



Review

Pd-catalyzed oxidation of alkynes

Jacques Muzart*

Institut de Chimie Moléculaire de Reims, UMR 6229, CNRS – Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

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ABSTRACT

This review surveys the different Pd-catalyzed procedures leading to the oxidation of the C≡C bonds. The reactivity and selectivity depend on the substitution of the triple bond, 1,2-diarylethynes being the most reactive. The main oxidation product, an 1,2-diketone, an ester or a furan, depends on both the used procedure and the substrate. Plausible mechanisms are, as far as possible, provided.

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1. Introduction

The oxidation of olefins in the presence of catalytic amounts of palladium salts or complexes has led to a plethora of reports, relating their allylic oxidation [1], epoxidation [2] or the formation of a ketone [3] or an aldehyde [4]. In contrast, the Pd-catalyzed oxidation of alkynes has been much less explored. Their most usually oxidation product is the corresponding 1,2-diketone. Since 1,2-diketones are structural moieties in numerous biologically interesting products [5], are broadly utilized for the construction of elaborated compounds [6] and as photoinitiators for the free-radical curing of polymer networks [7], it seems of interest to highlight, with an overview, the Pd procedures leading to their

synthesis [8]. The cleavage of the triple bond and the formation of tetrasubstituted furans are other reactions of alkynes under Pd-catalyzed oxidative conditions. These oxidation processes are gathered in the present review, which is organized in three main sections corresponding to the nature of the oxidized products with, mainly, a chronological account of the reports.

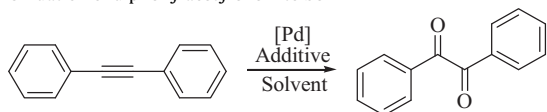
2. Formation of 1,2-dicarbonyl compounds

2.1. Oxidation with aqueous nitric acid

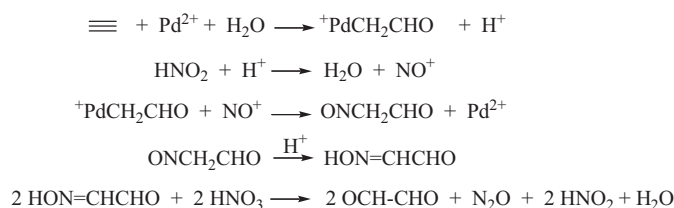
In 1970, Kukushkin et al. disclosed the formation of oxalic acid from the bubbling of acetylene into aqueous nitric acid containing catalytic amounts of Pd(NO₃)₂ (Eq. (1)) [9]. Fourteen years later, Kozlov et al. used also aqueous HNO₃, but with catalytic amounts of both PdCl₂ and NaNO₂ (Eq. (2)) [10]. These last conditions led to glyoxal as main product with a turnover number up to 100.

* Corresponding author. Fax: +33 3 2691 3166.
 E-mail address: jacques.muzart@univ-reims.fr

Table 1
Oxidation of diphenylacetylene into benzil



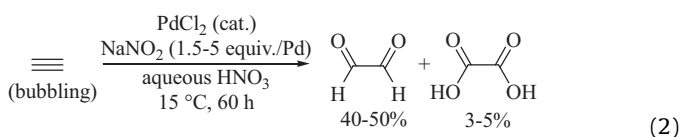
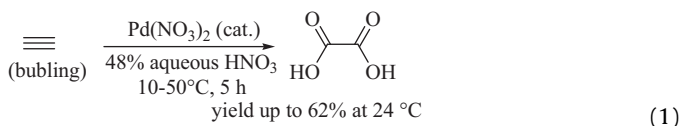
Entry	Catalyst (equiv.)	Additive (equiv.)	Solvent	T, °C	Time, h	Yield, %
1 [12]	PdCl ₂ (0.1)		DMSO	140	4	98
2 [13]	PdI ₂ (0.02)		DMSO	140	2	>96
3 [14]	PdBr ₂ (0.05)	CuBr ₂ (0.1), O ₂ (1 atm)	Dioxane/H ₂ O	60	24	97
4 [14]	PdBr ₂ (0.05)	CuBr ₂ (0.1), benzoquinone	Dioxane/H ₂ O	60	24	89
5 [14]	PdBr ₂ (0.05)	CuBr ₂ (0.1), O ₂ (1 atm)	DMF/H ₂ O	60	24	72
6 [14]	PdCl ₂ (0.05)	CuCl ₂ (0.1), O ₂ (1 atm)	DMF/H ₂ O	60	24	21
7 [14]	Pd(OAc) ₂ (0.05)	Cu(OAc) ₂ (0.1), O ₂ (1 atm)	DMF/H ₂ O	60	24	0
8 [15]	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	10	80
9 [16]	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	92



Scheme 1. Proposed mechanism for the oxidation of acetylene using the Pd^{II}–HNO₃–H₂O procedure.

The procedure was applied to the synthesis of methylglyoxal (25% yield) from methylacetylene [10]. Subsequently, K₂PdCl₄ instead of PdCl₂ was used by the same team, which thus obtained a mixture

of glyoxal (44–51%), acetic acid (13–15%) and acetaldehyde (traces) [11]. The proposed mechanism (Scheme 1) [10] of these oxidations remains unclear; the formation of [PdCH=CHOH]⁺ from Pd^{II}, acetylene and water, and its reaction with [NO]⁺ were suggested as key steps [10,11].

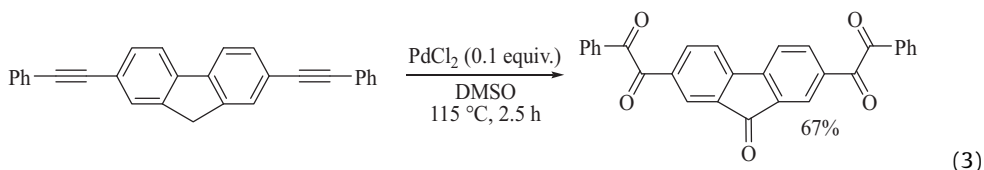


2.2. DMSO as the oxygen source

In 1994, Chi et al. disclosed the PdCl₂-catalyzed oxidation of tolan to benzil at 110–140 °C using DMSO as both solvent and oxidant (Table 1, Entry 1) [12]. They proposed that the reaction is catalyzed by Pd^{II} species because Pd(OAc)₂, which is reduced to metallic palladium under the reaction conditions, is inactive [12]. The process is compatible with tolan bearing substituents such as a *p*-hydroxyl, a *p*-nitro, a *p*-CHO (Table 2, Entries 1, 5 and

12), a *p*-chloro (Table 3, Entry 8), a *p*-methoxy, a *p*-phenyl or a *m,p*-crown-ether (Table 4, Entries 1 and 2) [12,17,19], but is sensitive to steric hindrance, 1,3,5-trimethyl-2-(phenylethynyl)benzene leading to the corresponding 1,2-diketone in a very low yield (Table 4, Entry 3) [17,20]. The PdCl₂–DMSO system allowed the chemoselective oxidation of the triple bond of (*E*)-1-(2-phenylethenyl)-4-(phenylethynyl)benzene (Table 2, Entry 23) [18]. In fact, 1,2-arylethenes are inert towards this oxidation method [12].

The process was used for the synthesis of tetraketones from the diynes shown in Table 5 and Eq. (3) [17]. It is surprising that the methylene group of bis(4-(phenylethynyl)phenyl)methane (Table 5, Entry 6) and of fluorene was unchanged under these conditions, while that of 2,7-bis(phenylethynyl)-9H-fluorene was oxidized (Eq. (3)) [17].



The PdCl₂–DMSO procedure has been used in 2000 by Lee's team to obtain 1,2-diketones, in low to moderate yields, from the heteroarylacetylenes depicted in Eq. (4) [21,22], the authors assuming that the oxidation of most of these substrates using KMnO₄ [8a,23], NBS–DMSO [24] or I₂–DMSO [25] was unsuccessful [26]. Subsequently, it was, nevertheless, observed that the oxidation of 2-*tert*-butylamino-4-[4-fluoro-phenylethynyl]pyrimidine occurred with the best yield in using an optimized procedure based on KMnO₄, the PdCl₂–DMSO system being interesting only on small scales because it required a too high Pd loading (Eq. (5)) [27]. Yusubov et al. have used their PdCl₂–DMSO method to oxidize, in fair to good yields, the heteroarylacetylenes shown in Eq. (6), while those depicted in Scheme 2 did not react or led to complex mixtures [19].

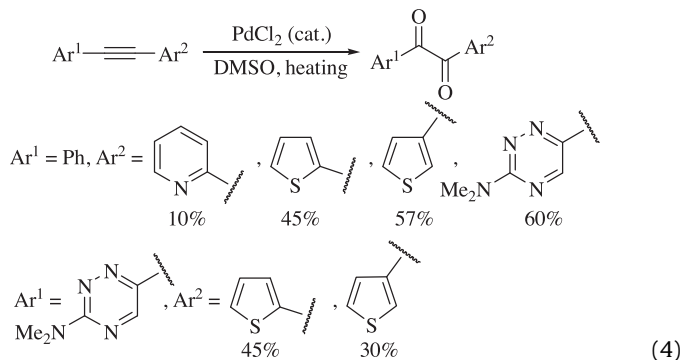
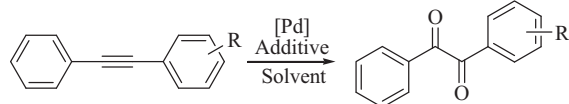
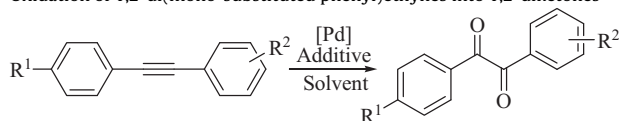


Table 2
Oxidation of 1-phenyl-2-(mono-substituted phenyl)ethynes into 1,2-diketones



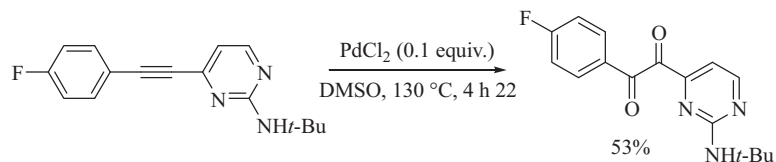
Entry	R	Catalyst (equiv.)	Additive (equiv.)	Solvent	T, °C	Time, h	Yield, %
1 [12]	<i>p</i> -OH	PdCl ₂ (0.1)		DMSO	140	2	84
2 [13]	<i>p</i> -OH	PdI ₂ (0.02)		DMSO	140	4	84
3 [16]	<i>p</i> -Cl	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	84
4 [14]	<i>p</i> -Br	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	97
5 [12]	<i>p</i> -NO ₂	PdCl ₂ (0.1)		DMSO	145	4	60
6 [16]	<i>p</i> -NO ₂	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	41
7 [13]	<i>p</i> -CO ₂ Et	PdCl ₂ (0.1)		DMSO	140	12	60
8 [13]	<i>p</i> -CO ₂ Et	PdI ₂ (0.02)		DMSO	140	3	96
9 [13]	<i>p</i> -OMe	PdI ₂ (0.02)		DMSO	140	2	98
10 [14]	<i>p</i> -OMe	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	90
11 [16]	<i>p</i> -OMe	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	85
12 [17]	<i>p</i> -CHO	PdCl ₂ (0.1)		DMSO	110	22	68
13 [13]	<i>p</i> -CHO	PdI ₂ (0.02)		DMSO	140	5	93
14 [17]	<i>p</i> -CHO	Pd/C (0.0075)	CuCl ₂ 2H ₂ O (0.2)	DMSO	140	15	69
15 [14]	<i>p</i> -CHO	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	90
16 [15]	<i>p</i> -Me	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	14	78
17 [16]	<i>p</i> -Me	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	74
18 [15]	<i>p</i> -Bu ^t	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	14	80
19 [15]	<i>p</i> -CN	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	10	87
20 [14]	<i>p</i> -CN	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	89
21 [16]	<i>p</i> -CN	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	49
22 [14]	<i>p</i> -CH(OH)Ph	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	89
23 [18]	<i>p</i> -CH=CHPh	PdCl ₂ (0.1)		DMSO	115	6	80
24 [14]	<i>o</i> -Me	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	77
25 [16]	<i>o</i> -OMe	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	61
26 [15]	<i>m</i> -OH	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	12	85
27 [16]	<i>m</i> -OMe	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	98
28 [15]	<i>m</i> -F	PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	9	83
29 [14]	<i>m</i> -CF ₃	PdBr ₂ (0.05)	CuBr ₂ (0.1) O ₂ (1 atm)	Dioxane/H ₂ O	60	24	93

Table 3
Oxidation of 1,2-di(mono-substituted phenyl)ethynes into 1,2-diketones



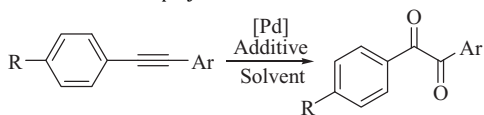
Entry	R ²	Catalyst (equiv.)	Additive (equiv.)	Solvent	T, °C	Time, h	Yield, %
R ¹ = Me							
1 [13]	<i>p</i> -NH ₂	PdI ₂ (0.02)		DMSO	140		0 ^a
2 [13]	<i>p</i> -NHAc	PdI ₂ (0.02)		DMSO	140	3	93
3 [13]	<i>o</i> -OMe	PdI ₂ (0.02)		DMSO	140	8	96
R ¹ = <i>p</i> -OMe							
4 [13]	<i>p</i> -CN	PdI ₂ (0.02)		DMSO	140	1	91
5 [16]	<i>p</i> -OMe	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	83
6 [16]	<i>p</i> -Ac	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	74
7 [16]	<i>p</i> -NO ₂	10% Pd/C (0.1)	O ₂ (1 atm)	DMSO	120	24	62
R ¹ = <i>p</i> -Cl							
8 [12]	<i>p</i> -Cl	PdCl ₂ (0.1)		DMSO	140	6	86

^a Formation of a complex mixture of unidentified products.

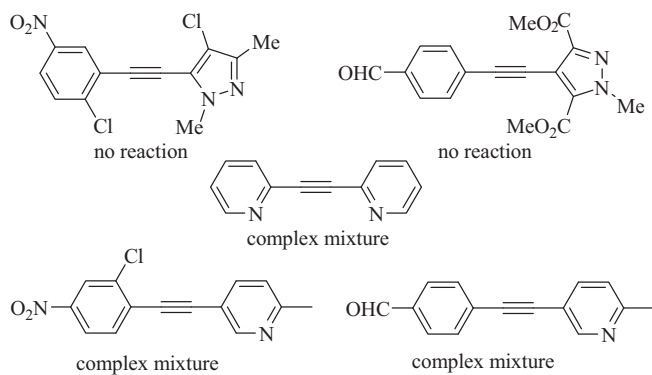


(5)

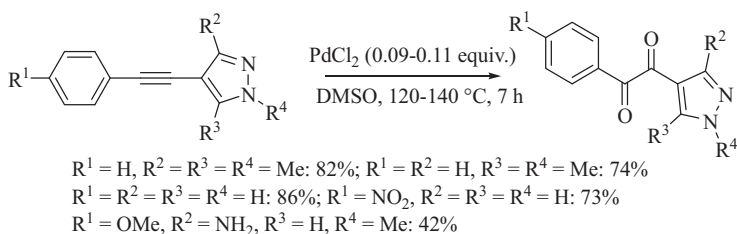
Table 4
Oxidation of other polysubstituted tolans



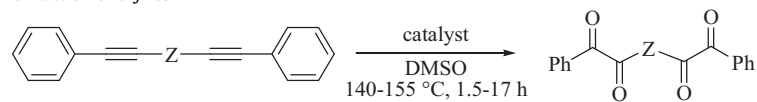
Entry	R	Ar	Catalyst (equiv.)	Additive (equiv.)	Solvent	T, C	Time, h	Yield, %
1 [19]	Ph		PdCl ₂ (0.09)		DMSO	120-125	7	84
2 [19] 3 [17]	OMe		PdCl ₂ (0.09)		DMSO	120-125	7	79
	H		PdCl ₂ (0.1)		DMSO	140	33	5
4 [14]	H		PdBr ₂ (0.05)	CuBr ₂ (0.1), O ₂ (1 atm)	Dioxane/H ₂ O	80	24	89
5 [15]	H		PdCl ₂ (0.05)	CuCl ₂ (0.05), air	PEG/H ₂ O	rt	10	82



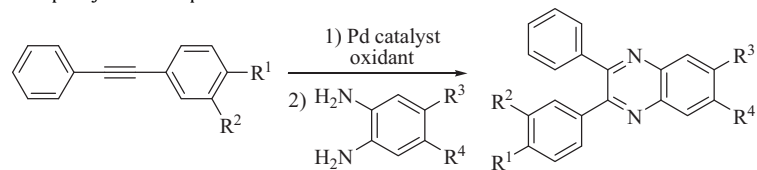
Scheme 2. Failures in the effective formation of α -diketones using the PdCl₂-DMSO procedure [19].



In 2008, Alami, Provot and co-workers reported that PdI₂ is more efficient than PdCl₂ to promote these oxidations [13]. Indeed, the amount of the catalyst was reduced from 0.1 to 0.02 equiv. (Table 1, Entry 2; Table 2, Entries 2 and 9; Table 3, Entries 2–4; Table 5, Entry 10) and some better yields were obtained (Table 2, Entries 8/7 and 13/12; Table 5, Entries 2/1, Eqs (7) and (8)) [28,29]. The authors used their procedure for the one-pot synthesis of various heterocycles via a cascade reaction involving oxidation followed by condensation with nitrogen nucleophiles (Table 6, Entries 1–5; Eq. (9)). We suggest that this efficient reaction between an α -diketone and 1,2-phenylenediamine could explain the formation of an intractable mixture from the oxidation of a substrate bearing a free amino group (Table 3, Entry 1).

Table 5
Oxidation of diynes

Entry	Z	Catalyst (equiv.)	T, °C	Time, h	Yield, %
1 [17]		PdCl ₂ (0.1)	145	10	80
2 [13]		PdI ₂ (0.02)	140	6	90
3 [17]		Pd/C (0.0075) CuCl ₂ ·2H ₂ O (0.2)	140	15	76
4 [17]		PdCl ₂ (0.1)	140	4	85
5 [17]		PdCl ₂ (0.1)	140	4	61
6 [17]		PdCl ₂ (0.1)	140	4	72
7 [17]		PdCl ₂ (0.1)	140	2.5	80
8 [17]		PdCl ₂ (0.1)	140	17	74
9 [17]		PdCl ₂ (0.1)	155	1.5	73
10 [13]		PdI ₂ (0.02)	140	9	57

Table 6
One-pot synthesis of quinoxaline derivatives

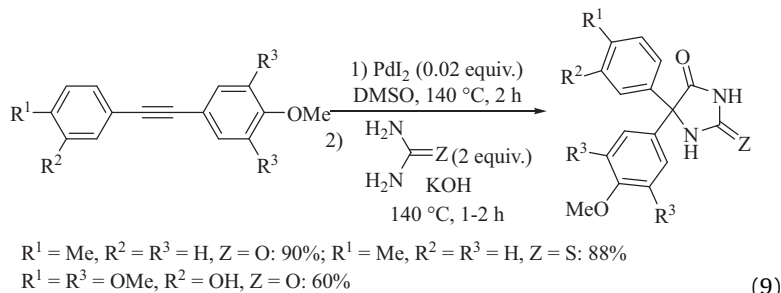
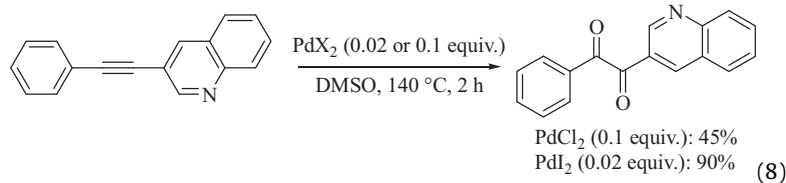
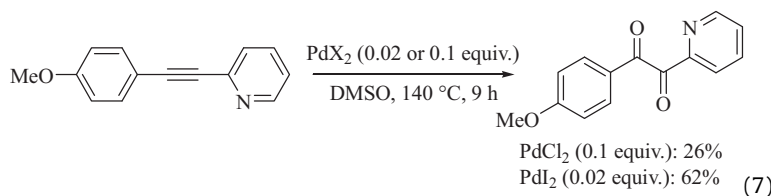
Procedure "DMSO": 1) PdI₂ (0.02 equiv.), DMSO, 140 °C, 2 h

2) diamine (2 equiv.), 140 °C, 2-8 h

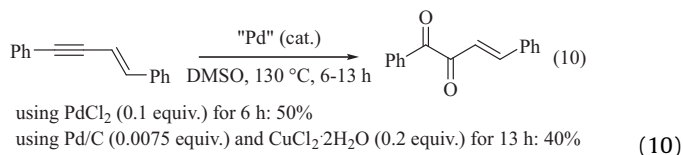
Procedure "PEG": 1) PdCl₂ (0.5 equiv.), CuCl₂ (0.5 equiv.), air, PEG/H₂O, rt

2) diamine (1 equiv.), rt, 14-20 h

Entry	R ¹	R ²	R ³	R ⁴	Procedure	Yield, %
1 [13]	H	H	H	H	"DMSO"	82
2 [13]	OMe	H	H	H	"DMSO"	80
3 [13]	OMe	H	Me	Me	"DMSO"	77
4 [13]	H	H	H	Me	"DMSO"	88
5 [13]	CN	H	H	H	"DMSO"	97
6 [15]	CN	H	H	H	"PEG"	81
7 [15]	H	OH	H	H	"PEG"	80
8 [15]	Me	H	H	H	"PEG"	75
9 [15]			H	H	"PEG"	78

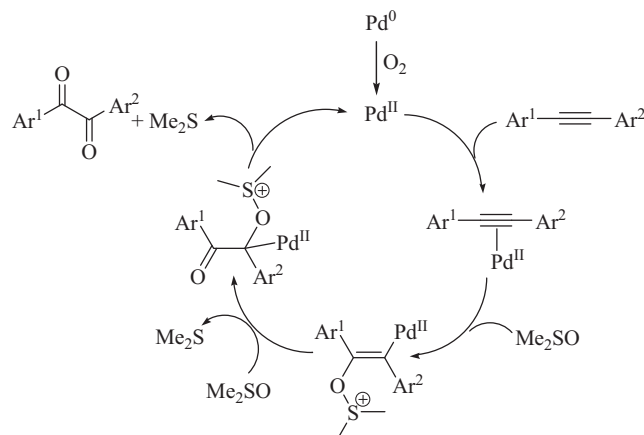


In 1995, Chi, Filimonov and co-workers proposed the association of Pd/C and a Cu^{II} halide as the catalyst [17,18]. The yields were similar to those obtained with PdCl₂ (Table 2, Entries 14/12; Table 5, Entries 3/1) [30], and the authors suggested a catalysis by Pd^{II} active species formed from Pd/C and Cu^{II} [17]. The Pd/C–CuCl₂ association and PdCl₂ have been used as catalysts for the chemoselective oxidation of the triple bond of (*E*)-1,4-diphenylbut-1-en-3-yne in 40–50% yield (Eq. (10)), whereas 1,4-diphenylbuta-1,3-diyne led to a mixture of compounds containing benzil and benzoic acid [18].

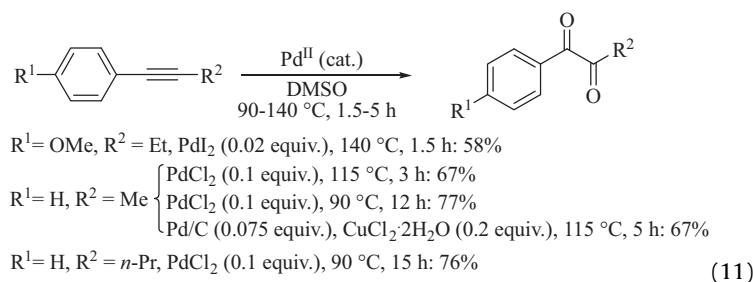


In 2010, Sajiki's team reported the preparation, in DMSO, of benzil derivatives from 1,2-diarylacetylenes, also with Pd/C as the catalyst but associated to oxygen instead of copper salts (Table 2, Entries 3, 6, 11, 17, 21, 25 and 27; Table 3, Entries 5–7) [16,31]. Whereas substrates with a *p*-OMe or *m*-OMe substituent led to high yields (Table 2, Entries 11 and 27), even better than with a *p*-Me (Table 2, Entry 17), the substitution with *o*-OMe decreased the yield (Table 2, Entry 25). This could be due to steric hindrance around the C≡C bond [16], or to the formation of benzofuran [16,32]. Compared to the PdCl₂ catalysis, the yield was slightly lower from diphenylacetylene (Table 1, Entries 9/1) but strongly decreased from a substrate with an electron-withdrawing substituent such as a cyano group (Table 2, Entries 6/5). Nevertheless, substrates bearing both electron-withdrawing and electron-donating on each ring underwent oxidation in good yields (Table 3, Entries 6 and 7). According to the authors, the role of oxygen is only to oxidize Pd⁰ into Pd^{II} species [16,33]. They however reminded that commercial Pd/C often contains traces of PdCl₂ [34,35]. The proposed mechanism (Scheme 3) involves DMSO as the stoichiometric oxidant, but does not inform on the nature of the anions associated to the cationic intermediates. To the best of our knowledge, this mechanism is the first proposal published in the literature for the Pd-catalyzed oxidation of alkynes with DMSO, but it is similar to the one previously proposed with a Lewis acid as the catalyst, especially FeBr₃ [36].

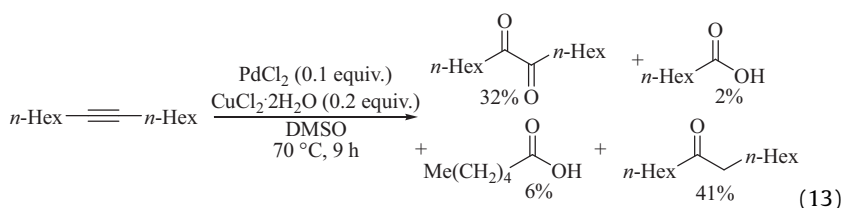
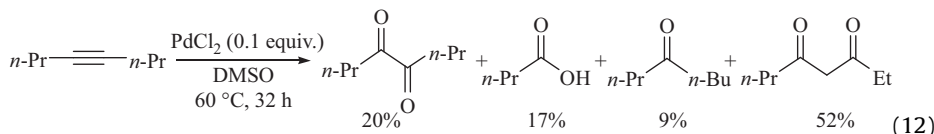
With PdI₂, PdCl₂ or Pd/C–CuCl₂ as the catalyst, 1,2-diketones can also be obtained when one of the aryl substituent was exchanged for an alkyl group (Eq. (11)) [13,20,37]. In contrast, the Pd/C–O₂ system did not catalyze such reactions [16]. This led us to suspect reaction mechanisms depending on the experimental conditions. No reaction was observed in using only CuCl₂ as the catalyst, whereas no more than 10% yield was obtained with only Pd/C as the catalyst [37]. This Pd/C-mediated oxidation could be due to traces of Pd^{II} contained in the catalyst [34]. The oxidation of pent-1-ynylbenzene which provides 1-phenylbutane-1,2-dione in 59–77% yield under PdCl₂ catalysis at 90–115 °C (Eq. (11)), affords benzoic acid in 86% yield at 105 °C with the Pd/C–CuCl₂ system [37]. It has been shown that palladium can induce the oxidative cleavage of the above α-diketone, leading to benzoic acid [37].



Scheme 3. Proposed mechanism for the oxidation of benzils into 1,2-diketones using the Pd/C–O₂–DMSO procedure.



The PdCl₂-catalyzed oxidation of dialkylacetylenes has a low selectivity (Eq. (12)), which is not improved by addition of catalytic amounts of a copper^{II} salt (Eq. (13)) [37].



2.3. Water as the oxygen source

In 2009, Wan's team disclosed the oxidation of alkynes using a PdBr₂/CuBr₂ combination as the catalyst, in a 5:1 dioxane/water mixture, under an oxygen atmosphere (Table 1, Entry 3; Table 2, Entries 4, 10, 15, 20, 22, 24 and 29; Table 4, Entry 4) [14,38]. While the Pd-catalyzed oxidations of arylalkynes with DMSO were carried out at temperatures higher than 100 °C, the oxidations with this method were, in most cases, performed at 60 °C. Furthermore, the exchange of one of the two aryls groups and even both by an alkyl group did not interfere with the production of the α-diketone, the yield being however lower from a dialkylethyne (Table 7, Entries 1, 2, 5 and 6) The authors suspect a Wacker-type mechanism but, despite the experiments carried out for its exploration, a detailed mechanism remains to be determined. Deoxybenzoin and benzoin would not be intermediates because they lead only to traces of benzil under the optimal reaction conditions. A highly informative experiment, performed with H₂O¹⁸, revealed that both oxygen atoms of the diketone origin from water. The formation of the diketone is hardly depreciated by addition of a radical trap, but requires the copper salt, deoxybenzoin instead of benzil being produced from 1,2-diphenylethyne in the absence of this cocatalyst. This led us to suspect that the active catalyst is a complex, either bimetallic or anionic, formed from the interactions between PdBr₂ and CuBr₂ [39,40]. The inertness of the Ar-Br bond (Table 2, Entry 4) and functional groups such as benzylic alcohol (Table 2, Entry 22) and aldehyde (Table 2, Entry 15), which are usually sensitive to Pd⁰ [41,42] or Pd^{II} [42,43] conditions, has to be noted. As oxidant, benzoquinone afforded results slightly lower than oxygen (Table 1, Entry 4) whereas PhI(OAc)₂, H₂O₂, *t*-BuOOH and DMSO led to much lower yields: 30, 12%, 18% and 14%, respectively, instead of 97% for the oxidation of 1,2-diphenylacetylene. Use of other co-solvents than dioxane (DMF, DME, THF, EtOAc, *i*-PrOH, MeCN, MeNO₂, Me₂CO) and PdCl₂ or Pd(OAc)₂ as the catalyst were also detrimental to the reaction efficiency (Table 1, Entries 5–7).

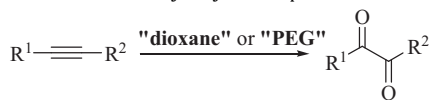
Subsequently, Chandrasekhar and co-workers proposed a recyclable catalytic system using catalytic amounts of both PdCl₂ and

CuCl₂ under air atmosphere in a PEG-400/H₂O mixture, which is effective even at room temperature (Table 1, Entry 8; Table 2, Entries 16, 18, 19, 26 and 28; Table 4, Entry 5), and also for the oxidation of 1-aryl-2-alkylethyne (Table 7, Entries 3 and 4) [15,44]. The recycling performance of this procedure, investigated with 4-(phenylethynyl)benzointrile as the substrate, showed, over five runs, a decrease of the yields from 87% to 75%. The procedure is also effective for the one-pot synthesis of quinoxaline derivatives (Table 6, Entries 6–9).

Compared to the Pd/C–O₂–DMSO and Pd/C–CuCl₂–DMSO procedures, the formation of the 1,2 diketones from 4-(phenylethynyl)benzaldehyde and 4-(phenylethynyl)benzointrile is strongly improved by the use of methods with water as the oxygen source (Table 2, Entries 14/15 and 19/20/21). This difference in the yields is greatly reduced for the oxidation of 1-methoxy-4-(phenylethynyl)benzene (Table 2, Entries 10/11).

Although 1,2-diketones are not produced, it seems of interest to here mention the Pd^{II}-catalyzed hydration of alkynes reported by Utimoto et al. in 1987 (Eq. (14)), which has been used for the synthesis of 5-oxo-prostaglandin E₁ methyl ester (Eq. (15)) [45]. The reactions were performed under ultrasonic irradiation, with PdCl₂(MeCN)₂ as the catalyst, at room temperature in aqueous acetonitrile. This procedure led unchanged 5-decyne, and did not give any hydrated product from 1-octyne [45]. This led the authors to propose an intramolecular assistance by the carbonyl to afford the oxypalladation product **A** shown in Scheme 4. Tsuji assumes that the hydration of **A** proceeds by addition of water to the oxonium unit [46]. Subsequent protonolysis leads to the regeneration of the catalyst and delivers the diketone [47].

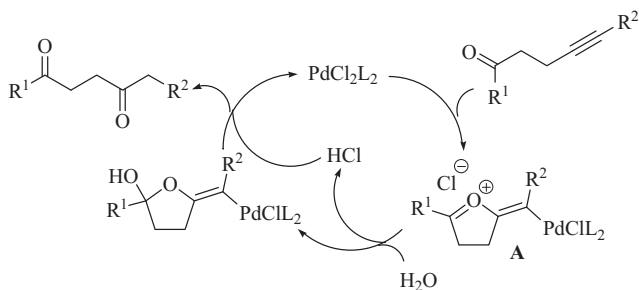
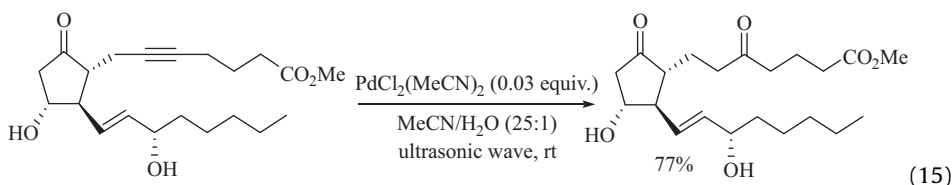
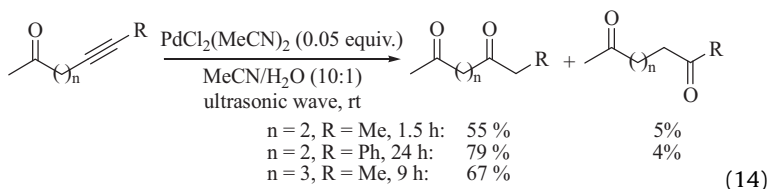
Table 7
Oxidation of mono- and di-alkylethyne in aqueous mixtures



Procedure "dioxane": PdBr₂ (0.05 equiv.), CuBr₂ (0.1 equiv.), O₂ (1 atm), dioxane/H₂O (5:1), 60–80 °C, 24 h

Procedure "PEG": PdCl₂ (0.05 equiv.), CuCl₂ (0.05 equiv.), air, PEG-400/H₂O (4:1), rt, 12 h

Entry	R ¹	R ²	Procedure	T, °C	Yield, %
1 [14]		<i>t</i> -Bu	"dioxane"	80	80
2 [14]		<i>n</i> -Bu	"dioxane"	60	73
3 [15]		<i>n</i> -Hex	"PEG"	rt	63
4 [15]			"PEG"	rt	68
5 [14]			"dioxane"	60	67
6 [14]			"dioxane"	60	41



Scheme 4. Carbonyl-assisted hydration of alkynes.

3. Formation of esters

The formation of esters from the Pd-catalyzed cleavage of C≡C bonds in alcohols was disclosed in 2008 by Wang and Jiang using a pressure of oxygen [48]. Optimization of the procedure, fulfilled with 1,2-diphenylethyne as the substrate, has shown that, to be

efficient, the reaction requires the presence of a co-catalyst, in particular ZnCl₂·2H₂O (Eq. (16)). With catalytic amounts of this Lewis acid, Pd⁰ and Pd^{II} are effective catalysts, the best one being Pd(OAc)₂. The methodology was used for the cleavage of various alkynes (Table 8) and 1,3-diyne (Eq. (17)).

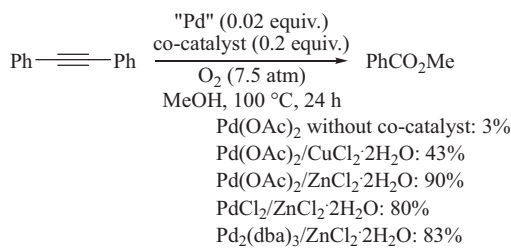
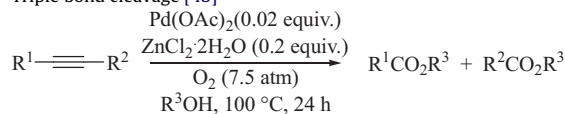
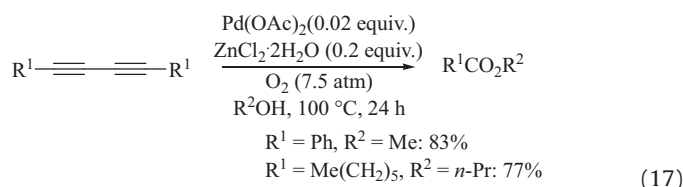
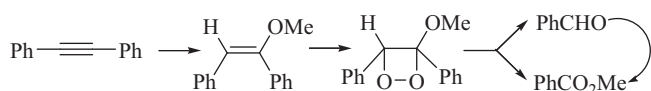
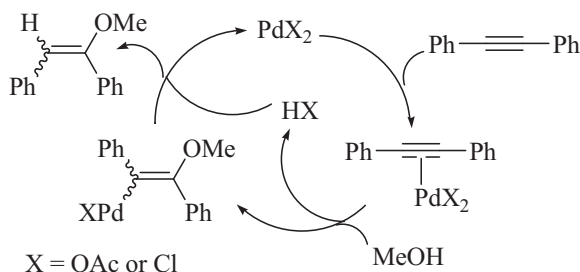
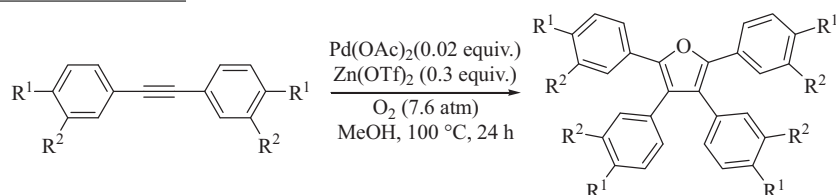


Table 8
Triple bond cleavage [48]

Entry	R ¹	R ²	R ³	R ¹ CO ₂ R ³ Yield %	R ² CO ₂ R ³ Yield, %
1	Ph	<i>p</i> -MeC ₆ H ₄	Me	89	89
2	Ph	<i>p</i> -MeOC ₆ H ₄	Me	85	85
3	Ph	<i>p</i> -O ₂ NC ₆ H ₄	Me	88	88
4	Ph	<i>p</i> -BrC ₆ H ₄	Me	86	86
5	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	Me	89	
6	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	Et	86	
7	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	<i>n</i> -Pr	79	
8	Ph	Me(CH ₂) ₅	<i>n</i> -Pr	87	87
9	Ph	H	Me	86	
10	Ph	CO ₂ Et	Me	90	
11	<i>n</i> -Pr	<i>n</i> -Pr	Me	18	
12	Me(CH ₂) ₅	H	<i>n</i> -Pr	73	



The mechanism of these oxidative reactions is not obvious. The quantitative recovery of benzil when submitted to the reaction conditions, ruled out the transient formation of α -diketones. Having detected 1-methoxy-1,2-diphenylethene in the course of the oxidation of 1,2-diphenylethyne in methanol, the authors proposed the intermediates shown in Scheme 5. According to them, the dioxetane, which would be issued from the reaction of the enol ether with palladium-activated molecular oxygen, undergoes fragmentation to afford methyl benzoate and benzaldehyde, this latter suffering further oxidation and esterification. We suspect that the enol ether is formed as depicted in Scheme 6.

**Scheme 5.** Plausible intermediates leading to the cleavage products of 1,2-diphenylethyne.**Scheme 6.** Pd-catalyzed hydromethoxylation of 1,2-diphenylethyne.

R¹ = H, R² = Me (56%); R² = H, R¹ = Me (75%), OMe (68%), F (79%), CF₃ (82%)

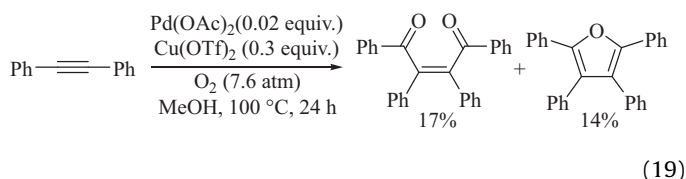
(18)

It is known that enol ethers are cleaved with molecular oxygen [49], even, for some of them, in the absence of any catalyst [50]. Wang and Jiang have subsequently shown that 1-methoxy-1,2-diphenylethene provided effectively methyl benzoate under their experimental conditions [48]. The catalyzed fragmentation of enol ethers has been particularly studied by Tokunaga and co-workers, who used an array of Lewis acids including Cu^{II} and Pd^{II} catalysts, and also proposed a dioxetane intermediate, but formed through reactions involving a radical cation and an electron transfer [49]. The formation of esters from the corresponding aldehydes requires comments because aldehydes are rather stable under 1 atm O₂ and Pd-catalysis [4,41,51,52]. Moreover, Wang and Jiang obtained benzaldehyde in 36% yield from the Pd(OAc)₂-catalyzed cleavage of the C=C bond of *E*-stilbene with oxygen (8 atm) in MeOH at 100 °C for 24 h [53]. In contrast, the same reaction, except the presence of ZnCl₂ as additive, led to the formation of methyl benzoate with a trace of benzaldehyde [53]. Consequently, it becomes obvious that Zn^{II} species are involved in the aldehyde → ester transformation. Svirskii and coll. having recently shown that PdCl₂ catalyzes the esterification of carboxylic acids [54], the Zn^{II} species could actually promote the aldehyde → acid transformation. We suspect that the mechanism could differ for substrates having the triple bond substituted by one or two alkyl groups, their reported intermolecular Pd-catalyzed hydroalkoxylation affording rather allylic ethers [55–57].

4. Formation of furans

In the course of their study on the above Pd(OAc)₂-catalyzed oxidative cleavage of the C≡C bonds of 1,2-diarylethyne [48], Jiang et al. detected small amounts of tetrasubstituted furans [58]. This observation urged them to investigate the reaction conditions leading to their effective synthesis. A screening of Lewis acids and solvents led them to retain Zn(OTf)₂ and MeOH, which have been used as shown in Eq. (18).

When $\text{Cu}(\text{OTf})_2$ was used instead of $\text{Zn}(\text{OTf})_2$, the reaction of 1,2-diphenylacetylene afforded a mixture of 2,3,4,5-tetraphenylfuran and (Z)-1,2,3,4-tetraphenylbut-2-ene-1,4-dione (Eq. (19)), this latter leading to the tetrasubstituted furan under the reaction conditions, even in the absence of $\text{Pd}(\text{OAc})_2\text{-O}_2$ (73% yield) [58]. In fact, the Lewis acid-mediated cyclocondensation of such diketones into furans was already known [59]. Consequently, the 1,4-dione was retained as intermediate; it seems that the authors envisaged its formation via the oxidation of a tetraphenylcyclobutadienepalladium complex [58]. We have to point out that the synthesis of tetraphenylcyclobutadienepalladium^{II} complexes from 1,2-diphenylacetylene and PdCl_2 has been reported forty years ago [60,61], as well as their transformation into 2,3,4,5-tetraphenylfuran [61], whereas (Z)-1,2,3,4-tetraphenylbut-2-ene-1,4-dione has been obtained from bis(tetraphenylcyclobutadiene)palladium⁰ [62,63].



5. Conclusions

Almost a quarter century separates the initial report on the Pd-catalyzed oxidation of alkynes, which used aqueous HNO_3 as the oxidant, from the discovery of the more convenient Pd^{II} -DMSO procedure. Most papers have been published in the last twenty years and concern the synthesis of benzils. With DMSO, the experimental conditions, despite the required high temperature, can be tolerant with the presence of various sensitive substituents. With water as the source of oxygen atoms, the temperature can be decreased, in particular when polyethylene glycol is used as the main solvent, this moreover leading to a recyclable system. A versatile possibility with some procedures is the one-pot synthesis of heterocycles. In contrast to 1,2-diarylethyne, the efficiency and selectivity of the oxidation of 1-aryl-2-alkylethyne and 1,2-dialkylethyne are more sensitive to the experimental conditions and substituents, α -diketones being obtained in good yields only from the former. The synthesis of esters via the cleavage of the triple bond can effectively occur whatever could be the nature of the substituents. Another interesting process is the cascade reaction leading to 2,3,4,5-tetraarylfurans but, as for the formation of the α -diketones and esters, the detailed mechanism of which remains elusive.

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