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Polyyne cyclization to form carbon cages: [16.16.16](1,3,5)cyclophanetetracosayne derivatives $C_{60}H_6$ and $C_{60}Cl_6$ as precursors to C_{60} fullerene

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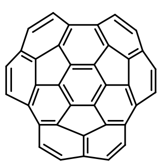
Abstract—[16.16.16](1,3,5)Cyclophanes fused by six [4.3.2]propellatriene units, which would serve as precursors to cage polyyne $C_{60}H_6$ and its perchloro derivative $C_{60}Cl_6$, respectively, were prepared. In the negative mode laser desorption mass spectra of the cyclophanes, the polyyne anions $C_{60}H_6^-$ and $C_{60}Cl_6^-$ were detected. Moreover, size-selective formation of C_{60}^+ as well as C_{60}^- was also observed, indicating the possible polyyne cyclization mechanism to form the fullerene cage. © 2001 Elsevier Science Ltd. All rights reserved.

C_{60} and some higher fullerenes are produced by arc-vaporization of graphite[1] and are readily available from commercial sources.[2] However, it is still important to synthesize fullerenes in a rational manner based on organochemical transformations, because it would be possible to manipulate carbon cages in 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,[3] which are of tremendous interest as new materials. In this respect, intensive studies have been conducted toward the designed synthesis of C_{60}. The first attempts were conducted by Chapman's group[4] well before the first observation of C_{60},[5] which was followed by several different approaches. However, despite the numerous efforts, the controlled chemical synthesis of fullerenes as well as that of endohedral metallofullerenes has not been achieved yet.

One of the most potential approaches to the rational synthesis of C_{60} is to build up six-membered rings around five-membered rings by intramolecular C–C bond formation under high-temperature pyrolytic conditions (FVP), leading to the formation of bowl-shaped molecules called 'bucky-bowls' or 'fullerene fragments'.[6] Scott and Rabideau have developed this method extensively. To date, the largest known fullerene fragment is $C_{36}H_{12}$ (**1**) synthesized by Scott.[6e,f] In view of the recent findings that curved polycyclic aromatic hydrocarbons exemplified by corannulene can be prepared efficiently without using the FVP technique,[7] this strategy will become more powerful than before. As an alternative approach to synthesize C_{60} from molecules already possessing sixty carbon atoms, a twisted $C_{60}H_{30}$ hydrocarbon, benzo[1,2-*e*:3,4-*e*′:5,6-*e*″]tribenzo[*l*:*l*′:*l*″]triacephenanthrylene (**2**), which represents a developed diagram of C_{60}, was prepared.[8] Partial dehydrogenation of **2** took place in the matrix-assisted laser-desorption ionization (MALDI) time-of-flight (TOF) mass spectroscopy down to $C_{60}H_{10}^+$ but complete dehydrogenation to C_{60}^+ was not observed.[8a] A mechanistically different approach from sixty-carbon-containing molecules, utilizing cyclization of highly reactive three-dimensional polyynes, was investigated by the groups of Rubin[9] and ours,[10] which is the topic of this report.[11]

Although the mechanism has not been clarified,[12] it has been proposed that monocyclic carbon clusters, called cyclo[*n*]-carbons,[13] are likely to play a key role during the early stages of the fullerene formation.[14] Inspired by this



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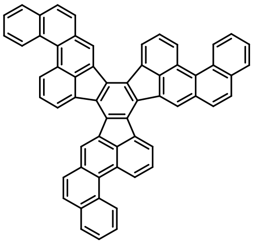

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Keywords: fullerene; cyclization; cyclophanes.

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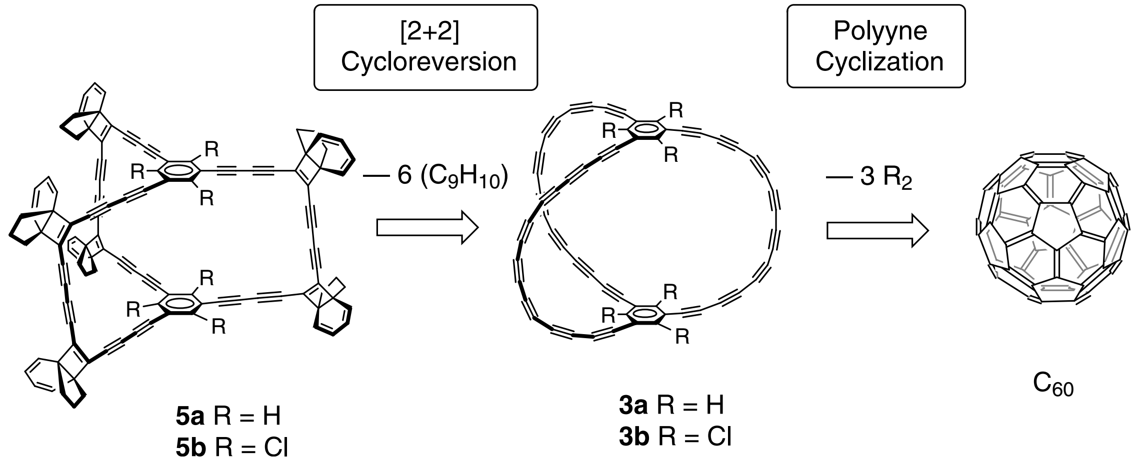
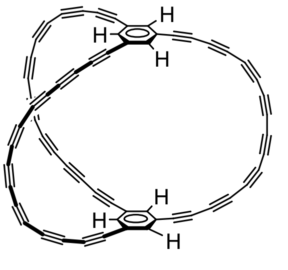
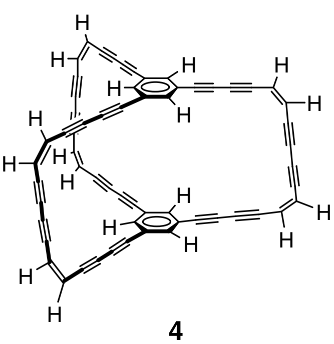


Scheme 1. Proposed formation of C_{60} from propellane-annelated cyclophanes **5a** and **b** by [2+2] cycloreversion followed by polyyne cyclization of three-dimensional polyynes **3a** and **b**. Only one of the diastereomers of **5a** and **b** is shown for clarity reasons.

proposal, Rubin proposed recently a new route to fullerene synthesis involving cyclization of reactive polyynes.[15] Thus the reactive cage polyyne $C_{60}H_6$ (**3a**) would isomerize to the most stable icosahedral structure of I_h symmetry by forming the five- and six-membered rings with the loss of hydrogen atoms, like the cascade rearrangement of $C_{10}H_{16}$ hydrocarbons called 'adamantane rearrangement'.[16] As an initial step to the synthesis of **3a**, Rubin prepared $C_{60}H_{18}$ (**4**) which contained two double bonds in each polyyne bridge. In the ion cyclotron resonance (ICR) mass spectrum (negative mode) of **4**, partial dehydrogenation down to $C_{60}H_{14}^-$ was observed,[15a] suggesting the possibility of complete dehydrogenation of $C_{60}H_6$ (**3a**) to C_{60}. As an extension of our strategy to generate highly reactive polyynes by [2+2] cycloreversion of [4.3.2]propellatriene derivatives,[13e] we report here the preparation of a stable hydrocarbon precursor **5a**, $C_{60}H_6(\text{Ind})_6$, and its perchlorinated derivative **5b**, $C_{60}Cl_6(\text{Ind})_6$, which would form cage polyynes $C_{60}H_6$ or $C_{60}Cl_6$, respectively, by extrusion of six aromatic fragments (indane). We also report the observation of C_{60} ions in the positive and negative modes of the laser desorption mass spectra of **5a** and **b**, an indication of the polyyne cyclization mechanism for the fullerene formation (Scheme 1).



3a



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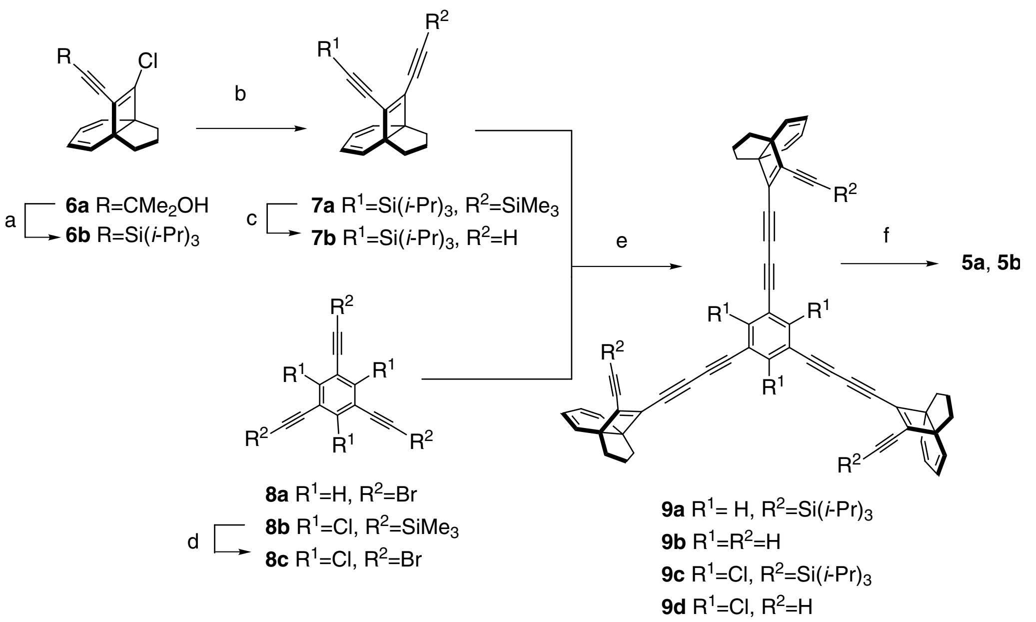
According to the semi-empirical calculations on the AM1 level,[17] cage polyyne **3a** has a heat of formation of 1341 kcal/mol which is about 500 kcal/mol larger than that of the known 1,2,33,41,42,50-hexahydrofullerene (ΔH_f^0 (AM1)=847.6 kcal/mol) prepared by dissolving metal reduction of C_{60}.[18] Although the bond angles of each sp carbon atom of **3a** (169.8–170.3°) are not severely distorted, the total strain for 48 sp carbon atoms must be tremendous. Moreover, the individual polyyne chain of **3a** can be envisioned as a diaryl-substituted hexadecaoctayne whose parent compound has been shown to lie on the isolation limit of the linear polyynes.[19] These data suggest that compound **3a** must be too reactive for isolation at room temperature. It is also worth noting that **3a** is a member of polyyne-bridged cyclophanes proposed recently as a new family of strained cyclophanes.[20]

The precursors **5a** and **b** were synthesized by oxidative dimerization of the corresponding tris(propellane)-substituted benzene derivatives **9b** and **d** which were obtained by hetero coupling of appropriate tris(bromoethynyl)-benzenes **8a** and **c** with unsymmetrically substituted dialkynylpropellatriene **7b** (Scheme 2). In order to prepare **7b**, the protective group of the known monoalkynylated propellatriene **6a**[13e] was changed to the more readily removable triisopropylsilyl group by deprotection followed by reprotection to give **6b**. Introduction of the second alkynyl group was achieved efficiently by the Sonogashira-type reaction using the recently reported P(t-Bu$)_3$ ligand,[21] and subsequent selective deprotection of the trimethylsilyl group of **7a** afforded monoprotected diyne **7b**. Pd-catalyzed hetero coupling of **7b** with tris(bromoethynyl)benzene (**8a**)[9a] under the protocol reported by Vasella[22] afforded 1,3,5-tris(propellanylethynyl)benzene **9a** in 67% yield. After removal of the triisopropylsilyl group, oxidative coupling of **9b** was performed under high dilution conditions to yield **5a** as a mixture of diastereomers[23] in 70% yield. In order to prepare the chloro derivative **5b**,



Scheme 2. (a) (i) KOH, benzene, reflux, 91%; (ii) BuLi, THF, 0°C, then $CF_3SO_3Si(i\text{-}Pr)_3$, rt, 99%; (b) $(CH_3)_3SiC{\equiv}CH$, $Pd(PhCN)_2$, CuI, $P(t\text{-}Bu)_3$, $NH(i\text{-}Pr)_2$, THF, 50°C, 85%; (c) K_2CO_3, MeOH–THF, rt, 96%; (d) NBS, $AgNO_3$, 67%; (e) $Pd_2(dba)_3{\cdot}CHCl_3$, CuI, 1,2,2,6,6-pentamethylpiperidine, benzene, rt, 67% for **9a**, 39% for **9c**; (f) (i) $Bu_4N^+F^-$, THF, rt, (ii) $Cu(OAc)_2$, pyridine, rt, 70% for **5a**, 29% for **5b**. Only one of the diastereomers of **9a**–**d** is shown for clarity reasons.

1,3,5-trichloro-2,4,6-triiodobenzene[24] was converted to tris(trimethylsilyl)ethynyl derivative **8b** under the normal Sonogashira conditions, which was converted to the bromoethynyl derivative **8c** by treatment with NBS and silver (I) nitrate. Hetero coupling[22] of **8c** with the propellane unit **7b** gave **9c** in 38% yield. After deprotection to **9d**, oxidative coupling of **9d** gave **5b** in 29% yield.[23] Solutions of **5a** and **b** are rather sensitive to room light; when a benzene solution of **5a** was allowed to stand under a fluorescent light for a few days, several unidentified products were detected by HPLC but no indane was detected. While the hydrocarbon **5a** was quite stable in the dark, the chloro derivative **5b** decomposed gradually even when it was stored in a refrigerator.[25]

Laser desorption time-of-flight (LDTOF) mass spectra of **5a** and **b** were measured using liquid paraffin as a matrix and the third harmonic of an Nd:YAG laser (355 nm, typically 3 MW/cm^2 with a 7 ns duration) for simultaneous desorption and ionization. Fig. 1a shows the positive mode laser desorption mass spectrum of hydrocarbon **5a**. A prominent peak due to C_{60}^+ formed by the loss of eight indane fragments and six hydrogen atoms is observed, although the signal to noise ratio of the spectrum is not large. 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.[26] The internal temperature of thermally excited C_{60}^+ was estimated to be as high as 2300–3000 K.[27] Since such C_2 loss down to C_{50}^+ is indeed observed in the positive mode spectrum of **5a**, indicating that the internal temperature of the C_{60}^+ is considerably high, it is hard to deduce whether the structure of the C_{60} cation retains the I_h symmetry of fullerene or not. However, it should be pointed out that this result represents one of few examples of size-selective formation of C_{60} cluster,[14c] because no larger cluster such as C_{70} was detected.

It was reported that perchlorinated polycyclic aromatic compounds served as good precursors to produce carbon cluster ions by electron impact induced fragmentation.[28] In this respect, we expected that the chloro derivative **5b** would serve as a better precursor to C_{60} cation although our ionization conditions were different from those reported. As shown in Fig. 1b, the positive mode LDTOF mass spectrum of **5b** exhibits a strong peak of C_{60}^+. The most important feature of the spectrum is that the S/N ratio is much improved from that of the spectrum of **5a**. The formation of C_{60}^+ is facilitated by the electron capture by the chlorine atoms, as supported by the observation of a strong peak of Cl^- in the negative mode spectrum in Fig. 2b. As in the case of **5a**, neither the parent peak nor $C_{60}Cl_6^+$ can be detected. In addition to the fragmentation down to C_{50}^+ due to the C_2 loss, ions up to C_{120}^+ were observed which might be formed by an ion-molecule reaction of C_{60} and the subsequent fragmentation of the dimeric cluster ion.

The negative mode LDTOF mass spectrum of **5a** is shown in Fig. 2a. In contrast to the positive mode spectrum, the negative mode spectrum exhibits peaks due to $C_{60}H_6^-$ and $C_{60}H_6(Ind)^-$ at *m/z* 726 and 844, respectively, though the parent peak is not detected. It has been documented that the internal temperature of negative ions is much lower than those of positive ions, and the negative ions represent better structures and populations of neutral species.[29] Consequently, it is reasonable to assume that the polycyclic cage structure of **3a** remains intact in the $C_{60}H_6$ anion observed. Fig. 2a also shows a small peak due to C_{60} anion. Judging from the isotope distribution of the C_{60} anion, there seems to be no intermediate species between

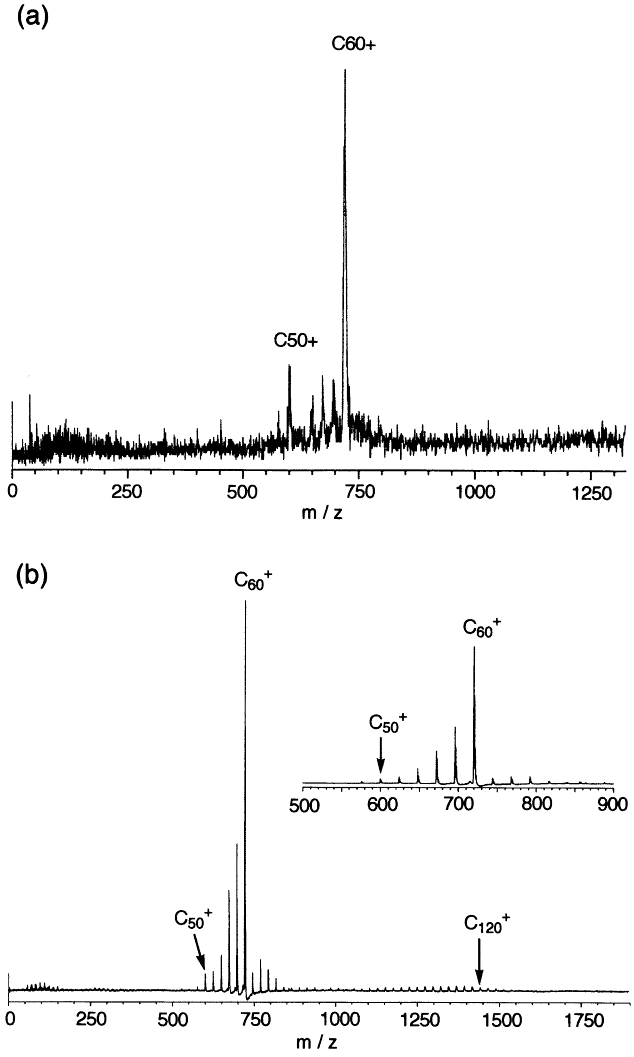


Figure 1. Positive mode laser desorption time-of-flight mass spectra of: (a) **5a** and (b) **5b**.

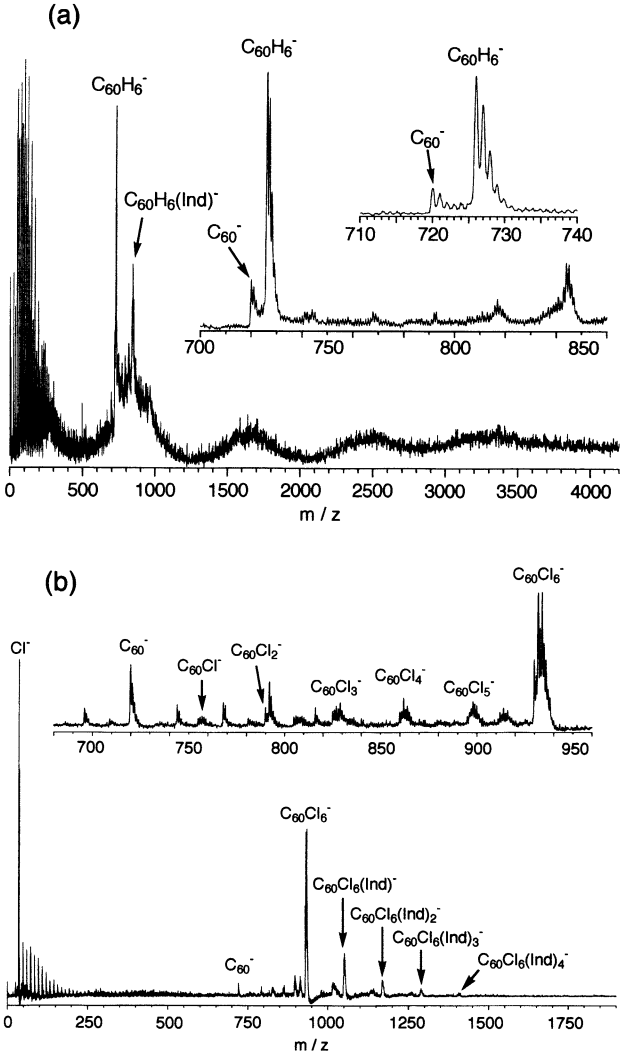
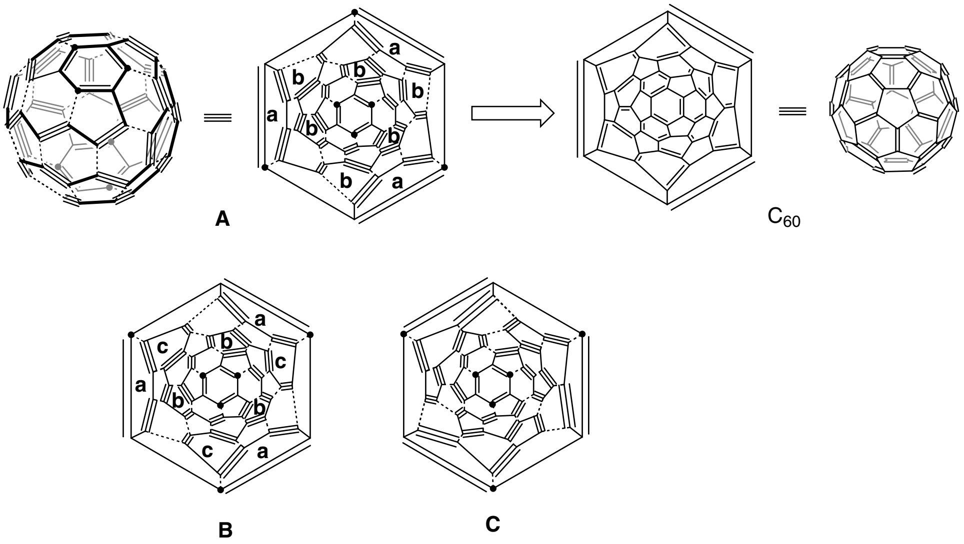


Figure 2. Negative mode laser desorption time-of-flight mass spectra of: (a) **5a** and (b) **5b**.

$C_{60}H_6^-$ and C_{60}^- like $C_{60}H_5^-$, $C_{60}H_4^-$, and so on. This means that the dehydrogenation takes place simultaneously to the drastic skeletal isomerization, leading to the formation of a fullerene-like structure. Similar results were reported by Rubin for the FT-ICR mass spectrum of a precursor having cyclobutenedione units which exhibited $C_{60}H_6^-$ and C_{60}^- more clearly than **5a**.[9]

Fig. 2b shows the negative mode LDTOF mass spectrum of **5b**. While the parent peak is not detected, the fragments from $C_{60}Cl_6(Ind)_4^-$ down to $C_{60}Cl_6^-$ are clearly seen due to the successive loss of the indane fragments. A small peak due to C_{60}^- was also detected. However, since the intermediate ions such as $C_{60}Cl_5^-$ and $C_{60}Cl_4^-$ are observed, the elimination of chlorine atoms from $C_{60}Cl_6^-$ to C_{60}^- is likely to take place stepwise, in contrast to the negative mode spectrum of **5a**. Since the bonding energy of a C–Cl bond (~3.1 eV) is lower than that of a C–H bond (~3.9 eV), the elimination of a chlorine atom takes place more easily than the case of hydrogen. It may occur even when the internal temperature of the precursory $C_{60}Cl_6$ molecule is not so high. However, the successive loss of six chlorine atoms would give an additional internal energy (~18 eV) to the molecule being able to heat it up to the temperature above ~1200 K which would be sufficiently high for the skeletal isomerization to form icosahedral C_{60}.[30]

Although there is no evidence on the mechanism of the fullerene formation from the precursors **5a** and **b** or **3a** and **b**, it is tempting to propose possible mechanisms. Taking into account the proposed mechanism of the conversion of cyclo[30]carbon into C_{60}, we can speculate a mechanism shown in Scheme 3 involving intramolecular cyclizations between the polyyne chains of **3a** and **b** to form the requisite five- and six-membered rings of the fullerene structure. The polyyne chains in the transition state geometry **A** of Scheme 3 do not seem too much constrained with regard to the bending, while the top and bottom benzene rings are twisted by 300° to each other. There are two other possible geometries **B** and **C**. Although the twist angle of the benzene rings (120°) in both **B** and **C** is smaller than that of **A**, these transition states seem to be highly strained because they have one or two small angle(s) in a polyyne chain.



Scheme 3. Schlegel diagrams **A**, **B** and **C** of the transition state geometries for possible cyclization mechanisms of three-dimensional polyynes **3a** or **b** to C_{60} fullerene. Filled circle denotes an sp^2 carbon bearing a hydrogen or chlorine atom. Lower case **a**, **b** and **c** in the hexagons indicate the six-membered rings being formed by a [4+2] transition state of butadiyne and benzene (**a**) or acetylene (**b**) and a 6π electrocyclic transition state (**c**).

In the transition state geometry **A** of Scheme 3, there are nine six-membered rings that are to be formed by formal [4+2] cycloaddition between a butadiyne fragment (4π) and a benzene or an acetylene moiety (2π) as indicated by the hexagons **a** and **b**, respectively, in the Schlegel diagram of **A**. Similarly, the geometry **B** has six [4+2] hexagons (**a** and **b**) and three 6π hexatriyne units (as indicated **c**) that would form six-membered rings by an electrocyclic reaction. It has been demonstrated by Johnson, both theoretically and experimentally, that [4+2] cycloaddition of butadiyne with ethylene or acetylene required high activation energy although the reaction was feasible.[31] These results may be related to the observation that C_{60} produced by the laser furnace method from graphite is best formed when the medium gas temperature is 700–900 K.[30] Accordingly, it is reasonable to assume that the polyyne cyclization of Scheme 3 would not occur at ambient temperature. Indeed, in contrast to the photodecomposition of **5a** by the visible light irradiation described above, photolysis of **5a** in benzene solution with a low-pressure mercury lamp at room temperature resulted in the formation of indane (ca. 50% yield by the ^1H NMR spectrum), indicating the formation of polyyne chains at least partially. However, only uncharacterized polymeric materials were obtained and no C_{60} was detected by HPLC. Though attempts to perform flash vacuum pyrolysis of **5a** were not successful so far owing to its low volatility, works in the preparative scale fragmentation of **5a** and **b** are under way.

In summary, we prepared stable precursors **5a** and **b** having [4.3.2]propellatriene units to cage polyyne $C_{60}H_6$ (**3a**) and its perchloro derivative $C_{60}Cl_6$ (**3b**) and succeeded in the observation of $C_{60}H_6^-$ and $C_{60}Cl_6^-$ in their negative mode laser desorption mass spectra. Size-selective formation of C_{60}^+ as well as C_{60}^- was also observed, particularly with remarkable clarity in the positive mode mass spectrum of **5b**, indicating the possible polyyne cyclization mechanism to form the fullerene cage. Although the preparative scale formation of C_{60} is yet to be achieved, we believe the present work marks a step forward toward designed synthesis of fullerenes.

1. Experimental

1.1. General

^1H NMR (400, 300 or 270 MHz) and ^{13}C NMR (100.5, 75 or 67.5 MHz) spectra were recorded on a JEOL JNM-AL-400, a Varian Mercury-300 or a JEOL JNM-GSX-270 spectrometer at 30°C. IR spectra were recorded as a KBr disk or a neat film on a JASCO FTIR-410 spectrometer. UV–Vis spectra were recorded on a Hitachi 220A spectrometer. EI and FAB mass spectral analyses were performed on a JEOL JMS-DX303HF spectrometer. LDTOF mass spectra were obtained on a home-built spectrometer equipped with an Nd:YAG laser (355 nm, typically 3 MW/cm^2 with a 7 ns duration).[13d] Elemental analyses were carried out with a Perkin–Elmer 2400II analyzer. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm×20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent.

1.1.1. 10-Chloro-11-[(triisopropylsilyl)ethynyl][4.3.2]-propella-2,4,10-triene (6b). A mixture of 13.1 g (50.2 mmol) of **6a**[13e] and 13.3 g (85%, 201 mmol) of powdered KOH in 600 mL of benzene was degassed by three freeze–thaw cycles. The mixture was heated at 90°C for 1 h while benzene was slowly distilled out under nitrogen. After being cooled, the mixture was diluted with water and the organic phase was separated, which was washed successively with saturated $NaHCO_3$ solution and saturated NaCl solution (brine) and dried over $MgSO_4$. Removal of the solvent followed by flash chromatography gave 9.23 g (91%) of 10-chloro-11-ethynyl[4.3.2]propella-2,4,10-triene as a colorless oil. ^1H NMR ($CDCl_3$) δ 5.76–5.96 (m, 4H), 3.15 (s, 1H), 1.93–2.02 (m, 2H), 1.34–1.67 (m, 2H), 1.15–1.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 132.2 (s), 128.5 (d), 127.3 (d), 125.1 (s), 122.7 (d), 121.7 (d), 82.4 (s), 73.3 (d), 59.5 (s), 55.7 (s), 32.1 (t), 31.5 (t), 18.4 (t); IR (neat) 3293, 2097, 1609, 1204, 1110, 1094, 938, 837, 757, 680 cm^{-1}.

To a solution of 2.76 g (13.6 mmol) of the above compound in 56 mL of THF was added 9.04 mL (15.0 mmol) of 1.66 M BuLi in hexane at 0°C. The mixture was stirred at 0°C for 3 h, then 4.81 g (15.6 mmol) of triisopropylsilyl trifluoromethanesulfonate was added dropwise. The mixture was stirred at room temperature for 30 min. Water was added and the mixture was extracted with ether. The extract was washed with saturated NaCl solution (brine) and dried over $MgSO_4$. Removal of the solvent followed by flash chromatography gave 4.87 g (99%) of **6b** as pale yellow oil. ^1H NMR ($CDCl_3$) δ 5.76–5.94 (m, 4H), 1.91–2.01 (m, 2H), 1.14–1.66 (m, 4H), 1.09 (brs, 21H); ^{13}C NMR ($CDCl_3$) δ 129.9 (s), 128.9 (d), 127.5 (d), 126.6 (s), 122.6 (d), 121.5 (d), 97.4 (s), 95.8 (s), 59.1 (s), 56.0 (s), 32.2 (t), 31.7 (t), 18.6 (q), 18.5 (t), 11.2 (d); IR (neat) 2143, 1612, 1203, 1125, 1007, 882, 839, 756, 666 cm^{-1}; EI MS *m/z* 359 (M^+). HRMS calcd for $C_{22}H_{31}ClSi$ 359.0263, found 359.0261.

1.1.2. 10-[(Triisopropylsilyl)ethynyl]-11-[(trimethylsilyl)-ethynyl][4.3.2]propella-2,4,10-triene (7a). A solution of 115 mg (300 μmol) of $Pd(PhCN)_2$, 38.1 mg (200 μmol) of CuI, and 3.59 g (10.0 mmol) of **6b** in 13 mL of THF was degassed by three freeze–thaw cycles and the flask was filled with argon. 162 mg (800 μmol) of $P(t\text{-}Bu)_3$, 1.21 g (12.0 mmol) of diisopropylamine, and 1.18 g (12.0 mmol) of (trimethylsilyl)acetylene were added in this order. The mixture was heated at reflux temperature for 8 h and at 50°C overnight. During the reaction, additional (trimethylsilyl)-acetylene (1.28 g, 13.0 mmol) was added. The mixture was diluted with water and ether and the aqueous phase was acidified with 1N HCl. The aqueous layer was separated and extracted with ether. The combined extract was washed with saturated $NaHCO_3$ solution and brine, and then dried ($MgSO_4$). The product was purified by flash chromatography, yielding 3.56 g (85%) of **7a** as a brown oil. ^1H NMR ($CDCl_3$) δ 5.81–5.86 (m, 4H), 1.88–2.00 (m, 2H), 1.39–1.63 (m, 2H), 1.07–1.34 (m, 2H), 1.08 (brs, 21H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 134.1 (s), 132.5 (s), 128.70 (d), 128.68 (d), 121.7 (d), 121.6 (d), 100.6 (s), 98.7 (s), 97.9 (s), 96.7 (s), 55.9 (s), 55.6 (s), 32.8 (t), 32.7 (t), 18.7 (t), 18.6 (q), 11.2 (d), 0.1 (q); IR (neat) 2143, 1250, 1029, 844, 670 cm^{-1}; EI MS *m/z* 421 (M^+). HRMS calcd for $C_{27}H_{40}Si_2$ 420.7856, found 420.7848.

1.1.3. 10-Ethynyl-11-[(triisopropylsilyl)ethynyl][4.3.2]-propella-2,4,10-triene (7b). To a suspension of 692 mg (5.00 mmol) of K_2CO_3 in 50 mL of MeOH was added a solution of 1.05 g (2.50 mmol) **7a** in 20 mL of THF. The mixture was stirred at room temperature for 1 h, then concentrated in vacuo to remove most of the MeOH. The mixture was diluted with ether and the extract was washed with water and brine, and dried ($MgSO_4$). Removal of the solvent followed by flash chromatography gave 834 mg (96%) of **7b** as a dark orange oil, which solidified in a refrigerator. Mp 39–40°C; ^1H NMR ($CDCl_3$) δ 5.78–5.89 (m, 4H), 3.16 (s, 1H), 1.90–2.00 (m, 2H), 1.40–1.63 (m, 2H), 1.11–1.28 (m, 2H), 1.08 (brs, 21H); ^{13}C NMR ($CDCl_3$) δ 134.8 (s), 130.9 (s), 128.5 (d), 128.4 (d), 121.9 (d), 121.8 (d), 98.24 (s), 98.20 (s), 82.2 (s), 75.9 (d), 56.2 (s), 55.5 (s), 32.7 (t), 32.6 (t), 18.7 (t), 18.6 (q), 11.2 (d); IR (KBr) 3263, 2132, 1244, 1020, 994, 882, 849, 671 cm^{-1}; EI MS *m/z* 348 (M^+). HRMS calcd for $C_{24}H_{32}Si$ 348.2273, found 348.2237.

1.1.4. 1,3,5-Tris{[11-(triisopropylsilyl)ethynyl[4.3.2]propella-2,4,10-trien-10-yl]butadiynyl}benzene (9a). To a flask filled with nitrogen containing 0.61 mg (3.2 μmol) of CuI and 3.30 mg (3.2 μmol) of $Pd_2(dba)_3\cdot CHCl_3$ was added a solution of 179 mg (0.514 mmol) of **7b** and 41 mg (0.106 mmol) of 1,3,5-tris(bromoethynyl)benzene (**8a**)[16a] in 4 mL of benzene followed by 46 mg (0.30 mmol) of 1,2,2,6,6-pentamethylpiperidine. The mixture was stirred at room temperature for 8 h, then poured into 100 mL of 1M HCl and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. A crude product obtained on the same scale was combined and purified by flash chromatography to afford 168 mg (67%) of **9a** as a yellow solid. Mp 74–75°C; ^1H NMR ($CDCl_3$) δ 7.56 and 7.53 (s, ratio 1:9, total 3H), 5.79–5.90 (m, 12H), 1.93–2.01 (m, 6H), 1.46–1.64 (m, 6H), 1.04–1.38 (brs, 63H); ^{13}C NMR ($CDCl_3$) δ 137.4 (s), 136.1 (s), 129.7 (s), 128.1 (d), 122.9 (s), 121.9 (d), 100.5 (s), 98.4 (s), 80.9 (s), 78.0 (s), 75.9 (s), 75.1 (s), 56.7 (s), 56.3 (s), 33.1 (t), 33.0 (t), 18.8 (q), 11.4 (d). Small signals with ca. one-tenth intensities are observed at 137.5 (s), 136.6 (d), 129.6 (s), 128.7 (d), 123.1 (s), 121.5 (d), 100.5 (s), 80.6 (s), 77.8 (s), 76.2 (s), 75.3 (s), 18.7 (q), 11.5 (d); IR (KBr) 2200, 2137, 2123, 1576, 1070, 1011, 881, 675 cm^{-1}; FAB MS *m/z* 1189 (M^+).

1.1.5. [4.3.2]Propellatriene-fused [16.16.16](1,3,5)cyclophaneoctadecaynehexaene (5a). To a solution of 186 mg (0.156 mmol) of **9a** in 8 mL of THF was added 134 μL (141 mg, 2.35 mmol) of acetic acid followed by 1.56 mL of 1.0 M solution of Bu_4NF in THF, and the solution was stirred at room temperature for 1 h. The mixture was diluted with water and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. In another run, to obtain an NMR sample of **9b**, the solvent was evaporated to dryness to give an oil which turned dark immediately owing to polymerization [^1H NMR ($CDCl_3$) δ 7.53 (s, 3H), 5.82–5.92 (m, 12H), 3.75 (s, 3H), 0.84–2.05 (m, 18H)].

Accordingly, the above extract was concentrated to ca. 5 mL and diluted with 5 mL of pyridine. The solvent was removed under reduced pressure again to ca. 5 mL and diluted with 80 mL of pyridine. This solution was added dropwise to a mixture of 2.83 g (15.6 mmol) of $Cu(OAc)_2$ in 210 mL of pyridine during a 5.5-h period. During the reaction and subsequent isolation procedures, the flasks and chromatography columns were covered with an aluminum foil to protect the product **5a** from room light, otherwise it readily changed into yet unidentified materials. After being stirred at room temperature for 19 h, the mixture was filtered through a short column of silica gel and the solvent was removed under reduced pressure. The product was purified by flash chromatography to give 78 mg (70%) of **5a** as a bright yellow solid. Dec. >140°C; ^1H NMR ($CDCl_3$) δ 7.49 (brm, 6H), 5.90 (brd, J=10.2 Hz, 12H), 5.81 (brd, J=7.8 Hz, 12H), 1.97–2.17 (m, 12H), 1.58–1.67 (m, 6H), 1.40–1.53 (m, 6H), 1.19–1.30 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 136.2 (d, smaller signals observed at

136.3 and 136.1), 135.2 (s, a small signal observed at 135.1), 127.6 (d, a signal with similar intensity observed at 127.7), 122.69 (s, smaller signals observed at 122.74, 122.71, 122.66, and 122.64), 122.2 (d, broad), 82.06 (s, smaller signals observed at 82.10, 82.03, 82.01), 80.4 (s), 80.0 (s), 77.1 (s), 75.47 (s, signals with similar intensities observed at 75.48 and 75.44, and smaller signals observed at 75.52 and 75.41), 74.6 (s), 56.8 (s, a smaller signal observed at 56.9), 33.1 (t), 18.8 (t); IR (KBr) 2200, 2163, 2127, 1572, 1375, 1244, 1078, 877, 738, 677 cm^{-1}; UV–Vis ($CHCl_3$) $\lambda_{\max}$ (log ϵ) 426 (4.65), 391 (4.78), 363 (4.71), 281 (5.24) nm; FAB MS *m/z* 1435 (M^+).

1.1.6. 1,3,5-Trichloro-2,4,6-tris[(trimethylsilyl)ethynyl]-benzene (8b). To a degassed solution of 11.2 g (20.0 mmol) of 1,3,5-trichloro-2,4,6-triiodobenzene,[25] 2.08 mg (1.80 mmol) of $Pd(PPh_3)_4$, and 686 mg (3.60 mmol) of CuI in 80 mL of THF was added under argon atmosphere 7.29 g (72.0 mmol) of diisopropylamine followed by 8.84 g (90.0 mmol) of (trimethylsilyl)acetylene, and the mixture was heated under reflux for 30 h. During the reaction additional (trimethylsilyl)acetylene (total 295 mg, 3.00 mmol) was added occasionally. Then the mixture was diluted with 1N HCl and ether, and the organic layer was separated. The aqueous layer was extracted with ether and the combined extract was washed with saturated $NaHCO_3$ solution and brine, and dried over $MgSO_4$. After removal of the solvent, the product was isolated by flash chromatography followed by recrystallization from hexane (and preparative HPLC for the mother liquor after several recrystallizations) to give 5.79 g (62%) of **8b** as a white solid. Mp 155–156°C; ^{1}H NMR ($CDCl_3$) δ 0.29 (s); ^{13}C NMR ($CDCl_3$) δ 138.9 (s), 122.6 (s), 107.9 (s), 97.2 (s), −0.23 (q); IR (KBr) 2168, 1251, 1069, 1035, 857, 758 cm^{-1}; EI MS *m/z* 472, 470, 468 (rel. intensity ca. 1:2:2, M^+).

1.1.7. 1,3,5-Trichloro-2,4,6-tris(bromoethynyl)benzene (8c). To a solution of 266 mg (0.570 mmol) of **8b** in 11 mL of acetone was added 354 mg (1.99 mmol) of NBS followed by 29 mg (0.17 mmol) of silver (I) nitrate and the mixture was stirred at room temperature for 10 h. During the reaction, the reaction flask was protected from light by wrapping with an aluminum foil. The same reaction was undertaken in another run, and the reaction mixture was combined and worked up as follows. The mixture was diluted with water and benzene, and the organic layer was washed with water and brine, and then dried ($MgSO_4$). Removal of the solvent in vacuo left a yellow solid which was recrystallized from benzene to give 430 mg (67%) of **8c** as a colorless solid. Dec. >167°C; No signal in ^{1}H NMR; ^{13}C NMR (benzene-d_6) δ 140.3 (s), 122.7 (s), 74.0 (s), 63.6 (s); IR (KBr) 2201, 1381, 1365, 1053, 788 cm^{-1}; EI MS *m/z* (rel. intensity) 496–486 (the most abundant peak at 490, M^+).

1.1.8. 1,3,5-Trichloro-2,4,6-tris[(11-ethynyl[4.3.2]propella-2,4,10-trien-10-yl)butadiynyl]benzene (9c). Hetero coupling of 194 mg (0.40 mmol) of **8c** with 628 mg (1.80 mmol) of **7b** was carried out as described for the preparation of **9b** using 124 mg (0.12 mmol) of $Pd_2(dba)_3{\cdot}CHCl_3$, 22 mg (0.12 mmol) of copper (I) iodide, and 174 mg (1.12 mmol) of 1,2,2,6,6-pentamethylpiperidine in 8 mL of benzene. The product was isolated by flash chromatography to afford 200 mg (39%) of **9c** as a dark yellow solid. Mp 96–97°C; ^{1}H NMR ($CDCl_3$) δ 5.78–5.92 (m, 12H), 1.93–2.05 (m, 6H), 1.40–1.68 (m, 6H), 1.21–1.33 (m, 6H), 1.09 (brs, 63H); ^{13}C NMR ($CDCl_3$) δ 140.9 (s), 138.6 (s), 129.5 (s), 128.11 (d), 128.06 (d), 122.2 (s), 122.01 (d), 121.99 (d), 101.3 (s), 98.5 (s), 85.2 (s), 78.3 (s), 75.4 (s), 56.9 (s), 56.3 (s), 33.1 (t), 32.9 (t), 18.9 (t), 18.7 (q), 11.3 (d); IR (KBr) 2197, 2137, 1290, 1072, 882, 841, 774, 672 cm^{-1}.

1.1.9. [4.3.2]Propellatriene-fused hexachloro[16.16.16]-(1,3,5)cyclophaneoctadecaynehexaene (5b). Deprotection of 259 mg (200 μmol) of **9c** was undertaken as described for the case of **9a** using 180 mg (3.00 mmol) of acetic acid and 2.00 mL (2.00 mmol) of 1.0 M THF solution of Bu_4NF in 10 mL of THF. The mixture was extracted with benzene, the organic phase was washed with saturated $NaHCO_3$ solution and brine, and dried over $MgSO_4$. The solution was concentrated to 100 mL by evaporation and was used in the subsequent reaction.

To a solution of 3.63 g (20.0 mmol) of $Cu(OAc)_2$ in 300 mL of pyridine was added dropwise the above solution during a 21-h period. The mixture was worked up as in the case of **5a**, except for the fact that final purification was carried out by preparative HPLC, to give 100 mg (61%) of **5b** as a bright yellow solid. *Caution!* A sample of this compound decomposed violently, catching fire when it was scratched with a spatula. Mp 96–97°C; ^{1}H NMR ($CDCl_3$) δ 5.89–5.92 (m, 12H), 5.81–5.83 (m, 12H), 1.97–2.17 (m, 12H), 1.58–1.67 (m, 6H), 1.40–4.53 (m, 6H), 1.19–1.30 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 141.5 (s), 135.9 (s), 134.8 (s), 127.8 (d), 122.8 (d), 122.5 (s), 122.2 (s), 84.9 (s), 80.9 (s), 79.6 (s), 77.9 (s), 77.3 (s), 57.2 (s), 57.1 (s), 33.2 (t), 29.4 (t), 18.8 (t); FAB MS *m/z* 1650–1638 (the most abundant peak at 1642, M^+).

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