J. Am. Chem. Soc. **1991**, *113*, 6943–6949

Solution-Spray Flash Vacuum Pyrolysis: A New Method for the Synthesis of Linear Polyynes with Odd Numbers of C≡C Bonds from Substituted 3,4-Dialkynyl-3-cyclobutene-1,2-diones

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Abstract: We report a new method for the preparation of a wide range of linear polyynes, **1a–1i**, with an odd number of C≡C bonds. This method is based on solution-spray flash vacuum pyrolysis (SS-FVP) of the readily available 3,4-dialkynyl-3-cyclobutene-1,2-diones **3a–3i**. It allows the synthesis of multigram quantities of a series of hexatriynes and decapentaynes from poorly volatile and thermally unstable precursors that cannot be subjected to conventional flash vacuum pyrolysis. Yields of the linear polyynes range from 42 to 99%. Similarly, the dodecahexayne **1j** was obtained in 31% yield by SS-FVP of the bis(3-cyclobutene-1,2-dione) **3j**. The synthesis of the new 3,4-dialkynyl-3-cyclobutene-1,2-diones **3h–3j** via the ketals **7**, **10**, and **13** is reported. The X-ray crystal structure of 1,10-diphenyl-1,3,5,7,9-decapentayne (**1c**) was solved, and the crystal packing structure provides valuable information to explain the thermal polymerization behavior observed for this compound in the crystalline state.

Introduction

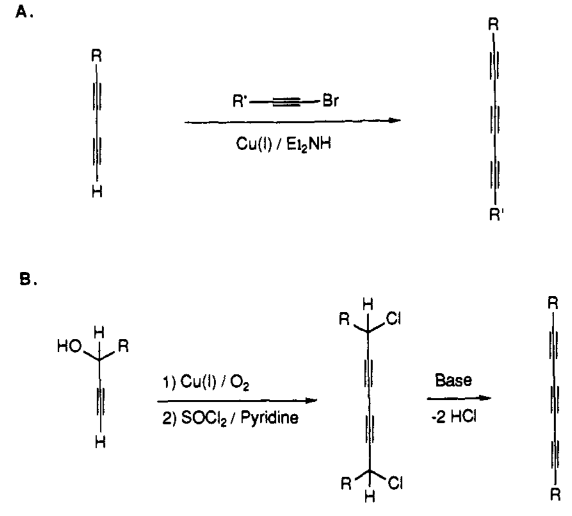
Since the initial work of Wegner on the polymerization of esters and carbamates of 2,4-hexadiyne-1,6-diol, linear polyynes have become important precursors to polymers possessing potentially unique and useful physical properties.[1,2] Accordingly, the polymerization of a variety of diynes has been studied extensively.[3–6] Patel et al. have proposed that the polymerization mechanism of diynes proceeds through an intermediate cumulene diradical.[3] Recently, Neuenschwander et al. have determined the X-ray crystal structure of the polymer formed by thermal treatment of a single crystal of a "push–pull" diyne.[4] The work of Hay[5a] on the oxidative coupling of 1,3-diethynylbenzene to give a soluble diyne oligomer has opened the way to the preparation of several other similar networks.[5b–e] The groups of Whitesides[5b–d] and Stille[5e] have studied the hardness and the thermal stability of hyper-cross-linked polymers with a large C/H ratio, formed by thermal treatment of these aromatic oligo(diynes). The study of the ferromagnetic properties of the polymer formed from a (piperidine-*N*-oxyl)-substituted diyne and of similar compounds has also received much attention.[6] It is clear that the area of organic material sciences would benefit from new, simple, and high-yielding synthetic entries into the class of the linear polyynes.

The area of natural product synthesis could also benefit from such developments since protected hexatriynes may be used as intermediates in the synthesis of the esperamicin, calicheamicin, and dynemicin families of anticancer *cis*-enediynes.[7] Selective reduction of the central triple bond in the triynes should afford the corresponding *cis*-enediynes.[8] In this regard, hexatriynes with two differentiated silyl protecting groups could be particularly useful because of the ease and selectivity with which the silyl groups can be removed, and the numerous possibilities for further functionalization.[9a,b]

However, the proposed applications of linear polyynes have so far been limited by the difficulty and the expense involved in the preparation of significant quantities of these molecules. While several methods for the synthesis of both symmetrically and unsymmetrically substituted polyynes with an *even number* of C≡C bonds have been developed,[9c,d,10–12] there is no convenient general method for the preparation of linear polyynes with an *odd number* of C≡C bonds.[9a,10,12]

The Cadiot–Chodkiewicz method for the coupling of terminal butadiynes with 1-bromoalkynes yields substituted hexatriynes (Scheme IA).[10,12] However, this method can suffer from the low yield of the desired coupling product.[12] Hexatriynes have also been prepared by double dehydrohalogenation of substituted

Scheme 1



[†] We dedicate this paper to Professor Ronald Breslow on the occasion of his 60th birthday.

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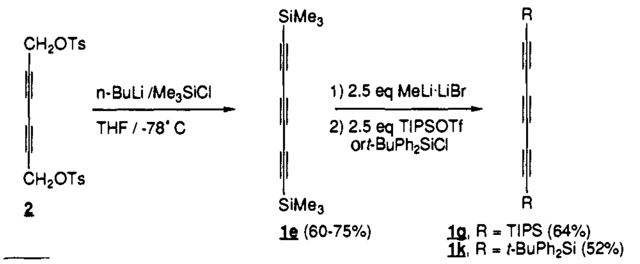
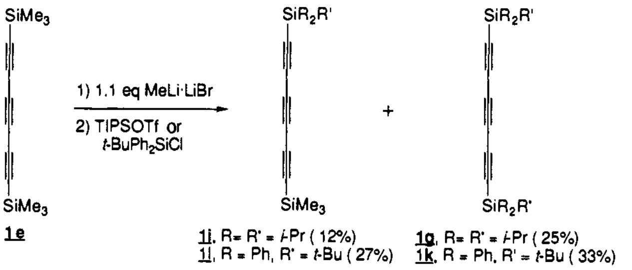
Scheme II



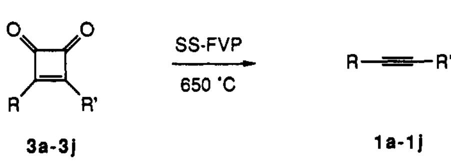
Scheme III



1,6-dichloro-2,4-hexadiynes, the latter being prepared by oxidative coupling of propargyl alcohols (Scheme IB).[10] This procedure is often lengthy for complex systems, and it uses intermediates like 1,6-dichloro-2,4-hexadiyne, which on occasion has exploded violently upon distillation and is a powerful skin irritant.[13]

In the course of our investigations into the synthesis of the cyclo[n]carbons[14a,b] and a hexanuclear cobalt complex of cyclo[18]carbon,[14c] we developed a general method for the preparation of symmetrically and unsymmetrically substituted odd-numbered polyynes. It was reasoned that 3,4-dichloro-3-cyclobutene-1,2-dione could be considered as a dichloroacetylene equivalent. Dichloroacetylene itself does not undergo Cadiot–Chodkievicz coupling with terminal alkynes.[15,16] However, the cyclobutenedione moiety can readily lose two carbonyl groups to give alkynes under either photolytic[17] or pyrolytic[14b,18] conditions. We found that "solution-spray flash vacuum pyrolysis" (SS-FVP) was the method of choice for the smooth elimination of the two carbonyl groups from substituted cyclobutenediones. In contrast to conventional flash vacuum pyrolysis (FVP),[19] this method allows the conversion of the relatively nonvolatile, high molecular weight cyclobutenediones **3a**–**3j** to the linear polyynes **1a**–**1j** in yields ranging from 31 to 99%.

Table I. Preparation of the Polyynes **1a**–**1j** from the 3-Cyclobutene-1,2-diones **3a**–**3j**



dione	R	R'	product yield (%)
3a[a]	Ph-	Ph-	**1a** (98%)[29]
3b[b]	$\mathrm{PhC{\equiv}C-}$	$\mathrm{PhC{\equiv}C-}$	**1b** (97%)[30]
3c[b]	$\mathrm{PhC{\equiv}CC{\equiv}C-}$	$\mathrm{PhC{\equiv}CC{\equiv}C-}$	**1c** (59%)[31]
3d[b]	n-$\mathrm{PrC{\equiv}C-}$	n-$\mathrm{PrC{\equiv}C-}$	**1d** (78%)
3e[b,c]	$\mathrm{Me_3SiC{\equiv}C-}$	$\mathrm{Me_3SiC{\equiv}C-}$	**1e** (99%)[20]
3f[b]	t-$\mathrm{BuMe_2SiC{\equiv}C-}$	t-$\mathrm{BuMe_2SiC{\equiv}C-}$	**1f** (99%)
3g[b]	i-$\mathrm{Pr_3SiC{\equiv}C-}$	i-$\mathrm{Pr_3SiC{\equiv}C-}$	**1g** (95%)[d]
3h	i-$\mathrm{Pr_3SiC{\equiv}CC{\equiv}C-}$	i-$\mathrm{Pr_3SiC{\equiv}CC{\equiv}C-}$	**1h** (42%)
3i	i-$\mathrm{Pr_3SiC{\equiv}C-}$	$\mathrm{Me_3SiC{\equiv}C-}$	**1i** (71%)
3j	e	e	**1j** (31%)

[a] Precursor **3a** prepared according to ref 25. [b] Precursors **3b**–**3g** prepared according to ref 14a. [c] Starting material **3e** was sublimed through a conventional FVP apparatus. [d] Yield on a 2-g scale was 69%. [e] For molecular structure, see Scheme VI.

Scheme IV

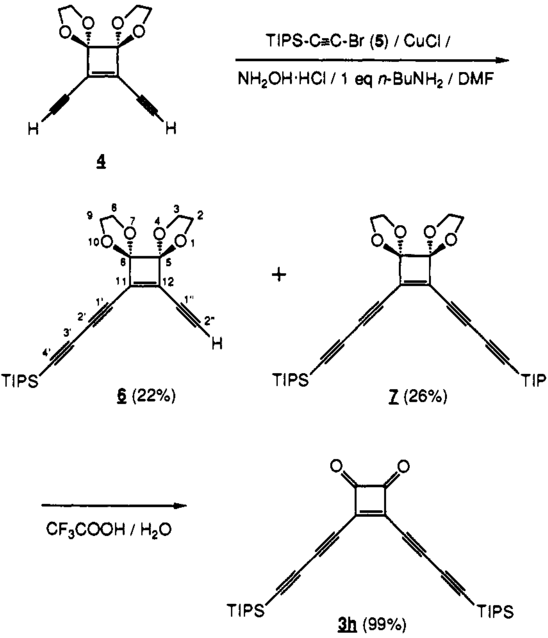


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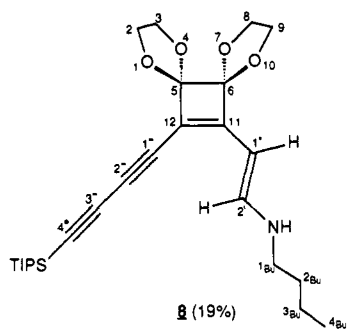
Chart I



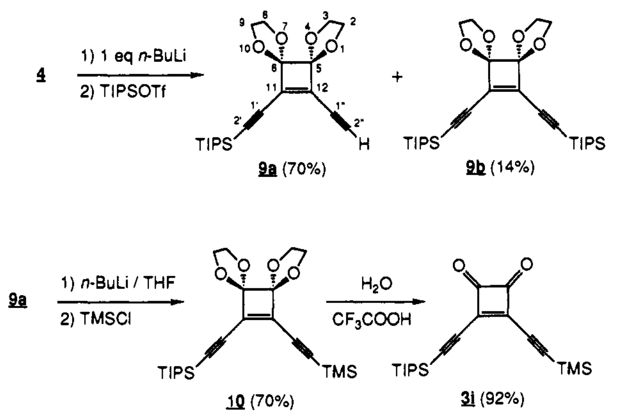
8 (19%)

Results and Discussion

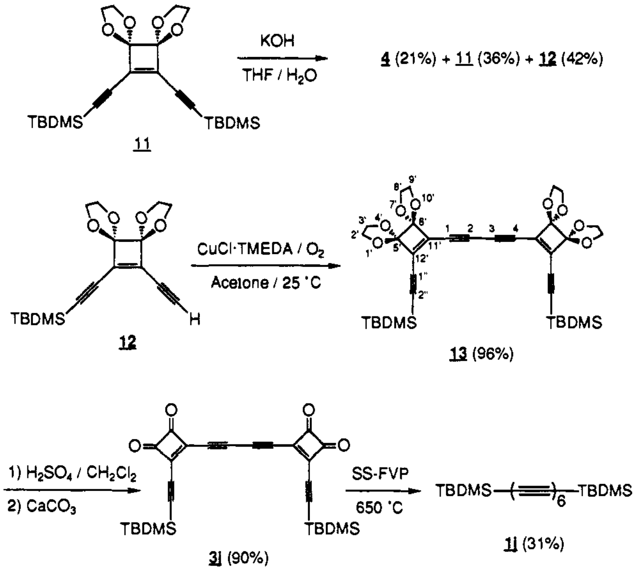
An Improved Synthesis of Silyl-Protected 1,3,5-Hexatriynes. Initially, we attempted to prepare several substituted hexatriynes by using 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (**1e**) as the starting material (Scheme II). Recently, Alberts improved the method for preparing this triyne,[20] starting from the bis(tosyl ester) of 2,4-hexadiyne-1,6-diol (**2**).[21,22] Even though greatly increased simplicity over the previous experimental procedure was achieved,[20b] the method still suffers from the low yield of crude product **1e** (16%) and the difficult purification subsequently involved.[20a] We were able to obtain a major increase in the yield of this reaction by adding the *n*-butyllithium reagent at −78 °C to the bis(tosylate) **2** *in the presence* of an excess of chlorotrimethylsilane (Scheme II). Up to 20-g quantities of pure **1e** were thus obtained in 60–75% yield after column chromatography. Furthermore, deprotection of the triyne **1e** with an excess of the methyllithium–lithium bromide complex[23] in THF (−78 → +20 °C, 3 h) and reaction of the intermediate dianion with triisopropylsilyl triflate (TIPSOTf) or *tert*-butyldiphenylsilyl chloride (TBDPS–Cl) afforded the symmetrically substituted hexatriynes **1g** and **1k**, respectively (Scheme II). However, clean and selective removal of only one trimethylsilyl group on **1e**, as described by Lewis et al.,[24] proved to be less straightforward. By using a variety of conditions (THF or diethyl ether; −78 °C or −78 → +20 °C; MeLi or MeLi·LiBr as reagents), either polymers or the disubstituted products **1g** or **1k** were obtained. In the best case, compound **1l** was prepared in 27% yield, next to unavoidable **1k** (33%, Scheme III). Similarly, monodeprotection of **1e** with MeLi·LiBr in THF at −78 °C and reaction with TIPSOTf afforded a mixture of **1i** and **1g**, which were difficult to separate (Scheme III). Although this method for the preparation of hexatriynes is straightforward, its unsatisfactory performance in the case of the unsymmetrically substituted derivatives **1i** and **1l** led us to investigate an alternative high-yielding method that is presented below.

Preparation of the 3,4-Dialkynyl-3-cyclobutene-1,2-diones. The 3-cyclobutene-1,2-diones **3b**–**3g** (Table I) were synthesized as reported earlier.[14a,25] For the preparation of the silyl derivatives **3e**–**3g**, the copper(I) acetylides of the corresponding silylated alkynes were added to $^1/_2$ equiv of 3,4-dichloro-3-cyclobutene-1,2-dione. Palladium-catalyzed coupling of the corresponding tributylstannylalkynes to this dione was the preferred method for the synthesis of the aryl and alkyl derivatives **3b**–**3d**.

Scheme V



Scheme VI



For the synthesis of dione **3h**, Cadiot–Chodkievicz coupling of the diketal **4**[14a] with 1-bromo-2-(triisopropylsilyl)acetylene (**5**)[26] in the presence of 1 equiv of *n*-butylamine gave the disubstitution product **7** next to **6** (Scheme IV). Interestingly, the use of more base in this reaction did not improve the yields. Instead, the amine-addition product **8** (Chart I) was the only product isolated when 10 equiv of *n*-butylamine were used. We observed a peculiar enhanced reactivity of systems like **4** and **6** toward addition in several instances with methanol and other nucleophiles.[16] However, deprotection of **7** with trifluoroacetic acid/water proceeded smoothly to afford dione **3h** in 99% yield.

In order to extend the scope of our method, the unsymmetrically substituted dione **3i** was prepared as a precursor for pyrolysis (Scheme V). Thus, diketal **4** was deprotonated at −78 °C with *n*-BuLi and reacted with TIPSOTf to afford the derivatives **9a** and **9b**. Compound **9a** was deprotonated once more under these conditions, and reaction of the resulting anion with TMS–Cl afforded **10**. Hydrolysis of the ketal functions of **10** with trifluoroacetic acid/water provided dione **3i** in 92% yield. This synthetic scheme demonstrates that similar functionalizations would readily give access to a number of other unsymmetrically substituted cyclobutenediones, and therefore to the corresponding hexatriynes.

Finally, we prepared the bis(dione) **3j** to assess whether 4-fold CO elimination under pyrolytic conditions could occur upon solution-spray flash vacuum pyrolysis (Scheme VI). This time, the

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(22) We encountered problems following Patel's procedure for the synthesis of the tosylate **2** (ref 21). A large amount of byproducts, presumably formed by competitive base-induced elimination of *p*-toluenesulfonic acid from **2**, always resulted when the tosylation reaction was carried at 5 °C in THF. We found that good yields of **2** (84%) could only be obtained when the addition of potassium hydroxide to a solution of 2,4-hexadiyne-1,6-diol was effected at −15 °C.

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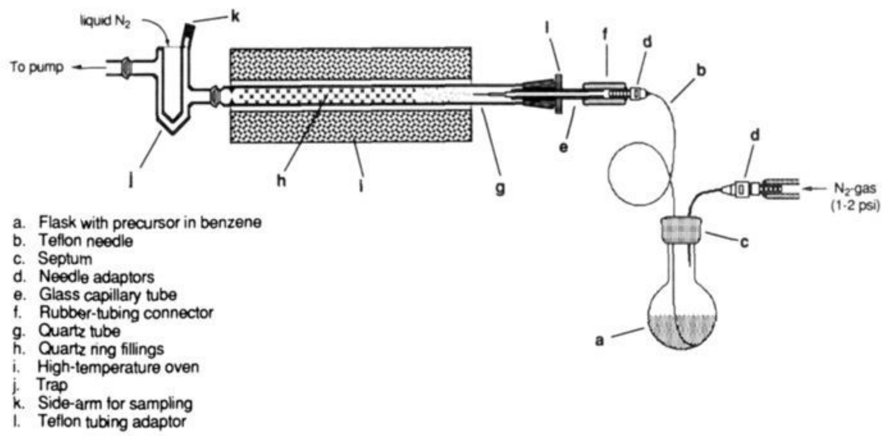

Figure 1. Schematic diagram of the solution-spray flash vacuum pyrolysis (SS-FVP) setup.

mono-protected diketal **12** was prepared through statistical deprotection of the TBDMS groups in **11**[14a] by KOH in THF/water. Diketal **4** and starting material **11** were the byproducts of this reaction. Separation by flash chromatography on silica gave the pure compounds **11**, **12**, and **4** in 36, 42, and 21% yields, respectively. The oxidative coupling of the mono(TBDMS) derivative **12** under the Hay[11c] coupling conditions proceeded in practically quantitative yield, affording the stable product **13**. The deprotection of ketal **13** could not be performed in trifluoroacetic acid/water since extensive decomposition and polymerization occurred. The reactivity of this bis(dione) is reminiscent of the high instability observed for the cyclic carbon oxides $C_{8n}O_{2n}$,[14b] and recourse to our sulfuric acid deprotection method once again gave surprisingly good results. Indeed, after stirring a dichloromethane solution of **13** with concentrated H_2SO_4, decantation, neutralization with calcium carbonate powder, and evaporation, compound **3j** was obtained in 90% yield as a dark orange oil, fully characterized by ^{1}H, ^{13}C, IR, and mass spectroscopy.

Solution-Spray Flash Vacuum Pyrolysis (SS-FVP). The conventional FVP procedure requires evaporation or sublimation of the precursor through a hot quartz tube,[19] which in our case could only be realized with the TMS-protected dione **3e** (Table I). Accordingly, when compound **3e** was sublimed at 70–110 °C (0.07 Torr) through a quartz tube filled with quartz rings and maintained at 600 °C, a quantitative yield of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (**1e**) was obtained. However, the diones **3b** and **3f** performed very poorly under these conditions. The starting materials polymerized almost completely without subliming even under high vacuum (2×10^{-5} Torr, 25–100 °C). The modified technique called "spray-pyrolysis" described by Meth-Cohn et al.[27] seemed unsuitable for our purposes, since either a liquid or a molten precursor are necessary to carry out this procedure. These researchers also noted that solutions were of no value in their pyrolyses. When we tried Fowler's "solvent-assisted sublimation",[28] appreciable amounts (up to 30%) of starting materials were always lost in the sublimation flask due to splattering on the wall and decomposition by excessive heat. Furthermore, the use of larger amounts (>2g) was always complicated by the poor conversion of the precursors.[28]

We found that the direct introduction of a solution of the compound in benzene as a *sprayed aerosol* inside a hot quartz tube maintained under a moderate vacuum (1–2 Torr) and filled with quartz rings gave conversions of the 3-cyclobutene-1,2-diones **3a**–**3j** to the corresponding alkynes **1a**–**1j** in 31–99% yield (Table I and Figure 1). Thus, diphenylacetylene **1a**[29] was prepared in 98% yield, and more significantly, triyne **1b**[30] and pentayne **1c**[31] were prepared analogously in 97 and 59% yield, respectively. In the silylated series, the triynes **1f** and **1g**,[14c] and the pentayne **1h**, are new compounds whose topochemical polymerization[1,3,4] will be studied later. Dione **3i** furnished the potentially useful unsymmetrically substituted triyne **1i** in 71% yield. Interestingly, even the bis(dione) **3j** was efficiently decarbonylated to the hexayne **1j** (31%) under these conditions. The lower yields for **1c**, **1h**, and **1j** were presumably caused by the poor volatility of the precursors and the products of decarbonylation, resulting in partial decomposition inside the hot quartz tube. Accordingly, the yield of biphenyl produced from benzene as a byproduct in these pyrolyses was proportional to the amount of material loss encountered, which can be explained by the formation of phenyl radicals from cumulene diradical intermediates.[3] However, these yields remain impressive in view of the high molecular weight and the very low thermal stability typical of compounds like **3j** (M_r = 486.7).

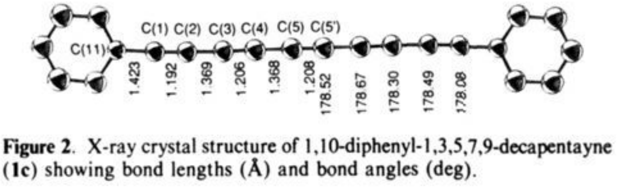

Figure 2. X-ray crystal structure of 1,10-diphenyl-1,3,5,7,9-decapentayne (**1c**) showing bond lengths (Å) and bond angles (deg).

The SS-FVP method offers the greatest advantage in that heat-sensitive and/or high molecular weight substrates, which otherwise cannot be evaporated or sublimed in the conventional FVP experiment, are converted to the desired products in up to quantitative yields. It is important that the pyrolysis quartz tube is filled with quartz rings for optimal heat transfer. As in Fowler's method, the sublimation of the solid substrate into the gas phase is assisted by the flash evaporation of benzene.[28] The scope of this method should reach far beyond the experiments described in Table I, and additional results will be reported later.

X-Ray Crystal Structure of 1,10-Diphenyl-1,3,5,7,9-decapentayne. Yellow needles of 1,10-diphenyl-1,3,5,7,9-decapentayne (**1c**) were grown by slow evaporation of a CCl_4 solution at 20 °C over 2 days. Compound **1c** crystallized in the monoclinic space group $P2_1/n$ with cell dimensions of $a = 8.805$ (2), $b = 5.218$ (1), and $c = 17.127$ (5) Å, $\beta = 94.563$ (9)°, $V = 784$ Å^3, and an occupation of $Z = 2$ in the unit cell.[32] The X-ray crystal structure of pentayne **1c** is shown in Figure 2. The C—C and C≡C bond lengths of the decapentayne moiety are within normal values for single and triple bonds in polyynes.[33] The decapentayne chain

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[27] (a) Clancy, M. G.; Hawkins, D. G.; Hesabi, M. M.; Meth-Cohn, O.; Rhouati, S. *J. Chem. Res., Synop.* **1982**, 78. (b) Clancy, M. G.; Hesabi, M. M.; Meth-Cohn, O. *J. Chem. Soc., Perkin Trans. 1* **1984**, 429–434.

[28] Magrath, J.; Fowler, F. W. *Tetrahedron Lett.* **1988**, *29*, 2171–2174.

[29] Cope, A. C.; Smith, D. S.; Cotter, R. J. *Organic Syntheses*; Wiley: New York, 1963, Collect. Vol. IV, pp 377–379.

[30] Armitage, J. B.; Entwistle, N.; Jones, E. R. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 147–154.

[31] Nakagawa, M.; Inui, T. *J. Chem. Soc. Jpn., Pure Chem. Sect.* **1952**, *73*, 143–145; *Chem. Abstr.* **1953**, *47*, 10512c.

[32] Data for **1c** ($C_{22}H_{10}$; M_r = 274.33) were collected at 20 °C on a Huber diffractometer constructed by Professor C. E. Strouse of this department, using Mo Kα radiation, to a maximum $2\theta = 50°$, giving 1378 unique reflections; the structure was solved by statistical methods (MULTAN80), yielding $R = 0.087$ and $R_w = 0.102$ for 624 independent reflections with $I > 3\sigma(I)$.

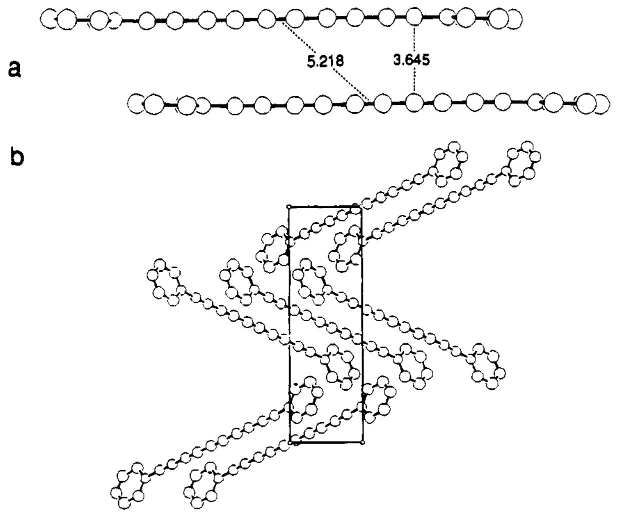

Figure 3. Crystal packing views for 1,10-diphenyl-1,3,5,7,9-decapentayne (**1c**): (a) in-plane arrangement showing the center-to-center distance and the closest distance between carbons of two neighboring decapentaynes; (b) as seen down the *a* axis of the unit cell, parallel molecules are within the same plane.

is nearly linear, the largest deviation from linearity being 1.92 (06)° for the C(02)–C(01)–C(11) angle. Views of the crystal packing structure of **1c** are shown in Figure 3. The arrangement of the molecules in the crystal is very interesting: The decapentayne units are disposed in a parallel fashion within a very close distance (Figure 3, upper). The closest distance between carbons of neighboring decapentayne chains is 3.645 Å. The center-to-center distance of two neighboring molecules is 5.218 Å. This distance is within the range of 4.7–5.2 Å found by Wegner in 1,3-diynes that undergo topochemical polymerizations.[1,4] Preliminary studies show indeed that needles of pentayne **1c** slowly polymerize between 130 and 150 °C in the air without gas evolution to a metallic black solid, retaining the original shape of the crystals. Attempts to determine the X-ray structure of a single crystal[4] of polymerized **1c** are being pursued.

In conclusion, this work describes a new simple route to the linear odd-numbered polyynes **1b–i** and the hexayne **1j** from readily available 3,4-dichloro-3-cyclobutene-1,2-dione via the stable 3,4-dialkynyl-3-cyclobutene-1,2-diones **3b–j**. The solution-spray flash vacuum pyrolysis (SS-FVP) described in this paper is a unique method for the pyrolysis of particularly nonvolatile and thermally sensitive compounds that can easily be carried out on a preparative scale. The X-ray crystal structure of 1,10-diphenyl-1,3,5,7,9-decapentayne (**1c**) shows that the molecules are favorably aligned in the crystal lattice for topochemical polymerization, a reaction that is now being investigated for all the new linear polyynes.

Experimental Section

General Procedure. All reactions were performed under argon. ^1H NMR spectra were recorded at 360 MHz and ^{13}C NMR spectra at 90.6 MHz; the solvent was $CDCl_3$ if not stated otherwise. Mass spectra were obtained at 20 eV under electron impact; *m/z* values are followed by relative intensities given in parentheses. IR spectra were measured in CCl_4 if not stated otherwise. Melting points are uncorrected. Elemental analyses were effected by Spang microanalytical laboratory, Eagle Harbor, MI, and by Desert Analytics, Tucson, AZ. Column chromatographies were made on silica gel 70–230 mesh or 230–400 mesh (flash) from E. Merck; thin-layer chromatographies (TLC) were all performed on plastic sheets coated with silica gel 60 F_{254} from E. Merck. Reaction workup included separation of the product-containing organic phase from aqueous layers, drying with $MgSO_4$, and evaporation of the solvent in vacuo.

Materials. Reagents and solvents used were reagent grade. *n*-Butylamine and CH_2Cl_2 were distilled over CaH_2 and tetrahydrofuran (THF) and Et_2O over sodium/benzophenone ketyl prior to use. DMF was dried over alumina activity 1 and maintained under vacuum for 5 min to remove amine impurities. Benzene was stored over molecular sieves (4 Å).

Synthesis. 1,6-Bis(*p*-toluenesulfonyloxy)-2,4-hexadiyne (2).[21] To a solution of 27.58 g (0.25 mol) of 2,4-hexadiyne-1,6-diol[13b] and 96.67 g (0.51 mol) of tosyl chloride in 1 L of THF was added dropwise at −15 °C a cold solution (0 °C) of 28.30 g (0.5 mol) of KOH in 80 mL of water. After 2 h, more KOH (11.15 g, 0.2 mol) was added in the same fashion over 1 h. After stirring further at −15 °C for 1 h, ice-cold water was added: 88.20 g (84%) of **2** as unstable pale pink crystals; ^1H NMR δ 2.45 (s, 6 H, CH_3), 4.73 (s, 4 H, CH_2), 7.36 (d, 4 H, J = 8.2 Hz, 3,5-H_{Pb}), 7.79 (d, 4 H, J = 8.2 Hz, 2,6-H_{Pb}); ^{13}C NMR δ 21.3, 57.3, 71.6, 72.1, 127.7, 129.8, 132.1, 145.4.

1,6-Bis(trimethylsilyl)-1,3,5-hexatriyne (1e). (a) From 1,6-Bis(*p*-toluenesulfonyloxy)-2,4-hexadiyne (2).[20a] To a solution of 54.40 g (0.13 mol) of **2** and 70.62 g (0.65 mol, 82.5 mL) of Me_3SiCl in 1.5 L of dry THF at −78 °C was added 375 mL (0.60 mol) of a 1.6 M solution of *n*-BuLi in hexane over 3 h. The brown solution was allowed to warm to −30 °C and quenched with saturated NH_4Cl. Workup and chromatography (hexane) afforded 16.70 g (59%; 73% on a 2-g scale) of **1e**: mp 64–66 °C (lit.[20a] mp 58–61 °C); IR ν (C≡C) 2160; ^1H NMR δ 0.21; ^{13}C NMR δ −0.6, 61.9, 87.4, 87.9; MS 218 (28, M^+), 203 (100, $M^+ - CH_3$).

(b) By Flash Vacuum Pyrolysis of 3,4-Bis[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione (3e). Compound **3e**[14a] (62.4 mg, 0.227 mmol) was sublimed over 3 h at 70–110 °C/0.07 Torr through a quartz tube packed with quartz rings and heated at 600 °C: 49.2 mg (99%) of **1e**.

1,6-Bis(triisopropylsilyl)-1,3,5-hexatriyne (1g). To a solution of 570.1 mg (2.6 mmol) of **1e** in 20 mL of THF at −78 °C was added dropwise 4.0 mL (6.0 mmol) of a 1.48 M solution of MeLi·LiBr in Et_2O. After 30 min, the solution was slowly warmed to 0 °C and stirred further for 1 h. TIPSOTf (1.84 g, 6.0 mmol, 1.6 mL) was added at once, and after 30 min at 20 °C, the yellow-brown solution was washed with saturated NH_4Cl. Workup and recrystallization gave 642.4 mg (64%) of **1g**: mp 148–149 °C (MeOH); IR ν (C≡C) 2150 cm^{-1}; ^1H NMR δ 1.0–1.1; ^{13}C NMR δ 11.3, 18.5, 61.3, 84.5, 89.8; MS 386 (12, M^+), 343 (100, $M^+ - C_3H_7$). Anal. Calcd for $C_{24}H_{42}Si_2$ (386.8): C, 74.53; H, 10.95. Found: C, 74.38; H, 11.06.

1-(Triisopropylsilyl)-6-(trimethylsilyl)-1,3,5-hexatriyne (1i). To a solution of 729.3 mg (3.34 mmol) of **1e** in 50 mL of THF was added dropwise 2.3 mL (3.4 mmol) of a 1.48 M solution of MeLi·LiBr in Et_2O at −78 °C. The solution was stirred for 3 h at −78 °C, and allowed to warm to 0 °C. TIPSOTf (1.04 g, 3.4 mmol, 0.91 mL) was added at once, and after 12 h at 20 °C, the pale brown solution was washed with saturated NH_4Cl. Workup and chromatography (hexane) gave 318.4 mg (25%) of **1g**. A second fraction afforded 124.8 mg (12%) of **1i** as a colorless oil containing 5–10% of 1-(triisopropylsilyl)-1,3,5-hexatriyne as an impurity arising from hydrolysis of **1i** on SiO_2. Chromatography on Florisil with hexane gave analytically pure material: IR ν (C≡C) 2157 cm^{-1}; ^1H NMR δ 0.20 (s, 9 H), 1.08 (m, 21 H); ^{13}C NMR δ −0.58, 11.2, 18.5, 60.9, 62.4, 85.1, 87.0, 88.0, 89.6; MS 302 (18, M^+), 259 (100, $M^+ - C_3H_7$); HRMS *m/z* (M^+, $C_{18}H_{30}Si_2$) calcd 302.1886, obsd 302.1885.

1,6-Bis(*tert*-butyldiphenylsilyl)-1,3,5-hexatriyne (1k). To a solution of 493 mg (2.25 mmol) of **1e** in 25 mL of THF at −78 °C, 3.35 mL (4.95 mmol) of a 1.48 M solution of MeLi·LiBr in Et_2O was added dropwise. After stirring for 1.5 h, 1.36 g (5.0 mmol, 1.3 mL) of TBDPS–Cl was added at 0 °C. The solution was stirred further overnight at 20 °C, quenched with a mixture of pentane and saturated NH_4Cl, and washed with saturated NaCl. Workup followed by flash chromatography (hexane) and recrystallization yielded 656 mg (52%) of **1k** as white needles: mp 126–127 °C (hexane); IR ν (C≡C) 2159 cm^{-1}; ^1H NMR δ 1.15 (s, 18 H), 7.35–7.45 (m, 12 H), 7.75–7.8 (m, 8 H); ^{13}C NMR δ 19.0, 27.0, 62.5, 83.7, 91.4, 127.9, 129.9, 131.9, 135.5; MS 550 (6, M^+), 493 (100, $M^+ - C_4H_9$). Anal. Calcd for $C_{38}H_{38}Si_2$ (550.9): C, 82.85; H, 6.95. Found: C, 82.96; H, 6.91.

1-(*tert*-Butyldiphenylsilyl)-6-(trimethylsilyl)-1,3,5-hexatriyne (1l). To a solution of 1.30 g (5.9 mmol) of **1e** in 50 mL of THF at −78 °C, 4.0 mL (5.9 mmol) of a 1.48 M solution of MeLi·LiBr in Et_2O was added dropwise. After 1.5 h of stirring, 1.82 g (6.6 mmol, 1.72 mL) of TBDPS–Cl was added at −78 °C. The solution was stirred overnight at 20 °C, quenched with saturated NH_4Cl, and washed with saturated NaCl. Workup and flash chromatography (hexane) gave 626 mg (27%) of **1l** as a brown oil: IR ν (C≡C) 2159 cm^{-1}; ^1H NMR δ 0.24 (s, 9 H), 1.13 (s, 9 H), 7.35–7.45 (m, 6 H), 7.77 (dd, J = 7.5 and 1.4 Hz, 4 H); ^{13}C NMR δ −0.6, 19.0, 27.0, 62.1, 62.4, 83.1, 87.8, 88.1, 91.5, 127.9, 129.9, 131.9, 135.5; MS 384 (7, M^+), 327 (100, $M^+ - C_4H_9$); HRMS *m/z* (M^+, $C_{25}H_{28}Si_2$) calcd 384.1730, obsd 384.1732. A second fraction yielded 1.07 g (33%) of **1k**.

1-Bromo-2-(triisopropylsilyl)ethyne (5). To a solution of 10.4 g (57 mmol) of TIPS-acetylene and 11.2 g (63 mmol) of NBS in 350 mL of acetone was added 50 mg (0.3 mmol) of $AgNO_3$.[26b] The solution was

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(33) Dale, J. In *The Chemistry of Acetylenes*; Viehe, H. G., Ed.; M. Dekker: New York, 1969; Chapter 1, pp 3–96.

stirred at 20 °C for 2 h, poured into ice–water/pentane, and washed with saturated NaCl. Workup afforded 15.1 g (96%) of **5** as a colorless liquid: IR ν ($C\equiv C$) 2120 cm^{-1}; ^{1}H NMR δ 1.0–1.1; ^{13}C NMR δ 11.3, 18.5, 61.7, 83.4.

11,12-Bis[4-(triisopropylsilyl)-1,3-butadiynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (7) and 12-Ethynyl-11-[4-(triisopropylsilyl)-1,3-butadiynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (6). To a stirred solution of 522 mg (2.39 mmol) of **4**[14a] in 20 mL of DMF were added sequentially 500 mg (7.2 mmol) of $NH_2OH \cdot HCl$, 600 mg, (6.1 mmol) of CuCl, 0.3 mL (222 mg, 3.0 mmol) of *n*-butylamine, and 1.36 g (5.2 mmol) of **5**. After 24 h of stirring at 20 °C, the solution was poured into H_2O/Et_2O and washed with more water and saturated NaCl. Workup followed by flash chromatography (CH_2Cl_2/hexane, 2:1) gave 359 mg (26%) of **7**: mp 132–134 °C; IR ν ($C\equiv C$) 2250, 2097 cm^{-1}; ^{1}H NMR δ 1.0–1.1 (m, 42 H), 3.95–4.05 (m, 4 H), 4.05–4.2 (m, 4 H); ^{13}C NMR δ 11.2, 18.5, 65.1, 66.1, 87.2, 88.7, 95.2, 115.8, 137.2; MS 578 (100, M$^+$). Anal. Calcd for $C_{34}H_{50}O_4Si_2$ (578.95): C, 70.54; H, 8.71. Found: C, 70.45; H, 8.63. As the second fraction, 208 mg (22%) of **6** were obtained as yellow needles: mp >105 °C (dec); IR ν ($\equiv C-H$) 3306, ($C\equiv C$) 2094 cm^{-1}; ^{1}H NMR δ 1.05–1.1 (m, 21 H), 3.67 (s, 1 H), 4.0–4.1 (m, 4 H), 4.1–4.2 (m, 4 H); ^{13}C NMR (gated decoupling) δ 11.1 (dm, ^1J = 119.8 Hz, ^2J = 3.8 Hz, $CH(CH_3)_2$), 18.4 (qm, ^1J = 126.4 Hz, $CH(CH_3)_2$), 64.6 (s), 66.06 (t, ^1J = 151.4 Hz, OCH_2), 66.08 (t, ^1J = 151.3 Hz, OCH_2), 73.7 (d,^2J = 49.8 Hz, C-1″), 86.2 (s), 88.6 (s), 90.7 (d, ^1J = 256.0 Hz, C-2″), 94.4 (s), 115.4 and 115.6 (2 × m, C-6, C-5), 136.2 (d, ^4J = 2.3 Hz, C-11), 137.6 (d, ^3J = 4.9 Hz, C-12); MS 398 (100, M$^+$); HRMS *m/z* (M$^+$, $C_{23}H_{30}O_4Si$) calcd 398.1913, obsd 398.1928.

11-[(*E*)-2-(*n*-Butylamino)ethenyl]-12-[4-(triisopropylsilyl)-1,3-butadiynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (8). A mixture of 282 mg (1.3 mmol) of **4**[14a] in 100 mL of DMF, 784 mg (3.0 mmol) of **5**, 21 mg (0.3 mmol) of $NH_2OH \cdot HCl$, 731 mg (10 mmol, 1.0 mL) of *n*-butylamine, and 30 mg (0.3 mmol) of CuCl was reacted as described for **6**. Workup followed by flash chromatography (hexane and hexane/EtOAc, 95:5) and recrystallization gave 116 mg (19%) of **8** as yellow crystals: mp 96–97 °C (hexane); IR ν ($N-H$) 3387, ($C\equiv C$) 2172, 2087 cm^{-1}; ^{1}H NMR δ 0.94 (t, J = 7.4 Hz, 3 H, 4-H_{Bu}), 1.08 (m, 21 H, TIPS), 1.37 (sext, J = 7.4 Hz, 2 H, 3-H_{Bu}), 1.55 (quint, J = 7.4 Hz, 2 H, 2-H_{Bu}), 3.04 (q, $J \approx$ 7.0 Hz, 2 H, 1-H_{Bu}), 3.85–3.9 (m, 2 H, OCH_2CH_2O), 3.95–4.0 (m, 2 H, OCH_2CH_2O), 4.05–4.1 (m, 2 H, OCH_2CH_2O), 4.1–4.15 (m, 2 H, OCH_2CH_2O), 4.63 (q, $J \approx$ 7.0 Hz, 1 H, NH), 5.03 (d, J = 13.6 Hz, 1 H, 1′-H), 7.07 (dd, J = 13.6 and 7.8 Hz, 1 H, 2′-H); ^{13}C NMR (gated decoupling) δ 11.3 (dm, ^1J = 123.7 Hz, $CH(CH_3)_2$), 13.7 (qt, ^1J = 125.0 Hz; ^2J = 4.0 Hz, C-4_{Bu}), 18.5 (qm, ^1J = 126.3 Hz, $CH(CH_3)_2$), 20.0 (tm, ^1J = 121.6 Hz, C-3_{Bu}), 31.0 (tm, ^1J = 126 Hz, C-2_{Bu}), 43.4 (br t, ^1J = 136 Hz, C-1_{Bu}), 65.3 (t, ^1J = 150.1 Hz, OCH_2), 65.5 (t, ^1J = 148.1 Hz, OCH_2), 68.7 (s), 81.7 (s), 87.7 (d, ^1J = 155.6 Hz, C-1′), 89.6 (s), 90.2 (s), 109.0 (d, ^2J = 4.4 Hz, C-11), 114.2 (m, C-5), 115.0 (sext, ^3J = 3.2 Hz, C-6), 144.9 (d, ^1J = 164.3 Hz, C-2′), 156.0 (d, ^3J = 4.7 Hz, C-12); MS 471 (100, M$^+$). Anal. Calcd for $C_{27}H_{41}NO_4Si$ (471.72); C, 68.75; H, 8.76; N, 2.97. Found: C, 68.66; H, 8.59; N, 3.12.

3,4-Bis[4-(triisopropylsilyl)-1,3-butadiynyl]-3-cyclobutene-1,2-dione (3h). A solution of 202 mg (0.35 mmol) of **7** in 10 mL of CF_3COOH and 1 mL of H_2O was stirred for 6 h at 20 °C. The solution was diluted with CH_2Cl_2 and washed with water and twice with saturated $NaHCO_3$. Workup yielded 169 mg (99%) of **3h** as a slightly unstable dark orange oil: IR ν ($C\equiv C$) 2196, 2170, 2095, ($C=O$) 1786 cm^{-1}; ^{1}H NMR δ 1.1–1.15; ^{13}C NMR δ 11.2, 18.5, 61.2, 87.7, 110.1, 110.7, 178.8, 194.9; MS 490 (25, M$^+$), 391 (100, M$^+$ – 2 CO, – C_3H_7); HRMS *m/z* (M$^+$, $C_{30}H_{42}O_2Si_2$) calcd 490.2723, obsd 490.2696.

12-Ethynyl-11-[(triisopropylsilyl)ethynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (9a) and 11,12-Bis[(triisopropylsilyl)ethynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (9b). To a solution of 359.7 mg (1.65 mmol) of **4**[14a] in 50 mL of THF at –78 °C was added dropwise 1.03 mL (1.65 mmol) of a 1.6 M solution of *n*-BuLi in hexane. After 15 min at –78 °C, 521 mg (1.7 mmol, 0.46 mL) of TIPSOTf was added at once. The solution was stirred for 30 min at 20 °C and poured into a mixture of hexane/water. Workup and flash chromatography (hexane/EtOAc, 9:1 and then 8:2) gave 119.0 mg (14%) of **9b** as a colorless oil: IR ν ($C\equiv C$) 2133 cm^{-1}; ^{1}H NMR δ 1.05–1.1 (m, 42 H), 4.0–4.2 (m, 4 H), 4.1–4.2 (m, 4 H); ^{13}C NMR δ 11.0, 18.4, 65.8, 96.4, 105.5, 115.0, 136.3; MS 530 (100, M$^+$). Anal. Calcd for $C_{30}H_{50}O_4Si_2$ (530.90): C, 67.87; H, 9.49. Found: C, 67.80; H, 9.69. A second fraction afforded 433.7 mg (70%) of **9a** as colorless plates: mp 119–120 °C (hexane); IR ν ($\equiv CH$) 3307, ($C\equiv C$) 2138 cm^{-1}; ^{1}H NMR δ 1.05–1.1 (m, 21 H), 3.55 (s, 1 H), 4.0–4.1 (m, 4 H), 4.1–4.2 (m, 4 H); ^{13}C NMR (gated decoupling) δ 11.0 (d, ^1J = 119.8 Hz, $CH(CH_3)_2$), 18.4 (qm, ^1J = 126 Hz, $CH(CH_3)_2$), 65.93 (t, ^1J = 151.2 Hz, OCH_2), 65.95 (t, ^1J = 151.0 Hz, OCH_2), 73.6 (d, ^2J = 49.9 Hz, C-1″), 89.0 (d, ^1J = 255.2 Hz, C-2″), 95.9 (s, C-1′), 106.5 (s, C-2′), 115.0 (m, C-6), 115.2 (m, C-5), 133.9 (d, ^3J = 4.8 Hz, C-12), 138.3 (d, ^4J = 2.4 Hz, C-11); MS 374 (100, M$^+$). Anal. Calcd for $C_{21}H_{30}O_4Si$ (374.56): C, 67.34; H, 8.07. Found: C, 67.54; H, 7.85.

11-[(Triisopropylsilyl)ethynyl]-12-[(trimethylsilyl)ethynyl]-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (10). To a solution of 133.1 mg (0.355 mmol) of **9a** in 30 mL of THF at –78 °C was added 0.22 mL (0.35 mmol) of a 1.6 M solution of *n*-BuLi in hexane. The reaction mixture was stirred at –78 °C for 30 min, and 54.3 mg (0.5 mmol, 63 μL) of TMSCl was added. After 30 min, the solution was allowed to warm to 20 °C and poured into hexane/saturated NH_4Cl. Workup and flash chromatography (CH_2Cl_2 and then CH_2Cl_2/EtOAc, 95:5) gave 113 mg (70%) of **10** as a colorless oil: IR ν ($C\equiv C$) 2134 cm^{-1}; ^{1}H NMR δ 0.20 (s, 9 H), 1.09 (m, 21 H), 4.0–4.1 (m, 4 H), 4.1–4.2 (m, 4 H); ^{13}C NMR δ –0.5, 11.0, 18.5, 65.9, 91.1, 96.4, 106.1, 108.6, 115.0, 115.1, 135.6, 137.4; MS *m/z* 446 (100, M$^+$). Anal. Calcd for $C_{24}H_{38}O_4Si_2$ (446.74): C, 64.53; H, 8.57. Found: C, 64.93; H, 8.44.

3-[(Triisopropylsilyl)ethynyl]-4-[(trimethylsilyl)ethynyl]-3-cyclobutene-1,2-dione (3i). A solution of 70.3 mg (0.157 mmol) of **10** in 6 mL of CF_3COOH and 0.5 mL of water was stirred at 20 °C for 2 h. The solvent was removed in vacuo below 20 °C, and the residue was redissolved in hexane and extracted twice with saturated $NaHCO_3$. Workup afforded 52.1 mg (92%) of **3i** as a pale yellow oil: IR ν ($C\equiv C$) 2160, ($C=O$) 1790 cm^{-1}; ^{1}H NMR δ 0.31 (s, 9 H), 1.1–1.2 (m, 21 H); ^{13}C NMR δ –0.9, 10.9, 18.5, 90.5, 92.7, 134.3, 135.8, 180.3, 180.5, 195.2, 195.5; MS 358 (36, M$^+$), 259 (100, M$^+$ – C_3H_7, – 2 CO); HRMS *m/z* (M$^+$, $C_{20}H_{30}O_2Si_2$) calcd 358.1784, obsd 358.1785.

11-[(*tert*-Butyldimethylsilyl)ethynyl]-12-ethynyl-1,4,7,10-tetraoxadispiro[4.0.4.2]dodec-11-ene (12). A solution of 5.25 g (11.7 mmol) of **11**[14a] in 100 mL of THF containing 1 mL (2 mmol) of 2.0 M KOH in water was stirred at 20 °C for 9 h. The solution was then poured into saturated NH_4Cl/Et_2O, washed with saturated NaCl, and worked up. Flash chromatography (10–50% of EtOAc in hexane) afforded first 1.891 g (36%) of **11**.[14a] Fraction 2 contained 1.620 g (42%) of **12** as off-white plates: mp 115–116 °C (hexane); IR ν ($\equiv CH$) 3306, ($C\equiv C$) 2140 cm^{-1}; ^{1}H NMR δ 0.15 (s, 6 H), 0.95 (s, 9 H), 3.55 (s, 1 H), 4.0–4.1 (m, 4 H), 4.1–4.2 (m, 4 H); ^{13}C NMR δ –5.1, 16.5, 25.9, 65.87, 65.88, 73.5, 89.3, 94.4, 107.9, 115.0, 115.2, 134.4, 137.7; MS 332 (100, M$^+$). Anal. Calcd for $C_{18}H_{24}O_4Si$ (332.48): C, 65.03; H, 7.28. Found: C, 65.17; H, 7.26. Fraction 3 gave 540 mg (21%) of **4**.[14a]

1,4-Bis[12-[(*tert*-butyldimethylsilyl)ethynyl]-1,4,7,10-tetraoxadispiro-[4.0.4.2]-11-dodecen-11-yl]-1,3-butadiyne (13). To a solution of 1.50 g (4.51 mmol) of **12** in 40 mL of acetone was added 15.0 mL (4.5 mmol) of a freshly prepared 0.3 M solution of CuCl·TMEDA in acetone.[34] The reaction mixture was stirred vigorously under oxygen for 30 min and poured into CH_2Cl_2/water, and the organic phase was washed with saturated $NaHCO_3$. Workup gave 1.433 g (96%) of **13** as yellow platelets: mp 181.5–182.5 °C (hexane); IR ν ($C\equiv C$) 2129 cm^{-1}; ^{1}H NMR δ 0.17 (s, 12 H), 0.95 (s, 18 H), 4.0–4.1 (m, 8 H), 4.1–4.2 (m, 8 H); ^{13}C NMR δ –5.1, 16.6, 25.9, 66.0 (for both OCH_2CH_2O), 75.4, 84.1, 94.8, 110.2, 115.39, 115.45, 133.3, 139.5; MS 662 (4, M$^+$), 446 (100). Anal. Calcd for $C_{36}H_{46}O_8Si_2$ (662.93): C, 65.23; H, 6.99. Found: C, 65.06; H, 6.83.

1,4-Bis[4-[(*tert*-butyldimethylsilyl)ethynyl]-1,2-dioxo-3-cyclobuten-3-yl]-1,3-butadiyne (3j). A solution of 679 mg (1.02 mmol) of **13** in 100 mL of CH_2Cl_2 was stirred vigorously with 4 mL of 96% H_2SO_4 for 20 h at 20 °C in the dark. The upper CH_2Cl_2 layer was decanted into another flask and stirred with dry $CaCO_3$ powder. The deep red solution was filtered and evaporated to give 446 mg (90%) of **3j** as a dark orange oil: IR ν ($C\equiv C$) 2145, ($C=O$) 1790 cm^{-1}; ^{1}H NMR δ 0.29 (s, 12 H), 1.02 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ –5.4, 16.7, 25.9, 80.4, 91.4, 103.7, 139.5, 175.5, 180.1, 192.7, 193.8; MS 486 (28, M$^+$), 147 (100); HRMS *m/z* (M$^+$, $C_{28}H_{30}O_4Si_2$) calcd 486.1683, obsd 486.1702.

General Procedure for Solution-Spray Flash Vacuum Pyrolysis (SS-FVP). The apparatus for SS-FVP experiments is assembled from four components (Figure 1): (1) Flask (a) contains the solution of the starting material. (2) A 1-mm inner diameter (6-mm outer diameter, 20-cm-long) capillary glass tube (e) is drawn into a fine capillary in the standard manner and then cut at the fine portion to a length of 5–7 cm. It is then inserted through a conventional thermometer adaptor or a pierced rubber stopper (l) fitting the quartz tube (g). The other end of the capillary tube (e) is attached with connector (f) to the needle adaptor (d) and the teflon needle (b) passing through the punctured septum (c) placed on flask (a). (3) The quartz tube (g) (20-mm outer diameter, 36-cm-long), filled with quartz rings (h, 4 mm by ~6-mm length) to two-thirds of its length, is heated to 650 °C in the high-temperature oven (i). It is essential to use quartz fillings to increase the contact time of the substrate. Otherwise, a large quantity of the starting material is usually recovered. (4) The

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

trap (j) is used in this setup to avoid the condensation of products on the walls of the quartz tube (g) in proximity to the oven. This problem occurs particularly when concentrated solutions (~0.1 M) and/or high molecular weight compounds are used. The side arm (k) on the trap is designed for easy sampling of the benzene solution collected in the trap.

To perform the SS-FVP experiment, nitrogen gas (100 mmHg reading at pressure gauge) was entered into flask (a) with the teflon needle (b) staying *above* the liquid level. The pyrolysis apparatus is placed under the vacuum of a mechanical pump, and the trap (j) is filled with liquid nitrogen. The quartz tube (g) is then heated in the oven (i). When the temperature reaches 650 °C (measured with an external iron–constantan thermocouple), the teflon needle (b) is placed below the level of the solution in flask (a), and rapid aspiration of the solution through the capillary occurs. As soon as the liquid reaches the tip of the capillary, a sprayed aerosol forms inside the hot tube. The products of pyrolysis condense together with benzene in the trap (j). Solutions in benzene can be relatively concentrated (up to 0.1 M). However, solutions of unstable and/or oily precursors tend to easily clog the capillary tube if they are >0.02 M. The tip of the capillary (e) should not be allowed to reach inside the oven, otherwise charring from the extreme heat and consequently clogging always occurs. At the end of the addition, a few milliliters of fresh solvent are added with a syringe to the flask (a) to complete the transfer of the starting material to the pyrolysis tube. After cooling of the oven (i), the products along with frozen benzene are allowed to thaw under nitrogen, collected, and worked up. Any black deposits inside the quartz tube are most conveniently removed by heating the tube under oxygen at normal pressure (balloon) between 25 and 700 °C. The poliynes were purified by flash chromatography on SiO_2 (**1a**–**1h** and **1j**) or on Florisil (**1i**). A mixture of hexane/CH_2Cl_2 (1:1) was the solvent in the separation of **1b** and **1c**; pure hexane was used in all other runs. Solid poliynes were further purified by recrystallization.

Diphenylacetylene (1a). Pyrolysis of 268 mg (1.14 mmol) of **3a**[25] in 10 mL of benzene gave 200 mg (98%) of **1a** as colorless crystals: mp 58.5–59 °C (lit.[29] mp 60–61 °C); ^1H NMR δ 7.3–7.35 (m, 6 H), 7.5–7.55 (m, 4 H); ^{13}C NMR δ 89.4, 123.2, 128.2, 128.3, 131.6.

1,6-Diphenyl-1,3,5-hexatriyne (1b). A total of 282 mg (1 mmol) of **3b**[14a] in 20 mL of benzene afforded 200 mg (88%) of **1b** as white needles: mp 91–92 °C (hexane; lit.[30] mp 96 °C); IR ν ($C\equiv C$) 2255, 2200 cm^{-1}; ^1H NMR δ 7.25–7.35 (m, 6 H, 2,4-H), 7.45–7.5 (m, 4 H, 3-H); ^{13}C NMR δ 66.5, 74.4, 78.6, 120.8, 128.4, 129.6, 132.9; MS 226 (100, M$^+$); HRMS *m/z* (M$^+$, $C_{18}H_{10}$) calcd 226.0773, obsd 226.0783.

1,10-Diphenyl-1,3,5,7,9-decapentayne (1c). The reaction of 55.0 mg (0.167 mmol) of **3c**[14a] in 10 mL of benzene gave 27.0 mg (59%) of **1c** as yellow needles (from CCl_4),[31] polymerizing between 130 and 150 °C in the air: IR ($CHCl_3$) ν ($C\equiv C$) 2175, 2075 cm^{-1}; ^1H NMR δ 7.3–7.35 (m, 4 H, 3-H), 7.4–7.45 (m, 2 H, 4-H), 7.5–7.55 (m, 4 H, 2-H); ^{13}C NMR δ 62.8, 64.4, 67.3, 74.4, 77.4, 120.2, 128.6, 130.2, 133.3; MS 274 (100, M$^+$); HRMS *m/z* (M$^+$, $C_{22}H_{10}$) calcd 274.0794, obsd 274.0783.

4,6,8-Dodecatriyne (1d). The reaction of 500 mg (2.3 mmol) of **3d**[14a] in 10 mL of benzene yielded 288 mg (78%) of **1d** as a colorless oil; IR (neat) ν ($C\equiv C$) 2214 cm^{-1}; ^1H NMR δ 0.99 (t, J = 7.4 Hz, 6 H, 1,12-H), 1.56 (sext, $J \approx 7.0$ Hz, 4 H, 2,11-H), 2.26 (t, J = 6.9 Hz, 4 H, 3,10-H); ^{13}C NMR δ 13.4, 21.3, 21.6, 60.3, 65.8, 79.1; MS 158 (99, M$^+$), 128 (100, M$^+$ – 2 CH_3); HRMS *m/z* (M$^+$, $C_{12}H_{14}$) calcd 158.1096, obsd 158.1091.

1,6-Bis(*tert*-butyldimethylsilyl)-1,3,5-hexatriyne (1f). The pyrolysis of 79.4 mg (0.22 mmol) of **3f**[14a] in 5 mL of benzene afforded 66.4 mg (99%) of **1f** as white crystals: mp 154–155.5 °C; IR ν ($C\equiv C$) 2155 cm^{-1}; ^1H NMR δ 0.14 (s, 12 H), 0.94 (s, 18 H); ^{13}C NMR δ –4.9, 16.8, 26.0, 61.7, 86.2, 88.6; MS 302 (16, M$^+$), 245 (100, M$^+$ – C_4H_9). Anal. Calcd for $C_{18}H_{30}Si_2$ (302.6): C, 71.45; H, 9.99. Found: C, 71.56; H, 10.11.

1,6-Bis(triisopropylsilyl)-1,3,5-hexatriyne (1g). The reaction of 3.60 g (8.13 mmol) of **3g**[14a] in 40 mL of benzene afforded 2.15 g (69%; 95% on a 0.5-g scale) of **1g**.

1,10-Bis(triisopropylsilyl)-1,3,5,7,9-decapentayne (1h). Pyrolysis of 26.8 mg (0.055 mmol) in **3h** in 40 mL of benzene gave 10.0 mg (42%) of **1h** as a light-sensitive yellow oil: IR ν ($C\equiv C$) 2098 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.05–1.15; ^{13}C NMR (CD_2Cl_2) δ 11.6, 18.6, 61.2, 62.5, 62.6, 87.4, 89.5; MS 434 (26, M$^+$), 391 (100, M$^+$ – C_3H_7); HRMS *m/z* (M$^+$, $C_{28}H_{42}Si_2$) calcd 434.2825, obsd 434.2806.

1-(Triisopropylsilyl)-6-(trimethylsilyl)-1,3,5-hexatriyne (1i). The reaction of 49.8 mg (0.138 mmol) of **3i** in 6 mL of benzene gave 30.0 mg (71%) of **1i**.

1,12-Bis(*tert*-butyldimethylsilyl)-1,3,5,7,9,11-dodecahexayne (1j). Pyrolysis of 399.6 mg (0.82 mmol) of **3j** in 20 mL of benzene gave 94.4 mg (31%) of **1j** as light-sensitive yellow crystals: mp 122–124 °C (dec); IR ν ($C\equiv C$) 2171, 2128, 2032 cm^{-1}; ^1H NMR δ 0.15 (s, 12 H), 0.95 (s, 18 H); ^{13}C NMR ($CDCl_3$/benzene-d_6 2:1) δ –5.2, 16.7, 25.8, 61.8, 62.52, 62.56, 62.65, 87.9, 88.4; MS 374 (34, M$^+$), 317 (100, M$^+$ – C_4H_9). Anal. Calcd for $C_{24}H_{30}Si_2$ (374.68): C, 76.94; H, 8.07. Found: C, 76.63; H, 8.12.

Acknowledgment. We thank the National Science Foundation for support of this work.

Registry No. **1a**, 501-65-5; **1b**, 20264-56-6; **1c**, 20264-57-7; **1d**, 134816-74-3; **1e**, 21752-86-3; **1f**, 134816-75-4; **1g**, 111409-80-4; **1h**, 134816-76-5; **1i**, 134816-77-6; **1j**, 134816-78-7; **1k**, 134816-79-8; **1l**, 134816-80-1; **2**, 32527-15-4; **3a**, 59973-06-7; **3b**, 125358-17-0; **3c**, 125358-34-1; **3d**, 125358-35-2; **3e**, 123002-90-4; **3f**, 123002-89-1; **3g**, 125358-37-4; **3h**, 134816-71-0; **3i**, 134816-72-1; **3j**, 134816-73-2; **4**, 123002-93-7; **5**, 111409-79-1; **6**, 134816-64-1; **7**, 134816-65-2; **8**, 134816-66-3; **9a**, 134816-67-4; **9b**, 134816-81-2; **10**, 134816-68-5; **11**, 123002-92-6; **12**, 134816-69-6; **13**, 134816-70-9; 2,4-hexadiyne-1,6-diol, 36060-65-8.

Supplementary Material Available: Experimental details of the crystal structure determination for **1c** and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (6 pages); table of calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.