Denitrogenative Ring Shrinkage of Heterocycles

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 carboxycles, 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.

Selected examples:

- 62% yield
- 42% yield
- 71% yield
- 86% yield
- 65% yield
- 84% yield
- 40% yield
- 29% yield
- 88% yield
dr > 20:1
ee > 99%
- 72% yield
dr > 20:1
- 55% yield
dr > 17:1
- 33% yield
dr > 20:1
- 56% yield
- 48% yield
- 49% yield
- 50% yield

Proposed mechanism: