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Easy Access to Esters with a Benzylic Quaternary Carbon Center from Diallyl Malonates by Palladium-Catalyzed Decarboxylative Allylation

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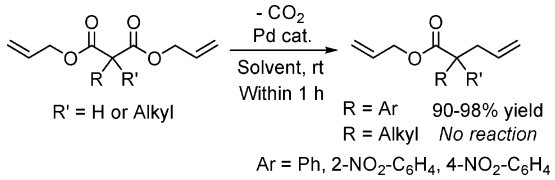
Received October 17, 2006

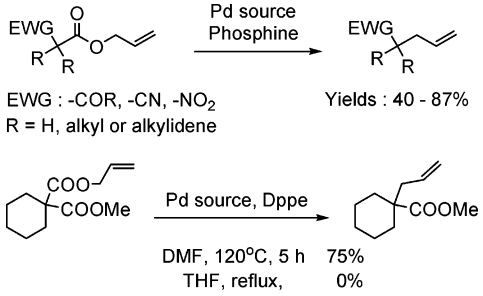


Diallyl 2-alkyl-2-arylmalonates underwent palladium-catalyzed decarboxylative allylation quickly under mild conditions. In contrast, no reaction took place with diallyl 2,2-dialkylmalonates under the same conditions. Electron-donating phosphine ligands were found to be vital for this reaction. Most of the solvents used did not affect the catalytic cycle. Catalysis in [bmim][BF_4], a well-known ionic liquid, was inhibited as a result of formation of a hydrogen bond between a carboxylate anion and a [bmim]$^+$ cation; however, the reaction in [bdmim][BF_4], in which the acidic proton of [bmim][BF_4] was replaced with a methyl group, proceeded smoothly. The catalytic mechanism was investigated using a tetradeuterated substrate and an enzymatically synthesized enantio-enriched allyl methyl 2-methyl-2-phenylmalonate. Even the electron-deficient phosphite ligand was found to be active for catalysis of diallyl 2-methyl-2-(2- or 4-nitrophenyl)malonates.

Introduction

Decarboxylation mediated by transition metal complexes is known to trigger irreversible formation of reactive carbanion species so effectively that it has been utilized to initiate many types of catalytic organic reactions even under neutral conditions.[1] Particularly in the area of palladium-phosphine complex catalysis, decarboxylative allylation reactions of allyl esters with an electron-withdrawing group at the α-position have been investigated extensively by Saegusa and Tsuji.[2] Although a series of electron-withdrawing groups, including cyano, keto, and nitro groups, have been found to show activity for this reaction, ester groups are rather less active; severe conditions are required for reaction of diallyl malonate derivatives (Scheme

SCHEME 1. Reactivities in Decarboxylative Allylation Reactions

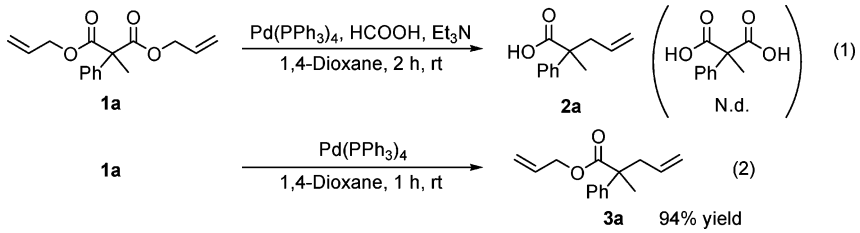


† Dedicated to the hearty memory of the late Professor Yoshihiko Ito of Doshisha University. Deceased on December 23, 2006.

(1) (a) McFadden, R. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 7738. (b) Trost, B. M.; Bream, R. N.; Xu, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3109. (c) Patil, N. T.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 6991. (d) Wang, C.; Tunge, J. A. *Org. Lett.* **2006**, *8*, 3211. (e) Ragoussis, V.; Giannikopoulos, A. *Tetrahedron Lett.* **2006**, *47*, 683. (f) Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510. (g) Nakamura, M.; Hajra, A.; Endo, K.; Nakamura, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7248. (h) Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6924. (i) Magdziak, D.; Lalic, G.; Lee, H. M.; Fortner, K. C.; Aloise, A. D.; Shair, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 7284. (j) Kuwano, R.; Ishida, N.; Murakami, M. *Chem. Commun.* **2005**, 3951. (k) Trost, B. M.; Xu, J. *J. Am. Chem. Soc.* **2005**, *127*, 2846. (l) Burger, E. C.; Tunge, J. A. *Chem. Commun.* **2005**, 2835. (m) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**. *6*, 433. For a recent review, see: (n) Tunge, J. A.; Burger, E. C. *Eur. J. Org. Chem.* **2005**, 1715. (o) You, S.-L.; Dai, L.-X. *Angew. Chem. Int. Ed.* **2006**, *45*, 5246.

10.1021/jo0621569 CCC: $37.00
Published on Web 01/30/2007

SCHEME 2



1: 120 °C in DMF with moderate yields; no reaction in boiling THF).[2b] Here, we report that diallyl malonates with an aryl group (aryl = Ph or 2- or 4-$NO_2C_6H_4$) at the α-position underwent efficient Pd-catalyzed decarboxylative allylation at room temperature with excellent yields, affording esters with a benzylic quaternary carbon center at the α-position, which can be transformed into many biologically active compounds.[3]

Results and Discussion

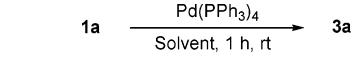
The initial finding was based on an attempt to synthesize 2-phenylpropionic acid for a different purpose from diallyl 2-methyl-2-phenylmalonate **1a** via allyl deprotection in 1,4-dioxane, catalyzed by a palladium complex and using formic acid as a reductant, followed by thermal decarboxylation. Despite the presence of the reductant, the palladium complex catalyzed decarboxylative allylation at a much greater rate than the deallylation reaction, affording mainly C-allylated monoacid **2a** (Scheme 2, eq 1).

To investigate this unexpected outcome, the same reaction was carried out in the absence of the reductant. The reaction took place very quickly to give **3a** in 94% isolated yield (Scheme 2, eq 2), despite the fact that decarboxylative allylation of diallyl 2,2-dialkylmalonate does not take place at room temperature, as mentioned above.

Next, we investigated solvent effects; the results are summarized in Table 1. It was found that the reaction could be carried out in all of the organic solvents tested, including an alcohol, a protic solvent, and a nucleophilic aldehyde, which can be considered to react with enolate carbanion species generated in situ.

A variety of substrates (**1b**−**1f**) were synthesized and applied in the reaction, using CH_2Cl_2 as a solvent (Table 2). All reactions afforded the corresponding products in excellent yields. In contrast, the reaction of diallyl 2-benzyl-2-methylmalonate **1g** was observed to give no product under the same conditions even after 1 day.

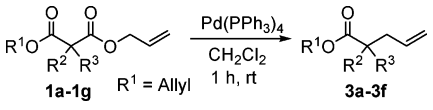
TABLE 1. Solvent Effect in Pd-Catalyzed Decarboxylative Allylation of 1a[a]



entry	solvent[b]	yield[c] (%)
1	1,4-dioxane	94
2	THF	97
3	CH_2Cl_2	95
4	$CHCl_3$	85
5	toluene	89
6	benzene	96
7	DMF	90
8	CH_3CN	94
9	acetone	89
10	propionaldehyde	94
11	*tert*-amyl alcohol	73
12	*tert*-amyl alcohol	95[d]

[a] $Pd(PPh_3)_4$ (2 mol %), **1a** (0.5 mmol). [b] 1 mL of solvent. [c] Isolated yield. [d] Reaction was carried out for 4 h.

TABLE 2. Effects of Substituents[a]



entry		R^2	R^3	yield[b] (%)
1	**1a**	Ph	Me	95 (**3a**)
2	**1b**	Ph	Et	91 (**3b**)
3	**1c**	Ph	Bn	93 (**3c**)
4	**1d**	Ph	$(CH_2)_2CO_2CH_3$	95 (**3d**)
5	**1e**	Ph	$(CH_2)_2CN$	96 (**3e**)
6	**1f**	Ph	H	98 (**3f**)
7	**1g**	Bn	Me	nr[c]

[a] $Pd(PPh_3)_4$ (2 mol %), substrate (0.5 mmol), CH_2Cl_2 (1 mL). [b] Isolated yield. [c] Reaction was carried out for 1 d.

A series of ligands were tested (Table 3), and phosphine ligands were found to be necessary for the reaction. Although the reaction with P(4-F-C_6H_4)$_3$ gave **3a** in excellent yield, it took 3 h for the reaction to be completed (entry 5). The use of phosphite and phosphinite, which have less electron-donating ability than phosphine, resulted in no reaction (entries 6 and 7), as also reported for allyl β-ketocarboxylates.[2g] From these results, it was concluded that the electron-donating phosphine ligands stabilize the π-allylpalladium cationic complex, allowing efficient release of a free carboxylate anion, from which decarboxylation occurs.

Next, we attempted to carry out the reaction in ionic liquid (IL), which is considered an environmentally friendly solvent.[4] Because of the simplicity of the reaction, it is easy to keep the

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SCHEME 3. Difference in Reactivity in [bmim][BF_4] and [bdmim][BF_4] and a Possible Explanation Based on ^{1}H NMR Analysis

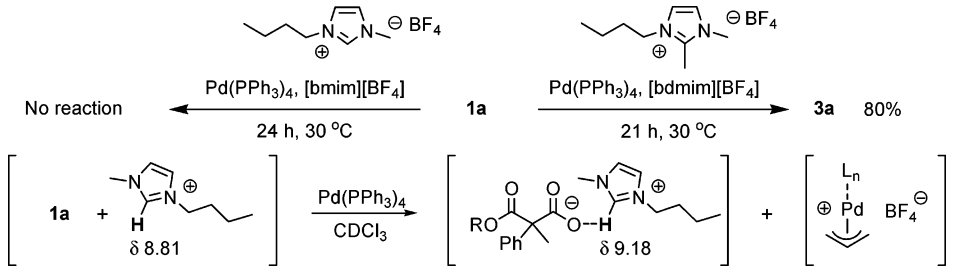
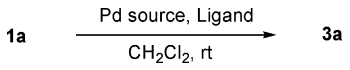


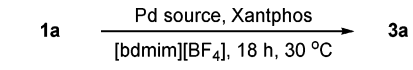
TABLE 3. Effects of Various Ligands on Catalytic Activity[a]



entry	ligand (mol %)	time (h)	yield[b] (%)
1	PPh_3 (8)	1	94
2	dppe[c] (2.4)	2	95
3	dppp[d] (2.4)	2	92
4	Xantphos[e] (2.4)	1.5	97
5	P(4-F-C_6H_4)$_3$ (8)	3	92
6	$P(OPh)_3$ (8)	1	nr
7	$PPh_2(OPh)$ (8)	1	nr

[a] $Pd_2(dba)_3$·$CHCl_3$ (dba = dibenzylideneacetone) (1 mol %), **1a** (0.5 mmol), CH_2Cl_2 (1 mL). [b] Isolated yield. [c] 1,2-Bis(diphenylphosphino)ethane. [d] 1,3-Bis(diphenylphosphino)-propane. [e] 9,9-Dimethyl-4,6-bis(diphenylphosphino)xanthene.

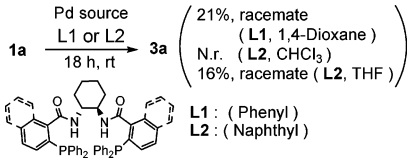
TABLE 4. Recycling of Catalytic System[a]



	run				
	1	2	3	4	5
recovery[b] (%)	0	0	0	0	33
yield[b] (%)	77	86	89	91	nd

[a] $Pd_2(dba)_3$·$CHCl_3$ (dba = dibenzylideneacetone) (1 mol %), Xantphos (2.4 mmol), **1a** (0.5 mmol), IL (1 mL). [b] Isolated yield.

SCHEME 4. Catalysis Using Ligands L1 and L2



reaction system clean; the catalyst simply converts the substrate to the product, along with gaseous CO_2, without the use of any other reagent, strong base, or additive. First, [bmim][BF_4] (1-*n*-butyl-3-methylimidazolium tetrafluoroborate), a well-known commercially available IL, was tested, but to our surprise, no reaction took place in this medium. Since it had previously been reported by Ross and Xiao that palladium-catalyzed allylic alkylation using allylic carbonates was retarded in [bmim][BF_4],[5] we assumed that the lack of reaction in this case might be for the same reason: formation of a hydrogen bond between a carboxylate anion and the acidic 2-H proton of the imidazolium cation results in a stable ion pair that protects the carboxylate anion from decarboxylation and interrupts the catalytic cycle. As supporting evidence for this, it was observed in the ^{1}H NMR spectrum ($CDCl_3$, 0.6 mL) that the 2-H proton peak shifted from $\delta = 8.81$ ppm (IL only, or with 0.5 equiv of malonate) to $\delta = 9.18$ ppm (with 0.5 equiv of malonate and 0.1 equiv (0.008 mmol) of $Pd(PPh_3)_4$) (Scheme 3).

Another IL, [bdmim][BF_4] (1-*n*-butyl-2,3-dimethylimidazolium tetrafluoroborate), in which the acidic 2-H proton is replaced with a methyl group, was synthesized to avoid this problem as Ross et al. did in Pd-catalyzed allylic alkylation[5] and as Hsu et al. did in Baylis−Hillman reaction.[6] As we expected, the reaction in [bdmim][BF_4] proceeded to give **3a** in 80% yield with a simple extraction procedure using hexane. Unfortunately, no product was obtained in a second run using the same system. A recyclable catalytic system was achieved using Xantphos, a rigid bidentate phosphine ligand,[7] instead of PPh_3; the results are summarized in Table 4. It was found that the catalyst could be recycled four times. The long reaction time is thought to be due to weak hydrogen bonding between the carboxylate anion and the 4- or 5-H proton of the [bdmim]$^+$ cation.[8] Further optimization is now in progress.

The next step was an attempt to achieve enantioselectivity in the reaction. Unfortunately, our first attempts using Trost ligands **L1** (phenyl) and **L2** (naphthyl), which are known to be efficient nucleophile-stereocontrolling ligands in allylic alkylation reactions,[9] gave racemic **3a** in low yield (Scheme 4). The use of catalysts containing other commercially available chiral phosphine ligands [(*R*)-BINAP, (*R*,*S*)-Josiphos, (*R*,*S*)-BPPFA, and (*S*)-*i*PrPHOX; see Supporting Information] also resulted in production of racemic **3a**. To utilize our efficient catalytic system to the best advantage by achieving efficient enantioselective synthesis without these ligands, it was necessary to investigate the details of the enolate-related mechanism[1n] in order to elucidate the optimum ligand structure for obtaining good to excellent ee.

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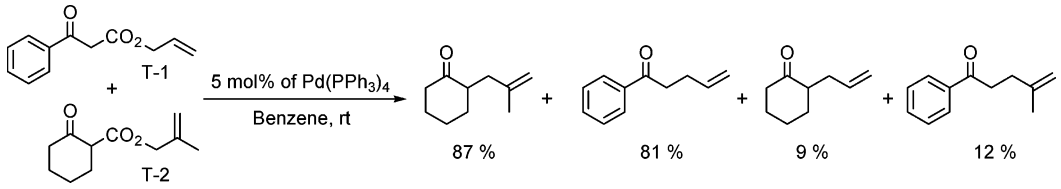
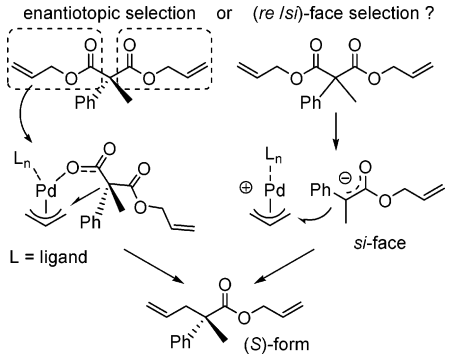
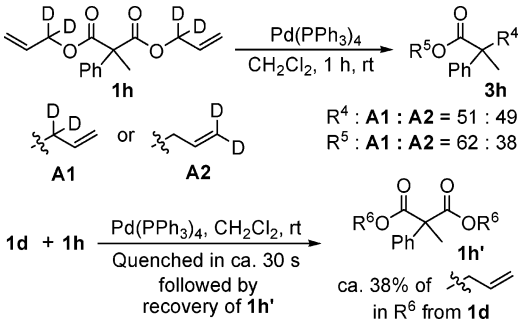
SCHEME 5. An Example of the "Boomerang Phenomenon"



SCHEME 6. Possible Enantioselective Steps



SCHEME 7. Scrambling Experiments

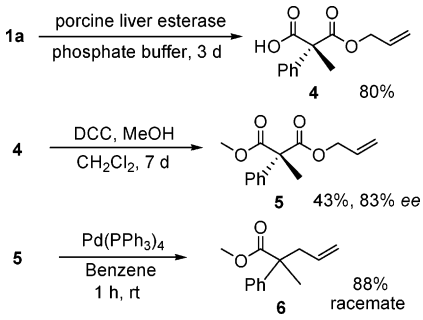


The example shown in Scheme 5 demonstrates the "boomerang phenomenon", the possibility of allylic moieties returning to their parent carbanion.[2j] On the basis of this result showing low crossover, we noticed that it was important to examine which type of enantioselectivity would be more effective, enantiotopic selectivity or enolate *re*/*si* face selectivity, because this is the first example of the application of diallyl malonates, which contain two enantiotopic ester groups, to palladium-catalyzed enantioselective decarboxylative allylation (Scheme 6).

To obtain mechanistic information, **1h** was synthesized from 1,1-dideuterated allyl alcohol and allowed to react to form **3h** (Scheme 7). Analysis of the product revealed that this transformation resulted in mixing not only of the alkylation position of allyl group R^4 but also of the *O*-alkylated position of the allyl moiety (R^5) in the ester group. When the reaction of a 1:1 mixture of **1d** and **1h** was quenched after ca. 30 s, ^{1}H NMR analysis of recovered substrate revealed that it was **1h′**, which contained a considerable amount of non-deuterated allyl group introduced from **1d**. From these results it was considered possible that formation of the free carboxylate anion may not always cause decarboxylation and that a fast equilibrium involving an ion-pair state results in quick allyl-scrambling.

Finally, when we enzymatically synthesized an enantioenriched substrate **5**[10] and subjected it to the catalysis carried out under the same reaction conditions drawn in Scheme 5 (Scheme 8), we obtained racemic product **6** from this reaction, indicating that there is no use in selecting one of two allyl ester groups enantiotopically, at least under these reaction conditions, and the carboxylate anion or carbanion/enolate is sufficiently separated from the π-allylpalladium cationic complex to cause it to racemize and lose its memory of chirality.[11]

SCHEME 8. Enzymatic Approach



We noticed that the conversion of **5** to give racemic **6** appeared to contradict the results shown in Scheme 5. Our results indicate that there is a relatively large distance between the carbanion and the cationic complex, which means it is almost impossible for them to "recognize" each other, so that the boomerang phenomenon does not occur. In order to explain these seemingly contradictory results, we synthesized dicrotyl 2-methyl-2-phenylmalonate **1i** and allowed it to react (3 h in benzene) as a 1:1 mixture of **1e** and **1i** (Scheme 9). The two TLC spots corresponding to **1e** and **1i** disappeared, and two new spots, corresponding to **3e′** and **3i′**, appeared; the products were separated by column chromatography. ^{1}H NMR characterization of **3e′** and **3i′** was found to be difficult, presumably because of allyl/crotyl scrambling and linear/branch mixing in the crotyl group. To simplify this problem, both products were transformed into the corresponding carboxylic acids under deallylation conditions using $Pd(PPh_3)_4$ and morpholine, followed by analysis by ^{1}H NMR.

Interestingly, ^{1}H NMR analysis of the acid derived from **3e′** revealed only the allylated product **2e** (R^7 = allyl), with no crotylated derivatives (**2j-b** or **2j-l**, R^7 = crotyl). In addition, ^{1}H NMR analysis of the acid derived from **3i′** revealed mainly **2a**, an allylated acid (R^8 = allyl), along with small amounts of crotylated products **2i-b** and **2i-l** (R^8 = crotyl). **PA**, 2-phenylpropionic acid, may be produced by decarboxylation of 2-methyl-2-phenyl malonic acid derived from **1i′** (derivatives of **1i**), which would be less active in decarboxylative allylic alkylation. From these observations, we considered that this predominant allylation to enolates generated from both **1e** and **1i** would suppose these ideas: (1) allyl and crotyl moieties in ester groups are catalytically exchangeable; (2) the exchange is slower than

(10) The absolute configuration of **4a** was determined by its transformation into known product and the comparison of their optical rotations. The detail is in Supporting Information.

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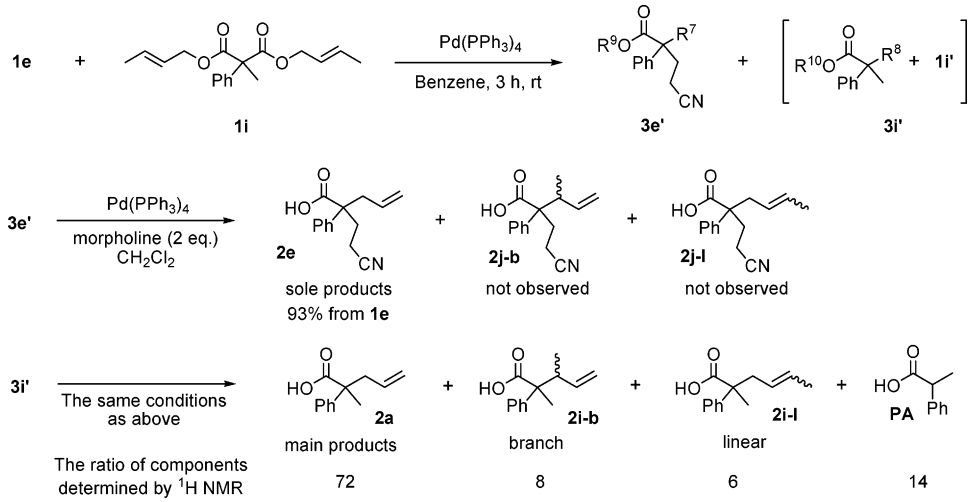
SCHEME 9. Scrambling of Symmetric and Unsymmetric Allylic Groups



catalytic decarboxylative allylation (not crotylation); and (3) a π-allylpalladium cationic complex is more effective than a π-crotylpalladium cationic complex in releasing carboxylate anions, causing decarboxylation. The last point may be related to the difference[12] in the ground-state structure of non-substituted and substituted allylic ligands in cationic π-allylpalladium complexes and may also help explain the speculation of Tunge et al.[1j] that the low crossover observed in Scheme 5 may be attributed to the differential reaction rates.

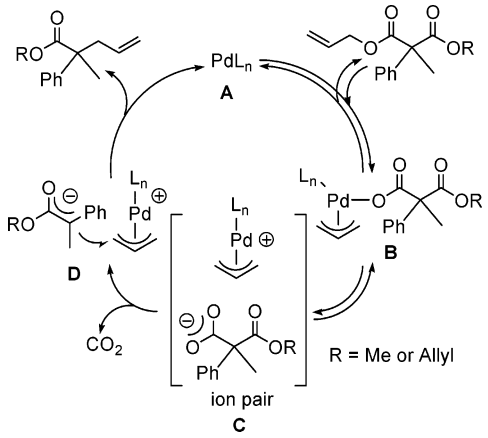
From these results we consider that the low crossover observed in Scheme 5 would possibly be attributed to a time lag between the reactions with T-1 and T-2 caused by difference of the carboxylate anion releasing rates of each π-(allylic)-palladium cationic complex. In Scheme 5 the release of carboxylate anion to form π-allylpalladium cationic complex might proceed much faster than the one to form π-(methallyl)-palladium cationic complex, causing a time lag in the reaction. The time lag would result in the low crossover, mimicking the boomerang phenomenon.

The rates of decarboxylation from the two carboxylate anion species, which sometimes causes stepwise alkylation,[1h,2g] could not be the reason for the low crossover because we observed no clear difference in decarboxylation reactivity between **1a** and **1e** in Table 2. At the same time, the reactivities of the two allylic esters toward the catalyst could also not be the reason because Tsuda also reported that almost complete crossover was observed when the same catalytic reaction (Scheme 5) was carried out in DMF, in which cationic complexes are well stabilized.[2j]

A plausible catalytic mechanism for the reaction is as follows (Scheme 10). First, the substrate undergoes oxidative addition with palladium−phosphine complex **A** to form a complex **B**. A carboxylate anion is released from **B** to form ion pair **C**. From the results obtained using a tetradeuterated substrate, it is possible that a fast equilibrium may exist between **A** and **C** via **B**, especially when using allyl esters. Decarboxylation takes place from **C**, and a reactive carbanion/enolate is formed (**D**). The carbanion then attacks the π-allylpalladium cation complex, affording the allylated product and the original catalyst.

From these findings, we deduced that the production of new enolate *re*/*si* face discriminating ligands was necessary, because

SCHEME 10. Plausible Catalytic Mechanism



Trost ligands demonstrated less activity and no selectivity in this reaction. Apart from chiral phosphine ligands, many chiral phosphite and phosphoramidite ligands have been shown to be effective in various asymmetric catalyses over the past decade. These ligands have recently been recognized as chiral tunable ligands,[13] because their various chiral building blocks are easily available, and these modular assemblies are promising for enantioselective catalysis.[14] For these reasons, it would be beneficial if these types of chiral ligands could be applied to our catalytic system, because these ligands are easy to synthesize, handle, and modify, allowing tailoring of an effective chiral pocket around the metal center.

On the basis of the proposed catalytic mechanism, it was envisioned that ion pair formation would be vital for catalysis

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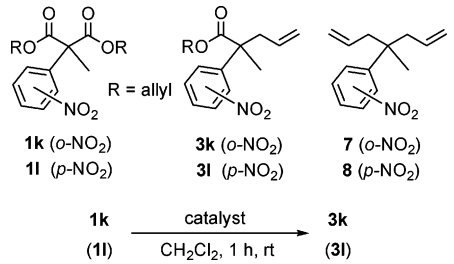
TABLE 5. Catalysis with Substrates Bearing *o*- or *p*-$NO_2C_6H_4$ Groups



entry	substrate	condition[a]	**3** (%)[b]
1	**1k**	A	88
2	**1k**	B	97
3	**1l**	A	80
4	**1l**	B	90

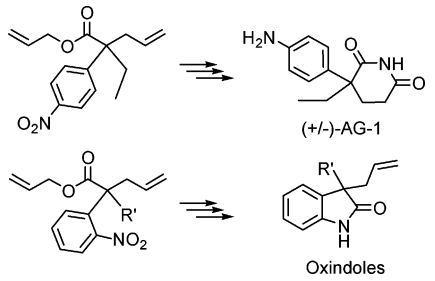
[a] Condition A: $Pd(PPh_3)_4$ (2 mol %), substrate (0.5 mmol), CH_2Cl_2 (1 mL). Condition B: $Pd_2(dba)_3{\cdot}CHCl_3$ (1 mol %), $P(OPh)_3$ (8 mol %), substrate (0.5 mmol), CH_2Cl_2 (1 mL). [b] Isolated yield.

to proceed with less active ligands. If the carboxylate anions could be made sufficiently stable to leave behind an unstable cationic complex, for example, π-allylpalladium(phosphite)$_n$, the use of a variety of chiral phosphite ligands would be possible. For this purpose, **1k** and **1l**, which were expected to generate stabilized carboxylate anions due to the electron-withdrawing effect of their nitro groups, were separately prepared and applied in the catalytic reaction. The results are summarized in Table 5. As we expected, the reactions took place smoothly even with $P(OPh)_3$ to afford the corresponding products **3k** and **3l**, respectively. Without $P(OPh)_3$, no reaction took place using **1l** under the same conditions, even after 3 h. The nitro group was found to be so effective that compound **8** (7%), presumably derived from double decarboxylative allylation of **1l**, was detected (entry 3). In contrast, the compound **7** was not detected by TLC analysis (entry 1).

These results seemed promising, not only because a variety of chiral phosphite and phosphoramidite ligands could be applied in the catalysis, but also because the nitro groups could be transformed into Ar-NH_2 groups, which would lead to the synthesis of useful compounds such as AG-1[15] and oxindole derivatives[16] (Scheme 11). Investigation of the application of **1k** and **1l** to asymmetric catalysis using a variety of chiral phosphite/phosphoramidite ligands is now in progress.

In summary, we found that the presence of an aryl group at the α-position of diallyl malonates enabled fast palladium-catalyzed decarboxylative allylation even at room temperature, affording esters with an all-carbon benzylic quaternary center. The catalyst was found to be recyclable when [bdmim][BF_4] was used as a reaction medium. Investigation of the reaction using a tetradeuterated substrate revealed some details of the catalytic mechanism. The use of an enzymatically synthesized

SCHEME 11. Possible Applications of Nitro-Substituted Compounds



enantioenriched substrate clarified that enolate *re*/*si* face selection is necessary to achieve asymmetric decarboxylative allylation, and that enantiotopic selection has no effect on enantioselectivity, at least under these reaction conditions. A previously reported catalytic system in which allylic moieties return to their parent carbanions was at first considered a likely possibility, invoking the possible predominance of enantiotopic selection for diallyl malonates derivatives, but the results obtained from a scrambling experiment with **1e** and **1i** revealed that the observed "boomerang phenomenon" was likely to be due to the difference in the ground-state structures of the two cationic (allylic)palladium complexes, which affects their anion release rates. The introduction of nitro groups on the phenyl ring of the substrate resulted in effective stabilization of the carboxylate anion species, even in catalysis using electron-deficient phosphite ligands.

Experimental Section

General Procedure for the Preparation of Diallyl 2-Phenylmalonate (1f). Phenylmalonic acid (15 g, 83 mmol), allyl alcohol (45 mL, 660 mmol), and *p*-toluenesulfonic acid monohydrate (1.7 g, 9.0 mmol) were dissolved in benzene (800 mL), and H_2O was azeotropically removed. After the reaction was complete, the apparatus was cooled to ambient temperature. The benzene solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl and was dried over anhydrous Na_2SO_4. A yellow oil remained after concentration and was purified by silica gel column chromatography (hexane/AcOEt = 4:1), affording **1f** (colorless oil) in 94% yield (20 g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.62 (ddd, A of AB system, J = 15, 5.7, 1.5, 2H), 4.67 (ddd, B of AB system, J = 15, 5.7, 1.5, 2H), 4.69 (s, 1H), 5.21 (dq, J = 10.5, 1.5, 2H), 5.27 (dq, J = 17.1, 1.5, 2H), 5.87 (ddt, J = 17.1, 10.5, 5.7, 2H), 7.32−7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 57.8, 66.3, 118.6, 128.2, 128.5, 129.2, 131.2, 131.3, 132.4, 167.5; HRMS (FAB$^+$) calcd for $C_{15}H_{17}O_4$ 261.1127 [M + H]$^+$, found 261.1127.

General Procedure for the Preparation of Diallyl 2-Alkyl-2-phenylmalonate (1). A variety of disubstituted malonates **1** except for **1f** were prepared by the conventional method for malonic ester synthesis (**1b** from ethyl iodide, **1c** from benzyl bromide, **1d** from methyl acrylate, **1e** from acrylonitrile as nucleophiles; **1g** was prepared by the same method using diallyl 2-methylmalonate).

General Procedure for the Preparation of Diallyl 2-Methyl-2-phenylmalonate (1a). Compound **1f** (8.0 g, 31 mmol) in anhydrous THF (80 mL) was added dropwise to NaH (1.1 g, 45 mmol) dissolved in ice-cooled anhydrous THF (80 mL). After the evolution of H_2 gas was complete, the apparatus was warmed to ambient temperature. To the reaction mixture was slowly added methyl iodide (4.5 mL, 72 mmol). The resulting mixture was stirred at 60 °C overnight. After the apparatus was cooled to ambient temperature, the reaction was quenched by adding 1 M aqueous HCl and was extracted with hexane. The collected organic layers were washed with dilute aqueous $Na_2S_2O_3$ saturated aqueous NaCl and was dried over anhydrous Na_2SO_4. A yellow oil remained after

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concentration and was purified by silica gel column chromatography (hexane/AcOEt = 5:1), affording colorless oil in 94% yield (7.9 g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, 3H), 4.66 (dt, J = 5.7, 1.5, 4H), 5.20 (dq, J = 10.2, 5.7, 2H), 5.26 (dq, J = 17.1, 5.7, 2H), 5.87 (ddt, J = 17.1, 10.2, 5.7, 2H), 7.29−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 58.9, 66.2, 118.4, 127.3, 127.6, 128.1, 131.4, 137.9, 170.9; HRMS (FAB$^+$) calcd for $C_{16}H_{19}O_4$ 275.1283 [M + H]$^+$, found 275.1265.

General Procedure for the Pd-Catalyzed Decarboxylative Allylation. To a solution (stirred for 30 min under argon) of catalyst (or Pd precursor (2 mol % per Pd) and ligand) was added substrate (0.5 mmol), and the mixture was stirred for 1 h at room temperature. Hexane was added after the reaction. The mixture was filtered through a thin silica gel pad, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with eluent (hexane/AcOEt) to give **3**.

Allyl 2-Methyl-2-phenyl-4-pentenoate (**3a**)**.** The product was obtained as a colorless oil (hexane/AcOEt = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 2.67 and 2.85 (dd, AB system, J = 13.8, 7.2, 2H), 4.55−4.58 (m, 2H), 5.02−5.21 (m, 4H), 5.54−5.68 (m, 1H), 5.76−5.89 (m, 1H), 7.20−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.6, 43.7, 49.9, 65.3, 117.8, 118.4, 125.9, 126.7, 128.3, 131.9, 133.8, 143.0, 175.2; HRMS (FAB$^+$) calcd for $C_{15}H_{19}O_2$ 231.1385 [M + H] $^+$, found 231.1397.

Acknowledgment. This work was partially supported by a grant to RCAST at Doshisha University from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: General experimental procedures and spectral data for all previously unreported starting materials and products. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0621569