CHEMISTRY LETTERS, pp. 1567-1570, 1990.

Selective Mono- and Dicarbonylation of Terminal Olefins Catalyzed by Pd-C in the Presence of Cu(II) or Cu(I) Chloride under Mild Conditions

Katsuhiko INOMATA,* Shiho TODA, and Hideki KINOSHITA
Department of Chemistry, Faculty of Science, Kanazawa University,
Kanazawa 920

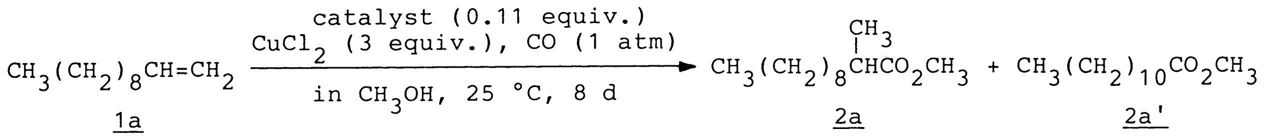
Pd-C can catalyze the carbonylation of terminal olefins with normal pressure of carbon monoxide at room temperature. The corresponding mono- and diesters (succinates) were selectively formed in excellent yields using Cu(II) and Cu(I) chloride, respectively, in alcohol.

It is well known that palladium chloride can catalyze the hydroesterification1) and hydrocarboxylation2) of olefins in acidic alcohol under mild conditions. In the course of our attempts to improve such hydroesterification reaction using various kinds of palladium catalysts (see Table 1) in the absence of hydrochloric acid under mild conditions (1 atom of CO, room temperature in methanol), we realized that palladium(0) black precipitates prior to the beginning or the completion of the reaction whenever the expected monoesters could be obtained in good yields from terminal olefins as shown in Table 1.

James and Stille found that the reaction of linear terminal olefins with 2-3 atm of carbon monoxide in methanol in the presence of palladium(II) chloride and copper(II) chloride as reoxidant afforded predominantly β-methoxy esters under neutral conditions on the contrary to our present result, and diesters (succinates) in the presence of base.3) They also described a similar precipitation of palladium(0) black in the same report,3) but only upon completion of the reaction, and it was regarded as an obstacle to decrease the catalytic efficiency. However, we eventually found that Pd-C is a favorable catalyst for the carbonylation of olefins (Entry 8 in Table 1), and further mono- and diesters can be selectively obtained in excellent yields in the presence of $CuCl_2$ or CuCl, respectively, with normal pressure of carbon monoxide at room temperature. We now describe the results of these investigations.

To a mixed dispersion of 5% Pd-C (58 mg, 0.11 equiv.) and anhydrous $CuCl_2$ (95% purity, 106 mg, 3.0 equiv.) in absolute methanol (4 ml) was

Table 1. Relationship between the Carbonylation of Terminal Olefins and the Precipitation of Palladium(0) Black



$$CH_3(CH_2)_8CH{=}CH_2 \xrightarrow[\text{in } CH_3OH,\ 25\ °C,\ 8\ d]{\text{catalyst (0.11 equiv.)},\ CuCl_2\ \text{(3 equiv.)},\ CO\ \text{(1 atm)}} CH_3(CH_2)_8\overset{CH_3}{\overset{|}{C}}HCO_2CH_3 + CH_3(CH_2)_{10}CO_2CH_3$$

1a 2a 2a'

Entry	Catalyst	Total yield of 2a and 2a'/%	Ratio of 2a/2a'[a]	Palladium (0) Black
1	$PdCl_2$	75	72/28	+
2	Li_2PdCl_4[b]	80[c]	71/29	+
3	-	no reaction	-	-
4	$PdCl_2(PPh_3)_2$	64	21/79	+
5	$PdCl_2$(dppe)	no reaction	-	-
6	$PdCl_2$(dppp)	trace	-	-
7	$Pd(PPh_3)_4$	9	23/77	-
8	Pd-C	quant.[d]	81/19	+

a) Determined by 400 MHz ^{1}H-NMR spectra and GLPC.

b) Complicated when the reaction mixture was refluxed for 1 h. The use of $CuCl_2$ was essential (no reaction in the absence of $CuCl_2$, 34% yield with 0.11 equiv. of $CuCl_2$).

c) 60% yield after 4 d.

d) No reaction in the absence of $CuCl_2$ or with 3 equiv. of $Cu(OAc)_2$ in place of $CuCl_2$.

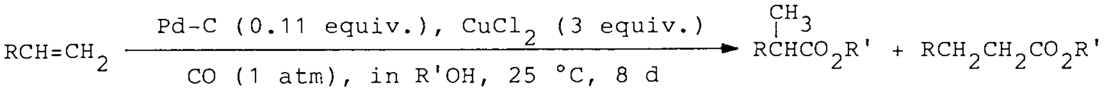
added 1-undecene (1a, 0.051 ml, 0.25 mmol) at 25 °C under carbon monoxide (1 atm). After stirring for 8 days at 25 °C, the reaction mixture was added dropwise to aqueous 10% $NaHCO_3$ solution. The filtrate through Celite was diluted with ethyl acetate and successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC (SiO_2, hexane : ethyl acetate = 10 : 1, v/v) to afford 54 mg of monoesters (2a and 2a', 81/19, quantitative yield) as a colorless oil. It is noteworthy that the ratio of 2a/2a' varies depending upon the catalysts used.

In a similar manner, other monoesters (2b-e and 2b-e') were prepared from the corresponding terminal olefins (1b-e) in excellent yields (Table 2).$^{4)}$

On the other hand, it was found that the use of CuCl in place of $CuCl_2$ in the above reaction gave exclusively α-monosubstituted succinates (3a-e) in high yields as shown in Table 3. Addition of THF to dissolve olefins was effective for higher olefins (1c,d, Entries 4 and 6).

James and Stille pointed out that the reduction of copper(II) to copper(I) in the presence of trialkylamines may decrease the catalytic activity of their carbonylation system cited above.$^{3)}$ It is not likely

Table 2. Preparation of Monoesters from Terminal Olefins



$$RCH=CH_2 \xrightarrow[\text{CO (1 atm), in R'OH, 25 °C, 8 d}]{\text{Pd-C (0.11 equiv.), CuCl}_2\text{ (3 equiv.)}} R\overset{CH_3}{CH}CO_2R' + RCH_2CH_2CO_2R'$$

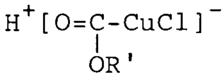
1a-e 2a-e 2a-e'

Entry	1a-e, R	R'OH	Total yield of 2 and 2'/%[a)]	Ratio of 2/2'[b)]
1	1a, $CH_3(CH_2)_8$	CH_3OH	quant.	81/19
2	1b, $CH_3(CH_2)_9$	CH_3OH	quant.	78/22
3	1c, $CH_3(CH_2)_{11}$	C_2H_5OH	quant.	72/28
4	1d, $CH_3(CH_2)_{15}$	C_2H_5OH	82	77/23
5	1e, $Ph(CH_2)_2$	CH_3OH	quant.	96/4

a) All the products gave the satisfactory spectral data.

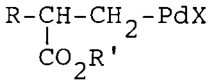
b) Determined by 400 MHz ^1H-NMR spectra.

that copper(I) chloride directly reacts with palladium(0) as an oxidant in the absence of oxygen. Taking into account the facts that (1) no reaction took place in the absence of copper salt [see foot note d) of Table 1], (2) 2% of 3a was obtained with CuCl in the absence of Pd-C [see foot note b) of Table 3], and (3) treatment of the dispersion of CuCl in methanol under carbon monoxide with stirring for 5 d prior to addition of olefin (1a) and Pd-C was effective to shorten the reaction time (3a was obtained in 97% yield for 5 d after addition of 1a and Pd-C, while 21 and 64% yields for 4 and 6.5 d, respectively, without the prior treatment with carbon monoxide), an active copper species, for example 4, seems to be formed.



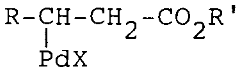
$H^+[O=\underset{OR'}{C}-CuCl]^-$

4



$R-\underset{CO_2R'}{CH}-CH_2-PdX$

5



$R-\underset{PdX}{CH}-CH_2-CO_2R'$

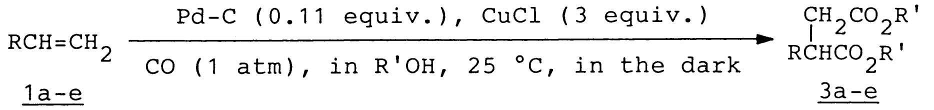
6

(X = Cl, H, etc.)

When $CuCl_2$ was used instead of CuCl, the predominant formation of branched monoesters (2) by formal Markovnikov addition to olefins (1) can be rationalized on the basis of the formation of carbonium ion intermediate[5)] or acidic decomposition of the intermediate (5) formed in preference to 6 by HCl evolved in the solution.[3)] This speculation was partially supported by the facts that the reaction mixture with $CuCl_2$ was strongly acidic, while weekly acidic with CuCl. Further, addition of methanolic hydrogen chloride (3 equiv.) to Pd-C/CuCl system shown in Table 3 afforded 46% of the monoester (2a/2a'=75/25) without formation of 3a accompanied by recovery of 20% of 1a.

As described above, it was found that Pd-C can catalyze the selective mono- and dicarbonylation of terminal olefins with normal pressure of carbon monoxide at room temperature, and they can be cleanly controlled by

Table 3. Preparation of α-Monosubstituted Succinates from Terminal Olefins



$$\mathrm{RCH{=}CH_2} \xrightarrow[\text{CO (1 atm), in R'OH, 25 °C, in the dark}]{\text{Pd-C (0.11 equiv.), CuCl (3 equiv.)}} \begin{array}{l}\mathrm{CH_2CO_2R'}\\ |\\ \mathrm{RCHCO_2R'}\end{array}$$

1a-e 3a-e

Entry	1a-e, R	R'OH	Time/d	Yield/%[a]
1	1a, $CH_3(CH_2)_8$	CH_3OH	9	3a, quant.[b]
2	1b, $CH_3(CH_2)_9$	CH_3OH	8	3b, 89
3	1c, $CH_3(CH_2)_{11}$	C_2H_5OH	8.5	3c, 56
4	"	CH_3OH/THF (1/1)	8	3c', 84
5	1d, $CH_3(CH_2)_{15}$	C_2H_5OH	9	3d, 67
6	"	CH_3OH/THF (1/1)	9	3d', 92
7	1e, $Ph(CH_2)_2$	CH_3OH	8	3e, 97

a) All the products gave the satisfactory spectral data.
b) 2% of 3a was obtained in the absence of Pd-C accompanied by recovery of 82% of 1a.

use of $CuCl_2$ or CuCl, even though the reactions are sluggish.

Related works including the detailed reaction mechanism and the attempts to speed up the reaction are in progress in our laboratory.

References

1) B. Despeyroux and H. Alper, Ann. N.Y. Acad. Sci., 415, 148 (1983); S. B. Fergusson and H. Alper, J. Chem. Soc., Chem. Commun., 1984, 1349.
2) H. Alper, J. B. Woell, B. Despeyroux, and D. J. H. Smith, J. Chem. Soc., Chem. Commun., 1983, 1270.
3) D. E. James and J. K. Stille, J. Am. Chem. Soc., 98, 1810 (1976). See also H. Urata, A. Fujita, and T. Fuchikami, Tetrahedron Lett., 29, 4435 (1988) and references cited therein.
4) Tsuji and his co-worker have also found that palladium metal such as Pd-C or palladium powder obtained prior reduction of palladium chloride with carbon monoxide is equally effective catalyst for the synthesis of esters from olefins under much more vigorous conditions (100 atm of CO, HCl (15%) in methanol, 80 °C) than ours: J. Tsuji, M. Morikawa, and J. Kiji, Tetrahedron Lett., 1963, 1437.
5) D. M. Fenton, J. Org. Chem., 38, 3192 (1973). Another mechanism involving $HPdL_nCl$ was proposed by Tsuji: J. Tsuji, Acc. Chem. Res., 2, 144 (1969).

(Received June 11, 1990)