ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1994, **4(1)**, 2–3

Mendeleev
Communications

A New Catalytic Reaction: Oxidative Carbonylation of Alkynes to Alkynylcarboxylic Acid Esters

Ton T. Zung, Lev G. Bruk and Oleg N. Temkin*

Moscow State Academy of Fine Chemical Technology, 117571 Moscow, Russian Federation. Fax: +7 095 430 7983

A new catalytic reaction – oxidative carbonylation of alkynes in the $PdCl_2$–CuCl system – and the reaction mechanism have been proposed based on the unusual effects of oxygen and copper(I) salts on this process and the key role of σ-alkynylcopper(I) complexes in the reaction.

The oxidative carbonylation of 1-alkynes to alkynylcarboxylic acid esters in the $PdCl_2$–$CuCl_2$–base system has already been reported in earlier work.[1,2]

$$\mathrm{RC{\equiv}CH + CO + 2CuCl_2 + 2NaOAc + R'OH} \xrightarrow[\mathrm{PdCl_2}]{20\,^{\circ}\mathrm{C},\ 1\ \mathrm{atm}} \mathrm{RC{\equiv}CCOOR' + 2CuCl + 2AcOH + 2NaCl} \quad (1)$$

Recently we have carried out studies on the mechanism of reaction (1) and have found the following experimental results,[3] which showed that σ-alkynylcopper(I) complexes are intermediates in the reaction.

(*a*) Addition of CuCl to the initial solution causes a significant decrease in the induction period.

(*b*) σ-Alkynylcopper(I) complexes prepared by a known method[4] can be carboxylated to alkynylcarboxylic acid esters by reaction (2); the reaction proceeds at a high rate and without an induction period.

Table 1 Oxidative carbonylation of PhC≡CH and MeC≡CH in the $\mathrm{PdCl_2}$–CuCl system.

Alkyne	Concentrations/mol $\mathrm{dm^{-3}}$							RC≡CCOOMe
	$\mathrm{PdCl_2}$	CuCl	LiCl	T/°C	$\%\mathrm{O_2}$	%CO	%MeC≡CH	Yield(%)
PhC≡CH	5.6×10^{-3}	0.5	0.3	11	60	40		82
PhC≡CH	5.6×10^{-3}	0.3	0.3	20	50	50		82
PhC≡CH	1.4×10^{-3}	0.4	0.2	26	42	58		86
MeC≡CH	5.6×10^{-3}	0.3	0.3	20	60	30	10	77
MeC≡CH	5.6×10^{-3}	0.3	0.3	20	50	30	20	45

$$\mathrm{RC{\equiv}CCu + CO + 2CuCl_2 + R'OH \xrightarrow[\text{20 °C, 1 atm}]{PdCl_2} RC{\equiv}CCOOR' + 3CuCl + HCl} \qquad (2)$$

(*c*) On studying the kinetics of PhC≡CCl and PhC≡CCOOMe formation in the $\mathrm{PdCl_2}$–$\mathrm{CuCl_2}$–CuCl–LiCl system in a buffer solution of MeOH–AcOH–$\mathrm{Et_3N}$, we found that the rates of oxidative carbonylation and oxidative chlorination of PhC≡CH changed in opposite directions on varying the $\mathrm{CuCl_2}$ and $\mathrm{PdCl_2}$ concentrations. This kinetic relation is in accordance with the hypothesis of a common intermediate in the formation of both these products. In addition, it is known that σ-alkynylcopper(I) complexes are intermediates in the oxidative chlorination of alkynes in the $\mathrm{CuCl_2}$–CuCl system.[5]

In this paper, we describe a new catalytic reaction of alkynylcarboxylate synthesis, catalysed by a two-component system of $\mathrm{Pd^{II}}$–$\mathrm{Cu^{I}}$ with the participation of oxygen.

It was shown that, in contrast to the well-known alkene oxidation process in the $\mathrm{Pd^{II}}$–$\mathrm{Cu^{II}}$–$\mathrm{O_2}$ system [6] (the so-called Waker process), the presence of oxygen in process (1) leads to an increase in the induction period and a decrease in the PhC≡CCOOMe yield.

The effect of oxygen on the process can be explained by the decrease in copper(I) concentration because of CuCl oxidation by oxygen.

The results of our kinetic studies, in particular, knowing the dependence of the reaction rate on CuCl and $\mathrm{CuCl_2}$ concentrations,[3] allowed us to propose a catalytic system of $\mathrm{PdCl_2}$–CuCl for the synthesis of alkynylcarboxylic acid esters, reaction (3).

$$\mathrm{RC{\equiv}CH + CO + \tfrac{1}{2}O_2 + R'OH \xrightarrow{PdCl_2,\ CuCl} RC{\equiv}CCOOR' + H_2O} \qquad (3)$$

We have determined the reaction conditions in which the alkyne oxidative carbonylation reaction (3) gives alkynylcarboxylic acid esters in good yields. The requirements for the stationary and selective synthesis process are as follows:

(i) A high concentration of copper(I) salts and low copper(II) concentration are required for high reaction rate and high selectivity.

(ii) An almost neutral pH.

(iii) Approximately equal rates of alkyne carbonylation and CuCl oxidation reactions.

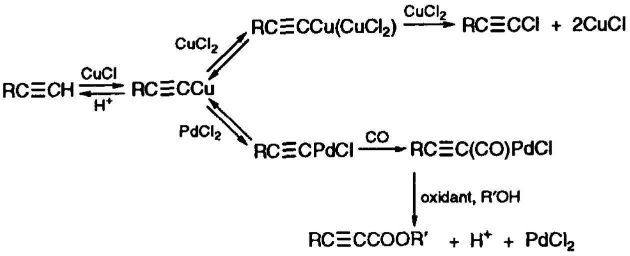
Reaction (3) proceeds intensely even in the absence of base. In this case, the stationary process (with constant $\mathrm{Cu^{I}}$ concentration and pH) must be maintained by a definite correlation between alkyne concentration and partial pressure of oxygen.

For instance, PhC≡CH was added dropwise to a mixture of $\mathrm{PdCl_2}$ (5.6×10^{-3} mol $\mathrm{dm^{-3}}$), CuCl (0.3 mol $\mathrm{dm^{-3}}$) and LiCl (0.3 mol $\mathrm{dm^{-3}}$) in methanol (10 ml) under atmospheric pressure (50% $\mathrm{O_2}$, 50% CO). The reaction was carried out at 20 °C and at a constant rate of ester formation during 3 h, and this allowed us to obtain 0.85 mol $\mathrm{dm^{-3}}$ ester solution. The yield of PhC≡CCOOMe was 82%. PhC≡CC≡CPh and PhC≡CCl were obtained as by-products. Under similar conditions, the oxidative carbonylation of MeC≡CH led to the formation of MeC≡CCOOMe.

In this carbonylation process, the correlation $[\mathrm{RC{\equiv}CH}]/p_{\mathrm{O_2}}$ is extremely important. The rate of MeC≡CCOOMe formation is decreased on decreasing the propyne partial pressure (propyne percentage of the gas) from 10% to 5%. But a higher $p_{\mathrm{MeC{\equiv}CH}}$ (*e.g.*, 20% MeC≡CH and 50% $\mathrm{O_2}$ in the gas) tends to reduce the carbonylation rate and ester yield, and to give rise to dimerization product (MeC≡CC≡CMe), Table 1.

Alkynylcarboxylic acid esters are usually produced from alkenylcarboxylic acids[7] or from sodium or magnesium alkynyl compounds (Iozitsch reaction).[8] Comparing both these traditional methods and process (1),[1,2] the reported one-pot synthetic method, based on the two-component $\mathrm{Pd^{II}}$–$\mathrm{Cu^{I}}$ catalytic system, is more effective and convenient.

The results of our studies on reactions (1)–(3) are in accordance with the following mechanism (Scheme 1) for the alkyne oxidative carbonylation.



Scheme 1

References

1 J. Tsuji and T. Takahashi, *Tetrahedron Lett.*, 1980, **21**, 849.
2 B. A. Trofimov, Yu. M. Skvortsov, A. G. Malkina and A. I. Gritsa, *Zh. Org. Khim.*, 1985, **21**, 2020 [*J. Org. Chem. USSR (Engl. Transl.)*, 1985, **21**, 1850].
3 Ton T. Zung, L. G. Bruk and O. N. Temkin, *Izv. Akad. Nauk, Ser. Khim.*, in press.
4 J. F. Norman, *Usp. Khim.*, 1973, **42**, 645 (in Russian); *Synthesis*, 1972, **2**, 63.
5 O. N. Temkin, G. K. Shestakov and Yu. A. Treger, *Atsetilen: khimiya, mekhanizmy reaktsii, tekhnologiya* (*Acetylene: Chemistry, Mechanisms of Reactions, Technology*), Khimiya, Moscow, 1991 (in Russian).
6 I. I. Moiseev, *π-Kompleksy v zhidkofaznom okislenii olefinov(π-Complexes in liquid-phase oxidation of olefines)*, Nauka, Moscow, 1970, pp. 52–63 (in Russian).
7 T. Abbott, *Sintezy organicheskikh preparatov, sbornik 2 (Organic Syntheses, V.2)*, Inostrannaya literatura, Moscow, 1949, pp. 71, 191, 520 (in Russian).
8 J. I. Iozitsch, *Zh. Fiz. Khim.*, 1910, **42**, 1491 (in Russian).

Received: Moscow, 16th August 1993
Cambridge, 2nd November 1993; Com. 3/05256G