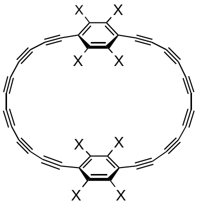
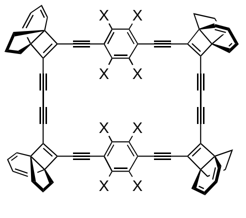
[12.12]Paracyclophanedodecaynes $C_{36}H_8$ and $C_{36}Cl_8$: The Smallest Paracyclophynes and Their Transformation into the Carbon Cluster Ion C_{36}^-**

Yoshito Tobe,* Ryutaro Furukawa, Motohiro Sonoda, and Tomonari Wakabayashi

Carbon clusters with magic numbers such as C_{20} and C_{36} have fullerene structures when they are produced from appropriate precursors or by vaporization of carbon materials under specific conditions. Thus the C_{20} fullerene cation was produced selectively by field evaporation of carbon nanotubes[1] and the positive and negative ions, C_{20}^+ and C_{20}^-, were formed by debromination of polybrominated dodecahedrane under mass spectrometric conditions.[2] A cage structure was characterized by photoelectron spectroscopy for the negative ion.[2] On the other hand, there remains controversy regarding the structure of C_{36}; C_{36} formed by arc discharge of graphite exists as a polymeric form with D_{6h} symmetry in solid state,[3] while high-temperature laser ablation of metal-doped graphite resulted in the isolation of $C_{36}H_6$.[4] However, no attempt has been made so far to produce C_{36} from an appropriate organic precursor. We and Rubin and co-workers have found independently that macrocyclic polyyne $C_{60}H_6$ formed C_{60} fullerene ions under mass spectrometric conditions, presumably by cyclization of the polyyne chain in an analogous manner to the mechanism proposed for fullerene formation from small carbon clusters.[5, 6] We envisaged that a similar cyclization of polyyne-bridged paracyclophane **1a** and subsequent dehydrogenation would give D_{6h}-symmetric C_{36}. In addition, the key intermediate **1a** is of substantial interest as a member of the highly unsaturated, alkyne-bridged paracyclophanes coined cyclophynes.[7, 8] In view of the fact that the smaller [8.8]paracyclophyne was elusive,[7] **1a** was expected to be too reactive for isolation, although the strain imposed on each sp carbon must be minimal (bending angle slightly larger than 10°).[9] It may, on the other hand, be capable of existence at low temperature in an inert atmosphere. We planned to generate **1a** from precursor **2a**, which contains [4.3.2]propellatriene units, by [2+2] cycloreversion of the cyclobutene ring, the method we have employed in generation of highly reactive polyynes such as cyclocarbons[10] and the C_{60} precursors.[5] Herein we report the synthesis of **2a** and its octachloro derivative **2b**, studies on the photolysis of **2a**, and generation of anions of **1a** ($C_{36}H_8^-$) and **1b** ($C_{36}Cl_8^-$) and subsequent formation of C_{36}^- under mass spectrometric conditions.

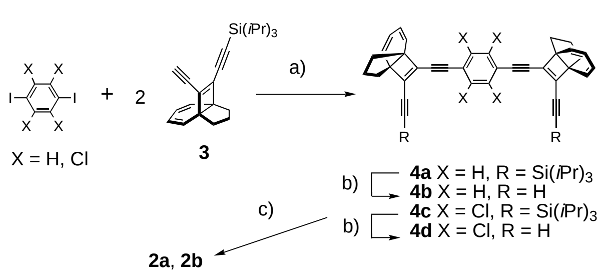


1a X = H
1b X = Cl



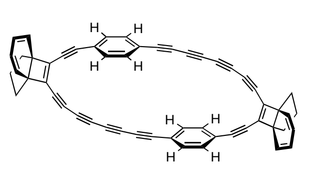
2a X = H
2b X = Cl

Palladium-catalyzed coupling of propellanediyne **3**[5] with 1,4-diiodobenzene gave **4a** (Scheme 1).[11] After removal of the protecting group of **4a**, the resulting compound **4b** was subjected to oxidative coupling under high dilution conditions to yield **2a** in good yield. Similarly, **2b** was prepared from **3** and 1,2,4,5-tetrachloro-3,6-diiodobenzene via **4c** and **4d**.



Scheme 1. a) For **4a**, $[Pd(PPh_3)_4]$, CuI, $(iPr)_2NH$, THF, RT, 93 %; for **4c**, $[Pd_2(dba)_3]\cdot CHCl_3$, CuI, PPh_3, Et_3N, 90 °C, 65 %; b) Bu_4NF, AcOH, THF, RT; c) $Cu(OAc)_2$, pyridine, RT, 79 % for **2a**, 75 % for **2b**. dba = *trans,trans*-dibenzylideneacetone.

When a solution of **2a** in $[D_8]$THF was irradiated with a low-pressure mercury lamp at 0 °C, indan was formed quantitatively as judged by the integration of its aromatic protons relative to the residual proton of THF. However, the aromatic protons of **2a** became small, broad signals, indicating that the products formed by [2+2] cycloreversion were intractable polymeric materials.[12] The photolysis was then carried out in furan with the aim of intercepting the reactive intermediates as Diels–Alder adducts of furan.[10] To our surprise, however, the major product **5**, isolated in 18 % yield as a labile orange solid, did not possess furan unit(s). The structure of **5**, which lost two opposite indan fragments from **2a**, was elucidated on the basis of the spectroscopic properties.[13] The alternative possibility **6** was excluded on stability grounds.[14] The effect of furan which allowed the isolation of **5** only in its presence is not clear yet, although **5** was detected as



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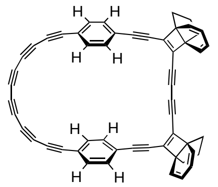

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one of products in the photolysis of **2a** in THF. At present, it appears that polyyne **5** is not strained enough to react thermally with furan.

Irradiation of **2a** at 77 K in a matrix, composed of 2-methyltetrahydrofuran and ethanol (6/1, v/v), resulted in a remarkable change in the absorption band at 350–420 nm (Figure 1), together with the monotonic increase of the absorption band of indan at 258–280 nm. The new absorption band at 350–420 nm did not change after irradiation for 24 h, but it was completely lost when the matrix was thawed by warming to room temperature and then refreezed (77 K). Subtracting the spectrum recorded after the thaw/refreeze cycle from that measured before the thaw leaves absorption maxima at 408, 379 and 367 nm (dotted line g in Figure 1). We attribute the absorption of this highly reactive species to cyclophyne **1a**, although additional evidence is needed for its full characterization.

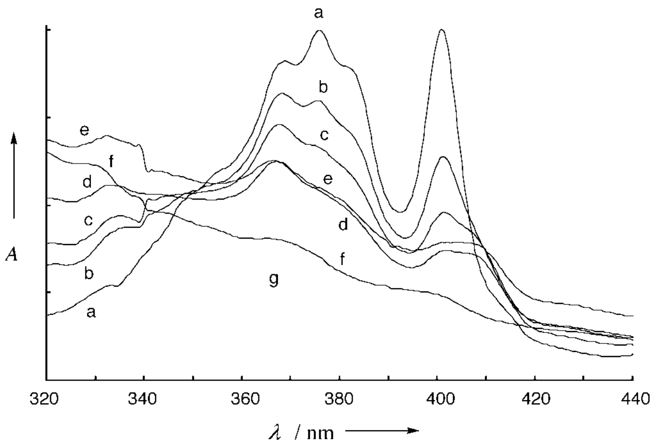

Figure 1. UV/Vis spectral changes for **1a** in a 2-methyltetrahydrofuran/ethanol (6:1) matrix at 77 K by irradiation with a low-pressure mercury lamp. a) before irradiation; b–e) after irradiation for 1, 3, 13, and 24 h, respectively; f) after irradiation for 24 h followed by thaw and refreeze; g) subtraction of line f from line e.

To generate the cyclophyne ions in the gas phase and to examine the possibility of their transformation into the carbon cluster C_{36}, laser-desorption time-of-flight mass spectra of **2a** and **2b** were measured. Figure 2a and 2b show the negative-mode mass spectra of **2a** and **2b**, respectively. As shown in Figure 2a, [2+2] cycloreversion of **2a** took place cleanly to form cyclophyne anion $C_{36}H_8^-$. However, in contrast to the case of $C_{60}H_6^-$,[5, 6] subsequent dehydrogenation leading to C_{36}^- was not observed. This can be ascribed to the difficulty of the structural rearrangement that would accompany the dehydrogenation for thermodynamic (C_{36} not as stable as C_{60}) and kinetic (the polyyne chains of **1a** located at para positions) reasons. By contrast, the mass spectrum of **2b**, which contains weaker C–Cl bonds, exhibits not only the peak of **1b** ($C_{36}Cl_8^-$) but also the peaks due to the stepwise loss of chlorine atoms down to C_{36}^- (Figure 2b), in analogy with the degradation of $C_{60}Cl_6^-$.[5b] Since the intensity of the C_{36}^- signal is considerably larger than those of $C_{36}Cl^-$, $C_{36}Cl_2^-$, and $C_{36}Cl_3^-$, we assume that the dechlorination is accompanied by a drastic skeletal change leading to possibly D_{6h}-symmetric C_{36}^-. Further work is in progress to confirm this by ultraviolet photoelectron spectroscopy.

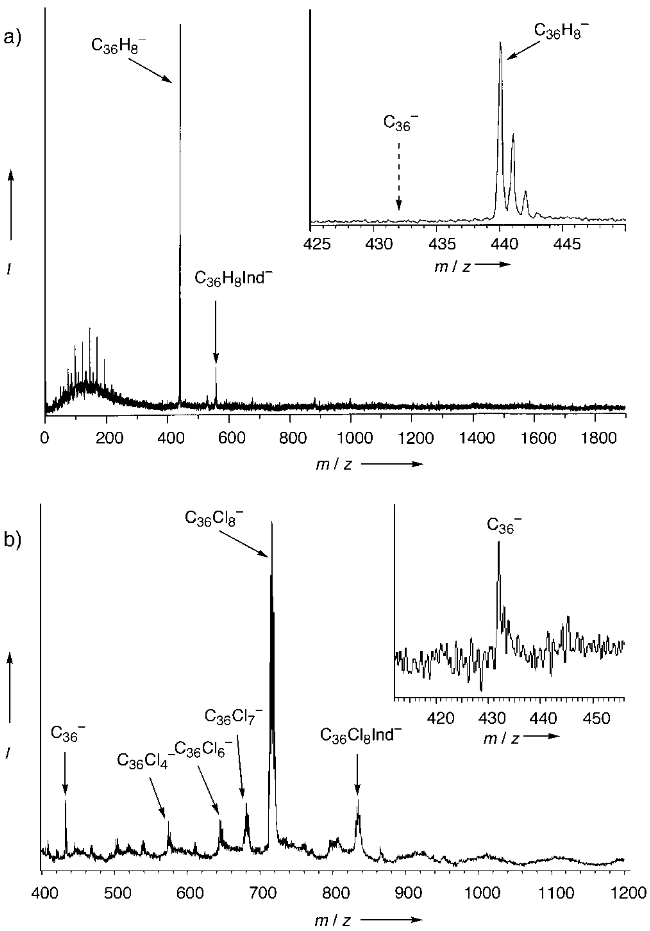

Figure 2. Laser-desorption time-of-flight mass spectra of a) **2a** and b) **2b** (Ind = indan). The compounds were dissolved in liquid parafin as a matrix. For simultaneous desorption and ionization, the third harmonic of a Nd:YAG laser (355 nm) was focused on an area of 3 mm^2.

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[9] The bond angles of the sp carbon atoms estimated from semiempirical AM1 calculations for the model compound of **1a**, in which the propellane units are substituted by cyclobutene, are 167.3–168.2°.

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[11] Compounds **2a**, **b**, **4a–d**, and **5** were obtained as mixtures of diastereomers, which were not separated, due to orientation of the propellane units. Only one of the isomers is drawn for each of the structures.

[12] Monitoring the reaction with HPLC showed several peaks during the initial stage of the photolysis, which then disappeared after prolonged irradiation, finally leaving only the peak of indan.

[13] The ^{1}H NMR spectrum exhibits an AA′BB′ pattern for the aromatic protons with the same integration value as that of the protons of the propelladiene unit. The ^{13}C NMR spectrum displays two signals for tertiary aromatic carbon atoms and ten signals for sp carbon atoms. The UV/Vis spectrum exhibits a few absorption maxima in the long wavelength region (λ_{max} (CHCl$_3$) 426 (ε 15000), 397 (50000), and 368 (90000) nm) which are reminiscent of those of the diphenyloctatetrayne chromophore (λ_{max} (CH$_2$Cl$_2$) 415 (ε 18600), 381 (33400), and 353 (43800) nm: M. M. Haley, M. L. Bell, S. C. Brand, D. B. Kimball, J. J. Pak, W. B. Wan, *Tetrahedron Lett.* **1997**, *38*, 7483). Finally, the mass spectrum exhibits a peak at m/z 677 [M^++1], which is attributed to the molecular ion of **5**. See Supporting Information for details.

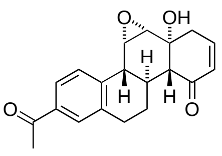
[14] The ΔH°_f values (AM1) for the model compounds of **5** and **6**, in which the propellane units are substituted by cyclobutene, are 660 and 675 kcal mol^{-1} and their bond angles around the sp carbon atoms are 173.1–173.7° and 164.1–170.2°, respectively.

The Zipper-Mode Domino Intramolecular Diels–Alder Reaction: A New 0→ABCD Strategy for Steroids and Related Compounds**

Marck Nörret and Michael S. Sherburn*

In the push towards more efficient syntheses of organic molecules, processes which lead to a rapid increase in structural complexity are playing an increasingly important role.[1] Multiple bond-forming processes involving parallel transformations (e.g. two-directional synthesis,[2] the generation of libraries of compounds) or sequential transformations[3] (e.g. domino reactions, multiple component couplings) are often utilized to achieve this goal.

Herein we report an efficient strategy for the one-step stereoselective synthesis of tetracycles of the perhydrochrysene class (i.e. D-homosteroid)—found in many biologically active naturally products such as the nicandrenones (e.g. NIC-10 **1**)[4] and scalarane sesterterpenes (e.g. scalarenedial **2**)[5]—from a simple and readily prepared acyclic precursor. This unprecedented domino sequence generates four rings, four C–C bonds, and eight contiguous stereocenters in a single operation and, as such, represents a new 0→ABCD strategy for the synthesis of steroids and related compounds.[6, 7]



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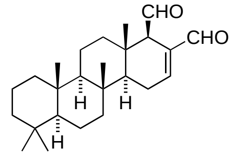

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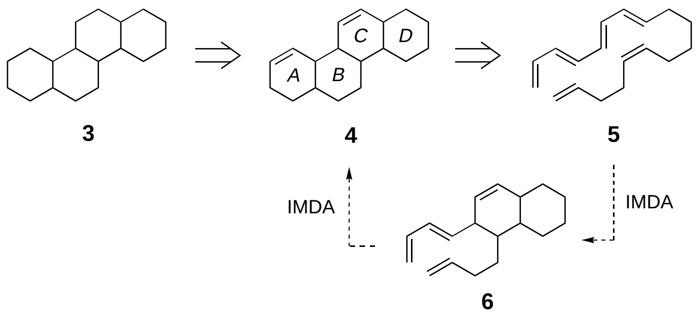
The essence of our approach is depicted in Scheme 1. Retrosynthetic introduction of disubstituted alkenes into the A and C rings of saturated tetracycle **3** permits the implementation of two intramolecular Diels–Alder (IMDA) transforms.[8–10] Thus, the tetracyclic diene **4** is retrosynthetically unzipped[11] to furnish simple acyclic precursor **5**, carrying a linearly conjugated tetraene (the bis-diene) tethered to an internal dienophile which, in turn, is tethered to a second, terminal dienophile.



Scheme 1. The domino zipper-mode IMDA reaction of hexaenes **5** to fused tetracycles **4**.

For a successful realization of the synthetic transformation of an acyclic hexaene **5** into a tetracycle such as **4**, a regioselective intramolecular cycloaddition of the more proximate, internal diene-internal dienophile pair must occur first (i.e. **5**→**6**). The bicyclic system thus formed has pendant diene and dienophile "arms" attached to neighboring ring atoms which must come together for the second IMDA reaction to ensue (ie. **6**→**4**). Inspection of molecular models reveals that cycloaddition transition states are readily adoptable for both of the expected diastereomers of bicyclic intermediate **6**.

We were concerned with the potential for generating many stereoisomers of tetracycle **4**. The parent 1,3,9-decatriene, for example, undergoes an unselective IMDA reaction at 250 °C (*cis*:*trans*-fused product ratio = 53:47).[12] Clearly, the judicious incorporation of functionality into unsubstituted system **5** was the key to obtaining stereocontrol in this domino reaction. Thus, we elected to prepare hexaene **12** to test this concept since both dienophile moieties of **12** carry activating groups which were anticipated to lead to facile and stereoselective IMDA reactions.[8]

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