Copper(II) Photocatalysis and Visible-Light Induced Homolysis Concept

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The successful application of Cu(II) complexes as visible light photoredox catalysts are shown. Following the seminal work of Kochi and co-workers (1), who demonstrated that CuCl₂ undergoes homolysis to Cu(I)Cl and Cl• upon UV irradiation, the activation of Cu(II) complexes endowed with suitable ligands to redshift absorption into the visible region can produce radicals (Z•) that initiate productive organic transformations (first column).(2)

Cu(II)-Complexes as Photoredox Catalyst

I) Oxo-azidation of vinylarenes

\[
\text{[Cu(dap)][Cl]} (1 \text{~mol}%) \\
\text{CHCl₃/MeCN, air, 25 °C, 530 nm, 12 h}
\]

0.5 mmol 2 equiv up to 85% yield

II) Chloro-sulfonation of Unactivated Olefins

\[
\text{[Cu(dap)][Cl]} (1 \text{~mol}%) \\
\text{Na₂S₂O₇} (1 \text{equiv})
\]

530 nm, CHCl₃, rt, 48 h 92% yield

With Cu(I)-Catalyst: [Cu(dap)][Cl] (1 mol%): 77% yield

With [Ru(bpy)₃]Cl₂ or Ir(ppy)₃, or Eosin y : <25% yield

In the absence of 1 equivalent Na₂S₂O₇ : 0% yield

Relevant Bio-active Organic Compounds

Cathinone

agelise (anti-oxidant activity)

thiamphenicol (an antibiotic)

setozol (a beta blocker)

(+)-teambamide (an antiviral natural product)

Substrate Scope and Limitation

20 h, 75%

R = 4-Br, 24 h, 68%

R = 4-Cl, 24 h, 69%

R = 3-Cl, 12 h, 67%

36 h, 85%

72 h, 10%

12 h, 67%

12 h, 67%

12 h, 67%

12 h, 67%

Proposed Reaction Mechanism

Sequential Functionalization of Two Different Alkenes

Synthetic Utility (Dehydrogenation Reactions)

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