An Improved Catalytic System, $Pd(PPh_3)_4$/PhCOOH Combined Catalyst, for the Allylation of Carbon Pronucleophiles with Allenes

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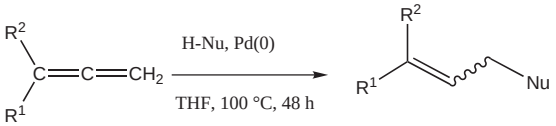
Abstract: The reaction of allenes with active methynes and methylenes proceeded smoothly in the presence of $Pd(PPh_3)_4$/PhCOOH combined catalyst to give the corresponding monoallylated products with *E*-stereoselectivity in good to high yields. This result is in marked contrast to the previous finding that the reaction of allenes with active methynes, in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$/dppb catalyst, affords the allylation products in lower yield with lower stereoselectivities.

Key words: palladium, carboxylic acids, catalysis, allenes, *C*-nucleophiles

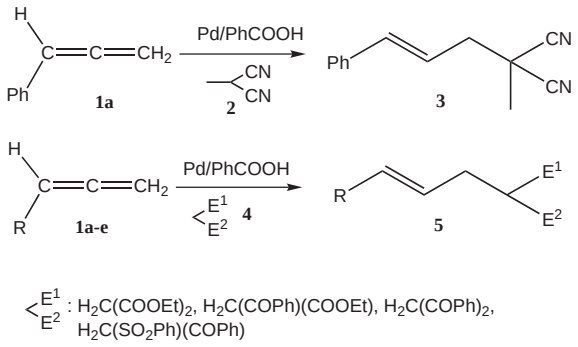
The formation of carbon-carbon bonds using transition metal catalysts is an important process in organic synthesis. The addition of a C-H bond to an unactivated C-C multiple bond to form a new carbon-carbon bond, i.e. hydrocarbonation, is a desirable method since it is an eco-chemical process with a high atom economy. Transition metals have been shown to be effective catalysts for promoting the addition of the C-H bond of carbon pronucleophiles to 1,3-dienes,[1] alkynes,[2] 1,3-enyne,[3] 3,3-dihexylcyclopropene,[4] methyleneaziridines,[5] methylenecyclopropanes[6] and allenes.[7] As a part of our continuing program on the transition metal catalyzed carbon-carbon bond formation, we previously reported the palladium catalyzed allylation of active methynes with allenes (Scheme 1).[7a] This new palladium-catalyzed transformation must become more useful, if the allylation of active methylenes becomes feasible. However, we encountered difficulties in the selective monoallylation of active methylenes; for example, a mixture of the mono- and diallylated products was obtained in the allylation of malononitrile, since the C-H bond of monoallylated product (allylmalononitrile) was more reactive than that of the starting malononitrile.



H-Nu = $HC(Me)(CN)_2$, $HC(Ph)(CN)(COOEt)$

Scheme 1

Furthermore, the method suffered from a low yield, poor stereoselectivity and long reaction time. In the course of our investigation, we found that the use of carboxylic acid as an additive improved dramatically the drawbacks mentioned above.[8a] Now we wish to report that the reaction of phenyl allene (**1a**) with an activated methyne, methyl malononitrile (**2**), proceeds stereoselectively in a higher yield (75%) with a shorter reaction time (12 h) by the use of $Pd(PPh_3)_4$ (5 mol%) and benzoic acid (10 mol%) combined catalyst (Scheme 2), and that the reaction of various allenes **1a**–**e** with activated methylenes **4** under the combined catalyst system proceeds very smoothly and gives selectively the mono-allylation products **5** in good to high yields with *E*-stereoselectivity (Scheme 2).



$\begin{matrix}E^1\\E^2\end{matrix}$: $H_2C(COOEt)_2$, $H_2C(COPh)(COOEt)$, $H_2C(COPh)_2$, $H_2C(SO_2Ph)(COPh)$

Scheme 2

In an initial experiment, phenyl allene (**1a**) was treated with 1 equivalent of methyl malononitrile (**2**), $Pd(PPh_3)_4$ (5 mol%) and benzoic acid (10 mol%) in dioxane at 100 °C to give the product **3** (*E*-isomer) in 75% yield (Scheme 2). No formation of the *Z*-isomer was observed, in contrast to the previous report[7a] in which a mixture of *E*- and *Z*-isomers was obtained in a ratio of 57:43. It is noteworthy that the addition of a catalytic amount of a simple carboxylic acid dramatically enhanced the rate and stereoselectivity of the reaction.[8]

Having the optimized condition in hand, we turned our attention towards active methylenes. As reported previously,[7a] the allylation of malononitrile with phenyl allene (**1a**) proceeded well in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$/dppb catalyst, however a mixture of mono- and diallylated products was obtained. At that stage, we believed that the synthetically useful allylation with allenes was restricted to active methynes only, and did not examine the allylation with other active methylenes. Later, it occurred to us

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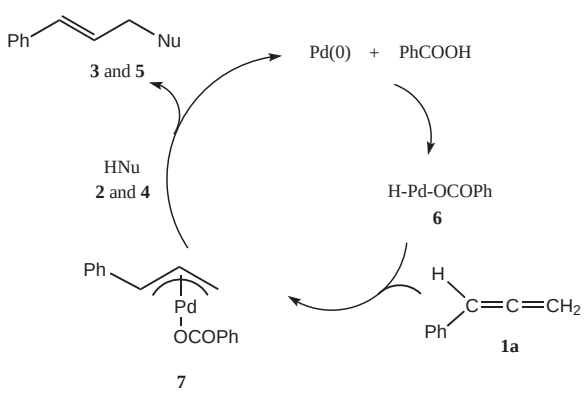
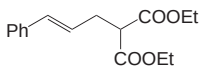
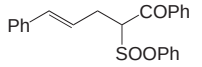
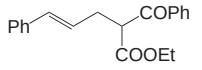
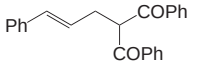
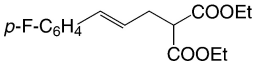
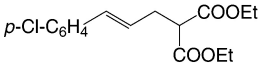
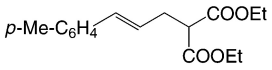
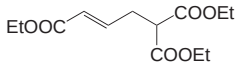
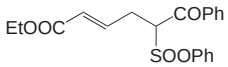
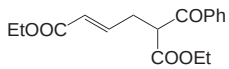
that diethyl malonate, less reactive than malononitrile, might react with **1a** pertinently without forming the double allylation product.

The reaction of diethyl malonate (**4a**) with phenyl allene **1a** in the presence of $Pd(PPh_3)_4$ and PhCOOH (10 mol%) in 1,4-dioxane at 100 °C for 12 hours afforded the monoallylated product **5a** in 90% isolated yield as a single *E*-isomer (Table 1, entry 1). Formation of the diallylated product was not observed at all under the conditions mentioned above. Similarly, the monoallylation of **4b**, **4c** and **4d** with phenyl allene (**1a**) also proceeded smoothly to give **5b**, **5c**, and **5d**, respectively, in good yields (entries 2–4). It should be noted that the functional groups on the aromatic ring of allenes did not affect the reaction efficiency. Thus, the allenes **1b**, **1c**, and **1d** with fluoro, chloro, and methyl substituents at the para position reacted smoothly with diethyl malonate (**4a**) to give the corre-



Scheme 3 Proposed mechanism for the allylation of C-nucleophiles with allenes

Table 1 $Pd(PPh_3)_4$/Benzoic Acid Catalyzed Allylation of Active Methylenes with Allenes[a]

Entry	Allenes (**1**)	H-Nu (**4**)[b]	Product (**5**)	Yield (%)[c]
1	**1a** R = Ph	**4a** $E^1 = E^2$ = COOEt	 **5a**	90
2	**1a** R = Ph	**4b** E^1 = COPh E^2 = SOOPh	 **5b**	85
3	**1a** R = Ph	**4c** E^1 = COPh E^2 = COOEt	 **5c**	82
4	**1a** R = Ph	**4d** $E^1 = E^2$ = COPh	 **5d**	85
5	**1b** R = *p*-F-C_6H_4	**4a**	 **5e**	70
6	**1c** R = *p*-Cl-C_6H_4	**4a**	 **5f**	72
7	**1d** R = *p*-Me-C_6H_4	**4a**	 **5g**	65
8	**1e** R = COOEt	**4a**	 **5h**	89
9	**1e** R = COOEt	**4b**	 **5i**	85
10	**1e** R = COOEt	**4c**	 **5j**	88

[a] All reactions were carried out with 5 mol% $Pd(PPh_3)_4$ and 10 mol% benzoic acid in 1,4-dioxane at 100 °C for 12 h.
[b] 1.2 Equivalent of pronucleophiles was used.
[c] Isolated yield.

sponding monoallylated products **5e**, **5f** and **5g** in 70%, 72%, and 65% yield, respectively (entries 5–7). Ethyl 2,3-butadienoate (**1e**) also reacted with the active methylenes **4a**, **4b**, and **4c** to give the monoallylated products **5h**, **5i**, and **5j**, respectively, in high yields (entries 8–10). It should be noted that the methodology reported herein is only applicable to activated allenes and in the case of unactivated allene such as deca-1,2-diene, starting material is recovered quantitatively.

A plausible mechanism for this allylation is illustrated in Scheme 3. The initial step is the formation of the hydridopalladium species **6** from Pd(0) and benzoic acid. The hydropalladation of phenyl allene (**1a**) with **6** would produce the π-allylpalladium species **7**. The π-allylpalladium species would reacts with the pronucleophiles **2** and **4** to give the products **3** and **5** with the liberation of Pd(0) and benzoic acid.[2] Another conceivable pathway is that the Pd-catalyzed addition of benzoic acid to allene **1a** takes place first[9] and then the resulting cinnamyl benzoate reacts with HNu in the Tsuji–Trost allylation manner to give the products **3** and **5**.

In conclusion, we have now improved our earlier allylation procedure for carbon pronucleophiles with allenes. Nowadays, a variety of methods are known for the synthesis of allenes, so we expect the present methodology can prove a good alternative to the existing methods for the allylation of carbon nucleophiles. Herein, we achieved selective mono-allylation of active methylenes with *E*-stereoselectivity and *E*-selective allylation of active methynes. The reason why the present catalytic system, Pd(0)/PhCOOH, gives high *E*-stereoselectivity while the previous catalyst, Pd(0) only, produces a mixture of *E* and *Z* stereomers is not clear at present. However, this difference may become a key for elucidating the precise mechanism for the previous reaction.[7a] Further investigation on the mechanism for the allylation with allenes and on the asymmetric allylation of carbon nucleophiles with allenes are now underway in our laboratory.

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz using $CDCl_3$ as solvent and are reported in ppm relative to $CHCl_3$ (δ = 7.26) for ^{1}H NMR and relative to the central $CDCl_3$ (δ = 77.00) resonance for ^{13}C NMR. Coupling constants in ^{1}H NMR data are given in Hz. The HRMS spectra were recorded at HITACHI M-2500S instrument. Dehydrated 1,4-dioxane were purchased from Wako Pure Chemical Inc. Structure of **5a**,[10] **5b**,[11] **5c**,[12] **5d**,[11] were confirmed by comparison with published spectral data. The allenes **1a**,[13] **1b**,[14] **1c**,[15] and **1d**[14] are known in literature. The allene **1e** is commercially available and was purchased from Aldrich.

Allylation of Diethyl Malonate (4a) with Phenyl Allene (1a); Typical Procedure

To a mixture of phenyl allene (**1a**, 0.20 g, 1.72 mmol), diethyl malonate (**4a**, 0.33 g, 2.07 mmol), $Pd(PPh_3)_4$ (0.099 g, 0.086 mmol) in anhyd 1,4-dioxane (5 mL) was added benzoic acid (0.021 g, 0.17 mmol), and the mixture was stirred for 12 h at 100 °C. The reaction mixture was then filtered through a short silica gel column using Et_2O as an eluent, and the filtrate was concentrated. The residue was purified by a silica gel column chromatography (hexane–EtOAc, 4:1) to give **5a** (0.43 g, 90%).

2-(3-Phenyl-allyl)-malonic Acid Diethyl Ester (5a)[10]

Oil.

IR (KBr): 3029, 1740 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.32 (m, 5 H), 6.46 (d, *J* = 15.9 Hz, 1 H), 6.14 (ddd, *J* = 15.9, 7.8, 7.8 Hz, 1 H), 4.18 (2 × q, *J* = 7.3 Hz, 4 H), 3.47 (t, *J* = 7.5 Hz, 1 H), 2.78 (t, *J* = 7.5 Hz, 2 H), 1.24 (2 × t, *J* = 7.3 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.6, 136.9, 132.6, 128.4, 128.3, 127.9, 127.2, 126.0, 125.4, 61.4, 51.9, 32.2, 14.09.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{20}O_4$: 276.1356; found: 276.1356.

2-Benzenesulfonyl-1,5-diphenyl-pent-4-en-1-one (5b)[11]

Solid; mp 116–117 °C.

IR (KBr): 3061, 1686, 1596 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.12–7.67 (m, 11 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 5.91 (ddd, *J* = 16.0, 7.5, 7.5 Hz, 1 H), 5.18 (dd, *J* = 12.0, 4.0 Hz, 1 H), 2.89–3.03 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 136.7, 136.3, 136.2, 134.1, 133.9, 133.8, 129.5, 128.7, 128.5, 128.2, 127.4, 125.9, 122.8, 69.3, 31.5.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{23}H_{20}O_3S$: 376.1128; found [M – SO_2Ph]: 235.1117.

2-Benzoyl-5-phenyl-pent-4-enoic Acid Ethyl Ester (5c)[12]

Oil.

IR (KBr): 3061, 1735, 1686 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 12 Hz, 2 H), 7.12–7.56 (m, 8 H), 6.42 (d, *J* = 15.5 Hz, 1 H), 6.18 (ddd, *J* = 15.5, 8.0, 8.0 Hz, 1 H), 4.41 (t, *J* = 8.0 Hz, 1 H), 4.11 (q, *J* = 7.5 Hz, 2 H), 2.86 (m, 2 H), 1.12 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 169. 1, 136.8, 136.0, 133.3, 132.4, 128.5, 128.4, 128.4, 128.3, 128.0, 127.1, 125.9, 125.9, 61.33, 54.2, 32.3, 14.0.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{20}H_{20}O_3$: 308.1407; found: 308.1407.

1,3-Diphenyl-2-(3-phenyl-allyl)-propane-1,3-dione (5d)[11]

Solid; mp 72–74 °C.

IR (KBr): 3085, 1690 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8 Hz, 4 H), 7.11–7.72 (m, 11 H), 6.48 (d, *J* = 16.0 Hz, 1 H), 6.26 (ddd, *J* = 16.0, 8.0, 8.0 Hz, 1 H), 5.37 (t, *J* = 8.0 Hz, 1 H), 3.04 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.3, 136.8, 135.8, 133.4, 132.3, 128.8, 128.4, 128.3, 127.2, 126.6, 126.0, 57.0, 33.0.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{24}H_{20}O_2$: 340.1458; found: 340.1455.

2-[3-(4-Fluoro-phenyl)-allyl]-malonic Acid Diethyl Ester (5e)

Oil.

IR (KBr): 3030, 1741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (dd, *J* = 8.8, 5.2 Hz, 2 H), 6.95 (t, *J* = 8.0 Hz, 2 H), 6.41 (d, *J* = 15.9 Hz, 1 H), 6.05 (ddd, *J* = 15.9, 7.4, 7.4 Hz, 1 H), 4.17 (2 × q, *J* = 7.2 Hz, 4 H), 3.46 (t, *J* = 7.5 Hz, 1 H), 2.76 (t, *J* = 7.4 Hz, 2 H), 1.25 (2 × t, *J* = 7.3 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 160.8, 133.1, 133.0, 131.5, 127.5, 125.2, 115.4, 115.2, 61.4, 51.9, 32.2, 14.2.

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{19}FO_4$: 294.1267; found: 294.1263.

2-[3-(4-Chloro-phenyl)-allyl]-malonic Acid Diethyl Ester (5f)
Oil.

IR (KBr): 3025, 1745 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.23 (m, 4 H), 6.34 (d, *J* = 16.0 Hz, 1 H), 6.08 (ddd, *J* = 16.0, 7.4, 7.4 Hz, 1 H), 4.11 (2 × q, *J* = 7.0 Hz, 4 H), 3.40 (t, *J* = 7.4 Hz, 1 H), 2.71 (t, *J* = 7.4 Hz, 2 H), 1.20 (2 × t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 135.4, 132.9, 131.5, 128.6, 127.3, 126.3, 61.5, 51.9, 32.2, 14.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{19}ClO_4$: 310.0972; found: 310.0974.

2-[3-(4-Methyl-phenyl)-allyl]-malonic Acid Diethyl Ester (5g)
Oil.

IR (KBr): 3029, 1743 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.47 (d, *J* = 16.0 Hz, 1 H), 6.12 (dt, *J* = 16.0, 7.6 Hz, 1 H), 4.23 (2 × q, *J* = 7.0 Hz, 4 H), 3.51 (t, *J* = 7.6 Hz, 1 H), 2.83 (t, *J* = 7.6 Hz, 2 H), 2.33 (s, 3 H), 1.32 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 137.0, 134.2, 132.5, 129.1, 125.9, 124.4, 61.4, 52.1, 32.3, 21.2, 14.2.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{22}O_4$: 290.1518; found: 290.1517.

5-Ethoxycarbonyl-hex-2-enedioic Acid Diethyl Ester (5h)
Oil.

IR (neat): 3065, 1735, 1710 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.85 (ddd, *J* = 12.9, 7.5, 7.5 Hz, 1 H), 5.85 (d, *J* = 12.9 Hz, 1 H), 4.18 (3 × q, *J* = 7.3 Hz, 6 H), 3.45 (t, *J* = 7.5 Hz, 1 H), 2.77 (t, *J* = 7.5 Hz, 2 H), 1.25 (3 × t, *J* = 7.3 Hz, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 165.6, 143.5, 123.6, 61.5, 60.1, 50.5, 30.9, 14.1, 13.9.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{20}O_6$: 272.1254; found [M + H]: 273.1333.

5-Benzenesulfonyl-6-oxo-6-phenyl-hex-2-enoic Acid Ethyl Ester (5i)
Oil.

IR (neat): 2931, 1710, 1690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.41–7.73 (m, 6 H), 6.65 (ddd, *J* = 12.8, 7.9, 7.9 Hz, 1 H), 5.78 (d, *J* = 12.8 Hz, 1 H), 5.15 (t, *J* = 8.0 Hz, 1 H), 4.07 (q, 7.3 Hz, 2 H), 2.95 (dd, *J* = 8.0, 7.9 Hz, 2 H), 1.19 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.6, 165.2, 141.2, 136.3, 135.9, 134.3, 134.0, 129.4, 128.9, 128.8, 128.6, 124.8, 124.8, 68.1, 60.3, 30.2, 14.0.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{20}O_5S$: 372.1026; found [M + H]: 373.1104.

5-Benzoyl-hex-2-enedioic Acid Diethyl Ester (5j)
Oil.

IR (neat): 3089, 1735, 1711, 1690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 2 H), 7.50–7.59 (m, 1 H), 7.44–7.49 (m, 2 H), 6.89 (ddd, *J* = 12.7, 7.5, 7.5 Hz, 1 H), 5.88 (d, *J* = 12.7 Hz, 1 H), 4.42 (t, *J* = 8.0 Hz, 1 H), 4.14 (2 × q, *J* = 7.3 Hz, 4 H), 2.88 (m, 2 H), 1.25 (t, *J* = 7.3 Hz, 3 H), 1.15 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.3, 168.5, 165.8, 144.1, 135.6, 133.9, 128.5, 123.6, 61.7, 60.2, 52.8, 31.08, 14.2, 13.9.

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{20}O_5$: 304.1305; found [M + H]: 305.1384.

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