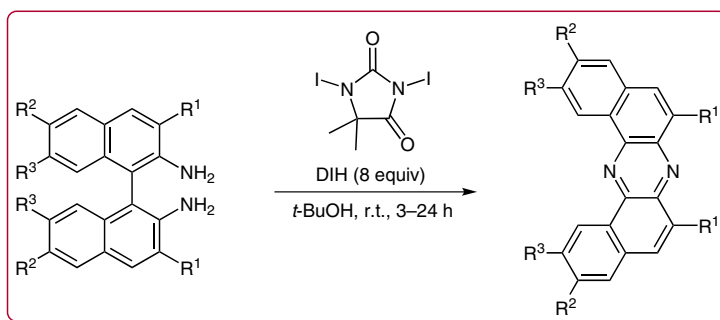


Personal Copy

Y. TAKEDA,* M. OKAZAKI, S. MINAKATA* (OSAKA UNIVERSITY, JAPAN)

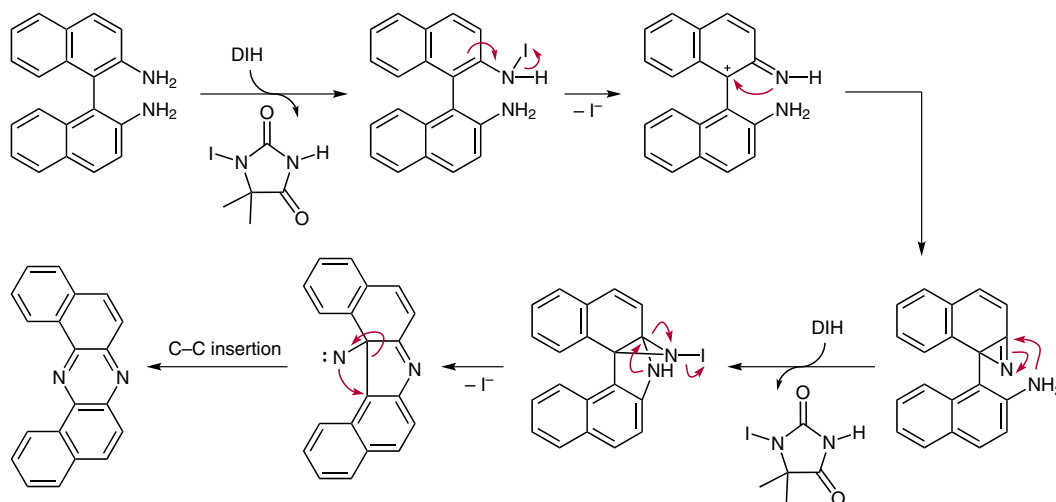
Oxidative Skeletal Rearrangement of 1,1'-Binaphthalene-2,2'-diamines (BINAMs) via C–C Bond Cleavage and Nitrogen Migration: A Versatile Synthesis of U-Shaped Azaacenes
Chem. Commun. **2014**, 50, 10291–10294.

Rearrange for a 'U'-seful Change



Entry	R ¹	R ²	R ³	Yield (%)
1	Ph	H	H	78
2	OMe	H	H	96
3	Br	H	H	37
4	H	Br	H	50
5	H	H	OMe	62
6	H			23

Proposed mechanism:



Significance: π -Conjugated azaacenes are promising electron-transporting materials for organic electronics, because the greater electronegativity of nitrogen compared to carbon increases their electron affinity and their oxidative stability. While a single report of the oxidative dimerization of 1-aminonaphthalenes is known, this procedure provides a mixture of U-shaped dibenzo[*a,j*]-phenazine and S-shaped dibenzo[*a,h*]phenazine (Y. Kosugi, K. Itoho, H. Okazaki, T. Yanai *J. Org. Chem.* **1995**, 60, 5690). Takeda and co-workers describe the selective synthesis of the U-shaped isomer through I⁺-mediated rearrangement of 1,1'-binaphthalene-2,2'-diamines (BINAMs).

Comment: The rearrangement proceeds best with electron-rich BINAMs; strongly electron-withdrawing groups such as esters are not tolerated. The bromo-substituted azaacenes, while produced in modest yield (entries 3 and 4), may be further elaborated by cross-coupling reactions. A cross-over experiment provided no cross-products, confirming that the rearrangement proceeds intramolecularly. A preliminary mechanism is presented in the paper. The substituted dibenzo[*a,j*]-phenazines emit fluorescence ranging from blue to yellow and display redox potentials compatible with commonly employed organic luminescence diode (OLED) materials.

SYNFACTS Contributors: Timothy M. Swager, Julia A. Kalow
Synfacts 2014, 10(10), 1036 Published online: 17.09.2014
DOI: 10.1055/s-0034-1379138; **Reg-No.:** S09514SF

2014 © THIEME STUTTGART • NEW YORK