



OXIDATIVE DIMERIZATION REACTIONS AND REACTIVITY OF TERMINAL ACETYLENIC ALCOHOLS

Tirkasheva Sarvinoz Isoq qizi

Doctor of Philosophy Chemistry, Acting Associate Professor,
Jizzakh State pedagogical universiteti

Parmanov Askar Basimovich

Doctor of Science, Associate Professor, National University of
Uzbekistan named after Mirzo Ulugbek

Abstract. *This review article provides a systematic analysis of literature data on the oxidative dimerization reactions and reactivity of terminal acetylenic alcohols. Particular attention is paid to the reactivity of the terminal $C(sp)-H$ bond, the chemical principles underlying the formation of conjugated diynediols, and the key stages of the oxidative coupling process. Catalytic systems, oxidants, ligands, bases, and solvents employed in oxidative dimerization are summarized with emphasis on their effects on reaction efficiency and selectivity. The influence of the molecular structure of terminal acetylenic alcohols, including the electronic and steric effects of the hydroxyl group and substituents, on their dimerization behavior is also discussed. Based on published studies, classical and modern catalytic approaches to the synthesis of hydroxyl-containing conjugated diynes are compared, and the prospects for further development of this transformation in organic synthesis are outlined.*

Keywords: *terminal acetylenic alcohols, oxidative dimerization, oxidative homocoupling, diynediols, conjugated diynes, $C(sp)-H$ bond, $C(sp)-C(sp)$ bond, catalysis, reactivity.*

Introduction and literature review

Oxidative homocoupling of terminal acetylenes is one of the fundamental approaches to conjugated 1,3-diynes. The reaction originates from the copper-mediated coupling reported by Glaser [1]. Hay subsequently developed catalytic variants employing copper(I) complexes and molecular oxygen [2], while the

introduction of bidentate amine ligands such as TMEDA significantly improved catalytic efficiency [3]. Palladium/copper systems further broadened the substrate scope, and propargyl alcohol was shown to undergo homocoupling to the corresponding hydroxyl-containing diyne [4]. Mechanistically, oxidative dimerization involves activation of the terminal C(sp)–H bond followed by formation of metal acetylide species. DFT studies of the Glaser reaction identified oxidation of copper acetylides and subsequent C(sp)–C(sp) bond formation as key events [5]. The nature of the amine strongly affects the process because amines may act simultaneously as bases, ligands and reaction media [6]. Solvent-free Cu(II)-catalyzed procedures were later developed [7], followed by CuCl/air protocols operating without palladium or additional ligands [8]. Cu(I)-catalyzed coupling with diaziridinone provided another mild, base-free route to 1,3-diynes [9]. Computational analysis of the Glaser–Hay reaction confirmed the importance of copper oxidation state, base strength and Cu/O₂ interactions in determining the reaction pathway [10].

The hydroxyl functionality makes terminal acetylenic alcohols distinct from conventional aryl- and alkylacetylenes. In a Cu(II)-modified clay system, many aromatic and aliphatic alkynes underwent efficient coupling, whereas propargyl alcohol displayed comparatively slower conversion [11]. This observation indicates that coordination and electronic effects associated with the hydroxyl group can influence catalytic activity. In contrast, CuCl-catalyzed coupling under air at room temperature demonstrated that highly mild conditions can be achieved [12]. Heterogeneous Cu₃(BTC)₂ MOF catalysts [13] and polymer-supported copper nanoparticles [14] further improved catalyst separation and recyclability.

A more substrate-oriented approach was demonstrated with the CuCl–TMEDA–CCl₄ system, which enabled the dimerization of a broad range of terminal acetylenes, including propargyl alcohol derivatives, in methanol under relatively mild conditions [15]. More recently, Ni(II)-catalyzed oxidative homocoupling has

emerged as an alternative to conventional copper-based systems, demonstrating that the range of metals applicable to C(sp)–C(sp) bond construction continues to expand [16].

Comparative analysis and review findings

Comparison of the reported methods indicates that copper-based catalysts remain the most versatile platforms for oxidative dimerization. Classical Glaser–Hay systems benefit from the use of molecular oxygen as a readily available oxidant, but their efficiency is sensitive to ligand, base and solvent selection. Pd/Cu systems generally offer mild conditions but are less attractive from the standpoint of catalyst cost and metal separation.

Heterogeneous Cu(II)-clay, Cu₃(BTC)₂ and supported copper nanoparticles provide clear advantages in catalyst recovery and reuse [11,13,14]. Nevertheless, the lower reactivity reported for propargyl alcohol in some heterogeneous systems indicates that results obtained for phenylacetylene cannot automatically be extrapolated to terminal acetylenic alcohols. Optimized CuCl–TMEDA–oxidant systems appear more suitable for hydroxyl-containing substrates [15]. Overall, the literature suggests that substrate structure, hydroxyl-group coordination, steric environment, copper speciation and oxidant properties jointly control the efficiency and selectivity of diyne diol formation.

Conclusion

Oxidative dimerization of terminal acetylenic alcohols provides an efficient route to hydroxyl-functionalized conjugated diynes through direct C(sp)–C(sp) bond formation. Copper(I)/copper(II) systems remain dominant, while recyclable heterogeneous catalysts and alternative Ni(II)-based approaches represent important developments. Future studies should focus on selective catalytic systems operating with low metal loading, environmentally acceptable oxidants and mild conditions specifically optimized for hydroxyl-containing terminal alkynes.

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