3-[(*E*)-1-Hexenyl]cyclohexanone (36) by Hydrozirconation/Transmetalation/Conjugate Addition. A suspension of Cp_2ZrHCl (390 mg, 1.51 mmol) in THF (8 mL) was treated with 1-hexyne (7, 123 mg, 1.50 mmol). The reaction mixture was stirred at 22 °C for 30 min and added at −23 °C to a mixture of flame-dried CuCN (134 mg, 1.50 mmol) and a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (6 mL, 3.0 mmol). This mixture was stirred for 5 min at −23 °C, and a solution of 2-cyclohexenone (4, 96 mg, 1.00 mmol) in THF (2 mL) was added dropwise. Stirring at −23 °C was continued for another 30 min. The mixture was quenched into a solution of saturated ammonium chloride/ammonium hydroxide (9:1) and extracted three times with Et_2O. The combined organic layers were dried ($MgSO_4$), filtered through silica gel, and chromatographed (EtOAc/hexane (1:9)) to yield 110 mg (61%) of **36**.

3-[(*E*)-5-[(*tert*-Butyldiphenylsilyl)oxy]-2-methyl-1-hexenyl]cyclohexanone (18) by Inverse Addition (IA) Protocol with 10 mol % CuCN. A suspension of CuCN (8.9 mg, 0.10 mmol) in THF (6 mL) was treated at −45 °C dropwise with a 0.5 M solution of 1-hexynyllithium in THF/hexane (5:1) (0.40 mL, 0.20 mmol). The reaction mixture was warmed to −23 °C, and a solution of 2-cyclohexenone (4, 96 mg, 1.0 mmol) in THF (1 mL) was added. After dropwise addition of a solution of alane **44** (approximately 1.5 mmol) in Et_2O (3 mL), stirring was continued for 30 min at −23 °C and for 30 min at 0 °C. Standard workup led to the isolation of 227 mg (52%) of **18**.

Acknowledgment. We thank Professor Robert E. Ireland for stimulating discussions.

Supplementary Material Available: ^{13}C NMR spectra for compounds **6**, **10**, **12a**, **14**, **16**, **18**, **24**, **26**, **28**, **30**, **31**, **35**, and **38** (14 pages). Ordering information is given on any current masthead page.

Highly Stereoselective 3 + 2 Annulations by Cyclopropanation of Vinyl Ethers with Rhodium(II)-Stabilized Vinylcarbenoids Followed by a Formally Forbidden 1,3-Sigmatropic Rearrangement

Huw M. L. Davies* and Baihua Hu

Department of Chemistry, Wake Forest University, Box 7486, Winston-Salem, North Carolina 27109

Received March 3, 1992

A highly stereoselective 3 + 2 annulation has been developed by cyclopropanation of vinyl ethers with rhodium(II)-stabilized vinylcarbenoids to generate vinylcyclopropanes followed by a Et_2AlCl-catalyzed 1,3-sigmatropic rearrangement. The success of this methodology rests on the remarkably stereoselectivity that is exhibited in both the cyclopropanation step and also the Et_2AlCl-catalyzed vinylcyclopropane rearrangement.

The development of general synthetic strategies for the construction of five-membered rings has been a very active area of research in recent years.[1] Particularly impressive are a number of approaches which proceed by means of carbenoid intermediates. A major contribution to this area has been Hudlicky's 4 + 1 annulation approach[2] based on intramolecular cyclopropanation of dienes followed by a 1,3-sigmatropic rearrangement of the resulting vinylcyclopropanes. A complimentary 3 + 2 annulation strategy by reaction of 4-bromocrotonates with α,β-unsaturated ketones in the presence of base has also been developed.[3] Harsh thermal conditions were originally required for ring expansion of the vinylcyclopropanes to the cyclopentenes, but since then, a number of milder procedures[2-7] using catalysts such as $(C_2H_4)_2Rh(acac)$[2a] or Et_2AlCl[7] have been reported. In the thermal reaction, the level of stereocontrol is substrate dependent.[2,3] However, improved stereoselectivity is possible with $(C_2H_4)_2Rh(acac)$,[2a] while the two examples of Et_2AlCl-induced rearrangement involving stereocontrol were highly stereoselective.[7a,b] An alternative and highly stereoselective 4 + 1 annulation was reported by Danheiser[8] using an anion-accelerated vinylcyclopropane rearrangement. 3 + 2 annulations have also been achieved through reaction of a nucleophilic vinylcarbene with electron-deficient alkenes[9] and by means of Fisher carbenes.[7c,10] Another carbenoid approach to cyclopentanes has been the intramolecular C–H insertion reaction reported by Taber.[11]

For some time we have been engaged in developing general synthetic procedures based on rhodium(II)-stabilized vinylcarbenoid intermediates.[12] From our results on the tandem cyclopropanation/Cope rearrangement sequence that we have employed for the stereoselective construction of seven-membered rings, it was evident that cyclopropanation with vinylcarbenoids can be remarkably stereoselective.[12] Extending the chemistry of vinylcarbenoids to their reaction with vinyl ethers was expected to produce donor–acceptor-substituted vinylcyclopropanes[13] that would readily rearrange to highly functionalized cyclopentenes (eq 1). In this paper we will

(1) (a) Ramaiah, M. *Synthesis* **1984**, 529. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React. (N.Y.)* **1985**, 33, 247. (c) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (d) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691.

(2) (a) Hudlicky, T.; Koszyk, F. J.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020. (b) Hudlicky, T.; Koszyk, F. J.; Dochwat, D. M.; Cantrell, G. L. *J. Org. Chem.* **1981**, *46*, 2911.

(3) (a) Hudlicky, T.; Heard, N. E.; Fleming, A. *J. Org. Chem.* **1990**, *55*, 2570. (b) Hudlicky, T.; Radesca-Kwart, L.; Li, L.; Bryant, T. *Tetrahedron Lett.* **1988**, *29*, 3283. (c) Hudlicky, T.; Sinai-Zingde, G.; Natchus, M. G.; Ranu, B. C.; Papadololous, P. *Tetrahedron* **1987**, *43*, 5685.

(4) Hashimoto, S.; Shinoda, T.; Ikegami, S. *Tetrahedron Lett.* **1986**, *27*, 2885.

(5) Sakito, Y.; Suzukamo, G. *Chem. Lett.* **1986**, 621.

(6) Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 2871.

(7) (a) Corey, E. J.; Myers, A. G. *J. Am. Chem. Soc.* **1985**, *107*, 5574. (b) Corey, E. J.; Kigoshi, H. *Tetrahedron Lett.* **1991**, *32*, 5025. (c) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1991**, *32*, 2871.

(8) (a) Danheiser, R. L.; Bronson, J. J.; Okano, K. *J. Am. Chem. Soc.* **1985**, *107*, 4579. (b) Danheiser, R. L.; Martinez-Davilla, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443.

(9) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695.

(10) (a) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660. (b) Wienand, A.; Reissig, H.-U. *Chem. Ber.* **1991**, *124*, 957.

(11) Taber, D. F.; Ruckle, R. E., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7686.

(12) (a) Davies, H. M. L.; Clark, D. M.; Smith, T. K. *Tetrahedron Lett.* **1985**, *26*, 5659. (b) Davies, H. M. L.; Clark, T. J.; Church, L. A. *Tetrahedron Lett.* **1989**, *30*, 5057. (c) Cantrell, W. R., Jr.; Davies, H. M. L. *J. Org. Chem.* **1991**, *56*, 723. (d) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817. (e) Davies, H. M. L.; Saikali, E.; Young, W. B. *J. Org. Chem.* **1991**, *56*, 5696. (f) Davies, H. M. L.; Clark, T. J.; Kimmer, G. F. *J. Org. Chem.* **1991**, *56*, 6440.

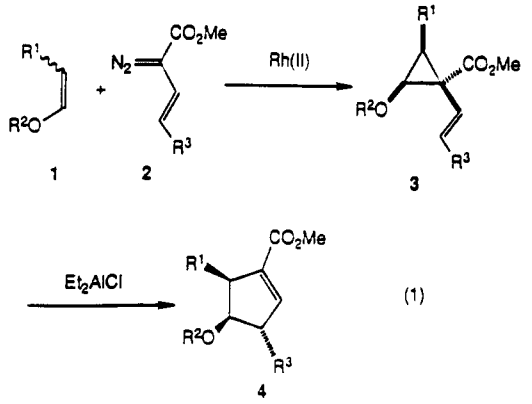
(13) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73.

0022-3263/92/1957-3186$03.00/0

Table I. Synthesis of Vinylcyclopropanes 3 and Cyclopentenes 4 According to Eq 1

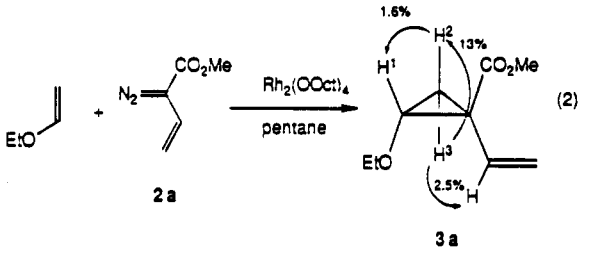
R_1	R_2	R_3	3 (yield, %)	4 (yield, %)
H	Et	H	**3a** (87)	**4a** (88)
	$-CH_2CH_2CH_2-$	H	**3b** (56)	**4b** (96)
Me	Et	H	**3c** (76)	**4c** (93)
H	Et	Me	**3d** (68)	**4d** (86)
	$-CH_2CH_2CH_2-$	Me	**3e** (73)	**4e** (89)
Me	Et	Me	**3f** (83)	**4f** (81)
H	Et	Ph	**3g** (75)	**4g** (68)
	$-CH_2CH_2CH_2-$	Ph	**3h** (66)	**4h** (67)
Me	Et	Ph	**3i** (80)	**4i** (77)
4-$MeOC_6H_4$	Me	Ph	**3j** (39)	**4j** (61)

describe the scope of such a 3 + 2 annulation protocol with emphasis on the remarkable stereocontrol that is possible.[14]

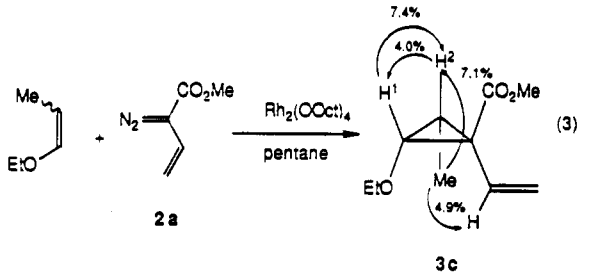


Results

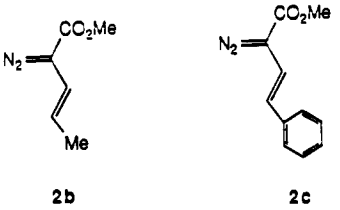
Rhodium(II) octanoate catalyzed decomposition of the vinyldiazomethane **2a** in the presence of ethyl vinyl ether using pentane as solvent resulted in the formation of the vinylcyclopropane **3a** in 87% yield (eq 2). Proton NMR analysis of the crude reaction mixture indicated that the stereoselectivity was 8:1. The stereochemical assignment for **3a** was based on distinctive coupling constants[15] ($J_{H^1H^2}$ = 6.1 Hz, $J_{H^1H^3}$ = 4.1 Hz) and NOE enhancement studies,[12b] the results of which are summarized in structure **3a**.



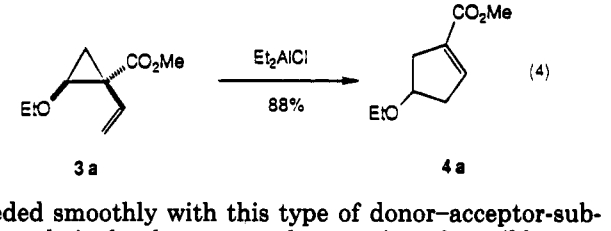
A highly stereoselective cyclopropanation (>20:1) was observed in the reaction of **2a** with 3,4-dihydro-2*H*-pyran, producing **3b** in 56% yield (Table I). The selectivity of vinylcarbenoid cyclopropanations was further demonstrated on decomposition of **2a** in the presence of an *E*/*Z* mixture (*E*/*Z* = 1:2.4) of ethyl propenyl ether (eq 3).[16] The cyclopropane **3c** was cleanly formed (76% yield, >20:1 isomeric purity), indicating that preferential reaction had occurred between the vinylcarbenoid and (*Z*)-ethyl propenyl ether. The stereochemical assignment of **3c** was

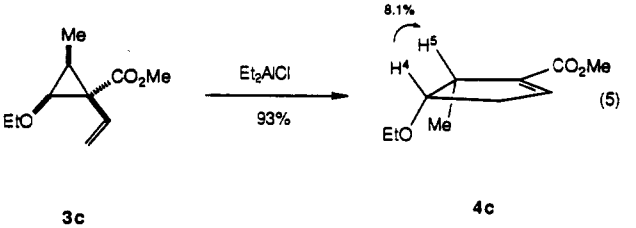


based on distinctive proton NMR coupling constant between H^1 and H^2 (J = 7.2 Hz)[15] and NOE difference experiments,[12b] as summarized in structure **3c**. The vinyldiazomethanes **2b** and **2c** were similarly decomposed in the presence of the vinyl ethers (Table I), and in all instances no evidence for isomeric mixtures of vinylcyclopropanes was observed in the proton NMR spectra of the crude reaction mixtures. The stereochemical assignments for **3d–j** were based on a combination of chemical shifts and coupling constants for the cyclopropane products and NOE enhancement studies. The reaction of **2c** with 1-(4-methoxyphenyl)-2-methoxyethylene mixture (*E*/*Z* = 1:1.1) to generate **3j** is noteworthy, because through this reaction it was possible to confirm that the vinylcarbenoid preferentially reacts with the (*Z*)-vinyl ether. Due to its lack of volatility, the residual vinyl ether was readily shown to be enriched in the *E* isomer (*E*/*Z* = 1:0.9) by NMR analysis of the concentrated crude reaction mixtures.



Having prepared a series of vinylcyclopropanes, their rearrangement to cyclopentenes was then examined. As mild reaction conditions were sought, the Et_2AlCl-catalyzed process reported by Corey[7a,b] appeared to be very attractive. Rearrangement of **3a** with Et_2AlCl at −78 °C to rt proceeded very cleanly to generate **4a** in 88% yield (eq 4). Having determined that the rearrangement proceeded smoothly with this type of donor–acceptor-substituted vinylcyclopropane, the question of possible stereocontrol in the more elaborate systems was then addressed. Et_2AlCl-catalyzed decomposition of **3c** proceeded cleanly to generate a single cyclopentene **4c** in 93% yield (eq 5). The stereochemistry of **4c**, which would require





that the 1,3-shift had occurred with retention of configuration at the migrating carbon, was based on a large NOE

(14) For a preliminary account of a portion of this work, see: Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 453.

(15) Generally, in cyclopropyl systems, J_{HHcis} = 6–10 Hz, $J_{HHtrans}$ = 3–5 Hz. See: Morris, D. G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, p 101.

(16) Normally, rhodium(II)-catalyzed cyclopropanations proceed with retention of alkene configuration. See: Maas, G. *Top. Curr. Chem.* **1988**, *137*, 75 and references cited therein.

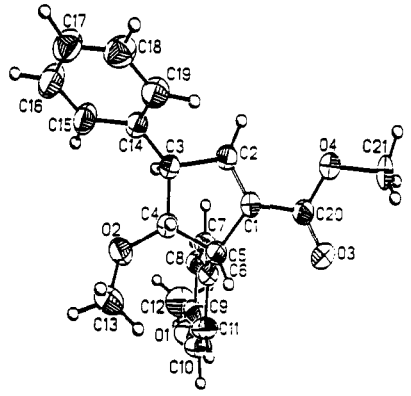
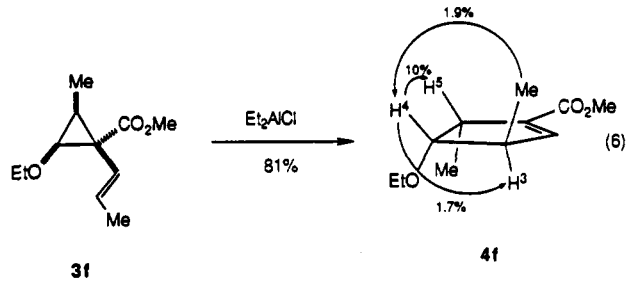


Figure 1. ORTEP drawing of **4j**.

enhancement between the cis protons H^4 and H^5 and the absence of an enhancement between the methyl group and H^4. The rearrangement of **3b** also proceeded in a stereodefined manner to give **4b**, without any evidence for the formation of isomeric cyclopentenes.

In the case of the vinylcyclopropanes derived from the vinyldiazomethanes **2b** and **2c**, an additional stereogenic center would be generated in the 1,3-sigmatropic rearrangement, but in all the cases studied the cyclopentene was formed in a stereodefined manner (Table I). For example, rearrangement of **3f** proceeded smoothly to generate **4f** in 81% yield (eq 6). The stereochemical



3f **4f**

assignment was once again based on distinctive NOE enhancements. A large enhancement (10%) was observed between the cis protons H^4 and H^5 while a much smaller enhancement (1.7%) was observed between the trans protons H^4 and H^3. Additionally, enhancement of H^4 occurred on irradiation of C^3-Me, but no enhancement of H^4 was observed on irradiation of C^5-Me. The stereochemistry of **4g–j** could be assigned in a similar manner. Further confirmation of these structural assignments was obtained by X-ray crystallographic analysis of the crystalline cyclopentene **4j**, the ORTEP drawing of which is presented in Figure 1.

Discussion

The spectacular levels of stereoselectivity are a distinctive feature of cyclopropanation reactions with ester-substituted vinylcarbenoids. From previous studies, we have found that vinyl ethers[12b] and alkoxy dienes[12c,f] result in excellent stereoselectivity, and in the cyclopropanations reported in this paper, except for the preparation of **3a**, no evidence for isomeric cyclopropanes was observed in the NMR of the crude reaction mixtures. These results contrast sharply with cyclopropanations of alkyl diazoacetates[17] where reasonable levels of stereoselectivity in cyclopropanation reactions occur only when extremely bulky alkyl groups are used.[18] Furthermore, a recent study

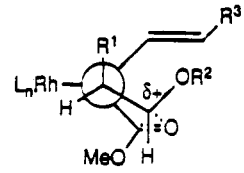


Figure 2.

of cyclopropanation of vinyl ethers with the parent vinyldiazomethane and chloro-substituted vinyldiazomethanes resulted in only moderate levels of stereoselectivity (1.1 to 6.1:1)[19] which would suggest that the presence of the ester functionality is a critical element for stereocontrol in vinylcarbenoid reactions.

A second intriguing feature of vinylcarbenoid cyclopropanations is the preferential reaction that occurs with (*Z*)-vinyl ethers when isomeric mixtures were used as substrates. Similar selectivity has been observed by us in tandem cyclopropanation/Cope rearrangements. For example,[12d] reaction of a vinylcarbenoid with (*E,Z*)-2,4-hexadiene produced a cycloheptadiene whose stereochemistry would have required initial cyclopropanation of the *Z* double bond, while (*E,E*)-2,4-hexadiene failed to react with the vinylcarbenoid.

These results are consistent with the mechanistic model that Doyle has proposed for cyclopropanations with alkyl diazoacetates.[17,20] In this model cyclopropanation is considered to occur in a nonsynchronous manner, and interaction between the ester carbonyl and the devloping positive charge is a crucial feature which sets up the moderate stereoselectivity that is observed with alkyl diazoacetates. Extending this model to the vinylcarbenoid system would lead to a proposed transition state as illustrated in Figure 2. Presumably, the steric requirements are much more exacting in the vinylcarbenoid system which leads to greater stereoselectivity. In the case of a trans vinyl ether, an unfavorable steric interaction would exist between the alkyl group and the nearby metal.

The thermal rearrangement of vinylcyclopropanes has been of great interest not only because of its synthetic potential but also because it has been a classic test for the Woodward Hoffman rules.[21] Several stereochemical studies have shown that formally forbidden pathways (suprafacial retention or antarafacial inversion) can be competitive with the allowed pathways (suprafacial inversion or antarafacial retention).[22,23] Due to the existence of several reaction pathways, rearrangement of simple vinylcyclopropanes tends to lead to mixtures of products, but good stereocontrol is possible in certain polycyclic systems. The examples by Corey[7a,b] of a highly stereoselective Et_2AlCl-catalyzed vinylcyclopropane rearrangement were in a highly substituted system en route to a total synthesis of tetracyclic lactones. Conceivably, the stereoselectivity may have been due to an inherent steric bias in the polycyclic system, and no explanation was given for the observed stereocontrol. In the systems described

(17) (a) Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H.; Buhro, W. E. *Tetrahedron Lett.* **1982**, *23*, 2261. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(18) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. L. *J. Am. Chem. Soc.* **1990**, *112*, 1906.

(19) de Meijere, A.; Schulz, T.-J.; Kostikov, R. R.; Graupner, F.; Murr, T.; Biefeldt, T. *Synthesis* **1991**, 547.

(20) For other discussions on the Doyle model, see: (a) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1989**, *54*, 3096. (b) Reference 12d.

(21) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(22) (a) Gajewski, J. J.; Squicciarni, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717. (b) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991**, *113*, 7432. (c) Mazzocchi, P. H.; Tamburin, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 7220.

(23) (a) Baldwin, J. E.; Ghatlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273. (b) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705.

herein, excellent stereocontrol was observed, which in all cases was consistent with a formal 1,3-sigmatropic rearrangement proceeding suprafacially with retention of configuration.

The vinylcyclopropanes prepared in this study are unusual in that they contain both electron-donor and -acceptor substituents bonded directly to the cyclopropane ring. A characteristic feature of donor–acceptor-substituted cyclopropanes is their facility for undergoing ring-opening reactions by means of stabilized dipolar intermediates.[13] Consequently, it would be reasonable to assume that the vinylcyclopropane rearrangements are proceeding through dipolar intermediates, but the stereochemical results clearly show that ring closure to the cyclopentene must be very rapid and is achieved before any bond rotation can occur.[5,8,24]

In summary, a highly stereoselective 3 + 2 annulation has been developed by reaction of vinylcarbenoids with vinyl ethers. The success of this methodology rests on the excellent stereoselectivity that is exhibited in both the cyclopropanation step and also the Et_2AlCl-catalyzed vinylcyclopropane rearrangement.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Column chromatography was carried out on silica gel 60 (230–400 mesh). The vinyldiazomethanes were prepared by methods that have been previously reported.[25]

Rhodium(II) Carboxylate Catalyzed Decomposition of Vinyldiazomethanes in the Presence of Vinyl Ethers. General Procedures. A solution of the vinyldiazomethane (1 equiv) in pentane (0.1–0.5 M) was added dropwise to a stirred mixture of rhodium(II) carboxylate (0.01 equiv) and the vinyl ether (5 equiv, 0.1–0.5 M) in pentane, heated under reflux in an argon atmosphere. After heating for a further 10–60 min, the solvent was evaporated under reduced pressure. The amounts of vinyldiazomethane, vinyl ether, and rhodium(II) catalyst used are presented in that order in abbreviated format. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parentheses.

Methyl (*E*)-1-Ethenyl-2-ethoxycyclopropane-1-carboxylate (3a). 2a (0.63 g, 5.0 mmol), ethyl vinyl ether (1.80 g, 25 mmol), octanoate (0.037 g, 0.05 mmol), (1:9), colorless oil, yield 0.74 g, 87%: ^1H NMR ($CDCl_3$) δ 6.29 (dd, J = 17.4, 11.0 Hz, 1 H), 5.13 (d, J = 11.0 Hz, 1 H), 5.07 (d, J = 17.4 Hz, 1 H), 3.67 (s, 3 H), 3.67 (dd, J = 6.1, 4.1 Hz, 1 H), 3.53–3.31 (m, 2 H), 1.69 (dd, J = 6.2, 6.1 Hz, 1 H), 1.45 (dd, J = 6.2, 4.1 Hz, 1 H), 1.12 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.7, 129.3, 115.1, 67.1, 66.9, 52.0, 31.9, 20.4, 14.8; IR (neat) 1725, 1640 cm^{-1}. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.31; H, 8.31.

Methyl *endo*-7-Ethenylbicyclo[4.1.0]heptane-7-carboxylate (3b). 2a (0.25 g, 2.0 mmol), 3,4-dihydro-2*H*-pyran (0.84 g, 10 mmol), octanoate (0.016 g, 0.02 mmol), (1:9), colorless oil, yield 0.20 g, 56%: ^1H NMR ($CDCl_3$) δ 5.89 (dd, J = 17.4, 10.6 Hz, 1 H), 5.56 (dd, J = 10.6, 2.4 Hz, 1 H), 5.50 (dd, J = 17.4, 2.4 Hz, 1 H), 4.02 (d, J = 6.9 Hz, 1 H), 3.78–3.68 (m, 1 H), 3.70 (s, 3 H), 3.40 (td, J = 11.1, 2.9 Hz, 1 H), 2.10–1.95 (m, 2 H), 1.90–1.75 (m, 1 H), 1.65–1.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 172.8, 128.6, 122.6, 64.7, 61.9, 52.1, 32.3, 24.8, 21.7, 16.2; IR (neat) 1705, 1630 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.01; H, 7.73.

Methyl 1β-Ethenyl-2β-ethoxy-3β-methylcyclopropane-1α-carboxylate (3c). 2a (0.25 g, 2.0 mmol), ethyl 1-propenyl ether (0.86 g, 10 mmol, E/Z ratio = 1:2.4), octanoate (0.016 g, 0.02 mmol), (1:9), colorless oil, yield 0.29 g, 76%: ^1H NMR ($CDCl_3$) δ 5.67 (dd, J = 18.1, 10.8 Hz, 1 H), 5.48 (dd, J = 18.1, 2.7 Hz, 1 H), 5.34 (dd, J = 10.8, 2.7 Hz, 1 H), 3.70 (d, J = 7.2 Hz, 1 H), 3.65 (s, 3 H), 3.55 (q, J = 7.2 Hz, 2 H), 1.90 (dq, J = 7.2, 6.6 Hz, 1 H), 1.19 (t, J = 7.2 Hz, 3 H), 1.08 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.2, 128.0, 119.5, 67.8, 66.7, 51.9, 32.0, 27.5, 14.9, 7.1; IR (neat) 1710, 1625 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.25; H, 8.78.

Methyl 2-Ethoxy-(*E*)-1-(1(*E*)-propenyl)cyclopropane-1-carboxylate (3d). 2b (0.70 g, 5.0 mmol), ethyl vinyl ether (1.80 g, 25 mmol), octanoate (0.037 g, 0.05 mmol), (1:9), colorless oil, yield 0.63 g, 68%: ^1H NMR ($CDCl_3$) δ 5.87 (dq, J = 15.5, 1.5 Hz, 1 H), 5.52 (dq, J = 15.5, 6.7 Hz, 1 H), 3.66 (s, 3 H), 3.60 (dd, J = 6.0, 3.9 Hz, 1 H), 3.55–3.30 (m, 2 H), 1.72 (dd, J = 6.4, 1.5 Hz, 3 H), 1.62 (dd, J = 6.4, 6.0 Hz, 1 H), 1.39 (dd, J = 6.4, 3.9 Hz, 1 H), 1.23 (t, J = 6.7 Hz, 3 H); ^{13}CNMR ($CDCl_3$) δ 173.4, 127.0, 122.0, 66.9, 66.3, 52.0, 31.3, 20.1, 18.1, 14.8; IR (neat) 1720, 1640 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.21; H, 8.76.

Methyl *endo*-7-(1(*E*)-Propenyl)bicyclo[4.1.0]heptane-7-carboxylate (3e). 2b (0.35 g, 2.5 mmol), 3,4-dihydro-2*H*-pyran (1.10 g, 12.5 mmol), octanoate (0.020 g, 0.025 mmol), (1:9), colorless oil, yield 0.37 g, 73%: ^1H NMR ($CDCl_3$) δ 5.77 (dq, J = 15.9, 6.5 Hz, 1 H), 5.38 (dq, J = 15.9, 1.7 Hz, 1 H), 3.87 (d, J = 7.1 Hz, 1 H), 3.68–3.55 (m, 1 H), 3.57 (s, 3 H), 3.29 (td, J = 10.7, 3.4 Hz, 1 H), 2.05–1.60 (m, 3 H), 1.75 (dd, J = 6.5, 1.7 Hz, 3 H), 1.40–1.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 173.5, 133.5, 121.2, 64.6, 61.7, 51.9, 31.3, 24.4, 21.6, 18.6, 16.3; IR (neat) 1710, 1630 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.03; H, 8.15.

Methyl 2β-Ethoxy-3β-methyl-1β-(1(*E*)-propenyl)cyclopropane-1α-carboxylate (3f). 2b (0.41 g, 3.0 mmol), ethyl 1-propenyl ether (1.27 g, 14.7 mmol, E/Z mixture = 1:2.4), pivalate (0.015 g, 0.03 mmol), (1:9), colorless oil, yield 0.48 g, 83%: ^1H NMR ($CDCl_3$) δ 5.84 (dq, J = 16.6, 6.5 Hz, 1 H), 5.25 (dq, J = 16.6, 1.6 Hz, 1 H), 3.62 (d, J = 7.1 Hz, 1 H), 3.62 (s, 3 H), 3.54 (q, J = 7.1 Hz, 2 H), 1.80 (dq, J = 7.1, 6.6 Hz, 1 H), 1.74 (dd, J = 6.5, 1.6 Hz, 3 H), 1.81 (t, J = 7.1 Hz, 3 H), 1.01 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.9, 131.4, 120.3, 67.2, 66.6, 51.9, 31.3, 26.7, 19.0, 14.8, 7.3; IR (neat) 1710, 1580 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.51; H, 9.18.

Methyl (*E*)-2-Ethoxy-((*E*)-2-phenylethenyl)cyclopropane-1-carboxylate (3g). 2c (1.62 g, 8.0 mmol), ethyl vinyl ether (2.90 g, 40 mmol), pivalate (0.045 g, 0.08 mmol), (1:9), colorless oil, yield 1.48 g, 75%: ^1H NMR ($CDCl_3$) δ 7.41–7.20 (m, 5 H), 6.75 (d, J = 16.1 Hz, 1 H), 6.43 (d, J = 16.1 Hz, 1 H), 3.78 (dd, J = 7.6, 4.6 Hz, 1 H), 3.73 (s, 3 H), 3.60–3.30 (m, 2 H), 1.88 (dd, J = 7.6, 6.4 Hz, 1 H), 1.63 (dd, J = 6.4, 4.6 Hz, 1 H), 1.11 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.7, 137.5, 129.5, 128.4, 126.9, 126.0, 121.6, 67.9, 67.1, 52.0, 31.6, 21.6, 14.7; IR (neat) 1710, 1640, 1600, 1580 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.38.

Methyl *endo*-7-((*E*)-2-Phenylethenyl)bicyclo[4.1.0]heptane-7-carboxylate (3h). 2c (1.62 g, 8.0 mmol), 3,4-dihydro-2*H*-pyran (3.36 g, 40 mmol), pivalate (0.045 g, 0.08 mmol), (1:9), colorless oil, yield 1.36 g, 66%: ^1H NMR ($CDCl_3$) δ 7.50–7.20 (m, 5 H), 6.75 (d, J = 16.5 Hz, 1 H), 6.21 (d, J = 16.5 Hz, 1 H), 4.05 (d, J = 6.8 Hz, 1 H), 3.62 (s, 3 H), 3.75–3.60 (m, 1 H), 3.32 (td, J = 10.7, 3.3 Hz, 1 H), 2.12–1.75 (m, 3 H), 1.50–1.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 172.8, 137.4, 136.9, 128.4, 127.4, 126.0, 120.1, 64.7, 62.0, 52.1, 31.8, 25.5, 21.8, 16.4; IR (neat) 1700, 1600, cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.12; H, 7.03.

Methyl 2β-Ethoxy-3β-methyl-1β-((*E*)-2-phenylethenyl)-cyclopropane-1α-carboxylate (3i). 2c (1.62 g, 8.0 mmol), ethyl 1-propenyl ether (3.45 g, 40 mmol, E/Z mixture = 1:2.4), pivalate (0.045 g, 0.08 mmol), (3:7), colorless oil, yield 1.67 g, 80%: ^1H NMR ($CDCl_3$) δ 7.40–7.20 (m, 5 H), 6.87 (d, J = 16.6 Hz, 1 H), 6.10 (d, J = 16.6 Hz, 1 H), 3.81 (d, J = 7.1 Hz, 1 H), 3.69 (s, 3 H), 3.61 (q, J = 7.1 Hz, 2 H), 2.02 (dq, J = 7.1, 6.8 Hz, 1 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.13 (d, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.3, 138.1, 134.0, 128.5, 127.1, 125.9, 120.3, 68.3, 66.8, 52.0, 31.9, 28.4, 14.9, 7.2; IR (neat) 1705, 1640, 1595, 1575 cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.58; H, 7.73.

Methyl 2β-Methoxy-3β-(4-methoxyphenyl)-1β-((*E*)-2-phenylethenyl)cyclopropane-1α-carboxylate (3j). 2c (0.20 g, 1.0 mmol), 1-(4-methoxyphenyl)-2-methoxyethylene (0.82 g, 5.0 mmol, E/Z mixture = 1:1.1), octanoate (0.0078 g, 0.01 mmol), (1:9), colorless oil, yield 0.13 g, 39%: ^1H NMR ($CDCl_3$) δ 7.40–7.15

(24) Goldschmidt, Z.; Grammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229.
(25) (a) Davies, H. M. L.; Hougland, P. W.; Cantrell, W. R., Jr. *Synth. Commun.* **1992**, *22*, 971. (b) Davies, H. M. L.; Saikali, E.; Clark, T. J.; Chee, E. H. *Tetrahedron Lett.* **1990**, *31*, 6299.

(m, 7 H), 6.86 (d, J = 8.8 Hz, 2 H), 6.74 (d, J = 16.6 Hz, 1 H), 6.06 (d, J = 16.6 Hz, 1 H), 4.16 (d, J = 7.3 Hz, 1 H), 3.82 (s, 3 H), 3.78 (s, 3 H), 3.45 (s, 3 H), 3.22 (d, J = 7.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 172.8, 158.2, 138.0, 133.5, 131.8, 128.2, 126.8, 125.9, 124.7, 120.0, 113.3, 70.4, 58.7, 55.0, 52.2, 36.6, 33.9; IR (neat) 1710, 1605, 1580 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.29; H, 6.50.

General Procedure for the Et_2AlCl-Catalyzed Rearrangement of Cyclopropanecarboxylates. A solution of cyclopropanecarboxylate (1 equiv, 0.1–0.4 M) in CH_2Cl_2 was added dropwise to a stirred solution of Et_2AlCl (1 M in hexane, 2 equiv) in CH_2Cl_2 at −78 °C under Ar. The mixture was maintained at −78 °C for 20–30 min and then warmed to room temperature for 3–4 h. After quenching with ethanol, water was added and the mixture was extracted twice with ether. The combined organic layers were extracted with water and saturated sodium chloride solution, dried (Na_2SO_4), and concentrated. All products were purified by column chromatography on silica using ether–petroleum ether as eluant in the ratio specified in parenthesis.

Methyl 4-Ethoxycyclopent-1-ene-1-carboxylate (4a). 3a (0.49 g, 2.9 mmol), (1:9), colorless oil, yield 0.43 g, 88%: ^{1}H NMR ($CDCl_3$) δ 6.69 (m, 1 H), 4.19 (tt, J = 6.8, 3.4 Hz, 1 H), 3.69 (s, 3 H), 3.50–3.30 (m, 2 H), 2.85–2.40 (m, 4 H), 1.15 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 141.0, 134.0, 78.5, 64.1, 51.4, 40.3, 38.2, 15.3; IR (neat) 1710, 1630 cm^{-1}; MS m/z (rel intensity) 170 (M^+, 100), 139 (23), 124 (44), 110 (68), 95 (21), 81 (77), 59 (41), 53 (74), 39 (50). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.32; H, 8.26.

Methyl (1Hα,6Hα)-5-Oxabicyclo[4.3.0]non-7-ene-7-carboxylate (4b). 3b (0.091 g, 0.5 mmol), (2:8), colorless oil, yield 0.088 g, 96%: ^{1}H NMR ($CDCl_3$) δ 6.80 (m, 1 H), 4.21 (q, J = 4.7 Hz, 1 H), 3.74–3.67 (m, 1 H), 3.71 (s, 3 H), 3.45 (ddd, J = 15.8, 8.1, 3.7 Hz, 1 H), 2.82–2.78 (m, 1 H), 2.51–2.48 (m, 2 H), 2.12–2.07 (m, 1 H), 1.93–1.81 (m, 1 H), 1.65–1.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 142.8, 136.9, 77.0, 64.7, 51.3, 42.8, 38.1, 22.9, 22.3; IR (neat) 1705, 1610 cm^{-1}; MS m/z (rel intensity) 182 (M^+, 89), 167 (2), 150 (77), 123 (27), 122 (100), 93 (23), 79 (29), 53 (16), 39 (25). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.01; H, 7.76.

Methyl (4α,5α)-4-Ethoxy-5-methylcyclopent-1-ene-1-carboxylate (4c). 3c (0.092 g, 0.5 mmol), (2:8), colorless oil, yield 0.086 g, 93%: ^{1}H NMR ($CDCl_3$) δ 6.61 (m, 1 H), 4.08 (ddd, J = 7.6, 7.6, 7.6 Hz, 1 H), 3.70 (s, 3 H), 3.46 (m, 2 H), 3.03 (br dq, J = 7.6, 7.1 Hz, 1 H), 2.60 (ddd, J = 18.0, 7.6, 3.2 Hz, 1 H), 2.40 (dddd, J = 18.0, 8.6, 2.0, 2.0 Hz, 1 H), 1.19 (t, J = 6.9 Hz, 3 H), 1.01 (d, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.0, 139.7, 139.6, 80.8, 65.2, 51.3, 39.7, 36.6, 15.4, 12.0; IR (neat) 1710, 1620 cm^{-1}; MS m/z (rel intensity) 184 (M^+, 86), 169 (5), 153 (19), 138 (37), 123 (66), 95 (100), 79 (39), 67 (56), 59 (38), 41 (53). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.34; H, 8.79.

Methyl (3β,4α)-4-Ethoxy-3-methylcyclopent-1-ene-1-carboxylate (4d). 3d (0.44 g, 2.4 mmol), (1:9), colorless oil, yield 0.38 g, 86%: ^{1}H NMR ($CDCl_3$) δ 6.57 (m, 1 H), 3.69–3.65 (m, 1 H), 3.68 (s, 3 H), 3.51–3.38 (m, 2 H), 2.90–2.78 (m, 2 H), 2.54–2.46 (m, 1 H), 1.15 (t, J = 7.0 Hz, 3 H), 1.06 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 146.3, 132.4, 86.0, 64.4, 51.4, 47.0, 37.3, 17.7, 15.4; IR (neat) 1710, 1640 cm^{-1}; MS m/z (rel intensity) 184 (M^+, 100), 169 (10), 155 (34), 138 (42), 123 (100), 95 (87), 79 (48), 67 (73), 59 (23), 41 (56). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.75. Found: C, 65.21; H, 8.71.

Methyl (1Hα,6Hα,9α)-9-Methyl-5-oxabicyclo[4.3.0]non-7-ene-7-carboxylate (4e). 3e (0.29 g, 1.5 mmol), (1:9), colorless oil, yield 0.26 g, 89%: ^{1}H NMR ($CDCl_3$) δ 6.60 (m, 1 H), 3.73 (t, J = 5.4 Hz, 1 H), 3.64 (s, 3 H), 3.63–3.47 (m, 2 H), 2.84–2.74 (m, 2 H), 1.95–1.30 (m, 4 H), 1.00 (d, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 147.4, 136.3, 83.2, 63.9, 51.2, 42.2, 40.7, 23.8, 22.5, 15.5; IR (neat) 1710, 1615 cm^{-1}; MS m/z (rel intensity) 196 (M^+, 100), 181 (19), 164 (52), 137 (87), 121 (19), 108 (23), 93 (30), 79 (38), 55 (18), 41 (38). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.17; H, 8.27.

Methyl (3β,4α,5α)-4-Ethoxy-3,5-dimethylcyclopent-1-ene-1-carboxylate (4f). 3f (0.18 g, 0.9 mmol), (1:9), colorless oil, yield 0.15 g, 81%: ^{1}H NMR ($CDCl_3$) δ 6.47 (m, 1 H), 3.70 (s, 3 H), 3.53 (dd, J = 8.6, 7.0 Hz, 1 H), 3.48–3.41 (m, 2 H), 3.02 (dq, J = 7.0, 7.0 Hz, 1 H), 2.80 (dq, J = 8.6, 7.0 Hz, 1 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.12 (d, J = 7.0 Hz, 3 H), 0.99 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 145.2, 138.1, 88.4, 65.6, 51.3, 43.0, 39.7, 16.7, 15.3, 12.2; IR (neat) 1715, 1620 cm^{-1}; MS m/z (rel intensity) 198 (M^+, 86), 169 (13), 152 (42), 137 (100), 123 (40), 109 (89), 81 (55), 79 (39), 53 (32), 43 (63). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.71; H, 9.19.

Methyl (4α,5α)-4-Ethoxy-5-phenylcyclopent-1-ene-1-carboxylate (4g). 3g (0.74 g, 3.0 mmol), (1:9), colorless oil, yield 0.50 g, 68%: ^{1}H NMR ($CDCl_3$) δ 7.40–7.12 (m, 5 H), 6.75 (m, 1 H), 4.10–4.00 (m, 2 H), 3.77 (s, 3 H), 3.48 (q, J = 7.0 Hz, 2 H), 3.05 (br dd, J = 17.0, 6.7 Hz, 1 H), 2.65 (br d, J = 17.0 Hz, 1 H), 1.18 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.1, 143.2, 141.3, 134.3, 128.6, 127.3, 126.8, 87.0, 64.7, 58.6, 51.6, 38.0, 15.4; IR (neat) 1715, 1630, 1600 cm^{-1}; MS m/z (rel intensity) 246 (M^+, 100), 217 (10), 185 (40), 173 (10), 157 (48), 129 (65), 115 (16), 91 (14). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.22; H, 7.42.

Methyl (1Hα,6Hα,9α)-9-Phenyl-5-oxabicyclo[4.3.0]non-7-ene-7-carboxylate (4h). 3h (0.77 g, 3.0 mmol), (1:9), colorless oil, yield 0.52 g, 67%: ^{1}H NMR ($CDCl_3$) δ 7.36–7.10 (m, 5 H), 6.85 (br s, 1 H), 4.11–4.09 (m, 2 H), 3.77 (s, 3 H), 3.86–3.60 (m, 2 H), 3.05–2.92 (m, 1 H), 2.18–1.95 (m, 1 H), 1.82–1.47 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.9, 143.8, 140.1, 138.7, 128.5, 127.4, 126.8, 84.2, 63.5, 52.4, 51.3, 40.8, 24.1, 22.3; IR (CCl_4) 1710, 1600 cm^{-1}; MS m/z (rel intensity) 258 (M^+, 100), 226 (22), 199 (98), 170 (24), 155 (18), 141 (23), 115 (19), 91 (16). Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.26; H, 7.05.

Methyl (3β,4α,5α)-4-Ethoxy-5-methyl-3-phenylcyclopent-1-ene-1-carboxylate (4i). 3i (0.63 g, 2.5 mmol), (1:19), colorless oil, yield 0.48 g, 77%: ^{1}H NMR ($CDCl_3$) δ 7.38–7.15 (m, 5 H), 6.72 (m, 1 H), 4.00–3.85 (m, 2 H), 3.75 (s, 3 H), 3.50–3.10 (m, 3 H), 1.18–1.07 (m, 6 H); ^{1}H NMR (C_6D_6) δ 7.20–7.00 (m, 5 H), 6.60 (m, 1 H), 3.87 (d, J = 8.5 Hz, 2 H), 3.77 (t, J = 7.7 Hz, 1 H), 3.45 (s, 3 H), 3.27–3.19 (m, 1 H), 3.15–2.93 (m, 2 H), 1.28 (d, J = 6.8 Hz, 3 H), 0.93 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.8, 142.3, 141.7, 139.8, 128.3, 127.4, 126.6, 89.1, 65.6, 54.3, 51.3, 40.0, 15.1, 12.3; IR (neat) 1710, 1620, 1600 cm^{-1}; MS m/z (rel intensity) 260 (M^+, 100), 228 (11), 199 (48), 171 (37), 155 (36), 128 (51), 115 (21), 91 (22), 43 (16). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.78; H, 7.75.

Methyl (3β,4α,5α)-4-Methoxy-5-(4-methoxyphenyl)-3-phenylcyclopent-1-ene-1-carboxylate (4j). 3j (0.19 g, 0.57 mmol), (3:17), colorless crystals, mp 78–80 °C, yield 0.12 g, 61%: ^{1}H NMR ($CDCl_3$) δ 7.40–7.15 (m, 7 H), 6.90–6.80 (m, 3 H), 4.38 (d, J = 6.8 Hz, 1 H), 4.13 (d, J = 7.8 Hz, 1 H), 4.07 (dd, J = 7.8, 6.8 Hz, 1 H), 3.78 (s, 3 H), 3.65 (s, 3 H), 3.07 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.5, 159.4, 143.7, 141.7, 139.3, 129.7, 128.8, 128.6, 127.5, 126.9, 113.6, 91.4, 58.2, 55.7, 55.0, 51.5 (two of the signals are superimposed); IR (neat) 1710, 1600, 1580 cm^{-1}; MS m/z (rel intensity) 338 (M^+, 100), 306 (52), 274 (39), 247 (66), 215 (24), 183 (6), 135 (14), 91 (15), 77 (9), 45 (8). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.54; H, 6.55. Found: C, 74.63; H, 6.57.

Acknowledgment. We thank Dr. Phirtu Singh from North Carolina State University for the X-ray analysis. Financial support of this work by the National Science Foundation (CHE 9024248) is gratefully acknowledged.

Supplementary Material Available: Crystallographic data including tables of the atomic positional and thermal parameters and bond distances and bond angles for **4j** (7 pages). This material is contained in many 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.