# Palladium-catalysed Reaction of Aryl-substituted Allylic Alcohols with Zinc Enolates of β-Dicarbonyl Compounds in the Presence of Titanium(IV) Isopropoxide

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The reaction of aryl-substituted allylic alcohols **1a–c** with $Zn(acac)_2$ using a catalytic amount of $PdCl_2(PPh_3)_2$ proceeds efficiently in the presence of lithium chloride and titanium(IV) isopropoxide to give the corresponding acetonylated products **3–5**. Similarly, benzoylmethylation and ethoxycarbonylmethylation of **1a** and **1b** can also be attained by using zinc enolates generated *in situ* from reactions of zinc chloride with dibenzoylmethane **8b** and ethyl benzoylacetate **8c**.

Palladium-catalysed reaction of allylic compounds with carbon nucleophiles such as metal enolates, forming a carbon–carbon bond, is of genuine synthetic utility.[1] The reaction is usually carried out using allylic esters and ethers. In contrast, and in spite of their ready availability, the reaction with allylic alcohols has been explored less thoroughly.[2,3] We have recently reported that carbonylation of allylic alcohols using a palladium complex smoothly proceeds in the presence of titanium(IV) isopropoxide and lithium chloride to give the corresponding isopropylprop-3-enoates (Scheme 1).[4] It was expected that allylic alcohols could react with appropriate metal enolates, by employing the same reagents under inert atmosphere in place of carbon monoxide. Consequently, as part of our study of transition metal catalysed carbon–carbon bond formation reactions,[5] we have examined the reaction of allylic alcohols with zinc enolates of β-dicarbonyl compounds (Schemes 2 and 3). The results are described herein.

$$R^1CH=C(R^2)CH(R^3)OH \longrightarrow R^1CH=C(R^2)CH(R^3)CO_2Pr^i$$
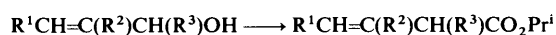
Scheme 1 *Reagents and conditions:* $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$, LiCl, $Ti(OPr^i)_4$, and THF, under CO (25 atm) at 100 °C

$$R^1CH=C(R^2)CH(R^3)OH \longrightarrow$$

1a $R^1 = Ph, R^2 = R^3 = H$
1b $R^1 = 2$-naphthyl, $R^2 = R^3 = H$
1c $R^1 = R^3 = H, R^2 = Ph$
1d $R^1 = R^2 = H, R^3 = Ph$
1e $R^1 = Pr, R^2 = R^3 = H$
1f $R^1 = R^3 = H, R^2 = Pr$
1g $R^1,R^3 = -(CH_2)_3-, R^2 = H$

$$R^1CH=C(R^2)CH(R^3)CH(COCH_3)_2, \quad R^1CH=C(R^2)CH_2CH_2COCH_3$$
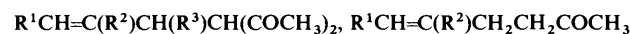
2 $R^1 = Ph, R^2 = R^3 = H$ **3** $R^1 = Ph, R^2 = H$
6 $R^1 = Pr, R^2 = R^3 = H$ **4** $R^1 = H, R^2 = Ph$
7 $R^1,R^3 = -(CH_2)_3-, R^2 = H$ **5** $R^1 = 2$-naphthyl, $R^2 = H$

Scheme 2 *Reagents and conditions:* $PdCl_2(PPh_3)_2$, $Zn(acac)_2$, $Ti(OPr^i)_4$ and/or LiCl, and 2-methoxyethyl ether of DME, under N_2 at 120 and 85 °C

Results and Discussion

*Reaction of Allylic Alcohols **1a–f** with* $Zn(acac)_2$.—When the reaction of cinnamyl alcohol **1a** (2 mmol) with $Zn(acac)_2 \cdot H_2O$ (4 mmol) was carried out in the presence of $PdCl_2(PPh_3)_2$ (0.05 mmol) and lithium chloride (1 mmol) in 2-methoxyethyl ether at 120 °C for 18 h under nitrogen, a mixture of 3-(3-phenyl-allyl)pentane-2,4-dione **2** (40%) and 6-phenylhex-5-en-2-one **3** (51%) was produced (Scheme 2 and Table 1). Addition of titanium(IV) isopropoxide to the reaction was found to favour the production of **3**. Thus, the monoketone **3** was exclusively

Table 1 Reaction of allylic alcohols **1a–g** with $Zn(acac)_2$[a]

Alcohol	Product(s) [yield (%)][b]
1a[c]	**2** (40), **3** (51)
1a[d]	**2** (10), **3** (72)
1a	**3** [85 (72)[e]]
1a[f]	**3** (80)
1a[g]	**3** (55)
1a[h]	**2** (19), **3** (61)
1a[i]	**2** (7), **3** [85 (78)[e]]
1a[j]	**3** (82)
1a[k]	**3** (84)
1b	**5** [85 (74)[e]]
1c	**4** (48)
1c[l]	**4** [79 (60)[e]]
1d	**3** (85)
1e[i]	**6** [55 (30)[e]]
1f[i]	**6** (60)
1g[i]	**7** (36)

[a] The reaction of **1** (1–5 mmol) with $Zn(acac)_2$ was carried out in 2-methoxyethyl ether in the presence of $PdCl_2(PPh_3)_2$, $Ti(OPr^i)_4$ and LiCl at 120 °C for 18 h unless otherwise noted. [1] : [$Zn(acac)_2$]:[$PdCl_2(PPh_3)_2$]:[$Ti(OPr^i)_4$]:[LiCl] = 1:2:0.025:1:0.5. [b] Determined by GLC analysis. Each product had (E)-configuration. [c] Without $Ti(OPr^i)_4$. [d] [$Ti(OPr^i)_4$] = 0.5. [e] Isolated yield. [f] [LiCl] = 1. [g] Without LiCl. [h] Reaction at 100 °C. [i] Reaction in 1,2-dimethoxyethane at 85 °C without $Ti(OPr^i)_4$. [j] [$Ti(OEt)_4$] = 1. [k] [$Ti(OBu)_4$] = 1. [l] Reaction in 1,4-dioxane at 100 °C for 40 h.
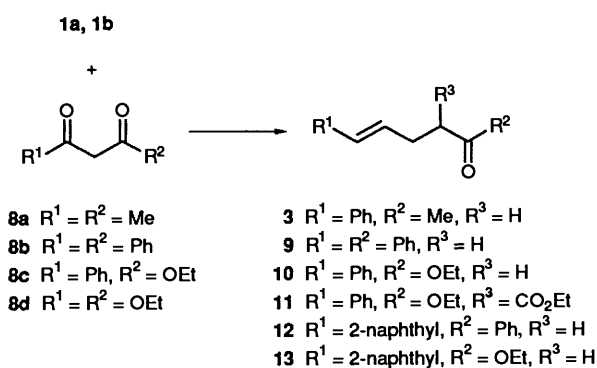
formed in a yield of 85% when 2 mmol of $Ti(OPr^i)_4$ was added. Reaction temperature also affected the product composition; the reaction at 100 °C using both lithium chloride and $Ti(OPr^i)_4$ gave **2** (19%) and **3** (61%) and that at 85 °C in 1,2-dimethoxyethane (DME) without $Ti(OPr^i)_4$ selectively afforded **2** (85%) along with **3** (7%). It was confirmed that (a) the reaction did not proceed in the absence of the catalyst or without both lithium chloride and $Ti(OPr^i)_4$, while without lithium chloride, **3** was selectively formed, although the yield was considerably lower; (b) the diketone **2** was transformed into **3** under the reaction conditions. These results indicate that both lithium chloride and $Ti(OPr^i)_4$ are capable of inducing the reaction of **1a** with $Zn(acac)_2$ under the influence of the palladium catalyst to give **2** which is, then, transformed into **3**, this process being favoured at a higher temperature in the presence of $Ti(OPr^i)_4$. Selective formation of **3** could be observed by use of $Ti(OEt)_4$ or $Ti(OBu)_4$ in place of $Ti(OPr^i)_4$. Tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$ showed also good catalytic activity, but with $PdCl_2$, $Pd(OAc)_2$ or $PdCl_2(PhCN)_2$, no coupling reaction occurred.

Reactions of aryl-substituted allylic alcohols **1b–d** with

Table 2 Reaction of **1a,b** with **8a–d**[a]

Alcohol	Dicarbonyl compound	Product(s) [yield (%)][b]
1a	**8a**	**3** (70)[c]
1a[d]	**8a**	**2** (70),[c] **3** (5)[c]
1a	**8b**	**9** (72)
1a[e]	**8c**	**10** (78)
1a[e]	**8d**	**10** (4),[c] **11** (70)[c]
1b	**8b**	**12** (92)
1b[e]	**8c**	**13** (84)

[a] The reaction of **1** (2 mmol) with **8** (4 mmol) was carried out in 2-methoxyethyl ether in the presence of $PdCl_2(PPh_3)_2$ (0.05 mmol), $ZnCl_2$ (2 mmol), $Ti(OPr^i)_4$ (2 mmol), and triethylamine (5 mmol) at 120 °C for 18 h unless otherwise noted. [b] Isolated yield. Each product had (E)-configuration. [c] Determined by GLC analysis. [d] Reaction in 1,2-dimethoxyethane at 85 °C without $Ti(OPr^i)_4$. [e] $Ti(OEt)_4$ (2 mmol) was used.

1a, 1b

+

8a R¹ = R² = Me   **3** R¹ = Ph, R² = Me, R³ = H
8b R¹ = R² = Ph   **9** R¹ = R² = Ph, R³ = H
8c R¹ = Ph, R² = OEt **10** R¹ = Ph, R² = OEt, R³ = H
8d R¹ = R² = OEt   **11** R¹ = Ph, R² = OEt, R³ = CO₂Et
                          12 R¹ = 2-naphthyl, R² = Ph, R³ = H
                          13 R¹ = 2-naphthyl, R² = OEt, R³ = H

Scheme 3 *Reagents and conditions:* $PdCl_2(PPh_3)_2$, $Ti(OPr^i)_4$, $ZnCl_2$, Et_3N and 2-methoxyethyl ether or DME, under N_2 at 120 or 85 °C

$Zn(acac)_2$ in the presence of $PdCl_2(PPh_3)_2$, LiCl and $Ti(OPr^i)_4$ at 120 °C selectively afforded the corresponding acetonylated products **4, 5** and **3**. Under the same conditions, reaction of alkyl-substituted substrates **1e–g**, however, gave intractable mixture of products, while diacetyl compounds **6** and **7** were obtained from reaction of **1e–g** in DME without $Ti(OPr^i)_4$ at 85 °C in modest yield. Formation of **3** and **6** from **1d** and **1f** may suggest the participation of π-allylpalladium intermediates in the reaction process.[1] The (E)/(Z) ratios of the allylic alcohols **1a, 1b** and **1e** employed were 98:2, 100:0 and 97:3, respectively. The products **2, 3, 5** and **6** were found to have (E)-configurations, no evidence for formation of the corresponding (Z)-isomers was obtained.

Reaction of **1a** *and* **1b** *with* β-*Dicarbonyl Compounds* **8a–d**.— The methyl ketone **3** could be also produced by reaction of **1a** with zinc acetylacetonate, generated *in situ* from acetylacetone **8a** and zinc chloride in the presence of triethyl amine, with $PdCl_2(PPh_3)_2$ and $Ti(OPr^i)_4$ in 2-methoxyethyl ether at 120 °C (Table 2 and Scheme 3). In this case, addition of lithium chloride showed no influence on the reaction. The reaction did not occur in the absence of zinc chloride.

Reactions of **1a** with dibenzoylmethane **8b** and ethyl benzoyl-acetate **8c** gave 1,5-diphenylpent-4-en-1-one **9** (72%) and ethyl 5-phenylpent-4-enoate **10** (78%), respectively, suggesting that debenzoylation from primary coupling products occurred smoothly, as did deacetylation from **2** [in the case of **8c**, $Ti(OEt)_4$ was employed]. Similarly, compounds **12** and **13** were isolated from reactions of **1b** with **8b** and **8c** in good yield. In these reactions, formation of isopropyl (or ethyl) benzoate in 40–55% yield was observed. Ethyl acetoacetate could not be used in place of **8c**, a complex mixture of products being formed.

Reaction of **1a** with diethyl malonate **8d** gave diethyl 2-(3-phenylallyl)malonate **11** (70%) as the predominant product along with **10** (4%). This indicates that the ethoxycarbonyl group in **11** is relatively stable under the reaction conditions.

Reaction Scheme.—A probable mechanism for the reaction of **1** with $Zn(acac)_2$ is illustrated in Scheme 4 in which the

Scheme 4
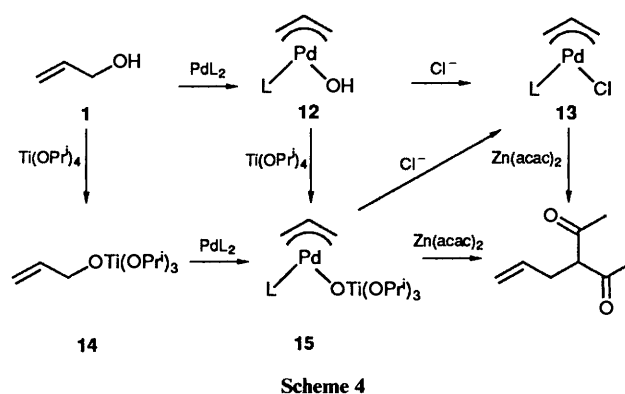
substituent on allyl alcohol is omitted. Reaction of **1** with palladium(0) species generated in the reaction medium gives an allyl complex **12**. In the presence of $Ti(OPr^i)_4$, **1** may react at first with the alkoxide to afford an allyl titanate **14**[6] followed by reaction with the palladium(0) species, giving a complex **15**. A possible role of added lithium chloride is that it would enhance the reaction with $Zn(acac)_2$ by ligand exchange with the chloride ion forming a complex **13**.[1] In the case of the reaction with zinc enolates generated from **8** and zinc chloride in the presence of triethyl amine, trimethylammonium chloride formed by the following equation may act as a chloride source.

$$8 + 2Et_3N + ZnCl_2 \longrightarrow Zn(R^1COCHCOR^2)_2 + 2Et_3NHCl$$
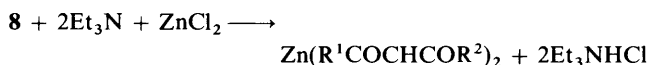
The intermediate **15** could also directly react with $Zn(acac)_2$; reaction of **1a** with the acetylacetonate proceeded without lithium chloride, although the yield of **3** was lower than that in the presence of the chloride. It should be noted that reaction of cinnamyl alcohol **1a** consisting predominantly of the (Z)-isomer [(E):(Z) = 3:97] with $Zn(acac)_2$ gave the ketone **3** having exclusively (E)-configuration in 80% yield. This fact suggests that *syn–anti* isomerization occurs in the π-allyl intermediates to give the more stable isomer preferentially.

A possible explanation for deacylation reaction of primary dicarbonyl products promoted by titanium alkoxides is illustrated in Scheme 5. It was found that **2** was transformed into **3** upon treatment with $Ti(OPr^i)_4$ and the reaction was

Scheme 5
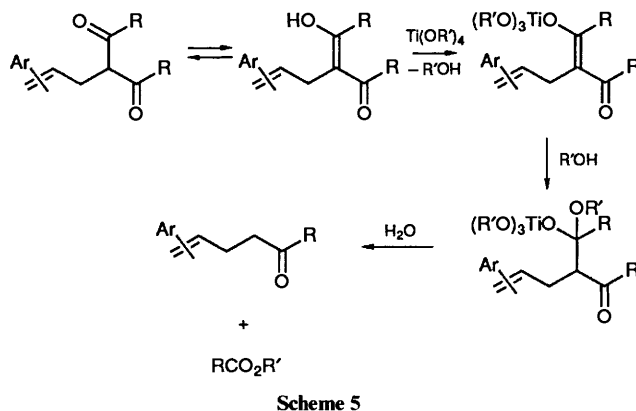
accelerated by a small amount of water. Thus, **3** was quantitatively formed from **2** in the presence of 1 equiv. of each of Ti(OPr^i)$_4$ and H$_2$O at 120 °C. It should be noted that, in the present reaction, the Zn(acac)$_2$ employed has crystallisation water and the hydroxide ion is formed from **1** during the reaction. It is known that titanium alkoxide reacts with water to give [Ti(OR)$_3$]$_2$O and higher polymeric alkoxides with liberating alcohol molecules.[6] Therefore, the polymeric alkoxides in place of the monomer may participate in the deacylation reaction.

Experimental

^{1}H NMR spectra were obtained with a JEOL JNM-GSX-400 spectrometer for CDCl$_3$ solutions. *J* Values are given in Hz. GLC–MS data were obtained with a JEOL JMS-DX-303 spectrometer. GLC analysis was carried out with a Shimadzu GC-8A gas chromatograph.

The alcohols **1a** [(*E*):(*Z*) = 3:97],[7] **1b**,[8] **1c**[9] and **1d**[10] were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details may be regarded as typical in methodology and scale.

*Reaction of Cinnamyl Alcohol **1a** with Zn(acac)$_2$.*—A mixture of substrate **1a** (268 mg, 2 mmol), Zn(acac)$_2$·H$_2$O (1126 mg, 4 mmol), PdCl$_2$(PPh$_3$)$_2$ (35 mg, 0.05 mmol), Ti(OPr^i)$_4$ (568 mg, 2 mmol) and LiCl (42 mg, 1 mmol) in 2-methoxymethyl ether (10 cm^3) was stirred under nitrogen at 120 °C for 18 h. Analysis by GLC and GLC–MS confirmed formation of 6-phenylhex-5-en-2-one **3** (295 mg, 85%). The product **3** (251 mg, 72%) was also isolated by column chromatography on silica gel with benzene–hexane (1:1) as eluent; oil;[11] *m/z* 174 (M$^+$); δ_H 2.17 (3 H, s), 2.48 (2 H, dt, *J* 6.8, 7.3), 2.61 (2 H, t, *J* 7.3), 6.19 (1 H, dt, *J* 16.1, 6.8), 6.41 (1 H, d, *J* 16.1) and 7.17–7.34 (5 H, m).

*Reaction of 3-(2-Naphthyl)prop-2-en-1-ol **1b** with Dibenzoylmethane **8b**.*—A mixture of substrate **1b** (368 mg, 2 mmol), **8b** (897 mg, 4 mmol), PdCl$_2$(PPh$_3$)$_2$ (35 mg, 0.05 mmol), Ti(OPr^i)$_4$ (568 mg, 2 mmol), ZnCl$_2$ (272 mg, 2 mmol) and triethylamine (505 mg, 5 mmol) in 2-methoxymethyl ether (10 cm^3) was stirred under nitrogen at 120 °C for 18 h. 5-(2-Naphthyl)-1-phenylpent-4-en-1-one **12** (526 mg, 92%) was isolated by column chromatography on silica gel with benzene–hexane (1:1) as eluent; m.p. 90–92 °C (from benzene–hexane) (Found: C, 87.85; H, 6.1. C$_{21}$H$_{18}$O requires C, 88.08; H, 6.34%); *m/z* 286 (M$^+$); δ_H 2.69–2.75 (2 H, m), 3.20 (2 H, t, *J* 7.3), 6.43 (1 H, dt, *J* 15.6, 6.8), 6.63 (1 H, d, *J* 15.6) and 7.25–8.01 (12 H, m).

Products.—3-(3-Phenylallyl)pentane-2,4-dione **2** was an oil;[12] *m/z* 216 (M$^+$); δ_H 2.15 (2.4 H, s; for enol), 2.21 (3.6 H, s; for keto), 2.75 (1.2 H, dt, *J* 1.5, 7.3; for keto), 3.16 (0.8 H, dd, *J* 1.5, 5.4; for enol), 3.80 (0.6 H, t, *J* 7.3; for keto), 6.07 (0.6 H, dt, *J* 15.6, 7.3; for keto), 6.21 (0.4 H, dt, *J* 16.1, 5.4; for enol), 6.34 (0.4 H, dt, *J* 1.5, 16.1; for enol), 6.45 (0.6 H, dt, *J* 1.5, 15.6; for keto), 7.21–7.36 (5 H, m) and 16.77 (0.4 H, s; for enol).

5-Phenylhex-5-en-2-one **4** was an oil; *m/z* 174 (M$^+$); δ_H 2.12 (3 H, s), 2.58 (2 H, t, *J* 7.8), 2.79 (2 H, t, *J* 7.8), 5.07 (1 H, s), 5.28 (1 H, s) and 7.25–7.40 (5 H, m).

6-(2-Naphthyl)-5-phenylhex-5-en-2-one **5** had m.p. 67–68 °C (from benzene–hexane) (Found: C, 85.75; H, 7.15. C$_{16}$H$_{16}$O requires C, 85.68; H, 7.19%); *m/z* 224 (M$^+$); δ_H 2.18 (3 H, s), 2.53 (2 H, dt, *J* 8.1, 6.8), 2.65 (2 H, t, *J* 6.8), 6.32 (1 H, dt, *J* 15.6, 8.1), 6.57 (1 H, d, *J* 15.6) and 7.38–7.78 (7 H, m).

3-Hex-2-enylpentane-2,4-dione **6** was an oil;[2c] *m/z* 182 (M$^+$); δ_H 0.77–0.84 (3 H, m), 1.21–1.32 (2 H, m), 1.84–1.94 (2 H, m), 2.04 (2.4 H, s; for enol), 2.17 (3.6 H, s; for keto), 2.44–2.48 (1.2 H, m; for keto), 2.84–2.85 (0.8 H, m; for enol), 3.60 (0.6 H, t, *J* 7.3; for keto) and 5.17–5.46 (2 H, m).

3-Cyclohex-2-enylpentane-2,4-dione **7** was an oil;[13] *m/z* 180 (M$^+$); δ_H 1.16–1.26 (2 H, m), 1.52–1.76 (2 H, m), 1.97–2.04 (2 H, m), 2.18 (3 H, s), 2.19 (3 H, s), 2.99–3.06 (1 H, m), 3.61 (1 H, d, *J* 10.3), 5.31 (1 H, dd, *J* 2.2, 5.0) and 5.74–5.79 (1 H, m).

1,5-Diphenylpent-4-en-1-one **9** was an oil;[11] *m/z* 236 (M$^+$); δ_H 2.66 (2 H, dt, *J* 6.8, 7.3), 3.15 (2 H, t, *J* 7.3), 6.29 (1 H, dt, *J* 15.6, 6.8), 6.46 (1 H, d, *J* 15.6), 7.16–7.48 (5 H, m) and 7.53–7.58 (5 H, m).

Ethyl 5-phenylpent-4-enoate **10** was an oil;[14] *m/z* 204 (M$^+$); δ_H 1.26 (3 H, t, *J* 7.1), 2.43–2.49 (2 H, m), 2.49–2.56 (2 H, m), 4.15 (2 H, q, *J* 7.1), 6.20 (1 H, dt, *J* 16.1, 6.5), 6.43 (1 H, d, *J* 16.1) and 7.17–7.34 (5 H, m).

Diethyl 2-(3-phenylallyl)malonate **11** was an oil;[15] *m/z* 276 (M$^+$); δ_H 1.18 (3 H, t, *J* 7.3), 1.18 (3 H, t, *J* 7.3), 2.73 (2 H, dd, *J* 6.8, 7.3), 3.42 (1 H, t, *J* 7.3), 4.13 (2 H, q, *J* 7.3), 4.13 (2 H, q, *J* 7.3), 6.08 (1 H, ft, *J* 15.8, 6.8), 6.40 (1 H, d, *J* 15.8) and 7.18–7.26 (5 H, m).

Ethyl 5-(2-naphthyl)pent-4-enoate **13** was an oil; *m/z* 254 (M$^+$); δ_H 1.26 (3 H, t, *J* 7.3), 2.49–2.53 (2 H, m), 2.59 (2 H, t, *J* 7.1), 4.16 (2 H, q, *J* 7.3), 6.34 (1 H, dt, *J* 15.6, 6.8), 6.59 (1 H, d, *J* 15.6) and 7.36–7.79 (7 H, m).

The free acid of **13** had m.p. 173–175 °C (from methanol) (Found: C, 79.35; H, 6.05. C$_{15}$H$_{14}$O$_2$ requires C, 79.62; H, 6.24%).

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