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

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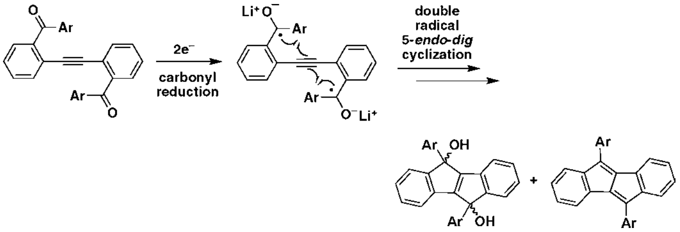
ABSTRACT



Upon the treatment of bis(arylcarbonyl)diphenylacetylenes with lithium naphthalenide, the carbonyl reduction dominantly occurs over the acetylene reduction. The produced bis(radical anion) intermediate undergoes a synchronous double-radical 5-*endo-dig* cyclization. This simple reduction procedure produces two intriguing classes of ladder π-conjugated skeletons, i.e., emissive methylene-bridged stilbenes and dibenzo[*a,e*]pentalenes regarded as a cyclic 1,4-diphenylbutadiene.

The intramolecular cyclizations of *o*-substituted phenylacetylenes to furnish a 5-membered ring fused to the benzene ring (eq 1)[1] are typical tools for the synthesis of indenes[2] and various benzoheterocycles, such as indole, benzofuran, and benzothiophene.[3] Simply doubling this methodology using *o,o′*-disubstituted diphenylacetylenes as precursors provides a new basis for the construction of fused polycyclic skeletons, as shown in eq 2.[4] The produced ladder-type bridged stilbenes have rigid and coplanar skeletons that give rise to intriguing properties, such as intense luminescence. These skeletons would be useful building units for new functional materials in organic electronics, including organic light-emitting diodes and organic transistors. Indeed, this double-cyclization methodology enabled us to synthesize a series of ladder π-electron systems containing NR,[5] SiR_2,[6] S and Se,[7−9] BR_2^- and PR_2^+,[10] and $P(=O)R$[11] as the bridging moieties. As a new family of these reactions, we now disclose

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[3] For recent examples, see the following. E = O: (a) Nakamura, I.; Mizushima, Y.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 15022. (b) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (c) Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem.—Eur. J.* **2004**, *10*, 518. (d) Bates, C. G.; Saejueng, P.; Murphy, J. M.; Venkataraman, D. *Org. Lett.* **2002**, *4*, 4727. (e) Dai, W.-M.; Lai, K. W. *Tetrahedron Lett.* **2002**, *43*, 9377. E = S: (f) Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 4081. (g) Hessian, K. O.; Flynn, B. L. *Org. Lett.* **2003**, *5*, 4377. (h) Larock, R. C.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011. E = NR: (i) Shimada, T.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10546. (j) Barluenga, J.; Trincado, M.; Rubio, E.; González, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2406. (k) Cacchi, S.; Fabrizi, G.; Parisi, L. M. *Org. Lett.* **2003**, *5*, 3843. (l) Rodriguez, A. L.; Koradin, C.; Dohle, W.; Knochel, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2488.

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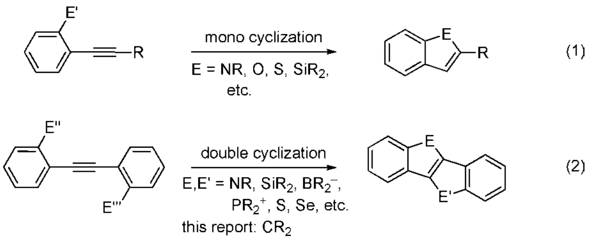
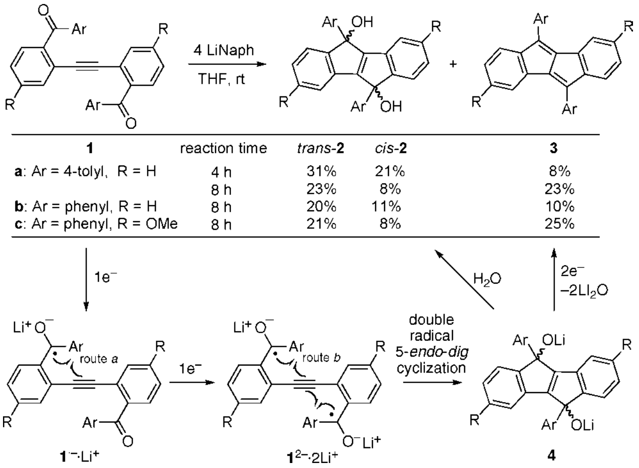
10.1021/ol901148p CCC: $40.75

an intramolecular reductive double cyclization of *o*,*o*′-bis(arylcarbonyl)diphenylacetylenes, as shown in Scheme 1. In addition to its novelty in the cyclization mode, this reaction produces two important classes of cyclized products, i.e., methylene-bridged stilbenes and dibenzo[*a*,*e*]pentalenes, both of which would be promising building units for extended π-electron materials. To demonstrate their potentials, we also carried out further derivatization of the cyclized skeletons.



Scheme 1. Reductive Double Cyclization of Bis(arylcarbonyl)diphenylacetylenes



1	reaction time	*trans*-**2**	*cis*-**2**	**3**
a: Ar = 4-tolyl, R = H	4 h	31%	21%	8%
	8 h	23%	8%	23%
b: Ar = phenyl, R = H	8 h	20%	11%	10%
c: Ar = phenyl, R = OMe	8 h	21%	8%	25%

We first examined the reaction of *o*,*o*′-bis(*p*-tolylcarbonyl)-diphenylacetylene **1a** with lithium naphthalenide (LiNaph) (Scheme 1). A THF solution of **1a** was reacted with 4 mol amounts of LiNaph at room temperature for 4 h. Aqueous workup followed by column chromatography produced the trans and cis isomers of hydroxymethylene-bridged stilbene **2a** in 31 and 21% yields, respectively, together with unexpected dibenzo[*a*,*e*]pentalene **3a** in 8% yield. Elongation of the reaction period from 4 to 8 h resulted in the increment of the yield of the dibenzopentalene **3a** up to 23%. However, use of an excess amount of LiNaph (8 mol amounts) only produced a trace amount of **3a**, and the bridged stilbene products were not obtained. When compound **1b** was reacted with 4 mol amounts of LiNaph for 8 h, compounds **2b** and **3b** were obtained in comparable yields. The stereochemistry of **2b** (trans and cis) was determined by X-ray crystallography.[12] These results demonstrate that this type of substrate indeed undergoes the double cyclization to give the cyclized products.

As a precedent of the reductive double cyclization, we previously reported the transformation from *o*,*o*′-bis(silyl)-diphenylacetylenes to silylene-bridged stilbenes (E = E′ = SiR$_2$ in eq 2),[6] which proceeds through a stepwise two-electron reduction of the acetylene moiety.[6c] In contrast, the present precursor **1** has two kinds of reducible functional moieties, i.e., the carbonyl groups as well as the acetylene moiety. Therefore, the similarity or dissimilarity between these reactions is interesting for us. We elucidate the reaction mechanism of the present cyclization based on the following theoretical and experimental considerations.

The first process of this cyclization should be the one-electron reduction. To gain an insight into the produced radical anion, theoretical calculations of **1b** were carried out at the UB3LYP/6-31+G(d) level. The optimized structure of the radical anion $\mathbf{1b}^{\bullet-}$ has a SOMO delocalized over the entire molecule (Figure 1a), suggesting that the carbonyl and acetylene moieties have a comparable susceptibility to reduction. However, the calculation of $\mathbf{1b}^{\bullet-}\cdot\mathrm{Li}^+(\mathrm{OMe}_2)_3$, taking a counter Li$^+$ ion and solvents into consideration, afforded a totally different structure, in which the radical and anion charge are localized mostly on one of the carbonyl groups, as shown in Figure 1b. This suggests that the Li$^+\cdots$carbonyl Lewis acid−base interaction makes the

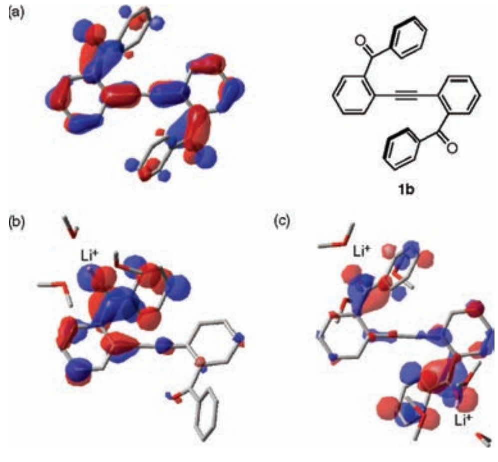


Figure 1. Optimized structures of (a) $\mathbf{1b}^{\bullet-}$, (b) $\mathbf{1b}^{\bullet-}\cdot\mathrm{Li}^+(\mathrm{OMe}_2)_3$, and (c) $\mathbf{1b}^{2-}\cdot2[\mathrm{Li}^+(\mathrm{OMe}_2)_3]$ with the pictorial drawings of SOMOs, calculated at the UB3LYP/6-31+G(d) level.

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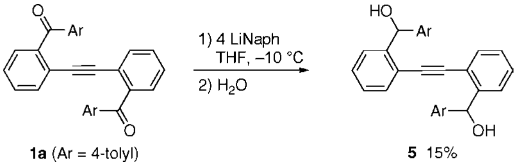
(12) Crystal data for *trans*-**2b**, *cis*-**2b**, and **7**: see the Supporting Information. CCDC-705782 (*trans*-**2b**), CCDC-705783 (*cis*-**2b**), and CCDC-705784 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 335033.

reduction of the carbonyl group dominant over the reduction of the acetylene moiety.

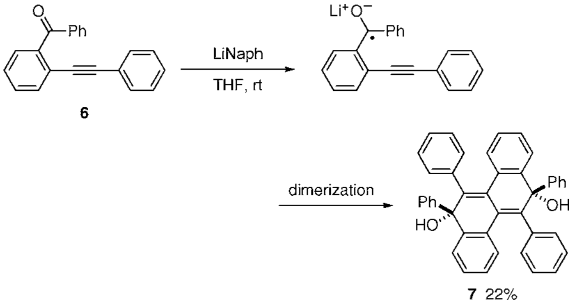
In addition, the cyclic voltammetry of **1b** in THF showed two-step irreversible one-electron reduction waves at the peak potential E_{pc} of -2.30 and -2.42 V (vs Fc/Fc$^+$). Considering the close proximity of these two reduction potentials, we should also consider a two-electron-reduced intermediate. The theoretical optimization of **1b**$^{2-}\cdot$2[Li$^+$(OMe$_2$)$_3$] demonstrated that this intermediate also has a two carbonyl group-reduced structure (Figure 1c). The formation of this dianionic intermediate was experimentally supported. Thus, the reaction of **1a** with 4 mol amounts of LiNaph at low temperature (-10 °C) followed by quenching with water produced dialcohol **5** in 15% yield (Scheme 2). This result also implies that a certain thermal condition is required to promote the subsequent cyclization.

Scheme 2. Reduction of Bis(arylcarbonyl)diphenylacetylene at Low Temperature



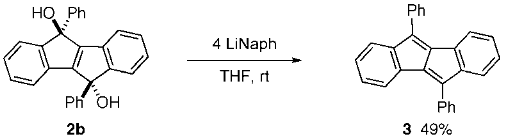
The next query is how the cyclization proceeds from these intermediates. To examine the possibility of the radical 5-*endo-dig* cyclization[13] from **1b**$^{\bullet-}\cdot$Li$^+$ (route *a* in Scheme 1), we conducted the reaction of *o*-(phenylcarbonyl)diphenylacetylene **6** with 1 mol amount of LiNaph (Scheme 3). However, we could not obtain any intramolecularly cyclized product but isolated a dimeric product **7** in 22% yield.[12] The other byproduct was an undefined complex mixture. Therefore, it is more likely that the present cyclization proceeds not through **1b**$^{\bullet-}\cdot$Li$^+$ but through **1b**$^{2-}\cdot$2Li$^+$ with a synchronous double-radical 5-*endo-dig* cyclization mechanism (route *b* in Scheme 1). This is a new mode of reaction for the double cyclization shown in eq 2.

Scheme 3. Reduction of Mono(arylcarbonyl)diphenylacetylene



The mechanism for the formation of the dibenzo[*a*,*e*]pentalene is also puzzling. We assume that the over-reduction of the cyclized intermediate **4** with the remaining LiNaph produces **3** through the elimination of Li$_2$O.[14] To confirm this possibility, we carried out the reaction of the isolated *trans*-**2b** with 4 mol amounts of LiNaph, which indeed gave **3b** in 49% yield (Scheme 4).

Scheme 4. Reduction of Dihydroxymethylene-Bridged Stilbene



Both cyclized products have intriguing π-conjugated skeletons. The methylene-bridged stilbenes are well-known to have intense luminescences.[15] Indeed, the hydroxy-substituted derivatives **2b** show intense blue emissions (*trans*-**2b**: $\lambda_{em} = 410$ nm, $\Phi_F = 0.55$; *cis*-**2b**: $\lambda_{em} = 410$ nm, $\Phi_F = 0.47$ in THF). On the other hand, the dibenzo[*a*,*e*]pentalene can be regarded as a fused-cyclic analogue of 1,4-diphenylbutadiene. Its fused-cyclic skeleton perturbs the electronic structure so as to make the HOMO−LUMO gap narrower than those of the noncyclized analogues (Supporting Information). In addition, the fused-cyclic structure would enhance the stability of both the oxidized and reduced species.[16] Because of these electronic features, this skeleton has attracted increasing attention.[16−18] However, while there are several reports on the modification of the substituents at the 5,10 positions,[18] only a little attention has been directed to the functionalization at other positions in the dibenzopentalene skeleton. As a new access to the π-extended materials containing this skeleton, we therefore examined further derivatization of **3**.

For the functionalization, we employed the orthometalation using the alkoxy group as the directing groups. Thus, the 3,8-dimethoxy-substituted **3c** was prepared by the double cyclization. After screening several bases, we found that ^{i}Bu$_3$Al(TMP)Li[19] was effective for the dimetalation of **3c**, without reacting with the reactive diene moiety. Subsequent

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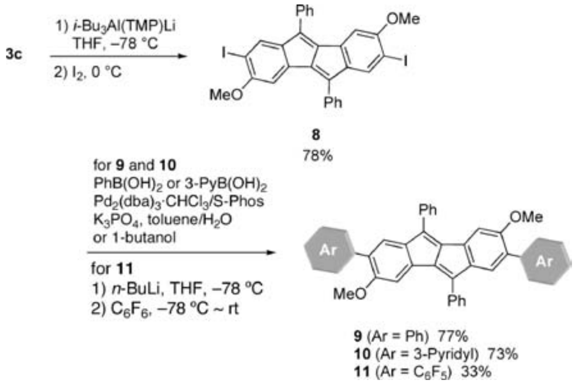
trapping with iodine gave the 2,7-diiodide **8**. This compound was readily transformed into the 2,7-diaryl-substituted derivatives **9**−**11** through the Pd-catalyzed cross-coupling or nucleophilic aromatic substitution, as shown in Scheme 5. These are just the examples of the functionalization of the dibenzopentalene skeleton. The present method would allow us to synthesize various types of the extended dibenzopentalene derivatives, some of which would be promising for the utilization in organic electronics. In fact, in the cyclic voltammetry, all of the produced dibenzopentalenes **9**−**11** show reversible one-electron reduction waves with the reduction potentials $E_{red}^{1/2}$ of −1.71, −1.66, and −1.59 V for **9**, **10**, and **11**, respectively (vs Fc/Fc$^+$) (Figure 2). These values demonstrate their high electron-accepting properties. Notably, **9** and **11** also show reversible oxidation waves at $E_{ox}^{1/2} = +0.58$ and +0.80 V, respectively, indicative of their potential use as an ambipolar carrier transporting material. Advantageously, these diaryl-extended derivatives exhibited relatively high decomposition temperatures (T_{d5}) with a 5% weight loss at 331, 321, and 313 °C for **9**, **10**, and **11**, respectively.

Scheme 5. Functionalization of Dibenzo[*a*,*e*]pentalenes



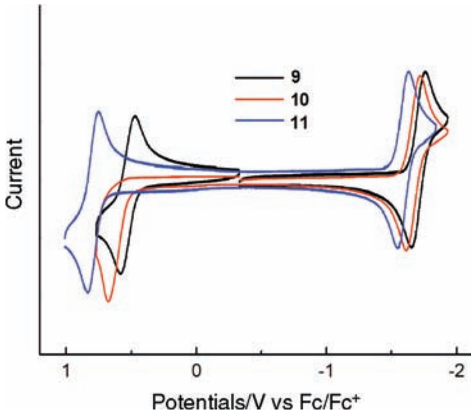


Figure 2. Cyclic voltammograms of **9**−**11** in CH_2Cl_2. Measurements conditions: sample (1 mM) with *n*-Bu_4NPF_6 (0.1 M) at a scan rate of 100 mV s^{-1}.

In summary, we have developed an intramolecular reductive double cyclization using *o*,*o*′-bis(arylcarbonyl)diphenylacetylenes. This methodology is valuable not only as a new example of the cyclization proceeding through a synchronous double radical 5-*endo*-*dig* cyclization mechanism but also as a simple synthesis of the two intriguing ladder π-skeletons. Further investigation on the application of the extended dibenzopentalenes to the organic electronic devices is currently in progress in our laboratory.

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Supporting Information Available: Experimental details, spectral data, and theoretical calculations, crystallographic data (CIF), and ORTEP drawings of *trans*-**2b**, *cis*-**2b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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