Precursors to the Cyclo[n]carbons: From 3,4-Dialkynyl-3-cyclobutene-1,2-diones and 3,4-Dialkynyl-3-cyclobutene-1,2-diols to Cyclobutenodehydroannulenes and Higher Oxides of Carbon

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Abstract: A series of novel cyclobutenodehydro[n]annulenes (n = 18, 24, 30) have been prepared as precursors in an organic approach to the cyclocarbons C_{18}, C_{24}, and C_{30}. On the way to these macrocycles, synthetic entries to three new classes of enediynes have been developed. Bis(1-propynyl)cyclopropenone was prepared in the reaction of 1-(trimethylsilyl)-1-propyne with trichlorocyclopropenylium tetrachloroaluminate. The 3,4-dialkynyl-3-cyclobutene-1,2-diones were prepared by the reaction of 3,4-dichloro-3-cyclobutene-1,2-dione either with (tri-*n*-butylstannyl)alkynes in the presence of catalytic amounts of $Pd(PPh_3)_4$ or with the soluble copper (I) acetylides of (trialkylsilyl)acetylenes. The peculiar downfield resonances of the terminal acetylenic carbon atoms in the ^{13}C NMR spectra of the 3,4-dialkynyl-3-cyclobutene-1,2-diones are discussed. The stereospecific and regiospecific reduction of these diones with cerium trichloride–sodium borohydride afforded exclusively the *cis*-3,4-dialkynyl-3-cyclobutene-1,2-diols. The oxidative Hay coupling of the acetonide of 3,4-diethynyl-3-cyclobutene-1,2-diol or of the bis(ethylene ketal) of 3,4-diethynyl-3-cyclobutene-1,2-dione gave two series of cyclobutenodehydroannulenes with 18π-, 24π-, and 30π-electron perimeters. In both series, the unusually stable octahydro[24]annulene perimeter is formed with the highest yield. Deprotection of the trimer and the tetramer, obtained in the oxidative coupling of the bis(ethylene ketal) of 3,4-diethynyl-3-cyclobutene-1,2-dione, was best effected in concentrated sulfuric acid and yielded quantitatively the (3-cyclobutene-1,2-dione)-annelated dehydroannulenes **4** ($C_{24}O_6$) and **5** ($C_{32}O_8$), novel higher oxides of carbon and direct precursors to the cyclocarbons C_{18} and C_{24}.

Ever since their first mass spectroscopic detection in the vapor phase of heated graphite,[1] all-carbon molecules C_n have exerted a considerable fascination on researchers in a number of fields.[2,3] With the advent of laser vaporization techniques in recent years, they have become the subject of an increasing number of experimental and theoretical studies.[4] Molecules of sizes ranging from C_2 to $>C_{600}$ have been detected in the supersonic beams produced by the vaporization of graphite, and theoretical investigations have been useful in assigning structures to these molecules.[5]

For the unambiguous determination of the chemical and physical properties of a single-sized all-carbon molecule, its chemical synthesis is required. Recently, we described the synthesis and the X-ray crystal structure of a direct precursor to the acetylenic molecule C_{18}.[6] The time-of-flight mass spectroscopic analysis of laser flash heating experiments on this precursor showed a sequence of retro-Diels–Alder reactions leading to C_{18} as the predominant fragmentation pattern. Therefore, we have provided structural evidence for an all-carbon molecule through its generation from a well-characterized organic precursor. Here, we present an alternative, more general approach to the cyclic structures C_{18}, C_{24}, and C_{30}.[7] These all-carbon molecules are members of the class of the *cyclo[n]carbons* in which n carbon atoms are connected to form monocyclic ring structures. For cyclo[18]carbon, ab initio calculations predict a relatively stable, cyclic D_{9h} ground-state geometry with alternating C—C and C≡C bonds.[6] Semiempirical calculations had previously predicted an enhanced relative stability for the larger closed-shell cyclo[n]carbons ($n \geq 10$) with $[4n + 2]$ atoms.[4d,8,9]

Our synthetic strategy to acetylenic cyclo[n]carbons is based on the known oxidative coupling of *cis*-3-hexene-1,5-diyne under Eglinton–Glaser conditions giving exclusively a cyclic trimer, 1,3,7,9,13,15-hexadehydro[18]annulene.[10,11] Substitution of the six remaining hydrogen atoms in this molecule with suitable leaving groups would give cyclo[18]carbon upon elimination.[12] We reasoned that diethynylcyclopropenone (**7a**) and 3,4-diethynyl-3-cyclobutene-1,2-dione (**8a**) would be ideal building blocks to construct the macrocycles **1–3** and **4–6**, all higher oxides of carbon, as direct precursors to the cyclo[n]carbons (Scheme I). Cyclopropenones and cyclobutene-1,2-diones are known to readily eliminate carbon monoxide in pyrolytic[12b,13] and photolytic processes[14,15] with the formation of acetylenes. Highly strained alkynes, e.g. benzyne or 1- and 2-naphthyne, have been generated from the corresponding cyclobutenediones in an argon matrix.[16] Thus, ketones **1–3** or **4–6**, if prepared, should readily give C_{18},

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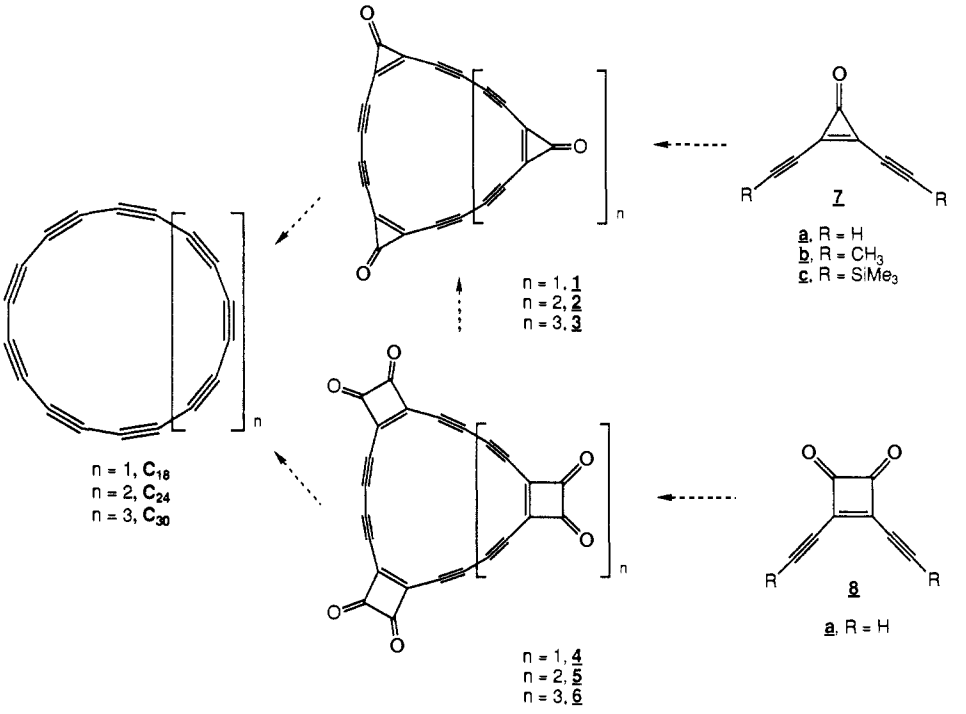
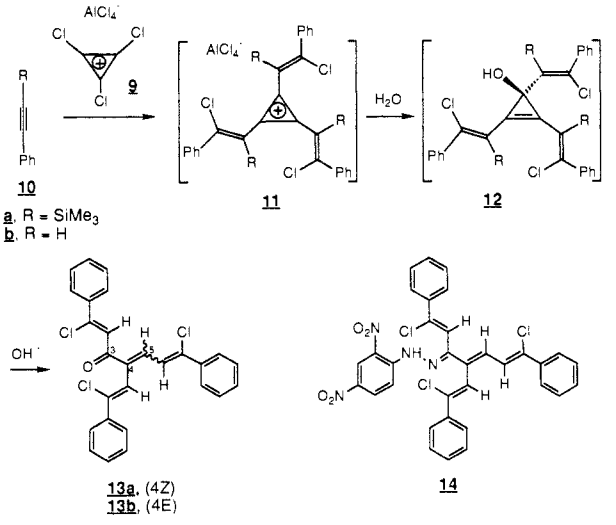
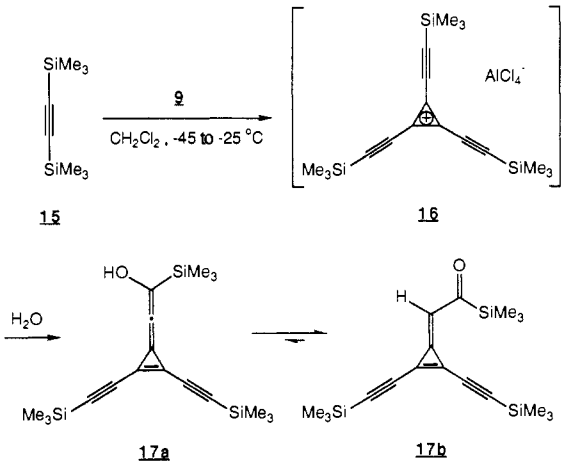
Scheme I



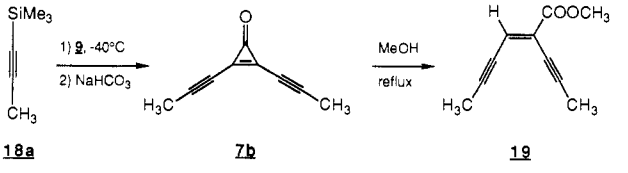
Scheme II



Scheme III



Scheme IV



C_{24}, or C_{30} by irradiation or flash vacuum pyrolysis, with the option of using matrix isolation techniques.

This paper describes novel synthetic entries to dialkynylcyclopropenones, 3,4-dialkynyl-3-cyclobutene-1,2-diones, and 3,4-dialkynyl-3-cyclobutene-1,2-diols. From these cyclobutenediyne derivatives, two series of cyclobutenodehydro[*n*]annulenes (n = 18, 24, 30) could be prepared. The synthesis of the macrocyclic ketones **4** and **5** from the corresponding dehydroannulenes with fused ethylene ketal protected cyclobutenediones is reported. With their molecular formulas of $C_{24}O_6$ and $C_{32}O_8$, respectively, **4** and **5** represent novel higher oxides of carbon and are direct precursors to the cyclocarbons C_{18} and C_{24}. The following paper discusses the unusual structural and electronic properties of the novel cyclobutenoannulenes, as studied in a combined experimental and theoretical approach.[17]

Results and Discussion

Dialkynylcyclopropenones. For the preparation of dialkynylcyclopropenones, e.g. **7a–c**, literature procedures were not available.[18] Disubstituted cyclopropenones, e.g. diphenylcyclopropenone, have previously been prepared by the reaction of arenes,[19] alkynes,[20] or alkenes[20,21] with trichlorocyclopropenylium salts, generated from tetrachlorocyclopropene[22] and a Lewis acid, e.g. aluminum chloride.[15d] On the other hand, alkynyltrimethylsilanes react with electrophiles like acyl halides to give alkynyl ketones.[23] Therefore, the reactions of the alkynylsilanes **10a**, **15**, and **18a** with the trichlorocyclopropenylium tetra-

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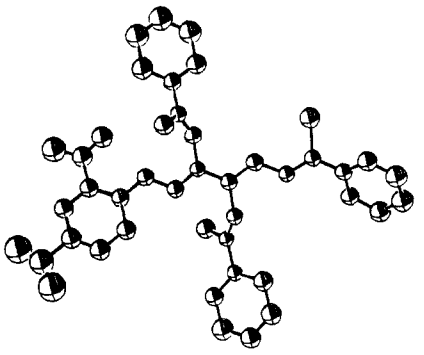


14

Figure 1. X-ray crystal structure of **14**.

chloroaluminate (**9**) were studied. The results are shown in Schemes II–IV.

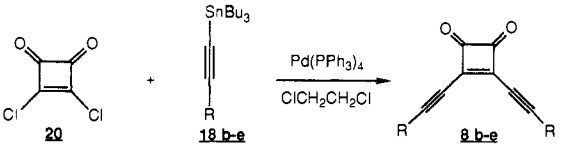
(Phenylethynyl)trimethylsilane (**10a**)[24] reacted with the salt **9** at 0 °C to give a mixture of two isomeric products **13a** and **13b** as yellow oils in 16% and 70% yield, respectively (Scheme II). Interestingly, a similar result was obtained by the reaction of phenylacetylene (**10b**) with the salt **9** under the same conditions (12% and 86% yield, respectively). Decreasing the reaction temperature to −78 °C did not change the results. The addition of a trace of acid to a solution of both isomers in CH_2Cl_2 leads to a complete conversion of **13a** to **13b**. Careful examination of all spectroscopic data [^{1}H NMR (2D COSY and NOESY), ^{13}C NMR, IR, and MS] of the unsaturated ketone **13b** did not allow us to determine the structure with full confidence. However, the (2,4-dinitrophenyl)hydrazone derivative **14**[25] gave fine red needles by recrystallization from ethanol, and its structure was shown by X-ray crystallographic analysis (Figure 1).[26]

The formation of the ketones **13a** and **13b** must occur through an addition instead of a substitution mechanism (Scheme II). This pathway has been previously observed with 2-butyne and **9**, leading to bis(1-methyl-2-chloro-1-propenyl)cyclopropenone.[20] With the alkynes **10a** and **10b**, apparently, the reaction does not stop at the mono- or the bisaddition stage, and the salt **11** is formed rapidly. Quenching the reaction with water presumably produces the unsaturated alcohol **12**, possibly observed by TLC (silica gel, CH_2Cl_2, R_f = 0.29) next to the already appearing products **13a** and **13b** (R_f = 0.56 and 0.69, respectively). Mild basic workup with aqueous sodium carbonate completes the hydrolysis of the trimethylsilyl groups and the cyclopropene ring opening, yielding quantitatively the ketones **13a** and **13b**.

When bis(trimethylsilyl)acetylene (**15**) was added to a suspension of the salt **9** in CH_2Cl_2 at −45 °C and then the solution warmed up, a deep purple solution, presumably of the trisubstituted salt **16**, resulted. Quenching with water gave the unstable acylsilane **17b** as a yellow oil in 75% yield (Scheme III). If not immediately quenched at −25 °C, the purple solution rapidly turned brown to give only decomposition products. Interestingly, the trisubstituted salt **16** is preferentially attacked by water at the terminal acetylenic carbon rather than at the cyclopropenylium ring.

Whereas all variations of the reaction conditions did not enable us to stop the reaction of **15** and **9** at the stage of the desired disubstitution product **7c**, bis(1-propynyl)cyclopropenone (**7b**) could be readily prepared in the reaction of 1-(trimethylsilyl)-1-propyne (**18a**) with **9** at −40 °C for 1 h (Scheme IV). Quenching of the resulting solution with water and workup with aqueous sodium bicarbonate gave the cyclopropenone **7b** in 50% yield. In an attempt to obtain the parent compound **7a**, the same reaction was tried with (trimethylsilyl)acetylene. However, no product could be isolated from the complex reaction mixture. The cyclopropenone **7b** may be useful since it reacts readily with nucleophiles, e.g. methanol, to give the enediyne **19**. The chemistry of enediynes has recently been used extensively in studies related to the mode of action of the esperamicin/calicheamicin class of anticancer drugs.[27]

Table I



20 18 b-e 8 b-e

R	conditions	yield, mp, aspect
b: Ph	20 °C/2 h	70%, 114–115 °C, orange needles
c: PhC≡C	20 °C/6 h	11%, >184 °C, deep red crystals
d: *n*-Pr	20 °C/2 h	51%, yellow oil
e: $SiMe_3$	20 °C/2 h	30%, 95–97 °C, yellow needles

3,4-Dialkynyl-3-cyclobutene-1,2-diones. Since we were unable to prepare the dialkynylcyclopropenones **7a** or **7c**, needed for the construction of **1–3**, we focussed our attention to the synthesis of the corresponding 3,4-dialkynyl-3-cyclobutene-1,2-diones **8a** or **8e**, needed for the macrocycles **4–6**. As for the cyclopropenone series, no 3,4-dialkynyl-3-cyclobutene-1,2-diones had previously been reported. Recently, Moore et al.[28a] and Liebeskind et al.[28b] published general routes for the synthesis of substituted cyclobutenediones by the addition of organolithium reagents to squaric acid esters. Using these methods, we tried to prepare the bis(phenylethynyl) derivative **8b** by the 2-fold addition of lithium phenylacetylide to diethyl squarate. However, reaction at −78 °C or higher temperature in THF led only to the monoaddition product 2-hydroxy-3,4-diethoxy-2-(phenylethynyl)-3-cyclobuten-1-one in 97% yield.[28b] Therefore, an approach based on the chemistry developed by Stille and Logue was used.[29] It was found that the vinylogous acyl halide 3,4-dichloro-3-cyclobutene-1,2-dione **20**[14a,31] reacted smoothly with a series of (tri-*n*-butylstannyl)alkynes in the presence of a catalytic amount of $Pd(PPh_3)_4$. The results are summarized in Table I. It is noteworthy that this method allows for the preparation of an extended chromophore such as **8c**. The starting material for the stable dione **8c**, 4-phenyl-1-(tri-*n*-butylstannyl)-1,3-butadiyne (**18c**), was prepared by using the homologation procedure recently published by Kende et al.[32] Direct elimination and deprotonation of the known *cis*-1-chloro-4-phenyl-1-buten-3-yne[32] with 2 equiv of *n*-butyllithium at −78 °C, and subsequent reaction with tri-*n*-butyltin chloride at 20 °C gave **18c** in 90% yield. In view of the encouraging results in the preparation of **8c**, a direct approach to the macrocyclic ketones **4–6** was attempted. However, the high dilution reaction of 1,4-bis(trimethylstannyl)-1,3-butadiyne[30] under the conditions of Table I only led to the formation of black polymers.

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(26) X-ray crystal data of **14** ($C_{33}H_{23}Cl_3N_4O_4$); M_r = 645.9; monoclinic; space group = $P2_1/a$; Z = 4; a (Å) = 8.478 (1); b (Å) = 19.319 (3); c (Å) = 19.236 (3); β = 101.182 (4)°; V = 3069 Å^3; D_c (g cm^{-3}) = 1.31. Data were collected on a Syntex P1 diffractometer modified by Professor C. E. Strouse, UCLA, using Cu Kα radiation, to a maximum 2θ = 100°, giving 3186 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was R = 0.070, R_w = 0.090 for 2238 independent reflections with $I > 3\sigma(I)$.
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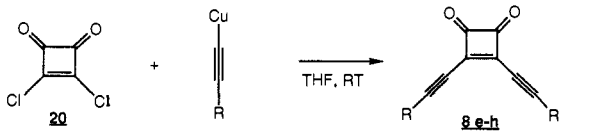
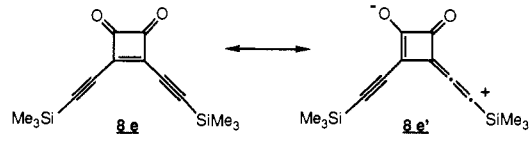
Table II



R	conditions	yield, mp, aspect
e: $SiMe_3$	20 °C/15 min	27%, 95–97 °C, yellow needles
f: $Me_3SiC{\equiv}C$	20 °C/15 min	21%, unstable brown oil
g: t-$BuMe_2Si$	20 °C/20 min	57%, 57–59 °C, orange crystals
h: $(i\text{-}Pr_3)Si$	20 °C/60 min	59%, 36.5–37.5 °C, yellow needles

Table III. ^{13}C NMR Chemical Shifts (in ppm) of the Cyclobutenediones **8b–h** and the Cyclobutenediols **21**, **24**, and **27** in $CDCl_3$

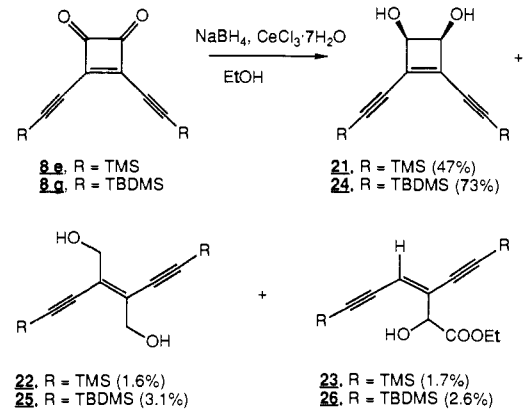


compd	C-1′	C-2′	C-3′	C-4′	C-3,4	C-1,2
8b	77.8	125.6	–	–	177.4	195.2
8c	73.0	99.9	67.6	110.6	178.2	194.8
8d	69.7	129.3	–	–	180.3	196.6
8e	90.5	135.8	–	–	179.4	195.1
8f	85.8	110.1	61.9	111.6	179.0	194.2
8g	91.2	134.9	–	–	180.1	195.1
8h	92.6	133.8	–	–	180.1	195.6
21	96.5	106.2	–	–	137.1	73.8
24	97.2	104.8	–	–	137.3	74.0
27	68.3	87.0	84.9	97.2	138.7	73.9

The desired trimethylsilyl derivative **8e** was also prepared in good yield from the corresponding stannane, but its purification proved to be rather difficult. Even after two chromatographies, an amount of 5–7% of tributyltin chloride was still present (^1H NMR). Since the dione **8e** rapidly hydrolyzes on silica, its yield after two chromatographies dropped to 30%. For a better entry into silyl-protected 3,4-diethynyl-3-cyclobutene-1,2-diones, we therefore investigated other methods that had previously been applied to the preparation of alkynyl ketones from acyl halides.[33]

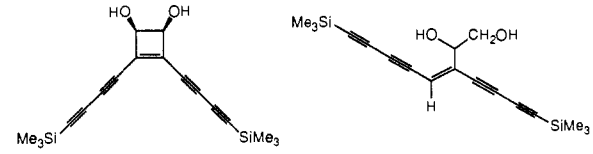
The zinc reagent generated in the reaction of lithium phenylacetylide with anhydrous zinc iodide in THF at 0 °C was added to a solution of **20** and $Pd(Ph_3)_4$ in THF at 20 °C to give **8b** in 47% yield.[33b] However, the same reaction with the zinc reagent from (trimethylsilyl)acetylene only led to traces of dione **8e**. After several attempts with other organometallic reagents,[33c–e] it was found that the soluble copper(I) acetylide[33a] of (trimethylsilyl)-acetylene[34a] reacted rapidly with **20** to give, after nonaqueous workup, the dione **8e** (Table II) in 27% yield. The product decomposes rapidly under the conditions it is produced, which explains the rather low yield. Presumably, the copper(I) salts cleave the TMS groups of **8e** to produce **8a**, which then undergoes fast polymerization (see below). The dione **8f** was prepared from 1,4-bis(trimethylsilyl)-1,3-butadiyne by selective deprotection of one silyl group with methyllithium/lithium bromide in THF,[35a] in situ reaction with copper(I) iodide,[35b] and addition of the dichloride **20**. Rapid nonaqueous workup afforded the dione **8f** as a brown oil (26% crude). Due to its great instability, analysis was made on the reduction product **27** described below. The dione **8f** and carbonyl-protected derivatives are of interest for the preparation of extended annulenes, e.g. [40]annulenes and, ultimately, of the corresponding cyclo[n]carbons.

Scheme V[a]



[a] TBDMS = *tert*-butyldimethylsilyl.

Chart I



The cyclobutenediones **8g** and **8h**, prepared from (*tert*-butyldimethylsilyl)acetylene[34b] and (triisopropylsilyl)acetylene[34c] possess enhanced stability toward nucleophilic reagents and, correspondingly, are isolated in higher yields (57% and 59%, respectively). In view of the planned conversion of **4–6** into the corresponding cyclocarbons, it is noteworthy that the EI and FAB mass spectra of all the 3,4-dialkynyl-3-cyclobutene-1,2-diones show strong peaks resulting from the loss of two carbon monoxide fragments.

^{13}C NMR Spectroscopy of 3,4-Dialkynyl-3-cyclobutene-1,2-diones. In the ^{13}C NMR spectra of all the cyclobutenediones **8b–h** (Table III), very unusual chemical shifts are observed for the resonances of the terminal acetylenic carbons. In particular, the silylated derivatives **8e–h** show the most deshielded absorptions for the terminal acetylenic carbons, e.g. δ 135.8 ppm for C-2′ in **8e**. We propose that dipolar resonance forms, e.g. **8e′**, account for this effect since, in the corresponding diols **21**, **24**, and **27**, such an effect is not observed (Table III). In the latter compounds, the alkyne carbons appear in the normal acetylenic absorption range of 70–110 ppm.[36]

3,4-Dialkynyl-3-cyclobutene-1,2-diols. All attempts (tetrabutylammonium fluoride in THF at −78 °C, aqueous potassium fluoride/ether, catalytic base (KOH or K_2CO_3) in methanol) to generate **8a** by deprotection of the silylated cyclobutenediones **8e** and **8g** only gave disappointing results. An instantaneous polymerization was always observed. Even the mildest deprotection methods [0.01 M $Na_2B_4O_7{\cdot}10H_2O$ in methanol, ethanolic silver nitrate, silver nitrate in anhydrous THF and addition of iodine to the bis(silver acetylide)] failed to give isolable amounts of **8a**.[23,37] In view of these discouraging results, a different approach to the annulenes **4–6** was considered for which cyclobutenediols or protected derivatives were required (see below).

The reduction of 3,4-diphenyl-3-cyclobutene-1,2-dione with lithium aluminum hydride has been described to give the corre-

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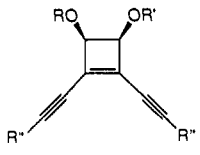
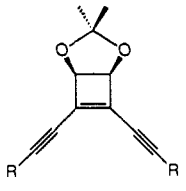
Chart II



29a, R = R' = Ac, R" = TMS
29b, R = Ac, R' = H, R" = TMS
30, R = R' = -CS-, R" = TBDMS
31, R = R' = R" = H



32, R = TBDMS
33, R = H

sponding *cis*- and *trans*-1,2-diols in low yields.[38] We found that the reduction of the diones **8e–g** with cerium trichloride–sodium borohydride (Luche reagent)[39] proceeded smoothly with great stereoselectivity and regioselectivity, giving the diols **21**, **24**, and **27** (Scheme V and Chart I). In the reduction of the 1,2-diketones **8e** and **8g**, two byproducts (**22**/**23** and **25**/**26**, respectively) were also formed, their structural assignment being fully supported by spectroscopic data and elemental analysis. In the reduction of compound **8f**, only the diol **28** was formed as a byproduct. The formation of these byproducts presumably arises from the homolytic cleavage of the C(1)–C(2) or the C(2)–C(3) bonds in the starting diones.

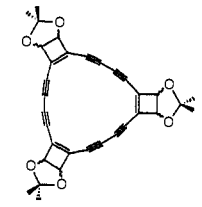
The stereochemistry of the diols **21**, **24**, and **27** was determined in three ways: (i) In the asymmetric monoacetate **29b** (Chart II) the coupling constant between the two methine protons 1-H and 2-H was found to be 3.5 Hz, a value similar to other cis-substituted cyclobutenes.[40] The monoacetate **29b** together with the diacetate **29a** were obtained upon acetylation of **21** with acetic anhydride. (ii) The coupling constants of the methine protons 1,2-H in the diols **21**, **24**, and **27** were determined from the ^{13}C satellites in the proton NMR spectra (**21**, J = 3.7 Hz; **24**, J = 3.6 Hz; **27**, J = 3.6 Hz).[36] (iii) The 3,4-H coupling constants in the five-membered cyclic derivatives **30** (J = 3.7 Hz) and **32** (J = 3.4 Hz), where the stereochemistry can only be cis, are close to those in the diols. The acetonide **32** was obtained in 91% yield in the reaction of the diol **24** with 2,2-dimethoxypropane under acid catalysis. The cyclic thiocarbonate **30** was prepared by the reaction of the diol **24** with 1,1'-thiocarbonyldiimidazole in a quantitative yield.[41]

We explain the exclusive formation of the *cis*-diols with the formation of a bulky alkoxycerium dichloride species after the first hydride attack, followed by an *anti* attack of the second hydride equivalent.

Synthesis of the Cyclobutenodehydroannulenes. Since the deprotection of the silylated diones **8e** and **8g** to give **8a**, the direct precursor to the macrocycles **4–6**, was not successful, two new approaches to annulene precursors of the cyclo[*n*]carbons were considered. One route involved the cyclization of 3,4-diethynyl-3-cyclobutene-1,2-diol (**31**) or hydroxy-protected derivatives to yield eventually the macrocyclic tris-, tetrakis-, or pentakis(cyclobutenediol) analogues of **4–6**, which then could be oxidized, e.g. in a Swern oxidation,[42] to the polyketones.

Therefore, the unstable diol **31** was prepared by deprotection of **21** (98%) with tetrabutylammonium fluoride (TBAF). When the cyclization of **31** was attempted under Eglinton–Glaser[43] or Hay conditions,[44] no cyclic product could be isolated. To circumvent the problems encountered with the deprotected diol **21**, the acetonide **32** was deprotected to **33** (TBAF, 89%), which proved to be a suitable cyclization component. The ketal function

Chart III



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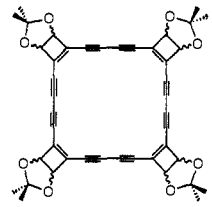
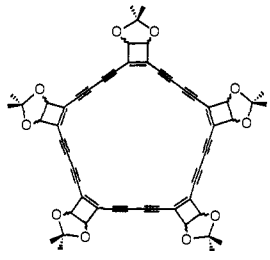
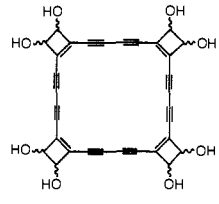


35



36



37

in **33** was rapidly hydrolyzed in pyridine in the presence of copper(II) acetate and the Eglinton–Glaser cyclization conditions could not be applied. However, the Hay cyclization [CuCl–*N,N,N',N'*-tetramethylethylene-1,2-diamine (TMEDA), O_2, [**33**] = 0.01 M in acetone] over 48 h at 20 °C gave three isolated products as mixtures of diastereomers, the unstable pale-yellow trimer **34** (2.1%), the orange-red tetramer **35** (6.6%), and the yellow pentamer **36** (1.8%) (Chart III). The presence of diastereomers in each of the compounds could only be detected by ^1H NMR and ^{13}C NMR, not by TLC. The trimer **34** is slightly unstable in the solid state and was best kept in dilute solution. Crystals of the tetramer **35** are stable at room temperature for months, and crystals of the pentamer **36** are stable if kept at 0 °C. It is remarkable that the tetramer is formed predominantly in this reaction and that it is an unusually stable [24]annulene. The reasons for these results are the subject of the following paper.[17]

The deprotection of the four ketal groups of the [24]annulene **35** was achieved quantitatively with concentrated HCl in THF, giving the octol **37** as a red powder with good solubility in THF and dimethyl sulfoxide. All attempts to oxidize **37** to **5** in an 8-fold Swern oxidation were unsuccessful. Neither the oxalyl chloride[42a] nor the milder trifluoroacetic anhydride[42b] activation methods gave any ketone **5**. Instead, the addition of triethylamine or the more hindered Hünig base diisopropylethylamine to the orange solution of the presumably formed octasulfoxonium intermediate gave immediately black polymers. We assume that the generated ketone **5** or the partially converted intermediates must be extremely sensitive to any nucleophile present even under the most strictly anhydrous conditions. Since it seemed that no nucleophilic oxidation reagent could be used, we tried to oxidize the octol **37** with a number of mild allylic oxidation reagents,[45] e.g. tetra-*n*-propylammonium perruthenate,[45a] barium manganate,[45b] manganese dioxide,[45c] silver oxide,[45d] or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone[45d] with no success.

The second route to direct precursors of the cyclo[*n*]carbons involved the cyclization of the bisketal **39** to the protected annulenes **41–43** and subsequent deprotection to give **4–6**. This approach, compared to the previous one, prevented the formation of nonseparable diastereomers and did not involve a problematic intermediate change in oxidation state of the oxygen functions.

Cava et al. effected the bis-ketalization of benzocyclobutenedione with ethylene glycol and *p*-toluenesulfonic acid.[46]

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(39) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226–2227.
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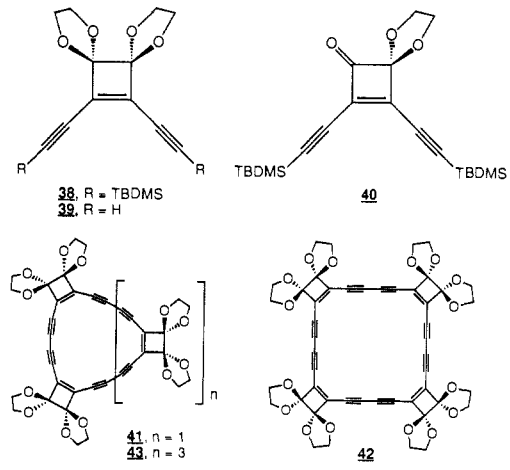
(46) Cava, M. P.; Stein, R. P. *J. Org. Chem.* **1966**, *31*, 1866–1869.

Chart IV



Attempts to effect this transformation on the diketone **8g** gave no reaction (2.5 equiv of $HOCH_2CH_2OH$, catalytic TsOH, benzene, 80 °C, 5 days). However, heating **8g** in bis(trimethylsilyloxy)ethane in the presence of trimethylsilyl triflate at 80 °C for 6 h gave the bisketal **38** (76%) as well as some monoketal **40** (5%, Chart IV).[47] The deprotection of the terminal alkyne carbons of the bisketal **38** was easily achieved (catalytic KOH, MeOH, 95%) to give the bisketal **39** as a stable solid. Hay coupling of **39** gave the pale-yellow trimer **41** (3.8%), the orange-red tetramer **42** (5.1%), and the bright-yellow pentamer **43** (0.8%). All three compounds are kinetically rather stable and can be kept at room temperature and ambient atmosphere for weeks without noticeable decomposition.

Higher Oxides of Carbon: Direct Precursors to the Cyclo[*n*]carbons. Preliminary studies cleary demonstrate that the route to **4–6** and ultimately to the corresponding cyclo[*n*]carbons via the polyketals **41–43** promises to be successful. We were unable to deprotect the polyketals **41–43** by standard methods. Partial deprotection of the octaketal **42** was accomplished with trifluoroacetic acid at room temperature over 48 h. In the IR spectrum of the deep red solution, the strong characteristic carbonyl absorption of four-membered ring ketones at 1780 cm^{-1} was present. Complete deprotection was accomplished upon stirring **41** or **42** with concentrated sulfuric acid for 30 min at room temperature. ^{13}C NMR experiments performed in D_2SO_4 leave no doubt that the ketal functions are split off very rapidly. After the 30 min needed to prepare the samples of **41** or **42**, respectively, and to accumulate the FIDs, only the macrocyclic polyketones **4** and **5** could be observed (Figure 2). In particular, the characteristic ^{13}C chemical shifts (ppm) for the 3-cyclobutene-1,2-dione moieties (180.9 and 194.6 for **4**, 180.0 and 194.5 for **5**) are observed next to the two acetylenic carbons (83.0 and 108.8 for **4**, 81.7 and 107.8 for **5**) and the resonance of the formed ethylene glycol (70.5). The protonation of the 1,2-dione functionalities in concentrated sulfuric acid apparently does not seem to have a large effect on the position of the cyclobutenedione ^{13}C resonances. These resonances for **8d** in D_2SO_4 (181.8 and 201.3 ppm) and in $CDCl_3$ (180.3 and 196.6, Table II) appear at similar positions.

The electronic absorption spectra provide additional support that sulfuric acid does not alter the annulene perimeters in **4** and **5**. The solutions of both macrocycles in sulfuric acid show highly structured spectra, and the characteristic strong bands between λ = 300 and 400 nm provide evidence that these oxides of carbon, in analogy to their precursors **41** and **42**, possess planar [4*n* + 2] and [4*n*]dehydroannulene perimeters, respectively.[7,17] These bands in **4** and **5** with their characteristic shapes[17] are bathochromically shifted by λ = 40–50 nm as compared to the spectra of the precursors **41** and **42**. In addition, more concentrated dark red solutions of **4** and **5** give end absorptions tailing up to $\lambda \approx 800$ nm. Solutions of **4** and **5** are extremely sensitive to light as shown by large changes in optical density upon exposure to daylight.

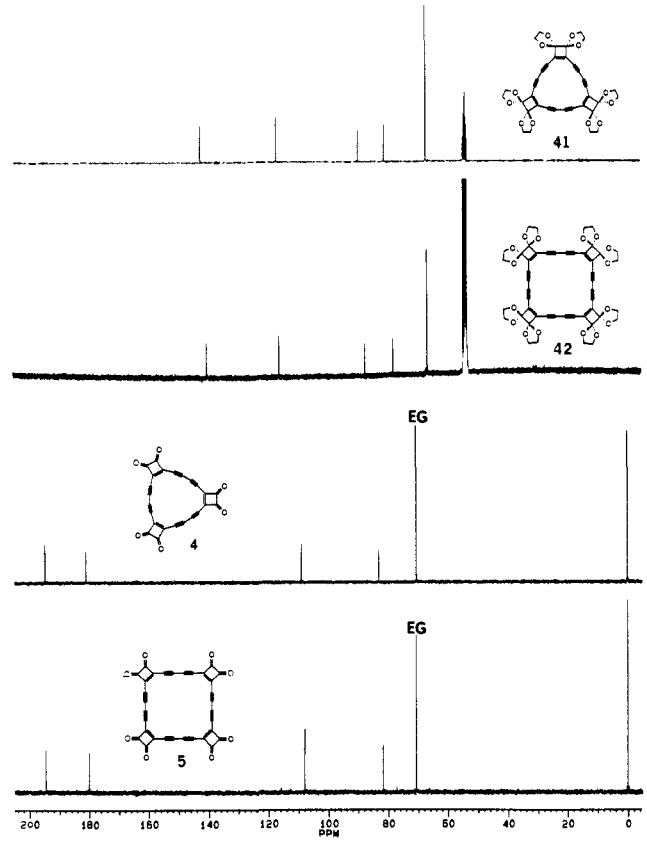


Figure 2. ^{13}C NMR spectra of the new oxides of carbon **4** and **5** in 98% D_2SO_4 (99.5% D, external Me_4Si as reference) as compared to the spectrum of the ketal precursors **41** and **42** in CD_2Cl_2. The peak designated EG in the spectra of **4** and **5** comes from the ethylene glycol generated during the deprotection reaction.

On attempted isolation of the octaketone **5** by aqueous workup at 0 °C, a considerable amount of polymers formed rapidly, and only a very low yield of an unstable dark red solid could be extracted with chloroform. An FT-IR spectrum of this material showed bands at 2254 (C≡C), 1790 (C=O), and 1602 (C=C) cm^{-1}, further supporting the structure of **5**. The hydrolysis of the ketals **41–43** by other methods, e.g. with trimethylsilyl iodide, trifluoromethanesulfonic acid, or Nafion resin in organic solvents, and the subsequent isolation and conversion of the oxides **4–6** are currently under way and will be the subject of another paper.

In conclusion, a series of cyclobutenodehydroannulenes have been prepared in an organic approach to the cyclo[*n*]carbons C_{18} C_{24}, and C_{30}. The unusual structural, electronic, and stability properties of these novel [4*n*] and [4*n* + 2]annulenes are the subject of the following paper. With the macrocyclic hexaketone **4** and the octaketone **5**, direct precursors to the cyclo[*n*]carbons C_{18} and C_{24} have been prepared. With their molecular formulas $C_{24}O_6$ (for **4**) and $C_{32}O_8$ (**5**), these molecules are by far the largest higher oxides of carbon reported.[48] On the way to the cyclobutenoannulenes, synthetic entries to three new classes of enediynes, the dialkynylcyclopropenones, the 3,4-dialkynyl-3-cyclobutene-1,2-diones, and the 3,4-dialkynyl-3-cyclobutene-1,2-diols have been developed. The new enediynes as well as their methods of preparation are of potential interest with regard to the developments of new enediyne-based anticancer drugs.

Experimental Section

General. ^1H NMR spectra were measured on Bruker AF200, AM360, and AM500 spectrometers with Me_4Si as internal standard. ^{13}C NMR spectra were taken with the solvent signal as reference unless specified

(47) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357–1358.

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otherwise. All NMR spectra were carried out at 296 K except for the experiments with D_2SO_4. EI mass spectra were recorded at 70 eV (if not stated otherwise) on AEI MS902 (UCLA) and VG-7070-EHF (UC Riverside) instruments. FAB mass spectra (matrix: *m*-nitrobenzyl alcohol) were carried out on a VGZAB-SE(UCLA) and a VGZAB-1FHF (UC Riverside) spectrometer. Melting points were measured on an Electrothermal apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer PE 580 apparatus. Electronic absorption spectra were taken on a Varian Cary 2300 spectrometer. Elemental analyses were effected by Spang Microanalytical Laboratory, Eagle Harbor, MI. Column chromatographies were made on silica gel, 70–230 mesh or 230–400 mesh (flash), from E. Merck. Although no exceptional instability was recorded, safety shields were used in all the preparations and characterizations of compounds with unprotected terminal acetylenes.

Materials. All reagents and solvents were purchased reagent grade and used without further purification, unless otherwise specified. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were dried and distilled prior to use.[49] Anhydrous magnesium sulfate was used as the drying agent after workup in all the experiments. The petroleum ether used in this study boils at 40–50 °C.

Synthesis. [1*Z*,4*Z*,6*Z*,1′*Z*]-1,7-Dichloro-1,7-diphenyl-4-[1-(2-chloro-2-phenylethenyl)]-1,4,6-heptatrien-3-one (13a) and [1*Z*,4*E*,6*Z*,1′*Z*]-1,7-Dichloro-1,7-diphenyl-4-[1-(2-chloro-2-phenylethenyl)]-1,4,6-heptatrien-3-one (13b). (a) from (Phenylethynyl)trimethylsilane. Trichlorocyclopropenylium tetrachloroaluminate (**9**) was formed[15d] from 547 mg (4.11 mmol) of aluminum chloride and 729 mg (4.11 mmol, 0.50 mL) of tetrachlorocyclopropene[22] in 10 mL of CH_2Cl_2. After 10 min, more CH_2Cl_2 (30 mL) was added. The suspension was cooled to 0 °C and 2.145 g (12.3 mmol) of (phenylethynyl)trimethylsilane[24] (**10a**) in 10 mL of CH_2Cl_2 was added dropwise over a period of 10 min. The brown solution was stirred for 30 min at 20 °C and poured into water. The organic layer was washed with water and with 1 M Na_2CO_3. A yellow spot with R_f = 0.29 (TLC, silica gel, CH_2Cl_2), presumably the hydroxycyclopropene intermediate **12**, was completely converted to the products **13a** and **13b** (R_f = 0.56 and 0.69) in this process and was not isolated. The organic solution was dried and the solvent evaporated. Flash chromatography with hexane/CH_2Cl_2 (2:1 to 1:1) gave two yellow compounds corresponding to the two isomers **13a** and **13b**. Fraction 1 gave 276 mg (16%) of **13a** as a dark yellow oil: IR ($CHCl_3$) ν (C=O) 1664, (C=C) 1586, 1570 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.98 (d, J = 1.1 Hz, 1 H, 1′-H), 7.08 (s, 1 H, 2-H), 7.22 (dd, J = 11.4 and 1.1, 1 H, 5-H), 7.35–7.4 (m, 9 H, *m,p*-H), 7.38 (d, J = 11.4 Hz, 1 H, 6-H), 7.65–7.7 (m, 6 H, *o*-H); MS (EI), *m/z* (relative intensity) 464 (2, M^+), 429 (21, $M^+ - Cl$), 393 (15, $M^+ - H - 2Cl$), 357 (9, $M^+ - 2H - 3Cl$), 78 (100, $C_6H_6^+$). Fraction 2 gave 1.24 g (70%) of **13b** as a dark yellow oil: IR ($CHCl_3$) ν (C=O) 1652, (C=C) 1586 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, J = 11.1 Hz, 1 H, 6-H), 7.07 (d, J = 1.4 Hz, 1 H, 1′-H), 7.15 (s, 1 H, 2-H), 7.35–7.5 (m, 9 H, *m,p*-H), 7.65–7.75 (m, 6 H, *o*-H), 7.79 (dd, J = 11.1 and 1.4 Hz, 1 H, 5-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ 120.3 (d), 121.9 (d), 122.2 (d), 126.8 (d), 126.9 (d), 127.2 (d), 128.5 (d), 128.6 (d), 128.7 (d), 129.5 (d), 130.1 (d), 130.4 (d), 136.0 (d), 137.0 (s), 137.1 (s), 137.2 (s), 137.9 (s), 138.1 (s), 142.3 (s), 142.7 (s), 189.5 (s); MS (EI) *m/z* (relative intensity) 464 (2, M^+), 429 (21, $M^+ - Cl$), 393 (15, $M^+ - H - 2Cl$), 357 (9, $M^+ - 2H - 3Cl$), 78 (100, $C_6H_6^+$). An analytically pure sample of **13a** or **13b** could not be obtained by careful chromatography. The isomer **13b** was analyzed as its (2,4-dinitrophenyl)hydrazone **14**.

(b) From Phenylacetylene. Following the procedure described above, a total of 1.41 g (13.8 mmol, 1.52 mL) of phenylacetylene in 15 mL of CH_2Cl_2 was added to a solution of **9** prepared from 622 mg (4.6 mmol) of aluminum chloride and 870 mg (4.9 mmol, 0.60 mL) of tetrachlorocyclopropene in 40 mL of CH_2Cl_2. After complete addition, the brown solution was stirred for 2 h at 20 °C and poured into water. After the workup described above, flash chromatography with hexane/CH_2Cl_2 (2:1 to 1:1) gave 240 mg (12%) of **13a** and 1.701 g (86%) of **13b**.

[1*Z*,4*E*,6*Z*,1′*Z*]-1,7-Dichloro-1,7-diphenyl-4-[1-(2-chloro-2-phenylethenyl)]-1,4,6-heptatrien-3-one (2,4-Dinitrophenyl)hydrazone (14). According to the general literature procedure,[25] this derivative was prepared from 654 mg (1.4 mmol) of **13b** and recrystallized twice from ethanol/CH_2Cl_2. Slow evaporation of the solvent afforded 780 mg (86%) of **14** as red needles suitable for X-ray diffraction: mp 172–173 °C; IR (CCl_4) ν (NH) 3280, (C=N) 1617, (C=C) 1593 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.73 (s, 1 H, 2-H), 7.02 (d, J = 11.1 Hz, 1 H, 6-H), 7.03 (d, J = 1.3 Hz, 1 H, 1′-H), 7.26 (dd, J = 11.1 and 1.3 Hz, 1 H, 5-H), 7.29 (m, 3 H, Ph), 7.43 (m, 6 H, Ph), 7.60 (m, 2 H, Ph), 7.76 (m, 4 H, Ph), 7.85 (d, J = 9.6 Hz, 1 H, 6-H_{DNPH}), 8.22 (ddd, J = 9.6, 2.6, and 0.8 Hz, 1 H, 5-H_{DNPH}), 9.05 (d, J = 2.6 Hz, 1 H, 3-H_{DNPH}), 11.59 (d, J = 0.8 Hz, 1 H, NH); MS (DCI, NH_3), *m/z* (relative intensity) 644 (2, M^+), 609 (5, $M^+ - Cl$), 574 (4 $M^+ - 2Cl$), 539 (6, $M^+ - 3Cl$), 105 (100), 77 (37, $C_6H_5^+$); MS (FAB) *m/z* 644 (31, M^+). Anal. Calcd for $C_{33}H_{23}Cl_3N_4O_4$ (645.9): C, 61.36; H, 3.59; N, 8.67. Found: C, 61.27; H, 3.69; N, 8.58.

1,2-Bis[(trimethylsilyl)ethynyl]-3-[[(trimethylsilyl)carbonyl]methylene]cyclopropene (17b). A solution of **9** in 5 mL of CH_2Cl_2 was prepared from 610 mg (4.6 mmol) of aluminum chloride and 814 mg (4.6 mmol, 0.56 mL) of tetrachlorocyclopropene. After 15 min, more CH_2Cl_2 (45 mL) was added, and the suspension was cooled to −45 °C. A solution of 1.57 g (9.2 mmol, 2.06 mL) of bis(trimethylsilyl)acetylene in 5 mL of CH_2Cl_2 was added at once via syringe. The solution was allowed to warm up slowly. At ~−35 °C, a deep purple color began to form, and the solution was allowed to warm up further until all of the formed cyclopropenylium salt had dissolved (at ~−25 °C). The solution was *immediately* quenched with ice–water, and the organic phase was separated, dried, and evaporated in vacuo at 20 °C. Rapid elution through a short flash silica gel column with hexane, then with hexane/benzene (9:1 to 4:1), gave **17b** as an unstable yellow oil: 1.19 g (75%); IR ($CHCl_3$) ν (C≡C) 2145, (C=O) 1647, (C=C) 1538, ($SiCH_3$) 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 9 H, CH_3), 0.23 (s, 9 H, CH_3), 0.24 (s, 9 H, CH_3), 7.09 (s, 1 H, 2-H); ^{13}C NMR (125.8 MHz, $CDCl_3$, gated decoupling) δ −1.0 (q, ^1J = 120.8 Hz, $SiCH_3$), −0.5 (q, ^1J = 120.7 Hz, $SiCH_3$), −0.3 (q, ^1J = 120.1 Hz, $SiCH_3$), 97.7 (d, ^4J = 11.6 Hz), 99.6 (s), 101.5 (s), 101.7 (d, ^4J = 4.4 Hz), 107.7 (d, ^3J = 4.6 Hz), 116.0 (d, ^3J = 5.6 Hz), 129.6 (d, ^1J = 168.8 Hz), 133.5 (s), 173.7 (d, ^2J = 7.2 Hz, C=O); MS (EI, 16 eV) *m/z* (relative intensity) 344 (100, M^+), 329 (59, $M^+ - CH_3$), 316 (8, $M^+ - CO$), 73 (77, $SiMe_3^+$); HRMS *m/z* (M^+, $C_{18}H_{28}OSi_3$) calcd 344.1448, obsd 344.1421.

Bis(1-propynyl)cyclopropenone (7b). A solution of **9** in 20 mL of CH_2Cl_2 was prepared from 1.33 g (10 mmol) of aluminum chloride and 1.96 g (11 mmol, 1.35 mL) of tetrachlorocyclopropene. After 15 min, more CH_2Cl_2 (80 mL) was added, and the suspension was cooled to −42 °C (acetonitrile/liquid N_2 bath). A total of 2.27 g (20 mmol, 3.0 mL) of 1-propynyltrimethylsilane was added dropwise over 30 min. The solution was stirred for 1 h at −42 °C and allowed to reach 20 °C over 1 h. The solution was poured into ice–water, and the organic layer was washed with more water and dried. After evaporation of the solvent, the remaining brown oil was purified by flash chromatography with hexane/ethyl acetate (95:5 to 80:20). Recrystallization from ether gave 647 mg (50%) of **7b** as moisture-sensitive colorless crystals: mp 109–110 °C; IR (KBr) ν (C≡C) 2223 (C=C) 1836, (C=O) 1602 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 2.10 (s, 6 H, CH_3); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ 5.1 (q, ^1J = 133.2 Hz, CH_3), 65.2 (q, ^3J = 4.7 Hz, C-1′), 108.0 (q, ^2J = 11.0 Hz, C-2′), 143.3 (s, C-2,3), 148.6 (s, C=O); MS (DCI, 50 eV) *m/z* (relative intensity) 131 (19, MH^+), 102 (100, $M^+ - CO$); HRMS (EI) (MH^+, C_9H_7O) calcd 131.0497, obsd 131.0509, (M^+, C_9H_6O) calcd 130.0419, obsd 130.0438.

Methyl 2-(1-Propynyl)-2-hexen-4-yn-1-oate (19). A solution of 477 mg (3.7 mmol) of bis(1-propynyl)cyclopropenone (**7b**) in 30 mL of dry methanol/chloroform (2:1) was heated to reflux for 1 h. The residue obtained after evaporation of the solvent was purified by flash chromatography with 5–10% ethyl acetate in hexane, and recrystallization from hexane gave 517 mg (87%) of **19** as colorless crystals: mp 67–68 °C; IR (CCl_4) ν (C≡C) 2230, 2215, (C=O) 1716, (C=C) 1570 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 2.04 (s, 3 H, CH_3-6), 2.06 (d, J = 2.5 Hz, 3 H, CH_3-3′), 3.73 (s, 3 H, OCH_3), 6.81 (q, J = 2.5 Hz, 1 H, 3-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ 4.8 (q, ^1J = 132.2 Hz, CH_3), 5.2 (q, ^1J = 132.0 Hz, CH_3), 52.5 (q, ^1J = 147.5 Hz, OCH_3), 74.3 (s, C-4), 77.4 (d, ^3J = 4.7 Hz, C-1′), 95.3 (q, ^2J = 11.0 Hz, C-5 or C-2′), 102.4 (q, ^2J = 10.8 Hz, C-2′ or C-5), 123.8 (s, C-2), 127.3 (d, ^1J = 169.3 Hz, C-3), 165.1 (s, C=O); MS (EI, 70 eV) *m/z* (relative intensity) 162 (100, M^+), 147 (6, $M^+ - Me$), 131 (20, $M^+ - MeO$); HRMS (M^+, $C_{10}H_{10}O_2$) calcd 162.0681, obsd 162.0682.

3,4-Bis(phenylethynyl)-3-cyclobutene-1,2-dione (8b). (a) Alkynyltributylstannane Method.[29] A solution of 302 mg (2 mmol) of **20**[14a,31] and 1.56 g (4 mmol) of (phenylethynyl)tributylstannane (**18b**)[29b] in 30 mL of dry 1,2-dichloroethane was degassed and stirred under an atmosphere of argon. Tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.06 mmol) was added, and the solution was stirred at 20 °C for 2 h. Silica gel was added, the solution was filtered, and the solvent was removed in vacuo. The residual orange crystals were washed with hexane to remove the tributyltin chloride. Recrystallization from CH_2Cl_2/hexane afforded 397 mg (70%) of **8b** as orange needles: mp 114–115 °C; IR (CCl_4) ν (C≡C) 2198 s, (C=O) 1783, (C=C) 1565 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.4–7.45 (m, 4 H, 3-H), 7.45–7.55 (m, 2 H, 4-H), 7.6–7.65 (m, 4 H, 2-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ 77.8 (s, C-1′), 120.5 (s, C-1_{Ph}), 125.6 (s, C-2′), 128.8 (d, C-3_{Ph}), 131.6 (d, C-4_{Ph}), 132.7 (d, C-2_{Ph}), 177.4 (s, C-3,4), 195.2 (s, C-1,2); MS (EI) *m/z* (relative intensity) 282 (65, M^+), 227 (67, $MH^+ - 2CO$), 226 (100, $M^+ - 2CO$). Anal.

(49) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1980.

Calcd for $C_{20}H_{10}O_2$ (282.3): C, 85.09; H, 3.57. Found: C, 85.07; H, 3.70.

(b) Alkynylzinc Iodide Method.[33b] A solution of 449 mg (4.4 mmol, 0.48 mL) of phenylacetylene in 15 mL of dry, degassed THF under argon was cooled to 0 °C in an ice bath. A 2.5 M solution of *n*-butyllithium (1.8 mL, 4.4 mmol) in hexane was added dropwise, and after 10 min, 1.40 g (4.4 mmol) of anhydrous zinc iodide was added at once. After stirring for 15 min at 0 °C, the solution was cannulated into a mixture of 302 mg (2 mmol) of **20** and 20 mg of tetrakis(triphenylphosphine)-palladium(0) in 40 mL of dry, degassed THF. The solution was stirred at 20 °C for 2 h and then filtered through a plug of silica gel with ether. After evaporation of the solvents, the residual solid was purified by flash chromatography with CH_2Cl_2/hexane (1:1). The first fraction gave 38 mg (9.4%) of diphenylbutadiyne: mp 86–88 °C (lit.[50] mp 87–88 °C); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 73.9, 81.5, 121.7, 128.4, 129.2, 132.5.[36] The second fraction gave 265 mg (47%) of **8b** as orange needles, mp 113–115 °C.

(4-Phenyl-1,3-butadiynyl)tri-*n*-butylstannane (18c). To a solution of 3.14 g (19.3 mmol) of *cis*-1-chloro-4-phenyl-1-buten-3-yne[32] in 60 mL of dry THF under argon at −78 °C was added dropwise a 1.64 M solution[51] of *n*-butyllithium in hexane (23.6 mL, 38.6 mmol). After 1 h at −78 °C, the solution was warmed up to 20 °C, and 6.29 g (19.3 mmol, 5.2 mL) of tributyltin chloride was added at once via syringe. After stirring for 1 h at 20 °C, the solution was diluted with hexane and washed with saturated ammonium chloride solution, followed by water. After drying and evaporation of the solvents, the crude oil was distilled under reduced pressure in a Kugelrohr apparatus at 185–190 °C (0.06 Torr) to give 7.20 g (90%) of **18c** as a pale yellow oil: IR (CCl_4) ν (C≡C) 2190, 2070, (C=C) 1588 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 9 H, 4-H_{Bu}), 1.05–1.15 (m, 6 H, 1-H_{Bu}), 1.37 (sext, J = 7.3 Hz, 6 H, 3-H_{Bu}), 1.55–1.7 (m, 6 H, 2-H_{Bu}), 7.3–7.35 (m, 3 H, 3,4-H_{Ph}), 7.45–7.5 (m, 2 H, 2-H_{Ph}); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 11.3 (C-1_{Bu}), 13.6 (C-4_{Bu}), 26.9 (C-3_{Bu}), 28.8 (C-2_{Bu}), 73.5 (C-4), 74.7 (C-2), 92.1 (C-3), 92.6 (C-1), 121.8 (C-1_{Ph}), 128.3 (C-3_{Ph}), 128.8 (C-4_{Ph}), 132.5 (C-2_{Ph}); MS (EI, 20 eV) m/z (relative intensity) 359 (100, $M^+ - C_4H_8$).

3,4-Bis(4-phenyl-1,3-butadiynyl)-3-cyclobutene-1,2-dione (8c). A solution of 1.05 g (6.9 mmol) of **20** and 5.70 g (13.7 mmol) of **18c** in 200 mL of dry 1,2-dichloroethane was degassed and placed under argon. Bis(triphenylphosphine)palladium(II) dichloride (140 mg, 0.2 mmol) was added, and the solution was stirred at 20 °C for 6 h. The solution was filtered through a plug of silica gel with CH_2Cl_2, and the solvents were removed. The dark oil was purified by flash chromatography with CH_2Cl_2/hexane (4:1 to 2:1) to give 249 mg (11%) of **8c** as moisture-sensitive deep red crystals: mp >184 °C (**explosion**); IR ($CDCl_3$) ν (C≡C) 2200, 2150, (C=O) 1793, 1780, (C=C) 1563 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.41 (t, J = 7.0 Hz, 4 H, 3-H), 7.49 (t, J = 7.0 Hz, 2 H, 4-H), 7.59 (d, J = 7.0 Hz, 4 H, 2-H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 67.6 (C-3′), 73.0 (C-1′), 99.9 (C-2′), 110.6 (C-4′), 120.1 (C-1_{Ph}), 128.8 (C-3_{Ph}), 131.1 (C-4_{Ph}), 132.9 (C-2_{Ph}), 178.2 (C-3,4), 194.8 (C-1,2); MS (EI) m/z (relative intensity) 330 (11, M^+), 274 (100, M^+ − 2CO); HRMS m/z (M^+, $C_{24}H_{10}O_2$) calcd 330.0681, obsd 330.0654, (M^+ − 2CO, $C_{22}H_{10}$) calcd 274.0783, obsd 274.0798.

3,4-Bis(1-pentyn-1-yl)-3-cyclobutene-1,2-dione (8d). A solution of 302 mg (2 mmol) of **20** and 1.4 g (4 mmol) of 1-pentynyltri-*n*-butylstannane (**18d**)[29a] in 30 mL of dry 1,2-dichloroethane was degassed and placed under argon. Tetrakis(triphenylphosphine)palladium(0) (70 mg, 0.06 mmol) was added, and the solution was stirred at 20 °C for 3 h. The solution was filtered through silica gel, and the solvents were removed. The oil was chromatographed twice with CH_2Cl_2/hexane (1:2) to give 219 mg (51%) of **8d** as a yellow oil: IR (film) ν (C≡C) 2215, (C=O) 1787, (C=C) 1562 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3 H, 5′-H), 1.63 (sext, J = 7.2 Hz, 2 H, 4′-H), 2.61 (t, J = 7.0 Hz, 2 H, 3′-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ 13.3 (q, C-5′), 21.2 (t, C-4′), 23.0 (t, C-3′), 69.7 (s, C-1′), 129.3 (s, C-2′), 180.3 (s, C-3,4), 196.6 (s, C-1,2); ^{13}C NMR (D_2SO_4, external TMS): δ 12.6; 20.6, 23.1, 70.1, 138.6, 181.8, 201.3; MS (EI) m/z (relative intensity) 215 (13, MH^+), 214 (89, M^+), 159 (15, MH^+ − 2CO), 158 (98, M^+ − 2CO), 129 (43, MH^+ − 2CO − C_2H_5), 128 (100, M^+ − 2CO − C_2H_5), 115 (54, M^+ − 2CO − C_3H_7). Anal. Calcd for $C_{14}H_{14}O_2$ (214.3): C, 78.48; H, 6.59. Found: C, 78.38; H, 6.56.

3,4-Bis[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione (8e). (a) Copper Acetylide Method.[33a] To a solution of 10.80 g (110 mmol, 15.6 mL) of (trimethylsilyl)acetylene[34a] in 150 mL of dry, degassed THF under argon at 0 °C was added dropwise 40 mL (100 mmol) of a 2.5 M solution of *n*-butyllithium in hexane over 10 min. After 20 min, 20.00 g (106 mmol) of copper(I) iodide was added under a positive pressure of argon, and the solution became deep yellow. After stirring for 10 min at 0 °C, 7.54 g (50 mmol) of **20** was added at once under a positive pressure of argon, and the solution was stirred for 20 °C for 15 min. At this point, TLC indicated complete conversion. The solution was poured *immediately* into a well-stirred suspension of 50 g of Celite in 700 mL of petroleum ether. Rapid filtration through a plug of Florisil with a mixture of petroleum ether/ether (9:1) gave 5.92 (43%) of crude **8e** as yellow needles, mp 90–95 °C. The compound was purified further by fractionated sublimation at 45–50 °C (0.10 Torr), giving 97 mg of bis-(trimethylsilyl)butadiyne, then at 60–70 °C (0.12 Torr), 3.71 g (27%) of **8e** as yellow crystals: mp 95–97 °C; IR ($CHCl_3$) ν (C≡C) 2150, (C=O) 1786, (C=C) 1552, ($SiCH_3$) 850 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.25 (s, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$, gated decoupling) δ −0.9 (q, ^1J = 120.9 Hz, CH_3), 90.5 (s, C-1′), 135.8 (decet, ^3J = 2.8 Hz, C-2′), 179.4 (s, C-3,4), 195.1 (s, C-1,2); MS (EI) m/z (relative intensity) 274 (61, M^+), 259 (5, $M^+ - CH_3$), 231 (5, $M^+ - CH_3$ −CO), 218 (78, M^+ −2CO), 203 (100, $M^+ - CH_3$ − 2CO), 73 (60, $SiMe_3^+$). Anal. Calcd for $C_{14}H_{18}O_2Si_2$ (274.5): C, 61.27; H, 6.61. Found: C, 61.30; H, 6.71.

(b) Alkynyltributylstannane Method.[29] To 302 mg (4 mmol) of **20** and 3.10 g (8 mmol) of **18e**[29b] in 25 mL of dry, degassed 1,2-dichloroethane under argon was added 25 mg of tetrakis(triphenylphosphine)palladium(0), and the solution was stirred at 20 °C for 2 h. After filtration and evaporation of the solvent, the brown oil was purified in two flash chromatographies with petroleum ether/ether (9:1) to give 330 mg (30%) of the product contaminated with 5–7% of tributyltin chloride (^1H NMR).

3-,4-Bis[4-(trimethylsilyl)-1,3-butadiynyl]-3-cyclobutene-1,2-dione (8f). To a solution of 1.94 g (10 mmol) of bis(trimethylsilyl)butadiyne in 30 mL of dry, degassed THF under argon at 0 °C was added dropwise over 10 min a total of 7.2 mL (10 mmol) of a 1.4 M solution of methyllithium–lithium bromide complex in ether.[35a] After 20 min, 2.14 g (11 mmol) of copper(I) iodide was added under a positive pressure of argon, and the solution became deep purple.[35b] After stirring for 15 min at 0 °C, 755 mg (5 mmol) of **20** was added at once under exclusion of air, and the solution was stirred at 20 °C for 20 min. At this point, TLC indicated complete conversion. The solution was poured *immediately* into a well-stirred suspension of 10 g of Celite in 300 mL of petroleum ether. The suspension was filtered rapidly through a column of Florisil with a mixture of petroleum ether/ether (9:1). Evaporation at 20 °C afforded 426 mg (26%) of **8f** as a very unstable brown oil contaminated with 14% of 1,8-bis(trimethylsilyl)-1,3,5,7-octatetrayne (^1H NMR, ^{13}C NMR)[23]: IR ($CDCl_3$) ν (C≡C) 2205, 2150, (C=O) 1784, ($SiCH_3$) 852 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.29 (s, 18 H, CH_3); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ − 1.0 (q of sept, ^1J = 120.9 and ^3J = 2.0 Hz, CH_3), 61.9 (s, C-3′), 85.8 (s, C-1′), 110.1 (s, C-2′), 111.6 (decet, ^3J = 2.8 Hz, C-4′), 179.0 (s, C-3,4), 194.2 (s, C-1,2); MS (FAB) m/z (relative intensity) 323 (30, MH^+), 295 (9, MH^+ − CO), 267 (14, MH^+ − 2CO), 266 (26, M^+ − 2CO), 251 (100, MH^+ − 2CO − CH_3). Since the product was unstable and very difficult to purify, the elemental analysis was made on the reduction product **27**.

3,4-Bis[(*tert*-butyldimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione (8g). To a solution of 33.16 g (0.24 mol) of (*tert*-butyldimethylsilyl)-acetylene[34b] in 400 mL of dry, degassed THF under argon at 0 °C was added dropwise over 30 min a total of 153 mL (0.23 mol) of a 1.5 M solution of *n*-butyllithium in hexane. After 20 min, 45.71 g (0.24 mol) of copper(I) iodide was added under a positive pressure of argon, and the solution became deep orange. After stirring for 15 min at 0 °C, 17.36 g (0.12 mol) of **20** was added at once, and the dark brown solution was stirred at 20 °C for 15 min. At this time, TLC indicated complete conversion. Celite (~20 g) was added to the solution, followed by saturated NaCl (500 mL). The mixture was filtered through a Celite pad, the aqueous phase was removed, and the organic phase was dried. After evaporation of the solvents in vacuo, the residual dark oil was dissolved in 100 mL of hexane and filtered through a plug of silica with hexane and then hexane/ether (9:1). The solvents were evaporated to give 23.68 g (57%) of **8g** as an orange oil that crystallized on standing, mp 54–58 °C. An analytically pure product was obtained by flash chromatography with hexane/ether (9:1): mp 57–59 °C; IR (CCl_4) ν (C≡C) 2060, (C=O) 1788, (C=C) 1552 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.20 (s, 6 H, $SiMe_2$), 0.21 (s, 6 H, $SiMe_2$), 0.97 (s, 18 H, *t*-Bu); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ −5.3 (qq, ^1J = 121.3 and ^3J = 2.1 Hz, $SiMe_2$), 16.6 (m, $C(CH_3)_3$), 25.9 (q of sept, ^1J = 125.7 and ^3J = 5.4 Hz, $C(CH_3)_3$), 91.2 (s, C-1′), 134.9 (sept, ^3J = 3.1 Hz, C-2′), 180.1 (s, C-3,4), 195.1 (s, C-1,2); MS (EI, 50 eV) m/z (relative intensity) 358 (13, M^+), 343 (2, $M^+ - CH_3$), 302 (3, M^+ − 2CO), 245 (100, M^+ − 2CO − C_4H_9); HRMS m/z (M^+, $C_{20}H_{30}O_2Si_2$) calcd 358.1784, obsd 358.1770. Anal. Calcd for $C_{20}H_{30}O_2Si_2$ (358.6): C, 66.98; H, 8.43. Found: C, 66.71; H, 8.31.

3,4-Bis[(triisopropylsilyl)ethynyl]-3-cyclobutene-1,2-dione (8h). To a solution of 10.94 g (60 mmol) of (triisopropylsilyl)acetylene[34c] in 300 mL

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(51) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.

of dry, degassed THF under argon at 0 °C was added a total of 37.5 mL (60 mmol) of a 1.6 M solution of *n*-butyllithium in hexane dropwise over 15 min. After 10 min, 12.38 g (65 mmol) of copper(I) iodide was added under a positive pressure of argon, and the solution became dark green. After stirring for 15 min at 0 °C, 7.54 g (50 mmol) of **20** was added at once, and the brown solution was stirred at 20 °C for 1 h. The solution was evaporated to dryness together with 50 g of silica gel. The solid was loaded on the top of a flash silica gel column packed with hexane as eluant. Elution with hexane/ether (9:1) gave 7.82 g (59%) of **8h** as yellow crystals: mp 36.5–37.5 °C; IR ($CHCl_3$) ν (C≡C) 2145, (C=O) 1784, (C=C) 1546 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.1–1.3 (m, 42 H, CH and CH_3); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 11.0, 18.5, 92.6, 133.8, 180.1, 195.6; MS (EI, 20 eV) *m/z* (relative intensity) 442 (23, M^+), 343 (100, $M^+ - 2CO - C_3H_7$). Anal. Calcd for $C_{26}H_{42}O_2Si_2$ (442.8): C, 70.53; H, 9.56. Found: C, 70.34; H, 9.62.

***cis*-3,4-Bis[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-diol (21), 3,4-Bis(hydroxymethyl)-1,6-bis(trimethylsilyl)-3-hexene-1,4-diyne (22), and Ethyl (*Z*)-2-Hydroxy-6-(trimethylsilyl)-3-[(trimethylsilyl)ethynyl]-3-hexen-5-yn-1-oate (23).** A solution of 15.65 g (42 mmol) of cerium(III) chloride heptahydrate in 150 mL of absolute ethanol was added at 20 °C to a solution of 5.80 g (21 mmol) of **8e** in 50 mL of ethanol. Sodium borohydride (1.70 g, 45 mmol) was added by small portions to control the hydrogen evolution. After stirring for 15 min at 20 °C, the suspension was poured into 0.1 M HCl/ethyl acetate (750 mL each). The organic phase was washed once with water and dried. The solvent was evaporated, and the resulting brown oil yielded three product fractions upon flash chromatography (2–5% of ethyl acetate in CH_2Cl_2). Fraction 1 afforded 113 mg (1.7%) of **23** as an unstable yellow oil: IR ($CHCl_3$) ν (OH) 3515, (C≡C) 2140, (C=O) 1731, (C—O) 1250, ($SiCH_3$) 846 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.14 (s, 18 H, CH_3), 1.24 (t, ABX_3, J = 7.1 Hz, 3 H, CH_3), 3.40 (s br, 1 H, OH), 4.18 (q, *A*BX_3, J = 7.1 Hz, 1 H, OCH_2), 4.19 (q, A*B*X_3, J = 7.1 Hz, 1 H, OCH_2), 4.55 (d, J = 1.2 Hz, 1 H, 2-H), 6.03 (d, J = 1.2 Hz, 1 H, 4-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ –0.4 (q, Si*C*H_3), 14.0 (q, CH_3), 62.3 (t, OCH_2), 72.6 (d, C-2), 99.4 (s, C≡), 101.5 (s, C≡), 104.0 (s, C≡), 105.0 (s, C≡), 118.2 (d, C-4), 132.4 (s, C-3), 171.5 (s, C=O); MS (EI, 50 eV) *m/z* (relative intensity) 322 (16, M^+), 307 (3, $M^+ - CH_3$), 293 (4, $M^+ - C_2H_5$), 249 (70, $M^+ - SiMe_3$), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{16}H_{26}O_3Si_2$ (322.6): C, 59.58; H, 8.12. Found: C, 59.38; H, 7.94.

Fraction 2, after recrystallization from hexane, afforded 92 mg (1.6%) of **22** as fine white needles: mp 115.5–116.5 °C; IR ($CHCl_3$) ν (OH) 3580, (C≡C) 2140, ($SiCH_3$) 845 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.19 (s, 18 H, CH_3), 2.18 (s, 2 H, OH), 4.34 (s, 4 H, CH_2); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ –0.3 (q of sept, ^1J = 120.4 and ^3J = 2.0 Hz, Si*C*H_3), 63.1 (t, ^1J = 146.8 Hz, CH_2), 100.2 (s, C-2,5), 108.9 (decet, ^3J = 2.7 Hz, C-1,6), 130.6 (m, C-3,4); MS (EI, 50 eV) *m/z* (relative intensity) 280 (12, M^+), 263 (12, $M^+ - OH$), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{14}H_{24}O_2Si_2$ (280.5): C, 59.95; H, 8.62. Found: C, 60.01; H, 8.69.

Fraction 3, after recrystallization from hexane, afforded 2.74 g (47%) of **21** as fine white needles: mp 105–105.5 °C; IR (CCl_4) ν (OH) 3615, 3310, (C≡C) 2146, 2138, ($SiCH_3$) 860, 850 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.23 (s, 18 H, CH_3), 2.56 (d, J = 7.3 Hz, 2 H, OH), 4.75 (d, J = 7.3 Hz, 2 H, 1,2-H); from the ^{13}C satellites of 1,2-H, the following coupling constants were observed: $J_{1\text{-}H,2\text{-}H}$ = 3.7 Hz, $^1J_{CH}$ = 160.7 Hz; ^{13}C NMR (125.8 MHz, $CDCl_3$, gated decoupling) δ –0.4 (q, ^1J = 120.3 Hz, CH_3), 73.8 (d, ^1J = 159.8 Hz, C-1,2), 96.5 (s, C-1′), 106.2 (decet, ^3J = 2.8 Hz, C-2′), 137.1 (m, C-3,4); MS (EI, 50 eV) *m/z* (relative intensity) 278 (8, M^+), 260 (12, $M^+ - H_2O$), 245 (23, $M^+ - H_2O - CH_3$), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{14}H_{22}O_2Si_2$ (278.5): C, 60.38; H, 7.96. Found: C, 60.11; H, 8.03.

***cis*-3,4-Bis[(*tert*-butyldimethylsilyl)ethynyl]-3-cyclobutene-1,2-diol (24), (*E*)-3,4-Bis(dihydroxymethyl)-1,6-bis(*tert*-butyldimethylsilyl)-3-hexene-1,4-diyne (25), and Ethyl (*Z*)-2-Hydroxy-3-[(*tert*-butyldimethylsilyl)ethynyl]-3-hexen-5-yn-1-oate (26).** A solution of 111.78 g (0.30 mol) of cerium(III) chloride heptahydrate in 400 mL of absolute ethanol was added at 20 °C to a solution of 54.02 g (0.15 mol) of **8g** in 200 mL of ethanol. Sodium borohydride (15.10 g, 0.40 mol) was added by small portions with vigorous stirring to control the hydrogen evolution. After 15 min at 20 °C, the suspension was poured cautiously into 2 L of ice-cold 0.1 M HCl/ethyl acetate (1:1). The organic phase was washed once with water and dried. The solvent was evaporated, and flash chromatography of the brown oil with CH_2Cl_2 gave three fractions. Fraction 1 afforded 1.59 g (2.6%) of **26** as an unstable yellow oil: IR ($CHCl_3$) ν (OH) 3510, (C≡C) 2140, (C=O) 1748 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.14 (s, 6 H, $SiMe_2$), 0.15 (s, 6 H, $SiMe_2$), 0.93 (s, 18 H, *t*-Bu), 1.29 (t, ABX_3, J = 7.1 Hz, 3 H, CH_3), 3.38 (d, J = 6.8 Hz, 1 H, OH), 4.21 (q, *A*BX_3, J = 7.1 Hz, 1 H, OCH_2), 4.24 (q, A*B*X_3, J = 7.1 Hz, 1 H, OCH_2), 4.57 (d, J = 6.8 Hz, 1 H, 2-H), 6.06 (d, J = 6.8 Hz, 1 H, 4-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ –4.8 (q, $SiMe_2$), –4.7 (q, $SiMe_2$), 14.0 (q, CH_3), 16.4 (s, *C*$(CH_3)_3$), 16.5 (s, *C*$(CH_3)_3$), 26.0 (C(*C*$H_3)_3$), 26.1 (s, C(*C*$H_3)_3$), 62.4 (t, O*C*H_2), 73.0 (d, C-2), 100.0 (s, C≡), 102.0 (s, C≡), 102.5 (s, C≡), 103.5 (s, C≡), 118.1 (d, C-4), 132.1 (s, C-3), 171.7 (s, C=O); MS (EI, 50 eV) *m/z* (relative intensity) 406 (2, M^+), 349 (41, $M^+ - C_4H_9$), 321 (22, $M^+ - C_4H_9 - CO$), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{22}H_{38}O_3Si_2$ (406.7): C, 64.97; H, 9.42. Found: C, 64.74; H, 9.44.

Fraction 2, after recrystallization from hexane, gave 1.70 g (3.1%) of **25** as white needles: mp 123–123.5 °C; IR ($CHCl_3$) ν (OH) 3590, (C≡C) 2140 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.16 (s, 12 H, $SiMe_2$), 0.96 (s, 18 H, *t*-Bu), 2.15 (br s, 2 H, OH), 4.39 (s, 2 H, 1,2-H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ –4.8 ($SiMe_2$), 16.6 (*C*$(CH_3)_3$), 26.0 (C(*C*$H_3)_3$), 63.3 (CH_2), 100.8 (C-2,5), 107.7 (C-1,6), 130.6 (C-3,4); MS (EI, 50 eV) *m/z* (relative intensity) 364 (9, M^+), 349 (4, $M^+ - CH_3$), 307 (28, $M^+ - C_4H_9$), 147 (100), 73 (65, $SiMe_3^+$), 57 (25, *t*-Bu^+). Anal. Calcd for $C_{20}H_{36}O_2Si_2$ (364.7): C, 65.87; H, 9.95. Found: C, 65.97; H, 10.07.

Fraction 3, after evaporation of the solvent, left 39.71 g (73%) of **24** as a pale yellow oil that crystallized on standing: mp 117–118 °C; IR ($CHCl_3$) ν (OH) 3590, 3360, (C≡C) 2150, 2135 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.11 (s, 6 H, $SiMe_2$), 0.12 (s, 6 H, $SiMe_2$), 0.93 (s, 18 H, *t*-Bu), 4.69 (d, J = 7.5 Hz, 2 H, OH), 5.00 (d, J = 7.5 Hz, 2 H, 1,2-H); from the ^{13}C satellites, the following coupling constants were observed: $J_{1\text{-}H,2\text{-}H}$ = 3.6 Hz, $J_{H,OH}$ = 7.5 Hz, $^1J_{CH}$ = 160.5 Hz; ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ –4.9 (q, ^1J = 120.6 Hz, $SiMe_2$), 16.5 (s, *C*$(CH_3)_3$), 26.0 (q of sept, ^1J = 125.3 and ^3J = 5.5 Hz, C(*C*$H_3)_3$), 74.0 (d, ^1J = 159.3 Hz, C-1,2) 97.2 (s, C-1′), 104.8 (sept, ^3J = 2.6 Hz, C-2′), 137.3 (dd, ^2J = 8.7 and ^3J = 4.5 Hz, C-3,4); MS (EI, 20 eV) *m/z* (relative intensity) 362 (4, M^+), 347 (2, $M^+ - CH_3$), 305 (100, $M^+ - C_4H_9$), 249 (10, $M^+ - C_4H_9 - C_4H_8$), 73 (54, $SiMe_3^+$). Anal. Calcd for $C_{20}H_{34}O_2Si_2$ (362.7): C, 66.23; H, 9.45. Found: C, 66.17; H, 9.49.

***cis*-3,4-Bis[4-(trimethylsilyl)-1,3-butadiynyl]-3-cyclobutene-1,2-diol (27) and (*Z*)-8-(Trimethylsilyl)-3-[4-(trimethylsilyl)-1,3-butadiynyl]-3-octene-5,7-diyne-1,2-diol (28).** A solution of 1.12 g (3 mmol) of cerium(III) chloride heptahydrate in 30 mL of absolute ethanol was added at 20 °C to 426 mg (1.3 mmol) of **8f** in 10 mL of ethanol. Sodium borohydride (228 mg, 6 mmol) was added by small portions. After stirring for 15 min at 20 °C, the suspension was poured into 200 mL of 0.1 M HCl/ethyl acetate (1:1). The organic phase was washed once with water and dried. The solvent was evaporated, and flash chromatography of the brown oil with 0–10% of ethyl acetate in CH_2Cl_2 afforded two fractions. Fraction 1, after recrystallization from ether/hexane, afforded 52 mg (12%) of **27** as tan needles: mp 153–154 °C; IR ($CDCl_3$) ν (OH) 3595, 3530, 3400, (C≡C) 2250, 2105, (C—O) 1257, ($SiCH_3$) 855 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.22 (s, 18 H, CH_3), 3.17 (s, br, 2 H, OH), 4.78 (s, 2 H, 1,2-H); from the ^{13}C satellites of 1,2-H, the following coupling constants were observed: $J_{1\text{-}H,2\text{-}H}$ = 3.6 Hz, $^1J_{CH}$ = 161.0 Hz; ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ –0.6 (q of sept, ^1J = 120.7 and ^3J = 2.0 Hz, Si*C*H_3), 68.3 (s, C-1′), 73.9 (d, ^1J = 161.0 Hz, C-1,2), 84.9 (s, C-3′), 87.0 (s, C-2′), 97.2 (decet, ^3J = 2.8 Hz, C-4′), 138.7 (dd, ^2J = 9.0 Hz; ^3J = 4.2 Hz, C-3,4); MS (EI, 20 eV) *m/z* (relative intensity) 326 (15, M^+), 311 (14, $M^+ - CH_3$), 73 (100, $SiMe_3^+$); HRMS *m/z* (M^+, $C_{18}H_{22}O_2Si_2$) calcd 326.1158, obsd 326.1172. Anal. Calcd for $C_{18}H_{22}O_2Si_2$ (326.5): C, 66.21; H, 6.79. Found: C, 66.27; H, 6.84.

Fraction 2, after evaporation of the solvent, afforded 76 mg (18%) of **28** as a yellow oil: IR ($CDCl_3$) ν (OH) 3600, 3420, (C≡C) 2255, 2200, 2100, (C—O) 1257, ($SiCH_3$) 855 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.23 (s, 9 H, CH_3), 0.24 (s, 9 H, CH_3), 2.73 (s, br, 1 H, OH), 3.33 (s, br, 1 H, OH), 3.62 (dd, J = 11.5 and 7.0 Hz, 1 H, 1-H), 3.81 (dd, J = 11.5 and 3.2 Hz, 1 H, 1-H), 4.31 (ddd, J = 7.0, 3.2, and 1.0 Hz, 1 H, 2-H), 6.26 (d, J = 1.0 Hz, 1 H, 4-H); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ –0.6 (q, ^1J = 120 Hz, CH_3), –0.5 (q, ^1J = 120 Hz, CH_3), 65.3 (td, ^1J = 143.2 and ^3J = 3.4 Hz, C-1), 72.1 (dd, ^2J = 13.2 and ^4J = 3.4 Hz, C-5), 73.5 (d, ^3J = 1.0 Hz, C-1′), 73.9 (dm, ^1J = 148.0 Hz, C-2), 82.6 (d, ^3J = 5.1 Hz, C-6), 84.0 (s, C-2′ or 3′), 87.2 (s, C-3′ or 2′), 87.7 (d, ^4J = 2.7 Hz, C-7), 94.5 (m, C-4′ or C-8), 95.5 (m, C-8 or C-4′), 117.5 (dd, ^1J = 170.4 and ^3J = 4.5 Hz, C-4), 135.8 (s, C-3); MS (EI, 20 eV) *m/z* (relative intensity) 328 (32, M^+), 311 (3, $M^+ - OH$), 310 (6, $M^+ - H_2O$), 297 (31, $M^+ - CH_2OH$), 73 (100, $SiMe_3^+$); HRMS *m/z* (M^+, $C_{18}H_{24}O_2Si_2$) calcd 328.1315, obsd 328.1312. Anal. Calcd for $C_{18}H_{24}O_2Si_2$ (328.6): C, 65.80; H, 7.36. Found: C, 65.51; H, 7.49.

***cis*-3,4-Diacetoxy-1,2-bis[(trimethylsilyl)ethynyl]-1-cyclobutene (29a) and *cis*-2-Acetoxy-3,4-bis[(trimethylsilyl)ethynyl]-3-cyclobuten-1-ol (29b).** A solution of 195 mg (0.7 mmol) of *cis*-1,2-diol **21**, 79 mg (0.77 mmol, 73 μL) of acetic anhydride, and 61 mg (0.77 mmol, 62 μL) of pyridine in 10 mL of dry CH_2Cl_2 was stirred at 20 °C for 5 days. The solution was extracted with 0.1 M HCl, washed with water, and dried. After evaporation of the solvent, the remaining oil was purified by flash chro-

matography with 0–5% of ethyl acetate in CH_2Cl_2 to give three fractions.

Fraction 1, after evaporation of the solvent, left 44 mg (15%) of **29a** as white crystals: mp 102–104 °C; IR ($CHCl_3$) ν (C≡C) 2130, (C=O) 1744, (C=C) 1590, ($SiCH_3$) 848 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.23 (s, 18 H, $SiCH_3$), 2.10 (s, 6 H, CH_3CO), 5.73 (s, 2 H, 3,4-H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ −0.4 ($SiCH_3$), 20.6 (CH_3CO), 73.6 (C-3,4), 95.5 (C-1′), 107.6 (C-2′), 134.1 (C-1,2), 169.8 (C=O); MS (EI, 20 eV) m/z (relative intensity) 362 (19, M^+), 347 (4, $M^+ - CH_3$), 320 (40, $M^+ - H_2CCO$), 289 (19, $M^+ - SiMe_3$), 278 (100, $M^+ - 2H_2CCO$), 73 (75, $SiMe_3^+$). Anal. Calcd for $C_{18}H_{26}O_4Si_2$ (362.6): C, 59.62; H, 7.23. Found: C, 59.55; H, 7.26.

Fraction 2 gave 128 mg (55%) of **29b** as white crystals: mp 99–100 °C; IR (CCl_4) ν (OH) 3570, (C≡C) 2145, 2130, (C=O) 1740, ($SiCH_3$) 847 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.22 (s, 9 H, $SiCH_3$), 0.23 (s, 9 H, $SiCH_3$), 2.16 (s, 3 H, CH_3CO), 2.63 (d, J = 9.3 Hz, 1 H, OH), 4.86 (dd, J = 9.3 and 3.5 Hz, 1 H, 3-H), 5.56 (d, J = 3.5 Hz, 1 H, 4-H); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ −0.4, 20.8, 73.6, 76.0, 95.8, 95.9, 106.4, 107.6, 132.2, 138.9, 170.5; MS (EI, 20 eV) m/z (relative intensity) 320 (10, M^+), 305 (26, $M^+ - CH_3$), 278 (100, $M^+ - H_2CCO$), 73 (66, $SiMe_3^+$). Anal. Calcd for $C_{16}H_{24}O_3Si_2$ (320.5): C, 59.95; H, 7.55. Found: C, 59.80; H, 7.45.

Fraction 3 gave 60 mg (29%) of the starting diol **21** as white needles.

***cis*-1,2-Bis[(*tert*-butyldimethylsilyl)ethynyl]-3,4-(thiocarbonyldioxy)-1-cyclobutene (30).** A solution of 179 mg (0.49 mmol) of **24** and 178 mg (1 mmol) of 1,1′-thiocarbonyldiimidazole in 5 mL of dry CH_2Cl_2 was stirred at 20 °C for 30 min. The solution was filtered through a plug of silica gel with CH_2Cl_2 and evaporated to give 198 mg (100%) of **30** as a colorless oil that crystallized on standing: mp 129–131 °C; IR ($CHCl_3$) ν (C≡C) 2205, 2130, (C=C) 1575, (C=S) 1283 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.10 (s, 6 H, $SiMe_2$), 0.11 (s, 6 H, $SiMe_2$), 0.89 (s, 18 H, t-Bu), 5.50 (s, 2 H, 3,4-H); from the ^{13}C satellites of 3,4-H, the following coupling constants were obtained: $^3J_{3\text{-}H,4\text{-}H}$ = 3.7 Hz, $^1J_{CH}$ = 178.6 Hz; ^{13}C NMR (90.6 MHz, $CDCl_3$, DEPT) δ −5.2 (q, $SiMe_2$), 16.3 (s, $C(CH_3)_3$), 25.8 (q, $C(CH_3)_3$), 82.9 (d, C-3,4), 94.9 (s, C-1′), 110.0 (s, C-2′), 137.9 (s, C-1,2), 193.1 (s, C=S); MS (EI, 20 eV) m/z (relative intensity) 404 (4, M^+), 348 (7, $M^+ - C_4H_8$), 303 (20, $M^+ - C_4H_9 - CS$), 287 (10, $M^+ - C_4H_9 - CSO$), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{21}H_{32}O_2SSi_2$ (404.7): C, 62.32; H, 7.97; S, 7.92. Found: C, 62.38; H, 8.10; S, 8.00.

***cis*-3,4-Diethynyl-3-cyclobutene-1,2-diol (31).** A 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added at 20 °C to a solution of 1.11 g (4 mmol) of **21** in 100 mL of wet THF. An instantaneous reaction occurred, and the solution was stirred further for 10 min. The solution was diluted with 100 mL of ethyl acetate and washed with water and saturated NaCl, and dried. The solvent was evaporated at 20 °C under reduced pressure to give unstable crystals that were immediately redissolved in petroleum ether/ether (1:2). Flash chromatography with this solvent gave 526 mg (98%) of **31** as unstable colorless crystals: mp >55 °C (**explosion**); IR (KBr) ν (OH) 3340, 3290, (≡C—H) 3220, (C≡C) 2085, (C=C) 1508 cm^{-1}; ^1H NMR (360 MHz, acetone-d_6) δ 4.39 (s, 2 H, H-2′), 4.61 (s, 2 H, H-1,2), 5.00 (s, br, 2 H, OH); ^{13}C NMR (90.6 MHz, acetone-d_6, gated decoupling) δ 74.4 (d, ^1J = 158.0 Hz, C-1,2), 76.5 (d, ^2J = 50.3 Hz, C-1′), 88.4 (d, ^1J = 254.6 Hz, C-2′), 138.6 (m, C-3,4); MS (EI, 16 eV) m/z (relative intensity) 134 (100, M^+), 116 (18, $M^+ - H_2O$); HRMS m/z (M^+, $C_8H_6O_2$) calcd 134.0368, obsd 134.0342.

1,2-Bis[(*tert*-butyldimethylsilyl)ethynyl]-3,4-(isopropylidenedioxy)-1-cyclobutene (32). A solution of 26.75 g (73.8 mmol) of *cis*-1,2-diol **24**, 10.42 g (100 mmol, 12.3 mL) of freshly distilled 2,2-dimethoxypropane, and 0.5 g of *p*-toluenesulfonic acid in 750 mL of dry CH_2Cl_2 was stirred at 20 °C for 2 h. The solution was filtered through a plug of silica gel with CH_2Cl_2 and evaporated to give 26.94 g (91%) of **32** as colorless crystals: mp 79–81 °C; IR ($CHCl_3$) ν (C≡C) 2150, 2135, (C—O) 1252 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.15 (s, 12 H, $SiMe_2$), 0.95 (s, 18 H, t-Bu), 1.43 (s, 3 H, Me), 1.56 (s, 3 H, Me), 5.16 (s, 2 H, 3,4-H); from the ^{13}C satellites of 3,4-H, the following coupling constants were obtained: $^3J_{3\text{-}H,4\text{-}H}$ = 3.4 Hz, $^1J_{CH}$ = 170.1 Hz; ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ −4.9 (qq, ^1J = 120.4 and ^3J = 1.9 Hz, $SiMe_2$), 16.6 (s, $C(CH_3)_3$), 26.0 (q of sept, ^1J = 125.3 and ^3J = 5.5 Hz, $C(CH_3)_3$), 28.6 (qq, ^1J = 123.8 and ^3J = 2.9 Hz, CH_3), 29.1 (qq, ^1J = 127.1 and ^3J = 3.3 Hz, CH_3), 82.0 (dd, ^1J = 169.9 Hz; $^{4(2)}J$ = 1.7 Hz, C-3,4), 97.3 (s, C-1′), 105.6 (sept, ^3J = 2.7 Hz, C-2′), 116.5 (sept, ^3J = 4.8 Hz, CMe_2), 138.4 (m, C-1,2); MS (EI, 50 eV) m/z (relative intensity) 402 (2, M^+), 387 (3, $M^+ - CH_3$), 373 (48, $M^+ - C_2H_5$), 287 (16, M^+ − TBDMS), 73 (100, $SiMe_3^+$). Anal. Calcd for $C_{23}H_{38}O_2Si_2$ (402.7): C, 68.60; H, 9.51. Found: C, 68.43; H, 9.65.

1,2-Diethynyl-3,4-(isopropylidenedioxy)-1-cyclobutene (33). A 1.0 M solution of tetrabutylammonium fluoride in THF (1 mL, 1 mmol) was added to a solution of 10.07 g (25 mmol) of **32** in 500 mL of wet THF at 20 °C. The solution was stirred for 30 min, then washed twice with water and once with saturated NaCl, and dried. The solvent was evaporated at 20 °C in vacuo to give an unstable oil that was redissolved in hexane. Flash chromatography with hexane/ether (95:5) gave 3.87 g (89%) of **33** as unstable colorless crystals: mp 53–54 °C; IR ($CHCl_3$) ν (≡C—H) 3285, (C≡C) 2100, (C—O) 1249, 1051 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.35 (s, 3 H, Me), 1.47 (s, 3 H, Me), 3.59 (s, 2 H, 2′-H), 5.12 (s, 3,4-H); from the ^{13}C satellites of 3,4-H and 2′-H, the following coupling constants were observed: $^3J_{3\text{-}H,4\text{-}H}$ = 3.5 Hz, $^1J_{HC\text{-}3,4}$ = 170.8 Hz, $^1J_{HC\text{-}2'}$ = 255.2 Hz, and $^2J_{2'\text{-}H,C\text{-}1'}$ = 49.5 Hz; ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ 28.6 (qq, ^1J = 126.8 and ^3J = 2.9 Hz, CH_3), 28.9 (qq, ^1J = 127.2 and ^3J = 3.4 Hz, CH_3), 75.4 (d, ^2J = 49.6 Hz, C-1′), 81.7 (d, ^1J = 170.7 Hz, C-3,4), 88.6 (d, ^1J = 255.3 Hz, C-2′), 116.7 (sept, ^2J = 4.8 Hz, CMe_2), 138.3 (m, C-1,2); MS (EI) m/z (relative intensity) 174 (16, M^+), 159 (33, $M^+ - CH_3$), 145 (99, $M^+ - C_2H_5$), 116 (100, $M^+ - Me_2CO$); HRMS m/z (M^+, $C_{11}H_{10}O_2$) calcd 174.0681, obsd 174.0676.

Cyclization of 33 to Trimer 34, Tetramer 35, and Pentamer 36. A solution of 3.85 g (22.1 mmol) of **33** with 10 mL of Hay catalyst[52] in 2 L of acetone was stirred vigorously at 20 °C for 2 days while a slow stream of dry oxygen was bubbled in. The acetone was evaporated at 20 °C in vacuo, and the residue was filtered through a plug of silica gel with CH_2Cl_2 to remove the baseline polymers. A flash chromatography of the remaining oil with CH_2Cl_2 afforded four identified fractions. Fraction 1 gave 54 mg (0.1%) of the starting material.

Fraction 2 gave 80 mg (2.1%) of **34** (mixture of diastereomers) as a slightly unstable pale yellow powder: mp >130 °C dec; IR ($CHCl_3$) ν (C≡C) 2100, (C=C) 1598, (C—O) 1262, 1250, 1077 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.19 (s, 9 H, Me), 1.54 (s, 9 H, Me), 5.97 (s, 6 H, CH), with 5.969, 5.973, 5.975, and 5.979 as indication for diastereomers of about equal intensities; ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 28.5, 29.1, 82.7, 83.0, 88.5, 117.9, 143.1; MS (FAB) m/z (relative intensity) 516 (9, M^+), 459 (33, $M^+ - H_2CCOCH_3$), 342 (100, $M^+ - 3\ Me_2CO$); HRMS m/z (M^+, $C_{33}H_{24}O_6$) calcd 516.1573, obsd 516.1571.

Fraction 3, after evaporation of the solvent and trituration of the red oil with hexane, gave 253 mg (6.6%) of **35** (mixture of diastereomers) as a red crystalline powder: mp >155 °C dec; IR ($CHCl_3$) ν (C≡C) 2255, 2120 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.33 (s, 12 H, Me), 1.60 (s, 12 H, Me), 4.92 (s, 8 H, CH), with 4.923 and 4.925 as indication for diastereomers; ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 28.6, 28.9, 80.1, 81.7, 86.2, 117.2, 141.5 (with 141.4, 141.6 as indication for diastereoisomers); MS (FAB) m/z (relative intensity) 688 (28, M^+), 456 (43, $M^+ - 4\ Me_2CO$), 344 (100, M^{2+}). Anal. Calcd for $C_{44}H_{32}O_8$ (688.7): C, 76.73; H, 4.68. Found: C, 76.44; H, 4.63.

Fraction 4 gave 68 mg (1.8%) of **36** (mixture of diastereomers) as a somewhat unstable yellow powder: mp >140 °C dec; IR ($CHCl_3$) ν (C≡C) 2115, (C—O) 1250, 1083 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.44 (s, 15 H, Me), 1.53 (s, 15 H, Me), 5.28 (s, 10 H, CH); ^{13}C NMR (90.6 MHz, $CDCl_3$) δ 28.68, 28.97, 78.93, 82.54, 85.10 (with 85.13), 117.26 (with 117.37), 139.22 (with 139.26, 139.30), peaks in parentheses indicate the presence of diastereomers; MS (FAB) m/z (relative intensity) 430 (42, M^{2+}), 429 (100). Anal. Calcd for $C_{55}H_{40}O_{10}\cdot CH_2Cl_2$ (945.9): C, 71.11; H, 4.48. Found: C, 71.82; H, 4.45.

Octol 37. A solution of 69 mg (0.1 mmol) of tetramer **35** in 50 mL of THF containing 2 mL of concentrated HCl was stirred at 20 °C under argon for 12 h. A progressive hydrolysis was observed by TLC (silica gel, ethyl acetate). The solution was poured into saturated ice-cold $NaHCO_3$/ethyl acetate, and the organic layer was washed with saturated NaCl and dried. Evaporation of the solvent at 20 °C in vacuo and rinsing the solid residue with ether gave 55 mg (99%) of **37** (mixture of diastereomers) as a stable red microcrystalline powder: mp >135 °C dec; IR (KBr) ν (OH) 3320, (C≡C) 2100, (C—O) 1275, 1083 cm^{-1}; ^1H NMR (360 MHz, Me_2SO-d_6) δ 4.44 (s, 8 H, CH), 5.55 (s br, 8 H, OH); ^{13}C NMR (90.6 MHz, Me_2SO-d_6, gated decoupling) δ 74.6 (d, ^1J = 157 Hz, CHOH) (with 74.7, d), 80.2 (s, C≡), 83.4 (s, C≡) (with 83.5, s), 140.9 (s, C=C) (with 141.0, s); UV/vis (tetrahydrofuran) λ_{max} (nm) 298 sh (ϵ 19 900), 313 (29 500), 331 (68 900), 356 (140 300), 399 sh (4730), 431 sh (3270), 471 (2490), 510 sh (1340); MS (FAB) m/z (relative intensity) 528 (3, M^+), 460 (100, $M^+ - 4OH$), 392 (4, $M^+ - 8OH$); HRMS m/z (M^+, $C_{32}H_{16}O_8$) calcd 528.0845, obsd 528.0842.

3,4-Bis[(*tert*-butyldimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione Mono(ethylene ketal) (40) and 3,4-Bis[(*tert*-butyldimethylsilyl)-ethynyl]-3-cyclobutene-1,2-dione Bis(ethylene ketal) (38). To 20.74 g (58 mmol) of **8g** and 30.96 g (150 mmol) of 1,2-bis[(trimethylsilyl)oxy]-ethane was added under argon 6.90 g (31 mmol, 6.0 mL) of trimethylsilyl trifluoromethanesulfonate. The mixture was heated at 80 °C for 6 h. After cooling, ether was added, and the solution was extracted twice with saturated $NaHCO_3$ and once with saturated NaCl. After drying and

(52) Jones, G. E.; Kendrick, D. A.; Holmes, A. B. *Org. Synth.* **1987**, *65*, 52–59.

evaporation of the solvents, the residual oil was subjected to flash chromatography, first with CH_2Cl_2/hexane (1:1), and then with pure CH_2Cl_2 to give two product fractions.

Fraction 1 afforded 1.14 g (5%) of monoketal **40** as yellow crystals: mp 101–103 °C; IR (CCl_4) ν (C≡C) 2140, (C=O) 1784, (C=C) 1577 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.17 (s, 6 H, $SiMe_2$), 0.21 (s, 6 H, $SiMe_2$), 0.96 (s, 9 H, *t*-Bu), 0.99 (s, 9 H, *t*-Bu), 4.1–4.2 (AA'BB', 4 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ −5.2 (qq, ^1J = 120.8 and ^3J = 1.8 Hz, $SiMe_2$), −5.1 (qq, ^1J = 120.8 and ^3J = 1.8 Hz, $SiMe_2$), 16.5 (m, $C(CH_3)_3$), 16.6 (m, $C(CH_3)_3$), 25.9 (q of sept, ^1J = 125.4 and ^3J = 5.4 Hz, $C(CH_3)_3$), 66.7 (t, ^1J = 151.6 Hz, CH_2O), 91.6 (s, C-1′ or 1″), 93.5 (s, C-1″ or 1′), 111.3 (sept, ^3J = 2.8 Hz, C-2′), 122.0 (quint, ^3J = 3.1 Hz, C-4), 126.1 (sept, ^3J = 2.8 Hz, C-2″), 144.3 (s, C-2), 163.2 (s, C-3), 193.3 (s, C-1); MS (EI) *m/z* (relative intensity) 402 (61, M^+), 387 (8, M^+ − Me), 374 (89, M^+ − CO), 233 (100). Anal. Calcd for $C_{22}H_{34}O_3Si_2$ (402.7): C, 65.62; H, 8.51. Found: C, 65.37; H, 8.57.

Fraction 2 gave 19.70 g (76%) of bisketal **38** as white crystals: mp 115–115.5 °C; IR (CCl_4) ν (C≡C) 2140, (C—O) 1032 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.14 (s, 12 H, $SiMe_2$), 0.95 (s, 18 H, *t*-Bu), 4.01–4.07 (AA'BB', 4 H, OCH_2CH_2O), 4.11–4.18 (AA'BB', 4 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ −5.2 (qq, ^1J = 120.6 and ^3J = 1.9 Hz, $SiMe_2$), 16.4 (m, $C(CH_3)_3$), 25.8 (q of sept, ^1J = 125.4 and ^3J = 5.5 Hz, $C(CH_3)_3$), 65.7 (t, ^1J = 150.8 Hz, CH_2O), 94.8 (s, C-1′), 107.2 (sept, ^3J = 2.7 Hz, C-2′), 114.9 (quint, ^3J = 3.1 Hz, C-1,2), 136.2 (s, C-3,4); MS (EI) *m/z* (relative intensity) 446 (100, M^+). Anal. Calcd for $C_{24}H_{38}O_4Si_2$ (446.7): C, 64.53; H, 8.57. Found: C, 64.41; H, 8.62.

3,4-Diethynyl-3-cyclobutene-1,2-dione Bis(ethylene ketal) (39). To a solution of 8.94 g (20 mmol) of **38** in 500 mL of wet THF under argon at 20 °C was added 0.5 mL (0.5 mmol) of a 1.0 M solution of tetrabutylammonium fluoride in THF. The solution became dark and was stirred at 20 °C for 20 min. The solvent was evaporated, and the brown solid was purified by flash chromatography with CH_2Cl_2. After evaporation of the solvent, the stable white crystals were washed with a small portion of hexane to give 4.14 g (95%) of **39**: mp >118 °C (**explosion**); IR ($CHCl_3$) ν (≡C—H) 3305, (C≡C) 2110 cm^{-1}; ^1H NMR (360 MHz, CD_2Cl_2) δ 3.71 (s, 2 H, 2′-H), 3.92–4.01 (AA'BB', 4 H, OCH_2CH_2O), 4.07–4.15 (AA'BB', 4 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, $CDCl_3$, gated decoupling) δ 65.9 (t, ^1J = 151.2 Hz, CH_2O), 73.1 (d, ^2J = 49.9 Hz, C-1′), 89.9 (d, ^1J = 255.9 Hz, C-2′), 115.0 (m, C-1,2), 136.4 (dd, ^3J = 4.7 and ^4J = 2.3 Hz, C-3,4); MS (EI, 16 eV) *m/z* (relative intensity) 218 (84, M^+), 174 (1 $M^+ - C_2H_4O$), 146 (100, $M^+ - C_2H_4O$ − CO), 144 (58), 130 (9, $M^+ - 2C_2H_4O$), 102 (32, $M^+ - 2CH_2H_4O$ − CO), 74 (59, $C_6H_2^+$); HRMS *m/z* (M^+, $C_{12}H_{10}O_4$) calcd 218.0579, obsd 218.0579; ($M^+ - 44$, $C_{10}H_6O_3$) calcd 174.0317, obsd 174.0301, ($M^+ - 72$, $C_9H_6O_2$) calcd 146.0368, obsd 146.0375, ($M^+ - 116$, C_7H_2O) calcd 102.0106, obsd 102.0100, ($M^+ - 144$, C_6H_2) calcd 74.0156, obsd 74.0149. Anal. Calcd for $C_{12}H_{10}O_4$ (218.2): C, 66.05; H, 4.62. Found: C, 65.99; H, 4.55.

Cyclization of 39 to Trimer 41, Tetramer 42, and Pentamer 43. A solution of 4.14 g (19 mmol) of **39** in 1 L of reagent grade acetone and 22 mL (4 mmol) of Hay catalyst[52] was stirred vigorously under an atmosphere of dry oxygen at 20 °C for 48 h. The solution was evaporated together with 50 g of silica gel at 20 °C in vacuo. The dry solid was loaded on the top of a flash chromatography column packed with chloroform/acetone (9:1). Elution with chloroform/acetone (9:1 to 8:2) gave three fractions.

The residue of fraction 1 was dissolved in CCl_4/CH_2Cl_2 and gave, after slow evaporation, 156 mg (3.8%) of the cyclic trimer **41** as stable pale yellow prisms: mp >100 °C dec (sealed tube); IR ($CHCl_3$) ν (C≡C) 2120, (C=C) 1566 cm^{-1}; ^1H NMR (360 MHz, CD_2Cl_2) δ 4.13–4.22 (AA'BB', 12 H, OCH_2CH_2O), 4.32–4.41 (AA'BB', 12 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, CD_2Cl_2) δ 66.8, 80.7, 89.4, 116.8, 142.1; MS (FAB) *m/z* (relative intensity) 649 (100, MH^+), 648 (57, M^+), 433 (8, $MH^+ - 3C_2H_4O - 3CO$), 432 (7); HRMS *m/z* (MH^+, $C_{36}H_{25}O_{12}$) calcd 649.1346, obsd 649.1340, (M^+, $C_{36}H_{24}O_{12}$) calcd 648.1268, obsd 648.1246.

Fraction 2, after evaporation of the solvent and washing the residual solid with a small amount of CH_2Cl_2, gave 208 mg (5.1%) of the cyclic tetramer **42** as a stable microcrystalline orange-red powder: mp >180 °C dec (sealed tube); IR (KBr) ν (C≡C) 2155, (C=C) 1615 cm^{-1}; ^1H NMR (360 MHz, CD_2Cl_2) δ 3.87–3.94 (AA'BB', 16 H, OCH_2CH_2O), 3.96–4.04 (AA'BB', 16 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, CD_2Cl_2) δ 66.4, 77.9, 87.3, 115.9, 140.1; MS (FAB) *m/z* (relative intensity) 865 (62, MH^+), 864 (33, M^+), 613 (100); HRMS *m/z* (M^+, $C_{48}H_{32}O_{16}$) calcd 864.1690, obsd 864.1734. Anal. Calcd for $C_{48}H_{32}O_{16} \cdot {}^1/_3CH_2Cl_2$ (893.1): C, 65.00; H, 3.69. Found: C, 65.06; H, 3.72.

Fraction 3, after slow evaporation from CH_2Cl_2, afforded 34 mg (0.8%) of the cyclic pentamer (**43**) as stable bright-yellow fine needles: mp >100 °C dec (sealed tube); IR ($CHCl_3$) ν (C≡C) 2160, (C=C) 1610 cm^{-1}; ^1H NMR (360 MHz, CD_2Cl_2) δ 3.95–4.04 (AA'BB', 20 H, OCH_2CH_2O), 4.10–4.18 (AA'BB', 20 H, OCH_2CH_2O); ^{13}C NMR (90.6 MHz, CD_2Cl_2) δ 66.6, 76.9, 86.1, 116.7, 137.5; MS (FAB) *m/z* 1081 (MH^+); HRMS *m/z* (M^+, $C_{60}H_{40}O_{20}$) calcd 1080.2113, obsd 1080.2098. Anal. Calcd for $C_{60}H_{40}O_{20} \cdot {}^1/_2CH_2Cl_2$ (1123.4): C, 64.68; H, 3.68. Found: C, 64.50; H, 3.77.

Hexaketone 4. A total of 31 mg (0.048 mmol) of **41** was dissolved in 0.5 mL of 98% D_2SO_4 (99.5% D) and transferred to a NMR tube (5-mm diameter). The formation of **4** was completed after a total of 1242 scans were taken at 313 K with neat Me_4Si in an external coaxial capillary tube as reference; ^{13}C NMR (D_2SO_4, gated decoupling) 83.0 (s), 108.8 (s), 180.9 (s), 194.6 (s), with 70.5 (t, ^1J = 155.1 Hz, for ethylene glycol); UV/vis spectrum (D_2SO_4) λ_{max} (nm) 216, 285, 340 sh, 358, 383, 436, 470 sh, 510 sh, absorption tailing to 800 nm, relative intensities of the three bands characteristic for the planar [18]π-electron perimeter:[17] 340 (47), 358 (65), 383 (100).

Octaketone 5. A total of 28 mg (0.032 mmol) of **42** was dissolved in 0.5 mL of 98% D_2SO_4 (99.5% D) and transferred to a NMR tube (5-mm diameter). The same conditions as described for **4** were used to record the ^{13}C NMR spectrum with a total of 1336 scans; ^{13}C NMR (D_2SO_4) δ 81.7, 107.8, 180.0, 194.5, with 70.5 for ethylene glycol; UV/vis spectrum (D_2SO_4) λ_{max} (nm) 227, 294, 350 sh, 373, 404, 485 sh, 536 sh, absorption tailing to 800 nm; relative intensities of the three bands characteristic for the planar [24]π-electron perimeter:[17] 350 (63), 373 (68), 400 (100).

An attempt to isolate **5** was made by dropping the sulfuric acid solution into a well-stirred mixture of ice/water/chloroform. The contact with water led to an almost complete polymerization of the product. On evaporation at 0 °C of the dried chloroform extract, only 2–3 mg of red solid were obtained. An FT-IR spectrum of this material, which was rapidly decomposing, showed bands at 2254 (C≡C), 1790 (C=O), and 1602 (C=C) cm^{-1}.

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Supplementary Material Available: Experimental details for the X-ray crystal structure determination of **14** and crystal data tables of atomic coordinates, equivalent isotropic thermal parameters, anisotropic thermal parameters, bond angles, and bond lengths (11 pages); table of independent reflections (10 pages). Ordering information is given on any current masthead page.