The Preparation and Structures of Several Cross-Conjugated Allenes ("Allenic Dendralenes")^[‡]

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isomerization reactions.

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The cross-conjugated allenes ("allenic dendralenes") 2allenylbuta-1,3-diene (2), 1,1-divinylallene (3, prepared here as the methyl derivative 49), and 1,1-diallenylethene (4) are prepared either by S_N2'-substitution processes from appropriate allenic or acetylenic precursors or by base-catalyzed isomerizations of propargylic substrates. Thermal elimi-

Introduction

With the successful synthesis of the first six members of the vinylogous series 1 (Scheme 1) by Sherburn and his students,^[2] the *dendralenes* have finally left their status of a "neglected class" of unsaturated hydrocarbons.^[3] Because the different routes developed by the Australian group provide preparative amounts of these oligoenes, we can expect many interesting studies on their chemical and physical properties in the near future.

Obviously, dendralenes are of great interest in their own right, but they can also serve as the basis of derived highly unsaturated hydrocarbon systems (i.e., compounds in which one or more of their ethylene moieties have been replaced by other unsaturated groups, in particular by acetylenic, allenic, and cumulenic functions). This is demonstrated in Scheme 1 for the case of [3]dendralene (1, n = 1).^[4] Replacement of one of the terminal double bonds of [3]dendralene leads to 4-methylenehexa-1,2,5-triene (2, 2-allenylbuta-1,3diene), whereas the exchange of the internal double bond of 1 (n = 1) provides 3-vinylpenta-1,2,4-triene (3, 1,1-divinylallene). Likewise, the introduction of two terminal allenic groups into [3]dendralene leads to 4-methylenehepta-1,2,5,6-tetraene (4), and when all double bonds of the parent hydrocarbon are replaced by allene groups the allenic counterpart of 1 (n = 1), the trisallene 5 (4-vinylidenehepta-1,2,5,6-tetraene), is the result.

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1(n = 1-6)n = 1multiple Diels-Alder adducts

nation/isomerization routes to these highly unsaturated hy-

drocarbons require reaction conditions under which these

allenes undergo secondary transformations. The new oli-

goolefins, the structures of which have been calculated by

MP2 methods, are interesting substrates for addition and

Scheme 1. From dendralenes (1) to the allenic dendralenes 2-5.

The hydrocarbon 2 is the allenic equivalent of 2-ethynylbuta-1,3-diene (6, Scheme 1), the simplest cross-conjugated enyne, about which we have already reported extensively.^[5] The divinylallene 3^[6] is of interest as a cycloaddition component, because in principle its reaction with dienophiles such as 7 could lead to phenalene derivatives such as 8 through diene-transmissive Diels-Alder additions.^[7] The bis(allene) 4 could be an interesting substrate for mechanistic studies, because the formation of a C-C bond between its allenic carbon atoms - as in the dimerization of allene

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itself^[8] – could result in the diradical intermediate **9**, which formally constitutes a hybrid of two classical diradical systems: trimethylenemethane (TMM)^[9] and tetramethyleneethane (TME).^[10] For the cross-conjugated all-allenic hydrocarbon **5** we would also expect interesting chemical behavior in, for example, addition reactions of all types (with 7, with metals or metal-containing fragments, in photoad-ditions, etc.).

Having described our efforts to prepare the hydrocarbons **2–4** in a short communication earlier,^[11] we now present our preparative work in full. As far as the tris(allene) **5** is concerned, to the best of our knowledge no efforts to prepare this hexaene have previously been undertaken.

4-Vinylpenta-1,2,4-triene (2)

In a first attempt directed towards 2, acrolein (10, Scheme 2) was treated with propargyl bromide under Barbier conditions to furnish the propargylic alcohol 11 in good yield. Although CrO₃ oxidation of 11 could also be performed satisfactorily and the cross-conjugated enone 12 could be obtained in 47% yield, Wittig methylenation of 12 with methyltriphenylphosphonium bromide/base failed. The reaction conditions were varied over a considerable range (base: potassium *tert*-butoxide or potassium carbonate; solvents: THF, diethyl ether; temperature from room temperature to 70 °C), but none of these experiments was successful, so this approach had to be abandoned.

The intermediates **11** and **12** were characterized by the usual spectroscopic methods as described in the Experimental Section. We assume that **12** is generated from **11** by initial oxidation of this alcohol to the corresponding ketone, the enol form of which could subsequently undergo a 1,5-hydrogen shift to yield the allenic ketone.

In the next set of experiments we attempted to exploit the high strain of four-membered cyclic intermediates, and in particular to "hide" the future butadiene subunit of 2 temporarily in a cyclobutene ring. For that purpose cyclobutanone (13, Scheme 3) was treated with propargyl bromide/magnesium in diethyl ether (Barbier conditions), and the resulting crude tertiary alcohol 14 was esterified to the acetate 15 with acetyl chloride/pyridine. The two steps proceeded in an acceptable combined yield; for analytical purposes a small amount of 14 was purified by distillation. When 14 was dehydrated with POCl₃ in pyridine, however, it mostly provided the conjugated enyne 17, together with only traces of 1-propargylcyclobutane (16; ratio 17/16 =93:7). The small amount of 16 obtained thwarted our original plan to subject it to thermal ring-opening to provide 19 and to isomerize this acyclic intermediate to 2 with base.



Scheme 3. Attempts to prepare 3-methylenehex-1-en-5-yne (19).

The acetate **15** (Scheme 3) was next subjected to lowpressure (0.01 mbar) gas-phase pyrolysis between 350 and 540 °C in a flow system. Product formation commenced at ca. 390 °C and provided the enyne **17** as the sole thermolysis product. When the temperature was increased further, three additional products were generated, and from 450 °C on these four components were present in sufficient amounts to allow their separation by preparative gas chromatography on a silver nitrate/PPG column at 70 °C. GC/MS analysis revealed that they were all C₇H₈ hydrocarbons (molecular ion peak at m/z = 92), and comparison with authentic compounds (if available) and analysis of spectroscopic data (see Experimental Section) allowed their



Scheme 2. Preparation of hexa-1,2,5-trien-4-one (12) and attempted Wittig reaction.



Scheme 4. Preparation of 4-methylenehexa-1,2,5-triene (2).

structure assignment as propynylidenecyclobutane (17), 2propargylbuta-1,3-diene (19), 2-ethynyl-1-methylenecyclobutane (22), and toluene (25). The hydrocarbons 19 and 22 were each formed in about 10% yield, the other two in about 40% yield. Whereas the proportion of 17 decreased with increasing temperature, toluene (25) became more and more the main product. The nonconjugated cyclobutene derivative 16 was not among the pyrolysis products but might very well have been generated as an unstable intermediate.

As far as the overall mechanism of the thermal elimination/isomerization is concerned, we propose that the process begins with the thermal elimination of acetic acid from 15 to afford 17. This crucial intermediate might subsequently undergo a concerted 1,5-hydrogen shift to provide the cyclic enallene 20. Isomerization of alkyl derivatives of enynes to vinylallenes has been described in the literature.^[12] At this point the reaction pathway could branch and lead to 19 through a 1,3-hydrogen shift, a process known to occur in, for example, the thermal interconversion of allene and propyne,^[13] followed by electrocyclic ring-opening. Of course, the same acyclic C7H8 isomer could also be produced by ring-opening of the undetected 16. Ring-opening of 20 could also lead to the target molecule 2, which does not survive, however, under the reaction conditions and yields the conjugated dienyne 23 through another 1,5-hydrogen shift. Unsaturated hydrocarbons of this type are known to aromatize by electrocyclization via isobenzene intermediates such as 24 and through terminal hydrogen shifts to aromatic compounds, in this case toluene (25). From substrate 15 on we therefore observe a cascade of *five thermally allowed processes* before the sequence comes to rest with a terminating 1,3-hydrogen shift. Because the intermediate 17 is also a strained hydrocarbon, the side path leading to 22 is also plausible: ring cleavage of 17 could generate the diradical 18, which from its resonance structure 21 could recyclize to the isolated product 22.

Although mechanistically remarkable, the pyrolysis of 15 did not lead to the desired cross-conjugated allene 2 or a useful precursor for it such as 19, and so we had to devise another approach.

As reported by Gore in 1984, an allene with a functional (leaving) group in its α -position can, on treatment with an organometallic compound, be attacked at the allenic carbon atom and provide a substituted buta-1,3-diene derivative

through an S_N2' -type mechanism.^[14] To use this process for the preparation of **2**, but-2-yne-1,4-diol (**26**) was converted via its monochloride **27** into the allenyl alcohol **28** by methods reported in the literature (Scheme 4).^[15,16]

To convert the hydroxy function into a good leaving group, 28 was treated with diethyl phosphorochloridate to provide buta-2,3-dien-1-yl diethyl phosphate (31), and on treatment with allenvlmagnesium bromide (32) in the presence of CuBr at low temperature, this did indeed lead to the desired cross-conjugated allene 2. Although the yield of the raw product was quite high (up to 60%), it was very difficult to isolate an analytically pure sample because of the very great instability of the hydrocarbon. It quickly begins to polymerize in ethereal solution at room temperature and is even less stable in neat form. On preparative gas chromatography on an OPN column at 60 °C the overwhelming majority of it is lost, and the yield is reduced to about 1% only. Still, all spectroscopic data for the tetraene could be recorded (see Experimental Section), and they clearly define the structure of the compound as given in Scheme 4.

3-Vinylpenta-1,2,4-triene (3, 1,1-Divinylallene)

Our first attempt to prepare this C_7H_8 hydrocarbon was modeled on the classic synthesis of [3]dendralene (1, n = 1) by Blomquist and Verdol,^[17] in which the two terminal double bonds are generated from 1,5-diacetoxy-3-methylenepentane (33, Scheme 5) by acetate pyrolysis in the last step. Application of this sequence to the synthesis of 3 required the preparation of the allene diacetate 38.

To obtain this precursor, the diester **33** was saponified to afford the diol **34**, the double bond of which could be dibromocyclopropanated to provide the dibromide **36** after the two hydroxy functions had been protected as *tert*-butyldimethylsilyl ethers as shown in **35**. Allene synthesis by methyllithium treatment then proceeded as expected and provided the doubly protected allene **37** in good yield. The ester groups were reintroduced by treatment of **37** with acetic anhydride in the presence of FeCl₃, and the bis(ester) **38** was ready for flash vacuum pyrolysis. However, at 550 °C, the only pyrolysis products we could identify were the ethynylbutadiene derivative **39** (70%) and toluene (**25**,



Scheme 5. Attempt to prepare 1,1-divinylallene (3) by acetate pyrolysis.

30%). The (Z) configuration of **39** follows both from an NOE experiment (increase of the ethynyl proton signal on saturation of the methyl signal) and from the chemical shift of the vinylic proton at C-4. It is highly likely that the secondary product **39** was produced from the intended **3** through a 1,5-hydrogen shift under the harsh reaction conditions. The formation of aromatic products from highly unsaturated acyclic precursors at high temperatures has often been observed, even if there is no simple connection from the starting material to its cyclic isomer.

If we wanted to proceed along this general route, we had to find a protocol by which the vinylic double bonds of 3 could be generated under milder reaction conditions.

For this we decided to employ selenoxide elimination, a process known to occur at temperatures as low as $0 \degree C$,^[18a-18g] and to start our approach with 1,1-bis(2-hydroxyethyl)allene (**42**) as the starting material (Scheme 6).

The allenic diol **42** is readily available by a route established by Gore and co-workers,^[19] who subjected the monoprotected diol **40** to a Claisen–Johnson rearrangement and subsequently reduced/hydrolyzed the obtained ester **41**. Treatment of **42** with freshly prepared *ortho*-nitrophenyl selenocyanate (**43**)^[18d] according to a procedure developed by Sharpless^[20] resulted in the formation of the diphenyl diselenide 44. Unfortunately, the next steps – oxidation, followed by elimination to 3 – could not be achieved. When 44 was oxidized with hydrogen peroxide at various temperatures, crude product mixtures that contained several reaction products were obtained. When these mixtures were subjected to IR analysis no allene bands could be detected; we assume that 44 or even 3, if formed under the reaction conditions, are readily oxidized with destruction of the allene moiety. We hence also had to abandon this approach.

An $S_N 2'$ -type process had been successful for the preparation of **2**, so we reasoned that a similar process might also be applicable for the synthesis of a 1,1-divinylallene such as **3**, provided that an appropriate precursor were available. Such a precursor is the ether **48** (Scheme 7), obtained in a few steps from 3-chloropropionyl chloride (**45**). This was first converted by a known Friedel–Crafts reaction with ethylene into the dichloro ketone **46**.^[21] When this was treated with a mixture of lithium amide and lithium ace-tylenide in liquid ammonia, prepared in situ, both dehydrochlorination and addition to the carbonyl group took place, and the tertiary alcohol **47** was formed in medium yield.

The methylation of the alcohol took place readily with sodium hydride/methyl iodide, and the ether **48** was isolated in good yield.



Scheme 6. Further attempts to prepare 1,1-divinyllene (3).



Scheme 7. Preparation of the first 1,1-divinylallene derivative 49.

On treatment of **48** with dimethyllithium cuprate at -78 °C an unstable product was formed. Even in dilute solutions (ca. 4%) this readily formed higher-molecular-weight products on standing, as shown by GC and GC/MS analysis. That this compound is the expected divinylallene derivative **49** is inferred from the following analytical and spectroscopic data: the compound has a molecular weight of 106 (C₈H₁₀), as demonstrated by GC/MS analysis, and was found to be a single product when a "fresh" reaction mixture was analyzed [an allene band at 1955 cm⁻¹ can be detected by IR spectroscopy, and in the ¹H NMR spectrum of a solution of **49** in deuteriochloroform the methyl group reveals itself as a doublet (³J = 7.5 Hz) at δ = 1.46 ppm].

Unfortunately, high-quality spectra of 49 could not be obtained, due to its great instability. However, when tetracyanoethylene (50, TCNE) was added to 49 in pentane at room temperature we isolated a monoadduct, the structure of which -52 – follows from the spectroscopic data given in the Experimental Section. So far we have been unable to prepare higher adducts of 49 with TNCE under these conditions. Note that 52 is also a cross-conjugated compound (a cyclic [3]dendralene), so the above Diels-Alder addition constitutes a dendralene-to-dendralene conversion. As far as the stereochemical orientation of the methyl group in 52 is concerned we do not at present have unambiguous proof that it points towards the vinyl substituent (rather than towards the cyano groups). We believe that the orientation shown in Scheme 7 is the more likely one, because in the transition state of the process – structure 51 – the dienophile 50 should approach the diene 49 from the less hindered side. When the addition is complete, the methyl group in the more or less planar adduct 52 should point away from the cyano substituents.^[22] Unfortunately, not enough material was available to subject 52 to further TCNE addition under rougher conditions.

However, in an exploratory experiment the cycloaddition was repeated in the presence of a large excess of maleic anhydride in THF solution at reflux. Although most of the diene **49** polymerized under these conditions, on mass spectrometric investigation of the solid residue remaining after workup and solvent removal we observed two peaks with the molecular masses of a mono- and a bis-adduct (m/z = 204 and 302, respectively). The bis-adduct should possess the structure **53**. In principle this diene-transmissive process should occur a third time to provide a phenalene derivative, as pointed out in the Introduction. Once the parent system (which lacks the presumably rate-retarding effect of the methyl substituent) becomes available this will certainly be one of the first experiments to be carried out.

4-Methylenehepta-1,2,5,6-tetraene (4)

The preparation of this bis-allene was easy, because one of its isomers, 4-methylenehepta-1,6-diyne (**55**, Scheme 8) had already been described in the literature. As described by Sondheimer and Looker, it can be prepared by treatment of the allylic dibromide **54** with ethynylmagnesium bromide (Scheme 8).^[23]

When 55 was treated with sodium methoxide in methanol at 64 °C for 30 min it isomerized to afford the singly rearranged allene 60 in 60% yield. The reaction obviously begins with the formation of the monoanion 56, which from its resonance structure 57 can be protonated to provide the vinylallene derivative 60. This interpretation is supported by a trapping experiment in which 55 was first lithiated at -78 °C with *n*-butyllithium in diethyl ether, and the resulting carbanion was subsequently quenched by the addition of trimethylsilyl chloride. In this case the TMS derivative 59 was produced. Both 60 and 59 were characterized



Scheme 8. Preparation of 4-methylenehepta-1,2,5,6-tetraene (4).

by the usual spectroscopic data (see the Experimental Section); the depicted (E) configuration of the enyne **59** follows from an NOE experiment in which the methylene group bearing the TMS substituent was irradiated. A clear increase in the signal intensity of the vinyl hydrogen atom was the consequence.

The best way to prepare the cross-conjugated bis(allene) 4 consisted of treatment of the substrate 55 with potassium tert-butoxide in THF at -78 °C for 30 min. The main problem with the hydrocarbon was again the workup. Although decomposition (by polymerization) could be reduced by carrying out all workup operations at low temperatures, it could not be completely prevented. Furthermore, all our samples of 4 contained small amounts of starting material and other unsaturated components (isomers of 4?). Although we were never able to obtain the bis(allene) in analytically pure form, our samples contained enough of the compound to allow unambiguous structure assignment (see the Experimental Section); in particular, the highly characteristic ¹H NMR and IR spectra of the molecule were helpful. As confirmation of the chemical structure, the addition of TCNE (50) to 4 was useful: the monoadduct 61 was isolated in fair yield and characterized by its spectroscopic data (Experimental Section). MS analysis of the addition product mixture gave no hint of the formation of a 2:1 adduct. Of course, it is conceivable that retro-Diels-Alder processes are occurring under the MS conditions.

In an attempt to trap the diradical 9 that could in principle be formed by intramolecular dimerization of the two allene moieties of 4, oxygen gas was passed through a solution of the hydrocarbon in pentane. Mass spectrometric analysis of the product mixture gave no hint that the *endo*peroxide had been produced as an adduct. Likewise, there were no indications that the triene 63 or products derived from it had been generated.

Further Base-Catalyzed Isomerizations

Success having been achieved with the preparation of **4** by base-catalyzed isomerization of the bis(acetylene) **55**, it was an obvious measure to apply this process to related terminal oligoalkynes. For this purpose we coupled the known tribromide $64^{[24]}$ (Scheme 9) with ethynylmagnesium bromide in the presence of CuCl and obtained the two isomeric hydrocarbons **65** and **66** in a combined yield of 53%.



Scheme 9. Attempted preparation of selected tri- and tetraallenes.

Separation of the two hydrocarbons by preparative gas chromatography provided pure **65**, which was characterized spectroscopically (see the Experimental Section). However, when treated under the conditions that had been successful for the **55** \rightarrow **4** isomerization, only the fully conjugated trienyne **68** was isolated, in quantitative yield. The depicted configuration was determined in an NOE experiment in which the proton at C-5 was irradiated, causing increases in signal intensity for the hydrogen atoms at C-3 and C-8. Of course, it is conceivable that **67** served as a precursor for **68**, but there are many other base-induced isomerizations through which **65** can be connected to the actually isolated product **68**.



Figure 1. Global minima for the allenic dendralenes 2-5, computed at the MP2/cc-pvtz level of theory.

In the case of the still more highly brominated substrate **70** we were unable to prepare the tetrayne **69** by the above coupling process. Treatment with acetylene Grignard reagent in this case furnished the bis(acetylene) **71**, a known compound described and used several times in the chemical literature.^[25] For its formation we assume that the intended reaction does indeed take place twice, but that the intermediately produced 1,4-dibromobutene derivative is debrominated by iodide, which is also present in the reaction mixture, in a 1,4-elimination reaction.

Theoretical Analysis of the Allenic Dendralenes 2, 3, 4, and 5

The conformation of [3]dendralene (1, n = 1) was determined by electron diffraction, and its most interesting feature is its nonplanar structure (Figure 1), with a vinyl substituent rotated by ca 40° out of the plane passing through its buta-1.3-diene moiety.^[30] In order to rank the cross-conjugated allenes 2, 3, 4, and 5 in terms of their geometrical distortion we started a theoretical investigation with the [3]dendralene (1, n = 1). All computations^[31] were conducted at the correlated MP2^[32] level of theory with application of a correlation-consistent basis set of triple-zeta quality (cc-pvtz).^[33] Although our ab initio calculation reproduced the nonplanar structure of [3]dendralene (1, n =1), the theoretical dihedral angel for the equilibrium geometry is considerably smaller (24.1°) . This discrepancy is due to a very soft dihedral potential, which becomes manifest a relaxed dihedral force constant^[34a,34b] in of 0.07 mdyn rad⁻¹. The analogous MP2 value in 2-methylbuta-1,3-diene adds up to $0.11 \text{ mdyn rad}^{-1}$.

Turning to the computed gas-phase structures of the allenic dendralene **2**, we observe a nearly planar structure (distortion of the dihedral angle: 10.1°) probably caused by an attractive C–H··· π interaction between the allene and the vinyl substituent.

The allenic dendralenes **3**, **4**, and **5** again exhibit nonplanarity, each adopting a chiral C_2 -symmetrical minimum structure, with subtle barriers of racemization for **4** (barrier: 0.4 kcalmol⁻¹) and **5** (barrier: 0.3 kcalmol⁻¹). In the case of the allenic dendralene **3** the barrier is a little more pronounced (2.2 kcalmol⁻¹), but still far too small to allow separation of single enantiomers. The electronic structures of the allenic units seem to be quite insensitive to cross-conjugation: the relaxed force constants for the C=C double bonds in the allenic dendralenes **2**, **3**, **4**, and **5** remain around 10.1 N cm⁻¹ throughout. This is exactly the same value as for the unsubstituted allene H₂CCCH₂ and reflects the well-known^[35] property of allenes to contain contracted (and hence stronger) C=C double bonds. For comparison, the relaxed C=C force constant in ethylene is computed to be 9.0 N cm⁻¹ at the same level of theory (MP2/cc-pvtz).

Conclusion

Cross-conjugated allenes, or "allenic dendralenes", such as 2-allenylbuta-1,3-diene (2), 1,1-divinylallene (3, prepared here as the methyl derivative 49), and 1,1-diallenylethene (4), are available either through $S_N 2'$ -substitution processes from appropriate allenic or acetylenic precursors or through base-catalyzed isomerizations of propargylic substrates. These reactions can be carried out under conditions sufficiently mild to prevent further reactions (polymerization, isomerization, additions) of these highly reactive hydrocarbons. Although gas-phase processes (thermal isomerizations, eliminations) are also attractive for their synthesis, because they avoid additional reagents and solvents and in principle require no workup, their reaction conditions are so harsh that subsequent thermal processes take place. The new allenes have been characterized by their spectroscopic data, as well as by selected chemical reactions (Diels-Alder cycloadditions). The structural properties of 2-5 were determined by quantum chemical calculations. Each of the studied allenic dendralenes exhibits a nonplanar minimum structure and a low barrier of inversion. Although - in comparison with an unperturbed C=C double bond - pronounced bond strengthening is observed, the electronic structures of the allenic C=C double bonds seem to be insensitive to substitution.

Experimental Section

1. General: Melting points: below 200 °C: Büchi 510 melting point apparatus; above 200 °C: Kofler apparatus. The values are uncorrected. NMR: Bruker AM 300: ¹H NMR (300.1 MHz), ¹³C NMR (75.5 MHz); Bruker WM 400: ¹H NMR (400.1 MHz), ¹³C NMR (100.6 MHz) in deuteriochloroform. ¹H chemical shifts in ppm, internal tetramethylsilane; ¹³C chemical shifts relative to CDCl₃ (δ = 77.01 ppm). IR: Perkin–Elmer 1420 and Nicolet 320 FT-IR spectrometers with KBr pellets or thin films. UV/Vis: HP 8452A Diode Array spectrophotometer and Beckman UV-5230. MS: Finnigan MAT 8430 (EI, 70 eV and FAB). GC/MS: Finnigan MAT 4515 (EI, 40 eV) attached to a Carlo Erba HRGC 5160. Elemental analyses: Institut für Pharmazeutische Chemie, TU Braunschweig.

2. 3-Hydroxyhex-1-en-5-yne (11): Magnesium turnings (28 g, 1.17 mol) were placed under N_2 in a three-necked flask (500 mL), and propargyl bromide (6.04 g, 50 mmol) in diethyl ether (20 mL) was added. After the reaction had started, the mixture was cooled to -30 °C, and a solution of propargyl bromide (54.3 g, 0.45 mol) and freshly distilled acrolein (10, 37.2 g, 0.66 mol) in diethyl ether (180 mL) was added at such a rate that the internal temperature did not rise above -20 °C. The mixture was stirred at -10 °C for 1 h and then hydrolyzed with satd. aqueous ammonium chloride solution (100 mL). The phases were separated, and the dried (sodium sulfate) organic phase was distilled under vacuum; compound 11 distilled at 50 °C/17 Torr (43.3 g, 90%) as a colorless oil. ¹H NMR (300.1 MHz): $\delta = 5.92$ (ddd, $J_1 = 17.2$, $J_2 = 10.5$, $J_3 = 6.1$ Hz, 1 H, 2-H), 5.30 (ddd, $J_1 = 17.2$, $J_2 = 1.4$, $J_3 = 1.4$ Hz, 1 H, 1-H_a), 5.17 (ddd, $J_1 = 10.5$, $J_2 = 1.4$, $J_3 = 1.4$ Hz, 1 H, 1-H_b), 4.26 (dt, J_1 = 6.1, J_2 = 6.1 Hz, 1 H, 3-H), 3.67 (s, 1 H, OH), 2.43 (dd, J_1 = 6.1, $J_2 = 2.6$ Hz, 2 H, 4-H), 2.11 (t, $J_1 = 2.6$ Hz, 1 H, 6-H) ppm. ¹³C NMR (100.61 MHz): δ = 138.7 (C-2), 115.3 (C-1), 80.2 (C-5), 70.5 (C-6), 70.3 (C-3), 26.8 (C-4) ppm. IR (film): $\tilde{v} = 3400$ (vs), 3310 (vs), 3005 (w), 2910 (m), 2110 (m), 1645 (m), 1425 (s), 1205 (m), 1125 (s), 1040 (s), 995 (s), 930 (s), 845 (m) cm⁻¹. The alcohol 11 is a known compound; spectroscopic data are listed here as an update.[26]

3. Hexa-1,2,5-trien-4-one (12): The alcohol 11 (17.3 g, 0.18 mol) was placed under nitrogen in a three-necked flask (1 L), and a mixture of acetone (540 mL) and pentane (60 mL) was added. With stirring, a solution of chromium trioxide (15.0 g, 0.150 mol) in sulfuric acid (96%, 13.8 mL) and water (36 mL) was slowly added at -5 °C. When the addition was complete, the mixture was stirred at 5 °C for 1 h. The black organic phase was separated and extracted three times with portions of pentane/diethyl ether (2:1, 200 mL), and the phases were combined, washed with a saturated ammonium chloride solution, and dried with MgSO4. After solvent removal, crude ketone 12 was obtained as a yellow oil. Purification by vacuum distillation resulted in decomposition; analytically pure material (colorless oil) was obtained by preparative gas chromatography on a squalane column (10 m) at 90 °C. ¹H NMR $(300.1 \text{ MHz}): \delta = 6.87 \text{ (dd, } J_1 = 17.2, J_2 = 10.4 \text{ Hz}, 1 \text{ H}, 5 \text{-H}), 6.33$ (dd, $J_1 = 17.2$, $J_2 = 1.6$ Hz, 1 H, 6-H_a), 5.97 (t, $J_1 = 6.5$ Hz, 1 H, 3-H), 5.72 (d, $J_1 = 10.4$, $J_2 = 1.6$ Hz, 1 H, 6-H_b), 5.30 (d, $J_1 =$ 6.5 Hz, 2 H, 1-H) ppm. ¹³C NMR (100.6 MHz): δ = 216.9 (C-2), 188.8 (C-4), 132.2 (C-5), 128.0 (C-6), 96.5 (C-3), 79.5 (C-1) ppm. IR (film): $\tilde{v} = 3070$ (w), 2990 (m), 1965 (s), 1935 (s), 1670 (vs), 1620 (vs), 1415 (s), 1405 (s), 1190 (vs), 985 (s), 970 (s), 875 (s), 855 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 233 (3.64) nm. MS (EI, 70 eV): m/z (%) = 94 [M]⁺ (16), 67 (8), 66 (26), 55 (100), 39 (47), 38 (21), 37 (10), 27 (48). The ketone is unstable in air, thus preventing an exact elemental analysis.

4. 1-Propargylcyclobutan-1-ol (14): Magnesium turnings (3.2 g, 0.13 mmol) were placed under nitrogen in a three-necked flask (250 mL), propargyl bromide (1.6 g, 15 mmol) was added, and the mixture was covered with a layer of diethyl ether (50 mL). As soon as the reaction had started, the main part of the halide (13.9 g, 0.13 mol), dissolved in diethyl ether (85 mL), was slowly added. When most of the Mg had reacted, a small amount (25 mg) of CuI was added, and the reaction mixture was cooled to 0 °C. At this temperature, cyclobutanone (13, 6.9 g, 99 mmol) in diethyl ether (20 mL) was added at such a rate as to keep the temperature constant. To complete the reaction, the mixture was stirred at room temperature for 18 h. For workup, a saturated aqueous solution of ammonium chloride was added, and the organic phase was separated, washed twice with water, and dried with sodium sulfate. Vacuum distillation provided 14 at 54 °C/11 Torr as a colorless liquid (7.8 g, 72%). ¹H NMR (300.1 MHz): δ = 2.53 (d, J = 2.6 Hz, 2 H, 5-H), 2.12 (m, 4 H, 2-H, 4-H), 2.04 (t, J = 2.6 Hz, 1 H, 7-H), 1.81 (m, 1 H, 3-H), 1.47 (m, 1 H, 3-H) ppm. ¹³C NMR $(100.6 \text{ MHz}): \delta = 80.7 \text{ (C-6)}, 73.7 \text{ (C-1)}, 70.4 \text{ (C-7)}, 34.9 \text{ (C-5)}, 30.4$ (C-2, C-4), 11.8 (C-3) ppm. IR (film): $\tilde{v} = 3390$ (s), 3310 (vs), 2995 (s), 2950 (s), 2120 (w), 1275 (s), 1110 (s), 970 (m), 915 (m) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 300 (1.21), 247 (1.62), 197 (2.59) nm. MS (EI, 70 eV): m/z (%) = 110 (3) [M]⁺, 91 (11), 82 (76), 71 (92), 54 (100), 44 (93), 41 (65), 39 (86). C₇H₁₀O (110.16): calcd. C 76.32, H 9.15; found C 76.40, H 9.32.

5. 1-Acetoxy-1-propargylcyclobutane (15): The alkoxide of 14 was prepared as described under 4., from 13 (3.5 g, 50.0 mmol), propargyl bromide (7.8 g, 66.0 mmol), magnesium turnings (1.6 g, 66.0 mmol), and CuI (25 mg) in diethyl ether (55 mL). This reaction mixture was cooled to 0 °C, and a solution of freshly distilled acetyl chloride (4.0 g, 44.0 mmol) and anhydrous pyridine (3.2 g, 41.0 mmol) in chloroform (15 mL) was added. When the addition was complete, the reaction mixture was stirred at room temperature for 1 h. A saturated solution of ammonium chloride in water was added (25 mL), and the organic phase was separated and washed thoroughly with dilute hydrochloric acid. After drying (sodium sulfate), the solvent was removed by rotary evaporation, and the remaining oil was distilled; at 86 °C/30 Torr the ester 15 was obtained as a colorless liquid (4.41 g, 58%). ¹H NMR (400.1 MHz): δ = 2.85 (d, J = 2.7 Hz, 2 H, 5-H), 2.33 (m, 4 H, 2-H, 4-H), 2.03 (s, 3 H, CH₃), 1.98 (t, J = 2.7 Hz, 1 H, 7-H), 1.86 and 1.72 (2×m, 2×1 H, 3-H) ppm. ¹³C NMR (100.6 MHz): δ = 169.8 (C-8), 79.9 and 79.8 (C-1 and C-6), 69.4 (C-7), 33.3 (C-2, C-4), 25.9 (C-5), 21.5 (CH₃), 13.7 (C-3) ppm. IR (film): $\tilde{v} = 3300$ (vs), 2998 (vs), 2950 (vs), 2120 (w), 1735 (vs), 1425 (s), 1375 (vs), 1275 (s), 1230 (vs), 1165 (s), 1110 (s), 1100 (s), 1015 (s), 955 (m), 930 (m) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 257 (1.67), 202 (2.31), 199 (2.30) nm. MS (EI, 70 eV): m/z (%) = 152 (0.1) [M]⁺, 137 (5), 124 (12), 113 (28), 92 (100), 91 (8), 85 (11), 82 (5).

6. Propynylidenecyclobutane (17): The alcohol **14** (3.8 g, 34.0 mmol) and anhydrous pyridine (40 mL) were placed under N₂ in a three-necked flask (250 mL), and the solution was cooled to 5 °C. Phosphoric trichloride (40.0 mmol, 6.12 g) was added with stirring at such a rate as to keep the internal temperature constant. After completion of the addition, the reaction mixture was stirred at 5 °C for a further 2 h. Pentane (10 mL) was added, followed by a saturated aqueous solution of ammonium chloride (40 mL). Drying with sodium sulfate, solvent removal, and distillation at normal pressure gave pure **17** (2.7 g, 84%) as a colorless oil (b.p. 112 °C). ¹H NMR (400.1 MHz): δ = 5.20 (m, 1 H, 3-H), 2.97 (m, 1 H, 1-H), 2.83 (m, 2 H, 5-H), 2.77 (m, 2 H, 7-H), 2.01 (m, 2 H, 6-H) ppm. ¹³C NMR (100.6 MHz): δ = 160.2 (C-4), 100.2 (C-3), 80.5 (C-2), 79.2 (C-1), 31.8 and 31.5 (C-5 and C-7), 16.6 (C-6) ppm. IR (film): \tilde{v} = 3325



(vs), 2994 (s), 2966 (vs), 2105 (m), 1663 (m), 1328 (m), 1186 (s), 833 (m) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 240 (3.72) nm. MS (EI, 70 eV): m/z (%) = 92 (7) [M]⁺, 91 (55), 84 (10), 57 (15), 49 (12), 39 (10), 32 (33), 28 (100). C₇H₈ (92.14): calcd. C 91.25, H 8.75; found C 91.07, H 8.74.

7. Pyrolysis of 17. 2-Propargylbuta-1,3-diene (19) and 1-Ethynyl-2methylenecyclobutane (22): At a pressure of 0.01 Torr the substrate 17 (460 mg, 5 mmol) was passed at 550 °C through a quartz pyrolysis tube filled with Raschig rings. The pyrolysate was frozen in a cold trap (-196 °C, 450 mg, 98% total yield) and analyzed by gas chromatography (15 m SPB-1 column, 60 °C); three products were obtained in a 1:3:5 ratio. Preparative GC (6 m 20% OPN column, 70 °C) gave analytically pure products. Fraction 1: Compound 19, colorless oil. ¹H NMR (400.1 MHz): $\delta = 6.45$ (dd, $J_1 = 17.6$, $J_2 =$ 10.9 Hz, 1 H, 3-H), 5.44 (m, J = 1.5 Hz, 1 H, 1-H_a), 5.23 (dd, J_1 = 17.6, $J_2 = 0.5$ Hz, 1 H, 4-H_a), 5.18 (d, J = 0.7 Hz, 1 H, 1-H_b), 5.12 (d, J = 10.9 Hz, 1 H, 4-H_b), 3.13 (m, 2 H, 5-H), 2.16 (t, J =2.7 Hz, 1 H, 7-H) ppm. ¹³C NMR (100.6 MHz): δ = 137.6 (C-3), 117.5 and 113.8 (C-1 and C-4), 71.1 (C-7), 21.5 (C-5) ppm; C-6 signal was not detectable. IR (film): $\tilde{v} = 3325$ (vs), 2994 (s), 2966 (vs), 2105 (m), 1663 (m), 1186 (s), 833 (s) cm⁻¹. MS (EI, 70 eV): m/z (%) = 92 (6) [M]⁺, 91 (45), 84 (10), 49 (13), 39 (10), 28 (100). C₇H₈ (92.14): calcd. C 91.25, H 8.75; found C 90.97, H 8.80. Fraction 2: Compound 22, colorless oil. ¹H NMR (400.1 MHz): δ = 5.00 (m, 1 H, 5-H), 4.85 (m, 1 H, 5-H), 3.65 (m, 1 H, 2-H), 2.65 (m, 2 H, 4-H) 2.24 (d, J = 2.5 Hz, 1 H, 7-H), 2.10 (m, 2 H, 3-H) ppm. ¹³C NMR (100.6 MHz): δ = 149.0 (C-1), 105.9 (C-5), 84.9 (C-6), 69.8 (C-7), 33.8 (C-2), 30.0 and 25.3 (C-3 and C-4) ppm. IR (film): $\tilde{v} = 3326$ (s), 2941 (vs), 2857 (m), 2126 (w), 1294 (m), 1252 (m), 861 (w) cm⁻¹. MS (EI, 70 eV): m/z (%) = 92 (5) [M]⁺, 91 (54), 83 (10), 57 (13), 49 (12), 44 (11), 32 (33), 28 (100). C₇H₈ (92.14): calcd. C 91.25, H 8.75; found C 90.97, H 8.80. Fraction 3: Toluene (25); identified by comparison with authentic material. When the acetate 15 was pyrolyzed under similar conditions at 450 °C, the hydrocarbons 17, 19, 22, and 25 were produced in the amounts given in the main section; the pyrolysis products were identified by comparison with the C7H8 hydrocarbons described above.

8. Buta-2,3-dien-1-ol (28): For the preparation of 28 we adopted a literature procedure^[27] and report the complete set of spectroscopic data here. A solution of 4-chlorobut-2-yn-1-ol (27, 36.4 g, 0.35 mol) in diethyl ether (225 mL) was placed under nitrogen in a threenecked flask (1 L). A suspension of lithium aluminium hydride (12.5 g, 0.44 mol) in diethyl ether (250 mL) was added at such a rate that the reaction mixture boiled under gentle reflux. After 1 h, the mixture was cooled to 0 °C with an ice bath, and water (150 mL) was added carefully. The diethyl ether phase was separated and the aqueous phase was extracted several times with diethyl ether (50 mL portions). The combined organic phases were dried (magnesium sulfate), the solvent was removed in vacuo, and the remaining oil was distilled; at 38 °C/12 Torr, compound 28 (23.0 g, 94%) was collected as a colorless liquid. ¹H NMR (400.1 MHz): δ = 5.29 (tt, J_1 = 6.5, J_2 = 6.5 Hz, 1 H, 2-H), 4.79 $(dt, J_1 = 6.5, J_2 = 2.8 \text{ Hz}, 2 \text{ H}, 4\text{-H}), 4.40 (s, 1 \text{ H}, -\text{OH}), 4.09 (dt, 1 \text{ H}, -\text{OH}), 4.09$ $J_1 = 6.5, J_2 = 2.8$ Hz, 2 H, 1-H) ppm. ¹³C NMR (100.6 MHz): $\delta =$ 207.7 (C-3), 90.1 (C-2), 75.7 (C-4), 59.5 (C-1) ppm. IR (film): v = 3600 (vs), 2990 (s), 2930 (s), 2870 (s), 1960 (s), 1440 (s), 1260 (m), 1130 (s), 845 (s) cm^{-1} .

9. Buta-2,3-dien-1-yl Diethyl Phosphate (31): A solution of the alcohol **28** (26.6 g, 0.370 mol) in dichloromethane (300 mL) and anhydrous pyridine (120 mL) was placed in a three-necked flask (1 L), and diethyl phosphorochloridate (130.4 g, 0.670 mol) in dichloromethane (125 mL) was added under N_2 with stirring at

0 °C. After the addition was complete, the mixture was stirred at room temperature for 12 h. For hydrolysis ice-cold water (100 mL) was carefully added, the phases were separated, and the organic phase was washed several times with dilute hydrochloric acid, neutralized, and dried (sodium sulfate). The solvent was removed by rotary evaporation, and the remaining oil was fractionated by vacuum distillation. At 66 °C/0.08 Torr, compound 31 (46.5 g, 61%) was collected as a colorless oil. ¹H NMR (400.1 MHz): δ = 5.34 (tt, $J_1 = 6.6$, $J_2 = 7.0$ Hz, 1 H, 2-H), 4.87 (dt, $J_1 = 6.6$, $J_2 =$ 2.3 Hz, 2 H, 4-H), 4.54 (dt, $J_1 = 7.0$, $J_2 = 2.3$ Hz, 2 H, 1-H), 4.12 $(dq, J_1 = 7.1, J_2 = 7.1 Hz, 4 H, 5-H), 1.35 (td, J_1 = 7.1, J_2 = 1.0 Hz)$ 6 H, 6-H) ppm. ¹³C NMR (100.6 MHz): δ = 209.2 (C-3), 86.9 (C-2), 76.4 (C-4), 64.8 (C-1), 63.4 (C-5), 15.7 (C-6) ppm. IR (film): v = 3060 (w), 2990 (vs), 2940 (s), 2910 (s), 1963 (s), 1480 (m), 1390 (s), 1280 (vs), 1170 (m), 1125 (m), 845 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 275 (2.14), 215 (2.68), 198 (2.93) nm. MS (EI, 70 eV): m/z (%) = 206 (1) [M]⁺, 178 (12), 155 (81), 150 (33), 127 (79), 109 (56), 99 (100), 91 (33), 81 (74), 65 (35), 52 (66). C₈H₁₅O₄P (206.18): calcd. C 46.60, H 7.33; found C 46.49, H 7.35.

10. 4-Methylenehexa-1,2,5-triene (2): Magnesium turnings (3.65 g, 60.0 mmol) in a three-necked flask (500 mL) were covered with a layer of diethyl ether (20 mL), and a few drops (0.7 g, 6 mmol) of propargyl bromide were added. After the reaction had started, the main fraction of the halide (6.5 g, 55.0 mmol), dissolved in diethyl ether (80 mL), was added. A catalytic amount of CuBr was added to the solution of the Grignard reagent, causing a color change to black. The solution was cooled to -10 °C, and 31 (10.3 g, 50.0 mmol) in diethyl ether (20 mL) was added dropwise. The mixture was stirred at room temperature for 12 h, and a saturated solution of ammonium chloride in water (40 mL) was added for hydrolysis. The inorganic phase was separated, neutralized, and dried (sodium sulfate). When the solvent was removed by rotary evaporation, polymerization set in, but the yield of the substitution could be estimated by NMR analysis as ca. 60%. Separation/purification by distillation failed because of the instability of 2. However, a small sample could be separated by preparative GC (6 m OPN, 60 °C), allowing the spectroscopic data to be recorded. ¹H NMR (400.1 MHz): δ = 5.99 (dd, J_1 = 16.2, J_2 = 10.2 Hz, 1 H, 5-H), 5.64 (t, J = 5.5 Hz, 1 H, 3-H), 5.56 (pseudo d, J = 16.2 Hz, 1 H, 6-H), 5.43 (d, J = 6.4 Hz, 2 H, 7-H), 5.06 (pseudo d, J = 10.3 Hz, 1 H, 6-H), 4.72 (d, J = 5.5 Hz, 2 H, 1-H) ppm. ¹³C NMR (100.6 MHz): δ = 210.7 (C-2), 135.3 (C-4), 131.0 (C-5), 120.8 (C-6), 120.4 (C-7), 89.1 (C-3), 77.0 (C-1) ppm. IR (film): v = 3020 (vw), 290 (vs), 2890 (w), 1955 (m), 1585 (s), 1425 (w), 1255 (vs), 1205 (s), 925 (m), 885 (m), 865 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 227 (3.76) nm. MS (EI, 70 eV): m/z (%) = 92 (78) [M]⁺, 91 (100), 86 (15), 76 (25), 53 (18), 47 (15), 44 (32), 41 (35), 39 (55). C₇H₈ (92.14): calcd. C 92.26, H 7.74; found C 91.70, H 7.90.

11. 1,5-Bis(*tert*-**butyldimethylsiloxy**)-**3-methylenepentane** (**35**): Imidazole (61.5 g, 0.9 mol) and *tert*-butyldimethylsilyl chloride (60.0 g, 0.40 mol) were added to a solution of the diol **34** (42.2 g, 0.36 mol, prepared from **33**^[28] according to a literature procedure) in DMF (30 mL), and the mixture was stirred at room temperature for 12 h. Diethyl ether (200 mL) was added, and the product mixture was carefully washed with water. After drying (sodium sulfate), the bis(ether) was purified by vacuum distillation at 98 °C/0.1 Torr to afford **35** (106.6 g, 85%) as a colorless oil. ¹H NMR (300.1 MHz): $\delta = 4.68$ (s, 2 H, 6-H), 3.61 (t, J = 6.9 Hz, 4 H, 1-H, 5-H), 2.16 (t, J = 6.9 Hz, 4 H, 2-H, 4-H), 0.88 (s, 18 H, *t*Bu), 0.0 (s, 12 H, CH₃) ppm. IR (film): $\tilde{v} = 3060$ (w), 2950 (vs), 1640 (w), 1460 (s), 1255 (s), 1095 (s), 835 (s) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 287 (15) [M – 57]⁺, 219 (96), 189 (100). 12. 1,1-Dibromo-2,2-bis[2-(tert-butyldimethylsiloxy)ethyl]cyclopropane (36): A suspension of potassium *tert*-butoxide (22 g, 0.18 mol, 2.5-fold excess) in a solution of 35 (25.0 g, 73.0 mmol) in anhydrous pentane (160 mL) was cooled to -30 °C under N₂ in a three-necked flask (500 mL). Bromoform (46.0 g, 0.18 mol, 2.5-fold excess) in pentane (40 mL) was slowly added with mechanical stirring, and the mixture was stirred for an additional hour at -30 °C. Water was added at 0 °C, and the dark red organic phase was washed with dilute hydrochloric acid and saturated hydrogencarbonate solution and dried (sodium sulfate). The solvent was removed by rotary evaporation, and starting material and bromoform were removed from the remaining oil by high vacuum distillation at 0.001 Torr. At a conversion of 80%, compound 36 (27.7 g, yield: 92%) was obtained as a yellow, highly viscous oil. ¹H NMR (300.1 MHz): δ = 3.66 (t, J = 6.9 Hz, 4 H, OCH₂), 1.79 (t, J = 6.9 Hz, 4 H, CH₂C), 1.34 (s, 2 H, cyclopropane), 0.84 (s, 18 H, tBu), 0.0 (s, 12 H, CH₃) ppm. IR (film): $\tilde{v} = 2950-2850$ (vs), 1460 (s), 1355 (m), 1255 (vs), 1100 (vs), 835 (vs) cm⁻¹. MS (EI, 70 eV): m/z (%) = 461 (0.3), 459 (0.6), 457 (0.3) [M]⁺, 287 (43), 147 (96), 89 (99), 73 (100).

13. 1,5-Bis(tert-butyldimethylsiloxy)-3-ethenylidenepentane (37): A solution of methyllithium in diethyl ether (32 mL, 2.2 N) was added at -20 °C under N₂ to a solution of **36** (28 g, 54.0 mmol) in anhydrous diethyl ether (120 mL) at such a rate that the reaction temperature stayed below -25 °C. Water (50 mL) was added, the aqueous phase was extracted twice with pentane, and the combined organic layers were treated with dilute hydrochloric acid and hydrogencarbonate solution. After solvent removal in vacuo, the remaining oil was vacuum-distilled at 123 °C/0.01 Torr to afford compound **37** (15.2 g, 79%) as a colorless oil. ¹H NMR (200.1 MHz): $\delta = 4.48$ (t, J = 2.95 Hz, 2 H, 6-H), 3.56 (t, J = 6.86 Hz, 4 H, 1-H, 5-H), 2.08 (m, 4 H, 2-H, 4-H), 0.85 (s, 18 H, tBu), 0.0 (s, 12 H, CH₃) ppm. ¹³C NMR (100.6 MHz): $\delta = 206.4$ (C-3), 91.07 (C-6), 75.29 (C-7), 61.90 (C-1, C-5), 35.70 (C-2, C-4), 25.96 and 18.32 (*t*Bu), -5.23 (CH₃) ppm. IR (film): $\tilde{v} = 3050$ (w), 2959–2850 (vs), 1955 (m), 1460 (s), 1255 (s), 1100 (vs), 835 (vs), 775 (vs) cm⁻¹. MS (EI, 70 eV): m/z (%) = 356 (8) [M]⁺, 299 (100).

14. 1,5-Diacetoxy-3-ethenylidenepentane (38): The bis(ether) 37 (6.32 g, 17.7 mmol) and freshly distilled acetic anhydride (21 mL) were placed under N₂ in a three-necked flask (250 mL), and the mixture was cooled to 0 °C. Anhydrous FeCl₃ (0.85 g, 5.0 mmol) was added, and the reaction mixture was stirred at this temperature. The dark brown, tarry product mixture was extracted with pentane, the solvent was removed in vacuo, and the remainder was distilled at 98 °C (0.01 Torr) to afford 38 (2.22 g, 59%) as a colorless oil. ¹H NMR (200.1 MHz): δ = 4.70 (t, J = 3.22 Hz, 2 H, 7-H), 4.12 (t, J = 6.80 Hz, 4 H 1-H, 5-H), 2.25 (m, $J_1 = 3.25$, $J_2 = 6.80$ Hz, 4 H, 2-H, 4-H), 1.99 (s, 6 H, CH₃) ppm. $^{13}\mathrm{C}$ NMR (100.6 MHz): δ = 205.1 (s, C-6), 169.7 (C=O), 95.3 (C-3), 76.1 (C-7), 61.6 (C-1, C-5), 30.6 (C-2, C-4), 20.1 (CH₃) ppm. IR (film): $\tilde{v} = 2950-2850$ (mw), 1955 (w), 1740 (vs), 1435 (m), 1370 (m), 1235 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 197 (3.30) nm. MS (EI, 70 eV): m/z (%) $= 152 (32) [M - 60]^+, 110 (73), 43 (100).$

15. (*Z*)-**3-Ethynylpenta-1,3-diene (39). Pyrolysis of 38:** A gaseous stream of the diacetate **38** (0.43 g, 2.0 mmol) was passed at 550 °C and 0.001 Torr through a quartz pyrolysis tube filled with Raschig rings. The pyrolysate was condensed in a cold trap at -196 °C and dissolved in diethyl ether, and the acetic acid was removed by washing the organic phase several times with water. Removal of the solvent by distillation resulted in the formation of a hydrocarbon mixture (170 mg, 92%), which was separated by preparative gas chromatography (10 m 4% squalane column). ¹H NMR (300.1 MHz): δ = 6.16 (m, 1 H, 2-H), 5.78 (q, *J* = 7.1 Hz, 1 H, 4-

H), 5.62 (d, J = 17.0 Hz, 1 H, 1-H), 5.05 (d, J = 11.0 Hz, 1 H, 1-H), 2.98 (s, 1 H, 7-H), 1.85 (s, J = 7.1 Hz, 3 H, CH₃) ppm. IR (film): $\tilde{v} = 3300$ (vs), 3010 (w), 2950–2850 (m), 2080 (w), 1710 (s), 1625 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 234 (2.76) nm. MS (EI, 70 eV): m/z (%) = 92 (96) [M]⁺, 91 (100), 77 (10), 65 (67), 51 (36).

16. 3-(2-Hydroxyethyl)penta-1,2-dien-5-ol (42): Although this diol has been described in the literature^[19] the procedure is lacking in detail, so we present our method of preparation here. Lithium aluminium hydride (1.00 g, 27.0 mmol) was placed in a three-necked flask (250 mL), and anhydrous diethyl ether (20 mL) was added under N₂. The suspension was cooled to 0 °C, and the allenic ester 41^[19] (12.7 g, 50.0 mmol) in diethyl ether (50 mL) was added over 1 h. The reaction mixture was stirred at room temperature for 3 h and cooled to 0 °C again before hydrolysis with a saturated solution of sodium sulfate in water (30 mL). The precipitate formed was removed by suction filtration, the organic phase was dried (magnesium sulfate), and the solvent was removed in vacuo. The remaining oil was dissolved in ethanol (70 mL), hydrochloric acid (1 N, 59 mL) was added, and the hydrolysis mixture was stirred at 30 °C for 30 min. The product mixture was dissolved in diethyl ether (250 mL), the solution was neutralized and dried (magnesium sulfate), and the solvent was removed by rotary evaporation; distillation (64 °C, 0.01 Torr) afforded pure 42 (4.49 g, 70%) as a colorless oil. ¹H NMR (100.1 MHz): δ = 4.73 (q, J = 3.0 Hz, 2 H, 1-H), 3.70 (t, J = 7.0 Hz, 4 H, 5-H), 3.00 (s, 2 H, OH), 2.25 (tt, $J_1 = 7.0$, $J_2 = 3.0$ Hz, 4 H, 4-H) ppm. IR (film): $\tilde{v} = 3350$ (vs), 2950 (s), 2880 (s), 1960 (m), 1440 (m), 1040 (s), 850 (m) cm⁻¹.

17. 1,5-Bis(2-o-nitrophenylselenyl)-3-ethenylidenepentane (44): Tri-nbutylphosphane (12.2 g, 60.0 mmol) was added slowly under N2 at room temperature to a solution of 42 (2.56 g, 20.0 mmol) and onitrophenyl selenocyanate (43, 13.6 g, 60.0 mmol) in anhydrous THF (50 mL). After 2.5 h, the solvent was removed in vacuo, and the remaining solid was recrystallized from ethanol (5.6 g, 59%). A sample of analytically pure 44 was obtained by silica gel column chromatography with pentane/diethyl ether (1:1, v/v); m.p. 118 °C, dark red needles. ¹H NMR (300.1 MHz): δ = 7.53 (m, 6 H, phenyl), 7.32 (m, 2 H, phenyl), 4.97 (t, J = 3.4 Hz, 2 H, 7-H), 3.04 (t, J =7.4 Hz, 4 H, 1-H, 5-H), 2.45 (tt, $J_1 = 7.4$, $J_2 = 3.4$ Hz, 4 H, 2-H, 4-H) ppm. ¹³C NMR (100.6 MHz): $\delta = 205.4$ (C-6), 133.6 (C-10), 133.4 (C-9), 133.3 (C-8), 129.1 (C-13), 126.5 (C-12), 125.5 (C-11), 102.4 (C-3), 79.5 (C-7), 31.1 (C-1,-5), 23.8 (C-2, C-4) ppm. IR (KBr): $\tilde{v} = 3050$ (vw), 2870 (vw), 1965 (w), 1585 (s), 1560 (s), 1505 (vs), 1330 (vs), 1305 (vs), 1090 (m), 850 (s), 735 (vs), 720 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 398 (4.01), 272 (4.10), 255 (4.41), 204 (4.38) nm. MS (EI, 70 eV): m/z (%) = 496 (5) [M]⁺, 376 (7), 310 (18), 202 (40), 186 (90), 184 (58), 156 (78), 109 (40), 106 (100), 91 (70), 77 (86). C₁₉H₁₈N₂O₄Se₂ (496.29): calcd. C 45.98, H 3.66; found C 46.22, H 4.14.

18. 3-Ethynylpenta-1,4-dien-3-ol (47): Liquid ammonia (350 mL) was condensed into a three-necked flask (1 L), a catalytic amount of iron nitrate was added, and lithium amide was prepared by addition of granulated lithium metal (7.63 g, 1.00 mol). Subsequently, dry acetylene was passed through the suspension until a deep black color had formed (ca. 15 min). 1,5-Dichloropentan-3-one (46, 52.0 g, 0.34 mol), prepared from 3-chloropropionyl chloride (45) according to a literature procedure,^[21] was added to the produced lithium acetylide suspension in portions. After 2.5 h, during which the temperature of the strongly exothermic reaction was kept at -33 °C, diethyl ether (300 mL) was added, followed by glacial acetic acid (35 g) in ice-cold water (100 mL). The organic phase was separated, neutralized, and dried with sodium sulfate. The solvent was

removed by rotary evaporation, and the remaining oil was subjected to fractional distillation. Fraction 1: Compound 47 (12.4 g, 34%), b.p. 55 °C/16 Torr, colorless liquid with aromatic odor. ¹H NMR (400.1 MHz): δ = 5.91 (dd, J_1 = 17.0, J_2 = 10.3 Hz, 2 H, 2-H, 4-H), 5.69 (dd, *J*₁ = 17.0, *J*₂ = 0.9 Hz, 2 H, 1-H, 5-H), 5.21 (dd, $J_1 = 10.3, J_2 = 0.9$ Hz, 2 H, 1-H, 5-H), 2.72 (s, 1 H, 7-H), 2.71 (s, 1 H, OH) ppm. ¹³C NMR (100.6 MHz): δ = 139.4 (C-2, C-4), 115.0 (C-1, C-5), 83.3 (C-6), 75.3 (C-7), 71.3 (C-3) ppm. IR (film): v = 3400 (vs), 3310 (vs), 3090 (m), 2990 (m), 2110 (m), 1635 (s), 1410 (vs), 1325 (s), 1180 (s), 1130 (s), 1020 (vs), 980 (vs), 940 (vs) cm^{-1} . UV (acetonitrile): λ_{max} (lg ε) = 246 (1.94), 199 (3.35) nm. MS (EI, 70 eV): m/z (%) = 108 (8) [M]⁺, 107 (66), 91 (10), 89 (10), 81 (84), 79 (100), 73 (30), 65 (20), 63 (17), 55 (58), 53 (48), 51 (22). C₇H₈O (108.14): calcd. C 77.75, H 7.46; found C 77.72, H 7.61. Fraction 2: 5-Chloro-3-ethynylpent-1-en-3-ol ("half"-ethynylated product of 46); 1.2 g (3%), b.p. 98 °C/16 Torr, colorless oil. ¹H NMR $(200.1 \text{ MHz}): \delta = 5.91 \text{ (dd, } J_1 = 17.0, J_2 = 10.2 \text{ Hz}, 1 \text{ H}, 2 \text{-H}), 5.58$ (dd, $J_1 = 17.1$, $J_2 = 0.9$ Hz, 1 H, 1-H), 5.24 (dd, $J_1 = 10.2$, $J_2 = 10.2$ 0.8 Hz, 1 H, 1-H), 3.69 (m, 2 H, 5-H), 2.95 (s, 1 H, -OH), 2.67 (s, 1 H, 7-H), 2.19 (m, 2 H, 4-H) ppm. 13 C NMR (100.6 MHz): δ = 140.0 (C-2), 115.5 (C-1), 83.6 (C-6), 74.9 (C-7), 70.3 (C-3), 44.7 (C-5), 39.6 (C-4) ppm. IR (film): $\tilde{v} = 3500$ (br.), 3300 (vs), 3020 (w), 2970 (m), 2110 (m), 1640 (m), 1455 (m), 1060 (s), 990 (s), 930 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 238 (2.36), 198 (2.77) nm. MS (EI, 70 eV): m/z (%) = 144 (0.4) [M]⁺, 143 (5), 117 (1), 115 (2), 91 (5), 81 (100), 77 (23), 55 (10).

19. 3-Ethynyl-3-methoxypenta-1,4-diene (48): A suspension of sodium hydride (4.56 g, 0.190 mol, 80% in paraffin oil) in anhydrous THF (210 mL) was placed in a three-necked flask (500 mL). A solution of 47 (12.4 g, 0.115 mol) in THF (140 mL) was added under N₂ over 15 min. A color change (to orange) and gas evolution were noted. After the mixture had been stirred at room temperature for 30 min, methyl iodide was added (10.5 mL, 0.169 mol), and the reaction mixture was stirred for an additional 3 h. A saturated aqueous solution of ammonium chloride was added (90 mL), the phases were separated, and the organic phase was neutralized and dried (sodium sulfate) overnight. Solvent removal by rotary evaporation furnished a pleasantly smelling oil, which was distilled at normal pressure; 48 (11.4 g, 81%), b.p. 118 °C. ¹H NMR (300.1 MHz): δ = 5.80 (dd, J_1 = 17.1, J_2 = 10.1 Hz, 2 H, 2-H, 4-H), 5.59 (dd, $J_1 = 17.1$, $J_2 = 1.2$ Hz, 2 H, 1-H, 5-H), 5.27 (dd, J_1 = 10.1, J_2 = 1.2 Hz, 2 H, 1-H, 5-H), 3.32 (s, 3 H, -OCH₃), 2.47 (s, 1 H, 7-H) ppm. ¹³C NMR (100.6 MHz): δ = 138.2 (C-2, C-4), 116.5 (C-1, C-5), 80.0 (C-3), 76.5 (C-6), 77.3 (C-7), 51.9 (OCH₃) ppm. IR (film): $\tilde{v} = 3300$ (vs), 3090 (m), 2950 (s), 2830 (s), 2110 (w), 1640 (m), 1410 (s), 1140 (m), 1075 (vs), 1020 (m), 985 (s), 935 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 232 (2.54), 199 (3.46) nm. MS (EI, 70 eV): m/z (%) = 124 (9) [M]⁺, 123 (10), 107 (62), 95 (35), 91 (78), 81 (76), 79 (100), 77 (40), 66 (12), 65 (59), 55 (58), 53 (66), 43 (14). C₈H₁₀O (122.17): calcd. C 78.65, H 8.25; found C 78.55, H 8.32.

20. 3-Vinylhexa-1,3,4-triene (49) and its TCNE Adduct 52: CuI was placed (3.70 g, 19.5 mmol) in a three-necked flask and covered with a layer of anhydrous diethyl ether (20 mL). Methyllithium (24.3 mL of a 1.6 N solution in diethyl ether) was added to the stirred suspension under N₂ at 0 °C. On addition, an intensely yellow precipitate formed immediately, dissolving with a color change (to grey-green) when all methyllithium had been added (homocuprate formation). The solution was cooled to -78 °C and the ether **48** (1.08 g, 10.0 mmol) in diethyl ether (25 mL) was added. When the addition was complete, the reaction mixture was stirred at -10 °C for 2.5 h. For workup, pentane (50 mL) was added to the reaction mixture, which was subsequently carefully hydrolyzed by addition of a saturated solution of ammonium chloride in water (50 mL) at -10 °C.



The pentane solution was investigated by GC/MS analysis and showed one new product with a molecular mass of 106 (C_8H_{10}). Because of its low stability, 49 could not be separated from the reaction mixture, and a solution of TCNE (50, 640 mg, 5.00 mmol, based on the assumption that the solution contained ca. 10 mmol of 49) in THF (50 mL) was added directly to the above product solution. The reaction mixture was heated to reflux for 30 min, the solvent was removed in vacuo, and the resulting yellow oil was purified by plate chromatography on silica gel with dichloromethane. The adduct 52 (ca. 26 mg) could be isolated as a colorless oil. ¹H NMR (300.1 MHz): δ = 6.66 (q, J = 7.4 Hz, 1 H, 9-H), 6.40 (dd, $J_1 = 17.2$, $J_2 = 10.7$ Hz, 7-H), 5.90 (t, J = 4.0 Hz, 1 H, 1-H), 5.43 (m, 1 H, 8-H), 5.33 (m, 1 H, 8-H), 3.32 (d, J = 3.7 Hz, 6-H), 2.05 (d, J = 7.3 Hz, 3 H, 10-H) ppm. ¹³C NMR (100.6 MHz): $\delta =$ 137.9 (C-7), 135.3 (C-1), 134.5 (C-2), 120.9 (C-3), 120.7 (C-9), 118.1 (C-8), 110.8 (C-11), 109.7 (C-12), 41.1 (C-4), 34.4 (C-6), 29.7 (C-5), 17.1 (C-10) ppm. IR (film): $\tilde{v} = 2957$ (s), 2928 (vs), 2855 (m), 1432 (s), 986 (m), 927 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 234 (3.88), 224 (3.92) nm. MS (EI, 70 eV): m/z (%) = 234 (50) [M]⁺, 219 (46), 206 (47), 192 (47), 179 (32), 165 (38), 155 (68), 141 (30), 129 (40), 116 (30), 106 (100), 91 (98), 77 (41), 63 (38), 51 (55). HRMS: calcd. 234.09055; found 234.09098.

21. 4-Methylenehepta-1,6-diyne (55): Although this hydrocarbon has been described several times in the literature,^[23a,29] the available information is incomplete, so we give our experimental and analytical details here in full. Ethylmagnesium bromide [from magnesium turnings (11.75 g, 484 mmol) and ethyl bromide (60.0 g, 0.590 mol)] in THF (300 mL) was prepared under N₂ in a three-necked flask (1 L). In a second three-necked flask, acetylene was passed through THF (200 mL) for 30 min. The ethyl Grignard reagent was added to this latter solution; the formed ethynylmagnesium bromide precipitated as a colorless solid below 35 °C. After the addition was complete, acetylene was passed through the suspension for additional 15 min, and CuCl (ca. 1 g) was added as a catalyst. A solution of 3-bromo-2-(bromomethyl)prop-1-ene (54, 35.4 g, 165 mmol)^[23a] in THF (30 mL) was added to the mixture, and the gray-green reaction mixture was stirred at 67 °C for 2.5 h. The mixture was cooled to 0 °C, hydrolyzed with a saturated solution of ammonium chloride in water (300 mL), and fractionated with a Vigreux column to afford 55 (12.2 g, 71%); colorless liquid, b.p. 44 °C/20 Torr, $n_{\rm D}$ (20 °C) = 1.4651. ¹H NMR (400.1 MHz): δ = 5.23 (q, J = 1.4 Hz, 2 H, 7-H), 3.03 (dq, $J_1 = 1.4$, $J_2 = 2.7$ Hz, 4 H, 3-H, 5-H), 2.14 (t, J = 2.7 Hz, 2 H, 1-H, 7-H) ppm. ¹³C NMR (100.6 MHz): δ = 138.1 (C-4), 113.2 (C-5), 80.5 (C-2, C-6), 71.0 (C-1, C-7), 25.1 (C-3) ppm. IR (film): $\tilde{v} = 3400$ (vs), 3080 (w), 2117 (w), 1658 (m), 1428 (m), 906 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 197 (2.89) nm. MS (EI, 70 eV): m/z (%) = 104 (9) [M]⁺, 103 (100), 78 (50), 77 (23), 63 (13), 40 (28), 19 (12). C₈H₈ (104.15): calcd. C 92.26, H 7.74; found C 92.65, H 7.33.

22. 4-Methylenehepta-5,6-dien-1-yne (60): Sodium (0.112 g, 4.87 mmol) was placed under N₂ in a three-necked flask (50 mL); subsequently, anhydrous methanol (10 mL) was injected through a septum. When the methoxide formation was complete, the hydrocarbon **55** was injected (104 mg, 1.00 mmol), and the reaction mixture was heated at 64 °C for 45 min. The mixture was allowed to cool to room temperature, and diethyl ether (10 mL) was added, followed by a saturated solution of ammonium chloride in water (10 mL). The phases were separated, and the organic phase was washed several times with water and then dried (sodium sulfate). The organic phase was concentrated to ca. 3 mL, and the product was separated by preparative gas chromatography (10 m squalane column, 110 °C) to afford **60** (60 mg, 60%); colorless liquid. ¹H NMR (400.1 MHz): $\delta = 5.92$ (t, J = 6.7 Hz, 2 H, 3-H), 5.26 (m, 1

H, 8-H), 5.07 (m, 1 H, 8-H), 5.01 (d, J = 6.7 Hz, 2 H, 1-H), 2.97 (d, J = 2.6 Hz, 2 H, 5-H), 2.17 (t, J = 2.6 Hz, 1 H, 7-H) ppm. ¹³C NMR (100.6 MHz): $\delta = 209.6$ (C-2), 136.6 (C-4), 114.0 (C-8), 95.5 (C-3), 81.0 (C-6), 78.6 (C-1), 71.1 (C-7), 22.8 (C-5) ppm. IR (film): $\tilde{v} = 3300$ (s), 3028 (w), 2130 (m), 1945 (vs), 1618 (s), 1416 (s), 1406 (s), 848 (vs), 828 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 230 (3.73) nm. MS (EI, 70 eV): m/z (%) = 104 (7) [M]⁺, 103 (100), 78 (48), 77 (27), 65 (12), 40 (14), 29 (11). C₈H₈ (104.15): calcd. C 92.26, H 7.74; found C 92.21, H 7.87.

23. (E)-4-(Trimethylsilylmethyl)hept-3-ene-1,6-diyne (59): A solution of 55 (1.04 g, 10.0 mmol) under N_2 in anhydrous diethyl ether (20 mL) was cooled to -78 °C in a three-necked flask (100 mL). n-Butyllithium solution (20 mL, 1 N in hexane) was added, and the temperature was raised to -20 °C. With stirring, a solution of trimethylsilyl chloride (2.18 g, 20.0 mmol) in diethyl ether (5 mL) was added to the deep red reaction mixture. The reaction mixture was brought to room temperature, and after 1 h of additional stirring, water was added (100 mL). The organic phase was separated and dried (sodium sulfate). The major part of the solvent was removed in vacuo, and the remainder was separated by preparative gas chromatography (4 m SE-30 column, 100 °C) to afford 59 (647 mg, 62%) as a colorless oil. ¹H NMR (400.1 MHz): δ = 5.16 (m, 1 H, 3-H), 3.27 (dd, $J_1 = 2.9$, $J_2 = 0.8$ Hz, 2 H, 5-H), 3.10 (d, J = 2.3 Hz, 1 H, 1-H), 2.04 (t, J = 2.9 Hz, 1 H, 7-H), 1.87 (d, J = 0.9 Hz, 2 H, 8-H), 0.07 [s, 9 H, (CH₃)₃Si] ppm. ¹³C NMR (100.6 MHz): δ = 150.7 (C-4), 102.9 (C-3), 81.2 (C-2), 81.1 (C-1), 69.7 (C-7), 26.8 (C-8), 24.6 (C-5), -1.3 (Me₃Si) ppm. IR (film): $\tilde{v} = 3320$ (vs), 2970 (s), 2900 (m), 2180 (w), 2120 (w), 1615 (m), 1295 (m), 1255 (vs), 1155 (m), 850 (vs), 755 (m), 650 (m) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 243 (4.02), 201 (3.34), 215 (3.58) nm. MS (EI, 70 eV): m/z (%) = $176 (2) [M]^+$, 161 (40), 159 (10), 133 (129), 73 (100), 45 (12). C₁₁H₁₆Si (176.34): calcd. C 74.92, H 9.70; found C 73.91, H 9.17.

24. 4-Methylenehepta-1,2,5,6-tetraene (4): A suspension of potassium tert-butoxide (228 mg, 2.00 mmol) in THF (15 mL) in a threenecked flask (50 mL) under N2 was cooled to -78 °C. A solution of 55 (104 mg, 1.00 mmol) in anhydrous THF (0.5 mL) was added slowly by syringe, and the mixture was stirred at this temperature for 30 min. Pentane (10 mL) and a saturated solution of ammonium chloride in water (10 mL) were added, and the reaction temperature was brought to 0 °C. The organic phase was thoroughly washed with water and dried with sodium sulfate, and the solvent was removed in vacuo at 0 °C. The bis(allene) 4 was isolated as a colorless oil (92 mg, 88%), which rapidly polymerized to form a solid. ¹H NMR (400.1 MHz): δ = 5.88 (m, 2 H, 3-H, 5-H), 5.09 (m, 2 H, 8-H), 5.01 (m, 4 H, 1-H, 7-H) ppm. $^{13}\mathrm{C}$ NMR (100.6 MHz): δ = 209.9 (C-2, C-6), 134.4 (C-4), 113.3 (C-8), 92.8 (C-3, C-5), 78.6 (C-1, C-7) ppm. IR (film): $\tilde{v} = 3300$ (s), 2130 (m), 1945 (vs), 1618 (s), 1416 (s), 1406 (s), 1216 (m), 848 (vs), 828 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 267 (3.82), 248 (3.74), 236 (3.69), 215 (3.58) nm. MS (EI, 70 eV): m/z (%) = 104 (7) [M]⁺, 103 (100), 78 (48), 77 (27), 65 (12), 40 (14), 29 (11). Because of the strong tendency of the hydrocarbon to polymerize, no satisfactory elemental analysis could be obtained.

25. TCNE Adduct of **4. 4,4,5,5-Tetracyano-3-methylene-1-propadienylcyclohexene (61):** TCNE (**50**, 1.02 g, 8.00 mmol) was added to a solution of **4** (208 mg, 2.00 mmol) in anhydrous THF (30 mL), and, after 12 h at room temperature, the reaction mixture was worked up. Extensive polymer formation was noted. The precipitate was removed by filtration, and compound **61** (120 mg, 26%) was isolated from the filtrate by preparative plate chromatography (silica gel, dichloromethane); m.p. 118 °C, slightly red needles. ¹H NMR (400.1 MHz): $\delta = 6.34$ (m, 1 H, 2-H), 6.02 (t, J = 6.7 Hz, 1

H, 7-H), 6.00 (m, 1 H, 10-H), 5.78 (m, 1 H, 10-H), 5.32 (d, J = 6.7 Hz, 2 H, 9-H), 3.25 (m, 2 H, 6-H) ppm. ¹³C NMR (100.6 MHz): $\delta = 211.1$ (C-8), 129.5 (C-1), 129.1 (C-3), 123.5 (C-10), 121.3 (C-2), 110.2 (C-12), 109.5 (C-11), 94.5 (C-7), 81.5 (C-9), 32.9 (C-6), 29.7 (C-4, C-5) ppm. IR (film): $\tilde{v} = 3110$ (vw), 2960 (m), 2930 (s), 2850 (m), 1955 (m), 1933 (vs), 1720 (m), 1625 (vs), 1425 (vs), 1415 (vs), 1255 (m), 1135 (m), 930 (vs), 895 (vs), 870 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 272 (4.23), 224 (3.90), 208 (3.72) nm. MS (EI, 70 eV): m/z (%) = 232 (92) [M]⁺, 204 (53), 190 (17), 178 (100), 165 (51), 140 (52).

26. 4-Propargyloct-4-ene-1,7-diyne (65) and 4-Ethynyl-5-methyleneocta-1,7-diyne (66): Ethynylmagnesium bromide was prepared from ethylmagnesium bromide (311 mL, 280 mmol, 0.9 N in diethyl ether) as described above (Experiment 21). After the addition of CuI (ca. 2 g, 10 mmol), a solution of the tribromide 64 (21.5 g, 70.0 mmol)^[25] in anhydrous THF (20 mL) was added, and the reaction mixture was stirred at room temperature for 1 h. To complete the substitution, the mixture was heated to reflux for 1 h. For workup, water was added at room temperature, the phases were separated, and the organic phase was dried (sodium sulfate). The solvent was removed by rotary evaporation, and the remaining oil was vacuum-distilled to afford a mixture of 65 and 66 (5.2 g, 53%); b.p. 75-77 °C/15 Torr, colorless oil, ratio 1.7:1, which could be separated by preparative gas chromatography on a 4 m SE-30 column at 120 °C. Fraction 1: Trivne 65: ¹H NMR (300.1 MHz): $\delta = 5.68$ (m, 1 H, 5-H), 3.10 (m, 4 H, 3-H, 9-H), 3.05 (m, 2 H, 6-H), 2.18 (t, J = 2.8 Hz, 1 H, 8-H), 2.024 and 2.019 (2 × t, J = 2.7 Hz, 2 × 1 H, 1-H and 11-H) ppm. ¹³C NMR (75.47 MHz): $\delta = 131.4$ (C-4), 122.4 (C-5), 81.7 (C-7), 80.5 (C-2), 80.3 (C-10), 71.4 (C-8), 69.5 (C-1), 68.6 (C-11), 25.8 (C-6), 19.6 (C-3), 17.4 (C-9) ppm. IR (film): v = 3300 (vs), 2990 (w), 2930 (m), 2120 (s), 1675 (w), 1420 (vs), 1280 (vs), 1085 (m), 925 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 272 (2.77), 237 (3.17), 226 (3.28), 199 (3.49) nm. MS (EI, 70 eV): m/z (%) = 142 (8) [M]⁺, 141 (70), 139 (10), 116 (18), 115 (100), 103 (44), 103 (12), 89 (15), 77 (48), 63 (21), 51 (38), 39 (19). C₁₁H₁₀ (142.20): calcd. C 92.91, H 7.09; found C 91. 74 H 7.04. Fraction 2: Trivne **66**: ¹H NMR (300.1 MHz): δ = 5.37 (m, 1 H, 11-H), 5.28 (m, 1 H, 11-H), 3.42 (td, $J_1 = 2.5$, $J_2 = 6.7$ Hz, 1 H, 4-H), 3.21 (m, 1 H, 6-H), 3.02 (m, 1 H, 6-H), 2.58 (dd, $J_1 = 2.6$, $J_2 = 6.7$ Hz, 2 H, 3-H), 2.29 (d, J = 2.5 Hz, 1 H, 10-H), 2.17 (t, J = 2.7 Hz, 1 H, 1-H), 2.08 (t, J = 2.6 Hz, 1 H, 8-H) ppm. ¹³C NMR (100.6 MHz): $\delta = 140.6$ (C-5), 114.5 (C-11), 83.2 (C-7), 80.8 (C-9), 80.6 (C-2), 72.0 (C-8), 71.5 (C-10), 70.6 (C-1), 36.8 (C-4), 24.3 (C-6), 23.6 (C-3) ppm. IR (film): $\tilde{v} = 3305$ (vs), 2990 (w), 290 (m), 2120 (m), 1655 (m), 1425 (s), 910 (vs) cm⁻¹. UV (acetonitrile): λ_{max} (lg ϵ) = 244 (3.18), 235 (3.28), 232 (3.27), 198 (3.26) nm. MS (EI, 70 eV): m/z (%) = 142 (6) [M]⁺, 141 (44), 115 (62), 103 (48), 102 (22), 77 (100), 75 (13), 63 (44), 62 (14), 51 (72), 50 (39), 39 (62), 38 (20). C₁₁H₁₀ (142.20): calcd. C 92.91, H 7.09; found C 92. 43, H 7.04.

27. 4-(Prop-1-ynyl)octa-1,3,5-trien-7-yne (68): A solution of **65** (71 mg, 0.50 mmol) in THF (1 mL) was added by syringe under N₂ at -78 °C to a suspension of potassium *tert*-butoxide (171 mg, 1.50 mmol) in anhydrous THF (2 mL) in a three-necked flask (50 mL). After the reaction mixture had been stirred at this temperature for 30 min, pentane (10 mL) was added, followed by a saturated solution of ammonium chloride in water (10 mL), and the mixture was warmed to 0 °C. The phases were separated, and the organic component was washed carefully with water and dried with sodium sulfate. The solvent was removed at 0 °C to yield **68** (68 mg, 96%) as a slightly yellow oil. ¹H NMR (400.1 MHz): δ = 6.90 (ddd, J_1 = 17.0, J_2 = 10.2, J_3 = 11.1 Hz, 1 H, 2-H), 6.65 (d, J = 15.6 Hz, 1 H, 5-H), 6.38 (d, J = 11.1 Hz, 1 H, 3-H), 6.06 (dd, J_1 = 15.6, J_2 = 2.4 Hz, 1 H, 6-H), 5.43 (d, J = 17.0 Hz, 1 H, 1-H),

5.33 (d, J = 10.2 Hz, 1 H, 1-H), 3.11 (d, J = 2.4 Hz, 1 H, 8-H), 2.08 (s, 3 H, CH₃) ppm. ¹³C NMR (100.6 MHz): $\delta = 143.3$ (C-2), 139.1 (C-5), 134.8 (C-3), 123.3 (C-4), 121.3 (C-1), 110.0 (C-6), 94.9 (C-9), 83.0 (C-7), 80.7 (C-8), 73.5 (C-10), 4.4 (C-11) ppm. IR (film): $\tilde{v} = 3310$ (vs), 2920 (m), 2230 (w), 1550 (s), 1255 (m), 1210 (m), 990 (s), 950 (s), 910 (s) cm⁻¹. UV (acetonitrile): λ_{max} (lg ε) = 311 (3.90), 297 (3.96), 286 (3.87), 257 (3.61), 243 (3.66), 231 (3.68), 215 (3.75), 201 (3.85) nm. MS (EI, 70 eV): m/z (%) = 142 (42) [M]⁺, 141 (100), 139 (111), 127 (10), 115 (74), 63 (12). C₁₁H₁₀ (142.19): calcd. C 92.91, H 7.09; found C 92.35, H 7.29.

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