Available online at www.sciencedirect.com

ScienceDirect

Tetrahedron Letters 48 (2007) 3433–3436

Tetrahedron Letters

Short-step syntheses and complexation properties of *Z*,*Z*-tribenzodidehydro- and *all*-*Z*-tribenzo[12]annulenes

Siriwan Sirintasak, Yoshiyuki Kuwatani, Shin-ichi Hoshi, Eigo Isomura,
Tohru Nishinaga and Masahiko Iyoda*

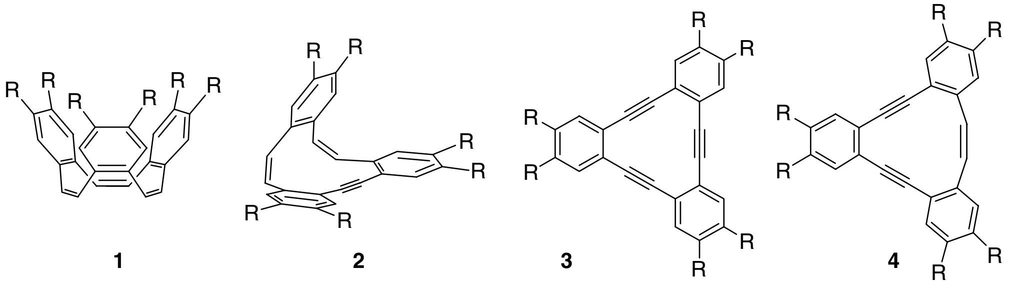
Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Received 14 February 2007; revised 3 March 2007; accepted 8 March 2007
Available online 12 March 2007

Abstract—Syntheses of *all*-*Z*-tribenzo[12]annulenes (**1a**–**c**) and *Z*,*Z*-tribenzodidehydro[12]annulenes (**2a**–**c**) by the reduction of the corresponding tribenzohexadehydro[12]annulenes **3a**–**c** were carried out using a low valent titanium complex generated from Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl. The unique structure of the first reduction products **2a**–**c** as well as **1a**–**c** was fully characterized. Complexation of these annulenes with silver(I) ions produces the corresponding silver complexes. Among them, the silver complexes of **2a**–**c** exhibit interesting monomer–dimer equilibrium.

Bowl-shaped cyclophanes play an important role in the supramolecular chemistry, because they can act as a host molecule for incorporation of guest molecules or ions using the electron rich cavity surrounded by aromatic rings.[1] They also form inclusion crystals which accommodate small molecules in the crystal lattice. Furthermore, they can be used as a component of designed artificial large host molecules for more efficient and practical applications in the molecular recognition, sensing, and catalysis. In this context, *all*-*Z*-tribenzo[12]annulene **1a** is an interesting candidate for the novel host molecules.[2] This compound forms a stable 1:1 metal complex with Ag(I) or Cu(I) ion by the use of 'pre-organized' three double bonds.[2c] We have been interested in this compound and investigated its synthetic pathways.[3] To develop new π-cavitands based on this structure, a new synthetic strategy has been investigated. The basic strategy reported here is the reduction of three triple bonds in tribenzohexadehydro[12]annulene **3a**, which is an easily accessible compound.[4]

Although the reduction of **3a** with the standard Lindlar catalyst was studied by Staab et al. to produce the corresponding *Z*,*Z*-dieneyne **2a** and *E*,*Z*,*Z*-tribenzo[12]-annulene,[5] the structure and properties of **2a** was not fully investigated, presumably due to low selectivity of



a: R = H, **b**: R = Me, **c**: R = *n*-Bu

Keywords: π-Conjugated system; Annulene; Metal reduction; Silver complex; X-ray crystal structure.

* Corresponding author. Tel.: +81 42 677 2547; fax: +81 42 677 2525; e-mail: iyoda-masahiko@c.metro-u.ac.jp

0040-4039/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2007.03.044

$$\mathbf{3} \xrightarrow[\text{THF}]{\text{Ti(O-}i\text{-Pr)}_4,\ i\text{-PrMgCl}} \mathbf{2} \xrightarrow[\text{ether}]{\text{Ti(O-}i\text{-Pr)}_4,\ i\text{-PrMgCl}} \mathbf{1}$$

3a: R = H	**2a**: R = H (83-99%)	**1a**: R = H (92%)
3b: R = Me	**2b**: R = Me (81%)	**1b**: R = Me (89%)
3c: R = *n*-Bu	**2c**: R = *n*-Bu (68%)	**1c**: R = *n*-Bu (87%)

Scheme 1. Synthesis of **2** and **1** by the reduction of benzodehydroannulenes **3**.

the reduction. To develop a selective and effective method for the conversion of **3a–c** into **1a–c** via **2a–c**, the reduction of **3a–c** was examined using a low valent titanium complex generated from Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl[6] (Scheme 1).

Reduction of **3a–c** with low valent titanium complex using a large excess of reagents yielded **2a–c** selectively.[7] Thus, the reaction of **3a** with Ti(O-*i*-Pr)$_4$ (50 equiv) and *i*-PrMgCl (100 equiv) in THF at −50 °C for 2 h or Ti(O-*i*-Pr)$_4$ (10 equiv) and *i*-PrMgCl (20 equiv) in THF at 0 °C for 2 h produced **2a** in 99% or 83% yield, respectively.[8] The reduction of hexamethyl derivative **3b** proceeded smoothly under the similar reaction conditions, and the reaction of **3b** with Ti(O-*i*-Pr)$_4$ (10 equiv) and *i*-PrMgCl (20 equiv) in THF at 0 °C for 2 h gave **2b** in 81% yield. The reduction of the hexabutyl derivative **3c** also produced the corresponding reduction product **2c** in 68% yield under the similar conditions.[8]

Further reduction of **2a–c** also proceeded smoothly to give *all-Z*-tribenzo[12]annulenes **1a–c**. Thus, the reaction of **2a** with Ti(O-*i*-Pr)$_4$ (5 equiv) and *i*-PrMgCl (10 equiv) in ether at −50 °C for 1 h afforded **1a** in 92% yield. The similar reaction of methyl derivative **2b** was relatively slow at −50 °C probably due to its low solubility under the reaction conditions and gave the corresponding reduction product **1b** in lower yield (68%). However, the reaction at 0 °C for 1 h gave **1b** in 89% yield. The similar reduction of more soluble **2c** at −50 °C for 1 h gave **1c** in 87% yield. It is worth noting that direct reduction of **3a–c** to **1a–c** was not successful possibly due to steric reasons for multiply titanium-coordinated intermediate.

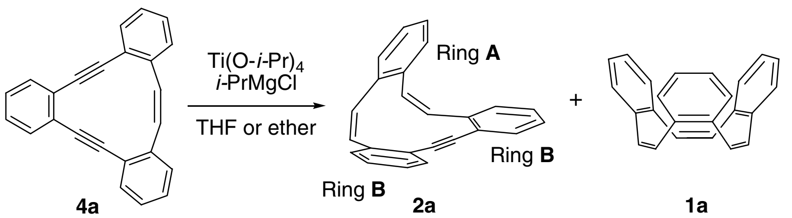
To examine the applicability of the same reduction for the synthesis of **1a** and **2a** from *Z*-tribenzotetradehydro[12]-annulene **4a**,[9] the reduction of **4a** with low valent titanium reagent was performed. Although the reaction of **4a** with Ti(O-*i*-Pr)$_4$ (3 equiv) and *i*-PrMgCl (6 equiv) in THF at 0 °C for 2 h gave a 4:6 mixture of **1a** and **2a** in totally 80% yield, similar reaction of **4a** with Ti(O-*i*-Pr)$_4$ (5 equiv) and *i*-PrMgCl (10 equiv) in ether at −50 °C for 1 h selectively produced **2a** in 92% yield.

Benzannulenes **2a–c** are considered to behave as a folded *Cs* symmetric structure. ^{1}H NMR spectra of **2a–c** show characteristic signals for the aromatic protons of benzene ring **A** (see Scheme 2) in a high field. Thus, the two aromatic protons of **2a** were observed at δ 6.89–6.86 and 6.74–6.72 as AA′BB′ multiplets. The corresponding signals of **2b** and **2c** were observed at δ 6.50 and 6.48, respectively. These high field shifts of the aromatic protons of ring **A** suggest that the protons locate in the shielding region of benzene ring **B** in the diphenylacetylene moiety.

The molecular and crystal structures of **2a** and **2b** were unambiguously determined by X-ray crystallographic analysis.[10,11] As shown in Figure 1, the diphenylacetylene moiety in **2a** shows a highly planar structure. The maximum atomic deviation from the least-squares plane defined by the 14 carbon atoms of **2a** is 0.04 Å. The molecular structure is totally V-shaped arrangement of the diphenylacetylene moiety and benzene ring **A** with a dihedral angle of 62°. This molecular structure is in good accordance with the higher field shift of benzene ring **A** (δ 6.72–6.74 and 6.86–6.89) in the ^{1}H NMR spectrum. The molecule forms a dimeric structure by the stacking of the diphenylacetylene moiety with a distance of 3.4 Å in the crystal (Fig. 1b and c).

As reported previously, the unique structure of *all-Z*-tribenzo[12]annulene **1a** was proved to be suitable for the metal complexation with Ag(I).[3] The substituted analogs **1b** and **1c** also formed stable Ag(I) complexes by the reaction with silver salts. The coordination to the silver ion occurred at the three double bonds, which were clearly shown by the lower field shift of the olefinic protons ($\Delta\delta = 0.7$–0.8 ppm) without significant changes for other signals.

Since didehydroannulenes (**2a–c**) possess a π-cavity composed of a triple bond and two double bonds, **2a–c** can be expected to behave as a π-cavitand. Actually, **2a–c** formed silver complexes with AgOTf, AgClO$_4$, and AgOCOCF$_3$. In the presence of AgOTf in CDCl$_3$, **2a** formed **2a**·AgOTf in which a triple bond and two double bonds can be expected to coordinate Ag(I) ion.



Scheme 2. Reduction of **4a** by Ti(O-*i*-Pr)$_4$ and *i*-PrMgCl.