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Ene-yne Cross-Metathesis for the Preparation of 2,3-Diaryl-1,3-dienes

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Received: 10 November 2017; Accepted: 21 November 2017; Published: 27 November 2017

Abstract: Ene-yne cross-metathesis from alkynes and ethylene is a useful method to produce substituted conjugated butadiene derivatives. If this method has been used with aliphatic alkynes, it has however never been used starting from diarylacetylenes as internal alkynes. We show that the ene-yne cross-metathesis catalyzed by the second generation Hoveyda ruthenium catalyst provides the 2,3-diarylbuta-1,3-dienes under 3 atm of ethylene at 100 °C. The scope and limitations of the reaction have been evaluated starting from unsymmetrical functionalized diarylacetylene derivatives hence leading to unsymmetrical 2,3-diarylbuta-1,3-dienes in a straightforward and environmentally acceptable manner.

Keywords: 1,3-dienes; ene-yne metathesis; ruthenium catalysis

1. Introduction

Depending on the substitution pattern of the 1,3-diene motif, different families of products in terms of electron delocalization are available. 2,3-Diarylbuta-1,3-dienes **A** consisting of branched π-electron frameworks are cross-conjugated compounds related to (4)-dendralenes featuring two terminal double bonds (Figure 1) [1], whereas 1,3-butadienes that are di-substituted in 1,4-position by aryl groups lead to highly conjugated compounds **B** with alternating single and double bonds. The 1,1-, 1,2-, and 1,3-diphenylbuta-1,3-dienes (**C**–**E**) present at the same time three conjugated double bonds and a cross-conjugated (3)-dendralene structure. Because of their conjugated 1,3-diene structure, these products are perfect starting substrates for the construction of complex molecules [2–4]. Besides the classical [4 + 2] cycloadditions, 1,3-butadiene itself and aliphatic 1,3-butadiene substrates have been efficiently transformed via transition metal-catalyzed reactions. Among them, ruthenium-catalyzed addition of aldehydes [5] and olefin metathesis [6], nickel-catalyzed multicomponent coupling with alkynes or aldehydes and dimethylzinc in the presence of carbon dioxide [7,8], rhodium-catalyzed asymmetric [4 + 3] cycloaddition with vinylcarbenoids [9], palladium-catalyzed telomerization with various nucleophiles [10–12], hydroamination [13,14] and hydroamidocarbonylation [15], are representative examples. However, monoarylated 1,3-dienes have been used for triflic acid-catalyzed synthesis of indenes [16], ruthenium-catalyzed isomerization [17], palladium-catalyzed hydroarylation with boronic esters [18], cobalt-catalyzed hydrosilylation [19], asymmetric hydrovinylation with ethylene [20] and enantioselective cycloaddition with internal alkynes [21]. 2-Aryl- and 2,3-diaryl-dienes of type **A** have been extensively studied for the access to cyclic products resulting from Diels–Alder [4,22]

and hetero-Diels–Alder reactions [23,24]. They have also been recently involved in iridium-catalyzed hydrohydroxymethylation [25] and ruthenium-catalyzed hydroxymethylation [26].

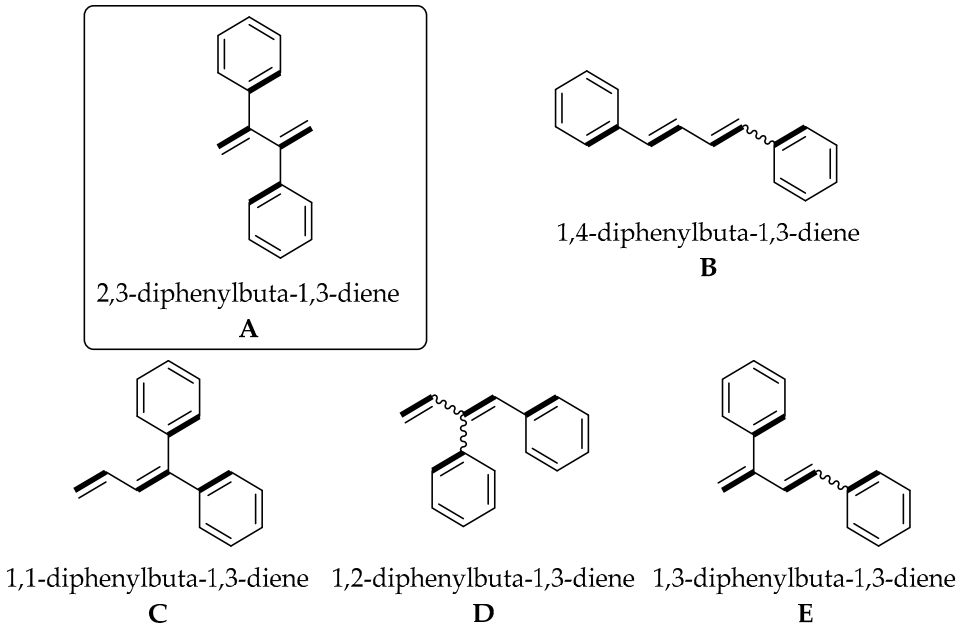


Figure 1. Different types of disubstituted 1,3-butadienes.

Elimination reactions such as the thermal decomposition of 3,4-diaryldihydrothiophene-1,1-dioxides [27] and the acid-catalyzed dehydration of 1,2-diol derivatives [28] have been used for the synthesis of 2,3-diaryl-buta-1,3-dienes of type **A**. But-2-yn-1,4-diol biscarbonates have been efficiently coupled with aryl and heteroaryl boronic acids in the presence of a palladium catalyst to give 2,3-diarylated 1,3-dienes [1,29,30]. 1,4-Dimethoxybut-2-yne was also found to be an excellent substrate for the copper(I)-catalyzed SN2'substitution with aryl Grignard reagents to produce symmetrical 2,3-diarylbuta-1,3-dienes [31]. Symmetrical 2,3-diaryl-1,3-dienes **A** have also been obtained by homocoupling methods starting directly from ketones or the corresponding hydrazones. These homocoupling reactions have been performed directly from acetophenone substrates upon treatment with SmI_2/Ac_2O [32], or from the derived hydrazones following a copper-mediated Shapiro reaction [33] or palladium-catalyzed coupling under oxidative conditions [34,35]. The preparation of 2,3-diaryllbuta-1,3-diene derivatives has been achieved by homocoupling of styrylmagnesium bromide in the presence of an organocatalyst [36], styryl bromide catalyzed by Pd/C in the presence of indium [37], and styrylboronic acid catalyzed by a palladium(II) complex in the presence of $KMnO_4$ or oxygen as oxidant [38]. The same symmetrical 1,3-dienes can be obtained by palladium-catalyzed cross-coupling of 2,3-bis(pinacolatoboryl)buta-1,3-diene with aryl iodides under basic conditions [39]. It is noteworthy that the preparation of unsymmetrical 2,3-diarylbuta-1,3-dienes with different aryl groups, is much less documented. The few reported methods rely on palladium-catalyzed cross-coupling of *p*-tolyl iodide with 3-silyl-3-phenylbuta-1,3-diene in 40% yield [39] and styryl triflates with styryl boronates [40]. An unsymmetrical 2,3-bis(2-nitrophenyl)-1,3-butadiene derivative has been prepared in 61% yield by a Pd-catalyzed Stille cross-coupling [41], whereas the tentative cross-coupling of two different hydrazones led to modest yields in the unsymmetrical product besides the symmetrical ones [16]. Because it is a straightforward atom economic reaction, ene-yne cross metathesis has been applied as an efficient method for the construction of 1,3-dienes [4,42–45]. Using ethylene as olefinic substrate allows the production of buta-1,3-dienes with two terminal methylene groups according to a catalytic cycle initially proposed by M. Mori [46] and further studied in more details by S. T. Diver [47,48]. However, if many examples involving ruthenium-catalysis have been

described starting from aliphatic including benzylic and propargylic alkynes [49–52], much less data are available from aromatic alkynes in the literature. A few mono-substituted 2-arylbuta-1,3-dienes have been obtained from terminal arylacetylenes [25,26,53–56], but to the best of our knowledge only one example of synthesis of 2,3-diphenylbuta-1,3-diene via ene-yne cross-metathesis starting from an internal alkyne has been reported [57].

Herein, we report on the application of ruthenium-catalyzed ene-yne cross-metathesis for the direct preparation of 2,3-diarylbuta-1,3-dienes of type **A** from ethylene and a variety of internal alkynes. We focused on a new preparation of unsymmetrical dienes performed in one step with atom economy from suitably designed internal alkynes. This process competes in terms of productivity and environmental impact with the methods based on palladium-catalyzed cross-coupling of functionalized alkenes that produce the desired products in moderate yields together with stoichiometric amount of wastes [39,41].

2. Results and Discussion

The feasibility of the ene-yne cross-metathesis between 1,2-diphenylacetylene with ethylene was first evaluated in the presence of the second generation Grubbs (I) and Hoveyda (II) ruthenium catalysts (Figure 2, Scheme 1).

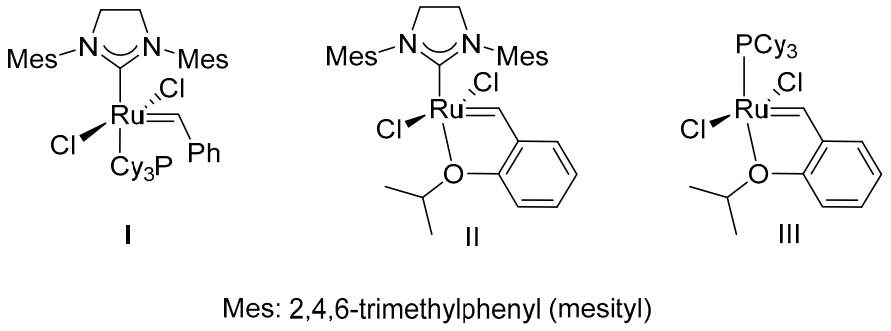
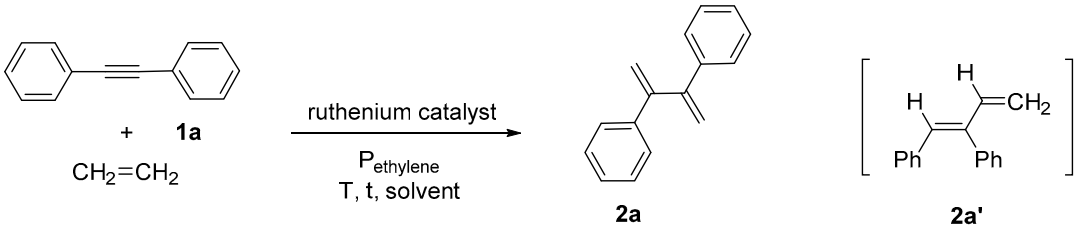


Figure 2. Ruthenium catalysts used in the screening experiments.



Scheme 1. Ene-yne cross-metathesis of 1,2-diphenylacetylene with ethylene.

The first attempts carried out with 1 atm of ethylene in the presence of 2 mol% of Grubbs catalyst I at room temperature in dimethyl carbonate (DMC) or dichloromethane (DCM) were not successful (Table 1, entries 1–3). Increasing the ethylene pressure to 5 atm and the temperature to 80 °C in DMC or 100 °C in toluene made the ene-yne cross-metathesis possible but with modest conversion (Table 1, entries 4 and 5). Further increase of reaction pressure and reaction time in DMC led to 90% conversion of the alkyne (Table 1, entry 6). A similar beneficial effect of increasing ethylene pressure from 1 to 6 atm had been observed during the ene-yne cross-metathesis of ethylene with terminal propargylic acetates [47]. These results indicated that the ene-yne metathesis of 1,2-diphenylacetylene required higher pressure than the ene-yne metathesis of the terminal phenylacetylene, which was carried out in short reaction time under 1 atm of C_2H_4 at 80 °C in toluene with catalyst I [26,53–55], and even at room temperature with a bimetallic ruthenium metathesis

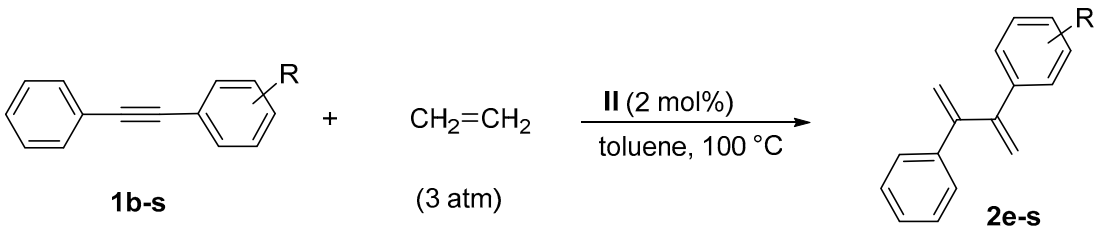
catalyst precursor [56]. The Hoveyda catalyst II was then evaluated under various experimental conditions. In dimethyl carbonate, the conversion of **1a** at 80 °C under 5 atm of C_2H_4 was similar to that obtained with catalyst I under related conditions (Table 1, entries 4 and 7). It was possible to improve the conversion of the alkyne by increasing the initial concentration of the substrate from 0.06 M to 0.3 M (Table 1, entries 8–10). It must be noted that in all the experiments performed in DMC solvent, the formation of 1,2-diphenylbuta-1,3-diene **2a**′ resulting from hydrovinylation of the alkyne by ethylene was observed as a byproduct in variable amounts. This side reaction might be attributed to the formation of Ru–H species resulting from the reaction of ruthenium species with MeOH arising from DMC decomposition. It is interesting to note that the formation of **2a**′ has been reported only once by reaction of alkynes with ethylene and that a ruthenium hydride was assumed to be essential for this catalytic reaction [58]. Such Ru–H species were also previously proposed to be responsible of carbon–carbon double bonds migration during olefin metathesis reactions performed in boiling DMC [59]. Toluene appeared to be a better solvent as the reaction carried out under 3 atm of ethylene at 100 °C for 17 h gave full conversion of the alkyne (Table 1, entry 11). Not only the conversion of the alkyne was better, but the selectivity in favor of the 2,3-diphenylbuta-1,3-diene was excellent since **2a**′ could not be detected. Optimization of the reaction in toluene revealed that 100 °C, 17 h were the optimum experimental conditions whereas a higher pressure of ethylene had a negative effect inhibiting the catalytic reaction, and lower catalyst loading led to decreased activity (Table 1, entries 12–15). The first generation catalyst III utilized in the conditions of entry 7 led to only 10% conversion [60] and a high proportion of hydrovinylation product **2a**′. The conditions reported in entry 11 appeared to be the best to investigate the scope of the reaction focused on the synthesis of unsymmetrical 2,3-diarylbuta-1,3-dienes.

Table 1. Optimization of the ene-yne cross-metathesis of 1,2-diphenylacetylene with ethylene [a].

Entry	Catalyst (mol%)	Ethylene Pressure (atm)	Solvent	*T* (°C)	*t* (h)	Conversion [c] (%)
1	I (2 mol%)	1	DMC 0.01 M	25	4	0
2	I (2 mol%)	1	DCM 0.06 M	25	4	0
3	I (2 mol%)	1	DMC 0.06 M	25	4	5
4	I (2 mol%)	5	DMC 0.06 M	80	17	60 [d]
5	I (2 mol%)	5	toluene 0.06 M	100	17	64 [d]
6	I (2 mol%)	7	DMC 0.06 M	80	22	90 [d]
7	II (2 mol%)	5	DMC 0.06 M	80	24	50 [d]
8	II (2 mol%)	5	DMC 0.1 M	80	23	94 [d]
9	II (2 mol%)	5	DMC 0.3 M	90 [b]	17	92 [d]
10	II (2 mol%)	3	DMC 0.3 M	90 [b]	17	95 [d]
11	II (2 mol%)	3	toluene 0.3 M	100	17	100 (90%) [e]
12	II (2 mol%)	3	toluene 0.3 M	70	17	67
13	II (2 mol%)	3	toluene 0.3 M	120	8	90
14	II (2 mol%)	25	toluene 0.3 M	100	72	0
15	II (1 mol%)	3	toluene 0.3 M	100	17	80

[a] Tolane (0.51 mmoles); [b] DMC boiling point under atmospheric pressure; [c] Determined by gas chromatography using tetradecane as internal standard; [d] presence of 1,2-diphenylbuta-1,3-diene **2a**′ (up to 15% determined by ^{1}H Nuclear Magnetic Resonance); [e] (isolated yield).

The unsymmetrical phenylacetylene derivatives **1b**–**s** were prepared according to the Sonogashira method from phenylacetylene and the desired substituted halogenated aryl derivatives in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI (See Supplementary Materials). Several alkynes presenting different electronic and steric properties were prepared in order to evaluate the full potential of the synthetic method. The results of the ene-yne cross-metathesis reactions of these substrates with C_2H_4 (Scheme 2) are gathered in Table 2.



Scheme 2. Ene-yne cross-metathesis of unsymmetrical diarylacetylenes.

The presence of an electron-donating or -withdrawing groups in *para*-position of one of the aryl groups did not inhibit the cross-metathesis with ethylene and the corresponding dienes **2b**–**h** were isolated in high yields after 17–24 h (Table 2, entries 1–7). Total conversion of the *para*-halogenated derivatives **1i**–**k** were obtained under similar conditions and the dienes **2i**–**k** were isolated in 89–90% yield without noticeable dehalogenation. Compounds **2i** and **2k** are particularly interesting for further cross-coupling reactions. The mixed phenyl 2-thiophenyl butadiene **2l** was isolated in 60% yield after complete conversion of the starting alkyne **1l** (Table 2, entry 11). Substitution at the *ortho*-position of one phenyl group was more problematic. Indeed, with the *o*-cyano group in **1m** a very low yield of 18% was obtained whereas no reaction took place with the *o*-OMe and *o*-NO_2 substrates **1n**,**o** (Table 2, entries 13 and 14) even when extended reaction time or higher temperatures were used. Both the steric hindrance and the potential catalyst inhibition by coordination of these *o*-substituents to the metal center might be at the origin of the low reactivity. Limitations were also observed with **1q**–**s** for which steric hindrance (**1q**) or substrate additional coordination site (**1r**,**s**) might be responsible from the lack of reactivity. On the contrary, the arylalkylacetylene hex-1-yn-1-ylbenzene **1p** led to full conversion and an excellent 97% isolated yield of **2p**, a class of 1,3-dienes scarcely reported employing olefin metathesis [57].

Table 2. Ene-yne cross-metathesis of unsymmetrical diarylacetylenes with ethylene [a].

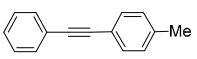
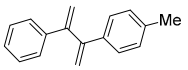
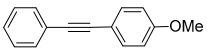
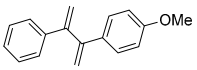
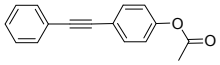
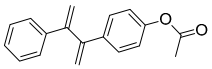
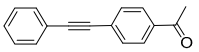
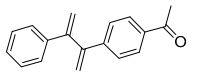
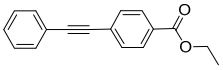
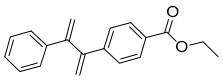
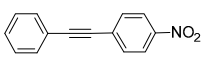
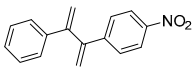
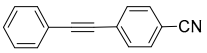
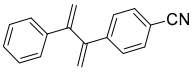
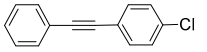
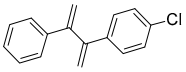
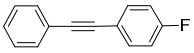
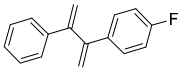
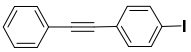
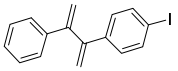
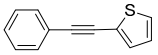
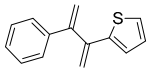
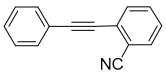
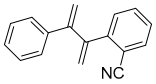
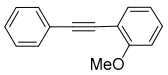
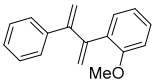
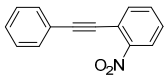
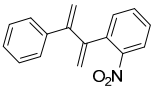
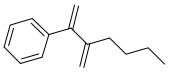
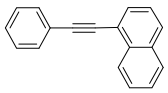
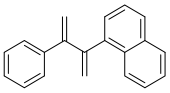
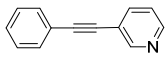
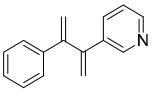
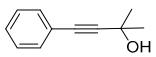
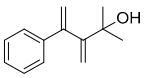
Entry	Substrate		*t* (h)	Conversion (%) [b]	Product		Yield (%) [c]
1		**1b**	24	100		**2b**	91
2		**1c**	17	100		**2c**	98
3		**1d**	17	100		**2d**	99
4		**1e**	17	100		**2e**	91
5		**1f**	17	100		**2f**	99
6		**1g**	24	100		**2g**	97

Table 2. *Cont.*

Entry	Substrate		*t* (h)	Conversion (%) [b]	Product		Yield (%) [c]
7		**1h**	24	92		**2h**	92
8		**1i**	17	100		**2i**	90
9		**1j**	22	100		**2j**	92
10		**1k**	17	100		**2k**	91
11		**1l**	27	100		**2l**	60
12		**1m**	48	40		**2m**	18
13		**1n**	24	0		**2n**	0
14		**1o**	24	0		**2o**	0
15		**1p**	24	100		**2p**	97
16		**1q**	17–48	10		**2q**	0
17		**1r**	24	0		**2r**	0
18		**1s**	17–48	0		**2s**	0

[a] Reaction conditions: alkyne (0.5 mmol), catalyst II (2 mol%), C_2H_4 (3 atm), temperature 100 °C, toluene (2 mL); [b] Conversion detemined by Gas Chromatography analysis with tetradecane as internal standard; [c] Isolated yield.

3. Conclusions

We have shown that 2,3-diarybuta-1,3-dienes could be prepared from diarylacetylenes using ene-yne cross-metathesis with Hoveyda second generation catalyst. The reaction requires a low ethylene pressure of 3 atm and a temperature of 100 °C. Toluene was found to be the best solvent allowing the selective formation of the desired products whereas in a greener solvent such as dimethyl carbonate the formation of hydrovinylation byproducts was observed. However, this side reaction presents a synthetic interest and will be investigated in more details. From unsymmetrical diarylacetylenes bearing one non-functionalized phenyl group, the reaction took place efficiently with

a variety of substituents on the other aryl group, except in the case of bulky aromatic substituents and substitution at the *ortho*-position.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/12/365/s1, (1) General information, (2) Alkyne syntheses, (3) 2,3-diarylbutadiene syntheses.

Author Contributions: C.B. and C.F. conceived and designed the experiments and wrote the paper; M.K.A. performed the experimental work and analyzed the analytical data. Z.K. supervised the work at the Université Frères Mentouri Constantine (Algeria).

Conflicts of Interest: The authors declare no conflict of interest.

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