[16.16.16](1,3,5)Cyclophanetetracosayne ($C_{60}H_6$): A Precursor to C_{60} Fullerene

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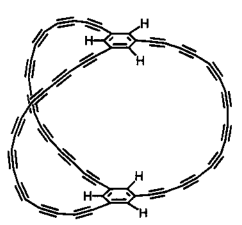
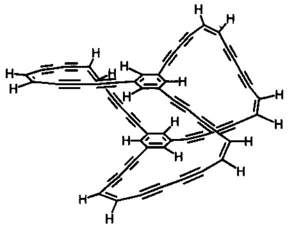
Although C_{60} and some higher fullerenes are now readily available from commercial sources, it is still important to synthesize fullerenes on the basis of organochemical transformations because it would be possible to manipulate carbon cages in a size-selective and structure-defined manner. It would also be possible to encapsulate transition metals into the cage leading to the yet-discovered endohedral transition metallofullerenes,[1] which are of tremendous interest as new materials. The first attempt to the total synthesis of isosahedral C_{60} was set up by Chapman's school[2] well before its first observation,[3] which was followed by several approaches.[4] However, despite the numerous efforts, the controlled chemical synthesis of fullerenes as well as that of endohedral metallofullerenes have not been achieved yet.

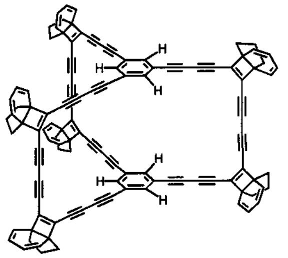
Recently, Rubin et al. proposed a new route to fullerene synthesis[5] inspired by a postulated mechanism of the fullerene formation, which includes intermolecular cycloaddition of cyclic polyynes (coalescence) followed by skeletal isomerization (annealing).[6] Thus, cage polyyne $C_{60}H_6$ (**1**) was proposed as a possible precursor to C_{60} fullerene, because it would cascade down to the most stable icosahedral structure of I_h symmetry[7] together with the loss of hydrogen, just like the similar cascade known as "adamantane rearrangement."[8] As an intial step to the synthesis of $C_{60}H_6$, they prepared $C_{60}H_{18}$ (**2**), in which two double bonds still remained in each of the polyyne bridge. In the ion cyclotron resonance mass spectrum (negative mode) of **2**, dehydrogenation down to $C_{60}H_{14}^-$ was observed,[5a] suggesting the possibility of complete dehydrogenation of $C_{60}H_6$ (**2**) to C_{60}. As an extension of our strategy to generate reactive polyynes by [2 + 2] cycloreversion of [4.3.2]propellatriene derivatives,[9] we disclose here the preparation of a stable precursor **3** [$C_{60}H_6(Ind)_6$] which would form $C_{60}H_6$ by extrusion of six aromatic fragments (indane = Ind) and the observation of C_{60} as well as $C_{60}H_6$ ions in the laser desorption mass spectra.[10]



$C_{60}H_6$ (**1**)



$C_{60}H_{18}$ (**2**)



$C_{60}H_6(Ind)_6$ (**3**)

According to the semiempirical calculations on the AM1 level, the title compound **1** has a heat of formation about 500 kcal/mol larger than that of the known hexahydrofullerene.[11] Moreover, since diaryl-substituted hexadecaoctaynes have been shown to be the isolation limit of the linear polyynes,[13] cage polyyne **1** must be too reactive for isolation at room temperature. It is also interesting to note that **1** is a member of polyyne-bridged cyclophanes, a new family of strained cyclophanes, proposed recently.[14]

To prepare unsymmetrically substituted diakynylpropellatriene, the protective group of the known monoalkynylated propellatriene **4a**[9b] was switched to the more readily removable $Si(i\text{-}Pr)_3$ group to give **4b**. Introduction of the second alkynyl group followed by selective deprotection of the $SiMe_3$ group of **5a** afforded diyne **5b**. Pd-catalyzed hetero coupling[15] of **5b** with tris(bromoethynyl)benzene (**6**)[5a] afforded trispropellane **7a** in 67% yield. After

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[7] Recently, a theoretical examination of a cascade isomerization mechanism, "fullerene rearrangement," from various C_{60} isomers to I_h C_{60} was undertaken: Osawa, E.; Ueno, H,; Yoshida, M.; Nishiyama, M. *J. Chem. Soc., Perkin Trans. 2* Submitted for publication.

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[10] Recently, we became aware that Rubin et al. synthesized a precursor to **1** annelated by cyclobutenedione units and observed $C_{60}H_6^-$ and C_{60}^- in the negative mode ion cyclotron resonance mass spectrum: Rubin, Y.; Parker, T. C.; Pastor, S.; Jalisatgi, S.; Boulle, C.; Wilkins, C. L. *Angew. Chem.* In press.

[11] The AM1-calculated $\Delta H_f°$ values for **2**, 1,2,33,41,42,50-hexahydrofullerene,[11a] and 1,2,5,10,21,24-hexahydrofullerene[11b] are 1341.5, 847.6, and 840.3 kcal/mol, respectively. Calculations were performed by SPARTAN version 5.0; Wavefunction Inc. For ab initio calculations of $C_{60}H_6$ isomers, see: Cahill, P. A. *Chem. Phys. Lett.* **1996**, *254*, 257−262.

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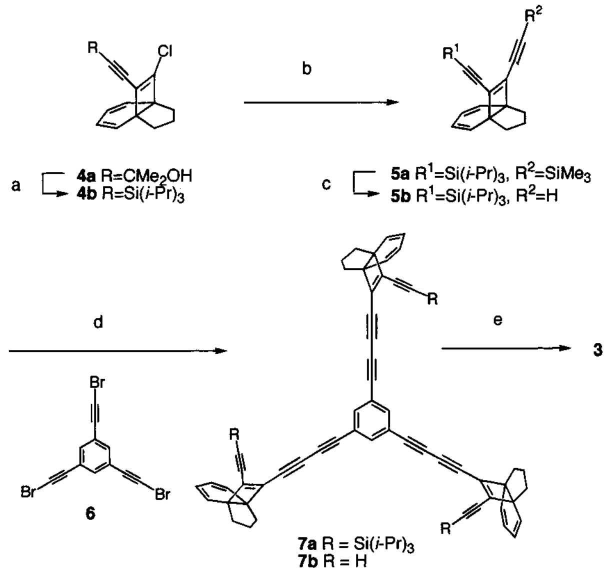
S0002-7863(98)00330-8 CCC: $15.00

Scheme 1[a]



[a] Key: (a) (i) KOH, benzene, reflux, 72%; (ii) BuLi, THF, 0 °C; (iii) $CF_3SO_3Si(i\text{-}Pr)_3$, rt, 99%; (b) $(CH_3)_3SiCCH$, $Pd(PPh_3)_4$, CuI, Et_3N, THF, rt, 78%; (c) K_2CO_3, MeOH−THF, rt, 96%; (d) $Pd_2(dba)_3{\cdot}CHCl_3$, CuI, 1,2,2,6,6-pentamethylpiperidine, benzene, rt, 67%; (e) (i) $Bu_4N^+F^-$, THF, rt, (ii) $Cu(OAc)_2$, pyridine, rt, 70%. Only one of the diastereomers (C_3) is shown for compounds **7a,b**.

removal of the $Si(i\text{-}Pr)_3$ group, oxidative coupling of **7b** under high dilution conditions furnished **3** as a mixture of diastereomers[16] in 70% yield (Scheme 1).

Figure 1a shows the positive mode laser desorption mass spectrum of **3**. While a prominent peak of C_{60}^+ is observed, neither the parent peak (*m/z* 1434) nor $C_{60}H_6^+$ (*m/z* 726) can be detected. It has been well-documented that, in general, carbon cluster cations generated by the laser desorption method are thermally highly excited, and, as a result, fragmentation due to C_2 loss is frequently observed.[17] The internal temperature of thermally excited C_{60}^+ was estimated to be as high as 2300−3000 K.[18] Since such C_2 loss down to C_{50}^+ was indeed observed in the present case, it is difficult to deduce the structure of C_{60} cation. However, it should be pointed out that this represents one of few examples of size-selective formation of C_{60} cluster,[6c,e] because no larger cluster such as C_{70} was observed.

The negative mode mass spectra of **3** are shown in Figure 1b. In contrast to the positive mode, the negative mode spectra exhibited peaks due to $C_{60}H_6^-$ and $(C_{60}H_6 + \text{indane})^-$ at *m/z* 726 and 844, respectively, though the parent peak was not detected. It has been documented that the internal temperature of negative ions is much lower than those of positive ions and negative ions represent better the structures and populations of neutral species.[19] Consequently, it is reasonable to assume that the polycyclic cage structure of **1** remains intact in the $C_{60}H_6$ anion observed.

Figure 1b also shows a small peak due to C_{60} anion was observed. Judging from the isotope distribution of the C_{60}^-, there are no intermediate species between $C_{60}H_6^-$ and C_{60}^- such as $C_{60}H_5^-$, $C_{60}H_4^-$, and so on. This means that the dehydrogenation probably takes place simultaneously to the drastic skeletal isomerization, leading to the formation of a fullerene-like structure. Though we are not able to figure out a rational pathway for such transformation at this moment, the large potential energy of **1** must be responsible for such cascade transformation.

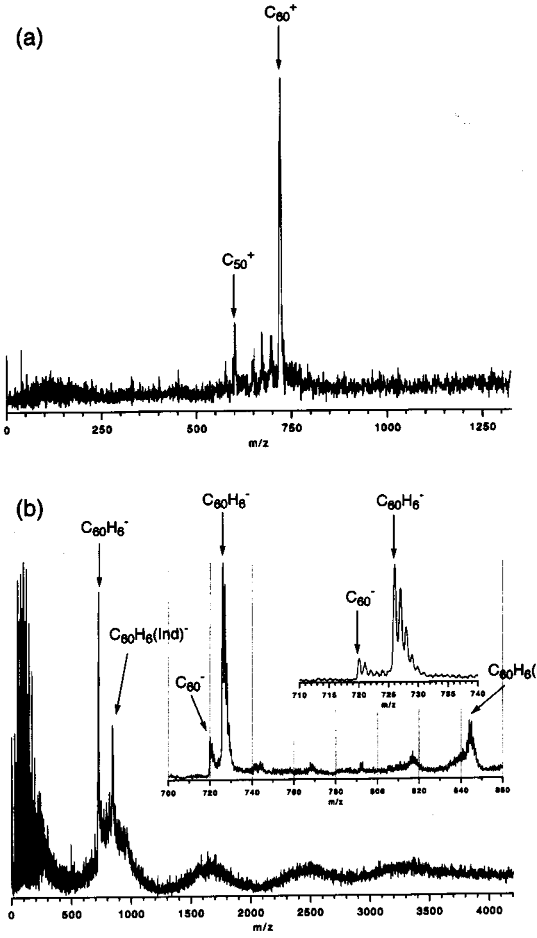


Figure 1. Laser desorption time-of-flight mass spectra of **3** (a) in positive mode and (b) in negative mode. Liquid paraffin was used as a matrix and the third harmonic of a Nd:YAG laser (355 nm, typically 3 MW/cm^2 with a 7 ns duration) was employed for simultaneous desorption and ionization.

In summary, we prepared a stable precursor to cage polyyne $C_{60}H_6$ (**1**) and succeeded in the observation of size-selective formation of C_{60}^+ and that of $C_{60}H_6^-$ as well. Although there still remains a lot to be done,[20] we believe the present work marks a step forward toward total synthesis of fullerenes.

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Supporting Information Available: Experimental procedures and spectral data for **3**, **4a**, **5a**,**b**, and **7a**,**b** (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(16) Eight diastereomers including **3** depicted (C_{3h}) are conceivable, none of which was separated.

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(20) Photolysis of **3** in benzene solution with a low-pressure mercury lamp resulted in the formation of indan (ca. 50% yield by ^{1}H NMR spectrum) and uncharacterized polymeric materials. So far we are not able to perform flash vacuum pyrolysis of **3** owing to its low volatility. Further work in the preparative scale fragmentation of **3** is under way.