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Palladium-Catalyzed Reactions of 3-Substituted Methylenecyclopropanes

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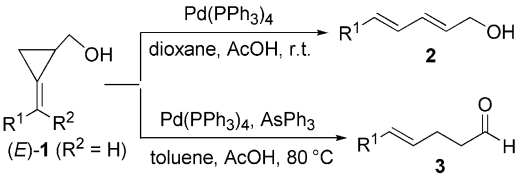
Pd-catalyzed reactions of 3-substituted methylenecyclopropanes (MCPs), in which the substituents can be either hydroxymethyl or formyl, have been thoroughly investigated in the presence or absence of an acid source. It was found that the Pd-catalyzed reactions of methylenecyclopropylcarbinols (*Z*)-**1** in the presence of acetic acid, acetic acid 2-methylene-but-3-enyl esters **4** can be formed in moderate yields. It was also found that Pd alone can catalyze the isomerization of methylenecyclopropylcarbinols (*E*)-**1** in the absence of an acid source to form pent-4-enals **3**. The Pd-catalyzed reactions of methylenecyclopropanecarbaldehydes **5** were also carried out in the presence of acetic acid. It was found that when (*E*)-**5** was used as the substrate, the isomerized product, penta-2,4-dienal **6**, could be obtained in good to high yields, whereas the use of (*Z*)-**5** gave 2-(3-formylpenta-2,4-dienylidene)cyclopropanecarbaldehyde **7** in moderate to good yields. Plausible mechanisms for all these transformations have been discussed on the basis of the obtained results and control experiments.

Introduction

Transition-metal-catalyzed reactions of methylenecyclopropanes (MCPs) have attracted much attention in the past decades and some excellent reviews have been reported.[1,2] In the past years, we have devoted ourselves to the chemistry of MCPs and have found some novel transformations of these substrates.[3,4] Previously, in the Pd-catalyzed isomerization reaction of 3-hydroxymethyl-substituted MCPs (i.e., methylenecyclopropylcarbinols) **1**,[5,6] we found that the regioselectivity of the isomerization reaction can be easily tuned by a subtle choice of the ligand and solvent.[7] Namely, for the $Pd(PPh_3)_4$-catalyzed isomerization of (*E*)-**1** in the presence of acetic acid, when dioxane is used as the solvent, penta-2,4-dien-1-ols **2**[8] are formed in high yields at room temperature, whereas when $AsPh_3$ is used as the ligand and toluene is used as the solvent, pent-4-enals **3**[9] are formed in good yields at 80 °C (Scheme 1). These results prompted us to further investigate the Pd-catalyzed reactions of other 3-substituted MCPs. In the continuing process, the Pd-catalyzed reactions were carried out in the presence of acetic acid by using (*Z*)-**1** as the substrates. It was found that acetic acid 2-methylene-but-3-enyl esters **4** can be formed in moderate yields. It was also found that Pd alone can catalyze the isomerization reaction of (*E*)-**1** in the absence of acetic acid to form pent-4-enals **3** under mild reaction conditions. Moreover, the Pd-catalyzed reactions of methylenecyclopropanecarbaldehydes **5** were also carried out in the presence of acetic acid. It was found that when using (*E*)-**5** as the substrates, the isomerized products, penta-2,4-dienals **6**, were obtained in good to high yields, whereas the use of (*Z*)-**5** gave 2-(3-formylpenta-2,4-dienylidene)cyclopropanecarbaldehydes **7** in moderate to good yields. Plausible mechanisms for all these transformations have been discussed on the basis of the obtained results and control experiments. Herein, we wish to report these results in detail.



Scheme 1. Pd-catalyzed isomerization of methylenecyclopropylcarbinols (*E*)-**1** in the presence of acetic acid.

Results and Discussion

Pd-Catalyzed Reactions of (*Z*)-1 in the Presence of Acetic Acid

Initially, the reactions of (*Z*)-**1** catalyzed by Pd catalyst were carried out in the presence of an excess amount of acetic acid. Interestingly, we found that the reactions proceeded smoothly to give 2-methylene-but-3-enyl esters **4** as

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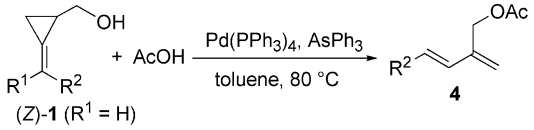
the sole products in moderate yields instead of the normal isomerized products as previously reported for substrates (*E*)-**1** (Table 1).[7]

Table 1. Pd-catalyzed reactions of substrates (*Z*)-**1** in the presence of acetic acid.[a]



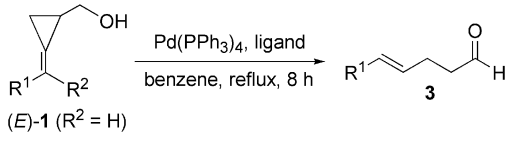
Entry	**1** (R^1/R^2)	Time [h]	Product, % Yield[b]
1	**1a** (H/C_6H_5)	6	**4a**, 60
2	**1b** ($H/4\text{-}FC_6H_4$)	8	**4b**, 57
3	**1c** ($H/4\text{-}ClC_6H_4$)	5	**4c**, 59
4	**1d** ($H/4\text{-}BrC_6H_4$)	24	**4d**, 50
5	**1e** ($H/4\text{-}MeC_6H_4$)	7	**4e**, 60
6	**1f** [$H/3,4,5\text{-}(MeO)_3C_6H_2$]	12	**4f**, 50

[a] All reactions were carried out by using (*Z*)-**1** (0.4 mmol), AcOH (5.0 mmol), $Pd(PPh_3)_4$ (0.02 mmol), $AsPh_3$ (0.16 mmol) in toluene (2.0 mL) at 80 °C for the listed time. [b] Isolated yield.

Pd-Catalyzed Isomerization of (*E*)-1 in the Absence of Acid

Differences between the Pd-catalyzed reactions of (*E*)-**1** and (*Z*)-**1** in the presence of acetic acid prompted us to further investigate other transformations of substrates **1**. Further studies showed that the Pd-catalyzed isomerization of (*E*)-**1** can also be achieved in the absence of acetic acid to form pent-4-enals **3** in acceptable to good yields (Table 2),[10] whereas substrates (*Z*)-**1** remained untouched under the same reaction conditions.

Table 2. Pd-catalyzed isomerization of (*E*)-**1**.[a]



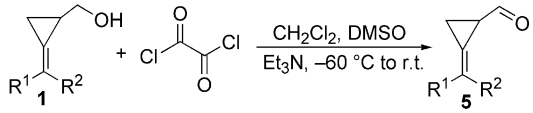
Entry	**1** (R^1/R^2)	Ligand	Product, % Yield[b]
1	**1g** (C_6H_5/H)	–	**3a**, 80
2	**1h** ($4\text{-}ClC_6H_4/H$)	$AsPh_3$	**3b**, 44
3	**1i** ($4\text{-}MeC_6H_4/H$)	$AsPh_3$	**3c**, 51
4	**1j** ($4\text{-}MeOC_6H_4/H$)	PPh_3	**3d**, 37

[a] All reactions were carried out by using (*E*)-**1** (0.25 mmol), $Pd(PPh_3)_4$ (0.025 mmol), the listed ligand (0.05 mmol) in benzene (1.0 mL) at reflux for 8 h. [b] Isolated yield.

Swern Oxidation of Methylenecyclopropylcarbinols 1 to Methylenecyclopropanecarbaldehydes 5

Because the Pd-catalyzed reactions of methylenecyclopropylcarbinols **1** dramatically depend on the substituents of substrates **1** (*E* or *Z* isomers), we also prepared another type of substituted MCPs, that is, methylenecyclopropanecarbaldehydes **5**, by Swern oxidation[11] of the corresponding substrates **1** to further investigate their reactivity upon treatment with Pd catalysts (Table 3). As can be seen from Table 3, oxidized products **5** can be obtained in good to high yields in almost all cases.

Table 3. Oxidation of methylenecyclopropylcarbinols **1**.[a]



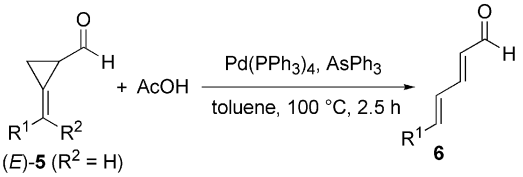
Entry	**1** (R^1/R^2)	Product, % Yield[b]
1	**1a** (H/C_6H_5)	**5a**, 82
2	**1c** ($H/4\text{-}ClC_6H_4$)	**5b**, 59
3	**1f** [$H/3,4,5\text{-}(MeO)_3C_6H_2$]	**5c**, 78
4	**1k** ($H/4\text{-}MeOC_6H_4$)	**5d**, 56
5	**1g** (C_6H_5/H)	**5e**, 85
6	**1h** ($4\text{-}ClC_6H_4/H$)	**5f**, 77
7	**1i** ($4\text{-}MeC_6H_4/H$)	**5g**, 78
8	**1j** ($4\text{-}MeOC_6H_4/H$)	**5h**, 78
9	**1l** ($4\text{-}FC_6H_4/H$)	**5i**, 58
10	**1m** ($4\text{-}BrC_6H_4/H$)	**5j**, 95
11	**1n** ($3\text{-}MeC_6H_4/H$)	**5k**, 68
12	**1o** [$3,4,5\text{-}(MeO)_3C_6H_2/H$]	**5l**, 51

[a] All reactions were carried out by using **1** (5.0 mmol), $(COCl)_2$ (8.7 mmol), DMSO (17.6 mmol), Et_3N (25 mmol) in CH_2Cl_2 (15.0 mL) at –60 °C to r.t. [b] Isolated yield.

Pd-Catalyzed Isomerisation of (*E*)-5 in the Presence of Acetic Acid

With the various methylenecyclopropanecarbaldehydes **5** in hand, we first carried out the Pd-catalyzed reaction of (*E*)-**5** in the presence of acetic acid. The results are summarized in Table 4. The corresponding isomerized products, penta-2,4-dienals **6**, were obtained in good to high yields within 2.5 h for a variety of substrates (*E*)-**5** (Table 4). The structure of compound **6h** was unambiguously confirmed by X-ray diffraction (Figure 1).[12]

Table 4. Pd-catalyzed isomerization of (*E*)-**5**.[a]



Entry	**5** (R^1/R^2)	Product, % Yield[b]
1	**5e** (C_6H_5/H)	**6a**, 83
2	**5f** ($4\text{-}ClC_6H_4/H$)	**6b**, 81
3	**5g** ($4\text{-}MeC_6H_4/H$)	**6c**, 80
4	**5h** ($4\text{-}MeOC_6H_4/H$)	**6d**, 92
5	**5i** ($4\text{-}FC_6H_4/H$)	**6e**, 93
6[c]	**5j** ($4\text{-}BrC_6H_4/H$)	**6f**, 40
7	**5k** ($3\text{-}MeC_6H_4/H$)	**6g**, 88
8	**5l** [$3,4,5\text{-}(MeO)_3C_6H_2/H$]	**6h**, 84

[a] Unless otherwise specified, all reactions were carried out by using **5** (0.5 mmol), AcOH (0.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and $AsPh_3$ (0.1 mmol) in toluene (2.0 mL) at 100 °C for 2.5 h. [b] Isolated yield. [c] The reaction time was 10 h.

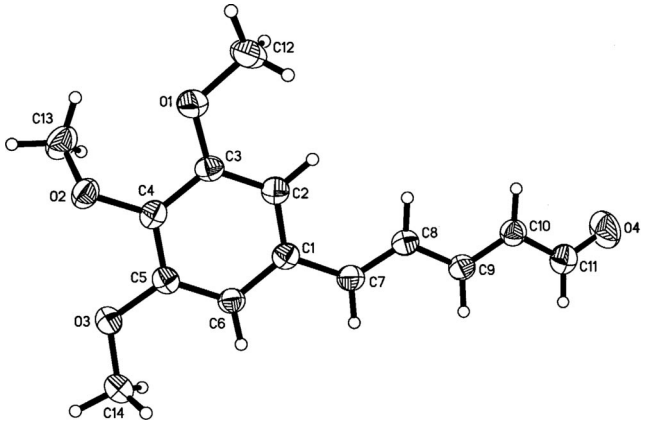
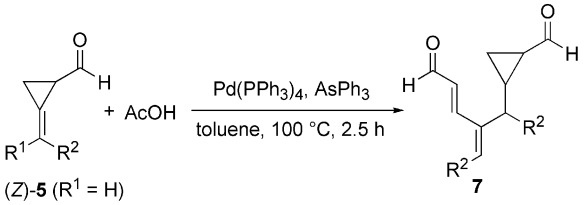


Figure 1. ORTEP drawing of compound **6h**.

Pd-Catalyzed Reactions of (*Z*)-5 in the Presence of Acetic Acid

On the basis of the previous diverse results on the Pd-catalyzed reactions of methylenecyclopropylcarbinols **1** (*Z* or *E* isomers) in the presence of acetic acid, we also carried out similar reactions by using (*Z*)-**5** as the substrates. The results are shown in Table 5, which are also far different from the results using (*E*)-**5** as the substrates. Corresponding products **7** were obtained in moderate to good yields under the optimized conditions (Table 5). Their structures were determined by ^{1}H and ^{13}C NMR spectroscopy, low-resolution and high-resolution mass spectrometry, and NOESY experiments (see the Supporting Information for details).

Table 5. Pd-catalyzed reactions of substrates (*Z*)-**5** in the presence of acetic acid.[a]

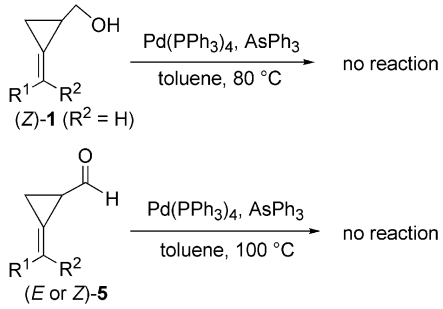


Entry	**5** (R^1/R^2)	Product, % Yield[b]
1	**5a** (H/C_6H_5)	**7a**, 73
2	**5b** (H/4-ClC_6H_4)	**7b**, 52
3	**5c** [H/3,4,5-(MeO)$_3C_6H_2$]	**7c**, 71
4	**5d** (H/4-MeOC_6H_4)	**7d**, 76

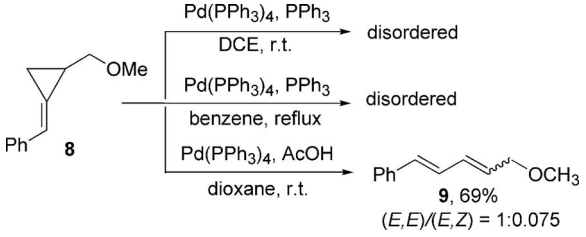
[a] All reactions were carried out by using (*Z*)-**5** (0.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), $AsPh_3$ (0.1 mmol), and AcOH (0.5 mmol) in toluene (2.0 mL) at 100 °C for 2.5 h. [b] Isolated yield.

Exploration of the Reaction Mechanism

To clarify the reaction mechanism, we also carried out several control experiments. In the following investigations, it was found that no reaction occurred if no acetic acid was added to the Pd-catalyzed reactions of methylenecyclopropylcarbinols (*Z*)-**1** and methylenecyclopropanecarbaldehydes **5** (*E* or *Z* isomers, Scheme 2). These results suggest that acetic acid is crucial for these Pd-catalyzed corresponding transformations. Compared to the Pd-catalyzed transformations of (*E*)-**1** with (*E*)-**5**, where one substrate possesses a hydroxymethyl group at the 3-position and the other a formyl group, it may be concluded that the hydroxy group is crucial for the acetic acid free isomerization of (*E*)-**1**,[13,14] and for the reactions of (*Z*)-**1**, (*E*)-**5**, and (*Z*)-**5**, acetic acid is necessary for the corresponding transformations (Tables 1, 4, and 5; Scheme 2). In fact, further studies showed that the palladium-catalyzed reactions of compound **8**, in which the hydroxy group of (*E*)-**1g** was transformed into a methoxy group, did not afford the desired isomerized product in the absence of acetic acid, whereas in the presence of acetic acid, corresponding isomerized product **9** was obtained in 69% yield (Scheme 3). These results clearly showed that the hydroxy group is essential for the acid-free isomerization of (*E*)-**1**.



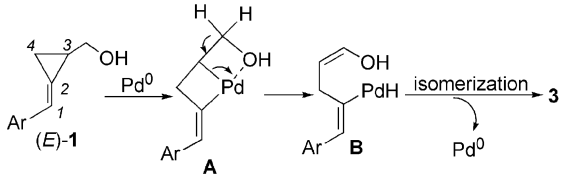
Scheme 2. Pd-catalyzed reactions of (*Z*)-**1** and **5** in the absence of acetic acid under the optimized conditions.



Scheme 3. Control experiments involving compound **8**.

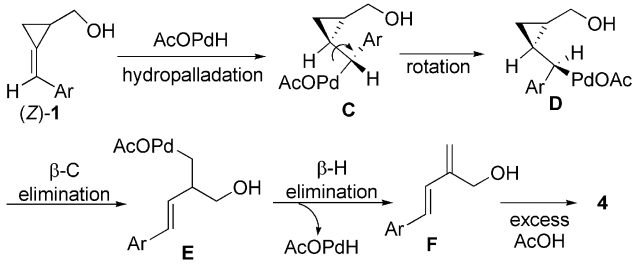
A plausible mechanism for the formation of products **3** is shown in Scheme 4, which is based on previous results.[13,14] Palladacyclobutane intermediate **A** is first formed from (*E*)-**1** and Pd^0 with the insertion of the metal into the proximal bond (C2–C3),[2a] which gives intermediate **B** through regioselective *anti*-β-hydrogen elimination.[15] Reductive elimination of **B** and isomerization will afford final products **3** (Scheme 4).

A possible mechanism for the formation of products **4** is illustrated in Scheme 5. First, hydropalladation of (*Z*)-**1** gives intermediate **C**, which will be transformed into intermediate **D** by rotation of the single bond. β-Carbon elimination of **D** gives intermediate **E**, which results in intermediate **F** through β-hydrogen elimination and release of the active catalyst AcOPdH. Finally, products **4** can be afforded by esterification of **F** in the presence of an excess amount

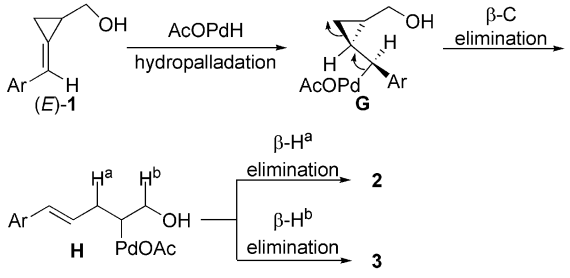


Scheme 4. Plausible mechanism for the palladium-catalyzed isomerization of (*E*)-**1**.

of acetic acid (Scheme 5). To compare the different reaction patterns between substrates (*E*)-**1** and (*Z*)-**1**, the mechanism of the palladium-catalyzed isomerization of substrates (*E*)-**1** in the presence of acetic acid is also cited in Scheme 6.[7] The difference between substrates (*E*)-**1** and (*Z*)-**1** can be considered by the steric repulsion between the sterically bulky aromatic and hydroxymethyl groups. For substrates (*Z*)-**1**, σ-bond rotation of intermediate **C** occurs before β-carbon elimination (the ring-opened process) because of the steric hindrance between the aryl group and the hydroxymethyl group in intermediate **C** (Scheme 5), whereas for substrates (*E*)-**1**, β-carbon elimination from intermediate **G**, which has less steric repulsion, occurs favorably to give intermediate **H** in spite of the priority of the σ-bond rotation to the β-carbon elimination step.[16] Elimination of intermediate **H** by β-H^a- or β-H^b-elimination will afford products **2** and **3**, respectively (Scheme 6).

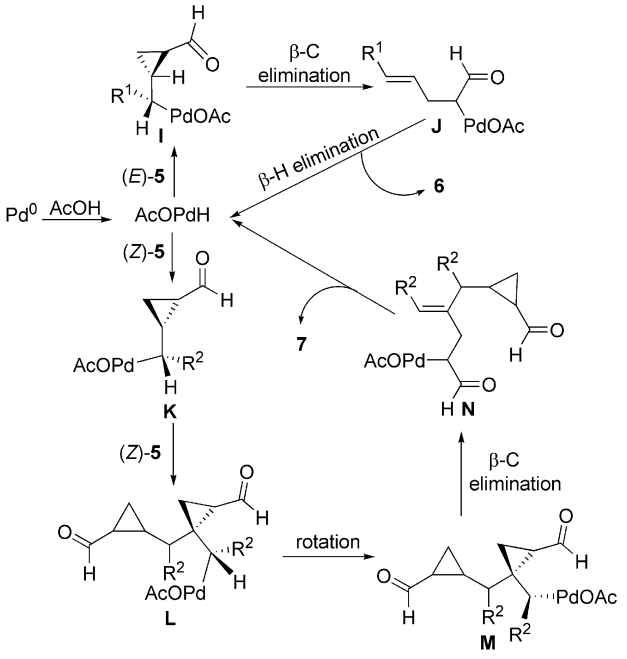


Scheme 5. Possible mechanism for the Pd-catalyzed reaction of (*Z*)-**1** in the presence of acetic acid.



Scheme 6. Possible mechanism for the Pd-catalyzed reaction of (*E*)-**1** in the presence of acetic acid.

The pathway for the Pd-catalyzed reactions of substrates **5** is shown in Scheme 7. Hydropalladation of (*E*)-**5** gives intermediate **I**. β-Carbon elimination of intermediate **I** occurs subsequently to afford intermediate **J**, which will release products **6** and regenerate the AcOPdH species to complete the catalytic cycle. In another way, hydropalladation of (*Z*)-**5** gives intermediate **K**, which cannot proceed in the β-carbon elimination pathway smoothly to give the ring-opened intermediate because of the steric repulsion between the aryl and formyl groups. Alternatively, intermediate **K** adds to another molecular of (*Z*)-**5** to give intermediate **L**. In this case, by single-bond rotation of intermediate **L**, β-carbon elimination of intermediate **M** and β-hydrogen elimination of intermediate **N** will afford products **7** and regenerate catalyst AcOPdH (Scheme 7). Another conclusion might also be drawn here: the steric hindrance between the aryl and formyl groups in intermediates **I** and **K**, which are derived from substrates (*E*)-**5** and (*Z*)-**5** by hydropalladation, respectively, results in the different pattern in these reactions.



Scheme 7. Plausible mechanism for the formation of products **6** and **7**.

Conclusions

In conclusion, we have carefully investigated the Pd-catalyzed reactions of 3-substituted MCPs in the presence or absence of an acid source. It was found that Pd-catalyzed reactions of methylenecyclopropylcarbinols (*Z*)-**1** in the presence of acetic acid can afford 2-methylene-but-3-enyl esters **4** in moderate yields, whereas palladium alone catalyzed reactions of (*E*)-**1** to give the isomerized products pent-4-enals **3** in acceptable to good yields. Isomerization of methylenecyclopropanecarbaldehydes (*E*)-**5** was achieved in the presence of a Pd catalyst and acetic acid, whereas for the reactions of (*Z*)-**5** under the identical reaction conditions, the corresponding product **7** was obtained as the sole product. Mechanisms for all the transformations were elucidated on the basis of the obtained results and control experiments. Efforts are underway to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

Experimental Section

General Procedure for the Pd-Catalyzed Reactions of Methylenecyclopropylcarbinols (*Z*)-1 in the Presence of Acetic Acid: Under an argon atmosphere, a mixture of methylenecyclopropylcarbinols **1a** (0.4 mmol), $Pd(PPh_3)_4$ (0.02 mmol), AcOH (5.0 mmol), $AsPh_3$ (0.16 mmol), and toluene (2.0 mL) was stirred at 80 °C for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography to give product **4a** as a colorless liquid.

General Procedure for the Pd-Catalyzed Isomerization of Methylenecyclopropylcarbinols (*E*)-1 To Give Pent-4-Enal in the Absence of Acetic Acid: Under an argon atmosphere, a mixture of methylenecyclopropylcarbinol **1g** (0.25 mmol), freshly prepared $Pd(PPh_3)_4$ (0.025 mmol), and benzene (1.0 mL) was stirred under reflux for about 8 h. Then, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography to give product **3a** as a yellow liquid.

General Procedure for the Preparation of Methylenecyclopropanecarbaldehydes 5: To a solution of oxalyl chloride (750 μL, 8.5 mmol) in CH_2Cl_2 (10.0 mL) at –60 °C was successively added a solution of DMSO (1.25 mL, 17.5 mmol) in CH_2Cl_2 (2.0 mL), and after the reaction mixture was stirred for about 2 min, a solution of methylenecyclopropylcarbinol **1a** (800 mg, 5.0 mmol) in CH_2Cl_2 (3.0 mL) was added within 5 min. Stirring was continued for 30 min and triethylamine (3.5 mL, 25.0 mmol) was added into the reaction solution dropwise. The reaction mixture was warmed to room temperature. An aqueous solution of 1.0 N hydrochloric acid (27.5 mL) saturated with sodium chloride was added into the reaction mixture, and the aqueous layer was extracted with CH_2Cl_2 (2×15 mL). The organic layers were combined and dried with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography to give product **5a** as a yellow liquid.

General Procedure for the Pd-Catalyzed Isomerization of Methylenecyclopropanecarbaldehydes (*E*)-5: Under an argon atmosphere, a mixture of **5e** (0.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and $AsPh_3$ (0.1 mmol) in toluene (2.0 mL) was heated to 100 °C. Then, AcOH (0.5 mmol) was added into the solution dropwise. The reaction mixture was stirred at 100 °C for 2.5 h. Then, the solvent was removed under reduced pressure, and the residue was purified on a silica gel column chromatography to give product **6a** as a yellow liquid.

General Procedure for the Pd-Catalyzed Reactions of Methylenecyclopropanecarbaldehydes (*Z*)-5: Under an argon atmosphere, a mixture of **5a** (0.5 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and $AsPh_3$ (0.1 mmol) in toluene (2.0 mL) was heated to 100 °C. Then, AcOH (0.5 mmol) was added into the solution dropwise. The reaction mixture was stirred at 100 °C for 2.5 h. Then, the solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography to give product **7a** as an orange liquid.

Supporting Information (see footnote on the first page of this article): General methods and procedures, results using HCOOH as the acid source, and spectroscopic data.

Acknowledgments

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[12] Crystal data of **6h**: Empirical Formula: $C_{14}H_{16}O_4$; Formula weight: 248.27; crystal color, habit: colorless, prismatic; crystal dimensions: $0.517 \times 0.505 \times 0.397$ mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 10.869(2) Å, b = 14.124(3) Å, c = 17.504(3) Å, α = 90°, β = 103.901(3)°, γ = 90°, V = 2608.5(9) Å^3; space group: $P2_1/c$; Z = 8; $D_{calcd.}$ = 1.264 g/cm^3; $F(000)$ = 1056; diffractometer: Rigaku

AFC7R; residuals: *R*; R_w: 0.0660, 0.1582. CCDC-266291 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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