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.

**Key words**
- reductive double cyclization
- methylene-bridged stilbenes
- dibenzo[a,e]pentalenes

**Chemical Structures**

1. 

2. 

3. 

4. 

**Table**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction time</th>
<th>trans-2</th>
<th>cis-2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Ar = 4-Tol, R = H</td>
<td>4 h</td>
<td>31%</td>
<td>21%</td>
<td>8%</td>
</tr>
<tr>
<td>1b Ar = Ph, R = H</td>
<td>8 h</td>
<td>23%</td>
<td>8%</td>
<td>23%</td>
</tr>
<tr>
<td>1c Ar = Ph, R = OMe</td>
<td>8 h</td>
<td>21%</td>
<td>8%</td>
<td>24%</td>
</tr>
</tbody>
</table>