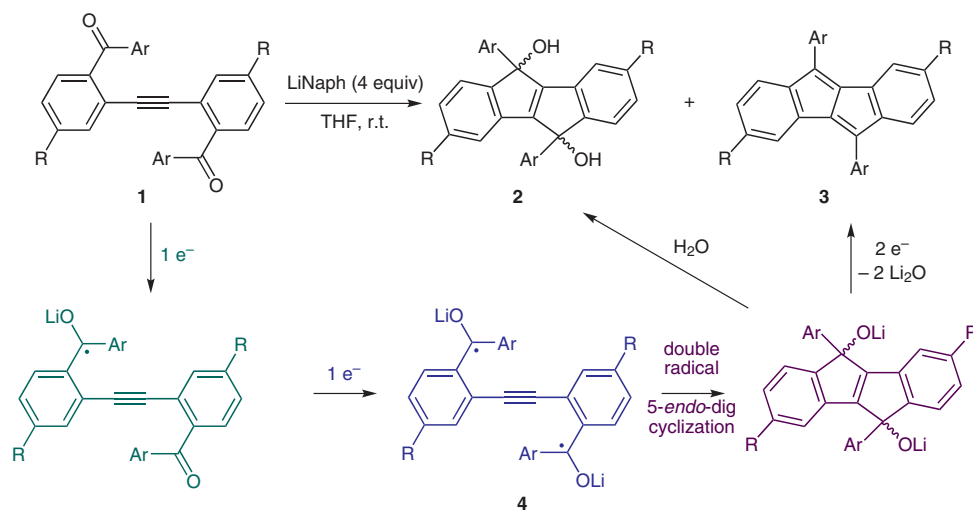


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Intramolecular Reductive Double Cyclization of *o,o'*-Bis(arylcarbonyl)diphenylacetylenes: Synthesis of Ladder π -Conjugated Skeletons

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Synthesis of Conjugated Ladder Systems by a Reductive Double Cyclization



Compound	Reaction time	<i>trans</i> -2	<i>cis</i> -2	3
1a Ar = 4-Tol, R = H	4 h	31%	21%	8%
	8 h	23%	8%	23%
1b Ar = Ph, R = H	8 h	20%	11%	10%
1c Ar = Ph, R = OMe	8 h	21%	8%	24%

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.

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