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Cobalt-Catalyzed Nitrogen Atom Insertion in Arylcycloalkenes *J. Am. Chem. Soc.* **2022**, *144*, 22433–22439, DOI: 10.1021/jacs.2c10570.

Turning Carbocycles into N-Heterocycles by Cobalt-Catalyzed Nitrogen Atom Insertion

Significance: A cobalt-catalyzed nitrogen atom insertion into arylcycloalkenes is disclosed. Trimethylsilyl azide (TMSN₃) serves as the nitrogen source. The reaction proceeds in the presence of air and water, providing a practicable synthetic route to 2-aryl-substituted pyridines and pyrroles. This method is also applicable to the late-stage modification of biologically active compounds.

Comment: Mechanistic investigations, including radical trapping, EPR analysis and deuterium labeling experiments, are in support of the shown mechanism. The presence of oxygen was shown to be crucial for turnover, initiating the catalytic cycle by formation of a superoxide radical, which subsequently generates an azido radical by abstraction of a silyl radical from TMSN₃.

Category

Metals in Synthesis

Key words

arylcycloalkenes

cobalt catalysis

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nitrogen atom

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pyrroles



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