Aromatic Carbon–Hydrogen Bond Activation. Novel Synthesis of 1-Naphthol Derivatives by Palladium Catalysed Cyclocarbonylation of Cinnamyl Compounds

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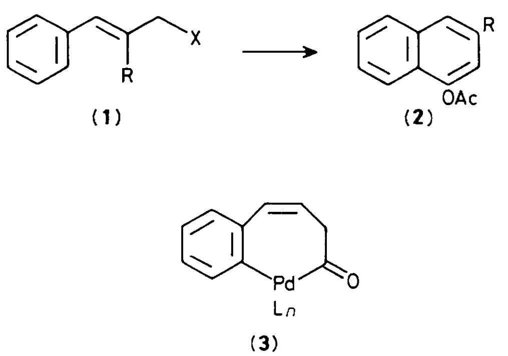
Palladium catalysed cyclocarbonylation of cinnamyl compounds gives 1-naphthol derivatives in good yields whereas the similar carbonylation of *trans*-β-bromostyrene yields a polymer containing benzindanone units.

Many organic reactions use palladium complexes. In particular, π-allyl palladium complexes, which are readily derived from allyl compounds, are important synthetic intermediates.[1] During our studies on carbonylation reactions catalysed by transition metal complexes,[2] we have discovered a novel synthesis of 1-naphthol derivatives by the palladium catalysed cyclocarbonylation of cinnamyl compounds (**1**) (Scheme 1). Several examples of the cyclocarbonylation of aromatic compounds have been reported, including the synthesis of anthraquinone from benzophenone with $PdCl_2$,[3] indanones

Table 1. Acetyl-1-naphthols from cinnamyl derivatives.[a]

(1)	Conversion[b] (%)	Yield[c] (%)
a	92	74 (46)
a[d]	85	69
b	69	59
b[e]	76	76 (44)
c	[f]	41

[a] Reaction conditions as Scheme 1. [b] Determined by g.l.c. [c] Determined by g.l.c., isolated yield in parentheses. [d] Ac_2O (50 mmol). [e] Ac_2O (50 mmol), 4 h. [f] Cinnamyl bromide was not detected by g.l.c. because it was converted into its ammonium salt.

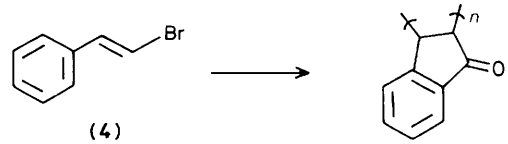


a; R = H, X = OAc
b; R = Me, X = OAc
c; R = H, X = Br

Scheme 1. *Reagents and conditions:* (**1**) (50 mmol), $PdCl_2(PPh_3)_2$ (0.3 mmol), Ac_2O (100 mmol), NEt_3 (100 mmol), benzene (20 ml), CO (60 kg/cm^2 at room temp.), 160 °C, 1 h.

from benzene and polyfunctional halides with $AlCl_3$,[4] an indanone from tetraphenylbutatriene with $Co_2(CO)_8$,[5] and indenones from benzene and diphenylacetylene with $Rh_4(CO)_{12}$.[6]

As shown in Table 1, 1-naphthyl acetate (**2a**) was obtained in good yield if cinnamyl acetate (**1a**) was treated with NEt_3 (2 equiv.) and Ac_2O (>1 equiv.) under CO pressure in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$. The reaction rate was much increased with increase in the amount of Ac_2O. In the case of β-methylcinnamyl acetate (**1b**), if 2 equivalents of Ac_2O were added, the reaction was four times faster than that with 1 equivalent. It is of interest that a combination of NEt_3 and Ac_2O is essential for this reaction. Only a low yield of 1-naphthyl acetate was formed from cinnamyl acetate in the absence of NEt_3, while the reaction without Ac_2O induced unfavourable side reactions and no 1-naphthyl acetate was formed. The rate of the cyclocarbonylation is also dependent on the structure of the starting cinnamyl derivatives. The reactivity decreases in the following order: cinnamyl acetate > cinnamyl bromide > β-methylcinnamyl acetate ≫ α-methylcinnamyl acetate, γ-methylcinnamyl acetate. In the case of the latter two compounds, no naphthol derivatives were formed under the reaction conditions shown in Table 1.



Scheme 2. *Reagents and conditions:* (**4**) (40 mmol), $PdCl_2(PPh_3)_2$ (0.3 mmol), NEt_3 (40 mmol), benzene (20 ml), CO (60 kg/cm^2), 180 °C, 24 h.

It seems plausible that the reaction proceeds through a cyclometallated complex (**3**) which is formed by oxidative addition of a cinnamyl derivative to a palladium(0) species followed by CO insertion and *ortho*-palladiation. However, we must await further investigations to elucidate the reaction mechanism.

A similar cyclocarbonylation using *trans*-β-bromostyrene (**4**) was also attempted (Scheme 2). However, the expected product, indene-1-one was not isolated, probably because the compound is thermally unstable and easily polymerizes. In fact a polymer was formed which exhibits an i.r. absorption band at 1710 cm^{-1} characteristic of a carbonyl group within a five-membered ring fused to an aromatic ring.

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