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N-Atom Deletion in Nitrogen Heterocycles

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## **Denitrogenative Ring Shrinkage of Heterocycles**

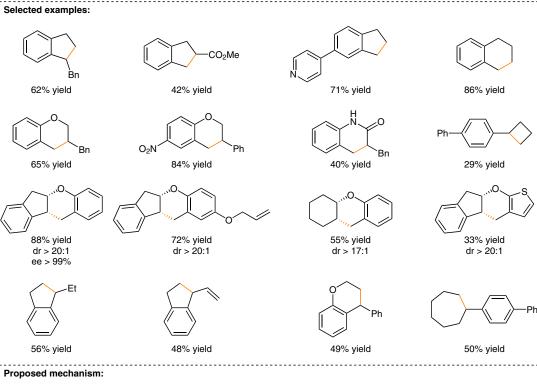


- 1. DBU (2.0 equiv)  $N_2SO_2N_3$  (5.0 equiv)  $CH_2Cl_2$ , 25 °C, 2–3 h
- 2. t-BuOLi (1.0 equiv) 1,4-dioxane, 120 °C, 3 h

n

n = 3 to 20

>30 examples up to 89% yield



$$\begin{array}{c|c}
 & N_2SO_2N_3 \\
\hline
 & via \\
 & via \\
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**Significance:** Lu et al. report a versatile method for N-atom excision from N-heterocycles. Rings containing 3–20 members and various types of cyclic structures including carbocycles, O-heterocycles, and N-heterocycles were obtained in moderate to excellent yields.

**Comment:** The authors propose a mechanism involving an initial N-sulfonylazidonation followed by a Curtius-type rearrangement to generate a 1,1-diazene intermediate. A second rearrangement gives a biradical intermediate that undergoes an intramolecular radical coupling reaction to give the desired product.

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**Metals in Synthesis** 

## Key words

nitrogen atom deletion

N-heterocycles

C-C coupling

skeletal editing

