Journal of Organometallic Chemistry, 325 (1987) C23–C26
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

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

NGUYEN D. TRIEU, CORNELIS J. ELSEVIER ** and KEES VRIEZE

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

(Received December 30th, 1986)

Summary

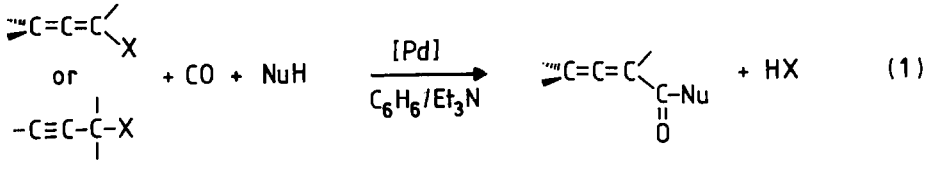
Allenyl esters $R^1R^2C{=}C{=}C(H)C(O)R$ (R = OMe) or amides ($R = NEt_2$) are formed with excellent selectivities and in good yields by carbonylation of propynyl and allenyl halides at 1–20 bar CO pressure in benzene, in the presence of MeOH or $HNEt_2$ and 1% of $Pd(PPh_3)_4$ or *trans*-$Me_2C{=}C{=}C(H)Pd(PPh_3)_2Br$.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

We recently reported that carbon–halogen bonds of allenyl halides C=C=CX and propynyl halides C≡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 alkoxycarbonylation 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 alkoxycarbonylation (and amidocarbonylation) of allenyl and propynyl halides (eq. 1).

* Dedicated to Prof. G.E. Coates on the occasion of his 70th birthday.
** To whom correspondence should be addressed.

0022-328X/87/$03.50



(1)

(X = Cl, Br; NuH = MeOH, EtOH, Et_2NH ; [Pd] = $Pd(PPh_3)_4$, $Me_2C{=}C{=}C(H)\text{-}Pd(PPh_3)_2Br$)

First, the palladium-catalyzed methoxycarbonylation of $Me_2C{=}C{=}C(H)Br$ was undertaken as a model reaction, using either $Pd(PPh_3)_4$ (**1**) or *trans*-$Me_2C{=}C{=}C(H)Pd(PPh_3)_2Br$ (**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

METHOXYCARBONYLATION OF $Me_2C{=}C{=}C(H)Br$ [a]

Entry	Catalyst	p(CO) (bar)	Time (h)	Temperature (°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% $Pd(PPh_3)_4$ (**1**) or 1% $Me_2C{=}C{=}C(H)\text{-}Pd(PPh_3)_2Br$ (**2**) as catalyst. Solvent C_6H_6. [b] Yield of $Me_2C{=}C{=}C(H)COOMe$ determined by ^1H NMR spectroscopy relative to added internal 1,3,5-$Me_3C_6H_3$; 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

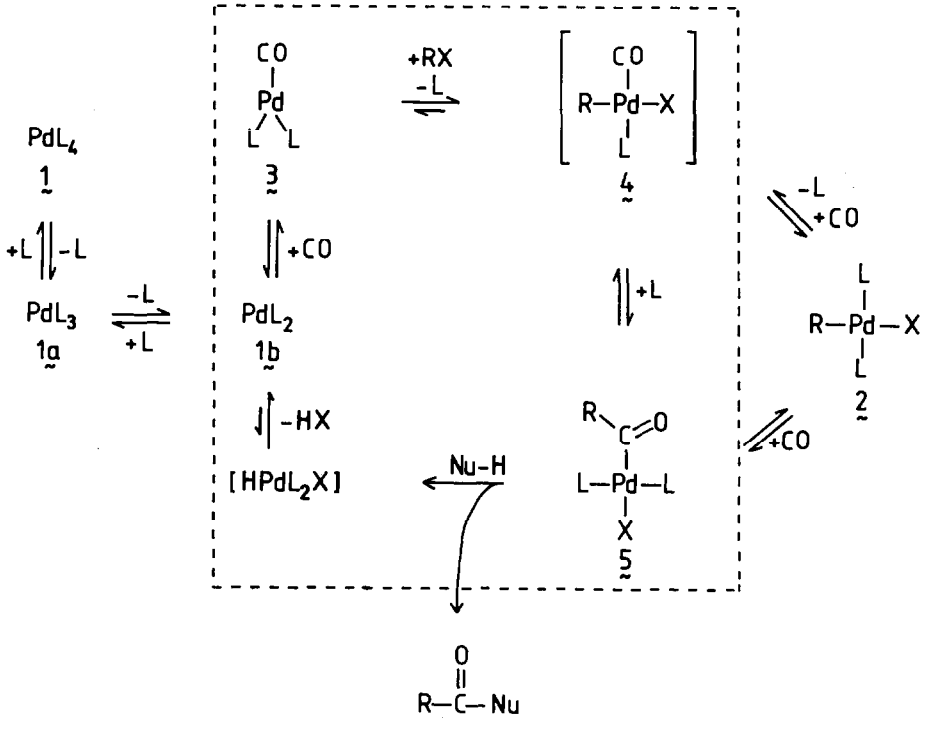
ALKOXYCARBONYLATION AND AMIDOCARBONYLATION OF ALLENYL AND PROPYNYL HALIDES [a]

Entry	Substrate	Catalyst	Product [b]	Yield
1	$Me_2C{=}C{=}C(H)Br$	**2**	$Me_2C{=}C{=}C(H)COOMe$	88
2	$Me_2C{=}C{=}C(H)Br$	**2**	$Me_2C{=}C{=}C(H)CONEt_2$	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	$HC{\equiv}CCH_2Br$	**1**	$H_2C{=}C{=}C(H)COOMe$	85 [c]
6	$HC{\equiv}CCH(Ph)Cl$	**1**	$Ph(H)C{=}C{=}C(H)COOMe$	63
7	$HC{\equiv}CCMe_2(OAc)$	**1/2**	$Me_2C{=}C{=}C(H)COOMe$	10

[a] In C_6H_6, with MeOH or Et_2NH 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 $HC{\equiv}CCH_2COOMe$ was formed.

interruption of the catalytic reaction. IR (KBr, $\tilde{\nu}$ (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 ($CDCl_3$): δ 7.8–7.3 (m, 30H, Ar), 5.27 (m, 1H, HC=C=C), 1.85 (d, 6H, $C{=}C{=}CMe_2$).

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 Pd^0 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 = $Me_2C{=}C{=}CH$; X = Cl, Br; L = PPh_3; NuH = MeOH, Et_2NH.

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 NEt_3 and 0.02 mmol of the catalyst **1** or **2** were added sequentially. For the amide synthesis, 2 ml of Et_2NH were added instead of MeOH and no NEt_3 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 $MgSO_4$ and evaporated. The residual liquid was analyzed. In several cases, pure products were obtained by chromatography (Al_2O_3/ether).

Acknowledgement. One of us (N.D.T.) thanks NUFFIC for a travel grant and the University of Hanoi for leave of absence.

References

1 C.J. Elsevier and P. Vermeer, J. Org. Chem., 50 (1985) 3042.
2 C.J. Elsevier, H. Kleijn, J. Boersma and P. Vermeer, Organometallics, 5 (1986) 716.
3 K. Ruitenberg, H. Kleijn, H. Westmijze, J. Meijer and P. Vermeer, Recl. Trav. Chim. Pays-Bas, 101 (1982) 405.
4 A. Schoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318, 3327.
5 D. Medema, R. v. Helden and C.F. Kohll, Inorg. Chim. Acta, 3 (1969) 255.
6 J.K. Stille and P.K. Wong, J. Org. Chem., 40 (1975) 532.
7 J. Tsuji, J. Organomet. Chem., 300 (1986) 281.
8 H.F. Schuster and G.M. Coppola, Allenes in Organic Synthesis, John Wiley, New York, 1984, p. 180.
9 G.K. Anderson and R.J. Cross, J. Chem. Soc., Dalton Trans., (1980) 1434.
10 K. Kudo, M. Sato, M. Hidai and Y. Uchida, Bull. Chem. Soc. Japan, 46 (1973) 2820.
11 D. Milstein, J. Chem. Soc., Chem. Commun., (1986) 817.
12 W.S. Wadsworth, Jr. and W.D. Emmons, J. Am. Chem. Soc., 83 (1961) 1733.
13 K.A. Parker, R.W. Kosley, Jr., S.L. Buchwald and J.J. Petraitis, J. Am. Chem. Soc., 98 (1976) 7104.
14 J.-C. Clinet and G. Linstrumelle, Synthesis, (1981) 875.
15 R.W. Lang and H.-J. Hansen, Helv. Chim. Acta, 63 (1980) 438.