2,2-Dihalovinylcyclopropanes as Highly Diastereoselective Three-Atom Addends in Phenylthio Radical Mediated Vinylcyclopentane Synthesis

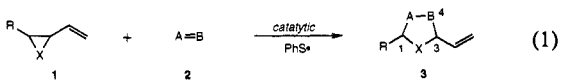
Ken S. Feldman,* Heidi M. Berven, and Paul H. Weinreb

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received May 21, 1993®

Abstract: 2,2-Dichloro- or 2,2-dibromovinylcyclopropane was condensed with electron-deficient alkenes in a phenylthio radical catalyzed process to afford 4-substituted and 4,5-disubstituted-1,1-dihalo-3-vinylcyclopentane derivatives in good yield and with good-to-excellent diastereoselectivity for the 3,4-cis isomer. Neither electron-rich nor β-substituted alkenes led to good yields of cyclopentane products. The diastereoselectivity and reactivity profiles of these transformations are satisfactorily rationalized by application of existing transition-state models of radical reactions.

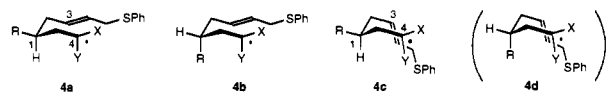
Our studies of the phenylthio radical catalyzed [3-atom + 2-atom] addition of substituted vinylcyclopropanes (or vinyloxiranes) with two-atom unsaturated addends (eq 1) have detailed



(1)

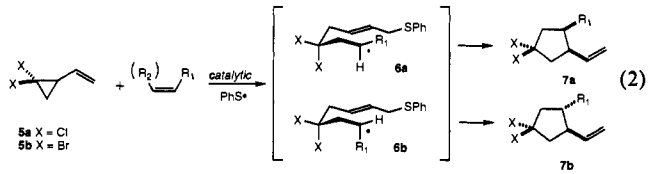
1 2 3

many of the salient regiochemical and stereochemical features of this transformation which, in turn, define its scope and limitations for complex molecule synthesis.[1,2] Specifically, the all-carbon series (X, A, B = carbon substituents) has proven to be particularly versatile for the synthesis of a wide range of functionalized vinylcyclopentane derivatives with moderate levels of stereoselectivity.[1b,f] In addition to providng access to substituted vinylcyclopentanes, these studies have helped illuminate the scope and magnitude of the critical steric interactions which, when taken together, determine the stereochemical outcome of cyclization of the putative intermediate 5-hexenyl radical **4**. With



4a 4b 4c 4d

one significant exception, the prevailing dogma[3] provides adequate rationalization for these observations. This exception arises upon consideration of the origins of 1,3 anti stereochemistry in product **3** upon cyclization of **4**. Houk[3a,b] and Beckwith[3c] have, independently, developed computational models based on parameter sets derived from simple, unadorned substrates which suggest that the boat-like/equatorial-R transition-state model **4c** is a viable alternative to the chair-like/axial-R species **4b** as a precursor to the 1,3-trans product. We have probed this issue experimentally[1f] with substrates more heavily functionalized than the Houk/Beckwith prototype systems and have found no evidence to support this contention. It is possible that the discrepancy between computational prediction and experimental result can be attributed to an unwarranted extrapolation from the simple system upon which the calculational model is based to our more highly substituted (and polarized) cases. In any event, our earlier experimental observations are relevant to the issue of C(3)–C(4) cyclopentane stereochemistry under investigation here, since the configuration about the forming C(3)–C(4) bond will now be dictated by the differential C(1)–C(4) steric interactions implied in **4a** and **4b** and not by (possibly conflicting) differential transannular interactions between the boat-like (e.g., **4c**) and chair-like (e.g., **4a**/**4b**) conformers. If this simplified "two-transition-state" model can be applied to related systems, then a means to predictably control vicinal (e.g., C(3)–C(4)) stereochemistry upon cyclization of **6** presents itself, eq 2. Thus,



5a X = Cl
5b X = Br

6a 6b 7a 7b

(2)

introduction of a dominant steric interaction between substituents on C(1) and C(4) (e.g., a 1,3 diaxial interaction (eq 2)) should direct the cyclization through a transition state resembling **6a** rather than **6b**, and hence the cis 3,4-substituted cyclopentane **7a** should result. In this report, we test this hypothesis by examining the scope and stereochemical consequences of [3-atom + 2-atom] addition between the dihalovinylcyclopropanes **5a**, **5b**, and **8** (eq 2) and a variety of representative mono-, 1,1-di-, and 1,2-disubstituted alkenes. These vinylcyclopropane derivatives present a halogen in the axial position at C(1) (cf. **6a**/**6b**, X = Cl or Br) and thus provide a meaningful test of this approach for stereochemical control upon cyclopentane formation.

Initial exploratory experiments (cf. eq 2) with both the dichloride **5a**[4] and, independently, the dibromide **5b**[4] and methyl acrylate as a typical alkene revealed that (1) the reaction proceeded in good yield under mild conditions similar to those defined previously[1f] and (2) the expectation of a high level of 3,4-cis stereochemistry was realized (Table I, entries a and b). In no

® Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) (a) Feldman, K. S.; Simpson, R. E.; Parvez, M. *J. Am. Chem. Soc.* **1986**, *108*, 1328. (b) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (c) Feldman, K. S.; Fischer, T. E. *Tetrahedron* **1989**, *45*, 2964. (d) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878. (e) Feldman, K. S.; Ruckle, R. E., Jr.; Romanelli, A. L. *Tetrahedron Lett.* **1989**, *30*, 5845. (f) Feldman, K. S.; Burns, C. J. *J. Org. Chem.* **1991**, *56*, 4601. (g) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Jean, G. *J. Org. Chem.* **1992**, *57*, 100. (h) Feldman, K. S.; Kraebel, C. M. *J. Org. Chem.* **1992**, *57*, 4574.

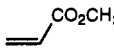
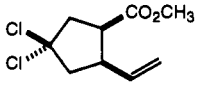
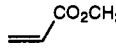
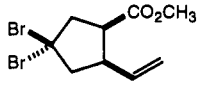
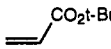
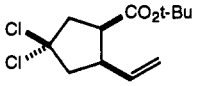
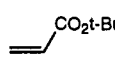
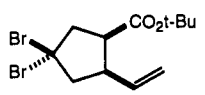
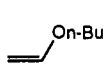
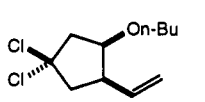
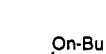
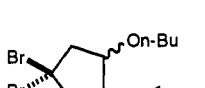
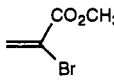
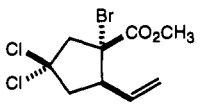
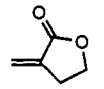
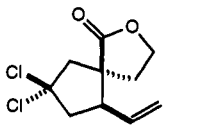
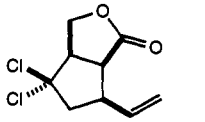
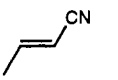
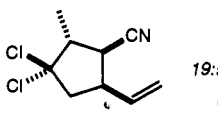
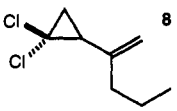
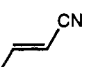
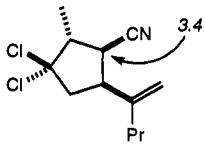
(2) Related studies have been reported: (a) Singleton, D. A.; Church, K. M. *J. Org. Chem.* **1990**, *55*, 4780. (b) Singleton, D. A.; Huval, C. C.; Church, K. M.; Priestley, E. S. *Tetrahedron Lett.* **1991**, *32*, 5765. (c) Singleton, D. A.; Church, K. M.; Lucero, M. J. *Tetrahedron Lett.* **1990**, *31*, 5551. (d) Saicic, R. N.; Cekovic, Z. *Tetrahedron* **1992**, *48*, 8975. (e) Miura, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 5139. (f) Chuang, C. P.; Hou, S. S.; Wu, R. R. *Synth. Commun.* **1992**, *22*, 467.

(3) (a) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. (b) Broeker, J. L.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 3651. (c) Beckwith, A. L. J.; Zimmermann, J. *J. Org. Chem.* **1991**, *50*, 5791.

(4) Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1957**, *79*, 2542.

0002-7863/93/1515-11364$04.00/0

Table I. Dihalovinylcyclopentane Synthesis from 2,2-Dihalovinylcyclopropanes and Alkenes

dihalovinylcyclopropane	alkene[a]	yield	vinylcyclopentane products (cis(**7a**)/trans(**7b**))[b]	
a)  **5a**		57 %		7.8:1 **9a/9b**
b)  **5b**		74 %		9:1 **10a/10b**
c) **5a**		71 %		3:1 **11a/11b**
d) **5b**		72 %		4.1:1 **12a/12b**
e) **5a**		24 %		1.1:1 **13a/13b**
f) **5b**		28 %		1.4:1 **14a/14b** *(unassigned)*
g) **5a**		61 %		14:1 **15a/15b**
h) **5a**		61 %		15:1 **16a/16b**
i) **5a**		32 %		6:1 **17a/17b**
j) **5a**		73 %		19:5:5:1 **18a/18b/18c/18d** *(major isomer shown)*
k)  **8**		69 %		3.4 : 1 **19a/19b**

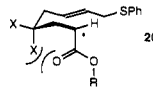
[a] Reagent ratios and experimental details can be found in the experimental section. [b] Product structure and stereochemistry were based on a combination of ^{1}H decoupling and DNOE experiments and, in the case of **11a/b**, **12a/b**, and **15a/b**, chemical transformations (see the experimental section and supplementary materials for details).

instance did we identify any products of cyclopropane ring opening toward the unsubstituted carbon. All the reactions reported herein were accomplished with similar protocols: 0.1–0.2 equiv of Ph_2S_2, 0.1 equiv of AIBN, 1–5 equiv of alkene per dihalovinylcyclopropane, in benzene or toluene at 35–45 °C with continuous sunlamp irradiation. Unlike previously studied alkene/vinylcyclopropane pairings,[1b,1f] these transformations did not show any significant improvement in yield and stereoselectivity upon exposure to various Lewis acids at low temperature (0 to −25 °C). Resubmission experiments with vinylcyclopentane products **9a** and **10a** revealed that product stereochemistry was not subject to equilibration under the specific reaction conditions. However, we were surprised to observe that the dibromocyclopentane products **10a/10b** were formed in good yield (57%) upon reaction of **5b** and methyl acrylate *without* inclusion of either Ph_2S_2 or AIBN. Furthermore, while the dichloro analog **5a** was completely unreactive under these conditions, small amounts of the dibromide **5b** (~5%) (or even bromine itself!) included with dichloride **5a** and methyl acrylate (but *no* Ph_2S_2 or AIBN) also led to good yields of the dichlorocyclopentane products **9a/9b** upon sunlamp irradiation. From these observations, we conclude that the dibromide **5b** produces a small amount of chain-carrying radical, presumably Br•, upon heat/irradiation, and that this radical efficiently catalyzes the multistep transformation. Since the stereochemical outcomes with the dibromide and dichloride species are quite similar in this and other cases (see Table I, entries a–f) and since the dichloride **5a** does not itself decompose under the reaction conditions, we have confined the majority of our studies to dichlorovinylcyclopropane **5a**.

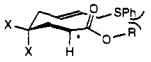
Vinylcyclopentane formation from dihalovinylcyclopropanes and substituted alkenes seems to require an electron-deficient alkene for a high-yielding reaction. Within this context, exam-

ination of the stereochemical results of the *tert*-butyl acrylate runs (Table I, entries c and d) vis-a-vis the methyl acrylate series reveals some of the subtle interplay of steric interactions which ultimately contribute to product stereochemistry. It is plausible that "transannular" torsional interactions along the forming bond destabilize a transition state resembling conformer **20b**. Since the ester residue R does not play a direct role in the competing destabilizing 1,3-type diaxial interactions shown in (the previously disfavored) conformer **20a**, an erosion in observed stereoselectivity for the bulkier *tert*-butyl ester would be expected.

As mentioned earlier, electron-rich alkenes (butyl vinyl ether, Table I, entries e and f) combine with dihalovinylcyclopropanes in only poor yield and, moreover, with essentially no stereochemical preference. The former observation perhaps can be attributed to less than optimal matching of orbital energies ($E_{somo}(^{\bullet}CHCl_2) = -9.75$ eV, compare $E_{somo}(^{\bullet}CH_2CHO) = -11.45$ eV, $E_{somo}(^{\bullet}CH_2OCH_3) = -9.09$ eV),[5] in that the dichloroalkyl radical derived from **5a** is actually more "electron rich" (similar to $^{\bullet}CH_2OCH_3$) than might have been supposed. The latter observation has been discussed elsewhere[1f] in a related context.

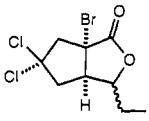


20a R = CH_3 or t-Bu

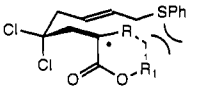


20b R = CH_3 or t-Bu

The 1,1-disubstituted electron-deficient alkenes examined in entries g and h (Table I) both afforded good yields of cyclopentanes with remarkably high diastereoselectivity. The stereochemical outcome of the reaction with α-methylenebutyrolactone was determined by DNOE measurements (see supplementary material), while conversion of the major bromoester **15a**, formed upon combination of 2,2-dichlorovinylcyclopropane **5a** with methyl α-bromoacrylate, to the iodolactone **21** defined the ester



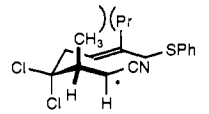
21



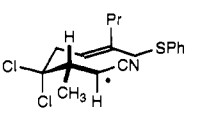
22

and vinyl appendages of **15a** as cis disposed. While the structural basis for the improvement in stereoselectivity in these two examples relative to the "parent" case, methyl acrylate (entry a), remains a matter of speculation, it is plausible that newly engendered torsional interactions shown in transition-state model **22** are contributing factors in further disfavoring the trans isomer. In any event, replacement of bromine with hydrogen in isomer **15a** (either SmI_2 or Bu_3SnH) largely furnishes the cis-substituted vinylcyclopentane derivative **9a**.

2-Substituted acrylates proved to be poor substrates for this transformation. Thus, 2-furanone combines with dichlorovinylcyclopropane **5a** in only 32% yield (entry i) while crotonaldehyde affords only 13% cyclopentane products in the analogous addition (not listed in Table I). However, the more reactive (but less sterically encumbered at the "carbonyl" carbon) crotononitrile series (Table I, entries j and k) proved serviceable. Combination of the dichloro species **5a** with crotononitrile led to all four possible stereoisomeric vinylcyclopentane products, which were not completely separable. Structural elucidation of partially purified isomers eliminated the possibility that these products resulted from *regioisomeric* [3-atom + 2-atom] addition and revealed the complete stereochemical details of the major isomer as shown. The "propylated" dichlorovinylcyclopropane **8** was explored in an attempt to influence the stereochemical outcome of the substituted 5-hexenyl radical cyclization in this series by judicious introduction of new, controlling steric interactions. Thus, the propyl substituent was designed to shift cyclization through a transition state resembling **23b** rather than **23a** as a consequence



23a



23b

of the indicated 1,3-type "diaxial" interaction (cf. **23a**). That such speculation was borne out experimentally can be seen in Table I, entry k, in which the methyl and pentenyl appendages are strictly trans disposed in the product cyclopentanes **19a/19b**. Unfortunately, the smaller size of the nitrile activating group compared with an ester resulted in a corresponding decrease in stereoselectivity at C(3). Nevertheless, the functionality pattern in cyclopentane **19a** and the complete trans C(2)–C(4) stereoselectivity are coincident with members of several terpene-derived classes of natural products, most notably the iridoids.[6]

In summary, we have demonstrated that 2,2-dichloro- and 2,2-dibromovinylcyclopropanes combine with electron-deficient alkenes to furnish substitued dihalovinylcyclopentane products in good yield and with excellent 3,4 stereoselectivity in most cases. Structurally more complex substrates can lead to more highly substituted cyclopentane products without substantially compromising stereochemical control. The documented utility of 1,1-dihalocycloalkenes in the synthesis of ketones,[7a,b] chloroalkenes,[7c] *gem*-dimethylalkanes,[7c] and alkanes[7d] underscores the potential versatility of these adducts in target-directed synthesis. The observed stereoselectivity upon cyclopentane product formation is completely consistent with the predictions of our refined model for substituted 5-hexenyl radical cyclization.[1f] It is now possible to impart higher levels of stereochemical control into an otherwise only modestly selective transformation (Table I, entries j and k).

Experimental Section

^{1}H NMR signals reported for mixtures include major and minor isomer peak designations. Low-resolution mass spectra (MS) were obtained at 50–70 eV by electron impact (EI). Gas–liquid chromatography (GLC) was performed with a capillary cross-linked methyl silicone column (25 m, i.d. 0.20 mm; film thickness 0.33 mm) or a 20M carbowax capillary column where specified, and a flame ionization detector. High-pressure liquid chromatography (HPLC) was performed with a ZORBAX-SIL^{tm} silica gel column (25 cm × 20 mm). Liquid (flash)[10] chromatography was carried out using 32–63-μM silica gel and the indicated eluent. Irradiation was provided by a 275-W sunlamp (Sylvania or General Electric).

Benzene (PhH), diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), pentane, tetrahydrofuran (THF), and toluene ($PhCH_3$) were purified by distillation from sodium/benzophenone ketyl under nitrogen. Diisopropylamine, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), and methylene chloride (CH_2Cl_2) were distilled from calcium hydride under nitrogen. Solvents for flash chromatography (diethyl ether and hexane) were distilled from calcium hydride prior to use. Moisture- and oxygen-sensitive reactions were carried out in predried glassware and under an inert atmosphere (N_2, Ar).

1,1-Dichloro-2-(2-pentenyl)cyclopropane (8). Dichlorocyclopropanecarboxaldehyde **5a** (4 g, 0.03 mol) in 200 mL of Et_2O was treated at −78 °C with propyl magnesium iodide which was generated from 1-iodopropane (6 g, 0.04 mol, 1.2 equiv) and magnesium filings (0.9 g, 0.04 mol,

(5) Pasto, D. J.; Krasnansky, R.; Zercher, C. *J. Org. Chem.* **1987**, *52*, 3062. The quantitative values provided by Pasto et al. have, in some cases, been superceded by the results of higher level calculations in recent years. However, this study is the only one complete enough to permit comparison of all the substituents of interest, and it is likely that their qualitative ranking will remain unaffected.

(6) Grayson, D. H. *Nat. Prod. Rep.* **1990**, *7*, 327 and references cited therein.

(7) (a) Hiyama, T.; Shinoda, M.; Nozaki, H. *Tetrahedron Lett.* **1978**, 771. (b) Wenkert, E.; Bakuzis, P.; Haviv, F. *J. Org. Chem.* **1970**, *35*, 2092. (c) Abudarham, J. P.; Meyet, J.; Smadja, W.; Levisalles, J. *Org. Magn. Reson.* **1977**, *10*, 192. (d) Reetz, M. T.; Steinbach, R.; Wenderoth, B. *Synth. Commun.* **1981**, *11*, 261. (e) Neumann, W. P. *Synthesis* **1987**, 665.

(8) (a) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482, 484. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(9) Khusid, A. K. *Zh. Org. Khim.* **1986**, *22*, 1195.

(10) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

1.2 equiv) in the usual manner. The reaction was quenched with ice-cold saturated NH_4Cl solution and extracted with 3 × 50 mL of Et_2O. The combined organic phases were washed with brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. Purification of the crude product via flash column chromatography on silica gel with hexane–Et_2O (4:1) as eluent provided 4 g (74% yield) of the alcohol as a pale-yellow oil. IR (CCl_4) 3320 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.34 (dt, J = 4.6, 7.8 Hz, 1 H), 2.55 (s, 1 H), 1.71 (dd, J = 9.1, 7.4 Hz, 1 H), 1.55 (m, 5 H), 1.18 (t, J = 7.2 Hz, 1 H), 0.89 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 59.7, 39.4, 37.8, 36.3, 25.2, 18.6, 13.9; MS m/z (relative intensity) 182 (M^+, 1), 165 ($M^+ - H_2O$, 25), 129 (98), 93 (100), 86 (54); HRMS calcd for $C_7H_{11}Cl_2O$ (M^+ – H), 181.0188; found, 181.0191.

This cyclopropyl alcohol (4 g, 20 mmol, 1 equiv) and PCC (14 g, 0.07 mol, 3 equiv) were combined in 200 mL of CH_2Cl_2. The resulting black solution was stirred at room temperature for 4 h, filtered through a plug of silica gel, and concentrated in vacuo. Flash column chromatography on silica gel eluting with hexane–Et_2O (4:1) provided 3.3 g (83% yield) of the product cyclopropyl ketone. IR (CCl_4) 1705 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.72 (t, J = 8.0 Hz, 1 H), 2.60 (t, J = 7.0 Hz, 2 H), 2.09 (t, J = 8.2 Hz, 1 H), 1.68 (m, 3H), 0.91 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 200.9, 58.1, 46.6, 38.7, 25.5, 16.9, 13.6; MS m/z (relative intensity) 181 (MH^+, 100), 145 (M^+ – HCl, 20), 111 (14), 81 (14), 71 (26); HRMS calcd for $C_7H_{10}Cl_2O$, 180.0109; found, 180.0099.

Titanium tetrachloride (6.2 mL, 56 mmol, 1.03 equiv) was added dropwise by addition funnel to a mixture of activated zinc (15.6 g, 24 mmol, 4.4 equiv) and dibromomethane (5.0 mL, 79 mmol, 1.4 equiv) in 50 mL of THF cooled to –40 °C under Ar. The mixture was allowed to warm to 5 °C and was stirred under Ar for 3 days. This stock solution of the methylating agent was stored in a freezer when not in use, and it retained its activity for several weeks.

A wide-bore cannula was used to transfer the methylating agent (54 mL, 56 mmol, 5 equiv) to a solution of the cyclopropyl ketone (2.0 g, 11 mmol) in 100 mL of CH_2Cl_2 cooled to –40 °C. The mixture was manually shaken (since magnetic stirring was impossible because of its viscosity) under Ar for 1 h. It was allowed to warm to 0 °C and diluted with 200 mL of hexane. The excess zinc–titanium reagent was quenched by careful addition of an ice-cooled solution of saturated $NaHCO_3$. The resulting mixture was partitioned between water and hexane. The hexane layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a yellow oil. The crude product was purified by column chromatography on silica gel eluting with hexane to give 1.4 g (70% yield) of the olefin **8** as a colorless oil. IR (CCl_4) 1600 (C=C) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.99 (s, 1H), 4.73 (s, 1H), 2.15 (t, J = 8.3 Hz, 2H), 2.13 (m, 1H), 1.63 (dd, J = 7.9, 5.3 Hz, 1 H), 1.58 (m, 1 H), 1.55 (t, J = 7.8 Hz, 2 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 112.5, 60.6, 53.2, 36.1, 24.8, 20.6, 13.9; MS m/z (relative intensity) 178 (M^+, 80), 143 (M^+ – Cl, 62), 107 (84), 101 (100).

Cyclopentane Synthesis. Dihalovinylcyclopropane (1 equiv), phenyl disulfide (0.1 equiv), AIBN (0.01 equiv), and the indicated olefin (1–15 equiv, see below) were dissolved in benzene (0.05–0.01 M based on vinylcyclopropane). The resulting solution was purged with Ar and then irradiated at the indicated temperature with a sunlamp for the indicated number of hours. Concentration of the reaction mixture gave an amber oil. The crude product was purified by flash column chromatography on silica get eluting with the indicated solvents. In some cases HPLC was necessary to give isomerically pure cyclopentane products.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with Methyl Acrylate. *gem*-Dichlorovinylcyclopropane **5a** (50 mg, 0.37 mmol), methyl acrylate (314 mg, 3.65 mmol, 10 equiv), phenyl disulfide (12.7 mg, 0.073 mmol, 0.2 equiv), and AIBN (1.2 mg, 0.004 mmol, 0.01 equiv) were combined in 5 mL of benzene at room temperature according to the general procedure to give 60 mg (74% yield) of the cyclopentanes **9a/9b**. GC (carbowax, 120 °C) of the mixture showed peaks at 2.07 and 2.12 min, corresponding to a 7.8:1 ratio of products. The isomers were separated by HPLC eluting with hexane–Et_2O (98:2).

Methyl 3,3-Dichloro-*c*-5-ethenyl-*r*-1-cyclopentanecarboxylate (9a). IR (CCl_4) 1715 (C=O) cm^{-1}; ^1H NMR (200 MHz, C_3D_6O) δ 5.65 (ddd, J = 17.4, 10.0, 7.5 Hz, 1 H), 5.18 (d, J = 17.6 Hz, 1 H), 5.07 (d, J = 11.3 Hz, 1 H), 3.68 (s, 3H), 3.32 (m, 1 H), 2.80 (m, 3H), 2.51 (dd, J = 16.1, 9.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 135.6, 117.4, 89.6, 52.9, 51.8, 50.5, 45.9, 43.7; MS m/z (relative intensity) 186 (M^+ – HCl, 55), 147 (38), 127 (100), 91 (78); HRMS calcd for $C_9H_{12}ClO_2$ (M^+ – HCl), 186.0448; found, 186.0438.

Methyl 3,3-Dichloro-*t*-5-ethenyl-*r*-1-cyclopentanecarboxylate (9b). IR (CCl_4) 1720 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.9 (ddd, J = 16.8, 10.2, 7.6 Hz, 1 H), 5.13 (d, J = 17.2 Hz, 1 H), 5.01 (d, J = 10.1 Hz, 1 H), 3.67 (s, 3H), 3.23 (pentet, J = 8.3 Hz, 1 H), 3.04 (dd, J = 16.7, 8.5 Hz, 1 H), 2.81 (m, 2 H), 2.79 (ddd, J = 5.3, 4.3, 3.2 Hz, 1 H), 2.51 (dd, J = 14.3, 9.3 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 173.5, 138.7, 115.9, 89.2, 53.9, 52.2, 51.4, 48.1, 45.1; MS m/z (relative intensity) 222 (MH^+, 6), 187 (MH^+ – HCl, 55), 147 (41), 127 (94), 91 (100); HRMS calcd for $C_9H_{12}Cl_2O_2$, 222.0214; found, 222.0224.

Reaction of *gem*-Dibromocyclopropane 5b with Methyl Acrylate. Following the general procedure, a solution containing the *gem*-dibromocyclopropane **5b** (50 mg, 0.22 mmol), methyl acrylate (0.300 mL, 3.32 mmol, 15 equiv), phenyl disulfide (8 mg, 0.04 mmol, 0.05 equiv), and AIBN (36 mg, 0.22 mmol, 1 equiv) was irradiated for 4 h. Purification of the residue by flash chromatography using Et_2O–hexane (5:95) as eluent yielded 51 mg (74%) of cyclopentanes **10a/10b** (diastereomer ratio 9.0 (**10a**):1 (**10b**)) as a clear oil. Partial separation of the two diastereomers was achieved by careful flash chromatography using Et_2O–hexanes (3:97) as eluent.

Methyl 3,3-Dibromo-*c*-5-ethenyl-*r*-1-cyclopentanecarboxylate (10a). IR (CCl_4) 1715 cm^{-1} (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 5.68 (ddd, J = 17.1, 10.1, 8.1 Hz, 1 H), 5.12 (d, J = 17.0 Hz, 1 H), 5.07 (d, J = 10.0 Hz, 1 H), 3.65 (s, 3 H), 3.36 (m, 2 H), 3.14 (dd, J = 14.5, 9.0 Hz, 1 H), 3.01 (m, 1 H), 2.93 (ddd, J = 14.2, 4.3, 2.3 Hz, 1 H), 2.63 (dd, J = 14.2, 9.9 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.5, 135.3, 117.5, 62.2, 56.0, 53.5, 51.8, 46.3, 44.2; MS m/z (relative intensity) 312 (M^+, 4), 233/231 (M^+ – Br, 71), 173/171 (M^+ – Br, CO_2CH_3, 70); HRMS calcd for $C_9H_{12}O_2Br_2$, 311.9184; found, 311.9156. GLC retention time with a carbowax 20M capillary column at 105 °C: 2.82 min.

Methyl 3,3-Dibromo-*t*-5-ethenyl-*r*-1-cyclopentanecarboxylate (10b). IR (CCl_4) 1715 cm^{-1} (C=O); ^1H NMR (500 MHz, C_6D_6) δ 5.59 (ddd, J = 17.4, 10.2, 7.6 Hz, 1 H), 4.91 (dt, J = 17.0, 1.2 Hz, 1 H), 4.83 (dd, J = 10.1, 1.2 Hz, 1 H), 3.25 (s, 3 H), 3.16 (ddd, J = 17.4, 8.6, 7.7 Hz, 1 H), 3.02 (ddd, J = 14.6, 7.9, 1.4 Hz, 1 H), 2.72 (dt, J = 14.0, 1.3 Hz, 1 H), 2.70 (dt, J = 14.0, 1.3 Hz, 1 H), 2.60 (heptet, J = 8.6 Hz, 1 H), 2.32 (ddd, J = 14.5, 8.6, 1.1 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 173.3, 138.6, 116.0, 61.4, 56.9, 54.4, 52.2, 48.5, 45.5; MS m/z (relative intensity) 281 (M^+ – OCH_3, 7), 233/231 (M^+ – Br, 47), 173/171 (M^+ – Br, CO_2CH_3, 61); HRMS calcd for $C_8H_9OBr_2$ (M^+ – OCH_3), 280.9000; found, 280.8993. GLC retention time with a carbowax 20M capillary column at 105 °C: 2.93 min.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with *tert*-Butyl Acrylate. *gem*-Dichlorovinylcyclopropane **5a** (110 mg, 0.48 mmol), *tert*-butyl acrylate (96 μL, 0.66 mmol, 1.5 equiv), phenyl disulfide (10 mg, 0.044 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.05 M) according to the general procedure to give 90 mg (71% yield) of the cyclopentanes **11a/11b** as a 3:1 mixture of cis/trans isomers by ^1H NMR integration. Purification of the isomeric mixture by flash column chromatography on silica gel eluting with hexane–Et_2O (95:5) gave a pure sample of the major isomer.

2,2-Dimethylethyl 3,3-Dichloro-*c*-5-ethenyl-*r*-1-cyclopentanecarboxylate (11a). IR (CCl_4) 1720 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (ddd, J = 17.0, 10.6, 8.1 Hz, 1 H), 5.17 (d, J = 17.1 Hz, 1 H), 5.05 (d, J = 10.3 Hz, 1 H), 3.29 (m, 1 H), 3.20 (pentet, J = 10.2 Hz, 1 H), 2.86 (dd, J = 14.4, 8.6 Hz, 1 H), 2.82 (dd, J = 14.5, 9.0 Hz, 1 H), 2.75 (ddd, J = 12.8, 6.4, 2.3 Hz, 1 H), 2.45 (dd, J = 13.7, 10.0 Hz, 1 H), 1.42 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 136.0, 117.1, 89.8, 81.3, 53.1, 50.6, 46.5, 43.9, 28.1; MS m/z (relative intensity) 265 (MH^+, 8), 209 (62), 173 (100), 127 (19); HRMS calcd for $C_8H_9ClO_2$ (loss of C_4H_9Cl), 171.0213; found, 171.0270.

Proof of Ring Stereochemistry for 11a/11b by $LiAlH_4$ Reduction. Pure samples of the cis and trans cyclopentane derivatives **9a** (2.0 mg, 9.0 μmol) and **9b** (2.0 mg, 9.0 μmol), respectively, were dissolved in Et_2O and treated with lithium aluminum hydride ($LiAlH_4$, 1 mg, 27 μmol, 3 equiv) at 0 °C until the starting material was consumed (TLC monitoring). The reaction mixtures were quenched by careful addition of a few drops of H_2O and dried over anhydrous Na_2SO_4. Analysis of the product alcohols in separate runs by GC (carbowax, 135 °C) gave retention times of 5.41 and 5.20 min corresponding to the cis and trans isomers, respectively.

A 4:1 isomeric mixture of the *tert*-butyl ester cyclopentane derivatives **11a/11b** (3.0 mg, 11 μmol) was then submitted to the same reduction procedure using $LiAlH_4$ (2 mg, 2.7 mmol, 2.5 equiv). GC analysis of the crude product (carbowax, 135 °C) gave signals with retention times of 5.45 and 5.25 min in a 3.7:1 ratio. The major product alcohol is therefore derived from the corresponding cis (major) ester derivative.

Reaction of *gem*-Dibromovinylcyclopropane 5b with *tert*-Butyl Acrylate. *gem*-Dibromovinylcyclopropane **5b** (80 mg, 0.35 mmol), *tert*-butyl acrylate (179 mg, 1.77 mmol, 5 equiv), phenyl disulfide (16 mg, 0.071 mmol, 0.2 equiv), and a crystal of AIBN were combined in 5 mL of benzene at room temperature and allowed to react according to the general procedure for 4 h. Purification of the crude reaction mixture by flash column chromatography on silica gel, eluting with hexane and then hexane–Et_2O (9:1), gave 90 mg (72% yield) of the cyclopentane product **12a/12b** as a 4.1:1 ratio of isomers by ^1H NMR integration. Stereochemistry was assigned by comparison of the ^1H NMR spectra of **12a/12b** with those of **11a/11b**.

2,2-Dimethylethyl 3,3-Dibromo-5-ethenyl-1-cyclopentanecarboxylate (12a/12b). ^1H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddd, J = 17.0, 10.2, 7.6 Hz, 1 H), 5.77 (ddd, J = 17.2, 10.1, 8.3 Hz, 1 H, major), 5.15 (d, J = 17.1 Hz, 1 H, major), 5.12 (d, J = 15.1 Hz, 1 H, minor), 5.08 (d, J = 10.1 Hz, 1 H, major) 5.05 (d, J = 10.5 Hz, 1 H, minor), 3.29 (m, 1 H), 3.09 (m, 3 H), 2.93 (m, 1 H), 2.62 (dd, J = 10.1, 4.0 Hz, 1 H), 1.45 (s, 9H, minor), 1.42 (s, 9 H, major); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 171.3, 138.9, 135.7, 117.2, 115.7, 81.4 (major and minor), 62.7, 61.9, 56.9, 56.2, 54.5, 53.7, 49.7, 46.8, 45.6, 44.3, 28.2, 28.0; MS m/z (relative intensity) 355 ((M + 2)H^+, 12), 299 ((M + 2) – C_4H_8, 44), 219 ((M + 2) – C_4H_8Br, 100); HRMS calcd for $C_8H_{10}Br_2O_2$ (M^+ – C_4H_9), 295.9057; found, 295.9044.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with Butyl Vinyl Ether. *gem*-Dichlorovinylcyclopropane **5a** (95 mg, 0.69 mmol), butyl vinyl ether (135 μL, 1.05 mmol, 1.5 equiv), phenyl disulfide (16 mg, 0.07 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.07 M) and heated at reflux for 4 h according to the general procedure to give 39 mg (24% yield) of the cyclopentanes **13a/13b** as 1.1:1 mixture of cis/trans isomers by ^1H NMR integration. These compounds decomposed upon attempted flash column chromatogrpahy (silica gel, alumina, florisil). Further purification of the material by HPLC, eluting with hexane–Et_2O (99:1), provided small amounts of partially purified minor product **13b**.

***t*-1-(Butyloxy)-3,3-dichloro-*r*-5-ethenylcyclopentane (13b).** IR (CCl_4) 1643 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddd, J = 18.5, 10.4, 6.8 Hz, 1 H), 5.11 (d, J = 17.3 Hz, 1 H), 5.09 (d, J = 7.8 Hz, 1 H), 3.96 (ddd, J = 6.2, 6.0, 4.3 Hz, 1 H), 3.36 (m, 2 H), 3.02 (ddd, J = 15.2, 6.1, 1.5 Hz, 1 H), 2.98 (m, 1 H), 2.68 (m, 2 H), 2.64 (m, 1 H), 1.50 (m, 2 H), 1.35 (m, 2 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 135.7, 116.3, 89.2, 80.3, 69.5, 55.9, 53.1, 46.9, 31.8, 19.3, 13.9; MS m/z (relative intensity) 237 (MH^+, 11), 201 (M^+ – Cl, 100), 145 (27), 127 (66); HRMS calcd for $C_{11}H_{18}ClO$ (M^+ – Cl), 201.1046; found, 201.1033.

Reaction of *gem*-Dibromovinylcyclopropane 5b with Butyl Vinyl Ether. *gem*-Dibromovinylcyclopropane (100 mg, 0.44 mmol), butyl vinyl ether (66 mg, 0.66 mmol, 1.5 equiv), phenyl disulfide (10 mg, 0.044 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.05 M) according to the general procedure. Purification of the crude material by flash column chromatography, eluting with hexane and then hexane–Et_2O (9:1), gave 41 mg (28% yield) of the cyclopentanes **14a/14b** as a 1:1.4 mixture of stereoisomers (unassigned) by ^1H NMR integration. The dibromo compounds were found to be as unstable as their dichloro counterparts **13a** and **13b** to chromatographic purification.

1-(Butyloxy)-3,3-dibromo-5-ethenylcyclopentane (14a/14b). IR (CCl_4) 1630 (C=C) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.96 (m, 1 H), 5.11 (m, 2 H), 3.98 (m, 1 H, isomer 1), 3.89 (m, 1 H, isomer 2), 3.42 (t, J = 6.5 Hz, 2 H, isomer 1), 3.35 (t, J = 6.5 Hz, 2 H, isomer 2), 3.33 (dd, J = 15.3, 10.3, Hz, 1 H, isomer 1), 3.30 (m, 1 H, isomer 1 and isomer 2) 3.18 (dd, J = 15.7, 7.6 Hz, 1 H, isomer 2), 3.09 (m, 1 H, isomer 1), 2.92 (m, 2 H, isomer 2 and isomer 1), 2.66 (dd, J = 13.2, 8.9 Hz, 1 H, isomer 2), 1.60 (m, 2 H, isomer 1 and isomer 2), 1.39 (m, 2 H, isomer 1 and isomer 2), 0.98 (t, J = 7.2 Hz, 3 H, isomer 1), 0.97 (t, J = 7.1 Hz, 3 H, isomer 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 135.3, 116.4, 115.8, 83.6, 80.4, 70.1, 69.6, 61.5, 60.3, 58.9, 57.2, 56.2, 55.9, 49.3, 46.9, 31.9, 31.8, 19.3, 19.2, 13.9, 13.8; MS m/z (relative intensity) 327 (MH^+, 20), 246 (MH^+ – HBr, 100), 173 (89), 81 (43).

Reaction of *gem*-Dichlorovinylcyclopropane 5a with Methyl α-Bromoacrylate. *gem*-Dichlorovinylcyclopropane **5a** (220 mg, 1.47 mmol), methyl α-bromoacrylate (318 mg, 2.21 mmol, 1.5 equiv), phenyl disulfide (33 mg, 0.015 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.07 M) at room temperature according to the general procedure. Purification of the crude material by flash column chromatography on silica gel eluting with hexane gave 111 mg (61% yield) of the cyclopentanes **15a/15b** as a 14:1 ratio of isomers by ^1H NMR integration.

Methyl *t*-1-Bromo-3,3-dichloro-*r*-5-ethenylcyclopentanecarboxylate (15a). IR (CCl_4) 1715 (C=O) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 5.83 (ddd, J = 17.0, 14.6, 10.6 Hz, 1 H), 5.25 (d, J = 10.0 Hz, 1 H), 5.22 (d, J = 18.6 Hz, 1 H), 3.81 (d, J = 13.9 Hz, 1 H), 3.77 (s, 3 H), 3.59 (m, 1 H), 3.39 (d, J = 16.5 Hz, 1 H), 2.98 (dd, J = 14.2, 6.4 Hz, 1 H), 2.78 (dd, J = 14.2, 10.1 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 169.3, 132.0, 119.0, 87.1, 62.7, 57.3, 53.4, 52.9, 52.8; MS m/z (relative intensity) 303 ((M + 2)H^+), 267, 221, 185; HRMS calcd for $C_9H_{11}BrCl_2O_2$, 299.9320; found, 299.9307.

Proof of Relative Ring Stereochemistry of Cyclopentane 15a by Iodolactonization. Iodine (254 mg, 1.40 mmol, 3 equiv) was added to an ice-cooled solution of bromocyclopentane **15a** (130 mg, 0.460 mmol), in 3 mL of dry acetonitrile. The mixture was stirred under Ar for 2 h. It was then taken up in 20 mL of Et_2O, washed with saturated $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude material was purified by flash column chromatography on silica gel, eluting with hexane and then hexane–Et_2O (9:1), to give the iodolactone **21** as a 1:1 mixture of stereoisomers. MS m/z (relative intensity) 415 ((M + 2)H^+), 333 (M^+ – HBr, 100), 297 (13); HRMS calcd for $C_8H_8BrCl_2IO_2$, 411.8132; found, 411.8139. The isomers were separated by flash column chromatography on silica gel eluting with hexane, but relative stereochemistry was not assigned.

Isomer 1. ^1H NMR (300 MHz, $CDCl_3$) δ 4.67 (ddd, J = 9.9, 4.5, 2.6 Hz, 1 H), 3.57 (dd, J = 10.1, 4.6 Hz, 1 H), 3.53 (d, J = 13.8 Hz, 1 H), 3.42 (m, 1 H), 3.40 (t, J = 10.0 Hz, 1 H), 3.22 (d, J = 15.2 Hz, 1 H), 3.14 (dd, J = 11.7, 9.4 Hz, 1 H), 2.65 (dd, J = 12.1, 6.2 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 173.9, 86.2, 82.8, 60.6, 54.0, 53.7, 52.8, 5.2.

Isomer 2. ^1H NMR (360 MHz, $CDCl_3$) δ 5.00 (m, 1 H), 3.66 (ddd, J = 11.1, 7.3, 5.6 Hz, 1 H), 3.41 (m, 3 H), 3.04 (t, J = 10.3 Hz, 1 H), 2.93 (dd, J = 13.9, 10.3 Hz, 1 H), 2.36 (dd, J = 13.9, 10.1 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 173.2, 86.4, 82.8, 60.6, 59.9, 54.1, 52.8, 5.2.

Reduction of Bromocyclopentane 15a: (1) With SmI_2. A slurry of SmI_2·2THF (188 mg, 0.343 mmol, 1.5 equiv) in 2.5 mL of THF was cooled to –78 °C under Ar, and the bromocyclopentane **15a** (65 mg, 0.23 mmol, 1 equiv) dissolved in 2.5 mL of THF was added dropwise by syringe. A color change from dark blue to yellow occurred within 5 min. The mixture was allowed to stir at –78 °C for an additional 30 min and was then quenched by addition of excess trifluoroacetic acid dissolved in dry Et_2O. The mixture was warmed to 0 °C , taken up in Et_2O, and washed with dilute $NaHCO_3$, water, and brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo to leave a yellow oil. The crude product was purified by flash column chromatography on silica gel, eluting with hexane and then hexane–Et_2O (9:1), to give 32 mg (66% yield) of cyclopentanes **9a/9b** as a clear oil, along with 9 mg of unreacted starting material. ^1H NMR analysis of reduction products **9a/9b** showed them to be a 12:1 mixture of stereoisomers. This spectrum was found to be identical to a standard spectrum of the unseparated cyclopentanes **9a/9b**, in which the major compound was identified as the cis isomer.

(2) With Bu_3SnH. (A) Photochemical Conditions. A solution of the bromocyclopentane **15a** (50 mg, 0.18 mmol), Bu_3SnH (67 mg, 0.23 mmol, 1.3 equiv), and a crystal of AIBN in 3 mL of toluene was purged with Ar, cooled to –30 °C, and irradiated with a sunlamp for 10 h. The mixture was then warmed to room temperature and concentrated in vacuo. The residue was dissolved in Et_2O and treated with saturated KF in ethanol. The mixture was filtered through Celite and concentrated in vacuo, leaving a yellow oil. The crude product was purified by flash column chromatography on silica gel, eluting with hexane, to give 22 mg (61% yield) of the cyclopentane as a colorless oil. ^1H NMR analysis of this product showed it to be a mixture of isomers **9a/9b** in a 7:1 ratio.

(B) Thermal Conditions. Bromocyclopentane **15a** (100 mg, 0.360 mmol) and *n*-Bu_3SnH (135 mg, 0.464 mmol, 1.5 equiv) were dissolved in 5 mL of benzene. The solution was purged with Ar and heated at reflux for 7 h. It was then cooled to room temperature and concentrated in vacuo. The crude product was purified according to part 2A to give 47 mg (64% yield) of the cyclopentanes **9a/9b**, the major isomer of which was assigned to be the cis compound **9a**, as above.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with α-Methylenebutyrolactone. *gem*-Dichlorovinylcyclopropane **5a** (80 mg, 0.59 mmol), α-methylenebutyrolactone (120 μL, 1.20 mmol, 2 equiv), phenyl disulfide (14 mg, 0.059 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.08 M) at room temperature for 3 h according to the general procedure. Purification of the crude material by flash column chromatography on silica gel eluting with hexane–Et_2O (5:1) gave 84 mg (61% yield) of the cyclopentanes **16a/16b** as a 15:1 ratio of isomers by ^1H NMR integration. The minor isomer was not further characterized.

8,8-Dichloro-*c*-6-ethenyl-2-oxaspiro[4.4]nonan-1-one (16a). IR (CCl_4) 1735 (C=O) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 5.80 (dt, J = 16.9, 9.1 Hz, 1 H), 5.28 (d, J = 14.0 Hz, 1 H), 5.15 (dd, J = 9.9, 1.4 Hz, 1 H), 4.25 (m, 1 H), 3.22 (d, J = 13.8 Hz, 1 H), 3.08 (m, 1 H), 2.65 (m, 3 H), 2.45 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 178.8, 135.3, 119.4, 88.8, 65.6, 57.9, 53.9, 53.4, 51.7, 38.7; MS m/z (relative intensity) 235 (MH^+, 79), 197 (M^+ – HCl, 100), 155 (26); HRMS calcd for $C_{10}H_{12}Cl_2O_2$, 234.0214; found, 234.0126.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with 2-Furanone. *gem*-Dichlorovinylcyclopropane **5a** (75 mg, 0.55 mmol, 1 equiv), 2 furanone (195 μL, 2.75 mmol, 5 equiv), phenyl disulfide (25 mg, 0.11 mmol, 0.2 equiv), and a crystal of AIBN were combined in 8 mL of benzene and heated at reflux for 3 h according to the general procedure to give 39 mg (32% yield) of the cyclopentane **17a/17b** as a 6:1 mixture of products by ^1H NMR integration. The isomers were separated by HPLC, eluting with hexane–Et_2O (98:2), to give the pure cis (major) isomer **17a** and the trans (minor) isomer **17b** contaminated with a small amount of an unsaturated compound (assigned by virtue of extra signals in the olefinic region of the ^{13}C spectrum) that was otherwise unidentified. Attempts to further purify the minor (trans) isomer by HPLC were not successful.

4,4-Dichloro-*c*-6-ethenyl-*r*-*cis*-1*H*-cyclopenta[*c*]furan-1-one (17a). IR (CCl_4) 1785 (C=O), 1630 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.85 (ddd, J = 16.8, 10.4, 6.5 Hz, 1 H), 5.22 (d, J = 16.8 Hz, 1 H), 5.15 (d, J = 10.4 Hz, 1 H), 4.47 (dd, J = 10.6, 9.8 Hz, 1 H), 4.23 (dd, J = 10.7, 6.9 Hz, 1 H), 3.74 (dddd, J = 10.1, 8.3, 6.7, 1.6 Hz, 1 H), 3.45 (m, 1 H), 3.32 (dd, J = 10.3, 8.6 Hz, 1 H), 2.77 (ddd, J = 14.1, 5.9, 1.3 Hz, 1 H), 2.41 (dd, J = 11.8, 5.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 133.9, 117.7, 90.2, 69.4, 56.8, 49.7, 46.3, 43.1; MS m/z (relative intensity) 220 (M^+, 10), 185 (32), 141 (100), 105 (100); HRMS calcd for $C_9H_{10}Cl_2O_2$, 220.0058; found, 220.0039.

4,4-Dichloro-*t*-6-ethenyl-*r*-*cis*-1*H*-cyclopenta[*c*]furan-1-one (17b). IR (CCl_4) 1780 (C=O), 1640 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.91 (ddd, J = 16.9, 10.0, 6.9 Hz, 1 H), 5.66 (d, J = 17.0 Hz, 1 H), 5.14 (d, J = 10.1 Hz, 1 H), 4.43 (dd, J = 10.7, 9.9 Hz, 1 H), 4.29 (dd, J = 10.9, 6.1 Hz, 1 H), 3.65 (ddd, J = 9.1, 6.1, 1.5 Hz, 1 H), 3.42 (pentet, J = 8.5 Hz, 1 H), 2.96 (ddd, J = 14.9, 8.3, 1.0 Hz, 1 H), 2.42 (dd, J = 15.0, 6.2 Hz, 1 H), 2.14 (dd, J = 13.3, 12.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 135.4, 125.4, 88.8, 72.2, 46.0, 41.2, 36.3, 32.1; MS m/z (relative intensity) 221 (MH^+, 100), 141 (41), 105 (25); HRMS calcd for $C_9H_{10}Cl_2O_3$, 220.0058; found, 220.0045.

Reaction of *gem*-Dichlorovinylcyclopropane 5a with Crotononitrile. *gem*-Dichlorovinylcyclopropane **5a** (75 mg, 0.55 mmol), crotononitrile (224 μL, 2.75 mmol, 5 equiv), phenyl disulfide (25 mg, 0.11 mmol, 0.1 equiv), and a crystal of AIBN were combined in benzene (0.07 M) at room temperature according to the general procedure to give 81 mg (73% yield) of the cyclopentanes **18a–d** as a mixture of isomers. GC analysis (carbowax, 105 °C) of the material gave three signals with retention times of 3.79, 6.28, and 8.00 min in a ratio of 3.8:1:1. HPLC separation of the isomers, eluting with hexane–Et_2O (9:1), gave clean samples of the first two isomers. The last component was found to be a mixture (5:1) of two cyclopentane products and was analyzed only by ^1H NMR and MS. Hence, the GC data notwithstanding, four stereoisomers were formed in a 19:5:5:1 ratio.

3,3-Dichloro-*c*-5-ethenyl-*t*-2-methyl-*r*-1-cyclopentanenitrile (18a). Retention time (105 °C, carbowax) 3.79 min; IR (CCl_4) 1660 (C=C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.85 (ddd, J = 16.8, 10.1, 9.6 Hz, 1 H), 5.23 (d, J = 10.1 Hz, 1 H), 5.17 (d, J = 14.6 Hz, 1 H), 3.12 (pentet, J = 8.3 Hz, 1 H), 2.98 (dd, J = 15.3, 6.1 Hz, 1 H), 2.92 (dd, J = 10.3, 6.9 Hz, 1 H), 2.70 (dq, J = 10.5, 6.4 Hz, 1 H), 2.45 (dd, J = 14.1, 9.9 Hz, 1 H), 1.38 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 118.4, 117.7, 92.3, 54.2, 52.8, 40.1, 38.2, 12.8; MS m/z (relative intensity) 167 (M^+ – HCl, 5), 113 (48), 83 (50), 55 (100). HRMS calcd for $C_9H_{10}ClN$ (M^+ – HCl), 167.0510; found, 167.0503.

3,3-Dichloro-*t*-5-ethenyl-*c*-2-methyl-*r*-1-cyclopentanenitrile (18b). Retention time (105 °C, carbowax) 6.28 min; ^1H NMR (300 MHz, $CDCl_3$) δ 5.80 (ddd, J = 17.7, 10.3, 6.8 Hz, 1 H), 5.25 (d, J = 17.0 Hz, 1 H), 5.18 (d, J = 10.1 Hz, 1 H), 3.24 (m, 1 H), 2.98 (dd, J = 10.0, 7.3 Hz, 1 H), 2.90 (dd, J = 13.9, 7.6 Hz, 1 H), 2.73 (m, 1 H), 2.35 (dd, J = 13.7, 10.9 Hz, 1 H), 1.45 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 118.5, 118.2, 92.1, 54.3, 52.8, 40.1, 38.2, 12.4; MS m/z (relative intensity) 167 (M^+ – HCl, 20), 132 (73), 113 (37), 87 (42), 55 (100); HRMS calcd for $C_9H_{11}Cl_2N$, 203.0269; found, 203.0275.

3,3-Dichloro-5-ethenyl-2-methyl-1-cyclopentanenitrile (no stereochemistry implied) **(18c).** Retention time (105 °C, carbowax) 8.00 min; ^1H NMR (200 MHz, $CDCl_3$) δ 5.80 (ddd, J = 17.3, 10.0, 7.5 Hz, 1 H), 5.27 (d, J = 17.3 Hz, 1 H), 5.19 (d, J = 10.3 Hz, 1 H), 3.25 (pentet, J = 7.2 Hz, 1 H), 2.90 (m, 3 H), 2.35 (dd, J = 13.4, 10.8 Hz, 1 H), 1.45 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 117.6, 88.8, 85.3, 52.2, 50.7, 45.3, 37.6; MS m/z (relative intensity) 204 (MH^+, 100), 167 (M^+ – HCl, 26), 132 (59); HRMS calcd for $C_9H_{11}Cl_2N$, 203.0269; found, 203.0261.

Reaction of *gem*-Dichlorovinylcyclopropane 8 with Crotononitrile. *gem*-Dichlorovinylcyclopropane **8** (20 mg, 0.11 mmol), crotononitrile (15 μL, 0.22 mmol, 2 equiv), phenyl disulfide (2.5 mg, 0.011 mmol, 0.1 equiv) and AIBN (2 mg) were combined in benzene (0.04 M) at room temperature according to the general procedure. Purification of the crude material by flash column chromatography on silica gel eluting with hexane gave 19 mg (69% yield) of the cyclopentanes **19a/19b** as a 3.4:1 mixture of isomers by ^1H NMR integration. The isomers were separated by HPLC using hexane–Et_2O (95:5) as eluent.

3,3-Dichloro-*t*-2-methyl-*c*-5-(1-propylethenyl)-*r*-1-cyclopentanenitrile (19a). IR (CCl_4) 2243 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (s, 1 H), 4.99 (s, 1 H), 3.15 (m, 1 H), 2.98 (t, J = 10.6 Hz, 1 H), 2.80 (dd, J = 12.8, 7.0 Hz, 1 H), 2.68 (m, 2 H), 2.06 (q, J = 6.4 Hz, 2 H), 1.39 (m, 2 H), 1.12 (d, J = 6.8 Hz, 3 H), 0.82 (t, J = 7.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 119.0, 112.8, 92.7, 55.1, 51.3, 46.1 42.6, 38.3, 21.0, 13.9, 12.8; MS m/z (relative intensity) 246 (M^+ – HCl, 35); HRMS calcd for $C_{12}H_{17}C_2N$, 245.0738; found, 245.0751.

3,3-Dichloro-*c*-2-methyl-*t*-5-(1-propylethenyl)-*r*-1-cyclopentanenitrile (19b). IR (CCl_4) 2242 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.93 (s, 1 H), 4.92 (s, 1 H), 3.23 (ddd, J = 13.4, 11.1, 6.9 Hz, 1 H), 3.03 (dd, J = 10.3, 7.4 Hz, 1 H), 2.85 (dd, J = 13.6, 7.1 Hz, 1 H), 2.70 (qd, J = 7.4, 6.8 Hz, 1 H), 2.44 (dd, J = 13.6, 11.9 Hz, 1 H), 2.06 (t, J = 6.3 Hz, 2 H), 1.50 (m, 2 H), 1.46 (d, J = 6.8 Hz, 3 H), 0.95 (t, J = 6.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 118.7, 112.8, 91.8, 54.7, 51.3, 42.5, 38.3, 37.9, 20.9, 13.9, 12.8; MS m/z (relative intensity) 246 (MH^+, 100), 210 (M^+ – HCl, 43), 174 (17); HRMS calcd for $C_{12}H_{17}Cl_2N$, 245.0738; found, 245.0716.

Acknowledgment. We thank the NIH (Grant GM37681) for financial support.

Supplementary Material Available: DNOE measurements for **9a, 9b, 10a, 13a, 16a, 17a, 18a, 18b, 19a,** and **19b,** copies of ^1H NMR spectra for **8, 9a, 9b, 10a, 10b, 11a, 13a, 15a, 21, 16a, 17a, 18a, 18b, 18c,** and **19b,** and copies of ^{13}C NMR spectra for **8, 9a, 9b, 10b, 11a, 13a, 15a, 21, 16a, 17a, 18a, 18b, 18c, 19a,** and **19b** (32 pages). Ordering information is given on any current masthead page.