[2 + 2] Cycloreversion of [4.3.2]Propella-1,3,11-trienes: An Approach to Cyclo[n]carbons from Propellane-Annelated Dehydro[n]annulenes

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Abstract: As a method to generate all-carbon molecules having highly reactive polyyne units from stable precursors, the [2 + 2] cycloreversion of [4.3.2]propella-1,3,11-triene derivatives was developed. To test the efficiency of this method, the reaction was first applied to simple diethynyl- and dibutadiynyl-substituted propellatrienes, which produced upon UV-irradiation linear hexatriyne and decapentayne derivatives, respectively. Next, dehydro[12]-, [16]-, [18]-, [20]-, and [24]annulene derivatives annelated by the [4.3.2]propellatriene units were prepared as precursors to the corresponding cyclo[n]carbons, a monocyclic form of carbon clusters. Laser-desorption mass spectra of the dehydroannulenes exhibited, in the negative mode, peaks due to the corresponding cyclo[n]carbon anions (n = 12, 16, 18, 20, and 24) formed by successive losses of aromatic indane fragments. Solution photolysis of the dehydro[16]annulene and dehydro[18]annulene derivatives formed reactive polyyne intermediates by [2 + 2] cycloreversion which were intercepted by furan to give the corresponding Diels−Alder adducts. The structures and spectroscopic properties of the dehydroannulenes annelated by the [4.3.2]propellatriene units, the precursors to cyclo[n]carbons, and those annelated by the oxanorbornadiene units, the products of the photolysis in furan, are discussed.

Introduction

There has been a long-standing interest in small carbon clusters (C_n: n < 10) in the fields of spectroscopy and theoretical chemistry in conjunction with the possible astrophysical significance of these species.[1] While extensive theoretical as well as spectroscopic studies have been carried out for the carbon clusters smaller than C_{10}, little was known for those having larger carbon atoms. However, with the discovery of the fullerene C_{60} as an unusually stable cluster[2] and its production in macroscopic quantities,[3] increasing interest has been focused on large carbon clusters in connection with the mechanism of fullerene formation. On the basis of the ultraviolet photoelectron spectroscopy[4] of carbon cluster anions and the mass chromatographic behavior[5] of cations generated by laser vaporization of graphite, it has been demonstrated that the

structures of carbon clusters are dependent on the number of carbon atoms.[6] The clusters smaller than C_9 are linear, those with the relatively narrow size regime of $C_{10}-C_{24}$ are believed to exist in the form of monocyclic rings. With increasing number of carbon atoms, bicyclic, tricyclic, and polycyclic structures become more abundant. Three-dimensional cage structures emerge from C_{30}, which become dominant with clusters larger than C_{60}.

Among the various forms of carbon clusters, monocyclic clusters, called cyclo[n]carbons, have been of exceptional interest from many points of view, ranging from spectroscopy and theoretical chemistry to synthetic organic chemistry, for the following several reasons, owing to their unique structure composed of two sets of cyclic arrays of p-orbitals, which are perpendicular to each other.[7] First, in the carbon cluster chemistry, little has been done for the larger clusters having monocyclic ring form, while extensive studies have been undertaken for the spectroscopic determination of the structures of linear carbon clusters with the carbon number smaller than ten.[1] Although the cyclic structure has been indicated by UPS[4]

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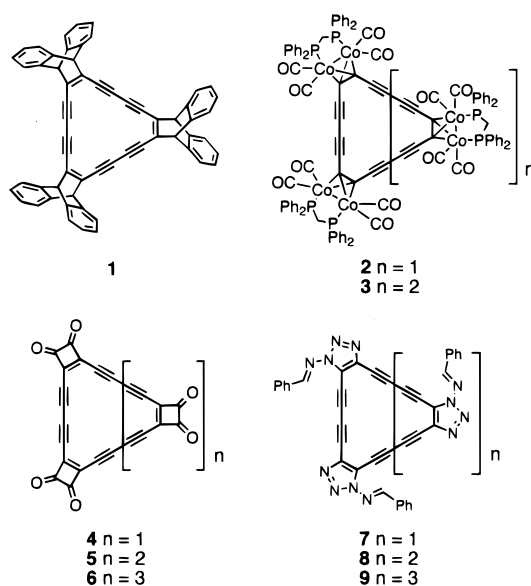
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and mass chromatographic investigations,[5] detailed geometrical, electronic, and vibrational information has not yet been obtained. Second, it is becoming more and more likely that monocyclic carbon clusters play a key role during the early stages of the mechanism,[8] although the mechanism of the fullerene formation has not been clarified. Namely, ample experimental[9] and theoretical[10] evidence has been accumulating which suggests that carbon nucleation occurs through coalescence of medium-sized carbon clusters, rather than sequential addition of small pieces such as C_2 and C_3, which is followed by annealing to form cage structures. Third, it is quite natural, from the viewpoint of organic chemistry, to ask whether the Hückel rule is valid for this class of novel π-systems composed of two sets of cyclic arrays of p-orbitals, which are perpendicular to each other.[11] In this respect, a number of theoretical calculations have been undertaken, but there still remains a controversy regarding the most stable geometries of cyclo[n]carbons with $4n + 2\pi$ electrons, particularly for cyclo[18]carbon.[12] Finally, Sarre reported recently, on the basis of the analysis of the ultrahigh-resolution absorption spectra of diffuse interstellar bands at 6614 and 5797 Å and the molecular rotational contour calculations, that large carbon ring molecules (i.e., cyclo[n]carbons) having planar oblate symmetric structures are good candidates for the carriers of these bands.[13]

It is, therefore, extremely important to synthesize and determine the molecular structures of cyclo[n]carbons by spectroscopic methods. In this context, a number of investigations have been undertaken to synthesize cyclo[n]carbons from organic precursors having dehydroannulene frameworks. A pioneering project to synthesize cyclo[n]carbons from organic precursors having the desired macrocyclic carbon framework was initiated by the Diederich's group more than a decade ago. The first precursor was dodecadehydro[18]annulene **1** fused by three dibenzobicyclo[2.2.2]octatriene units, from which elimination of three molecules of anthracene in a retro-Diels−Alder sense would generate cyclo[18]carbon.[14] The formation of C_{18} was indeed observed in the laser-desorption time-of-flight (LD-TOF) mass spectra of **1**. However, attempts to prepare macroscopic quantities of C_{18} by flash vacuum pyrolysis did not give C_{18}, and only anthracene and polymeric material were obtained. The second type of precursor is represented by the stable dinuclear cobalt complexes **2** and **3**, which can be regarded as transition metal complexes of C_{18} and C_{24}, respectively.[14b,15] Attempted decomplexation of **2** and **3** to give the corresponding cyclocarbons was unsuccessful. The third type of molecule is exemplified by dehydroannulenes **4**, **5**, and **6** annelated with cyclobutenedione units, which would produce C_{18}, C_{24}, and C_{30}, respectively, by multistep decarbonylation.[9d,14b,16] The formation

of C_{18}, C_{24}, and C_{30} ions was observed both in the positive and negative modes of the LD Fourier transform (FT) mass spectra of the respective precursors **4**−**6** together with the intermediate ions formed by the successive losses of carbon monoxide. It should be pointed out that, depending on the desorption conditions, C_{70}^+ was formed by the gas-phase ion molecule reaction of C_{18} and C_{24} (tetramerization or trimerization followed by loss of C_2) from **4** and **5**, respectively. More interestingly, C_{60}^+, which proved to possess the fullerene structure, was formed predominantly by coalescence (dimerization) between C_{30}^+ and C_{30} derived from the precursor **6**. A notable advantage of these carbon oxides is the fact that decarbonylation can, in principle, be carried out photochemically in rigid matrices at low temperatures to detect highly reactive cyclocarbons by spectroscopic methods. Indeed, irradiation of **4** isolated in a low-temperature matrix resulted in the formation of ketene intermediates which were characterized by the IR absorption at 2115 cm^{-1}.[14b] While subsequent loss of carbon monoxide took place as judged from the appearance of the absorption of CO at 2138 cm^{-1}, definite spectroscopic evidence for the formation of cyclo-[18]carbon has not been obtained. Rees planned to use the oxidative degradation of the 1-amino-1,2,3-triazole group to produce the triple bonds of cyclocarbons and prepared *N*-benzylidene-protected aminotriazole derivatives **7**−**9** as precursors to cyclocarbons C_{18}, C_{24}, and C_{30}.[17] However, attempts to remove the benzylidene protective group from **7** were not successful.

We planned to utilize the fragmentation of [4.3.2]propella-1,3,11-triene derivatives in a retro [2 + 2] sense ([2 + 2] cycloreversion) to generate highly reactive carbon−carbon triple bonds such as those involved in cyclo[n]carbons from appropriate precursors as shown in Scheme 1. The [2 + 2] cycloreversion of cyclobutane derivatives to generate a carbon−carbon double bond has been frequently utilized with success to produce highly unstable molecules such as cyclobutadiene.[18] The corresponding reaction of a cyclobutene derivative would form a carbon−carbon triple bond, but in this case electrocyclic ring-opening leading to a buta-1,3-diene would take place in competition with

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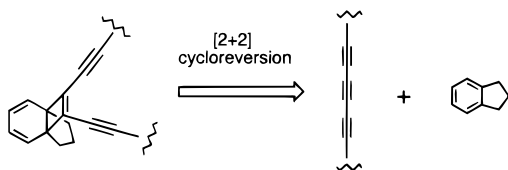
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Scheme 1

the desired cycloreversion.[19] This undesired reaction pathway can be suppressed by geometrical constraints. Namely, Paquette reported, as part of his extensive investigations in propellane chemistry, that photolysis of [4.4.2]propellapentaene **10a** and the corresponding triene **10b** takes place smoothly, leading to the formation of naphthalene and tetrahydronaphthalene, respectively, together with ethyne (not detected).[20] On the basis of our knowledge that [4.3.2]propellane derivatives can be readily prepared by means of [2 + 2] photocycloaddition of bicyclo[4.3.0]non-1(6)-en-2-one (**11**) to alkenes and alkynes,[21] we chose the [4.3.2]propellatriene system as the key structural element as shown in Scheme 1. Accordingly, we designed dehydro[12]-, [16]-, [18]-, [20]-, and [24]annulene derivatives **12**−**16** annelated by [4.3.2]propellatriene units as the precursors to the cyclo[*n*]carbons where *n* = 12, 16, 20, 18, and 24, respectively. In view of the presence of diastereomers in **12**−**16**, it was more desirable to prepare symmetric precursors composed of [4.4.2]propellapentaene unit like **10a**. However, we anticipated that the preparation of a building block such as diethynyl[4.3.2]propellatriene **17c** would be much easier than that of the corresponding [4.4.2] congener.[20]

10a   **10b**   **11**

12 n = 1
13 n = 2
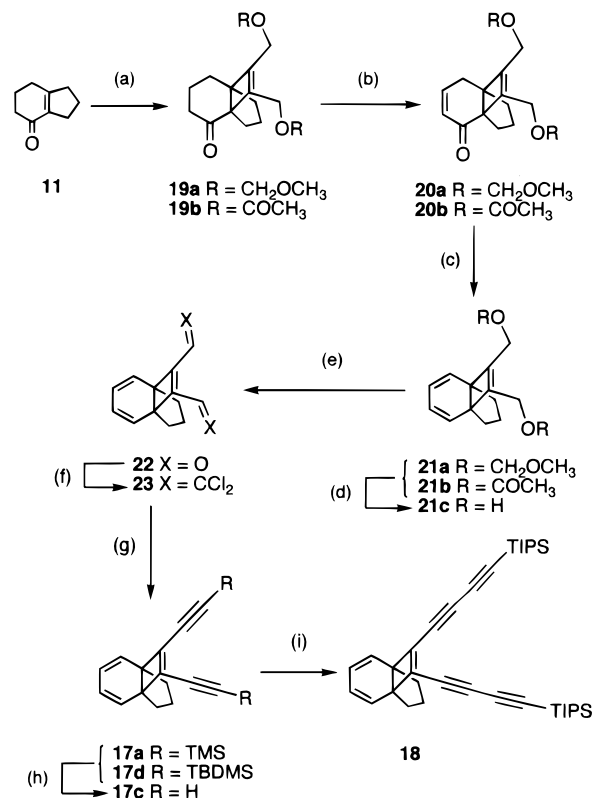**14** n = 3

15 n = 1
16 n = 2
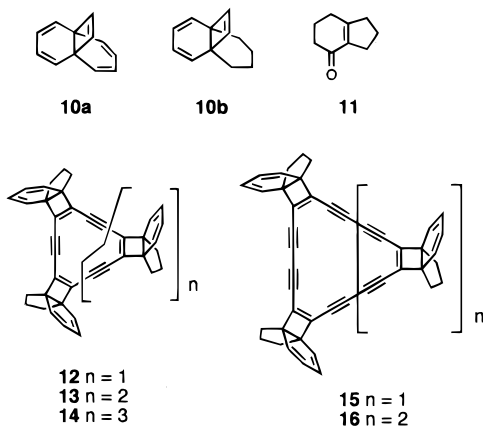
In this paper, we report the model study of the photochemical [2 + 2] fragmentation of simple 11,12-dialkynylated [4.3.2]-propellatriene derivatives **17a**, **17b**, and **18**, the synthesis and spectral properties of dehydro[12]-, [16]-, [18]-, [20]-, and [24]-annulene derivatives **12**−**16** annelated by [4.3.2]propellatriene units, and their fragmentation in the laser-desorption mass spectra and by ultraviolet irradiation.[22] The spectroscopic characterization and structural assignment of thus produced cyclo[*n*]carbon anions (*n* = 12, 16, 18, 20, 24) by ultraviolet

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Scheme 2[a]

11

19a R = CH$_2$OCH$_3$
19b R = COCH$_3$

20a R = CH$_2$OCH$_3$
20b R = COCH$_3$

22 X = O
23 X = CCl$_2$

21a R = CH$_2$OCH$_3$
21b R = COCH$_3$
21c R = H

17a R = TMS
17d R = TBDMS
17c R = H

18

[a] (a) For **19a**: 1,4-bis(methoxymethyl)-2-butyne, *hν*; for **19b**: 1,4-diacetoxy-2-butyne, *hν*. (b) for **20a**: i, TMSOTf, Et$_3$N; ii, Pd(OAc)$_2$; for **20b**: i, 5,5-dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione; ii, LiCl, Li$_2$CO$_3$. (c) i, NaBH$_4$, CeCl$_3$·7H$_2$O; ii, (2,4-dinitrophenyl)sulfenyl chloride. (d) for **21a**: HCl; for **21b**: NaOH. (e) MnO$_2$. (f) diethyl trichloromethylphosphonate, BuLi, −100 °C. (g) BuLi, TMSCl (for **17a**) or TBDMSCl (for **17b**). (h) Bu$_4$NF or LiOH·H$_2$O. (i) BrC≡CTIPS, CuCl, NH$_4$OH·HCl, aqueous EtNH$_2$.

photoelectron spectra have been reported elsewhere.[23] In addition, the structures and spectroscopic properties of the dehydroannulenes annelated by the [4.3.2]propellatriene units and/or oxanorbornadiene units are discussed.

Results and Discussion

Model Study for [2 + 2] Cycloreversion. Although the cycloreversion takes place exclusively in the simple systems **10a** and **10b**, it is expected that skeletal isomerization, well-known as di-*π*-methane rearrangement,[24] would take place in competition with the [2 + 2] cycloreversion, particularly when the desired pathway is hindered by strain. Accordingly, to test whether the cycloreversion pathway predominates in extensively conjugated *π* systems, we started with the model systems which would produce linear polyynes before investigating the carbon ring synthesis. Toward this end, diethynylpropellatrienes **17a**−**17c** were prepared according to the synthetic pathways shown in Scheme 2. Namely, photocycloaddition of enone **11**[25] with

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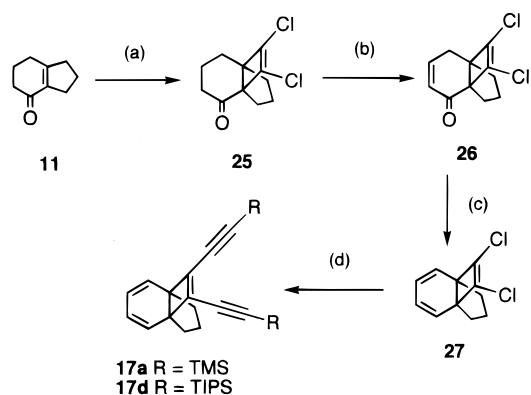
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1,4-bis(methoxymethyl)-2-butyne[26] gave cycloadduct **19a** which was oxidized to dienone **20a** through the silyl enol ether[27] and then transformed into propellatriene **21a** using the protocol of Reich et al.[28] Deprotection of the MOM group afforded diol **21c** which was oxidized by MnO$_2$ to give dialdehyde **22**. The formyl group was converted to the ethynyl group using the Normant protocol[29] through bis(dichloromethylene) compound **23**, giving diethynylpropellanes **17a** and **17b**. In the case of the preparation of **17b**, the trapping of the dianion, formed by elimination of HCl followed by chlorine−lithium exchange from **23**, with chloro-*tert*-butyldimethylsilane was carried out at 0 °C because of the low reactivity of the chlorosilane with the anion. As a result, we obtained bisallene **24** besides the desired product **17b**, which was formed presumably by nucleophilic attack of the excess butyllithium to an intermediate of the reaction.[30] Removal of the silyl-protecting groups of **17a** and **17b** yielded the unstable parent hydrocarbon **17c**. Alternatively, diol **21c** was prepared by the similar sequence of reactions by photocycloaddition of enone **11** with 1,4-diacetoxy-2-butyne (to give **19b**), bromination−dehydrobromination (to give **20b**), 1,2-reduction−1,4-dehydration (to give **21b**), and hydrolysis. The overall efficiencies of both procedures are almost identical. Bis-(butadiynyl)propellatriene **18** was prepared by the Cadiot−Chodkiewicz coupling[31] of **17c** with 1-bromo-2-(triisopropylsilyl)-ethyne.[32]
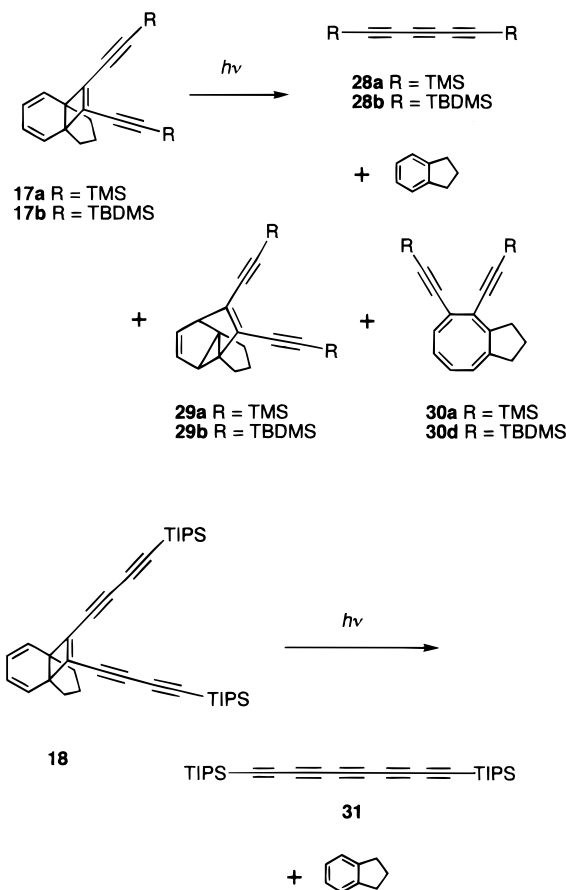

24
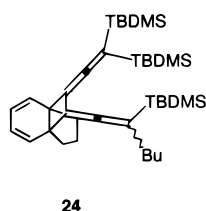
We developed another more efficient method for the preparation of diethynyl propellatrienes based on the Sonogashira coupling reaction[33] of dichloropropellatriene **27** with appropriate alkynes (Scheme 3). Thus, photoaddition of enone **11** with trichloroethene and subsequent elimination of HCl gave dichloroketone **25**. Bromination−dehydrobromination of **25** to dienone **26** followed by a 1,2-reduction−1,4-dehydration sequence yielded triene **27**. Reaction of **27** with appropriate trialkylsilyl-protected alkynes using Pd(0) and Cu(I) catalysts afforded **17a** and **17d** in good yields.

Irradiation of a hexane solution of **17a** with a low-pressure mercury lamp resulted in the formation of hexatriyne **28a**[32,34] in 66% isolated yield together with indane (Scheme 4). As byproducts, a small amount (14%) of a 1:1 mixture of isomerization products **29a** and **30a** was obtained. Although **29a** and **30a** could not be separated, their structures were

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(30) Although the mechanism of the formation of **24** is not certain, the possibility that it was produced by the nucleophilic attack of the organo-lithium reagent to the once formed **17b** was excluded, since diyne **17b** was inert to butyllithium under the reaction conditions.
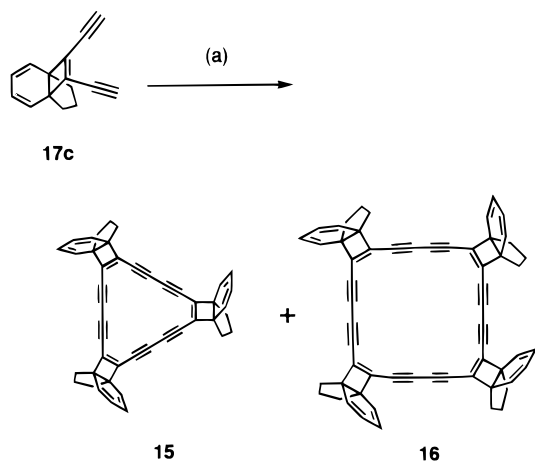(31) (a) Chodkiewicz, W.; Cadiot, P. *Compt. Rend.* **1955**, *241*, 1055. (b) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 213.
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Scheme 3[a]

17a R = TMS
17d R = TIPS

[a] (a) i, trichloroethylene, *hv*; ii, *t*-BuOK. (b) i, 5,5-dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione; ii, LiCl, Li$_2$CO$_3$. (c) i, NaBH$_4$, CeCl$_3$·7H$_2$O; ii, (2,4-dinitrophenyl)sulfenyl chloride. (d) HC≡CTMS (for **17a**) or HC≡CTIPS (for **17d**), Pd(PPh$_3$)$_4$, CuI, Et$_3$N.

Scheme 4

17a R = TMS
17b R = TBDMS

28a R = TMS
28b R = TBDMS

29a R = TMS
29b R = TBDMS

30a R = TMS
30d R = TBDMS

18

31

assigned on the basis of the NMR spectra. The salient feature of the ^{1}H NMR spectra of **29a** involves two methine signals at δ 3.34 and 2.69 ppm which couple with the vinyl protons at δ 5.90 and 5.58, respectively. The cyclooctatetraene structure of **30a** was elucidated on the basis of the presence of four vinyl proton signals in the ^{1}H NMR and eight sp^2 carbon signals (four quaternary and four tertiary carbons) in the ^{13}C NMR spectra. The compound **29a** can be envisioned as a product of vinylogous di-π-methane rearrangement of **17a**. Whether **30a** is a direct photochemical product or an isomerization product of **29a** by trace acid was not confirmed. Similarly, irradiation of *tert*-butyldimethylsilyl derivative **17b** gave hexatriyne **28b**[32] (67%) together with a mixture of **29b** and **30b** (6%). Photolysis of

Scheme 5. (a) Cu(OAc)$_2$, Pyridine or Cu(OAc)$_2$, CuCl, Pyridine

dibutadiynylpropellatriene **18** under similar conditions afforded decapentayne **31**[32] in 74% isolated yield. No isomerization product of the starting material was detected in this case. Thus, it was revealed that the desired [2 + 2] cycloreversion takes place predominantly in the model system even for the propellatrienes with extended conjugation, leading to the formation of linear polyynes.

We also examined the photolysis of bisallene **24** to generate a hexapentaene derivative **32**.[35] Thus, irradiation of **24** with a low-pressure mercury lamp in THF-d_8 at 0 °C resulted in the formation of an unstable product, together with indane, which was assigned to be **32** on the basis of the spectral properties characteristic to a cumulene; ^{13}C NMR δ 189.9, 174.9, 156.8, 154.1 ppm; IR 2060, 2040, 2000, 1960, 1880, 1820 cm^{-1}; UV–vis λ_{max} (cyclohexane) 584 and 527 nm. An attempt to isolate the product **32** was unsuccessful because of its rapid decomposition to form tarry brown materials.

32

Synthesis of Dehydroannulenes Annelated by [4.3.2]-Propellatriene Units. With the above results on the model study for the linear polyyne synthesis in hand, we investigated the cyclo[n]carbon synthesis using the [2 + 2] cycloreversion of [4.3.2]propellatriene derivatives. We started with the synthesis of precursors of cyclo[18]- and [24]carbons, dehydro[18]-annulene **15** and dehydro[24]annulene **16** which correspond to the trimer and tetramer of diethynylpropellatriene **17c**, respectively. Thus, copper(II)-mediated oxidative coupling of **17c** under Eglinton's conditions[36] gave the yellowish orange trimer **15** as the major product together with a small amount of carmine red tetramer **16** in total yield of 39% (Scheme 5). In an other run under modified conditions using copper(I) and copper(II) salts,[37] a nearly 1:1 mixture of **15** and **16** was obtained (56% yield). Both **15** and **16** were obtained as mixtures of diastereomers which were not separated and only those with highest

symmetry are drawn in the Scheme. The presence of dodeca-dehydro[18]- and hexadecadehydro[24]annulene cores in **15** and **16**, respectively, was confirmed by comparison of the ^{1}H NMR and electronic spectra with those of related compounds.[14–16,38,39]

Next, we synthesized the precursors of cyclo[12]-, [16]-, and [20]carbons, dehydro[12]-, [16]-, and [20]annulene systems **12**–**14** which correspond to the trimer, tetramer, and pentamer of chloroethynylpropellatriene **33b**. Monoethynylation of dichloropropellane **27** with 2-methyl-3-butyn-2-ol to furnish **33a** was accomplished in 60–70% yields by Pd(0)–Cu(I)-catalyzed coupling. The product was readily separated from the diethynylation product **17e** by chromatography. Removal of the terminal carbinol moiety gave alkyne **33b**. However, all attempts for cyclization of **33b** by Pd(0)–Cu(I)-catalyzed coupling under a variety of conditions failed to afford the desired cyclization products. Dimer **34**, formed by the oxidative coupling of the terminal alkyne moiety of **33b**, was obtained as an exclusive product. On the other hand, we were gratified to find that, when **33a** was subjected to the phase-transfer conditions[40] under which deprotection and coupling took place in one pot, the dehydroannulenes **12** (dark red), **13** (dark violet), and **14** (reddish orange) were obtained in 1, 11, and 1% yields, respectively (Scheme 6). These products were readily separated by chromatography, but individual compounds are also inseparable mixtures of diastereomers (only those with highest symmetry drawn in the scheme). The fact that the tetramer **13** was obtained in higher yield than the trimer **12** is explained in terms of the geometrical deformation which is smaller in the former than in the latter as described below. Trimer **12** was also prepared selectively in a stepwise manner by three successive Pd(0)–Cu(I)-catalyzed coupling reactions as shown in Scheme 7. Namely, the reaction of diethynylpropellane **17c** with an excess of **27** yielded the 1:2 coupling product **35** (50%), which was coupled with 2-methyl-3-butyn-2-ol to give monoethynylated compound **36** (47%) and disubstituted product **37** (36%). Finally, intramolecular cyclization of **36** under the phase-transfer conditions provided **12** in 16% yield.

Generation of Cyclo[n]carbons by [2 + 2] Cycloreversion of Propellane-Annelated Dehydroannulenes. With the cyclocarbon precursors **12**–**16** in hand, we investigated the generation of the corresponding cyclo[n]carbons by [2 + 2] cycloreversion. First, in the laser-desorption time-of-flight (LD TOF) mass spectra, we observed the formation of cyclo[n]carbons (n = 12, 16, 18, 20, 24) from the corresponding dehydroannulene derivatives **12**–**16** as shown in Figures 1 and 2. As shown in the inset of Figure 1, the positive mode of LD-TOF mass spectrum of **15** exhibited only the peak due to the indane fragment. Likewise, the peak due to indane was exclusively observed in the positive mode spectra of **12**–**14** and **16**. On the other hand, in the negative mode spectrum of **15** (Figure 1), we observed the peaks due to the parent ion (C$_{18}$R$_3^-$ where R denotes the indane fragment) and the anions resulting from

(35) For tetra-*tert*-butylhexapentaene, see: (a) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527. (b) Negi, T.; Kaneda, T.; Mizuno, H.; Toyota, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2398.

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(38) (a) Okamura, W. H.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 5991. (b) McQuilkin, R. M.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1970**, *92*, 6682. (c) Anthony, J.; Knobler, C. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 406. (d) Zhou, Q.; Carrol, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294. (e) Guo, L.; Bradshaw, J. D.; Tessier, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1994**, 243. (f) Haley, M. M.; Brand, S. C.; Pak, J. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 836. (g) Nishinaga, T.; Kawamura, T.; Komatsu, K. *J. Org. Chem.* **1997**, *62*, 5354. (h) Pak, J. J.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 8182.

(39) For recent reviews, see: (a) Haley, M. M. *Synlett* **1998**, 557. (b) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *201*, 82.

(40) (a) Rossi, A.; Carpita, A.; Quirici, M. G.; Gaudenzi, M. L. *Tetrahedron* **1982**, *38*, 631. (b) Huyne, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337.

Scheme 6[a]
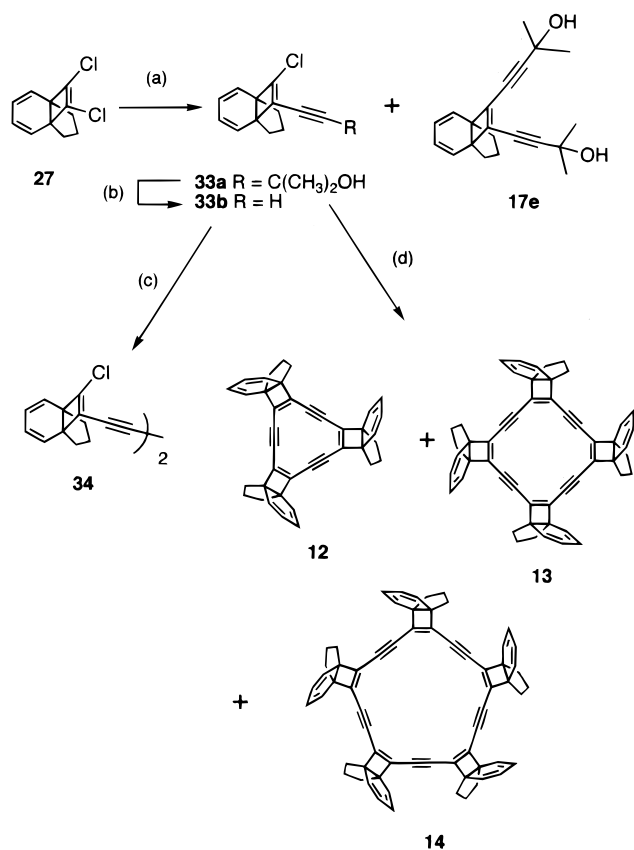
(a) 2-methyl-3-butyn-2-ol, Pd(PPh$_3$)$_4$, CuI, BuNH$_2$. (b) KOH. (c) Pd(PPh$_3$)$_4$, CuI, BuNH$_2$. (d) Pd(PPh$_3$)$_4$, CuI, aq. NaOH, benzyltriethyl-ammonium chloride.

Scheme 7[a]
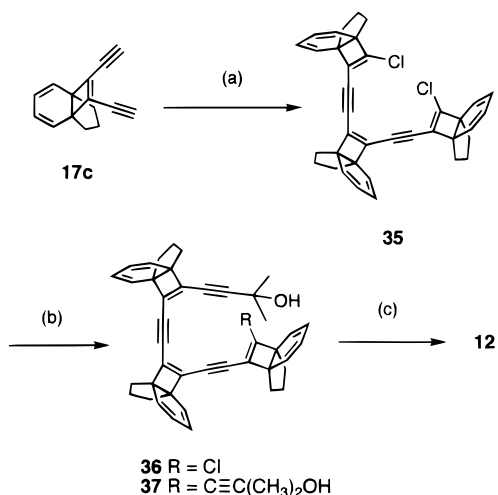
(a) **27** (excess), Pd(PPh$_3$)$_4$, CuI, Et$_3$N. (b) 2-methyl-3-butyn-2-ol, PdCl$_2$(PhCN)$_2$, CuI, piperidine. (c) Pd(PPh$_3$)$_4$, CuI, aq. NaOH, ben-zyltriethylammonium chloride.

the successive losses of one, two, and three indane fragments (C$_{18}$R$_2^-$, C$_{18}$R$^-$, and C$_{18}^-$, respectively). Also observed are the anions, C$_{36}^-$ and C$_{54}^-$, corresponding to the dimer and trimer of C$_{18}^-$, respectively. However, we have no information regarding the structure of these high molecular weight clusters at this moment.[41] The LD-TOF mass spectra of **12**−**14** and **16** exhibit essentially the same pattern of peaks as that of **15** as shown in Figure 2. Although the size-selective generation of cyclo[n]carbon anions with n = 6m carbon atoms (C$_{18}^-$, C$_{24}^-$,
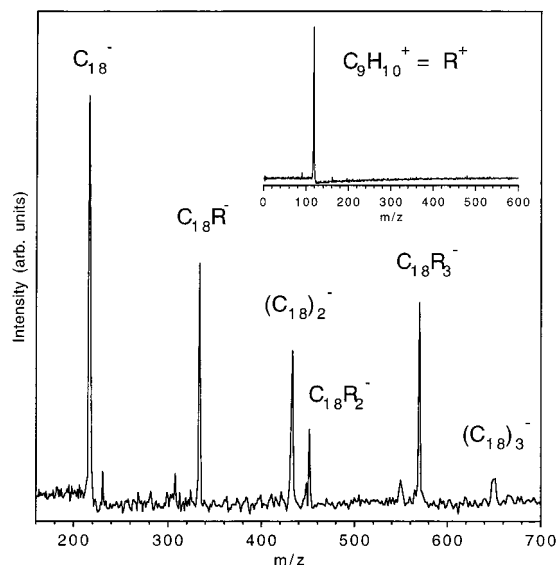

Figure 1. Negative and positive (inset) modes LD-TOF mass spectra of cyclo[18]carbon precursor **15**. R denotes the indane fragment.

and C$_{30}^-$) from the corresponding precursor molecules was reported previously,[9d,14,16] the formation of cyclo[n]carbon anions with n = 4m carbon atoms (C$_{12}^-$, C$_{16}^-$, and C$_{20}^-$) represents the first examples. The structures of the carbon cluster anions (C$_{12}^-$, C$_{16}^-$, C$_{18}^-$, C$_{20}^-$, and C$_{24}^-$) generated from the dehydroannulene derivatives **12**−**16** were investigated on the basis of the ultraviolet photoelectron spectra of the anions obtained by subjecting the mass selected anions to a second laser pulse (266 nm), which were compared with those of the anions of the same carbon numbers obtained by laser vaporiza-tion of graphite.[23] On the basis of the splitting frequencies due to vibrational excitation of the neutral cyclocarbons produced by detaching an electron from the corresponding anions, it was deduced that cyclo[n]carbons with 4m carbon atoms, that is, C$_{16}$, C$_{20}$, and C$_{24}$, should possess a polyyne structure with alternating single and triple bonds. Namely, the vibrational frequencies observed at 1775, 1930, and 1935 cm^{-1} were assigned to the tangential motion of the C−C bond in C$_{16}$ of C$_{8h}$, C$_{20}$ of C$_{10h}$, and C$_{24}$ of C$_{12h}$ symmetry, respectively. On the other hand, cyclo[18]carbon bearing 4m + 2 carbon atoms must be cumulenic, since its vibrational frequency at 645 cm^{-1} can be assigned to the totally symmetric C−C stretching (breathing) mode of C$_{18}$ of D$_{9h}$ symmetry. In the case of the smallest member C$_{12}$, it is not clear whether it is a polyyne or a cumulene because of the relatively low signal vs noise ratio of the spectra probably due to its decomposition to the linear isomer.[23]

To examine the possible formation of cyclo[n]carbons by photochemical [2 + 2] cycloreversion, a solution of **15** in THF-d$_8$ was irradiated with a low-pressure mercury lamp at 0 °C, yielding indane along with uncharacterized polymeric materials. Apparently, the intermediates formed by elimination of indane fragment(s) are too reactive at this temperature. To intercept reactive intermediates formed during the photolysis, irradiation was then carried out using furan as a solvent, giving three oxanorbornadiene-annelated products **38**−**40** in 15, 27, and 11% isolated yields, in which one, two, or all indane units are replaced by the furan moieties, respectively (Scheme 8). The structures of the products **38**−**40**, especially the regiochemistry

(41) The photoelectron spectrum of C$_{32}^-$ revealed that its structure was different from that of the carbon cluster generated from graphite by the laser vaporization; see ref 23.
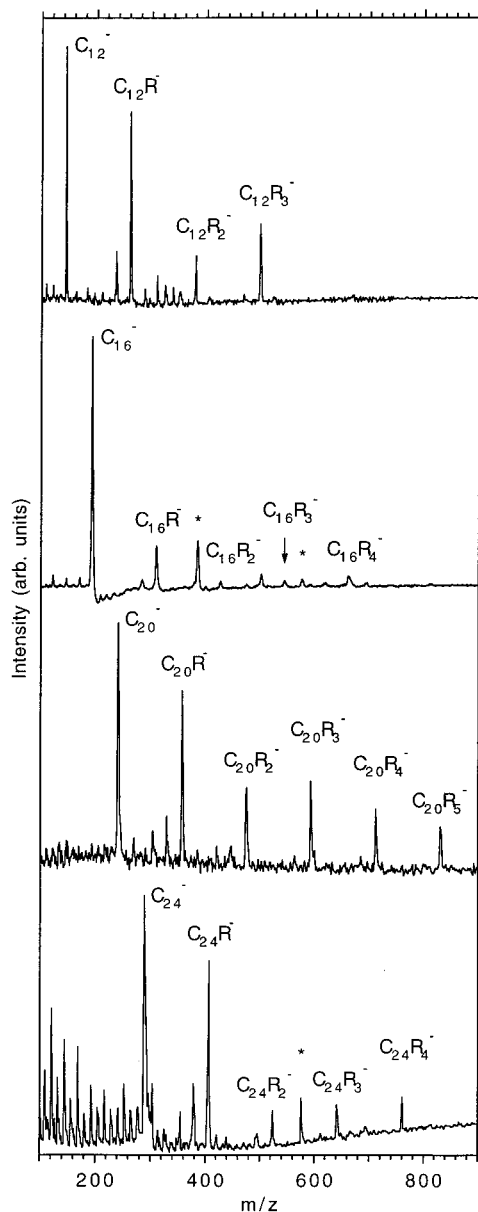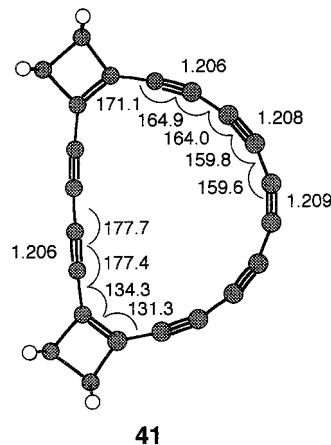
Figure 2. Negative mode LD-TOF mass spectra of cyclo[12]-, [16]-, [20]-, and [24]carbon precursors **12** (a), **13** (b), **14** (c), and **16** (d). R denotes the indane fragment.

Figure 3. AM1-calculated geometries of model compound **47** formed during photolysis of dehydro[18]annulene **15**. Bond lengths are in Å and bond angles in degrees.

Scheme 8

of the [4 + 2] cycloaddition of furan, were established by the ^{13}C NMR chemical shifts of their sp carbons. Namely, **38** and **39** exhibit only five clusters of the sp carbon signals (**38**: δ 95.3, 86.3, 84.0, 83.5, 82.0, 81.8 ppm, **39**: δ 96.1, 95.7, 87.6, 84.5, 82.9 ppm) and **40** (δ 97.0, 89.3 ppm) does only two, indicating that these compounds have an approximate C_3 symmetry. Monitoring the photochemical reaction of **15** in furan by HPLC suggests that **38** is formed initially, then it is converted to **39**, which finally gives **40**. Consequently, though these results do not imply the direct formation of cyclo[18]carbon by the photolysis of **15**, they clearly show that the elimination of at least one of the indane units takes place efficiently by [2 + 2] cycloreversion from **15** (and **38** and **39** as well) to produce highly reactive dehydro[18]annulene intermediates.
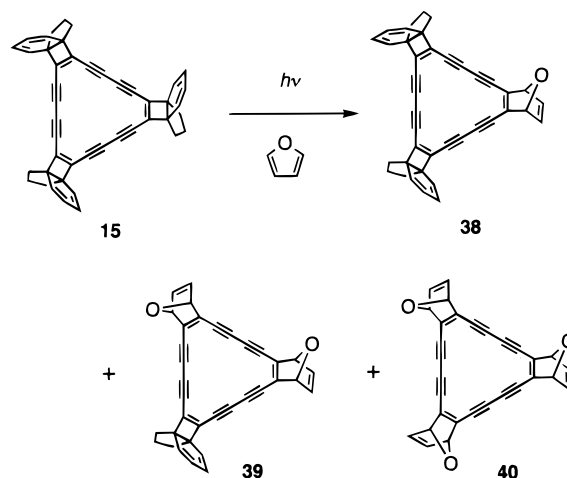
It should be noted that the [4 + 2] cycloaddition of furan takes place regioselectively giving the products **38**–**40**, in which the furan units are located at the same position as those occupied by the propellane units before they were extruded. To get insight into this regioselectivity, we undertook semiempirical AM1

calculations for the tetradecadehydro[18]annulene **41** (Figure 3), as a model compound for the reactive intermediate formed from **15** by elimination of one of the indane units. As shown in Figure 3, the calculated bond angle of the central triple bond of the decapentayne moiety of **41** is most severely deformed from linearity. In addition, [4 + 2] addition of furan to other position of the polyyne chain of **41** would lead to a structure which is apparently more strained than that actually formed.

We expected that the retro [4 + 2] fragmentation of the oxanorbornadiene unit in **40** would provide an alternative route to cyclocarbon chemistry. However, although such fragmentation was indeed observed in the LD-TOF mass spectrum of **40** as shown in Figure 4, it also exhibited fragmentation due to the loss of CO (or CHO) and C_2H_2 or (C_2H_3) units, leading to a complex spectrum pattern.

The photolysis of dehydro[16]annulene **13**, which was obtained most readily within the series of the compounds **12**–**14**, was also carried out in furan. In this case, the reaction was sluggish compared to the similar reaction of **15**, and only monosubstitution product **42** was isolated in 31% yield (30% of **13** recovered) (Scheme 9). Further irradiation led to the extensive formation of complex mixture of products and polymeric materials.

These results on the solution photolyses of **13** and **15** seem promising in view of the photochemical generation of cyclo-[*n*]carbons by UV irradiation in low-temperature matrices. However, the limited solubility, particularly in the case of
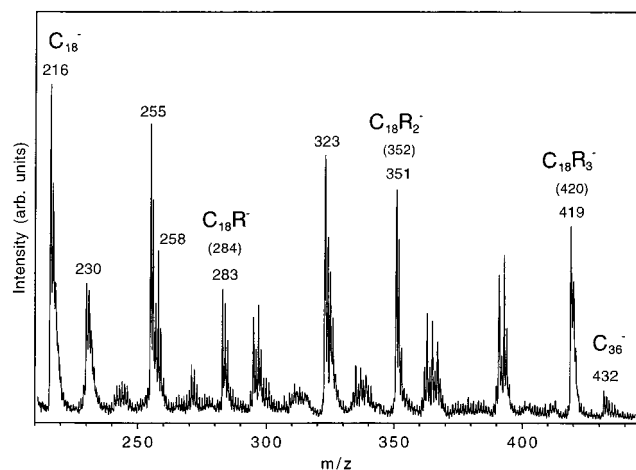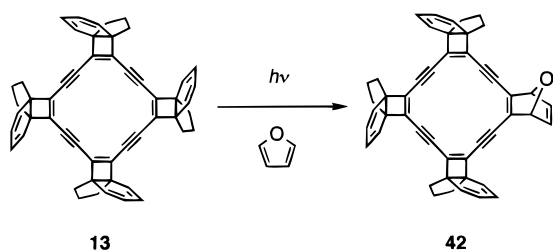
Figure 4. Negative mode LD-TOF mass spectrum of oxanorbornadiene-annelated dehydro[18]annulene **40**. R denotes the furan fragment.

Scheme 9

butadiyne-bridged compounds **15** and **16**, in conjunction with low volatility precluded their isolation in rigid glass as well as crystalline noble gas matrices. Also, low volatility of these compounds precluded experiments on the thermal fragmentation.

Structures and Spectroscopic Properties of Dehydroannulenes Annelated by [4.3.2]Propellatriene and Oxanorbornadiene Units. Finally, the structure and spectroscopic properties of the dehydroannulenes annelated by the propellatriene units and/or the oxanorbornadiene units are discussed. The parent hydrocarbons as well as a number of derivatives possessing dodecadehydro[18]- and hexadecadehydro[24]-annulene systems are known,[14−16,38,39] and the effect of fusion of cyclobutene rings on the structural and spectroscopic properties of these dehydroannulene ring systems has already been discussed.[42] The spectral properties of dehydroannulenes **15** and **16** are in accord with this view. Namely, the electronic spectra of **15** and **16** are similar to those of the corresponding cyclobutene-annelated dehydroannulenes.[42] In the ^{1}H NMR spectra, the signals due to the vinyl protons (H2 and H5 of the propellane unit) of **15** which are closer to the bridgeheads of the propellane units appear at about 0.3 ppm lower field than those of the reference compound **17c** owing to the diamagnetic ring current of the [18]annulene perimeters. On the other hand, the corresponding signals of **16** appear at about 0.3 ppm higher field than those of **17c** because of the paratropic character of the [24]annulene core.

To assess the geometries and stabilities of the propellatriene-annelated dehydroannulenes **12−14**, semiempirical AM1 calculations for the corresponding cyclobutene-annelated dehydroannulenes **43−45** were carried out (Figure 5). For comparison, AM1 calculations were also undertaken for the corresponding parent annulenes **46−48** which do not have the fused cyclobutene rings. Selected geometrical parameters, heats of

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formation, and HOMO−LUMO gaps of **43−48** are summarized in Table 1. In the cyclobutene-fused trimer **43**, the angle θ between the two $C(sp^2)−C(sp)$ bonds flanking the cyclobutene ring ($\sim80°$) is substantially reduced from the normal angle ($\sim90°$) of the diethynylcyclobutene system. Similarly, the triple bond is considerably deformed ($\beta = 170.2°$) from linearity, indicating the presence of considerable strain in this system. Accordingly, the heat of formation per one ethynylcyclobutene unit of **43** (98.3 kcal/mol) is larger than those of **44** (94.0 kcal/mol) and **45** (94.3 kcal/mol). On the contrary, there seems to be little strain in tetramer **44**, the most stable congener of this series, which has planar geometry of the annulene core because of the right angles at the corners. Moreover, tetramer **44** has the smallest HOMO−LUMO gap in accord with its planar structure. The structure of the pentamer **45**, however, is not planar; the angle θ is smaller than 90°, and the acetylene bond is bending slightly inward to the annulene ring. Despite the presence of the largest number of the π bonds, the HOMO−LUMO gap of **45** is the largest of the three, which is also indicative of nonplanarity of the annulene ring. On the other hand, in the series of the parent compounds **46−48**, trimer **46** turns out to be the least strained because of the best fit angle θ (65.8°) for the planar geometry. Planar **46** has the lowest HOMO−LUMO gap of the three. To reduce the angle strain around angles α and θ, the structures of tetramer **47** and pentamer **48** become nonplanar, rendering their heats of formation per enyne unit similar to one another (65.8, 65.0, and 65.7 kcal/mol, respectively).

In accord with the calculated HOMO−LUMO gaps for the model compounds, the end absorptions of the electronic spectra of planar **12** and **13** extend beyond 500 nm, while nonplanar **14** does not have absorptions at >500 nm as shown in Figure 6. In addition, in the ^{1}H NMR spectra, the vinyl protons (H2 and H5) adjacent to the bridgeheads of the propellane units of **12** and **13** appear about at 0.5 and 0.4 ppm higher field, respectively, than those of the reference compound **17c** owing to the paramagnetic ring current of the [12]- and [16]annulene perimeters. By contrast, the corresponding signals of **14** resonate at only 0.2 ppm higher field than those of **17c** because of its nonplanar structure, although **14** also has a 20π electronic system.

Within the series of dehydro[18]annulenes **15** and **38−40** annelated by the propellatriene and/or oxanorbornadiene units, the absorption bands in the electronic spectra exhibit steady bathochromic shifts with an increasing number of the oxanorbornadiene units in the molecule as shown in Figure 7, presumably as a result of through-bond interaction between the norbornadiene and dehydroannulene π systems. Moreover, the $\sigma−\pi$ conjugative interaction between the strained σ bonds of the oxanorbornadiene units and the π bonds of the annulene ring may also responsible for the bathochromic shift, because remarkable electron-donating effect of the bicyclo[2.2.2]octane unit was observed by Komatsu et al. in the dehydroannulene systems related to **38−40**.[38g] The kinetic stabilities of the dehydroannulenes **39** and **40** with more than one oxanorbornadiene unit are substantially less than those of **17** and **38**; the less sterically hindered compounds **39** and **40** exploded mildly when they were scratched with a spatula and decomposed gradually even in the solid state under inert atmosphere.

In conclusion, we have prepared dehydro[12]-, [16]-, [18]-, [20]-, and [24]annulenes **12−16** annelated by [4.3.2]propellatriene units as possible precursors to the corresponding cyclo[*n*]carbons of *n* = 12, 16, 18, 20, and 24. The model study of the photolysis for the simple propellatriene derivatives **17a**, **17b**,
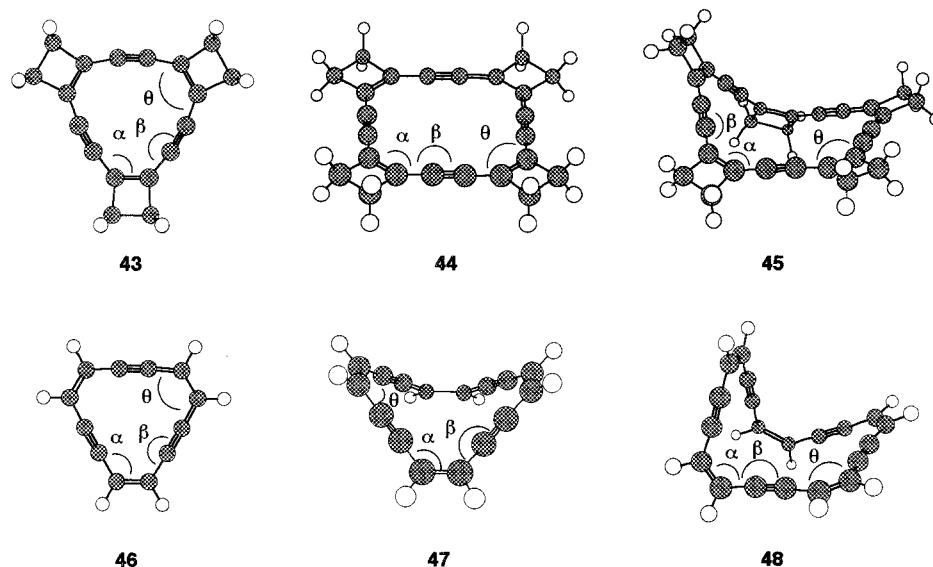
Figure 5. AM1-calculated geometries of the cyclobutane-annelated dehydroannulenes **43**−**45** and their parent compounds **46**−**48**.

Table 1. AM1-calculated Geometries and Energies for Cyclobutene-annelated Dehydroannulenes **43**−**45** and Their Parent Hydrocarbons **46**−**48**[a]

compd	bond angle (deg)			$\Delta Hf°$ (kcal/mol)	HOMO−LUMO gap (eV)
	α	β	θ		
43	129.8	170.2	79.6	294.8	6.42
44	135.6	179.7	91.2	375.9	6.23
45	137.1[b]	178.3[b]	94.1[b]	471.4	6.73
46	122.9	177.0	65.8	197.3	7.15
47	125.6	178.7	71.2	259.9	7.78
48	125.9[b]	175.7[b]	77.2[b]	328.7	7.81

[a] The angles α, β, and θ are indicated in Figure 1. [b] The averages of the angles because of the absence of symmetry in the optimized geometry.

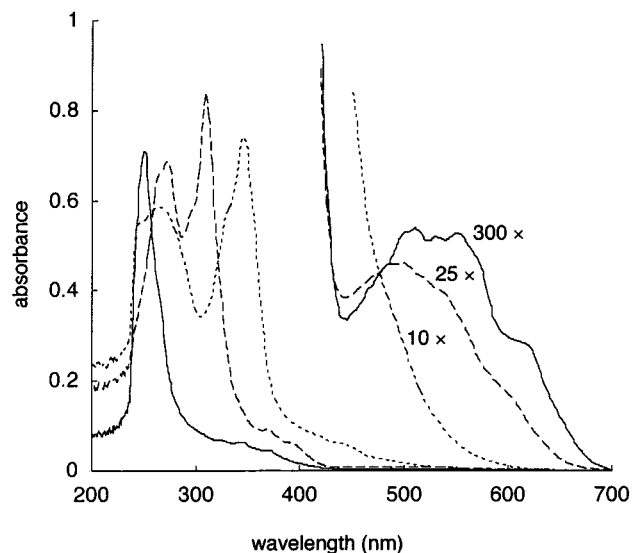**Figure 6.** UV−vis spectra of propellane-annelated dehydro[12]-annulene **12** (solid line, 1.04×10^{-6} M), dehydro[16]annulene **13** (dashed line, 3.43×10^{-6} M), and dehydro[20]annulene **14** (dotted line, 2.17×10^{-6} M) in chloroform.

and **18** by UV irradiation revealed that the [2 + 2] cycloreversion takes place efficiently to give the corresponding linear polyynes **28a**, **28b**, and **31**. The negative mode LD-TOF mass spectra of the cyclocarbon precursors **12**−**16** exhibit the corresponding cyclocarbon anions formed by the successive
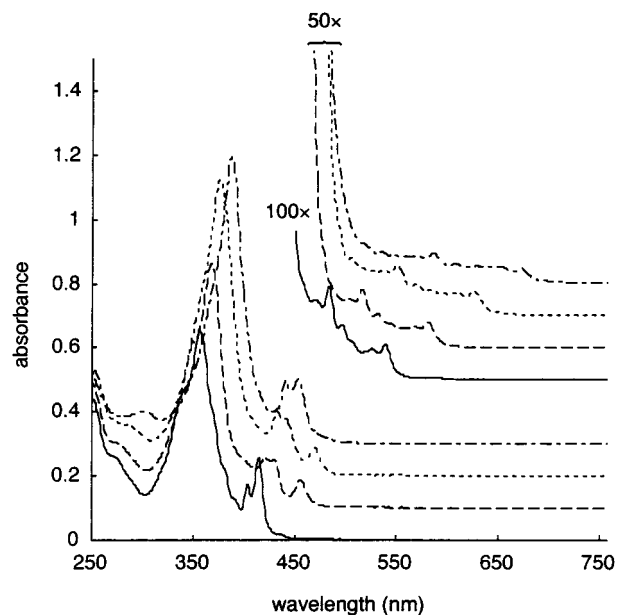

Figure 7. UV−vis spectra of propellane-annelated dehydro[18]-annulene derivatives **15** (solid line, 1.09×10^{-5} M), **38** (dashed line, 1.50×10^{-5} M), **39** (dotted line, 1.91×10^{-5} M), and **40** (dashed and dotted line, 1.57×10^{-5} M) in chloroform. The vertical scales for the spectra of **38**−**40** are shifted by 0.1, 0.2, and 0.3 units, respectively, for clarity.

losses of indane fragments. Solution photolysis of **13** and **15** in furan gave rise to the Diels−Alder adducts **38**−**40** and **42**, respectively, derived from reactive polyynes formed by [2 + 2] cycloreversion. Finally, it is worth noting that this technique was successfully applied to the generation of a three-dimensional polyyne $C_{60}H_6$ which eventually isomerized to C_{60} fullerene.[43]

Experimental Section

¹H NMR (500 or 270 MHz) and ¹³C NMR (125.65 or 67.5 MHz) were recorded on a JEOL JNM-GX-500 or a JNM-GSX-270 spectrometer. The assignments of the number of the attached hydrogen(s) to the carbon atoms in the ¹³C NMR spectra were determined by the

(43) Tobe, Y.; Nakagawa, N.; Naemura, K.; Wakabayashi, T.; Shida, T.; Achiba, Y. *J. Am. Chem. Soc.* **1980**, *102*, 4544. See also: Rubin, Y.; Parker, T. C.; Pastor, S. J.; Jalistagi, S.; Boulle, C.; Wilkins, C. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1226.

DEPT experiments, where the signs q, t, s, and p denote quaternary, tertiary, secondary, and primary carbons, respectively. IR and UV−vis spectra were taken on Hitachi 260-10 and 220A spectrometers, respectively. EI and FAB mass spectra were recorded on a JEOL JMS-DX303HF spectrometer. The laser-desorption time-of-flight (LD-TOF) mass spectra were obtained on a home-built spectrometer equipped with a Nd:YAG laser (266 nm, typically 0.6 mJ/pulse).[23] 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.

Preparation of 11,12-Diethynyl[4.3.2]propella-1,3,11-trienes (17a−c). Method A: Through Diformylpropellatriene 22. 11,12-Bis-[(methoxymethoxy)methyl][4.3.2]propell-11-en-1-one (19a). A solution of 5.29 g (39.0 mmol) of enone **11**[25] and 57.0 g (328 mmol) of 1,4-bis(methoxymethoxy)-2-butyne[26] in 40 mL of CH$_2$Cl$_2$ was irradiated through a Pyrex filter with a 500-W high-pressure mercury lamp at room temperature. After every 2 to 2.5 h, about a 5-g quantity of enone **11** in 20 mL of CH$_2$Cl$_2$ was added three times. The total amount of **11** used was 20.8 g (0.153 mol), and the irradiation was continued until GLC monitoring showed no change in the relative peak areas of the alkyne and the product. After evaporation of the solvent, the mixture was distilled under reduced pressure (79−81 °C/1 mmHg) to recover the unreacted alkyne. The residue was chromatographed on silica gel to afford 32.8 g (70%) of the cycloadduct **19a** as a pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 4.64 (s, 2H), 4.57 (AB, J = 6.4 Hz, $\Delta\nu$ = 9.3 Hz, 2H), 4.15 (s, 2H), 4.04 (AB, J = 13.1 Hz, $\Delta\nu$ = 38.0 Hz, 2H), 3.39 (s, 3H), 3.35 (s, 3H), 2.56 (ddd, J = 17.8, 6.0, 2.7 Hz, 1H), 2.23−1.33 (m, 10H), 1.13 (ddd, J = 12.4, 12.4, 6.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 214.0 (q), 143.8 (q), 137.0 (q), 95.9 (s), 95.8 (s), 64.8 (q), 60.9 (s), 60.5 (s), 56.9 (q), 55.04 (p), 54.99 (p), 38.7 (s), 31.7 (s), 30.7 (s), 25.5 (s), 22.7 (s), 20.0 (s); IR (neat) 1690, 1150, 1100, 1040 cm^{-1}; MS m/z 310 (M$^+$). Semicarbazone, mp 143−145 °C. Found: C, 58.96; H, 7.91; N, 11.44%. Calcd for C$_{18}$H$_{29}$O$_5$N$_3$: C, 58.83; H, 7.96; N, 11.11%.

11,12-Bis[(methoxymethoxy)methyl][4.3.2]propella-2,11-dien-1-one (20a). To a solution of 1.91 g (6.17 mmol) of **19a** and 1.25 g (12.3 mmol) of triethylamine in 12 mL of CCl$_4$ was added dropwise 1.51 g (6.79 mmol) of trimethylsilyl trifluoromethanesulfonate, and the resulting mixture was stirred at room temperature for 6 h. The mixture was diluted with NaHCO$_3$ solution and was extracted with CH$_2$Cl$_2$. The extract was washed with saturated NaCl solution and then dried over MgSO$_4$. The solvent was evaporated, and the residue was extracted with hexane (∼50 mL) to remove brown tarry material. The solvent was evaporated, and the residue was dissolved in 6 mL of acetonitrile. To this solution was added 680 mg (3.03 mmol) of Pd(OAc)$_2$ and a solution of 324 mg (3.00 mmol) of p-benzoquinone in 20 mL of the same solvent, and the mixture was stirred at 30 °C. After 16 h, another portion of Pd(OAc)$_2$ (450 mg, 2.00 mmol) was added, and the reaction was continued for another 29 h. The mixture was filtered, and the filtrate was concentrated under reduce pressure. The residue was chromatographed on silica gel to give 1.01 g (53%) of dienone **20a** as a pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 6.57 (ddd, J = 10.1, 5.4, 2.7 Hz, 1H), 5.94 (ddd, J = 10.1, 2.7, 1.7 Hz, 1H), 4.54 (s, 2H), 4.50 (AB, J = 6.4 Hz, $\Delta\nu$ = 9.5 Hz, 2H), 4.09 (s, 2H), 3.95 (s, 2H), 3.31 (s, 3H), 3.29 (s, 3H), 2.88 (ddd, J = 19.8, 5.7, 1.7 Hz, 1H), 2.28 (ddd, J = 19.8, 2.7, 2.7 Hz, 1H), 2.06−1.93 (m, 2H), 1.69−1.48 (m, 2H), 1.30 (ddd, J = 12.6, 12.6, 6.9 Hz, 1H), 1.12 (ddd, J = 12.4, 12.4, 6.7 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 202.2 (q), 144.7 (t), 142.7 (q), 141.5 (q), 127.4 (t), 95.8 (s), 62.7 (q), 60.6 (s), 60.4 (s), 55.2 (q), 55.1 (p), 52.0 (p), 33.8 (s), 32.9 (s), 25.7 (s), 22.5 (s); IR (neat) 1765, 1150, 1100, 1040, 940, 915, 835 cm^{-1}; MS m/z 308 (M$^+$). HRMS found, 308.1631. Calcd for C$_{17}$H$_{24}$O$_5$, 308.1623.

11,12-Bis[(methoxymethoxy)methyl][4.3.2]propella-1,3,11-triene (21a). To a solution of 950 mg (3.08 mmol) of **20a** in 15 mL of MeOH cooled in an ice bath was added 1.27 g (3.40 mmol) of cerium trichloride heptahydrate followed by portionwise addition of 114 mg (3.00 mmol) of sodium borohydride. After 1 h, the mixture was diluted with water and extracted with CH$_2$Cl$_2$. The extract was washed with water and dried over MgSO$_4$. The solvent was evaporated to give the corresponding alcohol, which contained only one diastereomer as judged from its ^{1}H NMR spectrum. ^{1}H NMR (CDCl$_3$) δ 5.72 (dd, J = 9.6, 3.0 Hz, 1H), 5.61 (br t, J = 9.4 Hz, 1H), 4.64 (AB, J = 6.4 Hz, $\Delta\nu$ = 21.2

Hz, 2H), 4.56 (AB, J = 6.4 Hz, $\Delta\nu$ = 15.1 Hz, 2H), 4.25 (d, J = 12.1 Hz, 1H), 3.99 (s, 2H), 3.97 (br s, 2H), 3.89 (br d, J = 12.1 Hz, 1H), 3.37 (s, 3H), 3.35 (s, 3H), 2.37 (dd, J = 16.3, 6.9 Hz, 1H), 2.05 (dd, J = 12.6, 5.9 Hz, 1H), 1.86−1.73 (m, 3H), 1.64−1.48 (m, 1H), 1.27 (ddd, J = 12.6, 12.6, 6.7 Hz, 1H), 1.09 (ddd, J = 12.4, 12.4, 6.7 Hz, 1H); IR (neat) 3450, 1640, 1215, 1150, 1100, 1040, 940, 920 cm^{-1}. To a solution of the above product dissolved in 15 mL of 1,2-dichloroethane was added 909 mg (9.00 mmol) of triethylamine followed by 2.11 g (9.00 mmol) of 2,4-dinitrophenylsulfenyl chloride. The resulting suspension was heated under reflux for 6 h. The mixture was diluted with hexane (30 mL) and filtered. The filtrate was concentrated, and the dark red residue was extracted several times with hexane. The solvent was evaporated, and the residue was chromatographed on silica gel to give 749 mg (83%) of triene **21a** as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 5.84−5.70 (m, 4H), 4.55 (AB, J = 6.9 Hz, $\Delta\nu$ = 8.0 Hz, 4H), 4.06 (AB, J = 12.9 Hz, $\Delta\nu$ = 15.0 Hz, 4H), 3.32 (s, 6H), 1.87 (dd, J = 12.6, 5.7 Hz, 2H), 1.58−1.29 (m, 2H), 1.13 (ddd, J = 12.2, 12.2, 6.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 141.8 (q), 130.4 (t), 120.6 (t), 95.5 (s), 60.0 (s), 55.1 (p), 53.2 (q), 32.2 (s), 18.8 (s); IR (neat) 1650, 1155, 1105, 1050 915, 720 cm^{-1}; MS m/z 292 (M$^+$). HRMS found, 292.1689. Calcd for C$_{17}$H$_{24}$O$_4$, 292.1675.

11,12-Bis(hydroxymethyl)[4.3.2]propella-1,3,11-triene (21c). To a solution of 5.68 g (19.4 mmol) of **21a** in 190 mL of THF was added 90 mL of 4N HCl, and the solution was stirred at 40 °C for 6 h. After most of THF was removed, the mixture was neutralized with NaHCO$_3$ and extracted with ether. The extract was washed with saturated NaCl solution and then dried over MgSO$_4$. The solvent was evaporated, and the residue was chromatographed on silica gel to give 2.69 g (68%) of diol **21c** as a white solid: mp 96−98 °C; ^{1}H NMR (CDCl$_3$) δ 5.76 (s, 4H), 4.26−4.04 (m, 4H), 4.02 (br s, 2H), 1.79 (dd, J = 12.9, 5.7 Hz, 2H), 1.62−1.35 (m, 2H), 1.14 (ddd, J = 12.3, 12.3, 6.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 142.0 (q), 130.3 (t), 121.0 (t), 56.2 (s), 53.4 (q), 31.7 (s), 18.8 (s); IR (KBr) 1570, 1065, 1000, 995, 775, 710 cm^{-1}; MS m/z 204 (M$^+$). HRMS found, 204.1151. Calcd for C$_{13}$H$_{16}$O$_2$, 204.1150.

Preparation of Diol 21c through Acetates 19b, 20b, and 21b. A solution of 2.30 g (16.9 mmol) of enone **11**[25] and 15.8 g (92.9 mmol) of 1,4-diacetoxy-2-butyne in 20 mL of CH$_2$Cl$_2$ was irradiated through a Pyrex filter with a 500-W high-pressure mercury lamp at room temperature for 9 h. After removal of the alkyne by distillation under reduced pressure (110−130 °C/15 mmHg), distillation (135−145 °C/0.5 mmHg) afforded 2.17 g (62%) of the cycloadduct **19b** as a pale yellow oil. IR (neat) 1740, 1680, 1220, 1020 cm^{-1}.

A mixture of 53.2 g (0.174 mol) of **19b** and 57.8 g (0.191 mol) of 5,5-dibromo-2,2-dimethyl-1,3-dioxane-4,6-dione[44] in 365 mL of CCl$_4$ was heated under reflux for 23 h. During the reaction another portion od bromide (15.6 g, 51.8 mmol) was added. The mixture was cooled, and a saturated solution of NaHCO$_3$ was added. The organic layer was separated, washed with 0.2 M Na$_2$S$_2$O$_3$ and saturated NaCl solutions, and then dried over MgSO$_4$. The aqueous solution was extracted with ether, and the ether extract was treated similarly. The crude bromo ketone obtained from both extracts was combined and used for the next step without purification. To a solution of anhydrous LiBr (74.2 g, 0.855 mol) and Li$_2$CO$_3$ (63.2 g, 0.855 mol) in 320 mL of DMF was added dropwise a solution of the above product in 65 mL of DMF. The mixture was heated at 80 °C for 2 h and then at 110 °C for 4 h. After cooling, the mixture was diluted with water and filtered. The filtrate was extracted with ether, and the extract was washed with saturated NaCl solution and then dried (MgSO$_4$). Chromatography on silica gel gave dienone **20b** as a yellow oil (30.4 g, 57%). ^{1}H NMR (CDCl$_3$) δ 6.62 (ddd, J = 10.3, 5.5, 2.8 Hz, 1H), 5.99 (ddd, J = 10.1, 2.8, 1.7 Hz, 1H), 4.65 (s, 2H), 4.57 (AB, J = 15.2 Hz, $\Delta\nu$ = 38.2 Hz, 2H), 2.85 (ddd, J = 19.8, 5.4, 1.7 Hz, 1H), 2.31 (ddd, J = 19.8, 2.8, 2.8 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.10−1.97 (m, 2H), 1.83−1.72 (m, 1H), 1.65−1.47 (m, 1H), 1.43−1.30 (m, 1H), 1.25−1.12 (m, 1H); IR (neat) 1730, 1660, 1220, 1020 cm^{-1}; MS m/z 308 (M$^+$ + 1). HRMS found, 305.1364. Calcd for C$_{17}$H$_{21}$O$_5$, 305.1389.

The transformation of 814 mg (2.67 mmol) enone **20b** into triene **21b** was carried out as described for the corresponding reaction of **20a**, giving **21b** (486 mg) in 66% yield as a pale yellow oil. ^{1}H NMR

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(44) Snyder, H. R.; Kruse, C. W. *J. Am. Chem. Soc.* **1958**, *80*, 1942.

(CDCl$_3$) δ 5.74 (s, 4H), 4.59 (s, 4H), 2.02 (s, 6H), 1.83 (dd, J = 5.6, 12.1 Hz, 2H), 1.53 (dt, J = 12.1, 6.6 Hz, 1H), 1.34 (dtt, J = 5.6, 6.6, 12.1 Hz, 1H), 1.12 (ddd, J = 6.6, 12.1, 12.1 Hz, 2H); IR (neat) 1740, 1220, 1020, 720, 710 cm^{-1}; MS m/z 288 (M$^+$). HRMS found, 288.1346. Calcd for C$_{17}$H$_{20}$O$_4$, 288.1362.

A solution of 11.5 g (39.9 mmol) of **21b** in 48 mL of MeOH was added dropwise to a solution of 5.0 g (0.12 mol) of NaOH in 20 mL of MeOH and 7.5 mL of water. The solution was stirred at room temperature for 1.5 h, diluted with water, and extracted with ether. The extract was washed with saturated NaCl solution and dried (MgSO$_4$). Chromatography on silica gel yielded 5.96 g (73%) of diol **21c** as a white solid.

11,12-Diformyl[4.3.2]propella-1,3,11-triene (22). To a solution of 122 mg (0.60 mmol) of **21c** in 8 mL of CH$_2$Cl$_2$ was added 1.36 g (15.6 mmol) of activated MnO$_2$, and the mixture was stirred at room temperature for 4 h. The mixture was filtered, and the filtrate was concentrated. Chromatography on silica gel gave 94 mg (78%) of dialdehyde **22** as a yellow solid: mp 118−120 °C dec; ^{1}H NMR (CDCl$_3$) δ 10.03 (s, 2H), 5.97−5.86 (m, 4H), 2.16−2.10 (m, 2H), 1.73−1.63 (m, 1H), 1.44−1.22 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 184.9 (t), 149.2 (q), 127.4 (t), 122.6 (t), 53.7 (q), 32.6 (s), 18.9 (s); IR (KBr) 1675, 1665, 1285, 1170, 715, 700 cm^{-1}; MS m/z 200 (M$^+$). HRMS found, 200.0824. Calcd for C$_{13}$H$_{12}$O$_2$, 200.0837.

11,12-Bis(2,2-dichloroethenyl)[4.3.2]propella-1,3,11-triene (23). To a solution of 710 μL (3.67 mmol) of diethyl trichloromethylphosphonate[45] in 1.4 mL of ether and 1.1 mL of THF, cooled to −100 °C in a MeOH−liquid N$_2$ bath, was added dropwise 1.9 mL (3.1 mmol) of 1.6 M BuLi in hexane. The mixture was stirred for 15 min, then a solution of 61 mg (0.30 mmol) of dialdehyde **22** in 1 mL of ether−THF (1:1, v/v) was added dropwise. The solution was stirred at −100 °C for 3 h and then warmed to room-temperature slowly. The mixture was diluted with 10% HCl and extracted with ether. The extract was washed with saturated NaCl solution and dried over MgSO$_4$. After removal of the solvent, the residue was chromatographed on silica gel to afford 79 mg (78%) of tetrachloride **23** as a white solid: mp 143−144 °C; ^{1}H NMR (CDCl$_3$) δ 6.48 (s, 2H), 6.16−6.12 (m, 2H), 5.90−5.86 (m, 2H), 2.30−2.14 (m, 2H), 1.49−1.24 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 140.3 (q), 129.3 (t), 122.1 (q), 121.4 (t), 120.3 (t), 54.7 (q), 35.2 (s), 18.7 (s); IR (KBr) 1585, 920, 895, 850, 780, 700 cm^{-1}; MS m/z 334 (M$^+$). Anal. Found: C, 53.73; H, 3.51. Calcd for C$_{15}$H$_{12}$Cl$_4$: C, 53.93; H, 3.62.

11,12-Bis[(trimethylsilyl)ethynyl][4.3.2]propella-1,3,11-triene (17a). To a mixture of ether and THF (1:1, v/v, 0.8 mL) cooled in an ethanol−dry ice bath was added 910 μL (1.48 mmol) of 1.6 M BuLi followed by a solution of 90 mg (0.27 mmol) of tetrachloride **23** in 1.5 mL of the same solvent. After 3 h, 200 μL (1.58 mmol) of Me$_3$SiCl was added dropwise, and the mixture was stirred for 1.5 h before NaHCO$_3$ solution was added. The mixture was warmed to room temperature and extracted with ether. The extract was washed with saturated NaCl solution and dried (MgSO$_4$). Removal of the solvent followed by flash chromatography gave 71 mg (78%) of **17a** as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 5.88−5.77 (m, 4H), 1.94 (dd, J =12.6, 5.7 Hz, 2H), 1.63−1.37 (m, 2H), 1.25−1.12 (m, 2H), 0.19 (s, 18H); ^{13}C NMR (CDCl$_3$) δ 133.2 (q), 128.7 (t), 121.7 (q), 101.1 (q), 96.5 (q), 55.8 (q), 32.7 (s), 18.7 (s), −0.1 (p); IR (neat) 2120, 1240, 1020, 870, 840, 750 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 303 (4.19), 287.5 (4.14), 265 (4.37), 255 (4.27) nm; MS m/z 336 (M$^+$). HRMS found, 336.1724. Calcd for C$_{21}$H$_{28}$Si$_2$, 336.1730.

11,12-Bis[(*tert*-butyldimethylsilyl)ethynyl][4.3.2]propella-1,3,11-triene (17b). To a mixture of ether and THF (1:1, v/v, 4.6 mL) cooled in an ethanol-dry ice bath was added 7.0 mL (11 mmol) of 1.6 M BuLi followed by a solution of 538 mg (1.61 mmol) of tetrachloride **23** in 12 mL of the same solvent. After 2 h, the mixture was warmed to 0 °C, and 1.60 g (10.6 mmol) of *t*-BuMe$_2$SiCl in 7 mL of ether was added dropwise, and the mixture was stirred for 2 h before NaHCO$_3$ solution was added. The mixture was extracted with ether, and the extract was washed with saturated NaCl solution and then dried (MgSO$_4$). Removal of the solvent followed by flash chromatography gave 325 mg (48%) of **17b** as a white solid together with 300 mg (31%) of bisallene **24** as a colorless oil.

17b: mp 75−78 °C; ^{1}H NMR (CDCl$_3$) δ 5.88−5.77 (m, 4H), 1.94 (dd, J = 12.6, 5.4 Hz, 2H), 1.63−1.38 (m, 2H), 1.25−1.13 (m, 2H), 0.93 (s, 18H), 0.11 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 133.2 (q), 128.7 (t), 121.7 (q), 99.4 (q), 97.3 (q), 55.8 (q), 32.8 (s), 26.1 (p), 18.7 (s), 16.6 (q), −4.7 (p); IR (KBr) 2130, 1250, 1020, 860, 840, 820, 810, 770 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 304 (4.22), 288 (4.18), 265 (4.38), 255 (4.28) nm; MS m/z 420 (M$^+$). HRMS found, 420.2669. Calcd for C$_{27}$H$_{40}$Si$_2$, 420.2668.

24: ^{1}H NMR (CDCl$_3$) δ 5.68−5.61 (m, 4H), 2.06−1.83 (m, 2H), 1.68−1.17 (m, 4H), 0.93, 0.90, 0.89, 0.886, 0.882, 0.876, 0.872 (s, total 30H), 0.12, 0.11, 0.094, 0.085, 0.07, 0.066, 0.045, 0.042, 0.032, 0.017 (s, total 18H); ^{13}C NMR (CDCl$_3$) δ 209.6, 209.5 (q), 202.7, 202.1 (q), 130.0, 129.7, 129.5 (t), 119.2, 119.1, 119.0, 118.9 (t), 106.9, 106.8 (q), 104.7, 104.7, 104.4 (q), 98.4, 98.3 (q), 94.4, 94.3 (q), 53.7, 53.5 (q), 52.40, 52.36 (q), 40.1, 40.0 (s), 39.7, 39.5 (s), 31.8, 31.7 (s), 31.4, 31.3 (s), 27.6, 27.4, 27.3, 27.2, 27.1, 26.9 (p), 22.8, 22.7 (s), 19.7 (s), 18.0, 17.8, 17.7, 17.5, 17.4 (q), 14.11, 14.10 (p), −2.5, −2.6 (p), −3.0, −3.1, −3.3 (p), −3.6, −3.8 (p), −5.5, −5.55, −5.64 (p); IR (neat) 1880, 1250, 1000, 870, 850, 830, 810, 770 cm^{-1}; UV (cyclohexane) λ_{max} (log ϵ) 304 (4.22), 288 (4.18), 265 (4.38), 255 (4.28) nm; MS m/z 420 (M$^+$). HRMS found, 420.2669. Calcd for C$_{27}$H$_{40}$Si$_2$, 420.2668.

11,12-Diethynyl[4.3.2]propella-1,3,11-triene (17c). To a solution of 56 mg (0.13 mmol) of **17b** in a mixture of THF and water (95:5, v/v, 3 mL) was added 330 mL (0.33 mmol) of 1.0M Bu$_4$NF solution in THF and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was directly subjected to flash chromatography to afford 20 mg (78%) of **17c** as a colorless oil which turned dark under vacuum at room temperature. Deprotection of **17a** was similarly undertaken. Because of its thermal lability, this compound was not thoroughly purified when it was used for the subsequent transformations. ^{1}H NMR (CDCl$_3$) δ 5.92−5.79 (m, 4H), 3.21 (s, 2H), 1.95 (dd, J = 12.9, 5.7 Hz, 2H), 1.66−1.35 (m, 2H), 1.28−1.16 (m, 2H); IR (neat) 3280, 840, 840, 780 cm^{-1}; MS m/z 192 (M$^+$). HRMS found, 192.0928. Calcd for C$_{15}$H$_{12}$, 192.0939.

Method B: Through Dichloropropellatriene 27. 11,12-Dichloro-[4.3.2]propellan-1-one (25). A solution of 27.4 g (0.201 mol) of enone **11** in 112 mL of trichloroethene (ca. 1.2 mol) was irradiated with a 500-W high-pressure mercury lamp for about 70 h. After removal of the solvent, the residue was distilled under reduced pressure (140 °C/1 mmHg) to give 44.2 g (82%) of the cycloadducts as a brown solid. A portion of this sample was purified by chromatography on silica gel to afford a white solid. NMR spectra of this product indicated that it was a mixture of three regio- and stereoisomers. ^{1}H NMR (CDCl$_3$) δ 5.03, 4.98, 4.53 (s, ratio 1:3:4.5, total 1H), 2.6−1.5 (m, 13H); ^{13}C NMR (CDCl$_3$) δ 211.0, 207.6, 207.2 (q), 93.6, 88.0, 87.8 (q), 74.2, 70.8, 70.0 (t), 68.8, 66.6, 65.8 (q), 59.7, 52.5, 51.9 (q), 40.1, 39.8, 39.6 (s), 37.5, 37.2, 37.0 (s), 36.9, 35.3, 33.1 (s), 34.0, 31.9, 26.0 (s), 26.9, 25.1, 24.0 (s), 21.5, 19.8, 18.6 (s); IR (KBr) 1700, 820, 725 cm^{-1}.

To a solution of 27.8 g (0.298 mol) of *t*-BuOK in 200 mL of DMSO was added dropwise a solution of the above ketone in 180 mL of THF. The mixture was stirred at room temperature for 1.5 h and then diluted with water and extracted with ether. The extract was washed with water and saturated NaCl solution and then dried (MgSO$_4$). After removal of the solvent, 34.9 g (92%) of **25** was isolated by distillation under reduced pressure (79−95 °C/0.3 mmHg) as a pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 2.62−2.51 (m, 1H), 2.25−2.12 (m, 2H), 2.01−1.75 (m, 5H), 1.65−1.36 (m, 3H), 1.24−1.12 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 209.5 (q), 129.4 (q), 122.0 (q), 68.8 (q), 62.6 (q), 38.7 (s), 30.6 (s), 29.0 (s), 24.9 (s), 22.0 (s), 19.3 (s); IR (neat) 1700, 1630, 1060, 1040, 1030, 970, 890, 820, 740 cm^{-1}; MS m/z 230 (M$^+$). HRMS found, 230.0206. Calcd for C$_{11}$H$_{12}$Cl$_2$O, 260.0265.

11,12-Dichloro[4.3.2]propella-2,11-dien-1-one (26). Bromination of 42.0 g (0.182 mol) of ketone **25** followed by dehydrobromination was carried out as described for the corresponding transformation of diacetate **19b** described above to give 31.9 g (75%) of **26** as a pale yellow oil which solidified on standing: bp 80 °C/0.6 mmHg; mp 88−89 °C; ^{1}H NMR (CDCl$_3$) δ 6.66 (ddd, J = 10.3, 5.6, 2.7 Hz, 1H), 6.04 (ddd, J = 10.3, 2.8, 1.8 Hz, 1H), 2.88 (ddd, J = 9.9, 5.6, 1.6 Hz, 1H), 2.33 (ddd, J = 9.8, 2.8, 2.8 Hz, 1H), 2.10 (ddd, J = 12.7, 5.4, 2.6 Hz, 2H), 1.88−1.79 (m, 1H), 1.66−1.34 (m, 2H), 1.29−1.18 (m, 1H); ^{13}C

(45) Kosolapoff, G. M. *J. Am. Chem. Soc.* **1947**, *69*, 1002.

NMR (CDCl$_3$) δ 197.8 (q), 144.4 (t), 128.1 (q), 127.2 (t), 125.6 (q), 66.7 (q), 57.5 (q), 32.5 (s), 31.3 (s), 24.9 (s), 21.8 (s); IR (KBr) 1660, 1630, 1060, 1000, 980, 970, 880, 810, 770, 720 cm^{-1}; MS *m/z* 228 (M$^+$). HRMS found, 228.0082. Calcd for C$_{11}$H$_{10}$Cl$_2$O, 228.109.

11,12-Dichloro[4.3.2]propella-1,3,11-triene (27). Sodium borohydride reduction of 24.8 g (0.108 mol) of **26** and subsequent dehydration was carried out as described for the corresponding transformation of **20a** to give 16.4 g (71%) of **27** as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 5.94−5.81 (m, 4H), 1.98 (dd, *J* = 5.8, 12.7 Hz, 2H), 1.67−1.58 (m, 1H), 1.47−1.29 (m, 1H), 1.25−1.14 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 127.7 (t), 124.5 (q), 122.3 (t), 59.1 (q), 31.0 (s), 18.3 (s); IR (neat) 1610, 1190, 1035, 970, 905, 855, 810, 740, 715 cm^{-1}; MS *m/z* 212 (M$^+$). HRMS found, 212.0152. Calcd for C$_{11}$H$_{10}$Cl$_2$, 212.0160.

11,12-Bis[(triisopropylsilyl)ethynyl][4.3.2]propella-1,3,11-triene (17d). A flask containing 188 mg (0.99 mmol) of CuI and 488 mg (0.42 mmol) of Pd(PPh$_3$)$_4$ was charged with argon. A solution of 1.50 g (7.04 mmol) of **27** in 15 mL of benzene was added followed by 2.1 mL (∼21 mmol) of triethylamine. To this solution was added 3.9 mL (∼18 mmol) of (triisopropylsilyl)ethyne, and the mixture was stirred at room temperature for 3 h. After dilution with ether, the mixture was filtered, and the filtrate was washed with 5% HCl, water, and saturated NaCl solution. After being dried (MgSO$_4$), the solvent was removed under reduced pressure. Flash chromatography gave 3.50 g (99%) of **17d** as a pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 5.91−5.81 (m, 4H), 1.97 (dd, *J* = 5.4, 12.6 Hz, 2H), 1.64−1.46 (m, 2H), 1.34−1.01 (m, 2H), 1.10 (s, 42H); ^{13}C NMR (CDCl$_3$) δ 133.0 (q), 128.8 (t), 121.6 (t), 98.8 (q), 97.4 (q), 55.8 (q), 32.8 (s), 18.8 (s), 18.6 (p), 11.2 (t); IR (neat) 2130, 1250, 990, 880, 850, cm^{-1}; MS *m/z* 504 (M$^+$). HRMS found, 292.1689. Calcd for C$_{17}$H$_{24}$O$_4$, 292.1675.

Similar reaction of 2.13 g (10.0 mmol) of **27** with (trimethylsilyl)-ethyne gave 1.99 g (59%) of **12a** which was identical to the sample prepared from dialdehyde **22**.

11,12-Bis[(triisopropylsilyl)butadiynyl][4.3.2]propella-1,3,11-triene (18). To a solution of 31 mg (0.43 mmol) of NH$_4$OH·HCl, 165 µL of 70% aqueous solution of ethylamine (2.05 mmol), and 6 mg (0.06 mmol) of CuCl in 400 µL of methanol and THF (2:1, v/v) was added a solution of 26 mg of diyne **17c** (0.14 mmol) in 1.4 mL of the same solvent. After 15 min, a solution of 118 mg (0.40 mmol) of 1-bromo-2-(triisopropylsilyl)ethyne^{32} in 800 µL of the same solvent was added dropwise. The mixture was stirred at room temperature for 1 h, diluted with dilute HCl, and then extracted with ether. The extract was washed with Na$_2$CO$_3$ solution and saturated NaCl solution and then dried (MgSO$_4$). Removal of the solvent followed by flash chromatography gave 71 mg (95%) of tetrayne **18** as a colorless solid: mp 145−147 °C; ^{1}H NMR (CDCl$_3$) δ 5.89−5.79 (m, 4H), 1.98 (dd, *J* = 12.9, 5.4 Hz, 2H), 1.64−1.10 (m, 4H), 1.09 (s, 42H); ^{13}C NMR (CDCl$_3$) δ 134.6 (q), 128.14 (t), 122.1 (t), 92.1 (s), 89.4 (q), 67.8 (q), 56.7 (q), 32.9 (s), 18.7 (s) 18.5 (p), 11.3 (t); IR (KBr) 2090, 995, 880, 760 cm^{-1}; MS *m/z* 552 (M$^+$). HRMS found, 552.3589. Calcd for C$_{37}$H$_{52}$Si$_2$, 552.3608.

Photolysis of 11,12-Diethynyl[4.3.2]propella-1,3,11-trienes 17a and 17b. A solution of 70 mg (0.21 mmol) of **17a** in 5 mL of hexane, placed in a quartz tube, was irradiated with a 20-W low-pressure mercury lamp under a nitrogen atmosphere in an ice bath for 5 h. After removal of the solvent, flash chromatography gave hexatriyne **28a**^{32,34} (30 mg, 66%) together with an inseparable mixture of the isomerization products **29a** and **30a** (∼1:1, 10 mg, 14%) as a yellow oil. Indane was detected in the crude product by ^{1}H NMR and GLC. Irradiation of **17a** with a 500-W high-pressure mercury lamp through a Pyrex filter afforded **28a** together with **30a** in 58 and 20% yields, respectively, while **29a** was not obtained under these conditions.

28a: ^{13}C NMR (CDCl$_3$) δ 87.9 (q), 87.4 (q), 61.9 (q), −0.6 (p).
^{1}H NMR (CDCl$_3$) δ for **29a**: 5.90 (dd, *J* = 4.8, 2.1 Hz, 1H), 5.58 (dd, *J* = 5.3, 2.8 Hz, 1H), 3.34 (d, *J* = 2.5 Hz, 1H), 2.69 (d, *J* = 3.0 Hz, 1H); for **30a**: 5.81 (br s, 2H), 5.75 (AB, *J* = 11.1 Hz, Δν = 44.8 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ for **30a**: 142.2 (q), 138.9 (q), 132.7 (t), 131.1 (t), 130.9 (t), 130.6 (q), 130.0 (t), 129.1 (q), 104.4 (q), 103.4 (q), 99.7 (q), 98.5 (q), 37.5 (s), 36.4 (s), 22.4 (t), 0.1 (p), 0.0 (p): MS (for 1:1 mixture of **29a** and **30a**) *m/z* 336 (M$^+$).

Irradiation of 66 mg (0.17 mmol) of **17b** with a low-pressure mercury lamp under similar conditions afforded 33 mg (67%) of triyne **28b**^{32}

and 4 mg (6%) a mixture of **29b** and **30b** in a ratio of 1:7 as a yellow oil. Irradiation of **17b** with a high-pressure mercury lamp gave 66% of **28b** and 6% of **30b**.

28b: ^{13}C NMR (CDCl$_3$) δ 88.6 (q), 86.2 (q), 61.7 (q), 26.0 (p), 16.8 (q), −5.0 (p).
^{1}H NMR (CDCl$_3$) δ for **29b**: 5.88 (ddd, *J* = 5.3, 2.3, 0.7 Hz, 1H), 5.58 (dd, *J* = 5.2, 3.0 Hz, 1H), 3.34 (d, *J* = 2.5 Hz, 1H), 2.68 (d, *J* = 3.0 Hz, 1H); for **30b**: 5.80 (br s, 2H), 5.73 (AB, *J* = 11.4 Hz, Δν = 42.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ for **29a**: 135.1 (t), 130.1 (q), 125.7 (t), 67.1 (q), 60.4 (q), 57.4 (t), 48.0 (t), 28.8 (s), 27.3 (s), 25.6 (s); for **30a**: 141.9 (q), 139.1 (q), 132.3 (t), 131.3 (t), 131.1 (t), 130.1 (q), 130.0 (t), 128.8 (t), 105.1 (q), 104.2 (q), 98.1 (q), 97.1 (q), 37.6 (s), 36.5 (s), 26.2 (p), 22.5 (s), 16.7 (q), 16.6 (q), −4.5 (p); MS (for 1:7 mixture of **29b** and **30b**) *m/z* 420 (M$^+$).

Photolysis of 11,12-Bis[(triisopropylsilyl)butadiynyl][4.3.2]propella-1,3,11-triene (18). A solution of 45 mg (0.081 mmol) of **18** in 5 mL of hexane, placed in a quartz tube, was irradiated with a 20-W low-pressure mercury lamp under a nitrogen atmosphere in an ice bath for 12.5 h. After removal of the solvent, flash chromatography gave decapentayne **31**^{32} (26 mg, 74%) as a white solid. Indane was detected in the crude product by ^{1}H NMR and GLC, but any isomerization product was not detected.

31: ^{13}C NMR (CDCl$_3$) δ 89.5 (q), 86.5 (q), 62.42 (q), 62.40 (q), 61.4 (q), 18.5 (p), 11.3 (t).

Photolysis of 11,12-Diethylidene[4.3.2]propella-1,3-diene (24). A solution of **24** (50 mg, 0.084 mmol) in 0.8 mL of THF-*d$_8$* was irradiated with a low-pressure mercury lamp as described above for **27** for 27 h. The color of the solution turned reddish purple. Since an attempt to isolate the product **32** by flash chromatography failed because of its lability, ^{13}C NMR spectra were recorded directly at −20 °C, which indicated the presence of only indane and **32**. An aliquot of the photolysate was diluted with cyclohexane to measure the UV−vis spectrum. IR spectrum was recorded quickly after removal of the solvent in vacuo.

32: ^{13}C NMR (THF-*d$_8$*, −20 °C) δ 189.9 (q), 174.9 (q), 156.8 (q), 154.1 (q), 148.3 (q), 137.3 (q), 38.8 (s),32.3 (s), 27.28 (p), 27.26 (p), 27.1 (p), 23.4 (s), 20.2 (q), 19.4 (q), 19.2 (q), 14.5 (p), −3.60 (p), −3.61 (p), −5.9 (p); IR (neat) 2060, 2040, 2000, 1960, 1880, 1820, 1600, 1250, 1060, 1020, 1000, 830, 800 cm^{-1}; UV (cyclohexane) λ$_{max}$ 584, 527 nm.

Oxidative Coupling of Diethynylpropellatriene 17c: Propellane-Annelated Dehydro[18]annulene 15 and Dehydro[24]annulene 16. A mixture of diyne **17a** (1.00 g, 2.97 mmol) and LiOH·H$_2$O (673 mg, 16.0 mmol) in 13.8 mL of THF and 3.7 mL of H$_2$O was stirred at room temperature for 1.5 h. After dilution with water, the mixture was extracted with a mixture of pentane and THF (1:1, v/v). The extract was dried over MgSO$_4$ and then passed through a column of silica gel. The solvent was evaporated and the residue, i.e., **17c**, was diluted immediately with 70 mL of a mixture of THF, methanol, and pyridine (1:1:2, v/v) for the subsequent coupling reaction. To a solution of 3.78 g (20.8 mmol) of Cu(OAc)$_2$ in 280 mL of a mixture of THF, methanol, and pyridine (1:1:2, v/v) was added the above solution of **17c** during a 9 h-period under nitrogen atmosphere. Another portion of Cu(OAc)$_2$ (1.62 g, 8.92 mmol) was added after 7 h. The mixture was stirred at room temperature for a total of 33 h, while the flask was covered with aluminum foils to protect the products from the room light. Most of the solvent was removed under reduced pressure, and the residue was treated with 10% HCl and benzene. The insoluble material was filtered off, and the organic layer was separated, washed with saturated NaHCO$_3$ solution, and then dried (MgSO$_4$). The solvent was removed, and the residue was chromatographed on silica gel. The product was washed with a small amount of benzene to give 127 mg of trimer **15** as an orange solid. Flash chromatography of the filtrate gave additional **15**, yielding a total amount of 211 mg. During the purification, care was taken to protect the product from room light. Final purification was conducted with preparative HPLC to give 166 mg (29% from **17c**) of **15** (mixture of two diastereomers). In an other run which was undertaken similarly, CHCl$_3$ was used for extraction instead of benzene. In this case a mixture of orange trimer **15** and carmine red tetramer **16** (mixture of four diastereomers) was obtained in a ratio of 13:1 (estimated by HPLC peak area, taking into account the relative extinction coefficient) in 39% yield from **17c**. Tetramer **16** was isolated

by preparative HPLC. The absence of tetramer in the first run can be ascribed to its low solubility of **16** in benzene.

15 (mixture of two diastereomers with C_{3v} and C_s symmetry in an approximate ratio of 1:3): dec 170 °C; ^{1}H NMR (CDCl$_3$) δ 6.22–6.17 (m, 6H), 6.00–5.95 (m, 6H), 2.29 (dd, J = 12.9, 6.0 Hz, 6H), 1.64 (ddd, J = 12.8, 6.6, 6.2 Hz, 6H), 1.58–1.50 (m, 3H), 1.16 (ddd, J = 24.7, 6.6, 6.2 Hz, 3H); ^{13}C NMR (CDCl$_3$) δ 137.89, 137.88, 137.87, 137.85 (q), 128.90*, 128.85 (t)*, 122.21, 122.19, 122.18, 122.16 (t), 83.37‡, 83.35‡, 83.34†, 83.33‡ (q), 81.08‡, 81.07†, 81.04‡, 81.03‡ (q), 57.70, 57.69, 57.68 (q), 34.37, 33.35 (s), 19.01 (s). The intensities of the signals marked by * are approximately twice as much as those of the signals of similar environment. The sp carbon signals (indicated by †) for the minor C_{3v} isomer was identified by using a 90° pulse radiation; under these conditions, the intensities of the signals of the C_{3v} isomer decreased relative to those of the corresponding signals (indicated by ‡) of the major C_s isomer: IR (KBr) 2140, 1070, 1045, 770, 720, 665 cm^{-1}; UV–vis (CHCl$_3$) λ_{max} (log ϵ) 539 (2.00) 484 (2.43), 415 (4.37), 403 (4.21), 356 (4.78) nm; LD-TOF MS see Figure 1.

16 (mixture of three diastereomers): dec 186 °C; ^{1}H NMR (CDCl$_3$: CS$_2$ = 1:3) δ 5.81–5.78 (m, 8H), 5.55–5.50 (m, 8H), 1.76 (dd, J = 12.6, 5.2 Hz, 8H), 1.6–1.0 (m, 16H); IR (KBr) 2120, 1070, 1050, 720, 670 cm^{-1}; UV–vis (CHCl$_3$) λ_{max} (log ϵ) 427 (3.76), 369 (4.92), 348 (4.70) nm; LD-TOF MS see Figure 2. Because of the extremely limited solubility of **16** in organic solvents, the ^{13}C NMR spectrum of this compound was not recorded.

Oxidative Coupling of Diethynylpropellatriene 17c Using Cu-(I)–Cu(II) Salts. To a solution of 400 mg (0.771 mmol) of diyne **17d** in 18 mL of THF was added dropwise 2.0 mL of 1.0 M Bu$_4$NF in THF (2.0 mmol). The mixture was stirred at room temperature for 1.5 h, diluted with water, and extracted with hexane. The extract was washed with saturated NaCl solution, dried (MgSO$_4$), and passed through a column of silica gel. The solvent was removed, and the residue (**17c**) was diluted with 20 mL of pyridine. This solution was added dropwise during a 2 h-period to a solution of 1.40 g (7.71 mmol) of Cu(OAc)$_2$ and 380 mg (3.84 mmol) of CuCl in 100 mL of pyridine, which had been bubbled with nitrogen for 20 min. The mixture was stirred at room temperature for 23 h and the solvent was removed under reduced pressure. The residue was treated as above (CHCl$_3$ used for extraction) to give 82 mg (56% from **17d**) of a mixture of **15** and **16** in a ratio of ca. 1:1.

11-Chloro-12-[1-(3-hydroxy-3-methylbutynyl)][4.3.2]propella-1,3,11-triene (33a). Reaction of 6.00 g (28.2 mmol) of **27** and 2-methyl-3-butyn-2-ol (6.20 g, 84.5 mmol) was carried out as described for the preparation of **17d** for 1.5 h at room temperature using 2.00 g (1.73 mmol) of Pd(PPh$_3$)$_4$ and 750 mg (3.94 mmol) of CuI in 25 mL of THF. The products were separated by flash chromatography to afford 5.10 g (70%) of **33a** and 272 mg (3%) of **17e** both as yellow solids. Final purification was conducted by preparative HPLC.

33a: ^{1}H NMR (CDCl$_3$) δ 5.94–5.76 (m, 4H), 2.19 (s, 1H), 2.00–1.91 (m, 2H), 1.66–1.13 (m, 4H), 1.15 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 133.3 (q), 128.8 (t), 127.5 (t), 125.5 (q), 122.5 (t), 121.6 (t), 98.9 (q), 71.7 (q), 65.4 (q), 59.3 (q), 55.7 (q), 32.1 (s), 31.5 (s), 31.3 (p), 18.4 (s); IR (neat) 3250, 1250, 1240, 1220, 1160, 1010, 960, 940, 900, 890, 750, 700 cm^{-1}; MS m/z 261 (M$^+$). HRMS found, 260.7628. Calcd for C$_{16}$H$_{17}$OCl, 260.7631.

17e: mp 130–134 °C; ^{1}H NMR (CDCl$_3$) δ 5.94–5.84 (m, 4H), 2.71 (s, 2H), 2.02–1.95 (m, 2H), 1.70–1.20 (m, 4H), 1.15 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 131.8 (q), 128.7 (t), 121.6 (t), 99.2 (q), 74.2 (q), 65.6 (q), 55.7 (q), 32.5 (s), 31.3 (p), 18.6 (s); IR (KBr) 3300, 1290, 1160, 1140, 960, 920, 900, 720 cm^{-1}; MS m/z 308 (M$^+$). HRMS found, 308.4211. Calcd for C$_{21}$H$_{24}$O$_2$, 308.4204.

11-Chloro-12-ethynyl[4.3.2]propella-1,3,11-triene (33b). To a solution of 521 mg (2.00 mmol) of **33a** in 45 mL of toluene was added a solution of 450 mg (8.0 mmol) of KOH in 3 mL of methanol, and the mixture was heated under reflux under nitrogen atmosphere for 30 min. After cooling, the mixture was diluted with water, and the organic layer was washed with saturated NaHCO$_3$ solution and NaCl solution and then dried (MgSO$_4$). The product was purified by flash chromatography to afford 293 mg (73%) of **33b** as a colorless oil. ^{1}H NMR (CDCl$_3$) δ 5.96–5.76 (m, 4H), 3.15 (s, 2H), 2.02–1.93 (m, 2H), 1.67–1.34 (m, 2H), 1.28–1.15 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 132.2 (q), 128.5

(t), 127.3 (t), 125.1 (q), 122.7 (t), 121.7 (t), 82.4 (q), 73.3 (t), 59.5 (q), 55.7 (q), 32.1 (s), 31.5 (s), 18.4 (s); IR (neat) 3293, 2097, 1609, 1204, 1109, 1094, 938, 827, 753 cm^{-1}; MS m/z 212 (M$^+$). HRMS found, 212.05271. Calcd for C$_{13}$H$_{11}$Cl, 212.0549.

Attempted Cyclization of 33b. To a solution of 10 mg (0.053 mmol) of CuI, 148 mg (0.257 mmol) of Pd(PPh$_3$)$_4$, and 0.76 μL (0.77 mmol) of butylamine in 2 mL of THF was added dropwise a solution of 52 mg (0.257 mmol) of **33b** in 2.5 mL of THF under argon atmosphere. The mixture was stirred at room temperature for 2 h and treated as described for the preparation of **17d** to yield 30 mg (58%) of the linear dimer **34** (mixture of two diastereomers) as a white solid. Attempted cyclization of **33b** under different conditions invariably gave **34** as the only isolable product but no cyclization products were detected. **34**: mp 145 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.96–5.76 (m, 8H), 2.02–1.93 (m, 4H), 1.67–1.31 (m, 4H), 1.30–1.11 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 135.0 (q), 128.4 (t), 127.0 (t), 124.7 (q), 122.9 (t), 121.8 (t), 78.2 (q), 72.8 (q), 59.7 (q), 56.5 (q), 34.2 (s), 31.8 (s), 18.5 (s); IR (KBr) 3300, 1290, 1160, 1140, 960, 920, 900, 720 cm^{-1}; MS m/z 402 (M$^+$). HRMS found, 402.0899. Calcd for C$_{21}$H$_{24}$O$_2$, 402.0942.

Coupling of Chloroethynylpropellatriene 33a under Phase-Transfer Conditions: Propellane-Annelated Dehydro[12]annulene 12, Dehydro[16]annulene 13, and Dehydro[20]annulene 14. A mixture of 2.60 g (9.96 mmol) of **33a**, CuI (190 mg, 1.00 mmol), Pd-(PPh$_3$)$_4$ (1.15 g, 1.00 mmol), benzyltriethylammonium chloride (91 mg, 0.40 mmol) in 30 mL of benzene and 10 mL of 5 N aqueous NaOH solution was heated at 80 °C with vigorous stirring for 140 h under nitrogen atmosphere. The mixture was diluted with water and extracted with CHCl$_3$. The extract was washed with 6 N HCl, water, and saturated NaCl solution and was dried (MgSO$_4$). After removal of the solvent the products were separated by flash chromatography followed by preparative HPLC purification to afford 18 mg (1%) of trimer **12** as a dark red solid, 183 mg (11%) of tetramer **13** as a dark violet solid, and 15 mg (1%) of pentamer **14** as a reddish orange solid.

12 (mixture of two diastereomers with C_{3v} and C_s symmetry): mp 117 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.77–5.83 (m, 6H), 5.28–5.35 (m, 6H), 1.96–2.06 (m, 3H), 1.50–1.63 (m, 9H), 0.80–0.88 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 139.91, 139.89, 139.78*, 139.76 (q), 126.26, 126.19, 126.17, 126.15 (t)*, 122.00, 121.98*, 121.97, 121.94 (t), 93.47, 93.35*, 93.33, 93.30 (q), 54.47, 54.46*, 54.45, 54.41 (q), 32.14, 32.11*, 32.08, 32.06 (s), 18.86, 18.81, 18.77* (s). The signals marked by asterisk are due to the C_{3v} isomer, because the intensities of these signals are slightly larger than those expected from the statistical distribution (1:3) of C_{3v} and C_s isomers: IR (KBr) 1250, 1070, 1020, 800, 750 cm^{-1}; UV–vis (CHCl$_3$) λ_{max} (log ϵ) 614 (sh, 1.96), 550 (2.23), 509 (2.24), 250 (4.83) nm; FAB MS m/z (%): 498 (100) [M$^+$], 261 (30) [M$^+$ − 2(C$_9$H$_{10}$) − H]; LD-TOF MS see Figure 2.

13 (mixture of four diastereomers with C_{4v}, C_s, C_{2v}, and C_{2h} symmetry): mp 218–221 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.76–5.81 (m, 8H), 5.37–5.44 (m, 8H), 1.68–1.74 (m, 4H), 1.54–1.66 (m, 12H), 0.92–1.01 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 135.65, 135.62, 135.58, 135.54, 135.53, 135.52, 135.51, 135.49* (q), 127.26, 127.25, 127.21, 127.14, 127.01* (t), 121.91, 121.90*, 121.87, 121.86, 121.85, 121.81 (t), 89.98, 89.95, 89.93, 89.92, 89.91, 89.91*, 89.90, 89.88 (q), 54.93, 54.90, 54.88, 54.87* (q), 32.49, 32.47, 32.45 (s), 18.73, 18.69, 18.66, 18.65 (s). Since the signals marked by * are due to the statistically least feasible C_{2v} isomer, these signals have apparently low intensities: UV–vis (CHCl$_3$) λ_{max} (log ϵ) 502 (2.72), 309 (4.39), 272 (4.30) nm; FAB MS m/z (%): 664 (100) [M$^+$], 309 (53) [M$^+$ − 3(C$_9$H$_{10}$) − H]; LD-TOF MS see Figure 2.

14 (mixture of four diastereomers): mp 108 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.82–5.88 (m, 10H), 5.68–5.65 (m, 10H), 1.84–1.87 (m, 10H), 1.59–1.61 (m, 10H), 1.14–1.22 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 132.99, 132.97, 132.95, 132.92, 132.86, 132.82, 132.80, 132.78 (q), 128.35, 128.33, 128.29, 128.25, 128.21, 128.20, 128.18, 128.16, 128.11 (t), 121.96, 121.94, 121.91, 121.89, 121.85 (t), 88.80, 88.79, 88.77, 88.75, 88.74, 88.73 (q), 56.08, 56.07, 56.06, 56.05, 56.04, 56.03, 56.02 (q), 32.94 (s), 18.74, 18.71, 18.67 (s); IR (KBr) 1100, 870, 760 cm^{-1}; UV–vis (CHCl$_3$) λ_{max} (log ϵ) 345 (4.53), 263 (4.43) nm; FAB MS m/z (%): 830 (37) [M$^+$], 357 (100) [M$^+$ − 4(C$_9$H$_{10}$) − H], 240 (65) [M$^+$ − 5(C$_9$H$_{10}$)]; LD-TOF MS see Figure 2.

Alternative Method for Preparation of Dehydro[12]annulene 12.
Coupling of **17c** (190 mg, 0.99 mmol) and an excess **27** (3.00 g, 14.1
mmol) was carried out as described for the preparation of **17d** using
90 mg (0.47 mmol) of CuI, 274 mg (0.24 mmol) of Pd(PPh$_3$)$_4$, and
586 μL (5.9 mmol) of triethylamine in 6 mL of THF. The 2:1 coupling
product **35** (mixture of three diastereomers) was isolated by flash
chromatography as a yellow solid: mp 68−70 °C; ^{1}H NMR (CDCl$_3$)
δ 5.77−5.95 (m, 12H), 1.96−2.03 (m, 6H), 1.16−1.67 (m, 12H); ^{13}C
NMR (CDCl$_3$) δ 133.03, 133.01, 132.98 (q), 131.91, 131.90, 131.83
(q), 128.83, 128.44 (t), 127.33, 127.31 (t), 125.67 (q), 122.61 (t), 121.85,
121.55 (t), 86.57 (q), 84.94 (q), 59.64 (q), 56.33, 56.31, 56.16 (q), 33.00
(s), 32.28, 31.83 (s), 18.78 (s), 18.50, 18.48 (s); IR (KBr) 2330, 1200,
1080, 1020, 980, 900, 850, 750 cm^{-1}; MS *m/z* 544 (M$^+$).

Coupling of **35** (440 mg, 0.81 mmol) with 2-methyl-3-butyn-2-ol
(75 mg, 0.89 mmol) was carried out as described for the preparation
of **33a** using 15 mg (0.081 mmol) of CuI, 15 mg (0.040 mmol) of
PdCl$_2$(PhCN)$_2$, and 1.38 g (16 mmol) of piperidine in 9 mL of THF to
afford 225 mg (47%) of monosubstitution product **36** and 191 mg (36%)
of disubstitution product **37** both as orange solids.

36 (mixture of three diastereomers): mp 97−100 °C; ^{1}H NMR
(CDCl$_3$) δ 5.76−5.95 (m, 12H), 2.12 (s, 1H), 1.91−1.99 (m, 6H), 1.64−
1.16 (m including singlet at 1.55, 10H); ^{13}C NMR (CDCl$_3$) δ 133.12,
133.09, 133.07, 133.03, 132.98, 132.97 (q), 132.62, 132.60, 132.57
(q), 131.87, 131.85, 131.81 (q), 128.73, 128.71, 128.67, 128.63, 128.57,
128.47, 128.45 (t), 127.29 (t), 125.66 (q), 122.64, 122.59 (t), 121.83,
121.81, 121.68, 121.64, 121.61 (t), 100.31 (q), 87.63, 87.61, 87.60,
87.58 (q), 86.92, 86.89 (q), 86.64, 86.63 (q), 84.87, 84.84 (q), 74.62
(q), 65.65 (q), 59.61, 59.38 (q), 56.31, 56.30, 56.16, 56.14, 56.09 (q),
33.00, 32.87, 32.76 (s), 32.28 (s), 31.80, 31.39, 31.36 (p), 18.73, 18.47
(s); IR (KBr) 3400, 2340, 1260, 1160, 1090, 1040, 860, 840, 760, 720
cm^{-1}; MS: *m/z* 593 (M$^+$).

37 (mixture of three diastereomers): mp 125−127 °C; ^{1}H NMR
(CDCl$_3$) δ 5.88−5.78 (m, 12H), 2.75 (s, 2H), 2.00−1.93 (m, 6H), 1.61−
1.17 (m including singlet at 1.55, 24H); ^{13}C NMR (CDCl$_3$) δ 133.15,
133.14, 133.11, 133.08 (q), 132.69, 132.67, 132.65, 132.63 (q), 131.66,
131.65 (q), 128.71, 128.51, 128.45 (t), 121.74, 121.67 (t), 100.54 (q),
87.55, 87.53 (q), 86.91, 86.89, 86.86 (q), 74.47, 74.45 (q), 65.70, 65.51
(q), 56.27 (q), 56.01 (q), 32.94, 32.78, 32.72 (s), 31.32, 31.30 (p), 18.64
(s); IR (KBr) 3350, 2340, 1260, 1160, 1080, 1050, 950, 910, 870, 860,
760, 720 cm^{-1}; MS: *m/z* 653 (M$^+$).

Intramolecular coupling of **36** was carried out as described for the
preparation of **12**−**14** using 105 mg (0.18 mmol) of **36**, 17 mg (0.089
mmol) of CuI, 102 mg (0.089 mmol) of Pd(PPh$_3$)$_4$, 8.0 mg (0.0035
mmol) of benzyltriethylammonium chloride in 20 mL of benzene and
900 μL of 5 N aqueous NaOH solution for 4 h. Flash chromatography
followed by preparative HPLC gave 14 mg (16%) of trimer **12** which
was identical with a sample prepared by coupling of **33a**.

Photolysis of Dehydro[18]annulene 15 in THF-d$_8$. A solution of
10 mg (0.018 mmol) of **15** in 0.8 mL of THF-d$_8$ was irradiated at room
temperature under nitrogen with a low-pressure mercury lamp for 43
h. The progress of the reaction was monitored by ^{1}H NMR, which
showed gradual formation of indane. Brown films of polymeric material
were formed on the wall of a NMR tube.

Photolysis of Dehydro[18]annulene 15 in Furan. A solution of
19 mg (0.033 mmol) of **15** in 40 mL of furan was irradiated with a
low-pressure mercury lamp in a quartz tube for 20 h. In a second run,
81 mg (0.14 mmol) of **15** was irradiated similarly. The combined
products were separated by flash chromatography followed by prepara-
tive HPLC to give **38** (yellowish orange solid, 12 mg, 15%), **39** (dark
orange solid, 20 mg, 27%), and **40** (dark orange solid, 7 mg, 11%).

38 (mixture of three diastereomers in an approximate ratio of 1:1:
2): dec 102 °C; ^{1}H NMR (CDCl$_3$) δ 7.38 (br s, 2H), 6.30−6.18 (m,
6H), 6.02−5.96 (m, 4H), 2.41−2.31 (m, 4H), 1.68−1.54 (m, 6H), 1.22−
1.08 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 146.16, 146.14, 146.13, 146.12
(q), 144.81, 144.80, 144.79* (t), 138.12, 138.10, 138.09, 138.08 (q),

137.41, 137.40*, 137.39 (q), 129.04, 129.02*, 128.99, 128.98, 128.96*,
128.94 (t), 122.22, 122.20, 122.19, 122.18 *, 122.16, 122.15, 122.14
(t), 95.30, 95.29, 95.26, 95.25 (q), 87.09, 87.07, 87.02, 87.00 (t), 86.36,
86.35, 86.29, 86.28 (q), 84.06, 84.04, 84.03, 84.02 (q), 83.55, 83.54,
83.53, 83.52 (q), 81.99, 81.97, 81.95, 81.94 (q), 81.80, 81.79, 81.70,
81.69 (q), 58.02, 58.01, 57.97, 57.96, 57.88, 57.87, 57.85, 57.84 (q),
34.58, 34.56, 34.54* (s), 19.06 (s). The intensities of the signals marked
by * are approximately twice as much as those of the signals of similar
environment: IR (KBr) 2140, 1270, 1030, 870, 835, 670 cm^{-1}; UV−
vis (CHCl$_3$) λ$_{max}$ (log ε) 580 (2.20), 516 (2.50), 456 (3.77), 429 (4.00),
421 (4.03), 367 (4.71) nm; LD-TOF MS *m/z* 520 (M$^+$).

39 (mixture of three diastereomers in an approximate ratio of 1:1:
2): dec 90 °C; *This compound once decomposed with mild explosion
when it was scratched with a spatula.* ^{1}H NMR (CDCl$_3$) δ 7.48−7.43
(m, 4H), 6.37−6.31 (m, 6H), 6.04−5.99 (m, 2H), 2.48−2.38 (m, 2H),
1.7−1.6 (m, 3H), 1.2−1.0 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 146.23, 146.21,
146.20, 146.17 (q), 145.35, 145.32, 145.30, 145.29 (q), 145.13‡, 145.07,
145.05, 145.03, 145.00 (t), 137.67, 137.66*, 137.65 (q), 129.24, 129.18,
129.17, 129.12 (t), 122.24, 122.22, 122.18, 122.16 (t), 96.17, 96.15,
96.13, 96.11 (q), 95.74, 95.73, 95.71, 95.69 (q), 87.59, 87.57†, 87.53,
87.52, 87.51 (q)*, 87.36, 87.33, 87.22†, 87.19, 87.15*, 87.08 (t), 84.51,
84.49*, 84.47 (q), 83.01, 83.00, 82.92, 82.89 (q), 58.29, 58.24, 58.23,
58.20 (q), 34.86*, 34.81, 34.80 (s), 19.17 (s). The intensities of the
signals marked by *, †, and ‡ are approximately twice, three, or four
times as much as those of the signals of similar environment,
respectively: IR (KBr) 2140, 1280, 1270, 1030, 870, 860, 830, 740,
710, 670 cm^{-1}; UV−vis (CHCl$_3$) λ$_{max}$ (log ε) 627 (2.04), 550 (2.26),
470 (3.66), 441 (3.97), 433 (4.02), 376 (4.68) nm; LD-TOF MS see
m/z 470 (M$^+$).

40 (mixture of two diastereomers with C_{3v} and C_s symmetry in an
approximate ratio of 1:3): dec 82 °C; *This compound once decomposed
with mild explosion when it was scratched with a spatula.* ^{1}H NMR
(CDCl$_3$) δ 7.55−7.50 (m, 6H), 6.52−6.49 (m, 6H); ^{13}C NMR (CDCl$_3$)
δ 145.46, 145.45, 145.39, 145.38 (t), 145.24, 145.22, 145.20, 145.16
(q), 97.02, 97.01, 96.99, 96.98 (q), 89.36, 89.35, 89.33, 89.31 (q), 87.51,
87.44, 87.36, 87.29 (t); IR (KBr) 2120, 1280, 1270, 1030, 880, 865,
830, 710 cm^{-1}; UV−vis (CHCl$_3$) λ$_{max}$ (log ε) 672 (2.01), 583 (2.26),
453 (4.11), 441 (4.10), 387 (4.76) nm; LD-TOF MS *m/z* 520 (M$^+$)
(see Figure 4).

Photolysis of Dehydro[20]annulene 13 in Furan. A solution of
180 mg (0.270 mmol) of **13** in 20 mL of furan was irradiated with a
low-pressure mercury lamp in a quartz tube for 32 h. The products
were separated by flash chromatography to afford 46 mg (25%) of
unreacted starting material **13** and 37 mg (31%) of monosubstitution
product **42** (a mixture of diastereomers) as an orange solid: mp 122
°C dec; ^{1}H NMR (CDCl$_3$) δ 6.84−6.80 (m, 2H), 5.85−5.75 (m, 6H),
5.45−5.34 (m, 6H), 4.69−4.66 (m, 2H), 1.91−1.49 (m, 12H), 1.05−
0.85 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 143.55, 143.50, 143.49, 143.47,
143.43, 143.40 (q), 140.95, 140.93, 140.91, 140.86, 140.78, 140.76, 140.74
(t), 136.21, 136.17, 136.14, 136.11, 136.08, 136.06, 136.03 (q), 135.61,
135.57, 135.55, 135.34 (q), 127.15, 127.09, 127.04, 126.98, 126.95,
126.91, 126.86, 126.84, 126.81 (t), 122.03, 121.99, 121.95, 121.91,
121.89, 121.87, 121.84, 121.81 (t), 102.06, 102.05, 102.02 (q), 91.48,
91.45, 91.44, 91.37 (q), 90.49, 90.45, 90.42, 90.40, 90.36, 90.34, 90.32,
90.29 (q), 85.75, 85.72, 85.70, 85.69, 85.67, 85.65 (t), 55.00, 54.98,
54.96, 54.92, 54.89, 54.85, 54.84, 54.82, 54.81, 54.78, 54.75 (q), 32.44,
34.42, 32.40, 32.38, 32.35 (s), 18.70, 18.66 (s).