# The Regio- and Stereoselectivities of the Reaction of Allyl Acetates and Silyl Ketene Acetals Catalyzed by Pd(0) Complexes: A New Route to Cyclopropane Derivatives

C. Carfagna, L. Mariani, A. Musco,* and G. Sallese

*Istituto di Scienze Chimiche, Università degli Studi di Urbino, p.zza Rinascimento 6, 61029 Urbino, Italy*

R. Santi*

*Istituto G. Donegani, via Fauser 4, 28100 Novara, Italy*

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Pd(0) complexes of chelating phosphines catalyzed the coupling of allyl acetates and ketene silyl acetals to yield α-allylated carboxylic acid esters. Unexpectedly alkylation of the central carbon atom (C2) of the allyl groups was also observed with concomitant formation of cyclopropane derivatives. In both cases the silyl enolate attacked the allyl group from the side opposite Pd. The yield of the reaction was sensitive to the nature of the ligand coordinated with palladium. The 1,1'-bis(diphenylphosphino)ferrocene–Pd complex was the most effective catalyst.

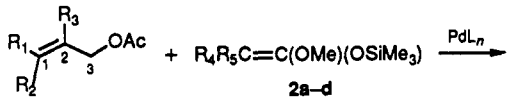
## Introduction

The reaction of $\eta^3$-allyl Pd complexes with carbon nucleophiles to stereoselectively form carbon–carbon single bond has found wide application in organic synthesis.[1] Allylation occurs when an appropriate allylic compound, e.g. an allyl acetate, carbonate, or phosphate, is allowed to react with a carbon nucleophile in the presence of a Pd(0)–phosphine complex.[1-4] As reported by several workers, the reaction takes place in two steps: the oxidative addition of the allylic compound to the Pd(0) complex and then attack of the nucleophile on one of the terminal carbon atoms of the coordinated allyl group. Although the first step occurs with inversion of configuration, the stereochemical course of the second step, depends on the nature of the carbon nucleophile. Thus, a resonance-stabilized carbon nucleophile, such as malonate, attacks the coordinated allyl group from the side opposite the metal to yield products with overall retention of configuration. Conversely, a nonstabilized carbon nucleophile, such as a vinyl,[5] an aryl,[6] or a methyl[7] organometallic, first attacks the metal and then couples with the coordinated allyl group intramolecularly to give products with overall inversion of configuration.

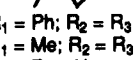
Here we report the results of a study of the Pd-catalyzed coupling of allylic acetates and ketene silyl acetals. It will be shown that, in contrast to the Pd(0)-catalyzed reaction of allyl carbonates and silyl ketene acetals,[8] the attack of the silyl enolate may also occur at the central carbon atom (C2) of the allyl group to yield cyclopropane derivatives.

## Results

Various allyl acetates and ketene silyl acetals were allowed to react in the presence of a Pd(0)–tertiary phosphine complex. The results are summarized in Table I. In most cases α-allylated carboxylic acid esters were formed (Table I, runs 1–16, 19–20) by nucleophilic attack of the silyl enolate on C1 or C3 of the allyl moiety (eq 1).



1a–e + $R_4R_5C{=}C(OMe)(OSiMe_3)$ (2a–d) $\xrightarrow{PdL_n}$ $AcOSiMe_3$ + $R_1R_2C{=}C(R_3)CH_2CR_4R_5COOMe$ (3) + $CH_2{=}C(R_3)CR_1R_2CR_4R_5COOMe$ (3') (1)

**1a**: $R_1 = R_2 = H$; $R_3 = Me$
**1b**: $R_1 = R_3 = (CH_2)_4$; $R_2 = H$
**1c**: $R_1$ =  ; $R_2 = Me$; $R_3 = H$
**1d**: $R_1 = Ph$; $R_2 = R_3 = H$
**1e**: $R_1 = Me$; $R_2 = R_3 = H$ and $R_1 = H$, $R_2 = Me$, $R_3 = H$ $E/Z = 2.6/1$
**2a**: $R_4 = R_5 = H$
**2b**: $R_4 = Me$; $R_5 = H$
**2c**: $R_4 = Ph$, $R_5 = H$
**2d**: $R_4 = R_5 = Me$

Preformed Pd(0) complexes were active catalysts. However, catalytically active species could also be conveniently prepared in situ (eq 2).

$$^1/_2(\eta^3\text{-}C_4H_7PdOAc)_2 + R_4R_5C{=}C(OMe)(OSiMe_3) + nL \longrightarrow PdL_n + CH_2{=}C(Me)CH_2CR_4R_5COOMe + AcOSiMe_3 \quad (2)$$

**The Effects of the Ligand and the Structure of the Ketene Silyl Acetal on the Course of the Reaction.** In order to determine the effect of the nature of the ligand on the natures and yields of the coupling products, the reaction of 2-methylallyl acetate (**1a**) and (*E*)-1-methoxy-1-(trimethylsiloxy)propene (**2b**) was investigated in detail. Table I shows the results (runs 2–6).

The yield of coupling products, from the reaction performed in THF at room temperature, as a function of the ligand bound to the metal, was 1,1'-bis(diphenylphosphino)ferrocene (DPPF) > 1,4-bis(diphenylphosphino)butane (DPPB) ≈ 1,3-bis(diphenylphosphino)propane (DPPP) ≫ 1,2-bis(diphenylphosphino)ethane (DPPE) ≫ $PPh_3$. Whereas the DPPF and DPPB complexes gave comparable yields of products when the reaction was performed in boiling THF, a very

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Table I. Reaction of Allyl Acetates (1) and Silyl Ketene Acetals (2) To Yield α-Allylic Esters (3, 3') and Cyclopropane Derivatives (4)[a]

| run | 1 | 2 | ligand[b] | 1/2 (molar ratio) | t (h) | product | yield (%)[c] | de[d] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 1a | 2a | DPPF | 1:1 | 5 | 3aa | 50 | |
| 2 | 1a | 2b | DPPF | 1:1 | 1 | 3ab | 85 | |
| 3 | 1a | 2b | DPPB | 1:1 | 1 | 3ab | 50 | |
| 4 | 1a | 2b | DPPP | 1:1 | 1 | 3ab | 50 | |
| 5 | 1a | 2b | DPPE | 1:1 | 1 | 3ab | 24 | |
| 6 | 1a | 2b | $PPh_3$[e] | 1:1 | 1 | 3ab | traces | |
| 7 | 1a | 2c[f] | DPPF | 1:1 | 2 | 3ac | 75 | |
| 8 | 1a | 2d | DPPF | 1:1 | 2 | 3ad | 73 | |
| 9 | 1b | 2a | DPPF | 1:1 | 4 | 3ba/3'ba (4:1) | 39 | |
| 10 | 1b | 2b | DPPF | 1:1 | 2 | 3bb/3'bb (9:1) | 53 | 26 |
| 11 | 1b | 2c | DPPF | 1:3 | 2 | 3bc | 75 | |
| 12 | 1c | 2c | DPPF | 1:1 | 2 | 3cc/3'cc (9:1) | 60 | |
| 13 | 1d | 2a | DPPF[g] | 1:1 | 5 | 3da/3'da (5:1) | 60 | |
| 14 | 1d | 2b | DPPF | 1:3 | 5 | 3db/3'db (5:1) | 80 | 35 |
| 15 | 1d | 2c | DPPF | 1:1 | 2 | 3dc/3'dc (3:1) | 65 | 8 |
| 16 | 1e[h] | 2c | DPPF | 1:1 | 2 | 3ec/3'ec (1:1) | 60 | 20 |
| 17 | 1f | 2a | DPPF | 1:3 | 4 | 3fa/4fa (1.5:1) | 60 | |
| 18 | 1f | 2b | DPPF | 1:3 | 1 | 3fb/4fb (4.5:1) | 90 | 33 |
| 19 | 1f | 2c | DPPF | 1:3 | 2 | 3fc | 85 | |
| 20 | 1f | 2d | DPPF | 1:3 | 1 | 3fd | 80 | |
| 21 | 1g | 2a | DPPF | 1:3 | 5 | 3ga/4ga (6.5:1) | 53 | |

[a] Reaction conditions: 1/2 ($\eta^3$-$C_4H_7PdOAc)_2$/ligand/1 = 1:2:20. $T$ = 25 °C. [b] DPPF = 1,1'-bis(diphenylphosphino)ferrocene; DPPB = 1,4-bis(diphenylphosphino)butane; DPPP = 1,3-bis(diphenylphosphino)propane; DPPE = 1,2-bis(diphenylphosphino)ethane. [c] Yields based on 1 are estimated by GC after introduction of an appropriate internal standard. [d] Diastereomeric excess. [e] 1/2($\eta^3$-$C_4H_7PdOAc)_2$/$PPh_3$/1 = 1:4:20. [f] 2c = 1:2 $E/Z$ mixture. [g] Reaction temperature = 65 °C. [h] 1e = 2.6:1 $E/Z$ mixture.

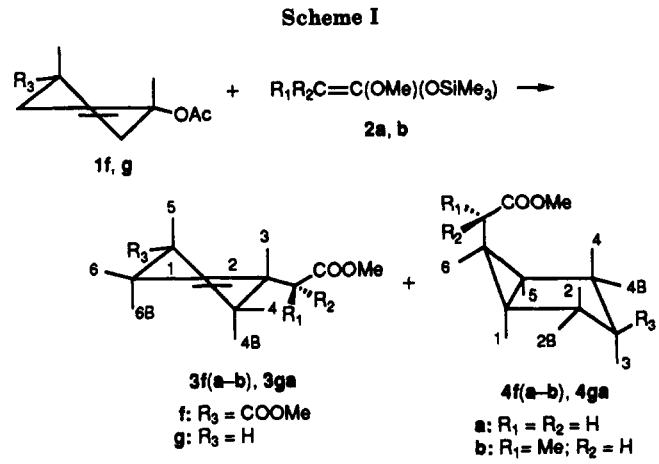
low yield of coupling products was obtained with the $PPh_3$ complex. As can be seen from Table I (runs 2–6), the DPPF complex gave the best results. Therefore, all subsequent reactions were performed with that complex as the catalyst.

The effectiveness of the DPPF complex in catalyzing carbon–carbon bond formation is not unprecedented. Its high catalytic activity has been related to the large value of the P–Pd–P bond angle.[9] Thus ketene silyl acetals **2a**, **2c**, and **2d** were allowed to react with methallyl acetate (**1a**). In all cases, good yields of coupling products were obtained (Table I, runs 1, 7, and 8).

**Regioselectivity of the Reaction.** The reaction of 1-(acetoxymethyl)-1-cyclohexene (**1b**) with ketene silyl acetals **2a–c** gave predominantly products of the alkylation of the exocyclic carbon atom. These results suggested that attack of the nucleophile on the complex occurred preferentially at the less substituted allylic carbon atom. The reaction of geranyl acetate (**1c**) (run 12) with ketene silyl acetal **2c** yielded **3cc** (54% yield), a result which confirmed that attack of the nucleophile occurred at the less substituted carbon atom. In this case GC/MS revealed the presence of a second, minor isomer to which structure **3'cc** was tentatively assigned.

The $^{13}C$ NMR spectrum[4] of the coupling product **3cc** indicated that the original geometry about the carbon–carbon double bond was retained in the product. Similarly, the original geometry about the double bond of the allyl compound was preserved in the products of the coupling of cinnamyl acetate (**1d**) and ketene silyl acetals **2a–c** (runs 13–15). On the other hand, a 2.6:1 mixture of the $E$ and $Z$ isomers of crotyl acetate (**1e**), on reaction with ketene silyl acetal **2c**, gave the coupling product **3ec**, which displayed $E$ stereochemistry. These results, taken together, indicated that the geometry that was generated about the carbon–carbon double bond of the coupling product was $E$, regardless of the original geometry about the double bond of the starting allyl acetate. The diastereoselectivity of the reaction was poor (runs 10, 14–16, 18).

Scheme I




**The Stereochemical Course of the Reaction and the Formation of Cyclopropane Derivatives.** In order to elucidate the stereochemical course of the coupling reaction, the reaction of *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene (**1f**) with ketene silyl acetals **2a–d** (Table I, runs 17–20; and Scheme I) was studied. Identification of the reaction products provided evidence of nucleophilic attack on the central carbon atom (C2) of the allyl group. Thus the reaction of **1f** with **2a** yielded two major products, the isomers *cis*-**3fa** (54%) and **4fa** (36%). GC/MS also showed the presence of a small (9%) quantity of a third isomer, which had a fragmentation pattern identical with that of *cis*-**3fa**.[10] It was assumed that this compound, which could not be isolated in pure form, was *trans*-**3fa**. Compounds *cis*-**3fa** and **4fa** were isolated by column chromatography and spectroscopically characterized. The cis stereochemistry of **3fa** was assigned after comparing the compound's $^1H$ NMR vicinal hydrogen coupling constants (Experimental Section) with those reported for compounds of similar structure.[4] That *cis*-**3fa** was formed implied that the nucleophile attacked **2a** externally. The assignment of a bicyclo[3.1.0]hexane structure to **4fa** was

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(10) Capillary GC (SE30, 0.25 mm × 30 m) showed, in order of increasing retention time, the supposed *trans*-**3fa**, *cis*-**3fa**, and **4fa**.

also based on NMR data (Experimental Section).

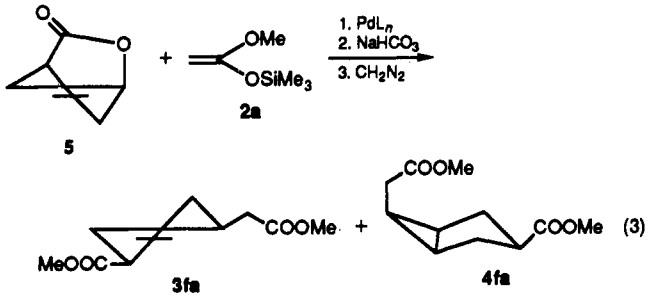
The results of DEPT and $^1H$–$^{13}C$ NMR correlation experiments permitted the assignment of the signals in the $^{13}C$ NMR spectrum of **4fa**. The chemical shifts of C-6 and C-1, $\delta$ 20.8 and 23.1, respectively, and the corresponding $^1J_{C-H}$, 165 Hz, were consistent with a three membered ring.[11]

The results of $^1H$ NMR spin decoupling and DNOES experiments were consistent with the existence of a syn relationship between the substituents at C-3 and C-6.

Although bicyclo[3.1.0]hexane derivatives can assume boat conformations,[12] a chair conformation for **4fa** seemed more likely due to steric repulsion between the substituents on C-3 and C-6. In conclusion all the NMR data were consistent with structure **4fa**. It followed that the attack of the silicon enolate on the internal carbon atom (C2) of the allyl group occurred from the side opposite palladium. Altogether, compounds *cis*-**3fa** and **4fa**, which arose from direct attack of ketene silyl acetal **2a**, accounted for 90% of the coupling products.

Although the presence of substituents on the nucleophilic carbon atom of the ketene silyl acetals inhibited the formation of **4**, the presence in the $^1H$ NMR spectra of the crude product mixtures of a signal at $\delta$ 3.34, which could be assigned to the H-3 proton, allowed the identification of **4**. GC/MS was also particularly useful in differentiating between **3** and **4**, for the relative abundance of the fragment $[M^{\bullet+} - (CR_1R_2COOMe)]$ in all of the cases examined was much greater in the spectra of **4** than in those of **3**.

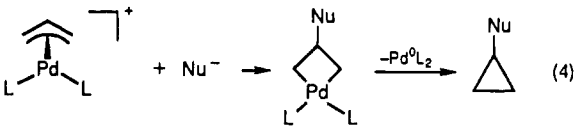
Similar results were obtained from the reaction of 7-oxabicyclo[3.2.1]oct-2-en-6-one (**5**) with ketene silyl acetal **2a** (eq 3). GC analysis of the reaction mixture showed




(3)

*cis*-**3fa** (53%), **4fa** (38%),[10] and a third, minor isomer (9%). It was assumed that the minor isomer was *trans*-**3fa** because no isomerization of **5** in the presence of Pd(0) complexes was possible. It was thus concluded that a minor side reaction may have been *intra*molecular attack of the silyl enolate on one of the terminal carbon atoms of the allyl group. This conclusion was supported by a recent report in which it was shown that, under certain conditions, nucleophiles that are known to attack the allyl group from the side opposite palladium can also attack from the side on which the metal is located.[13]

The reaction of 3-acetoxycyclohexene (**1g**) with **2a** also produced a bicyclo[3.1.0]hexane derivative **4ga**, but in lower yield than was the case for the reaction of **1f** (Table I, run 21; Scheme I). Separation of **3ga** and **4ga** by column chromatography proved to be difficult. However an enriched sample of **4ga** was obtained and was characterized by NMR. $^{13}C$ chemical shifts of $\delta$ 16.1 and 22.2 and the corresponding $^1J_{CH}$, 171.8 and $\approx$160 Hz, respectively, showed the presence of a three-membered ring in the structure. Hegedus et al.[14] reported that, under special reaction conditions and with stoichiometric quantities of the reactants, the attack of an enolate on the central carbon atom (C2) of $\eta^3$-allyl complex is possible. The existence of a palladiacyclobutane intermediate, which would yield a substituted cyclopropane through reductive elimination of palladium, was proposed (eq 4). This four-membered cyclic intermediate could be formed either by direct nucleophilic attack of the enolate on the central carbon (C2) of the allyl group or by attack on palladium followed by intramolecular attack of the palladium enolate on C2.




(4)

Tsuji et al.[8] found that Pd–DPPE complexes catalyzed the reaction of allyl carbonates and ketene silyl acetals to yield **3**. The involvement of a Pd enolate intermediate was proposed. However, the results of the present study suggest that attack of the enolate on either the terminal or the central carbon atom of the allylic system was preferentially external. Thus, the involvement of a Pd enolate intermediate is not supported by the experimental evidence.

In conclusion, it has been shown that the reaction of ketene silyl acetals with allylic acetates in the presence of Pd(0)–phosphine complexes occurred with inversion of configuration. This result is consistent with a direct attack by the nucleophile. A similar stereochemical course was observed in the reactions of tin, lithium and boron enolates.[15–17] Further work aimed at elucidating the factors that lead to attack on the central carbon of the allyl group is in progress. According to molecular orbital calculations, such a reaction should not be allowed for allylpalladium complexes.[18]

## Experimental Section

$^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AC-200 instrument. Mass spectra were recorded with a Varian MATT 112 F spectrometer. GC analyses were performed with a Dani 3800 instrument equipped with a 0.25 mm × 30 m capillary column coated with SE 30 or with a 2 mm × 2 m glass column packed with either 5% Carbowax on Chromosorb W-DMCS. Silica gel 60 (230–400 mesh) (E. Merck) was used for flash chromatography. Materials: 1,4-bis(diphenylphosphino)ferrocene was prepared by a literature method.[19] The other ligands were Fluka products and used as received. $(\eta^3\text{-}C_4H_7PdOAc)_2$ was prepared from $(\eta^3\text{-}C_4H_7PdCl)_2$ and thallium(I) acetate in $CH_2Cl_2$. Ketene silyl acetals,[20] *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene, and 7-oxabicyclo[3.2.1]oct-2-en-6-one[4,21] were prepared by published procedures. Allylic acetates were prepared by standard methods.

**Reaction of *cis*-3-Acetoxy-5-carbomethoxy-1-cyclohexene (1f) and 1-Methoxy-1-(trimethylsiloxy)ethylene (2a).** Com-

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pounds **1f** (0.199 g, 1 mmol) and **2a** (0.438 g, 3 mmol) were added at room temperature to a THF solution (12 mL) of $(\eta^3\text{-}C_4H_7PdOAc)_2$ (0.011 g, 0.025 mmol) and DPPF (0.055 g, 0.1 mmol). The mixture was left at room temperature for 4 h. The solvent was then evaporated, and the residue was extracted with 1:1 hexane/diethyl ether. The extract, which was shown by GC to contain a 1.5:1 mixture of **3fa** and **4fa**, was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1).

Methyl *cis*-(5-carbomethoxy-1-cyclohexen-3-yl)acetate (**3fa**) (0.015 g) was eluted first, followed by methyl *syn*-3-carbomethoxybicyclo[3.1.0]hexane-6-acetate (**4fa**) contaminated with **3fa** (0.025 g).

**Methyl *cis*-(5-Carbomethoxy-1-cyclohexen-3-yl)acetate (3fa).** MS $m/z$ (relative intensity): 212 ($M^{\bullet+}$, 6), 181 (21), 180 (19), 152 (39), 138 (15), 121 (11), 93 (91), 79 (94), 74 (100), 65 (12), 59 (27), 43 (25), 39 (19). $^1$H NMR ($CDCl_3$) (see Scheme I for numbering): $\delta$ 5.68 ($H_1$), 5.48 ($H_2$), 2.5–2.7 ($H_3$, $J_{3,7}$ = 6.9 Hz), 2.1–2.3 ($H_4$, $J_{4,4B}$ = 11.2 Hz), 1.27 ($H_{4B}$, $J_{4B,5} \approx J_{4B,3}$ = 14.0 Hz), 2.05–2.3 ($H_6$, $H_{6B}$), 2.28 ($H_7$, $J_{7,3}$ = 6.9 Hz), 2.26 ($H_{7B,3}$, $J_{7B,3}$ = 7.9 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 126.0 ($C_1$, $^1J_{C-H}$ = 161 Hz), 130.0 ($C_2$, $^1J_{C-H}$ = 160 Hz), 32.1 ($C_3$, $^1J_{C-H}$ = 136 Hz), 24.9 ($C_4$, $^1J_{C-H}$ = 128 Hz), 20.8 ($C_5$, $^1J_{C-H}$ = 127 Hz), 28.7 ($C_6$, $^1J_{C-H}$ = 132 Hz), 40.5 ($C_7$, $^1J_{C-H}$ = 129 Hz). Anal. Calcd for $C_{11}H_{16}O_4$: C, 52.26; H, 7.55. Found: C, 52.09; H, 7.48.

Supposed trans isomer, MS $m/z$ (relative intensity): 212 ($M^{\bullet+}$, 8), 181 (19), 180 (23), 152 (47), 139 (12), 121 (8), 93 (100), 79 (89), 74 (92), 65 (11), 59 (25), 43 (22), 39 (19).

**Methyl *syn*-3-Carbomethoxybicyclo[3.1.0]hexane-6-acetate (4fa).** MS $m/z$ (relative intensity): 212 ($M^{\bullet+}$, 3), 181 (16), 152 (28), 139 (43), 121 (20), 93 (87), 79 (100), 74 (41), 66 (19), 59 (39), 55 (23), 41 (26). $^1$H NMR ($CDCl_3$) (see Scheme I for numbering): $\delta$ 1.54 ($H_1 \equiv H_5$, $J_{1,2}$ = 1.4 Hz), 1.64 ($H_2 \equiv H_4$, $J_{2,2B}$ = 14.8 Hz, $J_{2,3}$ = 9.1 Hz), 2.23 ($H_{2B} \equiv H_{4B}$, $J_{2B,1}$ = 5.3 Hz, $J_{2B,2}$ = 14.8 Hz, $J_{2B,3}$ = 10.7 Hz), 3.31 ($H_3$, $J_{3,2B}$ = 10.7 Hz, $J_{3,2}$ = 9.1 Hz), 1.28 ($H_{6,1}$, $J_{6,1}$ = 8.4 Hz, $J_{6,7}$ = 7.4 Hz), 2.34 ($H_7$, $J_{7,6}$ = 7.4 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 23.1 ($C_1$,$C_5$ $^1J_{C-H}$ = 166 Hz), 28.1 ($C_2$,$C_4$, $^1J_{C-H}$ = 128 Hz), 50.6 ($C_3$, $^1J_{C-H}$ = 132 Hz), 20.8 ($C_6$, $^1J_{C-H}$ = 164 Hz), 28.1 ($C_7$, $^1J_{C-H}$ = 128 Hz). Anal. Calcd for $C_{11}H_{16}O_4$: C, 52.26; H, 7.55. Found: C, 52.12; H, 7.60.

**Reaction of 7-Oxabicyclo[3.2.1]oct-2-en-6-one (5) with 1-Methoxy-1-(trimethylsiloxy)ethylene (2a). A Typical Procedure.** Lactone **5** (0.496 g, 4 mmol) and silyl ketene acetal **2a** (1.752 g, 12 mmol) were added to a THF (35 mL) solution of $(\eta^3\text{-}C_4H_7PdOAc)_2$ (0.044 g, 0.1 mmol) and DPPF (0.222 g, 0.4 mmol). The mixture was stirred at room temperature for 24 h. The solvent was then evaporated. The residue was stirred with aqueous $NaHCO_3$ (2 mL) for 2 h, and then the mixture was extracted with chloroform. The aqueous phase was acidified with HCl and then was extracted with chloroform. Evaporation of solvent from the dried ($Na_2SO_4$) extracts yielded 0.52 g of an oil. This was allowed with an ether solution of diazomethane. GC analysis of the reaction mixture showed a 1:6:4 mixture of *trans*-**3fa**, *cis*-**3fa**, and **4fa**.

**Methyl 1-Cyclohexen-3-ylacetate (3ga) and Methyl Bicyclo[3.1.0]hexane-6-acetate (4ga). 3ga.** MS $m/z$ (relative intensity): 154 ($M^{\bullet+}$, 11), 123 (17), 122 (39), 94 (46), 81 (78), 80 (100). $^1$H NMR ($CDCl_3$) (see Scheme I for numbering): $\delta$ 5.72 ($H_1$, m), 5.54 ($H_2$, m), 2.6–2.8 ($R_3$ = H), 2.5–2.7 ($H_3$), 2.30 ($H_7$, $J_{3,7}$ = 6.8 Hz), 2.29 ($H_{7B}$, $J_{3,7B}$ = 8.2 Hz), 1.9–2.1 ($H_4$ and $H_{4B}$, $J_{3,4B}$ = 14.0 Hz), 1.4–2.0 ($H_5$, $J_{5-4B}$ = 14.0 Hz), 1.1–1.9 ($H_{6,6B}$). $^{13}$C NMR ($CDCl_3$): $\delta$ 128.1 ($C_1$, $^1J_{C-H}$ = 160 Hz), 130.0 ($C_2$, $^1J_{C-H}$ = 160 Hz), 32.1 ($C_3$, $^1J_{C-H}$ = 136 Hz), 24.9 ($C_4$, $^1J_{C-H}$ = 128 Hz), 20.8 ($C_5$, $^1J_{C-H}$ = 127 Hz), 28.7 ($C_6$, $^1J_{C-H}$ = 132 Hz), 40.5 ($C_7$, $^1J_{C-H}$ = 129 Hz).

**4ga.** MS $m/z$ (relative intensity): 154 ($M^{\bullet+}$, 0.5), 122 (43), 95 (39), 94 (46), 81 (100). $^1$H NMR ($CDCl_3$): $\delta$ 2.5–2.7 ($R_3$ = H), 2.24 ($H_7$, $J_{6,7}$ = 7.1 Hz), 1.9–2.0 ($H_2$, $H_{2B} \equiv H_4$, $H_{4B}$, $J_{2,1}$ = 1.5 Hz, $J_{2B,1}$ = 4.0 Hz, $J_{2,2B}$ = 14.8 Hz, $J_{2,3}$ = 9.1 Hz, $J_{2B,3}$ = 10.7 Hz), 1.45 ($H_1 \equiv H_5$, $J_{1,6}$ = 8.3 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.2 ($C_1$, $C_5$, $^1J_{C-H}$ = 160 Hz), 26.3 ($C_2$, $C_4$), 16.9 ($C_6$, $^1J_{C-H}$ = 172 Hz), 29.2 ($C_7$, $^1J_{C-H}$ = 128 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.28; H, 9.15.

**Methyl *cis*-2-(5-Carbomethoxy-1-cyclohexen-3-yl)-propanoate (3fb).** The masss spectrum shows overlapping peaks due to the presence of two diastereomers. MS $m/z$ (relative intensity): 226 ($M^{\bullet+}$, 4), 195 (8), 166 (36), 139 (10), 107 (73), 88 (55), 157 (100), 67 (6), 59 (20), 40 (15). $^1$H-NMR ($CDCl_3$) of the major isomer: $\delta$ 5.81–5.68 (m, 1 H), 5.64–5.53 (m, 1 H), 3.67 (s, 6 H), 2.70–2.50 (m, 2 H), 2.36 (quint, 1 H, $J$ = 6.9 Hz), 2.25–2.07 (m, 2 H), 2.05–1.85 (m, 1 H), 1.39 (dt, 1 H, $J$ = 11.3, 12.6 Hz), 1.09 (d, 3 H, $J$ = 6.95 Hz). $^1$H NMR ($CDCl_3$) of the minor isomer: $\delta$ 5.81–5.68 (m, 1 H), 5.50–5.40 (m, 1 H), 3.67 (s, 6 H), 2.70–2.50 m, 2 H), 2.38 (quint, 1 H, $J$ = 6.9 Hz), 2.25–2.07 (m, 2 H), 2.05–1.85 (m, 1 H), 1.32 (dt, 1 H, $J$ = 11.3, 12.6 Hz), 1.07 (d, 3 H, $J$ = 7.0 Hz). Supposed trans isomer (two diastereoisomers) MS $m/z$ (relative intensity): (i) 226 ($M^{\bullet+}$, 5), 195 (8), 166 (70), 135 (8), 107 (88), 91 (23), 79 (100), 67 (6), 59 (20), 44 (24), 40 (48); (ii) 226 ($M^{\bullet+}$, 4), 195 (7), 166 (62), 135 (6), 107 (81), 88 (51), 79 (100), 67 (10), 59 (21), 45 (6).

**Methyl *syn*-2-(3-Carbomethoxybicyclo[3.1.0]hex-6-yl)-propanoate (4fb).** MS $m/z$ (relative intensity): 167 (19), 139 (60), 107 (59), 91 (17), 88 (23), 79 (100), 67 (12), 59 (21), 55 (36), 41 (20). $^1$H NMR ($CDCl_3$): $\delta$ 3.35 (tt, $H_3$, $J$ = 10.1, $\simeq$9 Hz), 1.77 (m, $H_2$ and $H_4$), 1.52 ($H_1$ and $H_5$), 1.18 (d, 3 H, $J$ = 6.9 Hz); other signals were not assigned.

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**Supplementary Material Available:** Characterization data for *trans*-**3ec**,**3'ec**, *trans*-**3da**,**3'da**, *trans*-**3db**,**3db**, *trans*-**3dc**,**3'dc**, *trans*-**3cc**,**3fc**,**3fd**,**3'ba**,**3'bb**,**3bc**,**3aa**,**3ab**,**3ac**,**3ad** (7 pages). Ordering information is given on any current masthead page.