

# Copper (II) as catalyst for intramolecular cyclization and oxidation of (1,4-phenylene)bisguanidines to benzodiimidazole-diylienes

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A synthetically useful approach of catalytic intramolecular cyclization and oxidation of 2,2'-(1,4-phenylene)bis(1,3-dialkyl)guanidines (Alkyl = isopropyl 1 or cyclohexyl 2) catalyzed by copper acetate in acetonitrile under air was studied by on line monitoring of the reaction by ESI-MS. All-important intermediates organic species were intercepted during the experiment confirming for the first time the stepwise (1,4-phenylene)bisguanidines cyclization and oxidation mechanism. Moreover, performed collision-induced dissociation (CID) experiments were also applied as a structure elucidation tool. Bimetallic copper intermediates Cu<sub>1</sub> ([C<sub>28</sub>H<sub>48</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>10</sub> + H]<sup>+</sup>) of m/z 755 and Cu<sub>2</sub> [C<sub>22</sub>H<sub>36</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>4</sub> + H]<sup>+</sup> of m/z 575 were documented. The plausible key mechanistic steps involving the formation of organic and inorganic intermediates detected by in situ monitoring of the reaction are presented. © 2019 Elsevier Inc.

Catalysis

Copper acetate

Cyclization

ESI-MS

Guanidines

Catalysis

Catalytic oxidation

Copper compounds

Oxidation

Reaction intermediates

Collision induced dissociation

Copper acetates

ESI-MS

Guanidines

In- situ monitoring

Intramolecular cyclizations

Oxidation mechanisms

Structure elucidation

Cyclization