A New Entry into Cyclo[*n*]carbons: [2 + 2] Cycloreversion of Propellane-Annelated Dehydroannulenes

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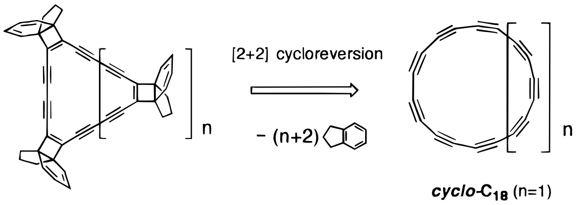
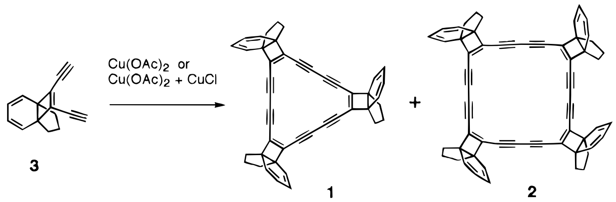
Increasing interest has been focused on cyclocarbons, the most stable form of carbon clusters in the relatively narrow size range from C_{10} through C_{20}.[1] Mechanistic studies on the formation of fullerenes suggest that the monocyclic species play a key role in the formation of carbon cages.[2] The novel topology of the *p* orbitals, composed of two sets of cyclic arrays of perpendicular *p* orbitals, stimulated a number of theoretical studies concerned with the Hückel rule.[3] For example, there are controversies regarding the most stable geometry of C_{18}, whether it is a polyyne of D_{9h} or C_{9h} symmetry or a cumulene of D_{9h} or D_{18h} symmetry.[3b−f] As an approach to the synthesis of cyclo[*n*]carbons from organic precursors of well-defined cyclic structure, Diederich synthesized three types of dehydroannulenes which would generate the corresponding all-carbon molecules by [4 + 2] cycloreversion, oxidative decomplexation, or decarbonylation.[3b,4] The formation of *cyclo*-C_{18}, *cyclo*-C_{24}, and *cyclo*-C_{30} was indeed observed by the laser-desorption time of flight (LD-TOF) mass spectra of some of these precursors, which generated fullerene cations (C_{60}^+ and C_{70}^+), indicating the relevance of monocyclic species to the mechanism of fullerene formation.[5] However, spectroscopic determination of the molecular structure of any cyclocarbon has not yet been achieved. In this connection, we designed dodecadehydro[18]annulene **1** and hexadecadehydro[24]annulene **2** annelated by [4.3.2]propellatriene units as new viable precursors of cyclo[18]carbon and cyclo[24]carbon, respectively. On the basis of our previous results on the photolysis of diethynyl-substituted [4.3.2]propellatrienes,[6] **1** and **2** should undergo photochemical [2 + 2] cycloreversion by elimination of indan molecules to produce the corresponding cyclocarbons. Moreover, the incorporation of the propellane units would considerably stabilize the inherently unstable (explosive) dehydroannulene core.[7] In this communication, we disclose the synthesis of **1** and **2**, detection of *cyclo*-C_{18} and *cyclo*-C_{24} anions by LD-TOF mass spectroscopy of **1** and **2**, and interception of reactive intermediates produced by the solution photolysis of **1** yielding an another class of dehydroannulenes **4−6** annelated by oxanorbornadiene units.



1 n=1 (+ diastereomer)
2 n=2 (+ diastereomers)

***cyclo*-C_{18}** (n=1)
***cyclo*-C_{24}** (n=2)

Copper-mediated oxidative coupling[8] of diethynyl[4.3.2]-propellatriene (**3**)[6] yielded the yellowish orange trimer **1** as the major product in 29% isolated yield along with a small amount of the reddish orange tetramer **2**. However when the coupling of **3** was undertaken under the modified conditions,[9] an approximately 1:1 mixture of **1** and **2** was obtained (total yield ca. 56%). The presence of dodecadehydro[18]- and hexadecadehydro[24]annulene cores in **1** and **2**, respectively, was confirmed by their spectroscopic data.[10] The ^{13}C NMR spectrum of **1** indicates that it is a mixture of two inseparable diastereomers with C_{3v} or C_s symmetry arising from relative orientation of the propellane units in the statistical ratio of 1:3.[12]



3

1
(+ diastereomer)

2
(+ diastereomers)

The positive mode LD-TOF mass spectrum of **1** shows only the peak due to the indan fragment (Figure 1a). On the other hand, in the negative mode, we observed the peaks due to the parent ion ($C_{18}R_3^-$ where R denotes the indan fragment) and the ions that resulted from the successive loss of one, two, and three indan fragments ($C_{18}R_2^-$, $C_{18}R^-$, and C_{18}^-, respectively). Moreover, small amounts of dimer (C_{36}^-) and trimer (C_{54}^-) were also detected. Since in our matrix-assisted laser-desorption system the desorbed molecule was relatively internally cool from evaporation of solvent molecules in the gas phase, the product of C_{36} (or C_{54}) in Figure 1a would not be a coalescence product, suggesting rather that the dimer (or trimer) is a weakly bound complex of two (or three) *cyclo*-C_{18}. Actually, we could not observe any trace of the "C_2-loss" fragmentation pattern which is supposed to occur upon excitation of a fullerene molecule.

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(10) Electronic spectra of **1** and **2** are similar to those of the corresponding cyclobutene-annelated dehydroannulenes.[11] The ^{1}H NMR spectra of **1** and **2** are also in accord with the diatropic and paratropic characters of the [18]-annulene and [24]annulene perimeters, respectively. Details are listed in the supporting information.

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(12) For clarity, only the highest symmetry isomers of **1** (C_{3v}) and **2** (C_{4v}) are shown, as well as one of the C_s isomers of **4** and **5** and the C_{3v} isomer of **6**.

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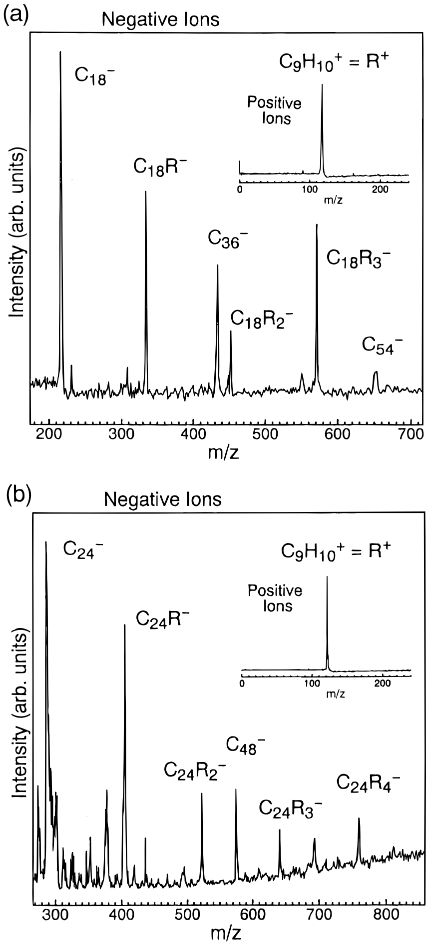


Figure 1. Laser-desorption time of flight mass spectrum of (a) **1** and (b) **2**. R denotes the indan fragment. For obtaining each spectrum, the compound **1** (or **2**) was first dissolved in liquid paraffin as a matrix. The solution was dropped into a small hole of a stainless steel disk and placed at the bottom of the acceleration plates. For simultaneous desorption and ionization, the fourth harmonic of a Nd:YAG laser (266 nm, typically 0.6 mJ/pulse) was focused on an area of 3 mm^2. The vacuum chamber was maintained at 1 × 10^{-6} Torr during the operation.

Likewise, the LD-TOF mass spectrum of **2** (Figure 1b) exhibits only the indan peak in the positive mode, while in the negative mode, the peaks due to C_{24}^- and its precursors generated by the stepwise loss of the indan fragments from **2** were observed.

As a preliminary study of the photochemical [2 + 2] cycloreversion, a solution of **1** in THF-d_8 was irradiated with a low-pressure mercury lamp at 0 °C to yield indan along with uncharacterized polymeric materials. In order to intercept reactive intermediates generated during the photolysis, irradiation was then carried out using furan as the solvent to afford three oxanorbornadiene-annelated products **4**−**6** in 15, 27, and 11% isolated yields, in which one, two, or all indan units are replaced by the furan moieties, respectively. Again, the ^{13}C NMR spectra of **4**−**6** indicate that these are mixtures of three (two C_s isomers and one C_1 for **4** and **5**) or two (C_{3v} and C_s for **6**) diastereomers.[12] Within the series of the dodecahydro[18]annulenes **1** and **4**−**6**, the absorption bands in the electronic spectra exhibit steady bathochromic shift with increasing number of the fused oxanorbornadiene units in the molecule,[13] presumably as a result of through-bond interaction[14] of the outer π bonds with the dehydroannulene system. Also, the kinetic stabilities of the dehydroannules **5** and **6** with more than one oxanorbornadiene unit are substantially more diminished than those of **1** and **4**; the less sterically hindered compounds **5** and **6** decomposed gradually even in the solid state under inert atmosphere. Monitoring the photochemical reaction of **1** in furan suggests that **4** is formed initially, and then it is converted to **5**, which finally gives **6**. It should be noted that the [4 + 2] cycloaddition of furan takes place regioselectively giving the products **4**−**6**, in which the furan units are located at the same position as those occupied by the propellane units before they were extruded. In order to gain insight into this regioselectivity, we undertook semiempirical AM1 calculations[15] for the tetradecadehydro[18]annulene **7** (Figure 2), a model compound for the reactive intermediate formed from **1** by elimination of one of the indan fragments. As shown in Figure 2, the calculated bond angle of the central triple bond of the decapentayne moiety of **7** is the most deformed from linearity of its triple bonds. This indicates that the observed regioselectivity is due to the highest reactivity of this bond because of its largest distortion. While these results do not necessarily imply the direct formation of *cyclo*-C_{18} by the photolysis of **1**, they clearly show that the elimination of at least one of the indan units takes place efficiently by [2 + 2] cycloreversion from **1** (and **4** and **5** as well) to produce highly reactive tetradecadehydro[18]annulene intermediates. Detailed characterization of the negatively charged and neutral cyclocarbon generated from **1** and **2** and synthesis of their homologues of different macrocyclic ring size are in progress.

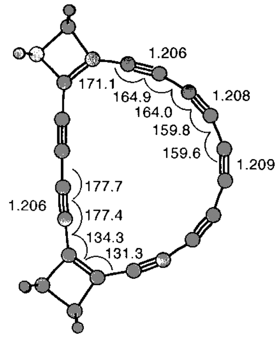
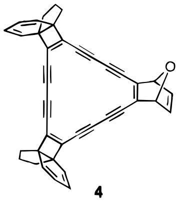
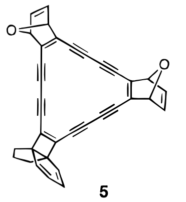
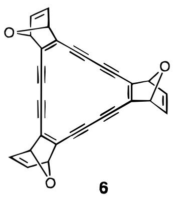


Figure 2. AM1-optimized geometries of tetradecadehydro[18]annulene model **7**. The bond angles are in degrees, and bond lengths are in angstroms.


4
(+ diastereomers)


5
(+ diastereomers)


6
(+ diastereomer)

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Supporting Information Available: Listing of spectral data of **1**, **2**, and **4**−**6** and full-scale LD-TOF mass spectra of **1**, **2**, and **4**−**6** (Figures 3 and 4) and UV−vis spectra of **1** and **4**−**6** (Figure 5) (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) For example, the most intense absorption bands (CHCl$_3$) of **1**, **4**, **5**, and **6** are observed at 356 (ϵ 60 200), 367 (ϵ 50 800), 376 (ϵ 48 200), and 387 (ϵ 57 000) nm, respectively. For details, see Figure 5 in the supporting information.

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