hz), 3.80 (dd, 1H, $J$ = 15.3, 6.0 Hz), 3.78 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 9.9, 11.9, 13.6, 17.0, 49.8, 53.8, 56.3, 119.0, 154.7, 156.0; MS *m*/*z* (rel intensity) 242 (0.1, $M^+$), 67 (86), 59 (100). Anal. Calcd for $C_{10}H_{14}N_2O_5$: C, 49.61; H, 5.83; N, 12.57. Found: C, 49.96; H, 6.06; N, 12.21.

***trans*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[[2-cyanomethyl)cyclopropyl]methyl]hydroxylamine (*trans*-7e)**: yield 49%; IR (film) 2249, 1793, 1726 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.6−0.7 (m, 2H), 1.0−1.2 (m, 2H), 2.34 (dd, 1H, $J$ = 17.3, 6.2 Hz), 2.48 (dd, 1H, $J$ = 17.3, 5.8 Hz), 3.46 (dd, 1H, $J$ = 15.1, 7.1 Hz), 3.64 (dd, 1H, $J$ = 15.1, 6.3 Hz), 3.78 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 10.0, 12.8, 16.0, 20.7, 53.7, 53.8, 56.2, 118.0, 154.8, 156.0; MS *m*/*z* (rel intensity) 242 (2, $M^+$), 67 (100), 59 (90); HRMS calcd for $C_{10}H_{14}N_2O_5$ [$M^+$] 242.0903, found 242.0904.

**General Method for FVT**.[5] Diacylated hydroxylamines **7** (10−300 mg) were first frozen in a liquid nitrogen bath, and then a vacuum was applied. Once the vacuum (0.01 Torr) had been established, the heater was turned on. The temperature of the hot tube was regulated by a temperature controller. When the set temperature reached to 450 °C, the receiver was placed in a liquid nitrogen bath, the reactant was heated until it thawed, and the reactant evaporated through the hot tube. The product was condensed and collected in the receiver at liquid nitrogen temperature and washed out with diethyl ether. The crude product was purified by column chromatography over silica gel using EtOAc/$C_6H_{14}$ as eluent to afford dienylcarbamates **9**. Scheme 4 provided the yields.

**Methyl *cis*-1,4-pentadienylcarbamate (9a)**: IR (film) 3322, 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.72 (br dd, 2H, $J$ = 7.6, 6.0 Hz), 3.72 (br s, 3H), 4.68 (br q, 1H, $J$ = 7.6 Hz), 5.0−5.2 (m, 2H), 5.80 (ddt, 1H, $J$ = 17.1, 10.0, 6.0 Hz), 6.3−6.7 (br m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 29.5, 52.4, 105.4, 115.2, 123.5, 135.6, 154.2; MS *m*/*z* (rel intensity) 141 (47, $M^+$), 82 (100), 59 (60); HRMS calcd for $C_7H_{11}NO_2$ [$M^+$] 141.0790, found 141.0791.

**Methyl 5-(trimethylsilyl)-*cis*,*trans*-1,4-pentadienylcarbamate** and **methyl 5-(trimethylsilyl)-*cis*,*cis*-1,4-pentadienylcarbamate mixture (9b)**: IR (film) 3324, 1717 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) for the major *cis*,*trans* isomer: $\delta$ 0.03 (s, 9H), 2.78 (br t, 2H, $J$ = 6.2 Hz), 3.70 (br s, 3H), 4.67 (br q, 1H, $J$ = 7.4 Hz), 5.72 (dt, 1H, $J$ = 18.5, 1.4 Hz), 5.89 (dt, 1H, $J$ = 18.5, 5.5 Hz), 6.3−6.8 (br s, 2H); $^{13}C$ NMR ($CDCl_3$) for the major *cis*,*trans* isomer $\delta$ −1.4, 32.5, 52.4, 105.2, 123.3, 131.1, 143.2, 154.1; MS *m*/*z* (rel intensity) 213 (21, $M^+$), 73 (100), 59 (15); HRMS calcd for $C_{10}H_{19}NO_2Si$ [$M^+$] 213.1185, found 213.1184.

**Methyl 5-phenyl-*cis*,*trans*-1,4-pentadienylcarbamate (9c)**: White solid; mp 72−74 °C (hexane); IR (film) 3335, 1699 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.89 (tt, 2H, $J$ = 7.0, 1.3 Hz), 3.73 (br s, 3H), 4.77 (br q, 1H, $J$ = 7.9 Hz), 6.17 (dt, 1H, $J$ = 15.9, 6.1 Hz), 6.45 (dt, 1H, $J$ = 15.9, 1.5 Hz), 6.2−6.7 (br m, 2H), 7.2−7.4 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 28.7, 52.5, 105.6, 123.7, 126.1, 127.2, 128.5, 128.6, 130.6, 137.2, 154.2; MS *m*/*z* (rel intensity) 217 (5, $M^+$), 142 (100), 59 (9). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.78; H, 7.17; N, 6.16.

**Methyl 5-methoxy-*cis*,*trans*-1,4-pentadienylcarbamate (9d)**: IR (film) 3323, 1714 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.60 (t, 2H, $J$ = 6.7 Hz), 3.50 (s, 3H), 3.72 (br s, 3H), 4.5−4.7 (br m, 1H), 4.69 (dt, 1H, $J$ = 12.7, 6.7 Hz), 6.34 (dt, 1H, $J$ = 12.7, 1.3 Hz), 6.3−6.6 (br s, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 23.8, 52.4, 55.9, 100.2,

(11) Baldwin, J. E.; Chang, G. E. C. *Tetrahedron* **1982**, *38*, 825.
(12) Kennewell, P. D.; Matharu, S. S.; Taylor, J. B.; Westwood, R.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2553.
(13) Baldwin, J. E.; Patapoff, T. W.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1421.
(14) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
(15) Bousquet, E. W. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. II, p 313.

107.3, 122.8, 147.9, 154.1; MS *m*/*z* (rel intensity) 171 (12, $M^+$), 80 (100), 59 (47); HRMS calcd for $C_8H_{13}NO_3$ [$M^+$] 171.0895, found 171.0894.

**Methyl 5-cyano-*cis*,*trans*-1,4-pentadienylcarbamate** and **methyl 5-cyano-*cis*,*cis*-1,4-pentadienylcarbamate mixture (9e):** IR (film) 3323, 2225, 1715 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) for the major *cis*,*trans* isomer $\delta$ 2.91 (br t, 2H, $J$ = 6.5 Hz), 3.74 (br s, 3H), 4.58 (br q, 1H, $J$ = 7.6 Hz), 5.41 (dt, 1H, $J$ = 16.3, 2.0 Hz), 6.72 (dt, 1H, $J$ = 16.3, 5.8 Hz), 6.3−6.8 (br s, 2H); $^{13}C$ NMR ($CDCl_3$) for the major *cis*,*trans* isomer $\delta$ 28.8, 52.7, 100.5, 101.1, 117.2, 125.7, 151.7, 154.1; MS *m*/*z* (rel intensity) 166 (15, $M^+$), 59 (100); HRMS calcd for $C_8H_{10}N_2O_2$ [$M^+$] 166.0742, found 166.0745.

***endo*-*N*,*O*-Bis(methoxycarbonyl)-*N*-(bicyclo[4.1.0]heptyl-7-methyl]hydroxylamine (*endo*-10)**. The analogous procedure for preparating diacylated hydroxylamines was followed, and *endo*-**10** was obtained in 80% yield: IR (film) 1795, 1725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.9−2.0 (m, 11H), 3.7−3.9 (br m, 2H), 3.80 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 10.5, 15.9, 18.5, 22.1, 47.6, 53.4, 55.9, 154.8, 156.2; MS *m*/*z* (rel intensity) 257 (33, $M^+$), 108 (100), 59 (55). Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.06; H, 7.45; N, 5.45. Found: C, 56.31; H, 7.58; N, 5.44.

***exo*-*N*,*O*-Bis(methoxycarbonyl)-*N*-(bicyclo[4.1.0]heptyl-7-methyl)hydroxylamine (*exo*-10)**. The analogous procedure for preparating diacylated hydroxylamines was followed, and *exo*-**10** was obtained in 70% yield: IR (film) 1795, 1725 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.7−1.9 (m, 11H), 3.49 (d, 2H, $J$ = 5.6 Hz), 3.78 (s, 3H), 3.91 (s, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 15.5, 20.6, 21.1, 22.8, 53.4, 54.9, 55.9, 154.8, 156.1; MS *m*/*z* (rel intensity) 257 (2, $M^+$), 108 (31), 67 (100), 59 (41). Anal. Calcd for $C_{12}H_{19}NO_5$: C, 56.06; H, 7.45; N, 5.45. Found: C, 56.29; H, 7.51; N, 5.39.

***cis*-3-[2-[(Methoxycarbonyl)amino]ethenyl]cyclohexene (11)**. By the general method for FVT, *endo*-**10** (257 mg, 1 mmol) gave **11** in 75% yield (136 mg) as a colorless liquid, whereas *exo*-**10** (257 mg, 1 mmol) gave **11** in 29% yield (52 mg): IR (film) 3321, 1701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.3−2.1 (m, 6H), 2.7−3.0 (br s, 1H), 3.71 (br s, 3H), 4.57 (br t, 1H, $J$ = 9.0 Hz), 5.4−5.9 (br m), 6.41 (br t, 1H, $J$ = 9.0 Hz), 6.3−6.8 (br s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.9, 24.7, 29.2, 32.9, 52.4, 112.9, 121.7, 128.3, 129.6, 154.1; MS *m*/*z* (rel intensity) 181 (29, $M^+$), 78 (100), 59 (39). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.30; H, 8.41; N, 7.68.

***cis*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-methyl-2-phenylcyclopropyl)methyl]hydroxylamine (*cis*-12)**. The analogous procedure for preparating diacylated hydroxylamines was followed, and *cis*-**12** was obtained in 71% yield: IR (film) 1795, 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.85 and 0.98 (dd, each 1H, $J$ = 8.3, 5.0, and 5.2, 5.0 Hz), 1.2−1.3 (m, 1H), 1.38 (s, 3H), 2.86 (dd, 1H, $J$ = 15.0, 8.6 Hz), 3.62 (dd, 1H, $J$ = 15.0, 5.5 Hz), 3.71 (s, 3H), 3.90 (s, 3H), 7.2−7.4 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.8, 22.3, 25.6, 27.7, 52.0, 53.2, 55.8, 126.1, 128.1, 128.8, 141.9, 154.6, 155.8; MS *m*/*z* (rel intensity) 293 (8, $M^+$), 144 (100), 59 (32). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.46; H, 6.53; N, 4.78. Found: C, 61.21; H, 6.59; N, 4.75.

***trans*-*N*,*O*-Bis(methoxycarbonyl)-*N*-[(2-methyl-2-phenylcyclopropyl)methyl]hydroxylamine (*trans*-12)**. The analogous procedure for preparating diacylated hydroxylamines was followed, and *trans*-**12** was obtained in 73% yield: IR (film) 1795, 1731 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.57 (dd, 1H, $J$ = 5.4, 5.0 Hz), 1.16 (dd, 1H, $J$ = 9.1, 5.0 Hz), 1.3−1.5 (m, 1H), 1.41 (s, 3H), 3.71 (dd, 1H, $J$ = 15.1, 8.1 Hz), 4.01 (dd, 1H, $J$ = 15.1, 6.1 Hz), 3.82 (s, 3H), 3.86 (s, 3H), 7.1−7.3 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 18.3, 20.6, 22.6, 24.7, 50.7, 53.6, 56.0, 125.8, 127.1, 128.2, 147.0, 154.8, 156.2; MS *m*/*z* (rel intensity) 293 (15, $M^+$), 144 (100), 59 (43). Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.46; H, 6.53; N, 4.78. Found: C, 61.35; H, 6.64; N, 4.70.

By the general method for FVT, *trans*-**12** (293 mg, 1 mmol) gave **13** in 61% yield (132 mg) as white solid, whereas *cis*-**12** (293 mg, 1 mmol) gave **13** in 43% yield (93 mg) and **14** in 7% yield (15 mg).

**Methyl 4-phenyl-*cis*-1,4-pentadienylcarbamate (13)**: white solid; mp 55−56 °C (hexane); IR (film) 3318, 1712 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.16 (br d, 2H, $J$ = 7.3 Hz), 3.73 (br s, 3H), 4.77 (br q, 1H, $J$ = 7.3 Hz), 5.16 (m, 1H), 5.40 (m, 1H), 6.3−6.8 (br m, 2H), 7.3−7.5 (m, 5H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 31.4, 52.5, 105.7, 112.8, 123.9, 125.9, 127.7, 128.3, 140.5, 145.5, 154.2; MS *m*/*z* (rel intensity) 217 (31, $M^+$), 142 (100), 59 (42). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.68; H, 6.98; N, 6.48.

***N*-(Methoxycarbonyl)-5-methyl-5-phenyl-2-pyrroline (14)**: IR (film) 1708 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) for major rotamer $\delta$ 1.91 (s, 3H, $CH_3$), 2.8−2.9 (br m, 2H), 3.65 (br s, 3H), 4.9−5.0 (br m, 1H), 6.6−6.7 (br m, 1H), 7.2−7.5 (m, 5H); MS *m*/*z* (rel intensity) 217 (25, $M^+$), 77 (23), 59 (100); HRMS calcd for $C_{13}H_{15}NO_2$ [$M^+$] 217.1103, found 217.1104.

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**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra of compounds **7** and **9**−**13** (40 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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