J. -L. YAO, Z. ZHANG, Z. LI^{*} (SHANGHAITECH UNIVERSITY, P. R. OF CHINA) Scalable Transition-Metal-Free Synthesis of Aryl Amines from Aryl Chlorides through X@RONa-Catalyzed Benzyne Formation J. Am. Chem. Soc. **2024**, 146, 8839–8846, DOI: 10.1021/jacs.4c00426.

Amination of Aryl Chlorides via Benzynes Catalyzed by Sodium Alkoxide Clusters



Significance: Amination of aryl chlorides took place with NaH in the presence of catalytic 1-methoxy-2-methylpropan-2-ol and *N*-ethylimidazole at 80 °C to give aryl amines (60 examples) via the corresponding benzynes in up to 98% yield (eq. 1). A molar scale reaction of 4-methylpiperidine (0.5 mol) with PhCl was performed to afford 4-methyl-1-phenylpiperidine in 80% yield (86.5 g). **Comment:** In this reaction, PhCl showed superior reactivity over PhF, PhBr, and PhI. ArCls with *ortho* or *meta* substituents provided *meta*-aminated products with high regioselectivity. The authors discovered that sodium tertiary alkoxides assemble to form dodecameric truncated octahedral clusters which dissolve NaH to promote the benzyne formation from aryl chlorides.

Category

Polymer-Supported Synthesis

Key words

aryl amines

aryl chlorides

benzynes

sodium alkoxide cluster

СТ

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