Carbenoid versus Vinylogous Reactivity in Rhodium(II)-Stabilized Vinylcarbenoids

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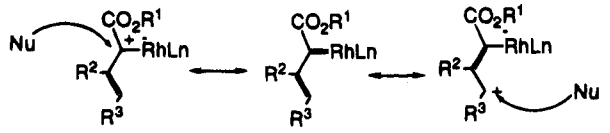
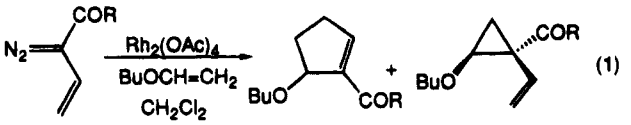
Rhodium(II)-stabilized vinylcarbenoid intermediates display electrophilic character at both the carbenoid site and the vinylogous position. The solvent and catalyst as well as the vinylcarbenoid structure have major effects on the regiochemical outcome of the reaction of vinylcarbenoids with alkenes and dienes. Reaction of vinylcarbenoids with vinyl ethers can lead to the formation of either cyclopropanes or cyclopentenes while reaction of vinylcarbenoids with cyclopentadiene can lead to the formation of either bicyclo[3.2.1]octadiene or bicyclo[2.2.1]heptene derivatives.

A number of studies on the chemistry of rhodium(II)-stabilized vinylcarbenoids have been reported in recent years.[1-5] Our interest in vinylcarbenoids has been primarily focused on developing a general route to seven-membered rings by the tandem cyclopropanation/Cope rearrangement that occurs on reaction of vinylcarbenoids with dienes.[1] The vinylcarbenoids used in our earlier studies were derived from vinyldiazomethanes containing two electron-withdrawing groups as these precursors are not prone to rearrangement to pyrazoles.[6] On extension of the chemistry to vinylcarbenoids containing a single electron-withdrawing group, it was discovered that these systems displayed electrophilic reactivity at the vinyl terminus in addition to the carbenoid site, as illustrated in structure **1**.[7,8] A systematic study to determine what factors are involved in controlling the site of electrophilic reactivity in rhodium(II)-stabilized vinylcarbenoids is the basis of this paper.[9]



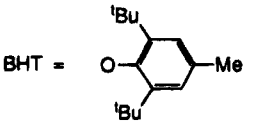
1

The reaction of vinylcarbenoids with butyl vinyl ether was used as the initial model system. Rhodium(II)-catalyzed decomposition of vinyldiazomethanes containing a substituent at the vinyl terminus (e.g. COOEt, Ph, Me) displayed normal carbenoid reactivity leading to cyclopropanation products in high yields.[10,11] Extending the reaction, however, to the less substituted system **2a** led to a more complicated reaction. Rhodium(II) acetate catalyzed decomposition of **2a** in the presence of butyl vinyl ether with CH_2Cl_2 as solvent gave rise to a mixture of the cyclopentene **3a** (24% yield) and the vinylcyclopropane **4a** (37% yield). Even though **4a** would be expected to readily undergo a vinylcyclopropane/cyclopentene rearrangement on account of the push-pull functionality present,[11,12] the expected cyclopentene from such a rearrangement would be a regioisomer of **3a**.[11] Confirmation that **3a** was not derived from **4a** was obtained by demonstrating that **4a** was stable under the reaction conditions for the rhodium(II)-catalyzed decomposition. Consequently, it was reasoned that in order to obtain the regiochemistry observed in the formation of **3a**, it would have been necessary for the initial interaction between the vinyl ether and vinylcarbenoid to have occurred at the vinyl terminus of the carbenoid instead of at the carbenoid center.



(1)

2a (R = OMe) **3a** (24%) **4a** (37%)
2b (R = OtBu) **3b** (22%) **4b** (33%)
2c (R = BHT) **3c** (90%) **4c** (0%)



In order to further probe the concept that the chemistry of vinylcarbenoids may originate at the vinyl terminus, the effect of increasing the size of the ester group on the regiochemistry was examined. Changing the ester from methyl to *tert*-butyl resulted in only minor changes in product ratio. However, increasing the size of the ester group to the very bulky 2,6-di-(*tert*-butyl)-4-hydroxytolyl (BHT) derivative[13] resulted in a profound effect. The cyclopentene **3c** was cleanly formed in 90% yield without

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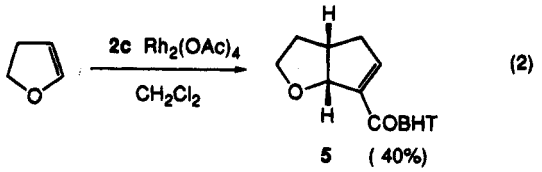
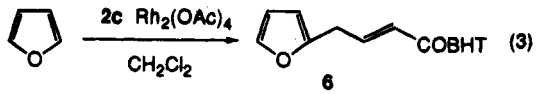
any evidence in the crude NMR of cyclopropane products. This result supports the notion that cyclopentene formation occurs through initial attack at the vinyl terminus of the vinylcarbenoid as large ester groups would be expected to sterically hinder attack at the carbenoid center.

The bulky vinyldiazomethane **2c** could be used in reactions with other vinyl ethers. Rhodium(II) acetate catalyzed decomposition of **2c** in the presence of dihydrofuran gave rise to the bicyclic system **5** in 40% yield. Further evidence to support that the site of initial reactivity was the vinyl terminus was seen in the reaction of **2c** with furan which led to the formation of the alkylation product **6** in 60% yield. For effective capture of the vinylcarbenoid from **2c** it is necessary to use electron-rich alkenes as decomposition of **2c** in the presence of styrene resulted in an uncharacterizable mixture.

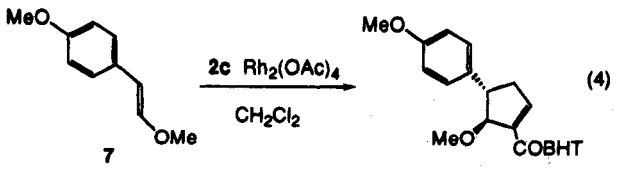


5 (40%) (2)

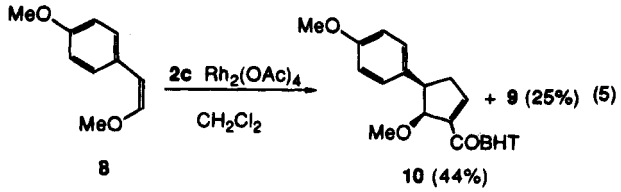


6 (3)

In order to gain some information about the likely intermediates that may be involved in these transformations, the question of stereocontrol was examined by decomposition of the vinyldiazomethane **2c** in the presence of either *E* or *Z* vinyl ethers, **7** and **8**. The reaction with the *E* vinyl ether **7** resulted in the exclusive formation of the trans cyclopentene **9** in 85% yield. On reaction with the *Z* vinyl ether **8**, however, a mixture of cis and trans cyclopentenes, **10** (44% yield) and **9** (25% yield), was formed. Formation of **9** was shown not to be due to isomerization of **10** as **10** remained unchanged on exposure to the rhodium(II) catalysis reaction conditions. These results are indicative that cyclopentene formation does not occur by a concerted process, and considering the nature of the reactants, this would mean that the involvement of zwitterionic intermediates would be most likely.



7 9 (85%) (4)



8 10 (44%) + 9 (25%) (5)

Reactions of vinylcarbenoids that proceed through zwitterionic intermediates may be strongly suppressed by the use of nonpolar solvents.[14,15] In order to test the likelihood that zwitterionic intermediates were involved in cyclopentene formation, the effect of solvent and catalyst on product distribution was examined. As described earlier, decomposition of **2a** in the presence of butyl vinyl ether under the standard reaction conditions of rhodium(II) acetate/CH_2Cl_2 gave a mixture of **3a** (24% yield) and **4a** (37% yield). When rhodium(II) octanoate/pentane was used, conditions that strongly disfavor formation of products derived from dipolar intermediates,[14,15] the cyclopropane **4a** was formed in 91% yield without any evidence of the cyclopentene **3a**.[9] Conversely, electron-withdrawing ligands on the metal seemed to enhance terminus reactivity and on using rhodium(II) perfluorbutyrate/CH_2Cl_2 a slightly improved yield of **3a** (32%) was obtained. The reaction was not very satisfactory, however, because it appeared that the rhodium(II) perfluorobutyrate was being deactivated during the course of the reaction. Similar effects of solvent and catalyst on the extent of formation of products involving terminus reactivity have been seen in the reaction between vinylcarbenoids and pyrroles.[8]

The next series of experiments were directed at vinyldiazomethanes with substituents at the central carbon. Introduction of a moderately sized group such as methyl enhanced the formation of the cyclopentene derivative. Thus, rhodium(II) acetate catalyzed decomposition of **11a** resulted in the preferred formation of the cyclopentene **12a** over the cyclopropane **13a** in a ratio of 4:1. On further increase of substituent size to the phenyl derivative **11b**, cyclopropane formation was completely inhibited but the yield of the cyclopentene **12b** was only 45%. A side product in this case was a mixture of cyclopropene dimers of undefined regiochemistry. The cyclopentene **12b** was still formed (12% yield) on changing the reaction conditions to rhodium(II) octanoate/pentane. This results is in sharp contrast to that observed with the vinyldiazomethane **2a**, where the use of pentane as solvent totally suppressed cyclopentene formation. On increasing the bulk at the central carbon even further to the *tert*-butyl derivative **11c**, neither **12c** nor **13c** were formed. Instead a very unstable compound was formed, which was tentatively assigned the cyclopropene structure **14c**. Convincing evidence that cyclopropenes **14** were generated in the reactions of **11b** and **11c** was obtained by decomposition of either **11b** or **11c** in the presence of the benzofuran **15**. Under these conditions, the suspected cyclopropenes **14** were readily trapped as their Diels–Alder cycloadducts **16**. Therefore, it would be reasonable to assume that the vinylcarbenoids derived from **11b** and **11c** are not efficiently trapped by butyl vinyl ether, particularly at the carbenoid site, and instead cyclize to the cyclopropenes. It should be stressed that even though vinylcarbenes in general readily rearrange to cyclopropenes,[16] the reactions described above were the first examples we had seen of rhodium(II)-stabilized vinylcarbenoids derived from vinyldiazomethanes undergoing rearrangement to cyclopropenes.

Having found that control of vinylcarbenoid reactivity could be achieved by appropriate structural modifications, the reaction of vinylcarbenoids with cyclopentadiene was then examined.[7] In this case, reaction at the

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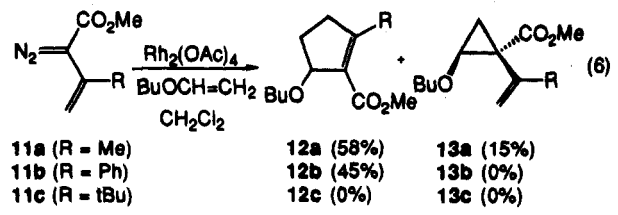
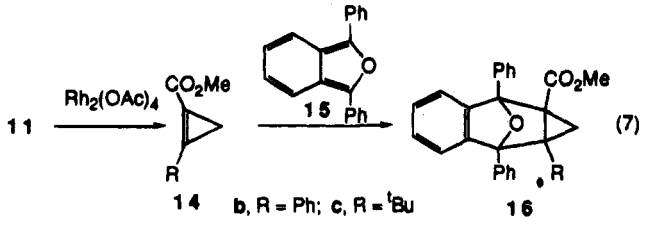
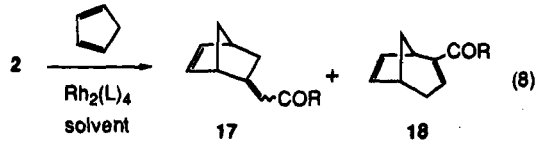


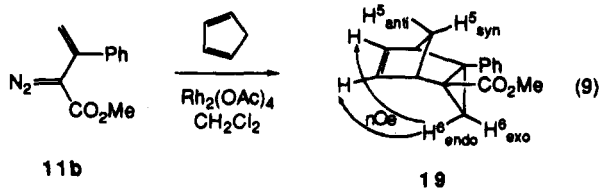


vinyl terminus of the vinylcarbenoid led to the [2.2.1]-bicycloheptadiene **17**, while the product derived from reactivity at the carbenoid center was the tandem cyclopropanation/Cope rearrangement product **18**. Once again, large ester groups enhanced reactivity at the vinyl terminus. As seen in Table 1, entries 1–3, the methyl ester **2a** gave a 1:2 ratio of **17a** and **18a** the *tert*-butyl derivative **2b** gave a 1:1 ratio of **17b** to **18b**, while the 2,6-di(*tert*-butyl)tolyl derivative **2c** gave exclusive formation of **17c**. The product distribution was also highly dependent on catalyst and solvent with ratios of **17a** to **18a** varying from 1:50 with rhodium(II) octanoate/pentane to 2:1 with rhodium(II) trifluoroacetate/CH_2Cl_2.[7]



a: R = OMe; b: R = OtBu; c: R = BHT

The reluctance of vinylcarbenoids with large substituents at the central carbon to undergo cyclopropanation reactions again became apparent on rhodium(II) acetate catalyzed decomposition of **11b** in the presence of cyclopentadiene. No products related to **17** or **18** were obtained but instead the cyclopropene cycloadduct **19** was formed in 62% yield. The stereochemical assignment for **19** was based on a detailed proton NMR and NOE analysis, the most characteristic element of which was the observation of a distinctive long-range coupling between H_{5anti} and H_{6endo}.[17]



11b 19

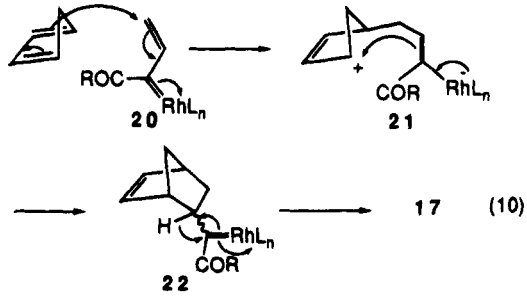
These studies show that the reactions of vinylcarbenoids with alkenes and dienes are highly dependent on vinylcarbenoid structure. Vinylcarbenoids containing functionality at the vinyl terminus react cleanly at the carbenoid center, while those unsubstituted at the vinyl terminus display electrophilic reactivity at either the vinyl terminus or the carbenoid center. Very bulky esters strongly favor reactivity at the vinyl terminus, presumably by sterically impeding attack at the carbenoid center. Introduction of functionality at the central carbon of the vinylcarbenoid leads to inhibition of reactivity at both the carbenoid center and the vinyl terminus, and cyclopropene formation may become the dominant process with these systems.

Table 1. Reaction of 2 with Cyclopentadiene (eq 8)

reaction conditions	R	17:18 ratio
$Rh_2(OAc)_4/CH_2Cl_2$	Me	33:67[7]
$Rh_2(OAc)_4/CH_2Cl_2$	$C(CH_3)_3$	48:52
$Rh_2(OAc)_4/CH_2Cl_2$	2,6-di(^{t}Bu)-4-MePh	100:0
$Rh_2(OOct)_4$/pentane	Me	2:98[7]
$Rh_2(TFA)_4/CH_2Cl_2$	Me	68:32[7]

Many features of the vinyl terminus reactivity are indicative of a stepwise mechanism that involves charged intermediates. Carbenoid reactions proceeding through charged intermediates are strongly suppressed by carrying out the reactions in nonpolar solvents instead of dichloromethane,[14,15] and this was very much the case here for the reactions with **2a** (but not for **11b**). The vinyl terminus reactivity can also be enhanced by using electron-withdrawing ligands which would stabilize negative charge on the rhodium. The loss of stereochemistry observed in the reaction of the *Z* vinyl ether **9** with **2c** is also consistent with a stepwise mechanism.

A reasonable mechanism for the formation of **17** from the reaction of **2** with cyclopentadiene is shown in eq 10. Electrophilic attack by the vinyl terminus of the vinylcarbenoid **20** on cyclopentadiene would generate the zwitterionic structure **21** which then could undergo ring closure to form a second carbenoid species (**22**). Rearrangement of **22** by a 1,2-hydride shift would generate the observed product **17**. The formation of alkylation products such as **6** and the parallel effects of solvent and catalysts on the reactions of vinylcarbenoids with both cyclopentadiene and butyl vinyl ether tend to disfavor an alternative mechanism involving a concerted cycloaddition between cyclopentadiene and the vinylcarbenoid **20**, even though such reactions are well precedented for the more stable Fisher carbene complexes.[18]



In order to test the mechanistic hypothesis, a precursor (**25**) for the unambiguous formation of the proposed carbenoid intermediate **22** was prepared as shown in Scheme 1. The direct cycloaddition between the vinyldiazomethane **2b** and cyclopentadiene failed to generate the precursor **25**, and so, an alternative synthetic approach was devised. Treatment of **2b** with rhodium(II) acetate/propylene oxide followed by a Diels–Alder cycloaddition between the resulting vinylglyoxylate and

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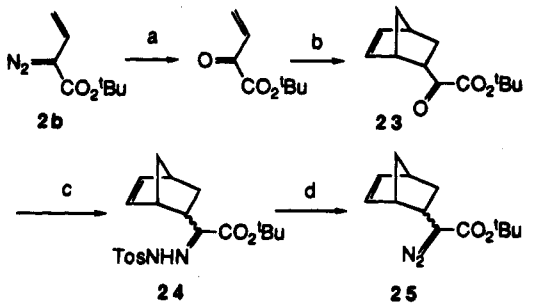
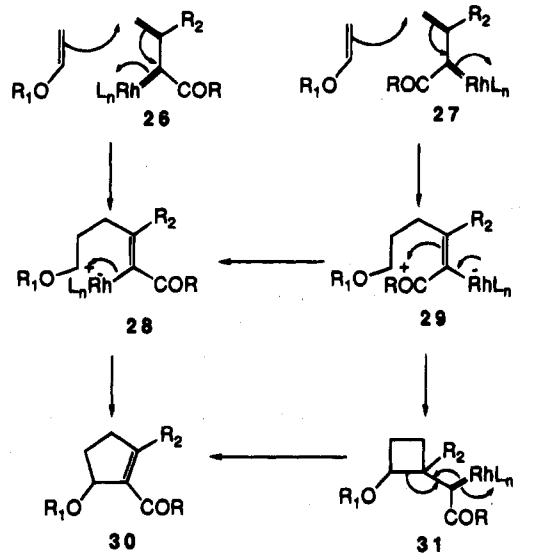
Scheme 1[a]

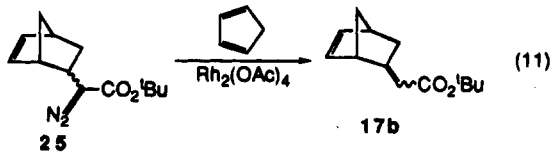


[a] (a) $Rh_2(OAc)_4$/butylene oxide; (b) cyclopentadiene; (c) TosNHNH$_2$/HCl; (d) NaH.

Scheme 2



cyclopentadiene generated the bicyclic product **23**. Treatment of **23** with tosylhydrazine followed by base generated the precursor **25**. Rhodium(II) acetate catalyzed decomposition of **25** in the presence of cyclopentadiene with CH_2Cl_2 as solvent resulted in the clean formation of the [2.2.1]bicycloheptene **17b** (81% yield), which demonstrated that the proposed second carbenoid species **22** is a viable intermediate for the formation of **17**.



(11)

The formation of cyclopentenes from the reaction of vinylcarbenoids with vinyl ethers can similarly be rationalized to occur by initial attack at the vinyl terminus of the vinylcarbenoid as illustrated in Scheme 2. Two possible zwitterionic intermediates, **28** and **29**, could be formed depending on which of the vinylcarbenoid conformations (**25** or **27**) is involved in the reaction with the vinyl ether. The zwitterionic intermediate **28** derived from the vinylcarbenoid in the s-*Z* configuration **26** has limited charge separation and is capable of direct closure to the cyclopentene **30**. The second zwitterionic intermediate **29** derived from the vinylcarbenoid in the s-*E* configuration **27** has increased charge separation and is incapable of direct closure to the cyclopentene **30**. Instead, either initial isomerization of **29** to **28** or closure to the cyclobutyl carbenoid **31** followed by ring expansion by a 1,2-alkyl shift would be required.

Some evidence that may distinguish between the two possible zwitterionic intermediates, **28** and **29**, is the solvent effect differences that were seen in the reactions of the various vinylcarbenoids with butyl vinyl ether. In the case of the vinyldiazomethane **2a**, cyclopentene formation is totally inhibited when pentane was the solvent, but this was not so for the phenyl-substituted vinyldiazomethane **11b**. This result may indicate that the reaction of **2a** proceeds via the charge-separated zwitterionic intermediate **29**, leading to dramatic solvent effects, while the reaction of **11b** proceeds through the alternative zwitterionic intermediate **28**. Certainly, it would be reasonable to expect the carbenoid from **11b** to preferentially adopt the s-*Z* configuration **26**, the presumed precursor to **28** as this would ensure that the phenyl ring is pointing away from the rhodium carboxylate core. Furthermore, cyclization of vinylcarbenoids to cyclopropenes would be expected to require the vinylcarbenoids to adopt the s-*Z* configuration **26**, which may explain why the vinylcarbenoids derived from **11b** and **11c** are so prone to form cyclopropenes.

In summary, rhodium(II)-stabilized vinylcarbenoid intermediates display electrophilic character at both the carbenoid site and the vinylogous position. Excellent regiocontrol is possible by judicious choice of solvent, catalyst, and vinylcarbenoid. These results help to define the scope and limitations of vinylcarbenoid transformations and lead to some insights about the reactive conformations of the vinylcarbenoids.

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. THF was freshly distilled from sodium benzophenone ketyl. Column chromatography was carried out on silica gel 60 (230–400 mesh). **2a**,[11] **2b**,[20] **2c**,[21] methyl 3-methyl-2-butenoate,[22] methyl 3-phenyl-2-butenoate,[23] and methyl 3-(dimethylethyl)-2-butenoate[24] were prepared by published procedures.

Rhodium(II) Carboxylate Catalyzed Decomposition of Vinyldiazomethane in the Presence of Alkenes. General Procedure. A solution of vinyldiazomethane (1 equiv) in solvent (0.1–0.5 M) was added dropwise to a stirred mixture of rhodium(II) carboxylate (0.01 equiv) and the alkene (5 equiv, 0.1–0.5 M) in solvent, and the solution was heated under reflux in an argon atmosphere. After a further 10–60 min of heating, the solvent was evaporated under reduced pressure. The amounts of vinyldiazomethane, solvent, alkene, 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 5-Butoxy-1-cyclopentene-1-carboxylate (3a) and Methyl 1β-Ethenyl-2β-butoxycyclopropane-1α-carboxylate (4a). **2a** (0.19 g, 1.5 mmol), CH_2Cl_2, butyl vinyl ether (0.75 g, 7.5 mmol), rhodium(II) acetate (0.007 g, 0.015 mmol), (1/9). Crude NMR shows **3a/4a** = 1/1.6. **3a**: 0.07 g (24% yield), colorless oil; ^1H NMR ($CDCl_3$) δ 6.96 (m, 1 H), 4.66 (br d, J = 6.8 Hz, 1 H), 3.73 (s, 3 H), 3.49 (t, J = 6.2 Hz,

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2 H), 2.75–2.55 (m, 1 H), 2.48–2.29 (m, 1 H), 2.20–1.90 (m, 2 H), 1.60–1.25 (m, 4 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.0, 148.0, 137.2, 82.4, 69.3, 51.4, 32.1, 31.3, 30.5, 19.4, 13.9; IR (neat) 1720, 1635 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.41; H, 9.23.

4a: 0.11 g (37% yield).[11]

Dimethylethyl 5-Butoxy-1-cyclopentene-1-carboxylate (3b) and Dimethylethyl 2β-Butoxy-1β-vinylcyclopropane-1α-carboxylate (4b). 2b (0.34 g, 2.0 mmol), CH_2Cl_2, butyl vinyl ether (1.0 g, 10 mmol), rhodium(II) acetate (0.0088 g, 0.02 mmol), (1/9). Crude NMR shows **3b/4b** = 1/1.5. **3b**: 0.16 g (22% yield), colorless oil; ^{1}H NMR ($CDCl_3$) δ 6.84 (m, 1 H), 4.59 (br d, J = 6.0 Hz, 1 H), 3.47 (t, J = 6.6 Hz, 2 H), 2.70–2.50 (m, 1 H), 2.40–2.23 (m, 1 H), 2.18–1.85 (m, 1 H), 1.60–1.40 (m, 5 H), 1.46 (s 9 H), 0.87 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.1, 146.7, 139.1, 82.4, 80.2, 69.5, 32.3, 31.1, 30.7, 28.2, 19.4, 13.9; IR (neat) 1700, 1635 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.72; H, 10.11.

4b: 0.24 g (33% yield).[20]

2,6-Bis(dimethylethyl)-4-methylphenyl 5-Butoxy-1-cyclopentene-1-carboxylate (3c). 2c (1.51 g, 3.7 mmol), CH_2Cl_2, butyl vinyl ether (1.83 g, 18.3 mmol), rhodium(II) acetate (0.016 g, 0.037 mmol), (1/9). **3c**: 1.27 g (90% yield), colorless gum; ^{1}H NMR ($CDCl_3$) δ 7.25 (br s, 1 H), 7.19 (s, 2 H), 4.85 (br d, J = 5.2 Hz, 1 H), 3.63 (t, J = 6.4 Hz, 2 H), 2.95–2.75 (m, 1 H), 2.68–2.45 (m, 1 H), 2.40–2.05 (m, 2 H), 2.38 (s, 3 H), 2.95–2.05 (m, 2 H), 1.65–1.50 (m, 2 H), 1.39 (s, 18 H), 0.94 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.6, 149.1, 145.7, 142.2, 138.3, 134.2, 126.7, 126.6, 82.3, 69.8, 35.1, 32.0, 31.6, 31.4, 30.4, 21.4, 19.2, 13.8; IR (neat) 1720, 1620, 1590 cm^{-1}. Anal. Calcd for $C_{25}H_{38}O_3$: C, 77.68; H, 9.91. Found: C, 77.52; H, 9.86.

2,6-Bis(dimethylethyl)-4-methylphenyl (1Hα,5Hα)-2-Oxabicyclo[3.3.0]oct-7-ene-8-carboxylate (5). 2c (0.72 g, 2.3 mmol), CH_2Cl_2, 2,3-dihydrofuran (0.83 g, 11.5 mmol), rhodium(II) acetate (0.010 g, 0.023 mmol), (1/3–1/1). **5**: 0.55 g (40% yield), pale yellow gum; ^{1}H NMR ($CDCl_3$) δ 7.13 (br s, 3 H), 5.47 (br d, J = 7.0 Hz, 1 H), 3.97–3.87 (m, 1 H), 3.60 (td, J = 9.6, 5.4 Hz, 1 H), 3.20–2.84 (m, 2 H), 2.44–2.31 (m, 1 H), 2.33 (s, 3 H), 2.20–2.10 (m, 1 H), 1.76–1.64 (m, 1 H), 1.34 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 164.7, 148.8, 145.7, 142.3, 142.1, 136.1, 134.3, 127.0, 126.6, 86.4, 65.7, 40.1, 39.7, 35.3, 35.2, 31.6, 31.4, 21.6; IR (neat) 1720, 1625, 1595 cm^{-1}. Anal. Calcd for $C_{22}H_{32}O_3$: C, 77.49; H, 9.05. Found: C, 77.55; H, 9.06.

2,6-Bis(dimethylethyl)-4-methylphenyl 4-(2-Furanyl)-2-butenoate (6). 2c (1.12 g, 3.6 mmol), CH_2Cl_2, furan (1.21 g, 17.8 mmol), rhodium(II) acetate (0.016 g, 0.036 mmol), (1/19–1/9). **6**: 0.75 g (60% yield); ^{1}H NMR ($CDCl_3$) δ 7.37 (m, 1 H), 7.23 (dt, J = 11.6, 6.6 Hz, 1 H), 7.11 (s, 2 H), 6.33 (m, 1 H), 6.15 (d, J = 11.5 Hz, 1 H), 6.10 (m, 1 H), 3.64 (d, J = 6.6 Hz, 2 H), 2.31 (s, 3 H), 1.31 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 166.5, 151.1, 146.0, 145.9, 145.6, 142.1, 142.0, 141.9, 134.5, 127.0, 124.0, 110.5, 106.7, 35.3, 31.6, 31.1; IR 1730, 1660, 1635, 1600 cm^{-1}. Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.70; H, 8.58.

2,6-Bis(dimethylethyl)-4-methylphenyl 5β-Methoxy-4α-(4-methoxyphenyl)-1-cyclopentene-1-carboxylate (9). 2c (1.01 g, 3.23 mmol) CH_2Cl_2, (*E*)-1-(*p*-methoxyphenyl)-2-methoxyethylene (**7**) (1.59 g, 9.7 mmol), rhodium(II) acetate (0.0142 g, 0.03 mmol), (1/9). **9**: 1.23 g (85% yield); ^{1}H NMR ($CDCl_3$) δ 7.32 (d, J = 8.5 Hz, 2 H), 7.24 (br s, 1 H), 7.12 (s, 2 H), 6.87 (d, J = 8.5 Hz, 2 H), 4.52 (br d, J = 5.9 Hz, 1 H), 3.81 (s, 3 H), 3.79–3.42 (m, 2 H), 2.97 (s, 3 H), 2.95–2.31 (m, 1 H), 2.31 (s, 3 H), 1.32 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 165.0, 158.4, 149.3, 145.7, 142.3, 142.2, 138.3, 134.4, 130.3, 126.9, 113.5, 85.1, 59.1, 55.2, 48.9, 38.2, 35.3, 35.2, 31.5, 21.5; IR (neat) 1720, 1610 cm^{-1}. HRMS *m/e* calcd for $C_{29}H_{38}O_4$: 450.2770. Found: 450.2774.

2,6-Bis(dimethylethyl)-4-methylphenyl 5β-Methoxy-4β-(4-methoxyphenyl)-1-cyclopentene-1-carboxylate (10). 2c (0.19 g, 0.61 mmol), CH_2Cl_2, (*Z*)-1-(*p*-methoxyphenyl)-2-methoxyethylene (**8**) (0.1056 g, 0.61 mmol), rhodium(II) acetate (0.003 g, 0.006 mmol), (1/19–1/7), NMR analysis of crude reaction mixture showed **9/8** = 1.3/1. **9**: 0.068 g (25% yield). **10**: 0.12 g (44% yield), pale yellow gum; ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 1 H), 7.14 (s, 2 H), 7.12 (d, J = 8.1 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 4.64 (br s, 1 H), 3.80 (s, 3 H), 3.51–3.48 (m, 1 H), 3.46 (s, 3 H), 3.25 (dddd, J = 19.3, 8.3, 2.2, 2.2 Hz, 1 H), 2.60 (ddd, J = 19.3, 2.9, 2.9 Hz, 1 H), 2.33 (s, 3 H), 1.36 (s, 9 H), 1.34 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 164.5, 158.0, 149.3, 145.4, 142.1, 141.8, 137.2, 136.5, 134.2, 127.3, 126.7, 126.6, 113.9, 91.9, 57.6, 55.0, 48.8, 40.2, 35.0, 34.9, 31.3, 31.1, 21.3; IR (neat) 1740, 1625, 1610 cm^{-1}. Anal. Calcd for $C_{29}H_{38}O_4$: C, 77.29; H, 8.51. Found: C, 77.23; H, 8.51.

General Procedure for the Synthesis of the Vinyldiazomethanes 11. A solution of *n*-butyllithium in hexane (50 mL, 1.6 M, 80 mmol) was added to a stirred solution of diisopropylamine (^{i}Pr$_2$NH) (9.1 g, 12.6 mL, 90 mmol) in THF (100 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min and then cooled down to −78 °C and HMPA (14.4 g, 14 mL, 80 mmol) was added. After 1 h of stirring, methyl 3-substituted-2-butenoate (40 mmol) was added and the solution was stirred for further 30 min. *p*-Tosyl azide (14.64 g, 80 mmol) was then added. After warming to room temperature over 3 h, the mixture was stirred overnight. Petroleum ether (500 mL) was added and the resulting mixture was filtered. The solution was washed with water and saturated sodium chloride solution, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica using the indicated solvent.

Methyl 2-Diazo-3-methyl-3-butenoate (11a). Petroleum ether as eluant. Orange oil (1.21 g, 22%): IR 2080, 1705, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.33 (s, 1 H), 4.88 (s, 1 H), 3.76 (s, 3 H), 1.92 (s, 3 H). The product was of insufficient stability to obtain elemental analysis.

Methyl 2-Diazo-3-phenyl-3-butenoate (11b). Ether–petroleum ether (1:9) as eluant. Orange oil (2.75 g, 34%): IR 2090, 1700, 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 5 H), 5.73 (s, 1 H), 5.29 (s, 1 H), 3.80 (s, 3 H). The product was of insufficient stability to obtain elemental analysis.

Methyl 2-Diazo-3-(dimethylethyl)-3-butenoate (11c). Ether–petroleum ether (1:19) as eluant. Orange oil (0.86 g, 12%): IR 2100, 1700, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.26 (s, 1 H), 5.15 (s, 1 H), 3.60 (s, 3 H), 1.00 (s, 9 H). The product was of insufficient stability to obtain elemental analysis.

Methyl 5-Butoxy-2-methyl-1-cyclopentene-1-carboxylate (12a) and Methyl 1β-(1-Methylethenyl)-2β-butoxycyclopropane-1α-carboxylate (13a). 11a (0.99 g, 7.0 mmol), CH_2Cl_2, butyl vinyl ether (3.51 g, 35 mmol), rhodium(II) acetate (0.039 g, 0.07 mmol), (1/9). Crude NMR shows **12a/13a** = 4.4/1. **12a**: 0.86 g (58% yield); ^{1}H NMR δ 4.65 (br d, J = 6.6 Hz, 1 H), 3.71 (s, 3 H), 3.50 (dt, J = 15.9, 6.6 Hz, 1 H), 3.39 (dt, J = 15.9, 6.6 Hz, 1 H), 2.69 (dt, J = 16.7, 7.5 Hz, 1 H), 2.30 (ddd, J = 18.3, 8.8, 2.9 Hz, 1 H), 2.11 (s, 3 H), 2.10–1.75 (m, 2 H), 1.60–1.40 (m, 2 H), 1.40–1.20 (m, 2 H), 0.87 (t, J= 7.3 Hz, 3 H); ^{13}C NMR δ 165.9, 160.5, 128.7, 84.5, 68.9, 50.8, 38.2, 32.0, 28.6, 19.3, 16.5, 13.8; IR (neat) 1710, 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.62; H, 9.55.

13a: 0.23 g (15% yield), colorless oil; ^{1}H NMR δ 5.10 (s, 1 H), 4.95 (s, 1 H), 3.73 (dd, J = 6.8, 4.6 Hz, 1 H), 3.64 (s, 3 H), 3.60–3.40 (m, 2 H), 1.90 (s, 3 H), 1.60–1.20 (m, 6 H), 0.87 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 173.2, 139.8, 116.8, 71.3, 63.9, 52.0, 35.5, 31.6, 22.6, 21.0, 19.2, 13.8; IR (neat) 1730, 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.60; H, 9.51.

Methyl 3-Butoxy-5-phenyl-1-cyclopentene-1-carboxylate (12b). 11b (0.52 g, 2.5 mmol), CH_2Cl_2, butyl vinyl ether (5.19 g, 51.9 mmol), rhodium(II) acetate (0.0114 g, 0.025 mmol), reaction temperature 0 °C, (1/9). **12b**: 0.32 g (45% yield). **11b** (0.52 g, 2.5 mmol), pentane/toluene (5:1), butyl vinyl ether (5.19 g, 51.9 mmol), rhodium(II) octanoate (0.0204 g, 0.025 mmol), reaction temperature 0 °C, (1/9). **12b**: 0.083 g (12% yield); ^{1}H NMR δ 7.40–7.27 (m, 5 H), 4.95–4.85 (m, 1 H), 3.69 (s, 3 H), 3.60–3.42 (m, 2 H), 3.08 (dddd, J = 17.1, 8.6, 6.1, 2.4 Hz, 1 H), 2.69 (ddd, J = 17.9, 8.6, 3.9 Hz, 1 H), 2.35–2.15 (m, 1 H), 2.05–1.90 (m, 1 H), 1.65–1.45 (m, 2 H), 1.45–1.30 (m, 2H), 0.91 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 166.2, 155.3, 136.0, 130.0, 128.3, 127.7, 127.6, 85.7, 69.1, 51.0, 37.1, 32.0, 29.0, 19.2, 13.8; IR (neat) 1710, 1630, 1600 cm^{-1}. Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.24; H, 8.14.

Methyl 6,7-Benzo-4-phenyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene-2-carboxylate (16b). 11b (0.61 g, 3.0 mmol), CH_2Cl_2, **15** (1.22 g, 4.5 mmol), rhodium(II) acetate (0.026 g, 0.06 mmol), (0/1–2/8). **16b**: 0.80 g (60% yield), mp 165–167 °C; ^{1}H NMR δ 7.82–7.72 (m, 2 H), 7.63–7.45 (m, 4 H), 7.34 (s, 5 H), 7.24–7.13 (m, 6 H), 6.51 (d, J = 7.6 Hz, 2 H), 3.29 (s, 3 H), 2.88 (d, J = 4.6 Hz, 1 H), 2.36 (d, J = 4.6 Hz, 1 H); ^{13}C NMR δ 170.34, 149.80, 147.78, 135.13, 134.92, 134.81, 130.73, 128.87, 128.42, 127.94, 127.86, 127.59, 127.55, 126.70, 126.42, 125.56, 123.74, 121.67, 90.30, 88.83, 53.57, 51.24, 44.03, 24.92; IR (CCl_4) 1720, 1540 cm^{-1}. Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44. Found: C, 83.63; H, 5.45.

Methyl 6,7-Benzo-4-(dimethylethyl)-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene-2-carboxylate (16c). 11c (0.36 g, 2.0 mmol), CH_2Cl_2, **15** (0.81 g, 3.0 mmol), rhodium(II) acetate (0.018 g, 0.04 mmol), (0/1–1/9). **16c**: 0.49 g (57% yield), mp 105–107 °C; ^{1}H NMR δ 7.82–7.72 (m, 2 H), 7.60–7.20 (m, 12 H), 3.50 (s, 3 H), 2.80 (d, J = 5.1 Hz, 1 H), 2.58 (d, J = 5.1 Hz, 1 H), 0.68 (s, 9H); ^{13}C NMR δ 172.60, 151.12, 147.53, 136.37, 135.29, 128.84, 128.78, 128.73, 128.63, 128.58, 128.45, 128.33, 126.10, 125.36, 124.26, 122.87, 92.10, 88.69, 55.59, 51.74, 42.18, 31.33, 31.19, 27.22; IR (CCl_4) 1720, 1600, 1540 cm^{-1}. Anal. Calcd for $C_{29}H_{28}O_3$: C, 82.05; H, 6.65. Found: C, 82.14; H, 6.69.

5-(2-Carbomethoxyethylidene)bicyclo[2.2.1]-hept-2-ene (17a). 2a (0.50 g, 3.98 mmol), CH_2Cl_2 (20 mL), cyclopentadiene (1.30 g, 20.0 mmol, prepared from cyclopentadiene dimer), rhodium(II) trifluoroacetate (0.027 g, 0.040 mmol). Purification by bulb-to-bulb distillation (110 °C (0.5 mmHg)) gave a mixture of **17a** and **18a** (0.35 g, 54% yield) that was inseparable by chromatography.

Confirmation that an *E*/*Z* mixture of **17a** was contained within the mixture was obtained by an independent synthesis of **17a**. A solution of methyl diethylphosphonoacetate (0.37 g, 1.8 mmol) and sodium hydride (0.04 g, 1.8 mmol, 60% mineral oil) in THF was stirred for 30 min at 0 °C. Norbornenone[25] (0.2 g, 1.8 mmol) was added and the mixture was stirred for 2 h at room temperature. Ammonium chloride (100 mL) was added and the mixture was extracted with ether (2×). The organic layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. Purification on silica gel column chromatography on silica (2/8 ether/petroleum ether) gave **17a** (0.22 g, 73% yield): ^{1}H NMR ($CDCl_3$) δ major isomer 6.27 (dd, J = 5.5, 3.1 Hz, 1 H), 5.98 (m, 1 H), 5.92 (s, br, 1 H), 3.66 (s, 3 H), 3.30 (m, br, 1 H), 3.05 (m, br, 1 H), 2.58 (br d, J = 16.7 Hz, 1 H), 2.30 (br d, J = 16.7 Hz, 1 H), 1.70–1.40 (m, 2 H); minor isomer 6.23 (dd, J = 5.5, 3.1 Hz, 1 H), 6.05 (m, 1 H), 5.65 (s, br, 1 H), 4.50 (m, 1 H), 3.67 (s, 3 H), 2.95 (m, br, 1 H), 2.32 (br d, J = 16.6 Hz, 1 H), 1.93 (br d, J = 16.6 Hz, 1 H), 1.70–1.40 (m, 2 H); IR (neat) 2940, 1710, 1450, 1100 cm^{-1}; MS *m*/*z* (rel intensity) 164 (100), 149 (12), 132 (80), 121 (10), 105 (57), 91 (10), 77 (17), 66 (22), 57 (7); HRMS calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0838.

Methyl Bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (18a). 2a (0.60 g, 4.78 mmol), pentane, cyclopentadiene (6.32 g, 95.60 mmol), rhodium(II) pivalate (0.058 g, 0.95 mmol), purified by bulb-to-bulb distillation (110 °C (0.5 mmHg)) to give **18a** (0.67 g, 86% yield): ^{1}H NMR ($CDCl_3$) δ 6.51 (m, 1 H), 6.23 (dd, J = 5.6, 2.9 Hz, 1 H), 5.73 (dd, J = 5.6, 2.7 Hz, 1 H), 3.72 (s, 3 H), 3.30 (t, J = 2.9 Hz, 1 H), 2.71 (m, 1 H), 2.45 (ddd, J = 20.0, 4.1, 4.1 Hz, 1 H), 2.04 (dt, J = 9.9, 4.6 Hz, 1 H), 1.91 (dd, J = 20.0, 4.4 Hz, 1 H), 1.62 (d, J = 9.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 166.6, 139.6, 137.5, 136.5, 131.1, 51.4, 39.9, 37.8, 37.2, 28.7; IR (neat) 2960, 1705, 1635, 1100 cm^{-1}; MS *m*/*z* (rel intensity) 164 (100), 149 (30), 132 (70), 121 (10), 105 (100), 91 (20), 77 (30), 66 (11), 51 (13), 39 (20); HRMS calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0834. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.05; H, 7.38.

(*E*/*Z*)-5-(2-((dimethylethoxy)carbonyl)ethylidene)-bicyclo[2.2.1]-2-ene (17b) and Dimethylethyl Bicyclo-[3.2.1]octa-2,6-diene-2-carboxylate (18b). 2b (0.84 g, 5 mmol), CH_2Cl_2, cyclopentadiene (3.30 g, 50 mmol), rhodium(II) acetate (0.022 g, 0.05 mmol). NMR analysis of the crude mixture shows a ratio of **17b**:**18b** = 48:52. Purification by silica gel chromatography (1/4 ether/petroleum ether) gave a mixture of three products (0.95 g, 92% yield). The mixture was partially separated by HPLC on silica gel using ethyl acetate–hexane (1/49–1/19) as eluant. **17b**: ^{1}H NMR δ (*E* isomer) 6.25 (dd, J = 5.6, 3.9 Hz, 1 H), 6.00 (dd, J = 5.6, 3.4 Hz, 1 H), 5.83 (dd, J = 2.0, 2.0 Hz, 1 H), 3.27 (br s, 1 H), 3.06 (br s, 1 H), 2.58 (ddd, J = 17.3, 2.0, 2.0 Hz, 1 H), 2.30 (ddd, J = 17.3, 2.0, 2.0 Hz, 1 H), 1.64 (br d, J = 8.6 Hz, 1 H), 1.46 (br d, J = 8.6 Hz, 1 H), 1.46 (s, 9 H); (*Z* isomer) 6.20 (dd, J = 5.5, 1.9 Hz, 1 H), 6.05 (dd, J = 5.5, 3.0 Hz, 1 H), 5.58 (br s, 1 H), 4.42 (br s, 1H), 2.90 (br s, 1 H), 2.30 (br d, J = 17.0 Hz, 1 H), 1.85 (br d, J = 17.0 Hz, 1 H), 1.70–1.40 (m, 2 H), 1.45 (s, 9 H); ^{13}C NMR δ 165.5, 163.7, 138.2, 131.6, 111.7, 78.4, 51.2, 49.7, 40.8, 34.6, 27.3; IR 1703, 1656, 1628 cm^{-1}; MS *m*/*z* (rel intensity) 206 (0.5), 166 (2), 150 (100), 132 (58), 105 (70); HRMS (EI$^+$) *m*/*e* calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1299. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.54; H, 8.77.

18b: ^{1}H NMR δ 6.42 (m, 1 H), 6.23 (dd, J = 5.5, 2.8 Hz, 1 H), 5.72 (dd, J = 5.5, 2.7 Hz, 1 H), 3.28 (m, 1 H), 2.52 (m, 1 H), 2.42 (ddd, J = 20.0, 4.1, 4.1 Hz, 1 H), 2.04 (dt, J = 9.9, 5.4 Hz, 1 H), 1.90 (dd, J = 20.0, 3.9 Hz, 1 H), 1.62 (d, J = 9.9 Hz, 1 H), 1.47 (s, 9 H); ^{13}C NMR δ 165.2, 139.4, 138.9, 134.7, 130.7, 79.5, 39.7, 37.6, 37.0, 28.0, 27.9; IR 1690, 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.56; H, 8.85.

(*E*/*Z*)-5-(2-((2,6-bis(dimethylethyl)-4-methylphenoxy)-carbonyl)ethylidene)bicyclo[2.2.1]-hept-2-ene (17c). 2c (0.63 g, 2 mmol), CH_2Cl_2, cyclopentadiene (0.99 g, 15 mmol), rhodium(II) acetate (0.0088 g, 0.02 mmol). NMR analysis of the crude mixture showed an *E*/*Z* ratio = 1.5:1. Purification by silica gel chromatography (1/19 ether/petroleum ether) gave an inseparable *E*/*Z* mixture of **17c**: 0.39 g (56% yield); ^{1}H NMR δ (*E* isomer) 7.11 (s, 2 H), 6.33 (dd, J = 5.3, 3.0 Hz, 1 H), 6.23 (br s, 1 H), 6.07 (dd, J = 5.3, 3.0 Hz, 1 H), 3.44 (br s, 1 H), 3.10 (br s, 1H), 2.62 (ddd, J = 16.0, 2.8, 2.8 Hz, 1 H), 2.55 (br d, J = 16.0 Hz, 1 H), 2.33 (s, 3 H), 1.80–1.70 (m, 1 H), 1.64–1.40 (m, 1 H), 133 (s, 9 H), 1.30 (s, 9 H); (*Z* isomer) ^{1}H NMR δ 7.14 (s, 2 H), 6.29 (dd, J = 5.6, 3.0 Hz, 1 H), 6.02 (dd, J = 5.6, 3.6 Hz, 1 H), 6.00 (br s, 1 H), 4.63 (br s, 1 H), 3.04 (br s, 1H), 2.60 (br d, J = 15.9 Hz, 1 H), 2.34 (s, 3 H), 2.08 (br d, J = 15.9 Hz, 1 H), 1.80 (br d, J = 9.0 Hz, 1 H), 1.55 (br d, J = 9.0 Hz, 1 H), 136 (s, 9 H), 1.33 (s, 9 H); IR (CCl_4) 1730, 1650, 1595 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 81.48; H, 9.19.

Methyl-4-Phenyltricyclo[3.2.1.0^{2,4}]oct-6-ene-2-carboxylate (19). 11b (0.202 g, 1.0 mmol), CH_2Cl_2, cyclopentadiene (0.66 g, 10 mmol), rhodium(II) acetate (0.0044 g, 0.01 mmol), (1/19). **19b**: 0.15 g (62% yield); ^{1}H NMR δ 7.50–7.20 (m, 5 H), 6.17–6.07 (m, 2H), 3.45 (br s, 1 H), 3.41 (s, 3 H), 3.00 (br s, 1 H), 2.55 (br d, J = 6.3 Hz, 1 H), 2.23 (dd, J = 5.5, 2.8 Hz, 1 H), 1.96 (br dd, J = 6.3, 2.8 Hz, 1 H), 1.56 (d, J = 5.5 Hz, 1 H); ^{13}C NMR δ 173.2, 139.4, 135.0, 134.8, 128.2, 128.0, 126.5, 63.2, 51.6, 51.4, 45.5, 42.7, 39.0, 28.6; IR (CCl_4) 1710, 1600 cm^{-1}; MS *m*/*z* (rel intensity) 240 (21), 208 (17), 181 (100), 165 (33); HRMS (EI$^+$) *m*/*e* calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1146.

Dimethylethyl α-Oxobicyclo[2.2.1]hept-5-ene-2-acetate (23). A solution of **2b** (8.00 g, 48 mmol) in benzene (50 mL) was added dropwise over 30 min to a stirred solution of butylene oxide (17.2 g, 238 mmol) and rhodium(II) acetate (0.2094 g, 0.48 mmol) in benzene (150 mL) heated at 60–64 °C under argon. After heating for a further 90 min, the mixture was cooled to room temperature. Freshly distilled cyclopentadiene (31.5 g, 476 mmol) was then added and the mixture was stirred at room temperature for 36 h. After evaporation of solvent under reduced pressure, the residue was purified by silica gel chromatography (1/9 ether/petroleum ether) to give **23** as a colorless oil (4.07 g, 38% yield): ^{1}H NMR δ 6.13 (dd, J = 5.6, 3.0 Hz, 1 H), 5.83 (dd, J = 5.6, 3.0 Hz, 1 H), 3.50 (ddd, J = 8.9, 4.2, 4.2 Hz, 1 H), 3.30 (br s, 1 H), 2.92 (br s, 1 H), 1.83 (ddd, J = 12.5, 8.9, 3.6 Hz, 1 H), 1.53 (s, 9 H), 1.50–1.30 (m, 3 H); ^{13}C NMR δ 196.0, 161.9, 137.7, 131.4, 83.5, 49.9, 48.4, 45.6, 42.5, 27.7, 27.4; IR 1720, 1630 cm^{-1}; MS *m*/*z*

(25) (a) Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289. (b) Bartlett, P. D.; Tate, B. E. *J. Am. Chem. Soc.* **1956**, *78*, 2473.

(rel intensity) 155 (8), 137 (11), 93 (7), 79 (14), 57 (100); HRMS (EI^+) *m/e* calcd for C_8H_9O ($M - C_5H_9O_2$) 121.0653, found 121.0654.

Dimethylethyl α-(*N*-(Toluenesulfonyl)hydrazo)bicyclo-[2.2.1]hept-5-ene-2-acetate (24). A solution of **23** (3.05 g, 13.7 mmol), tosylhydrazine (2.55 g, 13.7 mmol) and concd. HCl (1.5 mL) in methanol (50 mL) was stirred at room temperature for 2 d. The solvent was evaporated under reduced pressure, and the residue was recrystallized from methanol to give **24** as a white solid (3.18 g, 60%): mp 110–113 °C; ^1H NMR δ (major isomer) 7.83 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 5.88 (dd, J = 5.7, 2.7 Hz, 1 H), 5.46 (dd, J = 5.7, 2.9 Hz, 1 H), 3.33–3.13 (m, 1 H), 3.05 (br s, 1 H), 2.85 (br s, 1 H), 2.44 (s, 3 H), 1.53 (s, 9H), 1.80–1.10 (m, 4 H); IR (mix, in CCl_4) 3200–3000, 1740, 1600 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2SO_4$: C, 61.52; H, 6.71, N, 7.17. Found: C, 61.39; H, 6.76, N, 7.12.

Dimethylethyl α-Diazobicyclo[2.2.1]hept-5-ene-2-acetate (25). A solution of **24** (0.78 g, 2 mmol) and NaH (60% in mineral oil, 0.06 g, 2.5 mmol) in THF (50 mL) was stirred at room temperature for 24 h. Water was then added and the mixture was extracted with ether. The combined organic mixture was washed with water and saturated NH_4Cl solution. Purification by silica gel chromatography (1/19 ether/petroleum ether) gave **25** as a pale yellow oil (0.17 g, 36%): ^1H NMR δ (major isomer) 6.16 (dd, J = 5.8, 2.4 Hz, 1 H), 5.96 (dd, J = 5.8, 2.8 Hz, 1 H), 3.08 (br s, 1 H), 3.00–2.87 (m, 1 H), 2.87 (br s, 1 H), 2.13 (ddd, J = 12.8, 9.3, 3.6 Hz, 1 H), 1.45 (s, 9 H), 1.45–1.10 (m, 2 H), 0.90–0.70 (m, 1 H); IR 2077, 1688 cm^{-1}. Due to lack of stability **25** was used immediately in subsequent reactions.

Decomposition of 25 in the Presence of Cyclopentadiene. A solution of **25** (0.15 g, 0.64 mmol) in CH_2Cl_2 (5 mL) was added dropwise over 5 min to a stirred solution of cyclopentadiene (0.42 g, 6.4 mmol) and rhodium(II) acetate (0.0028 g, 0.006 mmol) in CH_2Cl_2 (10 mL) heated at reflux under argon. After a further 15 min of reflux, the solvent was evaporated under reduced pressure. Purification by silica gel chromatography (1/19 ether/petroleum ether) gave an *E* and *Z* mixture of **17b** (0.11 g, 81% yield).

Supplementary Material Available: Copies of ^1H NMR spectra of **9**, **11b**, **11c**, **17a**, **19**, **23**, and **25** (7 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.