**Aziridines Cross-Dimerize to Larger N-Heterocycles**

**Significance:** Azepines, dihydropyridinone, and uracil are key N-heterocyclic motifs found in numerous drug molecules. However, syntheses of these rings often require multistep routes and suffer from poor efficiency. The authors present a robust catalytic method to access these azaheterocycles in an enantiospecific manner via cross-dimerization of aziridines or diaziridinones with cyclopropenones or cyclobutenones. This ring-expansion strategy enabled step-efficient syntheses of several pharmaceutical agents and natural products, underpinning the broader synthetic utility.

**Comment:** Lewis acid-mediated, Pd-catalyzed cross-dimerization of sulfonlated aziridines to benzylocylobutane afforded the benzazepine skeleton. A synergistic Pd-Cu catalyst system was used to access the pyridinone and uracil motifs from cyclopropenone. A mechanistic study revealed a Pd$^{0}$/II/IV cycle starting with an oxidative C–C cleavage of the strained carbocycle followed by oxidative aziridine opening to form a Pd$^{IV}$ intermediate, which was supported by computational models. This protocol provided concise routes to useful drug precursors (e.g., SKF 38393, GSK 189254, ivabradine) with further synthetic modifications of the azepines, rendering this a potential retrosynthetic tool.

**Proposed mechanism:**

- **Oxidative addition of C–C bond**
- **SN2-type oxidative addition of C–N bond**
- **Nucleophilic attack of anionic sulfonamide**
- **Reductive elimination**