

Preliminary communication

CONVENIENT SYNTHESIS OF ALLENYL ESTERS AND AMIDES BY PALLADIUM CATALYZED ALKOXY- AND AMIDO-CARBONYLATION OF ALLENYL AND PROPYNYL HALIDES *

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Summary

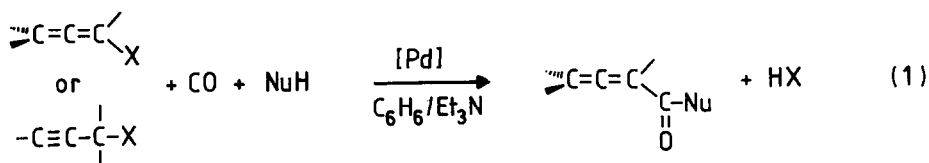
Allenyl esters $R^1R^2C=C=C(H)C(O)R$ ($R = OMe$) or amides ($R = NEt_2$) are formed with excellent selectivities and in good yields by carbonylation of propynyl and allenyl halides at 1–20 bar CO pressure in benzene, in the presence of MeOH or $HNEt_2$ and 1% of $Pd(PPh_3)_4$ or *trans*- $Me_2C=C=C(H)Pd(PPh_3)_2Br$. Possible organometallic intermediates are discussed.

We recently reported that carbon–halogen bonds of allenyl halides $C=C=CX$ and propynyl halides $C\equiv CCX$ ($X = Cl, Br, I$) are very prone to regio- and stereoselective substitution by d^{10} metal complexes like $Pd(PPh_3)_n$ [1,2]. The observed regioselectivity has been utilized in Pd^0 -catalyzed cross-coupling reactions of propynyl and allenyl compounds with organometallic reagents to give exclusively allenes, bearing e.g., aryl and alkynyl functions [3].

Effective Pd-catalyzed alkoxy carbonylation reactions (to give esters) have been described for aryl, alkenyl, allyl, and benzyl compounds [4–6], and recently decarboxylation-carbonylation of allyl and propynyl carbonates was observed [7]. However, no carbonylation of allenyl or propynyl halides has hitherto been reported. Nevertheless efficient synthesis of compounds containing a $C=C=CC=O$ moiety is of interest since these are versatile intermediates in the synthesis of e.g., unsaturated lactones [8]. Therefore, and to widen the scope of transition metal mediated synthesis of functionally substituted allenes, we attempted the palladium-catalyzed alkoxy carbonylation (and amidocarbonylation) of allenyl and propynyl halides (eq. 1).

* Dedicated to Prof. G.E. Coates on the occasion of his 70th birthday.

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(X = Cl, Br; NuH = MeOH, EtOH, Et₂NH; [Pd] = Pd(PPh₃)₄,

Me₂C=C=C(H)-Pd(PPh₃)₂Br)

First, the palladium-catalyzed methoxycarbonylation of Me₂C=C=C(H)Br was undertaken as a model reaction, using either Pd(PPh₃)₄ (**1**) or *trans*-Me₂C=C=C(H)Pd(PPh₃)₂Br (**2**) [2] as the catalyst (1 mole %). Representative results are shown in Table 1.

From entries 1 and 2 it is evident that smooth reaction occurs at 1 bar CO pressure, especially when larger amounts (5%) of catalyst are used. The reaction is accelerated, as expected, by increasing the CO pressure (entry 3) and/or the temperature (entries 4, 5). Furthermore, as shown by comparison of entries 5 and 7, the palladium(II) compound **2** seems to be slightly more effective than **1** (*vide infra*).

The results listed in Table 2 reveal that good to excellent yields of allenyl esters and amides can be obtained from a number of substituted allenyl and propynyl halides. Only propynyl esters (entry 7) give poor results. The regioselectivity is generally very good, and allenic products are exclusively obtained, but in case of 1-bromo-2-propyne (entry 5) a small amount of propynylic product is formed along with the allenyl ester.

The present results can be rationalized in terms of a catalytic cycle as depicted in Scheme 1, cf. [9,10], which may be entered via the pre-catalysts **1** or **2** respectively. The intermediacy of acyl-Pd^{II} compound **5** as the crucial species is likely, (cf. the intermediacy of comparable acyl species in analogous cases [4–7,11]), since we were able to isolate about 70% of the Pd as the yellow acylpalladium(II) complex **5** after

TABLE 1

METHOXYCARBOXYLATION OF Me₂C=C=C(H)Br ^a

Entry	Catalyst	p(CO) (bar)	Time (h)	Tempe- rature (°C)	Yield ^b (%)
1	2	1	72	20	26
2	2 ^c	1	72	20	98 ^c
3	2	20	72	20	98
4	2	20	2	20	19
5	2	20	2	80	65 ^d
6	1	20	2	20	20
7	1	20	2	80	32

^a With 1 mol% Pd(PPh₃)₄ (**1**) or 1% Me₂C=C=C(H)-Pd(PPh₃)₂Br (**2**) as catalyst. Solvent C₆H₆. ^b Yield of Me₂C=C=C(H)COOMe determined by ¹H NMR spectroscopy relative to added internal 1,3,5-Me₃C₆H₃; accuracy ±3%. Isolated yields were 80–90% of the values shown. All compounds gave satisfactory NMR and IR data. ^c 5% of **2** was used. ^d With THF as solvent the yield was 70%. With EtOH as nucleophile the yield was 60%.

TABLE 2

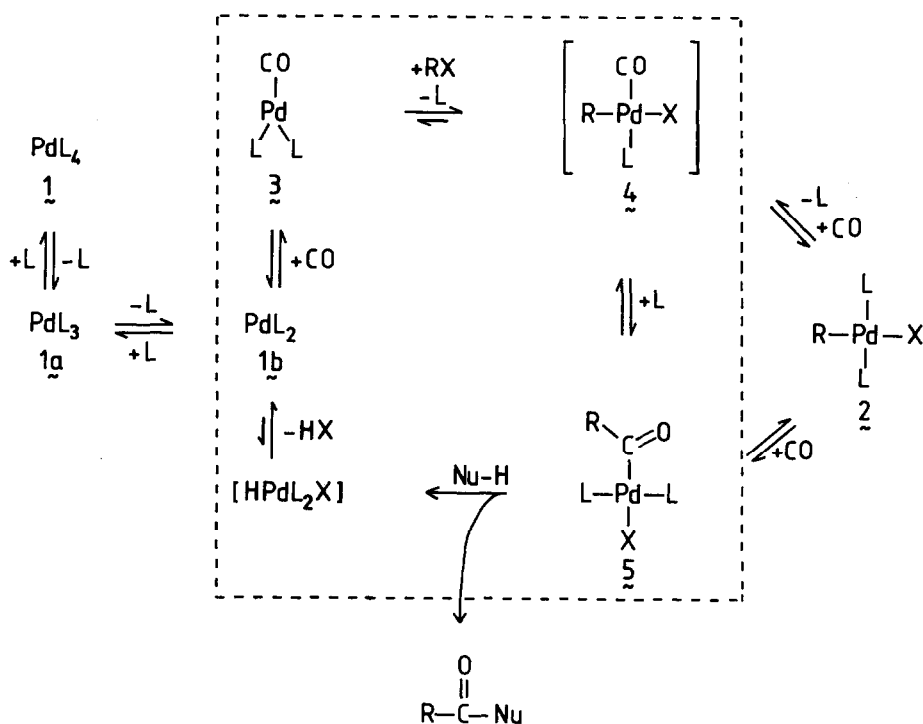
ALKOXYCARBONYLATION AND AMIDOCARBONYLATION OF ALLENYL AND PROPENYL HALIDES ^a

Entry	Substrate	Catalyst	Product ^b	Yield
1	Me ₂ C=C=C(H)Br	2	Me ₂ C=C=C(H)COOMe	88
2	Me ₂ C=C=C(H)Br	2	Me ₂ C=C=C(H)CONEt ₂	96
3	t-Bu(Me)C=C=C(H)Br	1	t-Bu(Me)C=C=C(H)COOMe	92
4	t-Bu(Me)C=C=C(H)Br	1	t-Bu(Me)C=C=C(H)CONEt ₂	85
5	HC≡CCH ₂ Br	1	H ₂ C=C=C(H)COOMe	85 ^c
6	HC≡CCH(Ph)Cl	1	Ph(H)C=C=C(H)COOMe	63
7	HC≡CCMe ₂ (OAc)	1/2	Me ₂ C=C=C(H)COOMe	10

^a In C₆H₆, with MeOH or Et₂NH as the nucleophile, 20 bar CO at 45 °C, 3 h. ^b NMR and IR data are in agreement with literature data [14,15]. ^c Ca. 8% of isomeric HC≡CCH₂COOMe was formed.

interruption of the catalytic reaction. IR (KBr, $\bar{\nu}$ (cm⁻¹)): 1960 (m, C=C=C), 1635 (vs, Pd(C=O)C=C; 1634–1665 [10]), 519 (s, Pd–C), 282 (m, Pd–Br). ¹H NMR (CDCl₃): δ 7.8–7.3 (m, 30H, Ar), 5.27 (m, 1H, HC=C=C), 1.85 (d, 6H, C=C=CMe₂).

Such an acylpalladium(II) complex is assumed to undergo nucleophilic substitution at the acyl carbon atom [11], yielding the organic product. After fast elimination of HX, the coordinatively unsaturated Pd⁰ species **1b** is obtained. When **2** is used as the catalyst, **1b** will readily take up CO to give **3**, which in turn undergoes oxidative addition of allenyl halide to give **4** [10]. Finally, 1,2-migration of the group

SCHEME 1. R = Me₂C=C=CH; X = Cl, Br; L = PPh₃; NuH = MeOH, Et₂NH.

R regenerates **5**. When **1** is applied as the precatalyst, the equilibria involving **1**, **1a** and **1b** may compete with coordination of CO to **1b**. This may make the catalytic reaction slower than when **2** is used, as is observed (*vide supra*). In the latter case, exactly two equivalents of phosphine are present per Pd entity, so formation of **1a** (and **1**) cannot occur.

The new method described can be regarded as competitive with established procedures for the preparation of allenyl esters, e.g. those involving Wittig-type reactions [12]. Such reactions require ketenes as starting materials, and these are less easy to prepare and handle than allenyl and propynyl halides. Allenyl amides can be conveniently prepared from propynylic alcohols and amide acetals [13] or using allenyllithium compounds *in situ* [14]. Our approach has the advantage of combining the use of stable, readily available materials with mild reaction conditions.

Typical procedure

A stainless steel autoclave (250 ml), flushed with nitrogen, was fitted with a stirring bar, and 30 ml of dry benzene, 2.0 mmol of allenyl or propynyl halide, 2 ml of MeOH, 0.3 ml of NEt₃ and 0.02 mmol of the catalyst **1** or **2** were added sequentially. For the amide synthesis, 2 ml of Et₂NH were added instead of MeOH and no NEt₃ was used. The autoclave was pressurized with CO to 20 bar. Experiments at 1 bar CO were performed in glass apparatus. The mixture was stirred for the times and at the temperatures indicated in Table 1. The experiments summarized in Table 2 were carried out at 45–50 °C for 3 h. The autoclave was cooled to 0 °C and depressurized and 1.0 mmol of mesitylene was added as a ¹H NMR integration standard. The mixture was poured into a separatory funnel and worked-up by washing with 0.5% hydrochloric acid (3 × 50 ml) and water (3 × 50 ml). The benzene fraction was dried over MgSO₄ and evaporated. The residual liquid was analyzed. In several cases, pure products were obtained by chromatography (Al₂O₃/ether).

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