Polycycles

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Oxidative Cyclodimerization After Tandem Cyclization of Dehydrobenzo[14]annulenes Induced by Alkyllithium**

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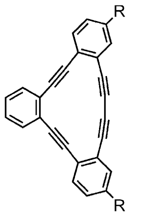
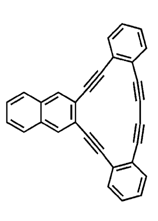
Highly ethynylated compounds have the potential to be transformed into polycyclic aromatic hydrocarbons by intramolecular cyclizations between the sp-carbon atoms because of the high reactivity of carbon–carbon triple bonds.[1] Particularly those with cyclic structures are useful for the construction of new carbon frameworks which are otherwise difficult to obtain. Moreover, cyclic precursors would limit the number of possible reaction pathways because of steric constraints. Indeed, a few examples of efficient transformations of dehydrobenzannulenes into polycyclic carbon frameworks were reported as exemplified for octadehydrodibenzo[12]annulene,[2] hexadehydrotribenzo[12]annulene,[3] and tetradehydrodibenzo[8]annulene.[4] The reactions are typically induced by attack of a nucleophile,[4a] an electrophile,[2,4b] or a radical,[3c] or initiated by reduction to generate a radical anion.[3a,b]

We envisaged that octadehydrotribenzo[14]annulene ([14]DBA) **1a**[5] and its congeners **2**–**4** would serve as intriguing substrates for multiple trasnannular bond formations to yield new polycyclic frameworks because of the presence of four closely located triple bonds. Additionally, the distorted butadiyne unit is expected to trigger reactions induced by an electrophile[2a] or a nucleophile,[4a] which would not occur for unactivated acetylenic bonds.[4a,6] We report herein the results of the reactions of **1** and its congeners, **2**–**4**, with butyllithium (*n*BuLi). We discovered an unprecedented oxidative cyclodimerization to form eight-membered ring products, in which two indeno[2,1-*a*]fluorene components are connected by a single and a double bond, following three transannular C–C bond formations.



1a : R = H
1b : R = *t*Bu



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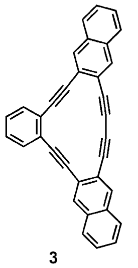

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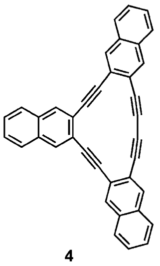

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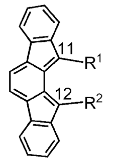

5a: $R^1 = R^2 = Ph$
5b: $R^1 = R^2 = Mes$

First we envisioned the possible pathways for the tandem transannular cyclizations of **1a** as shown in Scheme 1. In the initial step, we assume the formation of a five-membered ring after the addition of a nucleophile to the diyne moiety of **1a** to give the intermediate **7** on the basis of the previous reports.[2a,3,4a] For the second step, there are two options of transannular bond formation: 1) formation of a four-membered ring to give **9** or 2) a five-membered ring to form the 5/8/5 ring system **8**. In the former case, the resulting nine-membered ring can be further divided into 5/6 a ring system to afford the tetracyclic intermediate **11** bearing an indeno[2,1-*a*]fluorene substructure, or the 4/7 system **10** possessing two benzocyclobutene units. As to the indeno[2,1-*a*]fluorene framework, while Le Berre et al. reported the synthesis of the unstable 11,12-diphenylderivatives **5a**,[7] we succeeded recently in the synthesis of the robust dimesityl-substituted derivative **5b** and clarified its physical properties including its singlet diradical character.[8] These results suggest that the expected product **12**, formed by interception of **11** with an electrophile, must be substantially reactive.

When the di-*tert*-butyl[14]DBA **1b** was treated with *n*BuLi at −78 °C in THF and subsequently quenched with water or 1-iodobutane at the same temperature, the products **13a** and **13b** were obtained in 61 and 67 % yields, respectively (Scheme 2). The ^{13}C NMR spectra (see Figures S10 and S11 in the Supporting Information) of these products exhibited four

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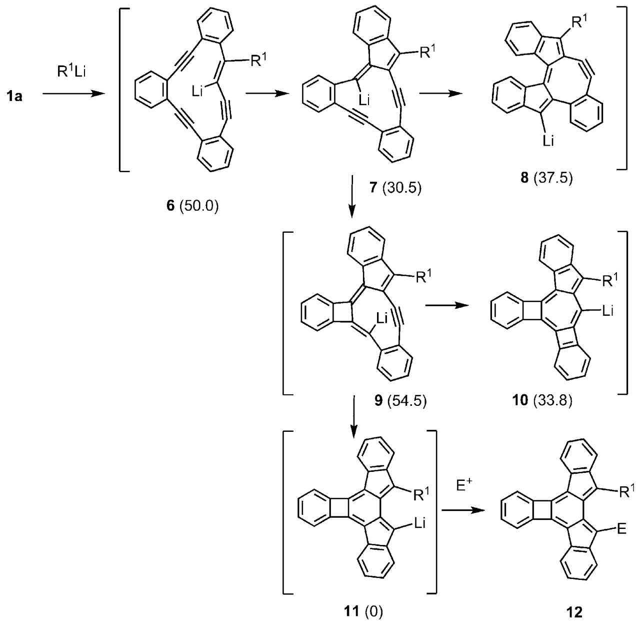
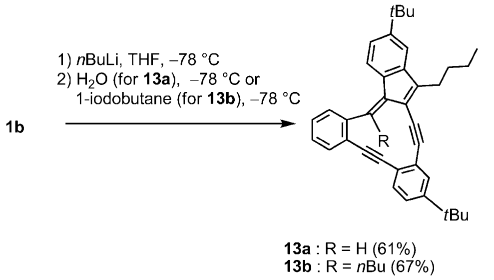
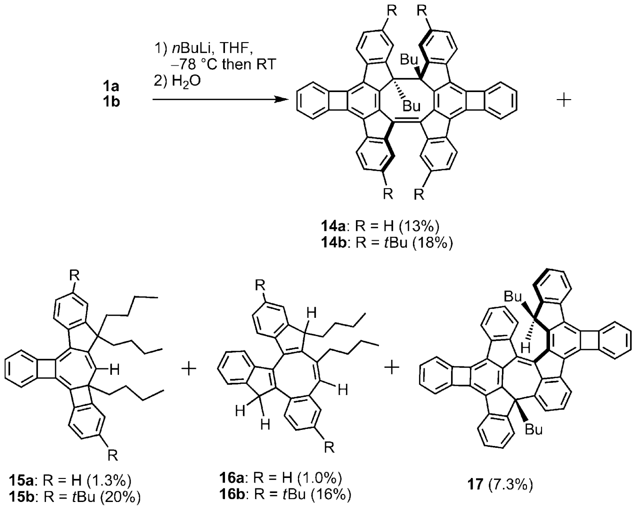


Scheme 1. A working hypothesis for tandem transannular cyclizations of **1a**. Energies (kcal mol^{-1}), relative to **11**, were calculated by a DFT ((R)B3LYP/6-31G*) method and are shown within parentheses.



Scheme 2. Transannular cyclization of **1b** at low temperature.



Scheme 3. Tandem transannular cyclization of **1a** and **1b** induced by *n*BuLi.

signals corresponding to sp-carbon atoms, thus implying that addition of *n*BuLi took place at the diyne moiety with a subsequent transannular cyclization to form a five-membered ring. In the ^{1}H NMR spectrum of **13a**, the signal for the vinyl proton appears at a high field ($\delta = 8.75$ ppm), which is consistent with the *E* configuration of the double bond in view of the similar anisotropic effects resulting from the proximate triple bonds reported for the related dehydroannulenes.[9]

On the contrary, when **1b** was treated with *n*BuLi (3 equiv)[10] at −78 °C and the mixture was warmed up to room temperature before quenching with water, three products **14b**, **15b**, and **16b** were isolated in 18, 20, and 16 % yields, respectively (Scheme 3). Most surprisingly, the mass spectrum of **14b** indicates that the molecular formula ($C_{76}H_{74}$) corresponds to a dimer of **1b** which is a two-electron oxidation product. ^{1}H and ^{13}C NMR spectra (see Figure S12 in the Supporting Information) of **14b** imply that **14b** has a symmetric structure, in which tribenzofused tetracyclic frameworks are connected with a single and a double bond. The final structural determination of **14b** was done by X-ray crystallographic analysis of the corresponding product **14a** which is derived from **1a** (see below).

The reaction of **1a** under similar reaction conditions afforded the corresponding products **14a**, **15a**, and **16a** in 13, 1.3, and 1.0 % yields, respectively (Scheme 3). In addition, the oxidative dimer **17** was isolated in 7.3 % yield. The NMR spectra of **17** indicate that it has an unsymmetric structure, which is in contrast to **14a**. The much lower yields of the products than those in the case of **1b** may be due to facile intermolecular reactions because of the absence of *tert*-butyl groups which would suppress such processes.

The structures of the dimers **14a** and **17** were determined by X-ray crystallographic analysis for the crystals obtained by recrystallization from a mixture of $CHCl_3$/MeCN and CH_2Cl_2/MeCN, respectively.[11] The structure of **14a** shows that it possesses two indeno[2,1-*a*]fluorene frameworks which are connected with a single and a double bond at the respective five-membered rings to form an eight-membered ring in the center (Figure 1a). The indenofluorene units are facing each other but twisted because of steric repulsion between the closely located benzene rings. The two *n*-butyl groups stretch above and below the plane of the molecule.

The crystal structure of **17** reveals that it also consists of two indeno[2,1-*a*]fluorene frameworks which are connected with a single and a double bond (Figure 1b). However, here the single bond is formed between a five-membered ring of one of the indenofluorene units and a benzene ring of the second indenofluorene unit, and the double bond is formed between two five-membered rings similar that in **14a**. The two indenofluorene units are oriented in opposite directions and are offset from each other to form a seven-membered ring in the center.

For the structures of **15a**,**b** and **16a**,**b**, the mass and ^{1}H and ^{13}C NMR spectra indicate that **15a**,**b** contain three *n*-butyl groups and one hydrogen atom, and are therefore a two-electron oxidation products from **1a**,**b**, whereas **16a**,**b** possess two *n*-butyl groups and four hydrogen atoms and are two-electron reduction products. However, because crystals

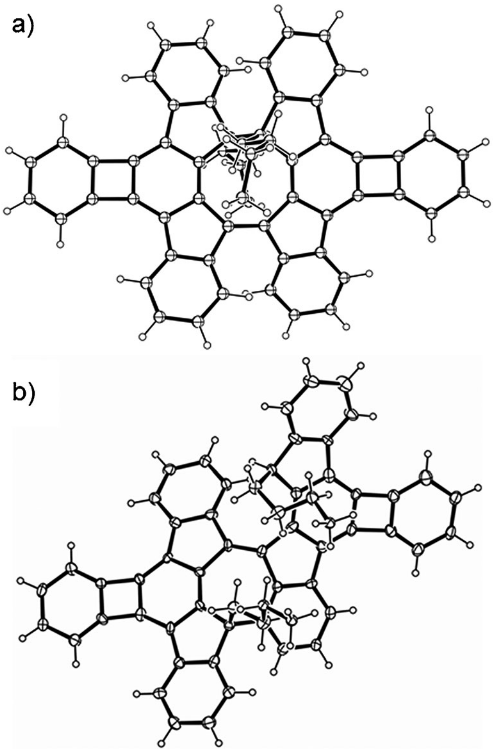
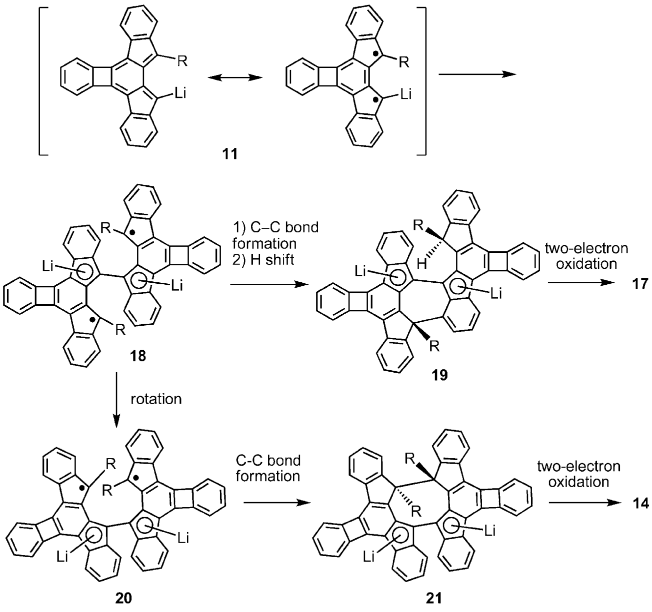


Figure 1. Top views of ORTEP drawings of a) **14a** and b) **17**. Displacement ellipsoids are drawn at 30% probability level.

suitable for X-ray analysis were not obtained, the structures of **15b** and **16b** were elucidated on the basis of HMQC and HMBC using the *tert*-butyl group as the pivotal groups for the correlations, as described in detail in the Supporting Information.[12] The structures of **15a** and **16a** were determined by the similarities of their spectra to those of **15b** and **16b**, respectively. As a result, we were able to propose the structures of **15a**,**b** to be tribenzofused tetracyclic 4/4/5/7 systems and those of **16a**,**b** to be tribenzofused tricyclic 5/5/8 systems formed by three and two transannular bond formations, respectively (Scheme 3).

The formation of the three types products, **14**–**16**, are interpreted in terms of the pathways shown in Scheme 1. The relative energies of the organolithium intermediates estimated by DFT calculations at the B3LYP/6-31G* level of theory are also shown in parentheses. The calculated energies suggest that the cyclization pathway leading to **7** is energetically favored though both of the second steps (**7**→**8** and **7**→**9**) are endoergic. This is consistent with the fact that **7** was intercepted as **13a**,**b** when the reaction was conducted at low temperature. Although the formation of **8** is energetically more favored than that of **9**, a considerable amount of product via the latter intermediate was obtained.[13] Addition of another *n*-butyl group to **8** accompanied by a two-electron reduction gives **16a**,**b** after quenching with water. In the third bond-formation step from **9**, though the formation of **10** is energetically much less favorable than the cyclization to **11**, substantial amounts of **15a**,**b** were obtained via **10**, after addition of two *n*-butyl groups accompanied by a two-electron oxidation.[13] In contrast, when the 5/6 rings are formed to generate **11**, it undergoes dimerization to give **14** and **17** through a pathway discussed below. Multiple additions of nucleophiles as well as dimerizations which proceed through redox processes are reported in a number of reactions of [60]fullerene with nucleophiles.[14]

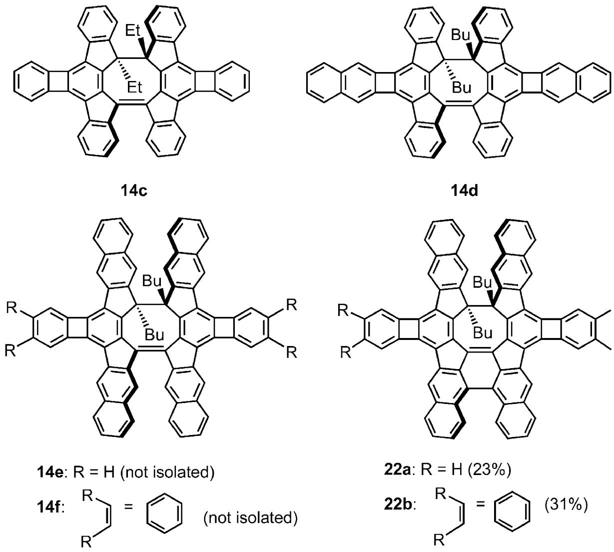
A tentative mechanism for the oxidative cyclodimerization step is shown in Scheme 4. It consists of initial C–C bond formation between intermediate **11** to give **18**, which undergoes rotation about the single bond to give **20** with subsequent bond formation to give **21**. Subsequent oxidation, either in situ by the species present in the reaction mixture or by oxygen during the workup,[15] furnishes the observed major dimeric product **14a**,**b**. In contrast, C–C bond formation in **18** at the proximal carbon atoms with subsequent hydrogen transfer and oxidation give the minor dimer **17** via **19**.[16]



Scheme 4. A tentative reaction mechanism for the oxidative dimer formation. For theoretical calculations using a model compound, see the Supporting Information.

To know the scope of the oxidation cyclodimerization with regard to nucleophiles, several reagents, including MeLi and *t*BuLi, were investigated.[17] However, only when the ethyllithium/*sec*-butyllithium complex[18] was used did the corresponding cyclic dimeric product **14c** form and was isolated in 23% yield (Scheme 5).

When the naphthalene homologue **2** was subjected to the reaction with *n*BuLi under similar reaction conditions, the corresponding dimeric product **14d** was isolated in 13% yield (Scheme 5).[19] Conversely, when **3**, having naphthalene units at different positions, was used, a blue color developed after quenching the reaction with water, thus suggesting the formation of **14e**, which gradually changed to orange during purification by silica gel chromatography to give **22a** as a final product (isolated in 23% yield).[19] The structure of **22a** was established by X-ray crystallographic analysis as shown in Figure S3 of the Supporting Information.[11] The formation of **22a** is explained by dehydrogenative C–C bond formation



Scheme 5. Oxidative cyclodimers derived from extended [14]DBAs.

between the proximate naphthalene units of **14e**. Similarly, **4** having naphthalene rings at both ends of the [14]DBA gave the dehydrogenated dimeric product **22b** in 31% yield.[19] These results clearly show that the anomalous oxidative cyclodimerization is a general reaction pathway for BuLi-induced cyclization reaction of [14]DBAs, thus leading to a new hydrocarbon framework consisting of indenofluorene substructures.

The absorption spectra and cyclic voltammograms of **14a**,**b**,**d** and **22a**,**b** are shown in Figures S8 and S9, respectively, in the Supporting Information. The optical and electrochemical data obtained from experiments and the relevant energy levels from calculations are summarized in Table S5 in the Supporting Information. Whereas the compounds **14a**,**b**,**d** exhibit absorption maxima at $\lambda = 605$ or 600 nm, the dehydrogenated dimers **22a**,**b** show absorption maxima at $\lambda = 513$ nm, which is substantially hypsochromic shifted from those of **14a**,**b**,**d**. These shifts are consistent with the larger HOMO–LUMO gaps of **22a**,**b**, as estimated by the DFT calculations (2.83 and 2.82 eV, respectively), relative to that of **14a** (2.32 eV). The TD-DFT calculations (see Table S6 in the Supporting Information) also support the hypsochromic shifts of **22a**,**b** (the lowest-energy transition at $\lambda = 503$ nm) compared with **14a**,**d** ($\lambda = 600$ and 602 nm, respectively). It is worth mentioning that the 9,9′-bifluorenylidene chromophore found in **14a**,**b**,**d** is reported by Heeger, Wudl, and co-workers as a promising nonfullerene electron acceptor component for bulk heterojunction (BHJ) organic solar cells,[20a,b] and its potential is supported by theoretical calculations.[20c]

In conclusion, tandem transannular cyclization of the [14]DBAs **1a**,**b** and **2–4** induced by an addition of *n*BuLi led to the discovery of an unprecedented cyclodimerization to form the eight-membered ring products **14a**,**b**,**d** in which two indeno[2,1-*a*]fluorene components are connected by a single and a double bond, following three transannular bond formations. In the case of the naphthalene congeners **3** and **4** the corresponding dimers **22a**,**b**, in which dehydrogenative C–C bond formation took place starting from the initial dimers **14e**,**f**, were obtained, thus demonstrating the generality of the reaction for [14]DBA derivatives. Though the mechanism of the reaction is not understood, and the selectivity of the reaction is not very good (up to 30%), the reaction provides a new approach to otherwise unaccessible hydrocarbon framework which may be of interest for optoelectronics.

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[11] CCDC 915201 (**14a**), 915203 (**17**), and 915204 (**22a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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distances are 2.82 and 3.24 Å, respectively. Though this explanation contradicts Baldwin's rules (i.e., 4-*exo-dig* vs. 5-*endo-dig* modes), the steric constraint resulting from the medium-sized rings of **7** and **9** would prevail. J. E. Baldwin, *J. Chem. Soc. Chem. Commun.* **1976**, 734–736.

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[17] The reaction of **1b** with MeLi, *t*BuLi, and PhLi only gave complex mixtures of products and did not contain products corresponding to **14**–**16**. The reason for this different reactivity is not clear.

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