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Palladium(0)-Catalyzed Cyclization-Carbonylation of 2,7-Octadienyl Acetate and Homologues

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Abstract: The palladium(0)-catalyzed carbonylations, in acetic acid as a necessary solvent, of 2,7-octadienyl acetate and homologues via π-allylpalladium species were preceded by their intramolecular olefin insertion to form mixtures of *cis*/*trans*-2-vinylcyclopentylacetyl- and *cis*/*trans*-cyclohexylacetylpalladium intermediates, which undergo further the intramolecular (5-exo) Heck reaction to give bicyclo-[3.3.0] and [4.3.0] skeletons, respectively, except for one case affording *trans*-2-vinylcyclopentylacetic acid as a major product.

INTRODUCTION

Despite ample examples of the palladium-catalyzed allylation of soft carbonucleophiles, there have been few reports that indicate possible insertion of an olefin (1,3-dienes[1]) and strained norbornadiene[2]) into π-allylic palladium complexes or intermediates. An intramolecular version of the olefin insertion into the π-allylpalladium species has first been suggested by Suzuki et al.[3] Oppolzer and coworkers have extensively been exploring the Pd(0)-catalyzed cyclization of dimethyl allyl(4-acetoxy-2-butenyl)malonate in acetic acid as an effective solvent to convert into 2-vinyl-methylenecyclopentane derivatives, referring to the cyclization as a palladium-ene reaction.[4] The process may well be regio- and stereoselective as well as entropically favored.

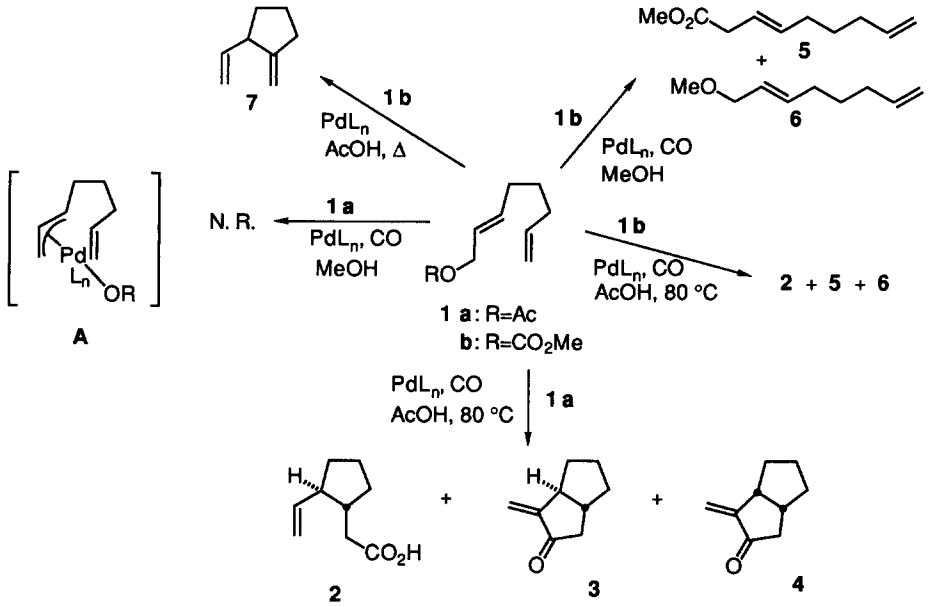
During the course of our study on the Pd(0)-catalyzed carbonylation of butadiene telomers,[5] it was found that in acetic acid the carbonylation via π-allylpalladium species can be preceded by cyclization to result in giving 2-vinylcyclopentylacetic acid. In order to look at the scope of this novel cyclization, the Pd(0)-catalyzed carbonylation of not only 2,7-octadienyl systems but also homologous 2,8-nonadienyl ones were undertaken and we wish to report here that the Pd(0)-catalyzed cyclization-carbonylation of these substrates proceeds only in acetic acid to give rise to mixtures of *cis*/*trans*-bicyclo[3.3.0] and [4.3.0] ring systems, respectively.[6] Similar and also nickel(0)-catalyzed cyclization-carbonylation sequences has been reported by Oppolzer and his coworkers[7] with highly stereocontrolled manner in some cases.

RESULTS AND DISCUSSION

2,7-Octadienyl acetate and carbonate

A butadiene telomer, 2,7-octadienyl acetate (**1a**), underwent the cyclization-carbonylation in the presence of $Pd(PPh_3)_3$, prepared in situ, under CO (2 atm) in AcOH at 80 °C to form *trans*-2-vinylcyclopentylacetic acid

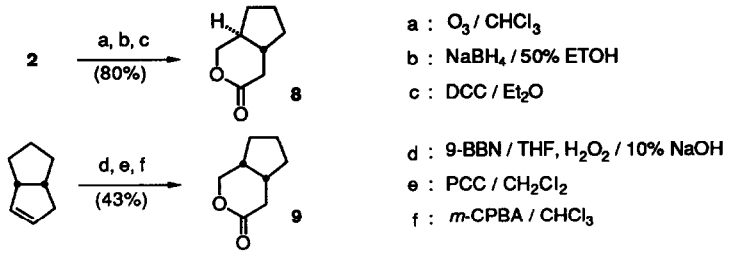
(**2**) in 50% yield, as a major product only in this particular case, along with *trans*-2-methylenebicyclo[3.3.0]octan-3-one (**3**) and the cis isomer (**4**) in a ratio 62 : 12 : 26 and in 80% combined yield. However, **1a** gave no significant product but rather resulted in recovery of **1a** in MeOH under otherwise the same conditions as above, whereas facile carbonylation of 2,7-octadienyl methyl carbonate (**1b**) took place in MeOH to form methyl 3,8-nonadienoate (**5**)[8] in 70% yield and a little 2,7-octadienyl methyl ether (**6**).[5b] Furthermore, **1b** underwent partly cyclization in AcOH to give **2** (20%) and mainly **5** and **6** (40% combined yield). Without CO the carbonate **1b** was converted to 2-vinylmethylenecyclopentane (**7**)[9] in 65% yield. The results are compiled in Scheme 1.



Scheme 1 (L = PPh_3)

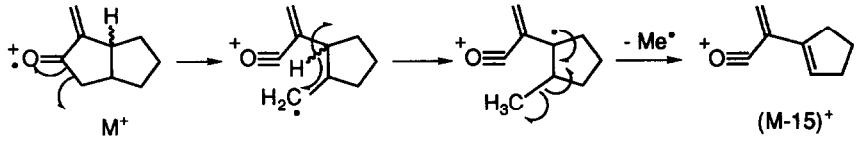
Characteristics of the reaction appear to rely mainly on the solvent employed. Although **1a** exhibited the novel cyclization-carbonylation in AcOH to afford **2**, **3**, and **4** (the stereochemistry will be identified below), the fact that no significant reaction of **1a** was observed in MeOH deserves to be mentioned; that is, π-allylpalladium acetate (**A**, R = Ac) once formed from **1a** may undergo reductive elimination to recover **1a** under CO in MeOH[10] and this is not the case in AcOH. On the other hand, it is evident that methoxycarbonylation under atmospheric pressure of CO is faster than olefin insertion using **1b** as a substrate in MeOH or even in AcOH, and that without CO in AcOH the carbonate **1b** eventually undergoes cyclization to form **7**.

The two substituents of the major product **2** are trans-related. This trans configuration of **2** was readily assigned by comparing the *trans*-3-oxabicyclo[4.3.0]nonan-4-one (**8**) derived from **2** with the cis isomer **9** which was prepared independently starting from *cis*-bicyclo[3.3.0]oct-2-ene as depicted in Scheme 2. Both



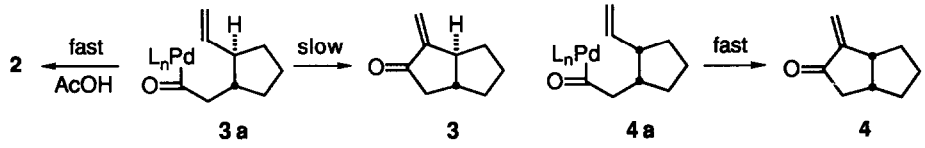
Scheme 2

trans and cis bicyclic products **3** and **4** were unequivocally characterized on the basis of ^{1}H NMR COSY spectra and of the presence of M-15 fragment of mass spectra (see Experimental). The fragmentation pattern for both **3** and **4** can most probably be given in Scheme 3.[11] It should be mentioned that the trans-disposed [3.3.0]



Scheme 3

system in **3** must be highly distorted[12] and that **3** is still formed kinetically from the σ-alkylpalladium intermediate **3a** as easily as **4** from the cis counterpart **4a** in a ratio ca. 1 : 2 as shown in Scheme 4. The major



Scheme 4

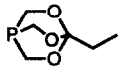
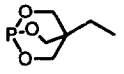
product **2** must arise from **3a** by way of a mixed anhydride, which is formed by reductive elimination with acetato ligand on Pd, and hydrolysis of the anhydride during workup. Although the *trans*-bicyclo[3.3.0]octane system has scarcely been reported so far, Bailey et al[13] have recently found that *trans*-2-allylcyclopentylmethyllithium does cyclize to give selectively, after methanolysis, *trans*-3-methylbicyclo[3.3.0]octane.

Thus, as for the stereochemistry at the stage of Pd-mediated 5-membered ring formation of **2**, **3**, and **4**, trans to cis ratio was found to be ca. 3 : 1 (**2** + **3**/**4**). In order to improve this diastereoselectivety of the cyclization, the effects of ligand variations and CO pressure were examined. The results are given in Table 1. It is seen that the best conditions so far is given in Entry 2. Three equivalents of PPh_3 to Pd can satisfactorily be used under an atmospheric CO pressure, while higher CO pressure did not exhibit significant effect on, at least, the yield of **2** (Entries 1 – 4). The ratio PPh_3/Pd = 1 appears to be enough for the cyclization-carbonylation of **1a** in shorter reaction time to form **2** and **4** in comparable yield (Entry 5), the fact being indicative of CO as a complemental ligand on Pd. Cage-like phosphine **B** is as effective ligand as PPh_3 and tri-

Table 1. Effects of Ligand Variation and CO Pressure on the Product Ratio from **1a**

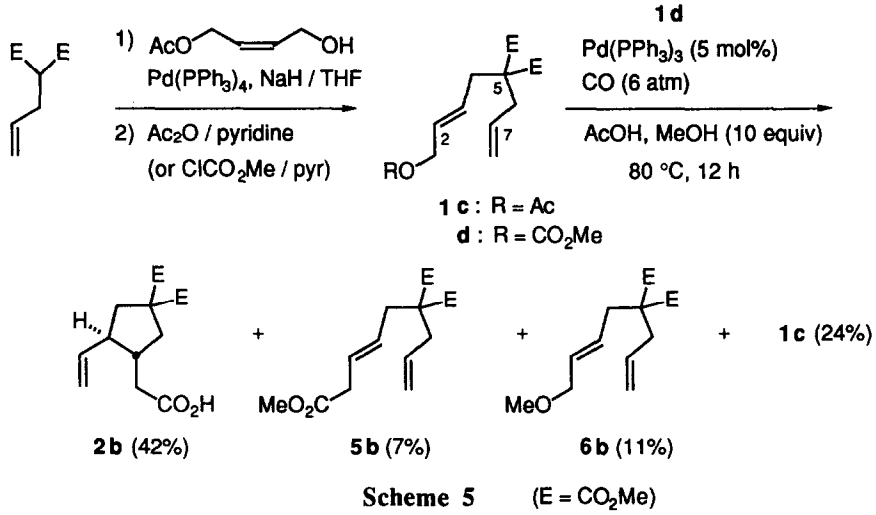
Entry	Lingand	Equiv[a]	Conditions			Yield (%)[b]		
			Time (h)	CO (atm)	Temp (°C)	**2**	**3**	**4**
1	PPh_3	3	20	1	80	50	6	13
2	PPh_3	3	20	2	80	50	9	21
3	PPh_3	3	14	5	reflux	40	–	11
4	PPh_3	3	12	20	80	39	–	–
5	PPh_3	1	5	1	80	33	–	29
6	B[c]	3	25	1	80	32	–	22
7	P(O-Tolyl-*o*)$_3$	3	28	1	80	17	–	–
8	C[d]	3	29	1	80		N. R.	
9	Dppe[e]	3/2	24	1	80		N. R.	

a) 1a (1.0 mmol) in AcOH (3 mL) : $Pd_2(dba)_3$•$CHCl_3$ (2.5 mol%) and ligand (15 mol%). b) Isolated yield.

c) B =  d) C =  e) Diphenylphosphinoethane

o-tolylphosphite is much less, whereas the phosphite **C** was found to be useless (Entries 6 – 8). Likewise, a bidentate ligand, dppe, is not effective (Entry 9). Solvent variations using 1 equiv of AcOH and/or AcONa to **1a** in MeCN have so far failed the cyclization to occur. Negishi et al,[14] however, have reported that cyclopentanol derivatives can be obtained from 4-hydroxy-2,7-octadienyl acetate via the Pd-catalyzed cyclization in MeCN, where the hydroxyl coordination to the Pd center is indispensable for the reaction, all attempts using the analogous substrates without the hydroxy substituent being in vain except in AcOH as a solvent. All results accommodated in Table 1 show that it is rather difficult to control the diastereoselective formation of the disubstituted cyclopentane derivatives. Trapping of the cyclized σ-alkylpalladium species by CO has also been studied by Oppolzer et al.[7b] Mainly, cis- or trans-substituted pyrrolidines or *cis*-3-aza-bicyclo-[3.3.0]octan-7-ones may be obtained in a highly diastereoselective manner from 5-aza-2,7-octadienyl acetates, depending on the metal (Ni or Pd) and its ligands.[15]

Dimethyl allyl(4-acetoxy-2-butenyl)malonate (**1c**) and 4-methoxycarbonyloxy analogue (**1d**) were prepared by a reported but modified procedure[15] from dimethyl allylmalonate and (*Z*)-4-acetoxy-2-buten-1-ol in the presence of $Pd(PPh_3)_4$, followed by protections using either acetic anhydride or methyl chloroformate (Scheme 5). Then, **1d** was subjected to the Pd(0)-catalyzed carbonylation to exhibit almost the same reaction patterns as those for **1b** as exemplified in Scheme 1. Typically, **1d** gave the cyclized product *trans*-4,4-bis(methoxycarbonyl)-2-vinylcyclopentylacetic acid (**2b**) in 42% yield as well as the linear methyl 6,6-bis(methoxycarbonyl)-3,8-nonadienoate (**5b**) and dimethyl allyl-(4-methoxy-2-butenyl)malonate (**6b**) in 7% and 11% yield, respectively, as depicted in Scheme 5. In addition, there was the 2,7-octadienyl acetate **1c** in 24% recovery. However, in MeOH **1d** did not undergo cyclization at all, giving **5b** (79%) and **6b** (11%), respectively. These results may imply that a facile ligand exchange from a methoxy (after decarboxylation) to an acetate ligand is taking place on the initially formed π-allylpalladium species (cf. **A** in Scheme 1) and that the π-

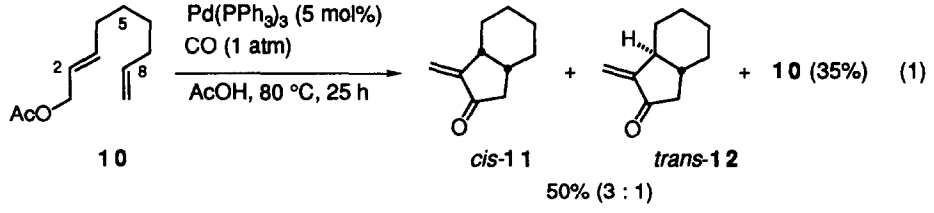


Scheme 5 (E = CO_2Me)

allylpalladium methoxide can undergo an immediate carbonylation to form **5b**, whereas the π-allylpalladium acetate directs towards reductive elimination under a CO pressure to recover **1c** or undergoes intramolecular olefin insertion prior to the carbonylation to afford eventually **2b** as observed above. Although the reaction conditions employed here are comparable to those for **1a** in Entry 3, Table 1, no cis-fused bicyclic product corresponding to **4** was obtained. It is uncertain whether the substituents attached on a 5-position of 2,7-octadienyl systems exhibit the stereodirecting effect on the product ratio. Oppolzer et al.[17] have discussed that the diastereoselectivity observed in their cases are consistent with either mechanistic alternatives; allylation of the alkene unit by an (*E*)-σ-allyl-(metallo-ene), or a *syn*-π-allylmetal (or internal σ-allyl) partner. However, the extent of diastereoselectivity in the cyclization of genuine 2,7-octadienyl systems to form disubstituted cyclopentane skeleton seems to be rather unpredictable.

2,8-Nonadienyl acetates

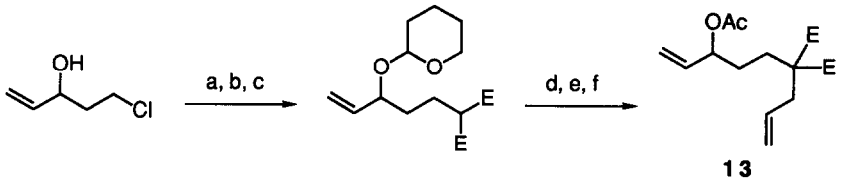
The Pd(0)-catalyzed carbonylation of plain 2,8-nonadienyl acetate (**10**)[18] in AcOH after prolonged heating for 25 h afforded *cis*- (**11**)[19] and *trans*-7-methylenebicyclo[4.3.0]nonan-8-one (**12**) in a ratio 3 : 1 in 50% combined yield (eq. 1). The second stage of cyclization (Heck reaction) must be so rapid that there was no



(1)

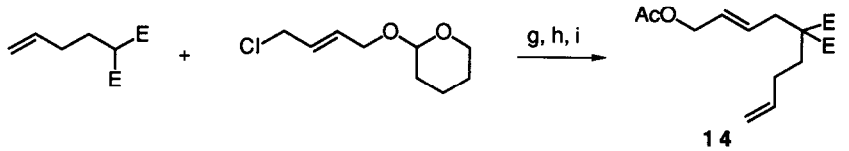
cyclohexylacetic acid at all. It was generally observed that the reactivity of **10** and its analogues toward cyclization decreased substantially (see below) not to complete the reaction under the same conditions as for **1a**. The cis-fused bicyclic enone **11** has been recorded in the literature.[19] Thus, in contrast to the cyclization of **1a**,

the major product was found to be the cis isomer **11**, diastereoselectivity being again not significant. Also in order to look at the effect of substituents attached on either 5- or 6-position of **10** on the stereochemical outcome of the present cyclization, related substrates **13** and **14** were prepared as shown in Scheme 6.



13

a : DHP / *p*-TsOH / CH_2Cl_2 ; b : NaI / NaOAc / Me_2CO ;
c : $CH_2(CO_2Me)_2$ / K_2CO_3 / Me_2CO (3 steps, 88%) ; d : CH_2=$CHCH_2Br$ / NaH / THF ;
e : *p*-TsOH / MeOH (3 steps, 74%) ; f : AcCl / pyr / CH_2Cl_2 (92%).

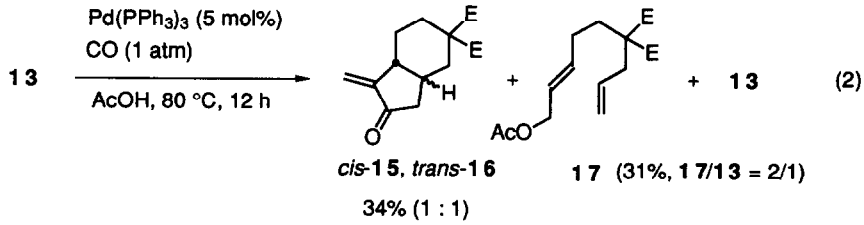


14

g : NaH / THF ; h : *p*-TsOH / MeOH ; i : AcCl /pyr / CH_2Cl_2 (3 steps 61%).

Scheme 6 (E = CO_2Me)

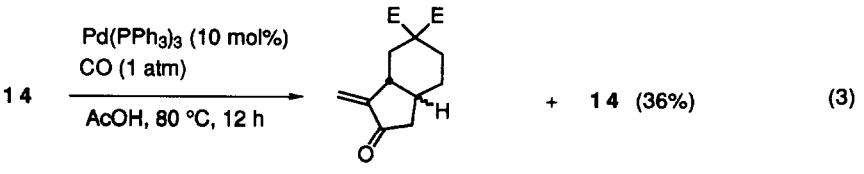
Reactions of **13** and **14** were found to proceed sluggishly to form the bicyclic enones **15**, **16**, and **18**, **19**, respectively, along with much recovery of the starting materials (eqs. 2 and 3). Recovery of **17** as a



cis-**15**, *trans*-**16**
34% (1 : 1)

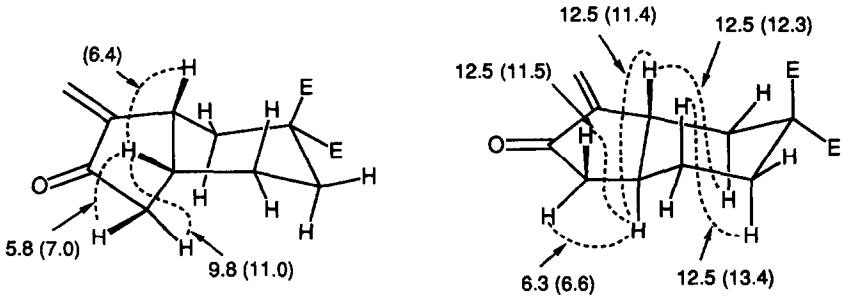
17 (31%, **17**/**13** = 2/1)

regioisomer of **13** (combined 31% recovery) again reinforces the facile reductive elimination from the π-allylpalladium acetate(cf. A, Scheme 1) which must undergo the intramolecular olefin insertion followed by the Heck reaction to give **15** and **16** in a ratio 1 : 1 in 34% combined yield. Compound **14** exhibited even less reactivity toward the Pd(0)-catalyzed cyclization to afford **18** and **19** in a ratio 1 : 1 in 23% yield under the same



cis-**18**, *trans*-**19**
23% (1 : 1)

conditions as for **13**. Stereochemistries of both **18** and **19** were assigned on the basis of ^1H NMR COSY spectra: The observed coupling constants are in satisfactory accordance with the expected ones based on the Macro Model calculations[20] as shown in Fig. 1. The diminished reactivity as well as the dull



18 (Steric energy = 13.3 kcal/mol) **19** (Steric energy =13.1 kcal/mol)

Fig. 1 $^3J_{H,H}$ **Coupling Constants.** Calculated ones in parentheses.

diastereoselectivity observed in the cyclizations of 2,8-nonadienyl acetate systems in comparison to the 2,7-octadienyl ones arises presumably from the difference in steric effects of CO_2Me substituents on the key steps of forming 6- vs. 5-membered ring by the intramolecular olefin insertion into the π-allylpalladium partner.

In conclusion, we wish to emphasize that, even before a full understanding of the diastereoselectivity in the intramolecular olefin insertion into π-allylpalladium intermediate arising especially from 2,7-octadienyl acetate is achieved, the observed cyclization-carbonylation may be effectively utilized in organic syntheses.

EXPERIMENTAL

General

IR spectra were recorded on a JASCO IR-700 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a JEOL FX-90Q or JNM GX 500 spectrometer with Me_4Si as an internal standard in $CDCl_3$. The former apparatus was generally used unless otherwise stated. GC-MS and HRMS data were obtained on a JEOL JSM-AX500 mass spectrometer. GLC analyses were performed on a Shimazu GC-4CPT (analytical) or Varian 920 (preparative) gas chromatograph equipped with a 15% Silicone DC-550 or PEG-20M on 60/80 Uniport B column (3 mm x 3 m for analytical, 5 mm x 3 m for preparative), He or H_2 was used as a carrier gas. Peak areas were calculated on Shimadzu Model C-R3A chromatopac integrator. Column chromatography was performed by using Fuji Davison BW-820 or Daiso IR-60 silica gel. HPLC separations were performed on a Nihon Seimitsu Kagaku apparatus using a Si-60 column.

Materials

$Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) was prepared according to the literature method.[21] PPh_3 was purified by recrystallization (EtOH). AcOH was distilled and stored under a nitrogen atmosphere. PhH, THF and Et_2O were distilled over benzophenone ketyl and MeOH was distilled over P_2O_5, respectively, before use. A butadiene telomer, 2,7-octadienyl acetate (**1a**) was prepared by the known procedure,[22] and 2,7-

octadienyl methyl carbonate (**1b**) was obtained from **1a** by hydrolysis followed by protection using methyl chloroformate in pyridine. *cis*-Bicyclo[3.3.0]oct-2-ene[23] (Scheme 2) and 5-chloro-1-pentene-3-ol[24] (Scheme 6) were prepared by the reported procedures. Also, dimethyl 3-butenylmalonate (Scheme 6) was prepared from 2-vinylcyclopropane-1,1-dicarboxylate[25] by the Pd-mediated hydrogenolysis.[26]

*Pd(0)-catalyzed cyclization-carbonylation of **1a** and **1b***

*a) Preparation of **2**, **3**, and **4**.* A mixture of $Pd_2(dba)_3$•$CHCl_3$ (26 mg, 2.5×10^{-2} mmol) and PPh_3 (39 mg, 0.15 mmol) were placed in a 30 mL two necked round-bottomed flask under Ar. To the flask was added deaeronated AcOH (2 mL) and the flask was flushed with CO. The solution was stirred for 15 min. To the catalyst solution was added **1a** (168 mg, 1.0 mmol) in AcOH (3 mL) and the whole mixture was heated at 80 °C for 20 h under an atmospheric pressure of CO. When CO pressure was applied, the reaction mixture was placed in a 50 mL glass-lined micro autoclave and heated for a given reaction time (see Table 1, Entries 2-4). All reactions using other phosphines or phosphites were performed under exactly the same conditions as above (Entries 6-9). A typical run (Entry 2) was given below. The catalyst deposited was filtered through a short Florisil plug. The filtrate was concentrated *in vacuo* and analyzed by GLC (Silicone DC-550 at 120 °C) to exhibit three peaks in a ratio 12 : 26 : 62 with retention times (T_R) in this order. The residue was neutralized with sat. $NaHCO_3$ and extracted with ether. The ethereal solution was washed with brine and dried ($MgSO_4$). Ether was removed to give enones **3** and **4** (42 mg, 30% combined yield). To the aqueous layer was added conc. HCl and the acidic aqueous layer was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated to give carboxylic acid **2** (77 mg, 50%).

2 : ^1H NMR (90 MHz, $CDCl_3$) δ 0.7-2.7 (m, 10H), 4.96 (dd, J = 10.0, 2.2 Hz, 1H), 5.00 (dd, J = 17.0, 2.2 Hz, 1H), 5.67 (ddd, J = 17.0, 10.0, and 7.5 Hz, 1H), and 11.2 (br s, 1H). ^{13}C (22.5 MHz, $CDCl_3$) NMR δ 23.4, 32.0, 32.6, 38.4, 42.2, 51.1, 114.6, 141.7, and 179.8. IR (neat) 3072, 2940, 2870, 1705, 1640, 1415, 1300, 955, and 915 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found : C, 69.83; H, 9,43.

3 : ^1H NMR δ 1.0-1.7 (m, 3H), 1.7-2.3 (m, 5H), 2.02 (dd, J = 16.0, 12.0 Hz, 1H), 2.51 (dd, J = 16.0, 5.5 Hz, 1H), 5.14 (dd, J = 1.6, 1.1 Hz, 1H), and 5.86 (dd, J = 2.8, 1.1 Hz, 1H). ^{13}C NMR δ 24.3, 25.8, 27.2, 42.8, 46.5, 54.8, 112.3, 148.2, and 208.2. IR (neat) 1725, and 1650 cm^{-1}. GC-MS (EI) *m/z* (%) 136 (M^+, 19.1), 121 ($M-15^+$, 1.7), 108 (26.5), 107 (21.4), 94 (61.8), 93 (60.1), 79 (100.0), 67 (45.7), and 54 (45.6). HRMS (EI) Calcd for $C_9H_{12}O$ 136.0888, Found 136.0892.

4 : ^1H NMR δ 1.2-1.4 (m, 1H), 1.5-1.7 (m, 3H), 1.9-2.0 (m, 1H), 2.0-2.2 (m, 2H), 2.5-2.7 (m, 2H), 3.0-3.4 (m, 1H), 5.28 (dd, J = 2.6, 1.1 Hz, 1H), and 6.01 (dd, J = 2.8, 1.1 Hz, 1H). ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 25.8, 34.0, 34.5, 36.9, 44.1, 45.4, 118.0, 150.3, and 208.1. IR (neat) 1720 and 1635 cm^{-1}. GC-MS (EI) *m/z* (%) 136 (M^+, 90.4), 121 ($M-15^+$, 2.4), 107 (68.8), 94 (69.3), 79 (100.0), and 67 (88.2). HRMS (EI) Calcd for $C_9H_{12}O$ 136.0888, Found 136.0821.

*b) Attempted cyclization-carbonylation of **1b**.* A mixture of $Pd(PPh_3)_3$ (0.05 mmol), prepared from $Pd_2(dba)_3$•$CHCl_3$ (26 mg) and PPh_3 (40 mg), and **1b** (184 mg, 1.0 mmol) in MeOH (3 mL) was heated at 60 °C under CO (1 atm) for 8 h. After complete consumption of **1b** by GLC analysis, the reaction mixture was worked up as described above. Columm chromatographic purification of the crude materials gave methyl 3,8-nonadienoate (**5**)[8] (118 mg, 70%) and 2,7-octadienyl methyl ether (**6**)[5b] (14 mg, 10%). From the acidified aqueous layer no **2** was detected. A mixture of **1b** (184 mg, 1.0 mmol) and $Pd(PPh_3)_3$ (2 mol%) in AcOH (3

mL) was heated at 80 °C for 4.5 h without CO. The product with low boiling point was 2-vinylmethylene-cyclopentane (**7**)[9] (65% by GLC).

c) Stereochemical assignment of **2**. *Preparation of* **8**: Into a solution of the acid **2** (100 mg, 0.65 mmol) in $CHCl_3$ was bubbled ozone for 15 min at -78 °C. A suspension of $NaBH_4$ (198 mg, 5.2 mmol) in 50% EtOH (3 mL) was added to the resulting solution at 0 °C. The mixture was stirred for 20 h at ambient temperature. The reaction mixture was quenched with 3 M HCl and aqueous layer separated was extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried ($MgSO_4$) and the solvent was removed to leave an alcohol (213 mg). To a solution of the alcohol in dry ether (13 mL) was added DCC (500 mg, 2.4 mmol) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. White precipitates formed were filtered through a celite plug and the filtrate was washed with brine and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed to afford the lactone **8** (73 mg, 80% in 2 steps). ^1H NMR δ 1.2-2.0 (m, 8H), 2.27 (dd, J = 17.8, 12.2 Hz, 1H), 2.91 (dd, J = 17.8, 4.9 Hz, 1H), 4.07 (dd, J = 10.5,10.5 Hz, 1H), and 4.61 (dd, J = 10.5, 4.6 Hz, 1H). ^{13}C NMR δ 23.5, 26.5, 31.1, 37.9, 41.7, 42.0, 74.8, and 170.3. IR (neat) 2940, 1720, 1470, and 1450 cm^{-1}.

Preparation of **9** : To a solution of *cis*-bicyclo[3.3.0]oct-2-one[23] (2 g, 18.5 mmol) in dry THF (50 mL) was added dropwise 9-BBN (0.43 M in THF, 55 mL, 23.5 mmol) at 0 °C. The reaction mixture was stirred for 8 h at room temperature. To the resulting mixture was added 35% H_2O_2 (20 mL) and 10% NaOH (20 mL) at 0 °C. After being stirred for 15 h at room temperature, the reaction mixture was washed with aq. $Na_2S_2O_3$. The aqueous layer was extracted with ether and the combined organic layer was washed with brine and dried ($MgSO_4$). The solvent was removed to give a mixture of *cis*-bicyclo[3.3.0]octan-3-ol and its regioisomer (2.3 g, 3 : 1 by GLC). To the solution of the alcohols (1g, 8 mmol) in CH_2Cl_2 (30 mL) was added PCC (2.6 g, 12 mmol) at 0 °C. After being stirred for 1 h, silica gel (2.6 g) was added and a brown solution was stirred for an additional 1 h.. The resulting mixture was filtered through a short silica gel column. The filtrate was concentrated *in vacuo* to give *cis*-bicyclo[3.3.0]octan-3-one and its regioisomer (945 mg). To a solution of the ketones (945 mg) in $CHCl_3$ (3 mL) was added dropwise a solution of *m*-CPBA (1.95 g, 11 mmol) in $CHCl_3$ (10 mL) at 0 °C. After being stirred for 12 h at room temperature, the reaction mixture was quenched with aq. $Na_2S_2O_3$ for 10 h. The aqueous layer was extracted with ether and the combined organic layer was washed with brine and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed to give **9** and its regioisomer (480 mg, 43% in 3 steps). The isomeric mixture was separated by HPLC to give pure **9**. ^1H NMR δ 1.0-3.0 (m, 10H), 4.01 (dd, J = 11.5, 6.6 Hz, 1H), and 4.29 (dd, J = 11.5, 4.8 Hz, 1H). ^{13}C NMR δ 25.8, 29.7, 34.4, 34.7(× 2), 36.7, 70.2, and 173.5. IR (neat) 2940, 2860, 1745, 1700, and 1470 cm^{-1}.

d) Preparation of **1c** *and* **1d** *(Scheme 5).* In a 200 mL three-necked flask under argon was placed NaH (50% in mineral oil, 2.5 g, 53 mmol), which was rinsed with dry hexane (15 mL × 2), dimethyl allylmalonate (7.8 g, 45 mmol) dissolved in THF (30 mL) was added slowly with stirring. $Pd(PPh_3)_4$ was prepared in situ from $Pd_2(dba)_3$•$CHCl_3$ (0.33 g, 0.32 mmol) and PPh_3 (0.68 g, 2.6 mmol) and dissolved in THF (10 mL). The catalyst solution was transferred into the sodiomalonate solution. A solution of (*Z*)-4-acetoxy-2-buten-1-ol (5.4 g, 42 mmol) in THF (10 mL) was added in one portion to the substrate solution at room temperature and the whole mixture was stirred for 6 h. After workup as usual, and column chromatographic purification afforded dimethyl allyl(4-hydroxy-2*E*-butenyl)malonate (**1e**) (3.9 g, 38%) yield. **1e**: ^1H NMR δ 2.02 (br s,

1H), 2.63 (br d, J = 7 H, 4H), 3.71 (s, 6H), 4.06 (d, J = 4.5 Hz, 2H), and 4.9-5.9 (m, 5H). Acetylation of **1e** (0.38 g, 1.6 mmol) with Ac_2O (0.3 mL) in pyridine (2 mL) at 0 °C for 0.5 h and usual workup gave **1c** in a quantitative yield. **1c**: ^{1}H NMR δ 2.05 (s, 3H), 2.63 (d, J = 7.0 Hz, 4H), 3.72 (s, 6H), 4.48 (d, J = 7.0 Hz, 2H), 5.07 (d, J = 12 Hz, 1H), 5.10 (d, J = 16 Hz, 1H), and 5.3-5.9 (m, 3H). A mixture of **1e** (1.31 g, 5.4 mmol), $ClCO_2Me$ (0.71 mL, 9.0 mmol) and pyridine (0.73 mL, 9.1 mmol) in ether (20 mL) was stirred at room temperature for 5 h. Workup as usual and chromatographic purification of the crude product afforded **1d** (1.05 g, 65%). **1d**: ^{1}H NMR δ 2.62 (br d, J = 7.0 Hz, 4H), 3.71 (s, 6H), 3.78 (s, 3H), 4.53 (d, J = 6.8 Hz, 2H), 5.08 (d, J = 18 Hz, 1H), 5.12 (d, J = 11 Hz, 1H), and 5.4-5.9 (m, 3H). IR (neat) 2930, 1740, 1640, 1435, 1250, 930, and 790 cm^{-1}.

*e) Pd(0)-catalyzed cyclization-carbonylation of **1d** (Scheme 5). In MeOH*: In a glass-lined 50 mL microautoclave with a stirring bar were placed under argon $Pd(PPh)_3$ (2.5×10^{-2} mmol), prepared in situ using $Pd_2(dba)_3$•$CHCl_3$ (13 mg) and PPh_3 (20 mg), and **1d** (153 mg, 0.5 mmol) dissolved in MeOH (4 mL). CO (10 atom) was introduced and the mixture was heated with stirring at 50 °C for 8 h. Pd catalyst deposited was filtered through a short Florisil plug, and the filtrate and MeOH washings were concentrated to leave a crude oil (149 mg). GLC analysis indicated two products **5b** and **6b** in a ratio 6 : 1. The crude products were separated by column chromatography to afford **5b** (112 mg, 79%) and **6b** (14 mg, 11%). **5b**: ^{1}H NMR δ 2.63 (d, J = 7.0 Hz, 4H), 3.04 (d, J = 6.0 Hz, 2H), 3.67 (s, 3H), 3.71 (s, 6H), and 4.9-5.9 (m, 5H). IR 3050, 2930, 2830, 1740, 1640, 1435, 1250, 1140, 930, and 785 cm^{-1}. **6b**: ^{1}H NMR δ 2.64 (d, J = 7.3 Hz, 2H), 3.29 (s, 3H), 3.72 (s, 6H), 3.84 (d, J = 4.6 Hz, 2H), and 4.8-5.9 (m, 5H). IR 3090, 2950, 2850, 1730, 1640, 1440, 1280, 1215, 1110, 975, and 900 cm^{-1}.

In AcOH: A solution of $Pd(PPh_3)_3$ (2.8×10^{-2} mmol, 5 mol%) and **1d** (166 mg, 0.55 mmol) dissolved in AcOH (5 mL) and MeOH (0.2 mL) was placed in a glass-lined 50 mL microautoclave. CO (6 atm) was introduced and the mixture was heated at 80 °C with stirring for 12 h. The catalyst deposited was filtered through a Florisil plug. The filtrate was diluted with water (10 mL) and the aqueous solution was extracted thoroughly with Et_2O. The ether extract was washed with sat. $NaHCO_3$, brine and the ether layer was separated from the aqueous solution. The ether layer was dried ($MgSO_4$) and concentrated to leave a crude oil (65 mg). GLC analysis (Silicone DC -550 at 200 °C) indicated three products **6b**, **1c**, and **5b**, (T_R in this order) in a ratio 26 : 57 : 17. Thus, the estimated yields can be **6b** (11%), **5b** (7%), and **1c** (24%), respectively. The aqueous layer was acidified with conc. HCl and extracted with Et_2O (20 mL × 3). The combined ether extract was washed with brine and dried ($MgSO_4$). The solvent was evaporated to leave a dense oil (105 mg). Pure **2b** was obtained as a colorless oil by column chromatography (63 mg, 42%).

2b: ^{1}H NMR δ 1.7–2.9 (m, 8H), 3.72 (s, 6H), 5.00 (dd, J = 9.8, 2.2 Hz, 1H), 5.04 (dd, J = 17.1, 2.2 Hz, 1H), 5.57 (ddd, J = 17.1, 9.8, 7.0 Hz, 1H), and 10.3 (br s, 1H). ^{13}C NMR δ 37.4, 39.9, 40.5, 41.1, 50.1, 52.8 (× 2), 58.5, 116.5, 139.0, 172.7, 172.9, and 178.4. IR (neat) 2950, 1735, 1710, 1640, 1440, and 1260 cm^{-1}. GC-MS (EI) *m/z* (%) 270 (M^+, 2), 252 (10), 239 (15), 224 (20), 210 (50), 192 (42), 178 (100), 164 (20), 150 (74), 119 (30), 105 (61), 91 (42), and 59 (38). HRMS (EI) Calcd for $C_{13}H_{18}O_6$ 270.1074. Found 270.1104.

*Pd(0)-catalyzed cyclization-carbonylation of **10**, **13**, and **14***

*a) Preparation of **11** and **12**.* To a solution of $Pd(PPh_3)_3$ (0.05 mmol, 5 mol%) dissolved in AcOH (2 mL) was added **10** (189 mg, 1.0 mmol) in AcOH (3 mL). The mixture was heated at 80 °C for 25 h under a

CO atmosphere. The reaction mixture was diluted with Et_2O and the Pd deposited was filtered. Work up including an alkali washing and removal of the solvent gave enones **11, 12** and the recovered **10**. Column chromatographic separation afforded **11** and **12** (72 mg, 50% combined yield) and **10** (65 mg, 35% recovery). GLC analysis indicated **11** : **12** in a ratio 3 : 1, and the products were separated by preparative GLC. **11**:[19] ^{1}H NMR δ 1.0–3.0 (m, 12H), 5.2 (dd, J = 3.0, 1.0 Hz, 1H), and 6.1 (dd, J = 3.0, 1.0 Hz, 1H). ^{13}C NMR δ 20.6, 23.9, 26.0, 28.7, 33.5, 41.1, 44.4, 116.5, 147.3, and 208.0. IR (neat) 2950, 1720, 1630, 1450, 1410, 1260, 1230, 1100, and 930 cm^{-1}. **12**: ^{1}H NMR δ 1.1–2.0 (m, 10H), 2.00 (dd, J = 17.0, 12.0 Hz, 1H), 2.41 (dd, J = 17.0, 6.0 Hz, 1H), 5.01 (dd, J = 3.0, 1.0 Hz, 1H), and 5.87 (dd, J = 3.0, 1.0 Hz, 1H). ^{13}C NMR δ 25.8, 26.3, 28.6, 31.5, 42.0, 44.4, 48.7, 112.9, 149.4, and 208.1. IR (neat) 1730 and 1650 cm^{-1}.

b) Preparation of 13. The starting material, 5-chloro-1-penten-3-ol[24] was distilled. Bp 60 °C/9 Torr. ^{1}H NMR δ 1.83 (s, 1H), 2.00 (m, 2H), 3.6-3.9 (m, 2H), 4.1-4.5 (m, 1H), 5.16 (ddd, J = 10.1, 1.7, 1,1 Hz, 1H), 5.28 (ddd, J = 17.1, 1.7, 1.1 Hz, 1H), and 5.90 (ddd, J = 17.1, 10.1, 5.9 Hz, 1H). ^{13}C NMR δ 39.4, 41.3, 70.1, 115.4, and 140.1. IR (neat) 3350, 2950, 1640, 1420, 1290, 1110, 1050, 990, 930, and 650 cm^{-1}. To a solution of the alcohol (6.4 g, 53 mmol), p-TsOH (0.5 g) in CH_2Cl_2 (55 mL) was added dropwise DHP (5.0 mL, 55 mol) at 0 °C over 5 min. The reaction mixture was stirred for 0.5 h and quenched with sat. $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried ($MgSO_4$). The solvent was removed to afford 5-chloro-3-tetrahydropyranyloxy-1-pentene (12.3 g, crude). ^{1}H NMR δ 1.4-1.8 (m, 6H), 1.8-2.3 (m, 2H), 3.4-4.0 (m, 4H), 4.1-4.3 (m, 1H), 4.6-4.8 (m, 1H), 5.1-6.1 (m, 3H). A slurry of the above chloride (5.0 g), NaI (16.2 g, 0.1 mol) and NaOAc(1.0 g, 12 mmol) in dry acetone (150 mL) was refluxed for 40 h. The reaction mixture was filtered, the filtrate was concentrated, and the residue was diluted with ether. The ethereal solution was washed with brine and dried ($MgSO_4$). The solvent was removed to give 5-iodo-3-tetrahydropyranyloxy-1-pentene (8.4 g). ^{1}H NMR δ 1.4-1.9 (m, 6H), 1.9-2.3 (m, 2H), 4.0-4.8 (m, 4H), 4.8-5.2 (m, 1H), 5.6-5.8 (m, 1H), and 5.0-6.1 (m, 3H).

Preparation of dimethyl 1-(3-tetrahydropyranyloxy-4-pentenyl) malonate: A mixture of the alkyl iodide (8.4 g, crude), dimethyl malonate (8.9 mL, 78 mmol), powdered K_2CO_3 (48 g, 0.35 mol) and dry acetone (350 mL) was refluxed for 19 h. The reaction mixture was filtered, the filtrate was concentrated, and the residue was diluted with ether. After workup as usual and removal of the solvent, the residue was chromatographed (eluent hexane/ether = 20/1) to afford the alkylated malonae (6.4 g, 88% in 3 steps). ^{1}H NMR δ 1.4-1.8 (m, 6H), 1.8-2.1 (m, 4H), 3.2-3.5 (m, 3H), 3.74 (s, 6H), 3.9-4.1 (m, 1H), 4.6-4.7 (m, 1H), and 5.0-6.1 (m, 3H). To a slurry of NaH (55% in mineral oil, 1.1 g, 25 mmol) in dry THF (220 mL) was added dropwise the alkylated malonate (6.4 g, 21.3 mmol) in dry THF (50 mL) at 0 °C. The mixture was stirred for 1 h. To the mixture was added allyl bromide (3.7 mL, 43 mmol) in one portion at 0 °C. The reaction mixture was stirred for 2 h at room temperature and quenched with 1 M HCl. After usual workup, the solvent was removed to give dimethyl 1-(3-tetrahydropyranyloxy-4-pentenyl)-(2-propenyl) malonate (8.1 g). ^{1}H NMR δ 1.3-1.7 (m, 6H), 1.7-2.1 (m, 4H), 2.61 (d, J = 7.0 Hz, 2H), 3.3-3.6 (m, 2H), 3.70 (s, 6H), 3.8-4.2 (m, 1H), 4.6-4.7 (m, 1H), and 4.9-5.0 (m, 6H). A solution of the above malonate (8.1 g), p-TsOH (0.5 g)in MeOH (150 mL) was stirred for 2 h at room temperature. After removal of MeOH, the residue was diluted with ether and washed with sat. $NaHCO_3$.

The aqueous layer was extracted with ether. The combined organic layer was washed with brine and dried ($MgSO_4$). After removal of ether, the residue was chromatographed (eluent hexane/ether = 1/1) to afford the alcohol, 1-(3-hydroxy-4-pentenyl)-(2-propenyl)malonate (4.0g, 74% in 3 steps). ^1H NMR δ 1.3-1.6 (m, 2H), 1.74 (s, 1H), 1.8-2.1 (m, 2H), 2.64 (d, J = 7.0 Hz, 2H), 3.71 (s, 6H), 3.9-4.1 (m, 1H), 5.66 (ddt, J = 17.4, 9.3, 7.0 Hz, 1H), and 5.50 (ddd, J = 17.4, 10.1, 6.1 Hz, 1H). ^{13}C NMR δ 28.5, 31.6, 37.5, 52.4 (× 2), 57.5, 72.9, 115.1, 119.0, 132.5, 140.7, and 171.6 (× 2). IR (neat) 3450, 2950, 1730, 1640, 1430, 1260, 1230, 1200, 1140, 990, 920, 740, 680, and 650 cm^{-1}.

To a solution of the above alcohol (3.0 g, 11.7 mmol), pyridine (2.0 mL, 24.7 mmol) in CH_2Cl_2 (40 mL) was added dropwise AcCl (0.9 mL, 12.6 mmol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, diluted with ether, and the ethereal solution was washed with 1 M HCl. After workup and removal of the solvent, the residue was chromatographed (eluent hexane/ether = 10/1) to give the acetate **13** (3.2 g, 92%). ^1H NMR δ 1.8-2.0 (m, 4H), 2.06 (s, 3H), 2.63 (d, J = 6.8 Hz, 2H), 3.72 (s, 6H), 5.0-5.4 (m, 5H), 5.57 (ddt, J = 17.7, 12.2, 6.8 Hz, 1H), and 5.77 (ddd, J = 18.3, 10.3, 6.4 Hz, 1H). ^{13}C NMR δ 21.1, 27.9, 28.7, 37.3, 52.3 (× 2), 57.3, 74.3, 117.2, 119.1, 132.3, 135.9, 170.0, and 171.3 (× 2). IR (neat) 2880, 2830, 1750, 1730, 1645, 1440, 1385, 1220, 1150, 1020, 930, and 860 cm^{-1}.

c) Pd(0)-catalyzed cyclization-carbonylation of 13. To a solution of $Pd(PPh_3)_3$ (0.05 mmol, 5 mol%), prepared from $Pd_2(dba)_3$•$CHCl_3$ (25.9 mg) and PPh_3 (39.5 mg), in AcOH (1 mL) was added **13** (297 mg, 1.0 mmol) in AcOH (4 mL) under a CO atmosphere. The reaction mixture was sirred for 12 h at 80 °C. The catalyst deposited was filtered through a Florisil plug. The filtrate was worked up as usual. After removal of the solvent, the residue was chromatographed to afford the enones **15** and **16** (89.4 mg, 34% combined yield) along with the starting material **13** and its regioisomer **17** (91.3 mg, 31%, **13** : **17** = 1 : 2). GLC analysis of the products indicated **15** : **16** = 1 : 1. **15**: ^1H NMR δ 1.6-3.2 (m, 10H), 3.68 (s, 3H), 3.78 (s, 3H), 5.28 (d, J = 2.6 Hz, 1H), and 6.18 (d, J = 2.6 Hz, 1H). ^{13}C NMR δ 21.7, 25.1, 30.7, 33.4, 39.4, 44.8, 52.5, 52.7, 54.4, 117.2, 145.0, 171.0, 172.1, and 206.0. IR (neat) 3028, 2952, 1729, 1646, 1452, 1434, 1240, 1092, 1062, 943, 921, and 520 cm^{-1}. **16**: ^1H NMR δ 1.2-2.8 (m, 10H), 3.73 (s, 3H), 3.76 (s, 3H), 5.10 (d, J = 2.2 Hz, 1H), and 5.90 (d, J = 2.2 Hz, 1H). ^{13}C NMR δ 25.1, 31.2, 36.1, 37.9, 43.7, 47.6, 52.7, 52.8, 55.5, 113.7, 148.0, 171.3, 172.2, and 204.5. IR (neat) 3028, 2952, 1720, 1648, 1451, 1435, 1270, 1069, 942, 913, and 545 cm^{-1}. **17**: ^1H NMR δ 1.9-2.0 (m, 4H), 2.06 (s, 3H), 2.65 (d, J = 7.3 Hz, 2H), 3.72 (s, 6H), 4.49 (d, J = 5.3 Hz, 2H), and 4.9-5.8 (m, 5H). ^{13}C NMR δ 20.9, 26.9, 31.8, 37.3, 52.3 (× 2), 57.4, 64.9, 119.0, 124.7, 132.3, 134.5, 170.7, and 171.4 (× 2). IR (neat) 2952, 1737, 1641, 1438, 1380, 1231, 657, and 608 cm^{-1}.

d) Preparation of 14. Another component for preparing **14**, (*E*)-4-(tetrahydropyranyloxy)-1-chloro-2-butene,[27] was prepared from (*E*)-1,4-diacetoxy-2-butene by conventional procedures involving patial methanolysis (K_2CO_3 in MeOH, 0 °C, 10 min), chlorination (PPh_3 in CCl_4, reflux, 20 h), methanolysis (same as above), and protection of the resulting alcohol (DHP, *p*-TsOH in CH_2Cl_2, 0 °C, 5 h) in 12% overall yield. To a suspention of NaH (0.39 g, 55% in mineral oil, 16 mmol) in dry THF (40 mL) was added dropwise dimethyl 3-butenylmalonate (1.5 g, 8.1 mmol) in THF (40 mL) at 0 °C and the mixture was stirred for 0.5 h. To the mixture was added the above 2-butenyl chloride (1.4 g, 7.3 mmol) in THF (20 mL). The whole reaction mixture was stirred for 12 h at room temperature and quenched with 0.5 M HCl. Workup and short column

chromatography afforded the crude dimethyl {4-tetrahydropyranyloxy-2(*E*)-butenyl}-3-butenylmalonate (2.6 g). ^{1}H NMR δ 1.5-1.8 (m, 6H), 1.8-2.1 (m, 4H), 2.5-2.7 (m, 2H), 3.7 (s, 6H), 3.4-4.2 (m, 4H), 4.4-4.6 (m 1H), 4.8-5.1 (m, 2H), and 5.5-6.0 (m, 3H). The product was deprotected (a catalytic amount of *p*-TsOH in MeOH for 2 h) and resulting alcohol was purified by column chromatography (eluent : hexane/ether = 1/2). ^{1}H NMR δ 1.58 (s, 1H), 1.8-2.0 (m, 4H), 2.5-2.7 (m, 2H), 3.72 (s, 6H), 4.07 (d, J = 4.4 Hz, 2H), 4.8-5.1 (m, 2H), and 5.5-5.8 (m, 3H). The alcohol (1.2 g, 4.7 mmol) was acetylated (AcCl/pyridine/CH_2Cl_2, 0 °C for 1 h) and the product was purified by column chromatography to give **14** (1.2 g, 87%). ^{1}H NMR δ 1.8-2.0 (m, 4H), 2.05 (s, 3H), 2.5-2.7 (m, 2H), 3.71 (s, 6H), 4.4-4.5 (m, 2H), 4.8-5.1 (m, 2H), and 5.5-5.9 (m, 3H). ^{13}C NMR δ 20.8, 28.3, 31.9, 35.8, 52.2 (× 2), 57.3, 64.3, 114.8, 128.2, 129.2, 137.0, 170.1, and 170.9 (× 2). IR (neat) 2895, 1730, 1640, 1420, 1210, 1030, 970 cm^{-1}.

e) Pd(0)-catalyzed cyclization-carbonylation of ***14****.* $Pd(PPh_3)_3$ (0.1 mmol), was prepared similarly from $Pd_2(dba)_3$·$CHCl_3$ (52 mg) and PPh_3 (79 mg) and rinsed with dry Et_2O. To the catalyst (10 mol%) was added **14** (307 mg, 1.03 mmol) dissolved in AcOH (5 mL) under CO. The reaction mixture was heated at 80 °C for 12 h. The catalyst deposited was filtered through a Florisil plug and the filtrate was worked up as usual. Chromatographic purification afforded the starting material **14** (109 mg, 36% recovery) and the enones **18** and **19** (62 mg, 23% combined yield). The ratio of **18** : **19** was 1 : 1 by GLC analysis. **18**: ^{1}H NMR (500 MHz) δ 1.6-1.7 (m, 2H), 1.78 (dd, J = 13.7, 9.8 Hz, 1H), 1.9-2.0 (m, 2H), 2.29 (dd, J = 13.7, 5.8 Hz, 1H), 2.34 (br s, 3H), 3.0 (m, 1H), 3.61 (s, 3H), 3.71 (s, 3H), 5.26 (s, 1H), and 5.94 (s, 1H). ^{13}C NMR (125 MHz) δ 23.3, 26.3, 31.4, 32.1, 38.6, 40.7, 52.8 (× 2), 53.4, 117.7, 148.8, 171.6, 172.1, and 206.0. **19**: ^{1}H NMR (500 MHz) δ 1.4-1.6 (m, 2H), 1.71 (dd, J = 12.5, 12.5 Hz, 1H), 1.78 (ddd, J = 12.5, 12.5, 3.1 Hz, 1H), 1.96 (dd, J = 15.9, 12.5 Hz, 1H), 2.0-2.1 (m, 1H), 2.18 (ddd, J = 12.5, 12.5, 3.1 Hz, 1H), 2.42 (dd, J = 15.9, 6.3 Hz, 1H), 2.54-2.58 (m, 1H), 2.83 (ddd, J = 12.5, 12.5, 3.1 Hz, 1H), 3.74 (s, 1H), 3.78 (s, 1H), 5.14 (d, J = 2.8 Hz, 1H), and 5.94 (d, J = 2.8 Hz, 1H). ^{13}C NMR (125 MHz) δ 27.8, 31.6, 33.5, 41.1, 43,7, 44.6, 52.9, 53.0, 55.2, 114.0, 148.0, 171.4, 172.3, and 205.1. IR (neat) 2952, 2860, 1735, 1648, 1450, 1248, 788, and 764 cm^{-1}.

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18. Preparation of **10**: Ethyl 2,8-nonadienoate was prepared in 28% yield by the consecutive Wittig reactions with 1,6-hexanedial using methylenetriphenylphosphorane and triethyl phosphonoacetate ylid, respectively, in THF. Reduction of the ester with DIBAL (2.6 equiv) in THF at -60 °C and acetylation of the resulting 2,8-nonadienol with Ac_2O/pyridine at 0 °C gave **10** in 66% overall yield. NMR data of **10** given: ^1H NMR (90 MHz, $CDCl_3$) δ 1.3-1.6 (m, 4H), 1.9-2.3 (m, 4H), 2.06 (s, 3H), 4.50 (d, J = 5.3 Hz, 2H), 4.94 (ddt, J = 10.0, 1.3, and 1.0 Hz, 1H), 4.98 (ddt, J = 17.0, 2.3, and 1.3 Hz, 1H), 5.6 (m, 2H), and 5.72 (ddt, J = 17.0, 10.0, and 6.8 Hz, 1H). ^{13}C NMR (22.5 MHz) δ 20.9, 28.4(×2), 32.1, 33.6, 65.2, 114.4, 124.1, 136.2, and 138.8. IR (neat) 2925, 2850, 1740, 1540, 1440, 1375, 1230, 1030, 970, 910 cm^{-1}.
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27. Spectral data of (*E*)-4-(tetrahydropyranyloxy)-1-chloro-2-butene given: ^1H NMR δ 1.4-2.0 (m, 6H), 3.3-4.4 (m, 6H), 4.5-4.7 (m, 1H), and 5.6-6.1 (m, 2H). ^{13}C NMR δ 19.4, 25.5, 30.6, 44.4, 62.1, 66.4, 98.1, 127.9, and 131.3. IR (neat) 2950, 1450, 1360, 1210, 1140, 1030, 980, 760, and 690 cm^{-1}.

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