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Chemo- and Stereoselective Palladium-Catalyzed Allylic Alkylations Controlled by Silicon

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A series of 2-silylbut-2-ene-1,4-diol derivatives **2** bearing different substituents on the silicon atom have been prepared and tested in palladium-catalyzed alkylations with dimethyl malonate. Totally chemo- and stereoselective, these high yielding reactions are strongly influenced by the presence of the silicon group on the allyl moiety. The preparation and reactivity of two analogues **9** where the silyl group is replaced by a *tert*-butyl group were also examined. Their difference of reactivity toward the nucleophile can be ascribed to the ability of the silicon group to stabilize a β-carbocation. Indeed, both steric and electronic factors are responsible for this behavior.

Introduction

Palladium plays an important role in organic chemistry as a result of the broad applications of its catalytic activity and the versatility of its utilization,[1] which has been exhaustively illustrated in a recent two-volume handbook containing more than 150 authored sections.[2] Among others, palladium-catalyzed allylations of various nucleophiles are one of the major achievements in this field. The possibility of controlling the chemo-, regio-, and enantioselectivity of the attack of the nucleophiles onto the η^3-allyl ligand is still a challenging research area. A lot of work has dealt with the variation of the ligands around the metal,[3,4] the steric and electronic influence of the substitutents of the allyl moiety,[5] or the role of the solvent.[6] Organosilicon compounds are versatile and powerful reagents with many applications in organic synthesis.[7] Moreover, silanes have attracted considerable attention not only as biologically acceptable analogues of natural products[8] but also because silicon acts as a directing atom that increases[9] or reverses selectivities usually observed for its carbon analogues.[10] Recently, organosilanes have been extensively studied in cross-coupling reactions catalyzed by palladium.[11,12] For example, Tietze took advantage of the presence of a silicon group to direct the last step of a domino-Heck double cyclization process.[13] On the other hand, Hirao et al. reported first, nearly 2 decades ago, that 1- or 3-trimethylsilylallyl acetates in the presence of a palladium catalyst could react regio- and stereoselectively with stabilized carbon nucleophiles, giving the corresponding vinylsilanes as the only product.[14] It was shown that the nucleophilic attack occurred at the carbon γ relative to

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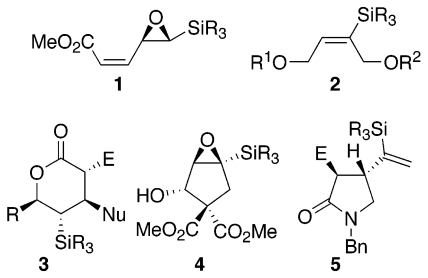
the silicon. Sometime later, for other 1- or 3-silyl-substituted allylic derivatives, Trost,[15] Murahashi,[16] and Tsuji[17] reported the utility of the silicon group to direct the nucleophilic attack in favor of the formation of the corresponding vinylsilane. In 1993, Sato extended this powerful reaction to the synthesis of optically active γ-trimethylsilyl allylamine derivatives.[18] More recently, Branchadell et al. published theoretical studies dealing with silyl-substituted π-allyl palladium complexes.[19] Finally, Yamamoto and co-workers noticed that a silicon group attached to the central position of a π-allyl system could influence the reactivity and regioselectivity during palladium-catalyzed carbonylations.[20] The first example of the highly chemo- and stereoselective alkylation of 2-triethylsilylbutenyl acetates was reported in 1996.[21]

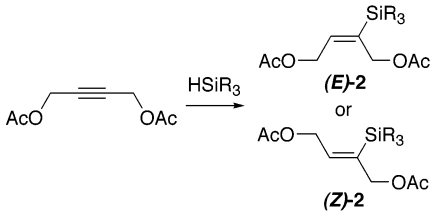
Our interest in the use of vinylepoxides in palladium-catalyzed reactions[22] as cheap starting materials for synthesis[23] was significantly enhanced when we observed the unusual reactivity of 1-silyl-substituted vinylepoxides **1**.[24] We extended our effort to triethylsilylated bisallylic derivatives **2**.[25] Gratifyingly, these substrates have been successfully used as synthons for the stereoselective synthesis of highly substituted lactones **3**,[26] cyclopentanols **4**,[27] or pyrrolidones **5**[28] (Scheme 1).

In this article, we describe our study on the influence of the silicon and its substituents on the chemo- and stereoselectivities observed during palladium-catalyzed allylations of 2-silylbut-2-ene-1,4-diol derivatives **2**. Depending on its position, the silicon group strongly influences the formation and the reactivity of the cationic π-allyl palladium complex. The main goal of this work was to demonstrate that steric as well as electronic factors are responsible for this behavior.

SCHEME 1



SCHEME 2[a]



[a] Reagents and conditions: $HSiR_3$ (1.1 equiv); THF (4 M); 60 °C; 8 h; catalyst (cf. Table 1).

Results and Discussion

The different precursors required for our study were obtained from commercially available 2-butyne-1,4-diol diacetate. *Syn* hydrosilylation of the triple bond using the Speier catalyst[29] gave, in excellent yield, the (*E*)-silyl-substituted diacetates **2** (Scheme 2). When not commercially available, the desired silanes were prepared from dimethylchlorosilane and aryl Grignard reagents. The (*Z*)-triethylsilyl diacetate **2a** was prepared from the same precursors using a cationic ruthenium complex[30] as a stereoselective *trans* hydrosilylation catalyst.[31]

These precursors **2** present two potential leaving groups that are differentiated only by their position relative to the silicon group. Anticipating that there might be an interesting high chemoselectivity in the presence of palladium, we began our study with compound (*E*)-**2a** using dimethyl malonate as the nucleophile (Scheme 3). In neutral (BSA) or basic (NaH) conditions, (*E*)-**2a** led to the corresponding adduct **6a** in 95% yield. In this reaction, catalysts prepared from both $Pd(OAc)_2$ and PPh_3 or diphenylphosphinoethane (dppe) are ef-

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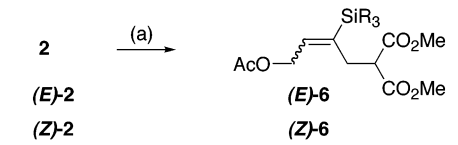
TABLE 1. Isolated Yields in Preparation of Vinylsilanes 6

entry	$HSiR_3$	catalyst[a]	precursor **2** (%)[b]	time (h)	vinylsilane **6** (%)[b]	*E*/*Z* ratio[c]
1	$HSiEt_3$	A	(*E*)-**2a** (100)	3	**6a** (95)	98/2
2	$HSiEt_3$	B	(*Z*)-**2a** (91)	3	**6a** (72)	10/90
3	$HSiMe_2t$-Bu	A	(*E*)-**2b** (85)	0.25	**6b** (100)	100/0
4	$HSiMe_2Ph$	A	(*E*)-**2c** (100)	3	**6c** (94)	95/5
5	$HSiMePh_2$	A	(*E*)-**2d** (100)	3	**6d** (>98)	100/0
6	$HSiPh_3$	A	(*E*)-**2e** (72)	88	**6e** (0)	
7	$HSiMe_2$(4-MeO-C_6H_4)	A	(*E*)-**2f** (100)	3	**6f** (82)	95/5
8	$HSiMe_2$(4-CF_3-C_6H_4)	A	(*E*)-**2g** (72)	3	**6g** (64)	98/2

[a] Catalyst A: $H_2PtCl_6 \cdot 6H_2O$ (0.01 mol %). Catalyst B: $[Cp^*Ru(PPh_3)(CH_3CN)_2]PF_6$ (1 mol %). [b] Isolated yields. [c] *E*/*Z* ratio determined by ^1H NMR and GC analysis on the crude reaction mixture.

SCHEME 3[a]



[a] Reaction conditions: dimethyl sodiomalonate (1.2 equiv), 5 mol % $Pd(dppe)_2$, THF, 0 °C, 0.25−3 h.

ficient. The palladium loading could be reduced from 5 to 2 mol % on a large scale. Gratifyingly, the silicon group totally differentiated the two potential leaving groups: only the β-acetate relative to silicon is displaced.[32] The structure of (*E*)-**6a** was determined by spectroscopic analysis. For example, in the ^1H NMR, we observed the disappearance of the singlet at 4.70 ppm, attributed to the reactive methylene in **2a**, and the appearance of a doublet at 2.76 ppm in (*E*)-**6a**. Moreover, (*E*)-**6a** has a doublet at 4.70 ppm corresponding to the nonreactive methylene, whereas (*E*)-**2a** has its doublet at 4.74 ppm. The configuration of the double bond was assigned as (*E*) after separation of the (*E*) and (*Z*) isomers and analysis of their ^{13}C NMR spectra.[33] These configurations were later confirmed chemically by the transformation of (*E*)-**6a** into the cyclopentanol **4**.[34]

In addition, we were pleased to observe high stereoselectivity in this reaction. Starting from (*E*)-**2a**, **6a** was obtained in a *E*/*Z* ratio varying from 90/10 at room temperature to 98/2 at 0 °C (entry 1, Table 1). Moreover, in the case of the isomer (*Z*)-**2a**, the configuration of the double bond is also mainly retained. In this case too, the *E*/*Z* ratio is strongly dependent on the temperature of the reaction, varying from 25/75 at room temperature to 10/90 at 0 °C. From both stereoisomers **2a**, the yields are good with a slightly better yield for the (*E*)-isomer (95% vs 72%) (entries 1 and 2, Table 1). Subsequently, the alkylation of dimethyl malonate with a number of variously substituted silanes was performed; the results are summarized in Table 1. All reactions except one (entry 6, Table 1) afforded the vinylsilanes **6** in good yields. Both alkyl and aryl derivatives are tolerated. The presence of one or two phenyl groups on the silicon atom gave similar reactivity and stereoselectivity (entries 4 and 5, Table 1). On the other hand, a significant break comes with the triphenylsilyl derivative **2e** (entry 6, Table 1). No reaction took place under the same conditions. Even after 4 days of reflux, the starting vinylsilyl diacetate was recovered; no trace of the expected product nor degradation was observed. It seems that the presence of three phenyl groups on silicon completely inhibits the coordination of the palladium to the double bond. To explore the possibility of an electronic control, we prepared and tested two vinylsilanes with electron-donating or electron-withdrawing aryl substituents. Both are tolerated and gave the corresponding products in 82% and 64% yields, respectively (entries 7 and 8, Table 1). These results clearly demonstrate that the silicon group plays an important role in the reactivity of the cationic π-allylic palladium complexes. It completely controls the ionization of only one of the two possible leaving groups and in addition the *syn*-*anti* isomerization of the π-allyl palladium intermediates. As a matter of fact, relatively few studies have been reported in the literature concerning the total transfer of the *Z* geometry of the double bond in palladium-catalyzed alkylation with classical ligands. Usually, this goal has been successfully achieved by the use of ligands having large bite angles or with special electronic factors such as Xantphos or phenanthroline derivatives.[35]

To better determine the relative importance of electronic and/or steric factors responsible for such selectivity, we decided to replace the silyl group by a *tert*-butyl group (Scheme 4).

To achieve this goal, the diacetate and the dicarbonate were prepared by first carbocupration of 1,4-butynediol with 4 equiv of a 1.8 M THF solution of *tert*-butylmagnesium chloride in the presence of 10 mol % of CuBr·Me_2S as catalyst.[36] We were pleased to isolate the expected diol **7** in 50% yield[37] with only 27% yield of the corresponding allene **8** as byproduct. The simple functionalization of **7** using acetyl chloride or methyl chloroformate gave the desired diacetate **9a** or dicarbonate **9b** in high yields (Scheme 4). These two new dielectrophiles were mixed with the sodium salt of dimethyl malonate and a catalytic amount of the palladium complex. The reactions were very slugglish with low conversion even

(32) The same chemoselectivity was observed with a vinylsilane bearing an acetate in the β position and a carbonate in the γ position. This specific dielectrophile reacts in an unusual manner because the acetate is, in this special case, a better leaving group than the carbonate; see: Thorimbert, S.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 8483−8486.

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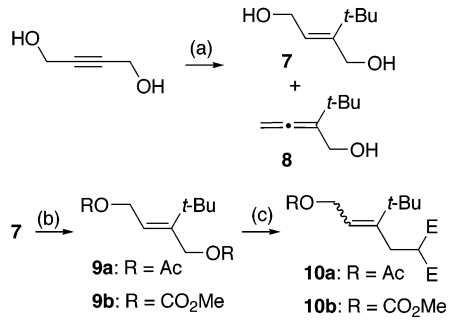
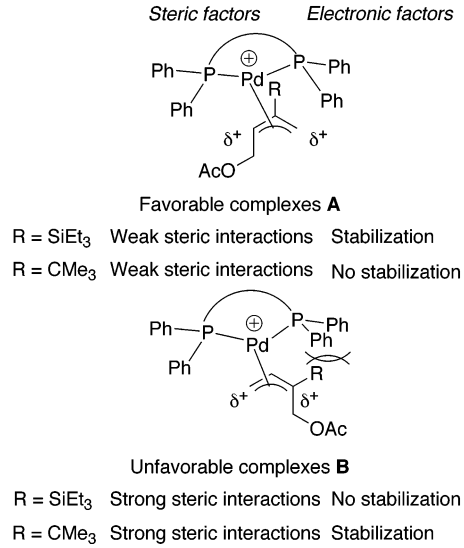
SCHEME 4[a]



[a] Reaction conditions: (a) *tert*-BuMgCl (4 equiv), CuBr·Me_2S (10 mol %), THF, −30 °C (1 h) to rt (12 h); **7**: 50%, **8**: 27%; (b) (i) Ac_2O (3 equiv), pyridine (3 equiv), CH_2Cl_2, 12 h; **9a**: 100%; (ii) $ClCO_2Me$ (2.4 equiv), pyridine (2.4 equiv), DMAP (5 mol %), CH_2Cl_2; **9b**: 85%; (c) compound **9a**, dimethyl sodiomalonate (1.1 equiv), 5 mol % $Pd(dppe)_2$, THF, reflux, 3 days; **10a**: 25%, *Z*/*E* ratio: 48/52. Compound **9b**, dimethyl malonate (1.1 equiv), 5 mol % $Pd(dppe)_2$, THF, (i) no base added, reflux, 3 days; **10b**: 20%. *Z*/*E* ratio: 43/57; (ii) NaH as base, reflux, 12 h; **10b**: 45%, *Z*/*E* ratio: 83/17.

at reflux, and we isolated the alkylated products in relatively poor yields after 3 days. Under basic conditions, the acetate **10a** and the carbonate **10b** were obtained in 25% and 45% yield, respectively. In the absence of base, the carbonate **10b** was isolated in a poorer yield of 20%. However, NMR analysis of the crude products showed that only the leaving group in the vicinal position relative to the *tert*-butyl function had been replaced. In the case of the carbonate **9b**, a slight difference in the stereoselectivity was observed depending on the conditions used for the alkylation. Without preforming the sodium salt of the dimethyl malonate, a nearly 1/1 mixture of both possible stereoisomers of **10b** was isolated, whereas under basic conditions **10b** was obtained with a *Z*/*E* ratio of 83/17. The high chemoselectivity but the relatively low stereoselectivity observed for these reactions (vide supra) in comparison with the high chemo- and stereoselectivity observed for the silicon analogues could be explained by both steric and electronic effects affecting the ionization process. Indeed, in the carbon or silicon series, depending on which acetate is involved, two possible π-allylic cationic palladium complexes **A** and **B** could be generated. In **B** there are strong interactions between the aryl groups on the phosphorus atom and the SiR_3 or CMe_3 groups (Scheme 5), whereas in complex **A** the phosphorane ligands surround the substituent at the central position of the allyl moiety.[38] Electronic effects also play an important role in view of the relative reactivity of the different electrophiles. Reactions take place at low temperature with fast rates and good yields for the silicon-substituted acetates **2**, whereas the same alkylations require higher temperature and longer reaction time and give only moderate yields for the alkyl derivatives **9a** and **9b**. Silicon is well-known to stabilize a β positive charge.[39]

SCHEME 5



Such a stabilization could be present in **A**, whereas in **B** the silicon group is directly bonded to a terminal, partially positive carbon atom. In this process, steric and electronic effects due to the silicon atom act in a synergistic manner, thereby explaining the fast and high yielding alkylation. Finally, the retention of the configuration of the double bond during the alkylation from the diacetates **2** probably results from the presence of the silicon atom, which allows a relatively faster attack of the nucleophile than the $\pi-\sigma-\pi$ isomerization usually observed in palladium-catalyzed alkylations.[40] In comparison, in the *tert*-butyl series, where the electronic and steric factors are opposite, the alkylation takes place with lower reactivity.

Conclusion

In conclusion, we have reported that 2-silylbut-2-ene-1,4-diol derivatives are suitable substrates for palladium-catalyzed allylic alkylations. (*Z*)- or (*E*)-Vinylsilanes are easily prepared by stereoselective hydrosilylations using either platinum or ruthenium catalysts. In all of the precursors, the presence of the silyl group allows the fast and highly selective differentiation of both potential allylic leaving groups. The formation of only one π-allylic palladium complex could be ascribed to steric and electronic factors that work in the same direction. Moreover, the presence of the silicon atom, which overall speeds up the attack of the nucleophile, allows the retention of the configuration of the double bond. Coupled with palladium-catalyzed cross-coupling reactions, this efficient alkylation will surely find new development in the field of organic chemistry applied to synthesis.

Experimental Section

General Procedure A for Hydrosilylation. (*E*)-Acetic Acid 4-Acetoxy-2-(triethylsilanyl)but-2-enyl Ester [(*E*)-2a]. To a stirred solution of 2-butyne-1,4-diol diacetate (7 g,

(37) (a) Without CuBr, the preparation of an *iso*-propyl analogue of diol **7** has been reported in 12% yield; see: de Silva, A. N.; Francis, C. L.; Ward, D. A. *Aust. J. Chem.* **1993**, *46*, 1657−1672. (b) For the use of 2-*iso*-propylbutenylene dicarbamates in palladium-catalyzed cyclization, see: Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1987**, *28*, 4837−4840.

(38) For the first report on the "ligand pocket effect" in palladium-catalyzed alkylation, see: Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143−1145. See also refs 1, 2, and 22b.

(39) (a) Lambert, J. B.; Emblidge, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 1317. (b) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677−2689.

(40) (a) Ogasawara, M.; Takizawa, K.-I.; Hayashi, T. *Organometallics* **2002**, *21*, 4853−4861. (b) van Haaren, R. J.; van Strijdonck, G. P. F.; Oevering, H.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Eur. J. Inorg. Chem.* **2001**, 837−843.

41.1 mmol) in THF (12 mL) were added triethylsilane (7.3 mL, 45.2 mmol) and a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ (0.4 mL, 0.01 mol %) in THF. The mixture was heated at 50 °C for 12 h, cooled, and filtered over Celite. The solvent was removed under vacuum, and the residue was purified by flash chromatography on a silica gel column to yield 11.14 g of (*E*)-**2a** (95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.93 (t, 1H, J = 6.0 Hz); 4.74 (d, 2H, J = 6.0 Hz); 4.71 (s, 2H); 2.07 (s, 3H); 2.05 (s, 3H); 0.91 (t, 9H, J = 7.6 Hz); 0.63 (q, 6H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8; 170.7; 138.6; 137.1; 62.7; 61.5; 21.0; 7.3; 3.0. IR (neat), cm^{-1}: 2950; 1740; 1610; 1430; 1220; 1150; 1020; 730. Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.81; H, 9.15.

(*Z*)-Acetic Acid 4-Acetoxy-2-triethylsilanyl-but-2-enyl Ester [(*Z*)-2a]. Following the general method A, except for the catalyst [Cp*Ru(PPh_3)(CH_3CN)$_2$]PF_6 (1 mol %). The product was obtained as a colorless oil. Yield: 1.05 g, 91%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.31 (tt, 1H, J = 7.1 and 1.5 Hz); 4.60 (d, 2H, J = 7.1 Hz); 4.54 (s br, 2H); 2.02 (s, 6H); 0.89 (t, 9H, J = 7.6 Hz); 0.64 (q, 6H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7; 170.5; 138.8; 137.2; 69.2; 63.2; 21.0; 20.9; 7.3; 3.7. IR (ATR), cm^{-1}: 2954; 2876; 1739; 1458; 1364; 1217; 1079; 1020; 959; 721. Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70; H, 9.15. Found: C, 58.28; H, 9.28.

General Procedure B for Alkylation of Diacetate by Dimethylmalonate. (*E*)- and (*Z*)-2-[4-Acetoxy-2-(triethylsilanyl)but-2-enyl]-malonic Acid Dimethylester (6a). At 0 °C, under argon, to a suspension of sodium hydride 60% in mineral oil (3.14 g, 78.9 mmol) in THF (190 mL) was added dropwise dimethylmalonate (6.3 mL, 79 mmol), and the reaction mixture was warmed to room temperature for 30 min. In a separate flask, $Pd(OAc)_2$ (235 mg, 2 mol %) was dissolved in THF (25 mL), diphenylphosphinoethane (1.67 g, 8 mol %) was added, and the solution was stirred for 30 min. Then, diacetate (*E*)-**2a** (15 g, 52.6 mmol) was added, and the resulting mixture was added dropwise by cannula to the malonate anion. After completion of the alkylation, the solution was diluted with diethyl ether and washed with a satured solution of ammonium chloride. The aqueous phase was extracted with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure, and the product was purified by flash chromatography on a silica gel column to afford (*E*)-**6a** (17.9 g, 95%) as a colorless oil. Data identical to the literature.[21]

(*E*)-2-*tert*-Butyl-but-2-ene-1,4-diol (7). To a solution of but-2-yne-1,4-diol (3.87 g, 45 mmol) and CuBr·Me_2S (0.92 g, 10 mol %) in THF (22 mL) was added dropwise at −30 °C a 1.8 M THF solution of *tert*-butylmagnesium chloride (100 mL, 180 mmol). The mixture was stirred at −30 °C for 1 h and then warmed to room temperature overnight. The reaction was quenched with a saturated solution of ammonium chloride and concentrated H_2SO_4 (0.1 mL). The aqueous phase was extracted with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure, and the crude reaction was purified by flash chromatography to yield 3.27 g of **7** (50%) and 1.55 g of allene **8** (27%), both as colorless oils. Data for **7**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.59 (t, 1H, J = 6.6 Hz); 4.18 (d, 2H, J = 6.6 Hz); 4.04 (s, 2H); 3.43 (s br, 2 × 1H); 1.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0; 123.2; 65.4; 58.6; 30.2; 21.4. IR (ATR), cm^{-1}: 3331; 2957; 1713; 1464; 1364; 1201; 1017; 986.

(*E*)-Acetic Acid 4-Acetoxy-2-*tert*-butyl-but-2-enyl Ester (9a). All glassware was flame-dried and cooled under Ar. At 0 °C, to a 1 M solution of **7** (1.44 g, 10 mmol) in CH_2Cl_2 were successively added pyridine (2.42 mL, 3 equiv) and Ac_2O (2.82 mL, 3 equiv). The mixture was stirred for 30 min at 0 °C and warmed to room temperature overnight. After completion of the reaction, the solution was diluted with CH_2Cl_2 and washed with a solution of HCl (10%). The organic phase was washed with $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure, and the product was purified by flash chromatography on a silica gel column to yield 2.28 g of **9a** (98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.53 (t, 1H, J = 6.0 Hz); 4.82 (d, 2H, J = 6.0 Hz); 4.53 (s, 2H); 2.07 (s, 3H); 2.06 (s, 3H); 1.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9; 170.7; 144.0; 125.4; 67.9; 61.9; 35.1; 30.1; 21.2; 21.0. IR (ATR), cm^{-1}: 2967; 1736; 1462; 1368; 1219 (br); 1022. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.13; H, 8.78.

(*E*)-Carbonic Acid 3-Methoxycarbonyloxymethyl-4,4-dimethyl-pent-2-enyl ester Methyl Ester (9b). All glassware was flame-dried and cooled under Ar. At 0 °C, to a solution of **7** (0.72 g, 5 mmol) in CH_2Cl_2 (5 mL) were successively added pyridine (0.97 mL, 2.4 equiv), $ClCO_2Me$ (0.93 mL, 2.4 equiv), and DMAP (5 mol %). The mixture was stirred for 30 min at 0 °C and warmed to room temperature overnight. After completion of the reaction, the solution was diluted with CH_2Cl_2 and washed with a solution of HCl (10%). The organic phase was washed with $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure, and the crude reaction was purified by flash chromatography to yield 1.1 g of **9b** as a colorless oil (85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.53 (t, 1H, J = 5.9 Hz); 4.85 (d, 2H, J = 5.9 Hz); 4.55 (s, 2H); 3.73 (s, 3H); 3.72 (s, 3H); 1.13 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.7; 155.4; 143.7; 125.3; 70.9; 65.1; 54.8; 35.0; 30.0. IR (neat), cm^{-1}: 2950; 1750; 1435; 1260; 950 (br); 790. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.32; H, 7.92.

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Supporting Information Available: Full characterization for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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