

Chapter 10

Recent Trends of Catalysts for Synthesis of Ynones

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10.1 Importance of Ynones:

α , β -Acetylenic ketones or ynones have become extremely important in last few years because of their versatile applications in various fields such as click chemistry, pharmaceutical, organic synthesis and natural products etc. Ynones are the construction blocks of organic chemistry, used to prepare many biologically active compounds, heterocyclic components for synthesis of various reaction intermediates so forth. ^[1]

10.2 Previous Work on Ynones Synthesis:

Ynones can also be used in the synthesis of various important organic moieties such as isoxazoles,^[2a] pyrimidines,^[2b] quinolones,^[3] furans,^[4] pyrazoles,^[5] flavones,^[6] oximes,^[7] polyfunctionalized pyrroles,^[8] chiral propargylic alcohols^[9] and many more. There are a number of procedures for the response to the synthesis of the ynones including oxidation of propargylic alcohols,^[10] coupling of terminal alkynes with organic halides in the presence of carbon-monoxide gas,^[11] oxidation of alkynes,^[12] reaction of terminal alkynes with nitriles,^[13] and the most important method is the reaction between terminal alkynes and carboxylic acid derivatives in the presence of various strong bases^[14] and elements like silver,^[15] zinc,^[16] tin,^[17] silicon,^[18] lithium,^[19] copper,^[20]

magnesium,^[21] cadmium,^[22] aluminum,^[23] thallium,^[24] gallium,^[25] stibium,^[26] indium,^[27] and so on.

10.3 Recent Developments in Ynone Synthesis:

Recently the synthesis of ynone, catalyzed by palladium catalysts such as palladacycle complexes^[28a] Pd/^[28b] Pd/C,^[28b] Pd(PPh₃)Cl₂/CuI,^[28c] PdNPs-PPS,^[28d] PdCl₂(PPh₃)₂,^[28e] Pd(OAc)₂,^[28f] palladium(II)acyclicdiaminocarbene complex,^[28g] Pd(PPh₃)₄/ZnCl₂,^[28h] polystyrene-supported palladium(0) complex,^[28i] palladium chloride–cryptand-22 complex,^[28j] Pd-PhI-phoxide,^[28k] have got much more attention. But the palladium catalyzed reactions have faced various problems, first of all high cost of palladium, separation problem during product isolation, palladium black formation etc. For the most of the part in industrial practice, palladium catalysts are maintained a strategic distance in the synthetic process of a complexed molecule whenever necessary.^[20b]

Wang et al. have recently reported a protocol for synthesis of ynone, the using copper nanoparticles supported on mesoporous polymer^[20e], beside that only a few number of copper catalyzed methodologies are reported yet for the synthesis of ynone.^[20]

The above mentioned reported methods suffer from various disadvantages such as high temperatures requirement, prolong reaction time, use of air and moisture sensitive catalysts like phosphorous containing catalysts, necessity of additives, use of hazardous organic solvents, use of toxic carbon-monoxide gas, harsh reaction conditions etc.

Practically speaking, the best strategy from environmental and financial perspectives is the reaction protocol without solvent. In this regard solvent free reaction methodologies irrefutably have turned out to be frequent and concentrated over late years.

10.4 Cryptands in Ynone Synthesis:

Cryptands have various applications in different fields like sensing, ^[29a] biological activity ^[29b] etc. Recently it has been observed that cryptand has great catalytic activity ^[30, 28j, 20e] in various reactions along with synthesis of ynone. This is because of many advantages like their versatile processing capabilities, separation and recycling etc.

The chelating effect of nitrogen and oxygen present in macrocycles along with its flexibility give support in stabilizing the complex. B. Movassagh with his co-worker M. Navidi ^[31] developed a palladium chloride–cryptand-22 complex, which was found to be an efficient catalyst for the copper-, phosphorus- and solvent-free coupling reaction of terminal alkynes with different acyl chlorides in the presence of triethylamine as base, at room temperature and under aerobic conditions. E. Mohammadi, B. Movassagh and M. Navidi ^[32] used an air-stable CuI/cryptand-22 complex for the solvent-free cross-coupling reaction of terminal alkynes with different acyl chlorides in the presence of Et₃N to give the corresponding ynone. S. J. Bora and B. Chetia ^[33] together synthesized CuCl₂-cryptand [2.2.2.2.2.2] complex for coupling of acyl chloride and terminal alkynes in presence of triethyl amine (TEA) which had a dual role of base and solvent.

This protocol was found to be an efficient, environmentally benign and operationally simple. In comparison to the other methods it was found that it catalyzed the reaction with a very low amount of catalyst loading without solvent.

This protocol was efficient, greener and more economically viable which can be applied in broad manufacturing planning. High yield, solvent free, phosphorus-free, palladium free and recyclable up to 5th cycle without heat requirements made this protocol highly advantageous. The catalyst was air stable and remains effective for a long period of time without loss of its catalytic activity and properties.

This beneficial protocol used for the synthesis of ynones was never reported before in any scientific article.

10.5 Conclusion:

Ynones have a rich history, it is become clear from this discussion that ynones can be synthesized in a variety of ways. Ynones are prime entrants for a variety of cyclization reactions. This makes them interesting starting materials and intermediates for both natural product synthesis and methodology and become very popular topics in the literature.

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