H. ZHANG, T. KARASAWA, H. YAMADA, A. WAKAMIYA, S. YAMAGUCHI* (NAGOYA UNIVERSITY, JAPAN)

Intramolecular Reductive Double Cyclization of o,o'-Bis(arylcarbonyl)diphenylacetylenes: Synthesis of Ladder π-Conjugated Skeletons


Synthesis of Conjugated Ladder Systems by a Reductive Double Cyclization

Significance: The intramolecular cyclization of ortho-substituted benzene rings is a popular synthetic technique for the formation of benzene-fused five-membered rings. The authors have extended this technique to the synthesis of ladder-type polycyclic compounds by employing diaryl acetylene precursors. In previous reports, reduction of the acetylene moiety led to a double cyclization with heteroatoms. In the current paper, carbonyl substituents on the benzene ring act as the reducible moiety and are used to generate methylene-bridged stilbenes (2) and dibenzo[a,e]pentalenes (3).

Comment: The authors used computational studies to determine that the carbonyl groups in compounds of type 1 are more readily reduced than the acetylene moiety. Cyclic voltammetry demonstrated close proximity of the two irreversible one-electron reduction potentials; therefore, the authors propose a mechanism involving synchronous double cyclization through biradical 4. Compound 3 is formed by the overreduction of compound 2 by lithium naphthalenide. The π-conjugation of these polycyclic hydrocarbons can be extended further via cross-coupling chemistry, presenting interesting candidates for organic electronics.