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A concise overview towards synthesis of Buta-1, 3-diynes

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Abstract
This consize overview will provide synthetic chemists the recently developed ideas for the cross-coupling and homo-coupling reactios towards the synthesis of Buta-1.3-diynes using terminal alkynes, dibromo alkenes, diiodoalkenes and other synthones. Buta-1,3-diynes have been widely applied as intermediate building blocks in organic transformations.

Keywords: Cross-coupling reactions, homo-coupling reactions, buta-1, 3-diynes synthesis, terminal alkynes, dibromo and diiodoalkenes

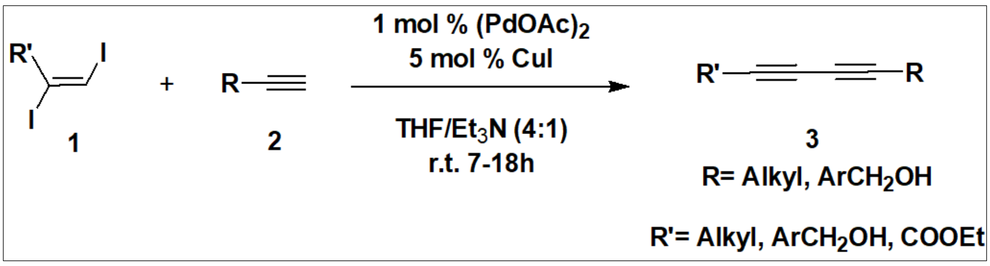
Introduction

Buta-1, 3-diyne and its derivatives have been found important intermediates and have attracted great importance in the field of biological sciences as well as in synthetic organic chemistry [1]. These moities have been widely applied as intermediate building blocks in organic transformations such as in the synthesis of natural products [2], pharmaceutical [3], and heterocyclic compounds [4]. As already discussed in the literature [5] that buta-1, 3-diynes have been utilized for the construction of carbocycles such as benzene [6] and naphthalene [7], nitrogen containing 5/6-membered heterocycles such as pyrrole [8], pyrazole [9], triazole [10], napththatriaazoles [11], benzo[a]phenanthridine [12], benzoquinolines [13], oxygen based heterocyles such as furan [14] and pyrone [15], and selenium and sulphur containing heterocycles selenothiophenes and thiophenes [16]. The Buta-1, 3-diyne based well-characterised compounds, threonyl-hydroxamate derivatives, LPC-009 is a representative LpxC inhibitors [17]. LPC-009 with aminoguanidine, shows antibacterial and anticancer activity [18].

Recently developed methodologies for the synthesis of buta-1, 3-diynes

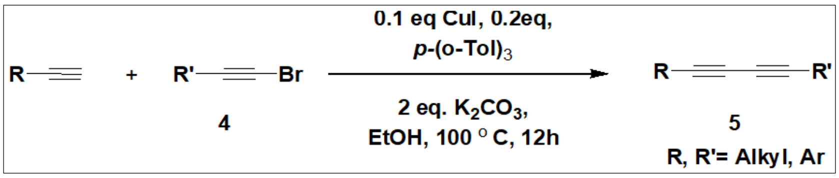
In this concise review here in we are reporting recently developed methodologies for the synthesis of buta-1, 3-diynes.

Li and coworkers reported the synthesis of unsymmetrical buta-1,3-diynes 3 in presence of palladium (II)acetate and copper (I) iodide, from the reaction of (*E*)-1,2-diiodoalkenes 1 with terminal alkynes 2 in moderate to good yields at room temperature [19].



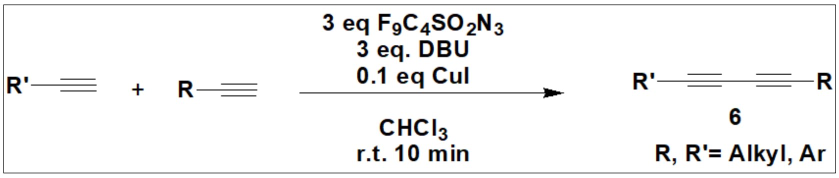
Scheme 1: Synthesis of unsymmetrical buta-1,3-diynes reported by Li and coworkers

Wang *et al.* [20] reported a cross-coupling of terminal alkynes with 1-bromoalkynes 4 in the presence of copper(I)iodide and tris(*o*-tolyl)phosphine enables the synthesis of unsymmetrical buta-1, 3-diynes 5 in good yields under simple and mild reaction conditions.



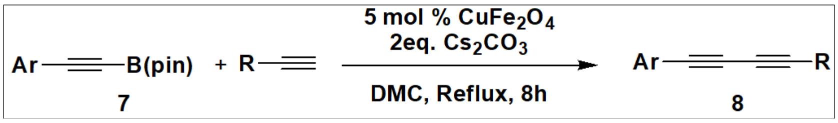
Scheme 2: Synthesis of unsymmetrical buta-1, 3-diynes reported by Wang *et al.*

Chiara and coworkers [21] used nonafluorobutane sulfonyl azide as a shelf-stable highly reactive oxidant for the copper-catalyzed synthesis of buta-1, 3-diynes 6 from terminal alkynes.



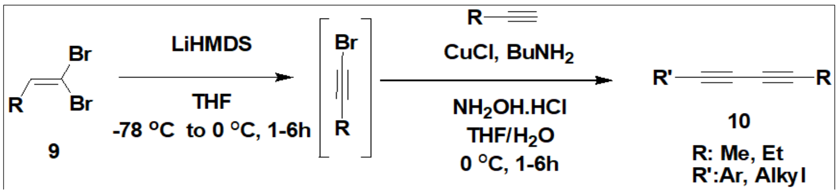
Scheme 3: Synthesis of unsymmetrical buta-1, 3-diynes reported by Chiara and coworkers

Ranu *et al.* reported an efficient cross-coupling of alkynyl bromides and boronates **7** to produce unsymmetric 1, 3-diynes 8 is catalyzed by $CuFe_2O_4$ nanoparticles in dimethyl carbonate [22].



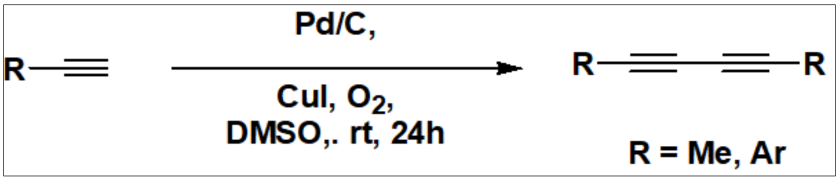
Scheme 4: Synthesis of unsymmetrical buta-1, 3-diynes reported by Ranu *et al.*

A convenient Cadiot-Chodkiewicz protocol method for the synthesis of internal 1,3-diyne 10 using low molecular weight alkyne coupling partners entails an in situ elimination from a dibromoolefin 9 precursor and immediate subjection to copper-catalyzed conditions reported by Ferreira *et al.* [23]



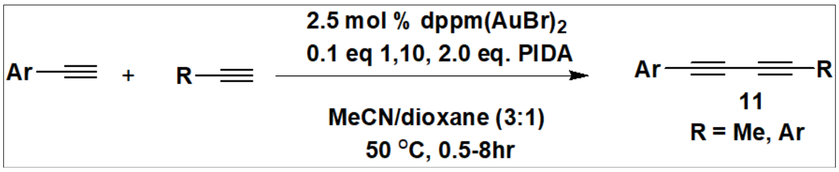
Scheme 5: Synthesis of unsymmetrical buta-1, 3-diynes reported by Ferreira *et al.*

A facile and environmentally friendly synthetic method for a variety of symmetrical 1, 3-diyne derivatives is based on a Pd/C-CuI-catalyzed homocoupling reaction of terminal alkynes reported by Sajiki *et al*. The reaction was efficiently catalyzed by an extremely low loading of Pd/C and CuI in the presence of molecular oxygen as the oxidant without any phosphine ligands and bases [24].



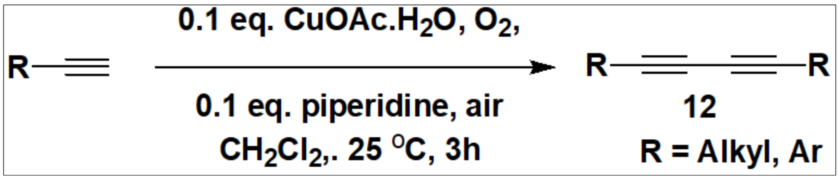
Scheme 6: Synthesis of unsymmetrical buta-1, 3-diynes reported by Sajiki *et al*.

Peng *et al.* reported Gold-catalyzed oxidative cross-coupling of alkynes to unsymmetrical diynes 11 has been achieved in the presence of 1,10-Phen as ligand and PhI(OAc)2 as oxidant giving the desired cross-coupled conjugated diynes in excellent heteroselectivity (>10:1), in good to excellent yields [25].



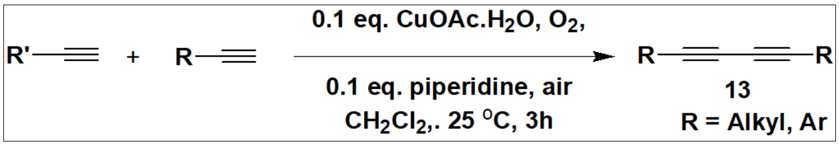
Scheme 7: Synthesis of unsymmetrical buta-1, 3-diynes reported by Peng *et al*.

Balaraman *et al* reported synthesis of symmetrical 1, 3-diynes 12 in quantitative yields using the copper (II) acetate catalyzed homocoupling of terminal alkynes in the presence of a stoichiometric amount of piperidine at 25 °C under aerobic conditions [26].



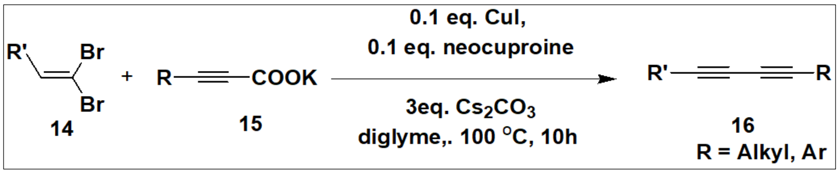
Scheme 8: Synthesis of unsymmetrical buta-1, 3-diynes reported by Balaraman *et al*.

Same research group reported facile synthesis of unsymmetric 1, 3-diynes 13 by heterocoupling terminal alkynes under the same reaction conditions.



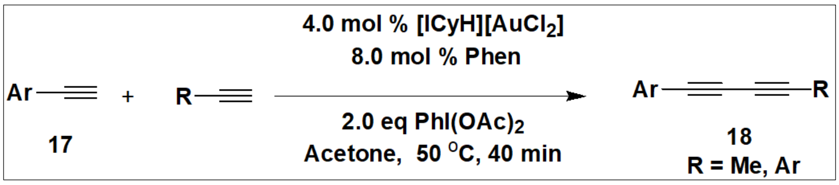
Scheme 9: Synthesis of unsymmetrical buta-1, 3-diynes reported by Balaraman *et al.*

In a copper-catalyzed decarboxylative coupling reaction, a broad range of aryl, alkenyl, alkynyl, and alkyl substituted 1, 1-dibromo-1-alkenes 14 react smoothly with aryl and alkyl substituted potassium propiolates 15 to produce unsymmetrical 1, 3-diynes 16 with high selectivity and good functional group compatibility reported by Huang *et al.* [27]



Scheme 10: Synthesis of unsymmetrical buta-1, 3-diynes reported by Huang *et al*.

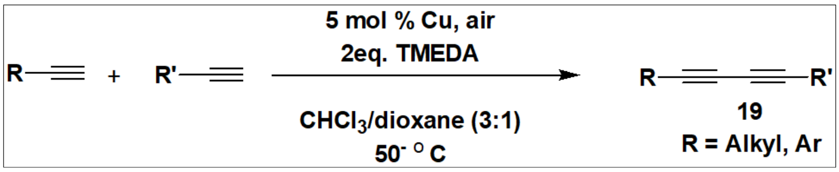
Low loadings of imidazol(in)iumauratescatalyze a simple and efficient oxidative coupling of aromatic 17 and aliphatic terminal alkynes.



Scheme 11: Synthesis of unsymmetrical buta-1, 3-diynes reported by Ma *et al*.

This approach displays high functional group tolerance and leads to a broad range of 1, 3-diyne 18 compounds in good yields in air under mild and sustainable conditions reported my Ma *et al*. [28]

Su *et al.* reported a Cu-catalyzed aerobic Glaser-Hay reaction enables a selective heterocoupling of terminal alkynes to provide a broad range of unsymmetrical 1, 3-diynes 19 in good to excellent yields [29].



Scheme 12: Synthesis of unsymmetrical buta-1,3-diynes reported by Su *et al*.

Conclusion: The recently developed synthetic methodologies towards the synthesis of buta-1, 3-diynes have been described in this concise review. This review will be beneficial for the chemists related to alkyne chemistry.

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