# Towards the synthesis of monocyclic carbon clusters: [2+2] cycloreversion of propellane-annelated dehydroannulenes

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*Abstract:* We have synthesized the propellane-annelated hexadehydro[12]-, octadehydro[16]-, dodecadehydro[18]-, decadehydro[20]-, and hexadecadehydro-[24]annulenes which serve as stable precursors of monocyclic carbon clusters $C_{12}$, $C_{16}$, $C_{18}$, $C_{20}$, and $C_{24}$, respectively.

Recently, tremendous interest has been focused on the monocyclic carbon clusters from several points of view (1). Firstly, they are novel form of carbon allotropes that are believed to be the most stable form in the narrow size range of $C_{10}$ to about $C_{20}$. Secondly, increasing evidences have been accumulating concerning the crucial role of monocyclic clusters in the fullerene formation (2). Finally, from the stand point of novel aromatics, the novel topology of the pi-orbitals which are perpendicular to each other would, certainly explore our view of novel aromatics. In this context, a number of theoretical predictions have been made, in particular for those having 4n+2 carbons (3).
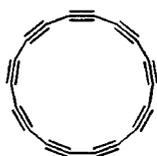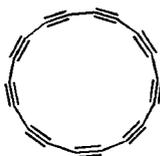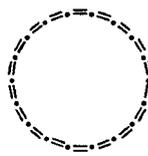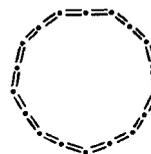


$C_{18}$ ($D_{9h}$)    $C_{18}$ ($C_{9h}$)    $C_{18}$ ($D_{18h}$)    $C_{18}$ ($D_{9h}$)

Although microscopic quantities of small clusters can be generated by the vaporization of graphite and detected using the mass selection technique, in order to prepare them in macroscopic quantities and to achieve full characterization, they must be generated from suitable precursor molecules of well-defined structure. In this connection, Diederich took the first move to prepare these precursor molecules **1-3** that would generate cyclic $C_{18}$, $C_{24}$ and $C_{30}$ by means of retro Diels-Alder reaction (4), oxidative decomplexation (5), and decarbonylation (6), respectively. Particularly interesting is the polyketone **3**, because the decarbonylation can be carried out at low temperature by photochemical reaction. However, because of the lability of the precursor itself, full characterization of monocyclic carbon clusters has not yet been achieved. Inspired by these pioneering work, we planned to design new precursors that are stable and are capable of generating the cluster molecule by photochemical reaction.
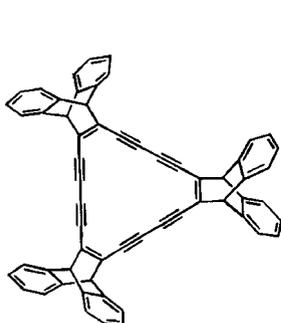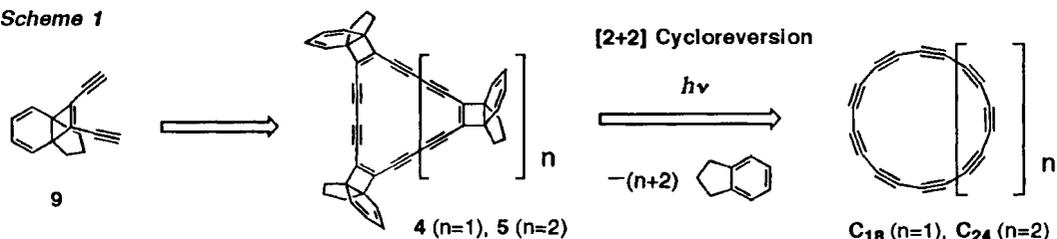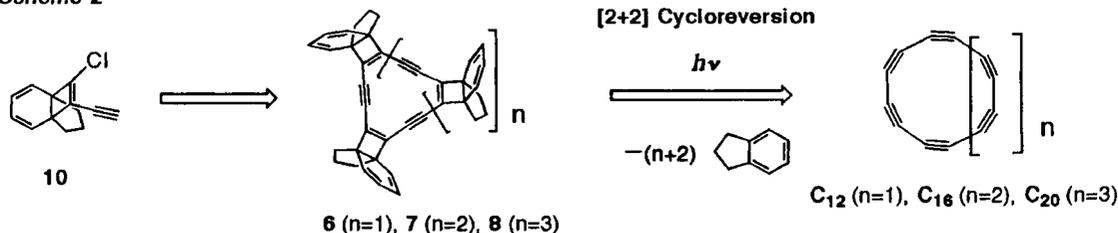


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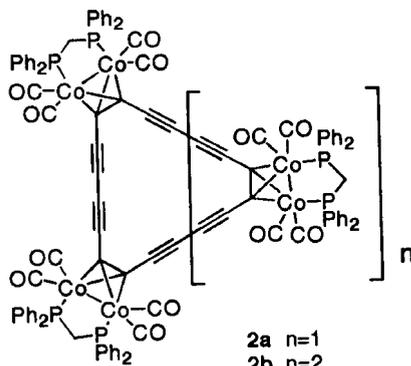
2a n=1
2b n=2
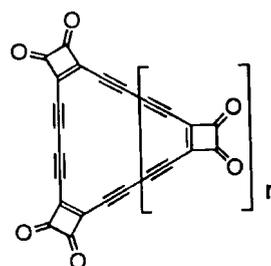
3a n=1
3b n=2
3c n=3

It has been well documented that photochemical [2+2] cycloreversion is one of the most efficient methods to generate such reactive species as cyclobutadiene (7). In this connection, we first designed precursors **4** and **5**, propellane-annelated dehydroannulenes, which would generate $C_{18}$ and $C_{24}$, respectively, by [2+2] cycloreversion extruding three or four molecules of indane (Scheme 1) (8). Next, we planned to prepare the precursors **6, 7,** and **8** of $C_{12}$, $C_{16}$, and $C_{20}$, respectively (Scheme 2) (9). The precursors **4** and **5** would be prepared by the oxidative coupling of diethynylpropellane **9** and **6-8** would be obtained by the palladium-catalyzed cyclization of chloroethynylpropellane **10**.

*Scheme 1*



**4** (n=1), **5** (n=2)

[2+2] Cycloreversion

$h\nu$

$-(n+2)$

$C_{18}$ (n=1), $C_{24}$ (n=2)

*Scheme 2*



**6** (n=1), **7** (n=2), **8** (n=3)

[2+2] Cycloreversion

$h\nu$

$-(n+2)$
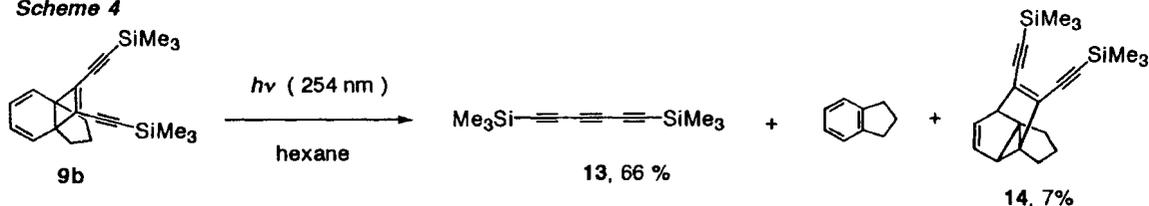
$C_{12}$ (n=1), $C_{16}$ (n=2), $C_{20}$ (n=3)

The diethynylpropellane **9** was prepared as shown in Scheme 3. Namely, photocycloaddition of the bicyclic enone with trichloroethylene and the subsequent dehydrochlorination afforded the dichloroketone **11**, which was converted to the dichlorotriene **12** by (i) alpha-bromination, (ii) dehydrobromination, (iii) 1,2-reduction, and (iv) formal 1,4-dehydration. Palladium catalyzed coupling of the chloride **12** with appropriately protected acetylenes gave the diethynyl propellatrienes **9** in good yields.
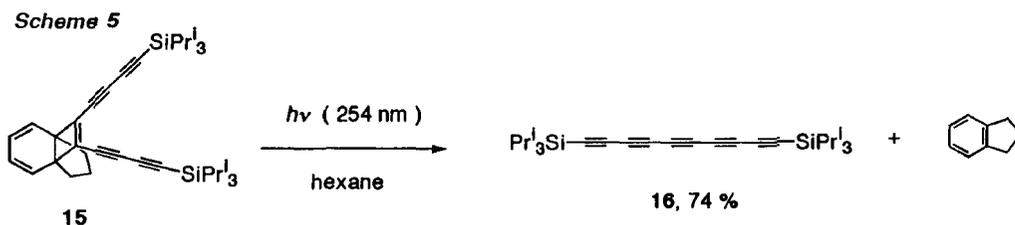
*Scheme 3*



**9b** R = SiMe₃, 63 %
**9c** R = SiPr$^i_3$, quantit
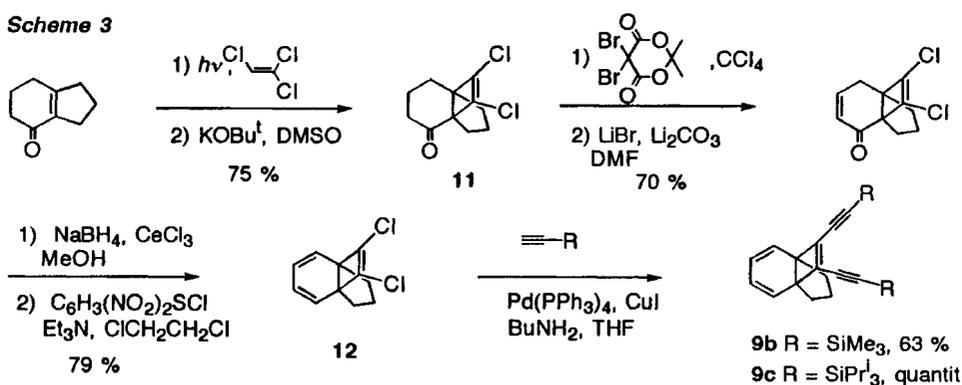
We next carried out the model study of the photolysis which produce linear polyynes (10). For example, photolysis of a diethynyl propellatriene **9b** gave a hexatriyne **13** by extrusion of indane in good yield as we expected. However we also found that a small amount of by a product **14** formed which was formulated as vinylogous di-pi-methane rearrangement product (Scheme 4). Photolysis of dibutadiynylpropellatriene **15**, however, afforded only indane and a decapentayne **16** (Scheme 5).

*Scheme 4*



**9b**

$h\nu$ ( 254 nm )

hexane

$Me_3Si \!-\!\equiv\!-\!\equiv\!-\!\equiv\!- SiMe_3$

**13, 66 %**

+

+

**14, 7%**

**Scheme 5**



Coupling of the diethynylpropellatriene **9** under the Eglinton's conditions afforded the 18-membered trimer **4** as the major product in about 30% yield. Besides this product, a small amount of the tetramer **5** was also obtained. Due to the orientation of the propellane units, the trimer was a statistical (1:3) mixture of the diastereomers. Coupling of **9** according to the Breslow's modification yielded about 1:1 ratio of the trimer **4** and tetramer **5**. Again, the tetramer is assume to be a mixture of three diastereomers. For the sake of clarity, only the isomers with the highest symmetry are drawn in this paper. As we expected, both **4** and **5** are stable which starts to decompose over 170 °C.



**[ all mixture of diastereomers ]**
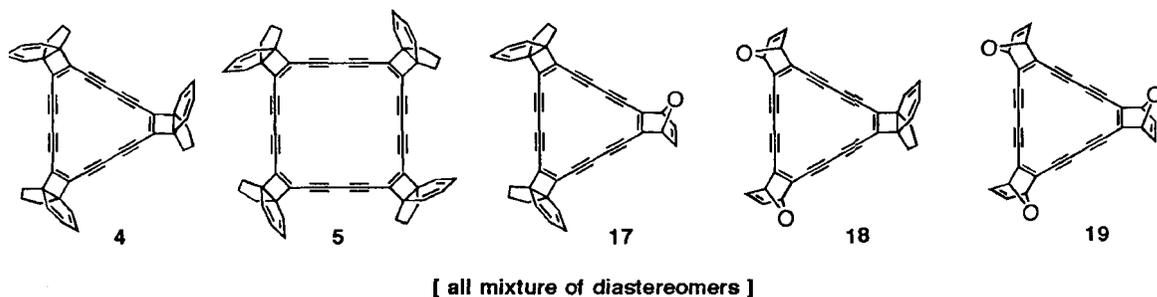
When the trimer **4** was subjected to the laser-desorption time-of-flight (LD-TOF) mass spectroscopy, we observed the formation of $C_{18}$ anion along with the parent ion $C_{18}R_3$ and the fragments due to the successive loss of the indane fragments ($C_{18}R_2$ and $C_{18}R$) in the negative mode as shown in Fig. 1, where R denotes the indane molecule. In the positive mode, on the other hand, only indane fragment was observed. Similarly, LD-TOF mass of the tetramer **5** exhibits, in the negative mode, the parent peak, the fragments due to the stepwise loss of indane, and finally $C_{24}$ anion (Fig. 2).
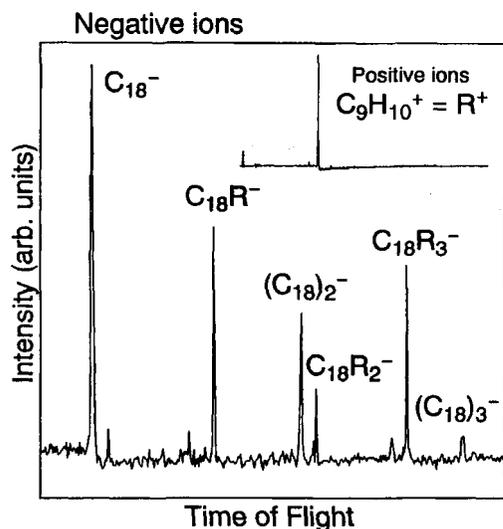


Fig. 1. LD-TOF mass spectrum of trimer **4**.
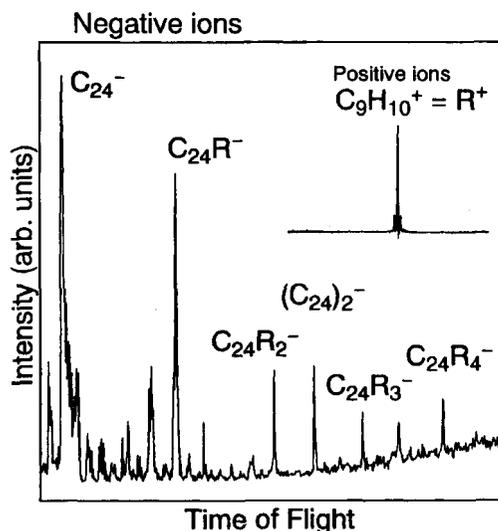R denotes the indane fragment.

Fig. 2. LD-TOF mass spectrum of ttetramer **5**.
R denotes the indane fragment.

When a solution of the trimer **4** in THF was irradiated at 0 °C, we observed the formation of indane, but we were not able to characterize any other products. While, when we irradiated **4** in a furan solution, we obtained products **17, 18** and **19**, which are derived by the capture of reactive intermediates. These results do not necessarily indicate the formation of $C_{18}$ during the photolysis, but they indicate that elimination of at least one of the indane fragments takes place readily from the trimer **4**.

We turned attention to the other members of monocyclic carbon clusters. Toward this end, we carried out the palladium catalyzed coupling of the dichloropropellane with dimethylbutynol to give the monosubstitution product **20** in a good yield. Palladium catalyzed coupling of **19** under the phase transfer conditions afforded the tetramer **7** as the major product along with the trimer **6** and pentamer **8** in small amounts (Scheme 6). It should be pointed out that although the parent hexadehydro[12]annulene is known (11), the tetramer **7** and the pentamer **8** are the first examples of octadehydro[16]- and decadehydro[20]annulenes, respectively. The LD-TOF mass spectra of the **6-8** exhibit the indane fragment in the positive mode and, on the other hand, the parent peak and the fragments due to the successive loss of the indane fragments to yield $C_{12}$, $C_{16}$, and $C_{20}$ anions, respectively (12).

**Scheme 6**



[ all mixture of diastereomers ]
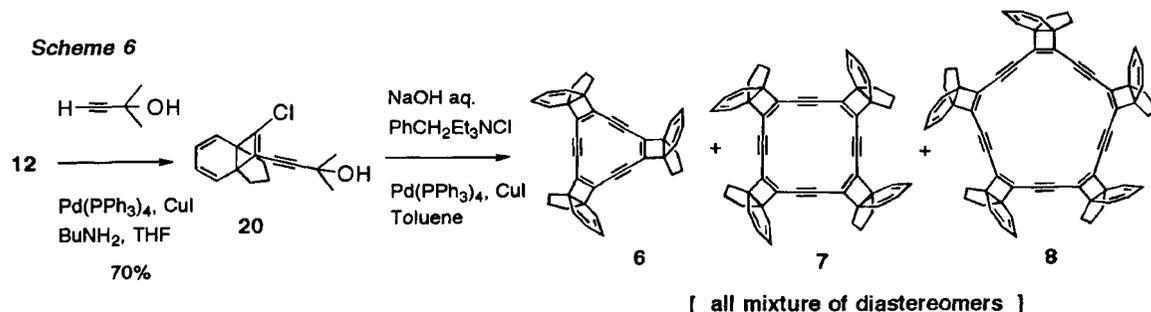
In summary, we have synthesized the propellane-annelated [12]-, [16]-, [18]-, [20]-, and [24]dehydroannulenes which served as stable precursors of monocyclic carbon clusters at least in microscopic quantities. The structure confirmation as well as the macroscopic preparation of the clusters are now undertaken in our laboratories.

## Acknowledgments

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