56. 1,1,2,2-Tetraethynylethanes: Synthons for Tetraethynylethenes and Modules for Acetylenic Molecular Scaffolding

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Dedicated to *Nikolai S. Zefirov* on the occasion of his 60th birthday

(18.I.96)

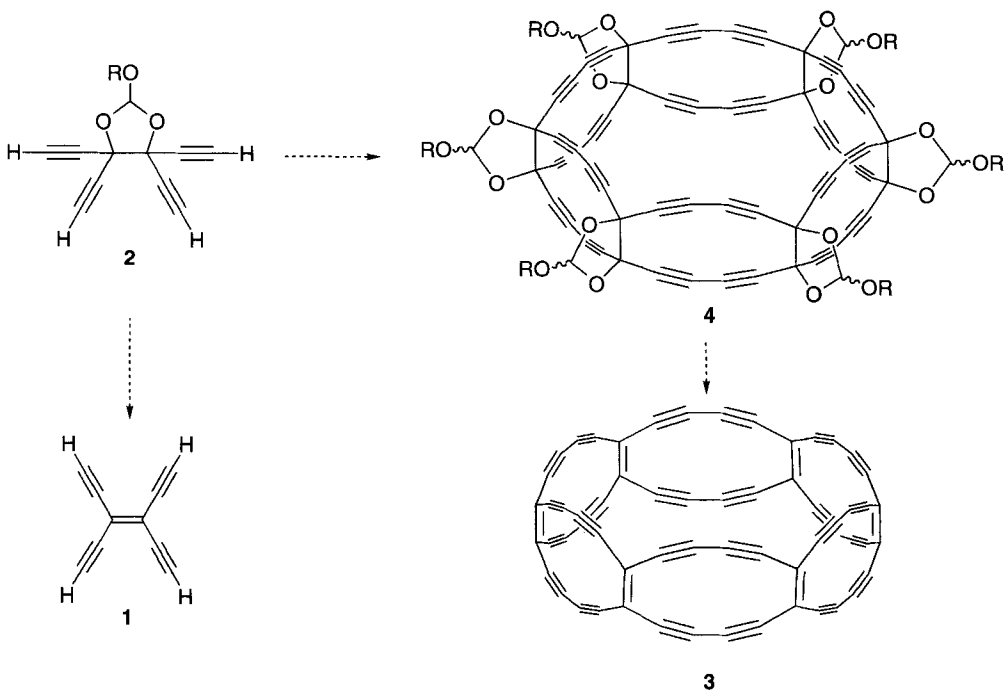
The synthesis of functionalized 1,1,2,2-tetraethynylethanes (= 3,4-diethynylhexa-1,5-diynes) as synthons for tetraethynylethenes (3,4-diethynylhex-3-ene-1,5-diynes) and as building blocks for three-dimensional acetylenic molecular scaffolding targeting the synthesis of the molecular carbon belts **3** and **4** is reported (*Scheme 1*). Reaction of diethyl oxalate and (trialkylsilyl)ethynyl *Grignard* reagents afforded the silyl-protected 3,4-diethynylhexa-1,5-diyne-3,4- diols **7** and **8** which were transformed in high yields into the cyclic carbonate **9** and the cyclic orthoesters **10**–**13**, respectively (*Scheme 2*). The solid-state structures of **9** and **10** were elucidated by X-ray crystallography. The alkyne protecting groups in **9**, **10**, and **12** were smoothly removed to give the free tetraynes **14**–**16** as relatively stable oils in nearly quantitative yields (*Scheme 3*). Orthoesters **15** and **16** underwent Pd-catalyzed cross-coupling with iodobenzene to give the tetraphenyl derivatives **17** and **18** (*Scheme 4*). Thermal acid-catalyzed elimination of the orthoester moieties in **12** and **13** produced the silyl-protected tetraethynylethenes **19** and **20** and concluded a novel, simple three-step synthesis of these fully two-dimensionally conjugated π-chromophores (*Scheme 5*).

1. Introduction. – With their diverse and unique properties, the known allotropes of carbon, *i.e.*, diamond, graphite, fullerenes, and the structurally related carbon nanotubes, which are available in macroscopic quantities, continue to intrigue chemists, physicists, biologists, as well as materials scientists [1–3][1]). In an attempt to emulate such properties, the synthesis of new molecular and polymeric carbon allotropes has been a primary focus of research in our laboratory [5] [6] as well as in others [7]. A variety of regular two-dimensional C-networks display the C-atom frame of tetraethynylethene (= 3,4-diethynylhex-3-ene-1,5-diyne, **1**) [8] as the infinite repeat unit [6]. The preparation of **1** as well as a rich variety of functional derivatives [8] [9] provided versatile building blocks for the construction of novel, multinanometer-sized functional and polymeric materials with extended C-cores [10–13]. However, the planar core of tetraethynylethenes, composed of sp- and sp^2-hybridized C-atoms, restricts their use to the formation of two-dimensional molecules and networks only.

To circumvent this limitation and to target the construction of three-dimensional molecular objects containing tetraethynylethenes as structural components, we sought the development of nonplanar synthons for the planar tetraethynylethenes. Suitably

[1]) For an entire Journal issue devoted to carbon nanotubes, see [4].

Scheme 1. *1,1,2,2-Tetraethynylethane Derivative* **2** *as a Possible Precursor to Tetraethynylethene* **1** *and the Cyclic C_{60} Isomer* **3**



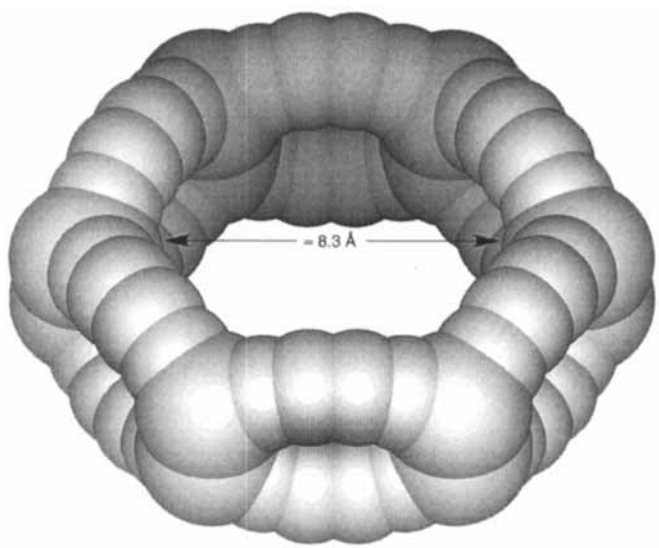


Fig. 1. *Space-filling molecular model of the molecular belt* **3**, *a C_{60} isomer*

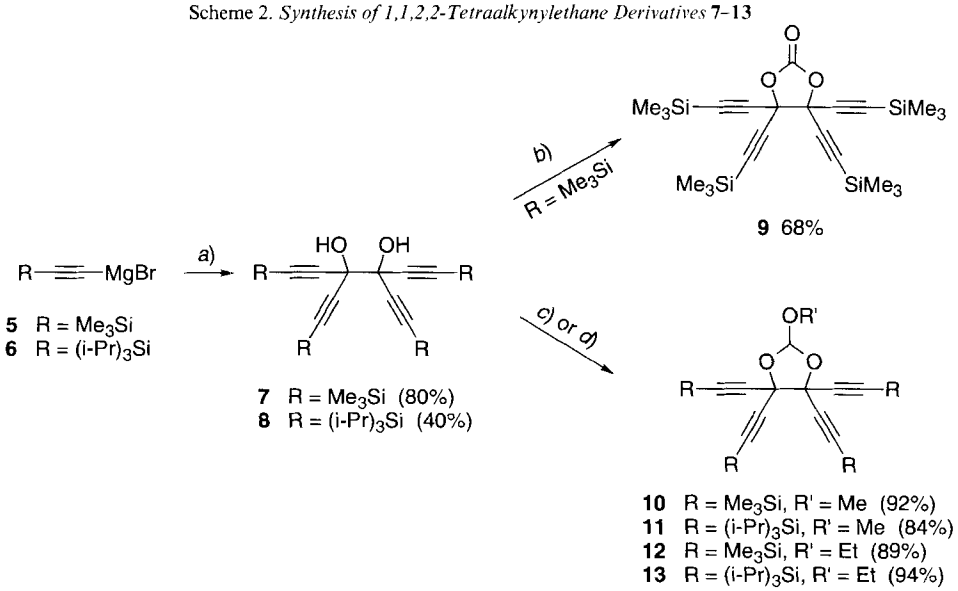
functionalized derivatives of 1,1,2,2-tetraethynylethane (= 3,4-diethynylhexa-1,5-diyne) [14] such as the orthoester-protected diol **2** (*Scheme 1*) seemed ideal to serve this purpose.

A prime target in this research is the molecular conjugated belt **3**, an isomer of C_{60}, which is composed of six fused octadehydro[12]annulene perimeters (*Scheme 1*) [11]. Starting from **2**, three-dimensional, strain-free construction to **4** would occur *via* oxidative cyclo-oligomerization [15] [16], and subsequent elimination of the masking orthoester functionality in the final step of the synthesis would produce the desired, fully conjugated sp^2-C-atom core. Force-field calculations [17] indicated that **3** has an interior circular cavity with an open space of *ca.* 8.3 Å in diameter (*Fig. 1*). Therefore, in the solid state, formation of porous crystals [18] for substrate inclusion, separation, or catalysis could be expected. Additional interest in **3** arised from theoretical calculations, which predicted superconductivity [19] for conjugated oligo-acene molecular belts [20]. Furthermore, the strained all-C-belt **3** could undergo thermal or photochemical rearrangement to the thermodynamically more stable, spherical C_{60} isomer, providing a stepwise, controlled synthesis of buckminsterfullerene.

Here, we describe the synthesis and structural properties of a series of protected 3,4-diethynylhexa-1,5-diyne-3,4-diols as potential precursors to **3** and **4** and demonstrate their synthon character for the corresponding tetraethynylethene derivatives.

2. Results and Discussion. – The protected vicinal diols **9** and **10–13** were chosen as first target compounds (*Scheme 2*), since elimination of both cyclic carbonate and orthoesther groups *via* known methods [21–24] could potentially afford the corresponding C=C bond and thus the desired tetraethynylethene molecular frame. The free diol precursors **7** and **8** were readily obtained as stable, colorless solids by reaction of the

Scheme 2. *Synthesis of 1,1,2,2-Tetraalkynylethane Derivatives* **7–13**



a) EtO_2CCO_2Et, Et_2O, r.t. *b*) *N,N'*-Carbonyldiimidazole, $PhCH_3$, reflux. *c*) $(MeO)_3CH$, cat. camphorsulfonic acid (CSA), CH_2Cl_2, r.t. *d*) $(EtO)_3CH$, cat. CSA, CH_2Cl_2, r.t.

alkynyl *Grignard* reagents **5** or **6** with diethyl oxalate in Et_2O [14e]. The structure of **7** was confirmed by a preliminary X-ray analysis of a single crystal grown from benzene at −20° [25]. The solid-state structure at room temperature showed a staggered conformation with an *anti*-orientation of the two OH groups; however, severe disorder resulting from the Me_3Si moieties and benzene solvent, incorporated into the lattice, precluded refinement to a level sufficient for meaningful bond-length and bond-angle determination or analysis of the H-bonding network formed by the OH groups.

Reaction of Me_3Si-protected diol **7** with *N*,*N*′-carbonyldiimidazole [26] in refluxing toluene gave carbonate **9** in 68% yield (*Scheme 2*). In contrast, $(i\text{-}Pr)_3Si$-protected diol **8** only provided low and poorly reproducible yields of the corresponding cyclic carbonate. In the reaction of **8**, a number of unidentified side-products formed, but the instability of the cyclic carbonate on chromatographic supports precluded its purification and isolation. While carbonate **9** was also unstable to chromatography, its purification could be achieved by crystallization from hexane at −20°.

The reactions of **7** or **8** with trimethyl or triethyl orthoformate in the presence of catalytic amounts of camphorsulfonic acid (CSA) afforded the corresponding orthoesters

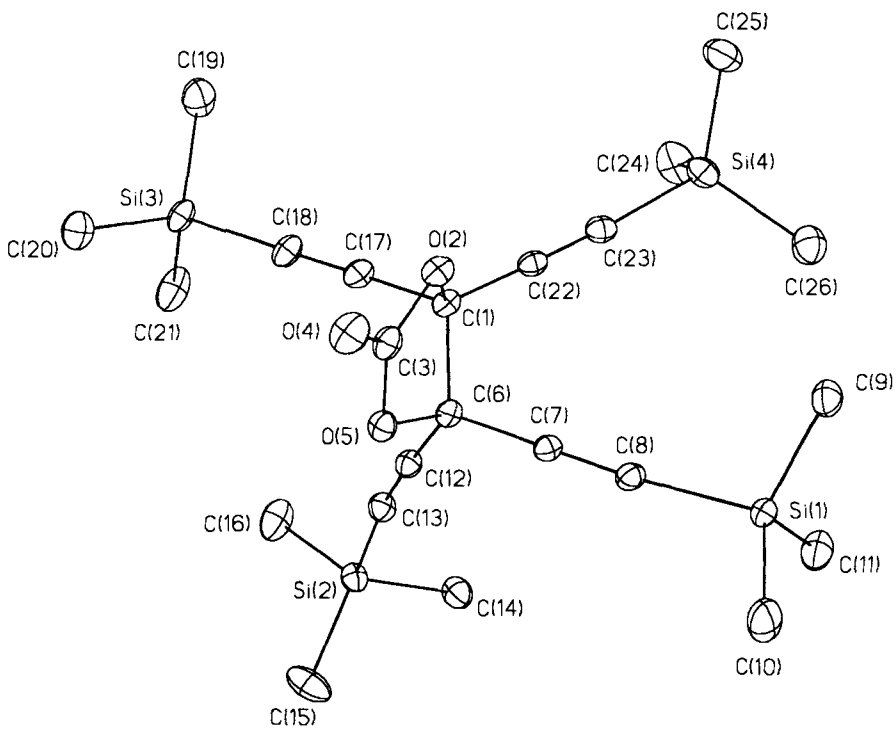


Fig. 2. *Molecular structure of* **9**.

Vibrational ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C(1)–C(6) 1.577(2), C(6)–C(7) 1.466(2), C(7)–C(8) 1.199(2), C(6)–C(12) 1.460(3), C(12)–C(13) 1.204(3), C(1)–C(17) 1.471(2), C(17)–C(18) 1.201(2), C(1)–C(22) 1.458(2), C(22)–C(23) 1.202(3), C(1)–O(2) 1.470(2), O(2)–C(3) 1.350(2), C(3)–O(4) 1.192(3), C(3)–O(5) 1.351(3), O(5)–C(6) 1.467(2); C(1)–C(6)–C(7) 111.4(1), C(1)–C(6)–C(12) 115.2(1), C(6)–C(1)–C(17) 111.4(1), C(6)–C(1)–C(22) 115.1(2), C(7)–C(6)–C(12) 112.0(2), C(17)–C(1)–C(22) 113.2(1), C(1)–C(6)–O(5) 99.7(1), O(2)–C(1)–C(6) 99.8(1), O(2)–C(3)–O(5) 111.6(2).

10–**13** (*Scheme 2*) in high yields as stable solids which could be stored without decomposition for months under normal laboratory conditions [23] [24].

The solid-state structures of carbonate **9** and orthoester **10** were solved in order to determine the ability of the alkynyl groups, after deprotection, to favorably orient for oxidative cyclizations leading to belt-shaped molecules such as **4**. Single crystals of **9** suitable for X-ray structural analysis were grown by slow evaporation of a hexane solution at room temperature. An ORTEP drawing of **9** and selected bond angles and bond lengths are shown in *Fig. 2*. The exocyclic ≡C–C–C and ≡C–C–C≡ angles at the puckered five-membered ring are slightly enlarged and adopt values between 111 and 115°. Correspondingly, the two endocyclic O–C–C angles are compressed to values close to 99°. Similar bond angles have been reported for cyclic five-membered ring carbonates bearing alkyl substituents [27a]. As a result of the puckering of the pentagon, the *cis*-alkynyl residues in **9** are not fully eclipsed, and the relevant torsional angles C(7)–C(6)–C(1)–C(22) and C(12)–C(6)–C(1)–C(17) amount to 34.9° and 36.7°. This distortion from coplanarity of the *cis*-alkynyl residues is, however, not expected to unfavorably influence the outcome of oxidative cyclizations which, after alkyne deprotection, should lead to the desired molecular belts.

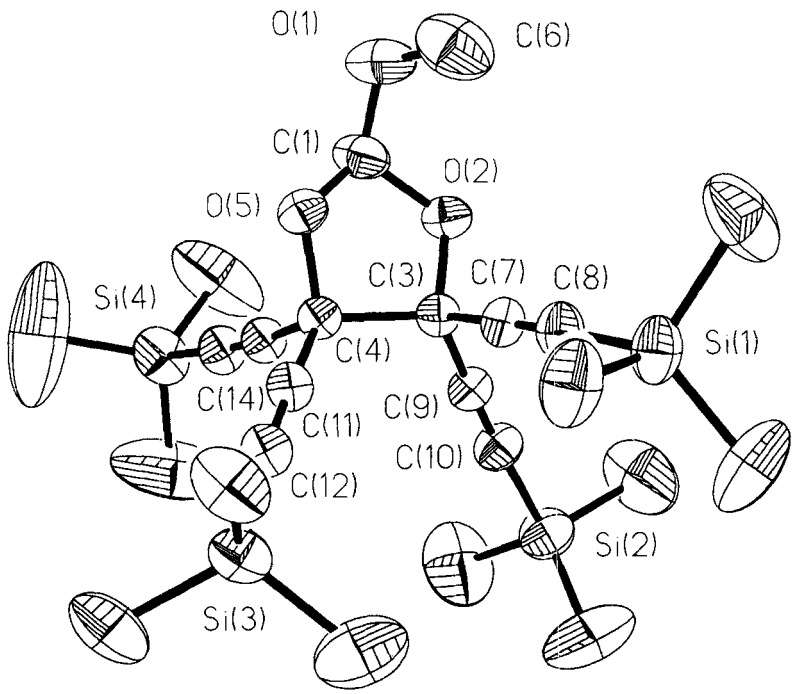


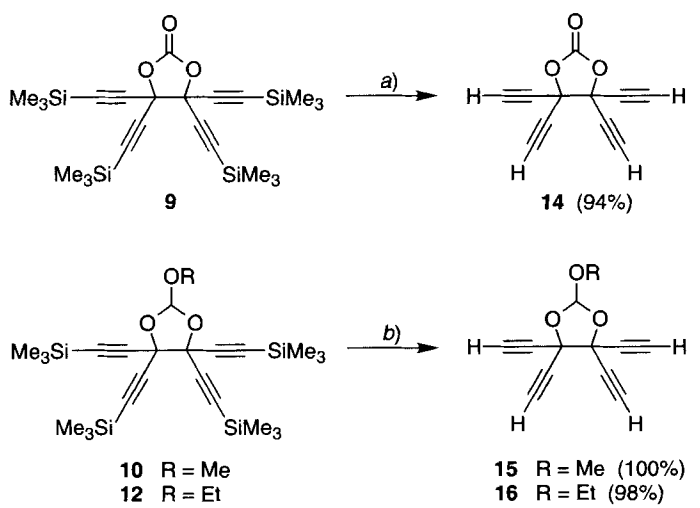
Fig. 3. *Molecular structure of* **10**.

Vibrational ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: C(3)–C(4) 1.578(7), C(3)–C(7) 1.477(6), C(7)–C(8) 1.200(7), C(3)–C(9) 1.468(7), C(9)–C(10) 1.179(8), C(4)–C(11) 1.458(7), C(11)–C(12) 1.198(8), C(4)–C(13) 1.479(7), C(13)–C(14) 1.179(7), C(1)–O(1) 1.302(9), C(1)–O(2) 1.419(8), O(2)–C(3) 1.435(6), C(1)–O(5) 1.422(8), C(4)–O(5) 1.438(6); C(3)–C(4)–C(11) 113.6(4), C(3)–C(4)–C(13) 111.2(4), C(4)–C(3)–C(7) 111.1(4), C(4)–C(3)–C(9) 114.5(4), C(7)–C(3)–C(9) 110.2(4), C(11)–C(4)–C(13) 112.1(4), C(3)–C(4)–O(5) 99.5(4), O(2)–C(3)–C(4) 101.0(4), O(2)–C(1)–O(5) 105.7(5).

Single crystals of orthoester **10** were grown by slow evaporation of an EtOH solution at room temperature, and an ORTEP drawing of the molecular structure and selected bond angles and bond lengths are shown in *Fig. 3*. The geometry of **10** resembles that of **9**, and comparable bond lengths, and endocyclic and exocyclic bond angles adopt similar values in both compounds. The torsional angles C(9)–C(3)–C(4)–C(13) and C(7)–C(3)–C(4)–C(11), which determine the deviation from coplanarity of the *cis*-alkynyl residues, amount to 37.9° and 35.9°, respectively [27b] [27c].

In a next step, we determined whether the silyl protecting groups at the terminal alkynes could be successfully removed to provide the direct precursors for the cyclization to the molecular belts. Attempts to remove the Me_3Si moieties in **9** *via* protodesilylation (catalytic amounts of K_2CO_3 in wet MeOH) revealed that the cyclic carbonate functionality was unstable to the use of MeOH as a solvent. Quantitative removal of the Me_3Si groups with formation of **14** was accomplished by reacting **9** with catalytic amounts of Bu_4NF in wet THF (*Scheme 3*). Tetrayne **14** was isolated as a viscous oil that slowly

Scheme 3. *Formation of the 1,1,2,2-Tetraethynylethanes* **14**–**16**

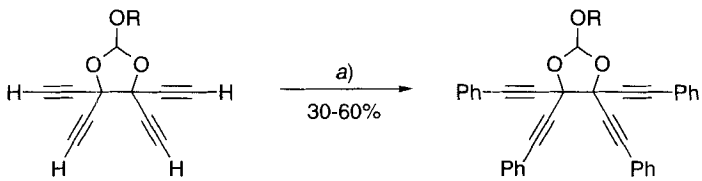


a) Bu_4NF, wet THF, r.t. *b*) K_2CO_3, wet MeOH, r.t.

darkened when kept neat at room temperature, but could be stored in Et_2O at −20° for months with only minimal decomposition. The cyclic orthoester moieties in **10** and **12** were stable to the conditions of the methanolic protodesilylation which afforded tetraynes **15** and **16** in quantitative yields. Compounds **15** and **16** were isolated as viscous oils that slowly darkened when kept neat at room temperatures. They were, however, sufficiently stable over several hours in solution for further synthetic elaboration and could also be stored as pure oils under refrigeration without decomposition.

We next investigated the ability of the 1,1,2,2-tetraethynylethanes **15** and **16** to undergo Pd-catalyzed cross-coupling (*Scheme 4*) [28]. It was of interest to test the stability of these compounds, with four unprotected terminal alkynyl groups, to cross-coupling

Scheme 4. *Cross-Coupling of 1,1,2,2-Tetraethynylethanes* **15** *and* **16** *with PhI*



15 R = Me
16 R = Et

17 R = Me
18 R = Et

a) PhI, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, r.t.

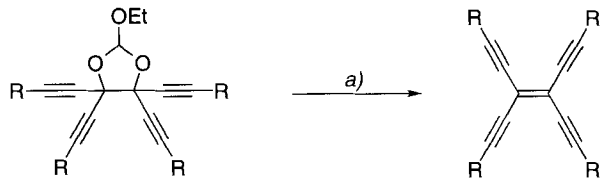
conditions, since transformations such as the *Cadiot-Chodkievicz* reaction [29] could be useful in a stepwise synthesis of molecular belts such as **4**. Cross-coupling with PhI gave the tetraphenyl derivatives **17** and **18** in moderate yields (30–60%) as clear oils that resisted all attempts of crystallization (*Scheme 4*). Thin-layer-chromatographic (TLC) monitoring of the reaction progress showed that the lower than expected isolated yields of **17** and **18** did not result from eventual decomposition of the starting materials. Rather, the products themselves appeared to be unstable to workup and concentration. Compounds **17** and **18** turned dark after several days when kept neat or in solution at room temperature.

We finally investigated the potential of the functionalized 1,1,2,2-tetraethynylethanes as synthons for tetraethynylethenes. In first attempts, orthoesters **12** and **13** were heated to 120° in Ac_2O for several hours, according to *Ando et al.* [22]. In the reaction of Me_3Si-protected **12**, mainly decomposition occurred, whereas no conversion was observed with the more robust $(i\text{-}Pr)_3Si$-protected **13**, even over the course of 16 h.

The method of *Hoffmann* and *Reiffen* [23b], which affects elimination of the orthoester moiety *via* thermolysis in the presence of aryl isocyanates, was then attempted. Heating of **12** or **13** in PhNCO at 150–160°, however, resulted only in the formation of numerous unidentifiable products, from which the formation of the desired tetraethynylethenes could hardly be discerned.

Alternatively, orthoesters have been shown to eliminate in the presence of catalytic amounts of strong acids [21] [24]. Thus, when **12** or **13** were heated as intimate mixtures with CSA, elimination of the orthoester moieties and formation of the corresponding tetraethynylethenes occurred in a reaction that was found to be highly temperature-dependent. Initial results from heating the mixture to 160–180° for more than 1 h showed almost complete decomposition of both starting materials and/or products. Investigations at varying temperatures revealed that elimination from both **12** and **13** occurred rapidly above 140°. It was also found that performing the elimination under vacuum (*ca.* 0.1 Torr) slightly reduced the amount of decomposition. Thus, the best results were obtained when **12** was heated with CSA under vacuum to 150° until evolution of gas from the mixture was no longer observed, which usually took *ca.* 5 min. (*Scheme 5*). Following workup, **19** [8] was obtained in 20–26% yield. Likewise, reaction of **13** under the same conditions gave **20** in slightly higher yields of 25 to 33%. Reactions of orthoesters **10** and **11** under similar conditions were also investigated, but the yields of the corresponding

Scheme 5. *Formation of Tetraethynylethenes* **19** *and* **20** *from 1,1,2,2-Tetraethynylethanes* **12** *and* **13**



12 R = Me_3Si
13 R = $(i\text{-}Pr)_3Si$

19 R = Me_3Si (20–26%)
20 R = $(i\text{-}Pr)_3Si$ (25–33%)

a) CSA, 150°/0.1 Torr, 5 min.

tetraethynylethenes were consistently lower. At temperatures below 140°, the elimination reactions of all four orthoesters **10**–**13**, as described, were prohibitively slow.

3. Conclusions. – Suitably functionalized 1,1,2,2-tetraethynylethanes provide versatile carbon-rich building blocks for three-dimensional acetylenic molecular scaffolding. The cyclic carbonate **9** and orthoester-protected diols **10**–**13** were readily prepared in a two-step synthesis, and the Me_3Si-protecting groups at the four terminal alkyne residues in **9**, **10**, and **12** could be removed in nearly quantitative yield giving the free tetraynes **14**–**16** as relatively stable oils. Orthoesters **15** and **16** underwent Pd-catalyzed cross-coupling reactions, and this opens the way to a stepwise construction of molecular C-belts such as **4** and, ultimately, **3**, which are the fascinating target compounds of this research program. Finally, 1,1,2,2-tetraethynylethanes **12** and **13** are synthons for the corresponding tetraethynylethenes **19** and **20**, and elimination of their orthoester moieties concludes a novel, simple three-step synthesis of these versatile, fully two-dimensionally conjugated [13b] π-chromophores. Based on these promising results, the synthesis of the challenging molecular belts **3** and **4** is now further pursued.

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Experimental Part

General. Reagents and solvents were purchased reagent-grade and used without further purification. Evaporation and concentration *in vacuo* was done at H_2O-aspirator pressure. All reactions were performed in standard glassware under an inert atmosphere of N_2. A positive pressure of N_2 was essential to the success of Pd-catalyzed reactions. Degassing of solvents was accomplished by vigorously bubbling N_2 through the soln. for at least 45 min. Column chromatography: silica gel *H* from *Fluka*. TLC: glass sheets covered with silica gel *60* F_{254} from *E. Merck*; visualization by UV light or anisaldehyde stain. M.p.: *Büchi SMP-20* apparatus; uncorrected. IR [cm^{-1}]: *Perkin Elmer-1600-FTIR*. ^1H- and ^{13}C-NMR: *Varian Gemini-200* and *-300* instruments at r.t. in $CDCl_3$; solvent peaks (7.24 ppm for ^1H and 77.0 ppm for ^{13}C) as reference. MS [*m/z*]: *VG-Tribrid* instrument for EI and a *VG-ZAB-2SEQ* instrument for FAB in a 3-nitrobenzyl-alcohol matrix. Elemental analyses were effected by the Mikrolabor in the Laboratorium für Organische Chemie at ETHZ.

X-Ray Crystal Structure of **9**. Single crystals were grown by slow evaporation of a hexane soln. at r.t. Low-temperature X-ray crystal data for $C_{23}H_{36}O_3Si_4 \cdot \frac{1}{2}(C_{23}H_{36}O_3Si_4)$ ($M_r = 709.3$): monoclinic space group $C2/c$ (No. 15), $D_c = 1.05$ g cm^{-3}, $Z = 8$, $a = 46.468(9)$, $b = 11.102(2)$, $c = 19.076(4)$ Å, $\beta = 113.64(3)°$,

$V = 9015(3)$ Å^3, CuK_α radiation, $\lambda = 1.5418$ Å, $\theta \leq 70°$, 8539 unique reflections, $T = 100$ K. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis using an isotropic extinction coefficient and an exponentially modified weight factor $r = 5$ Å^2 (heavy atoms anisotropic, H-atoms isotropic, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.037$, $wR(F) = 0.048$ for 461 variables and 6569 observed reflections with $I > 3\sigma(I)$.

X-Ray Crystal Structure of **10**. Single crystals were grown by slow evaporation of an EtOH soln. at r.t. X-Ray crystal data for $C_{24}H_{40}O_3Si_4$ ($M_r = 488.9$): monoclinic space group $P2_1/c$, $D_c = 0.978$ g cm^{-3}, $Z = 4$, $a = 10.517(2)$, $b = 17.641(6)$, $c = 18.377(5)$ Å, $\beta = 103.22(2)°$, $V = 3319.1(16)$ Å^3, MoK_α radiation, $\lambda = 0.71073$ Å, $3 \leq 2\theta \leq 40°$, 3108 unique reflections, $T = 293$ K. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares analysis using experimental weights (heavy atoms anisotropic, H-atoms fixed, whereby H-positions are based on stereochemical considerations). Final $R(F) = 0.048$, $wR(F) = 0.060$ for 280 variables and 2097 observed reflections with $F > 4\sigma(F)$. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, GB–Cambridge CB2 1EZ (UK), on quoting the full journal citation.

1,6-Bis(trimethylsilyl)-3,4-bis[2-(trimethylsilyl)ethynyl]hexa-1,5-diyne-3,4-diol (**7**). A 2M soln. of EtMgBr (102 ml, 204 mmol) in Et_2O was slowly added to a soln. of (trimethylsilyl)acetylene (21.0 g, 214 mmol) in Et_2O (150 ml) at 0°, then the mixture was warmed to r.t. and stirred for 4 h. The soln. was cooled to 0°, and freshly distilled EtO_2CCO_2Et (7.0 g, 48 mmol) in Et_2O (10 ml) was added. The mixture was warmed to r.t., stirred overnight, refluxed for 2 h, cooled to r.t., and poured into cold (0°), sat. aq. NH_4Cl soln. Extraction with Et_2O, drying ($MgSO_4$), and evaporation gave a light yellow oil. Addition of MeOH and refrigeration afforded **7** (17.1 g, 80%) as a colorless solid. M.p. 112–113°. IR (CCl_4): 3508, 2954, 2172, 1251. ^{1}H-NMR (200 MHz): 0.18 (*s*, 36 H); 2.95 (*s*, 2 H). ^{13}C-NMR (50 MHz): –0.68; 71.21; 90.75; 100.24. EI-MS (70 eV): 446 (0.4, M^+), 134 (100).

1,6-Bis(triisopropylsilyl)-3,4-bis[2-(triisopropylsilyl)ethynyl]hexa-1,5-diyne-3,4-diol (**8**). A 2M soln. of EtMgBr (20 ml, 40 mmol) in Et_2O was slowly added at r.t. to (triisopropylsilyl)acetylene (7.3 g, 40 mmol) in Et_2O (50 ml), and the mixture was stirred for 4 h. The soln. was cooled to 0°, and freshly distilled EtO_2CCO_2Et (1.5 g, 10 mmol) in Et_2O (10 ml) was added. The mixture was warmed to r.t., stirred overnight, refluxed for 4 h, cooled to r.t., and poured into cold (0°), sat. aq. NH_4Cl soln. Extraction with Et_2O, drying ($MgSO_4$), and evaporation left a light-yellow oil which was chromatographed (SiO_2, hexane/(CH_2Cl_2 2:1) to give **8** (3.1 g, 40%). R_f 0.4. White solid. M.p. 158–160°. IR (CCl_4): 3549, 2939, 2166, 1244. ^{1}H-NMR (200 MHz): 1.06 (*s*, 84 H); 2.96 (*s*, 2 H). ^{13}C-NMR (50 MHz): 11.11; 18.62; 71.12; 87.78; 103.04. EI-MS (70 eV): 782 (0.3, M^+), 347 (100). Anal. calc. for $C_{46}H_{86}O_2Si_4$ (783.53): C 70.52, H 11.06; found: C 70.57, H 11.28.

4,4,5,5-Tetrakis[2-(trimethylsilyl)ethynyl]-1,3-dioxolan-2-one (**9**). A soln. of **7** (2.2 g, 5.0 mmol) and *N,N'*-carbonyldiimidazole (0.81 g, 5.0 mmol) in toluene (60 ml) was refluxed for 30 min. The mixture was cooled to r.t., washed with sat. aq. NH_4Cl soln., dried ($MgSO_4$), and evaporated to yield a yellow oil. The oil was dissolved in hexane (10 ml), and cooling to –20° overnight gave **9** (1.6 g, 68%) as clear, colorless crystals. M.p. 66–68°. IR (CCl_4): 2964, 2105, 1830, 1252, 1204, 1005. ^{1}H-NMR (200 MHz): 0.22 (*s*). ^{13}C-NMR (50 MHz): –0.63; 77.10; 94.89; 97.06; 150.67. EI-MS (70 eV): 472 (0.1, M^+), 428 (7, $[M - CO_2]^+$), 412 (4, $[M - CO_3]^+$), 206 (100, $[(Me_3SiC{\equiv}C)_2C]^+$). X-Ray: *Fig. 2*.

2-Methoxy-4,4,5,5-tetrakis[2-(trimethylsilyl)ethynyl]-1,3-dioxolane (**10**). A soln. of **7** (1.04 g, 2.33 mmol), $(MeO)_3CH$ (1 ml, 9 mmol), and CSA (20 mg, 0.086 mmol) in CH_2Cl_2 (4 ml) was stirred for 16 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 3:2) gave **10** (1.04 g, 92%). R_f 0.4. White solid. M.p. 76–77°. IR (CCl_4): 2961, 2176, 1251, 1060. ^{1}H-NMR (200 MHz): 0.16 (*s*, 18 H); 0.17 (*s*, 18 H); 3.41 (*s*, 3 H); 6.03 (*s*, 1 H). ^{13}C-NMR (50 MHz): –0.50; –0.46; 50.54; 75.97; 92.98; 93.13; 98.21; 98.48; 115.06. EI-MS (70 eV): 488 (0.02, M^+), 428 (7, $[M - OCHOCH_3]^+$), 412 (2, $[M - C_2H_4O_3]^+$), 206 (100, $[Me_3SiC{\equiv}C)_2C]^+$). Anal. calc. for $C_{24}H_{40}O_3Si_4$ (488.92): C 58.96, H 8.25; found: C 58.72, H 8.02. X-Ray: *Fig. 3*.

2-Methoxy-4,4,5,5-tetrakis[2-(triisopropylsilyl)ethynyl]-1,3-dioxolane (**11**). A soln. of **8** (0.145 g, 0.185 mmol), $(MeO)_3CH$ (0.5 ml, 4.6 mmol), and CSA (10 mg, 0.043 mmol) in CH_2Cl_2 (4 ml) was stirred for 4 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **11** (0.127 g, 84%). R_f 0.6. White solid. M.p. 74–75°. IR (CCl_4): 2943, 2171, 1054. ^{1}H-NMR (200 MHz): 1.05 (*s*, 84 H); 3.48 (*s*, 3 H); 6.10 (*s*, 1 H). ^{13}C-NMR (75 MHz): 11.16; 18.63; 50.94; 75.86; 89.82; 90.47; 100.92; 100.97; 115.11. EI-MS (70 eV): 825 (0.5, M^+), 765 (9, $[M - OCHOCH_3]^+$), 749 (5, $[M - C_2H_4O_3]^+$), 157 (100, $[(i\text{-}Pr)_3Si]^+$). Anal. calc. for $C_{48}H_{88}O_3Si_4$ (825.57): C 69.83, H 10.74; found: C 69.78, H 10.47.

2-Ethoxy-4,4,5,5-tetrakis[2-(trimethylsilyl)ethynyl]-1,3-dioxolane (**12**). A soln. of **7** (0.50 g, 1.1 mmol), $(EtO)_3CH$ (1 ml, 6 mmol), and CSA (10 mg, 0.043 mmol) in CH_2Cl_2 (4 ml) was stirred for 8 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **12** (488 mg, 89%). R_f 0.6. White solid. M.p. 48–49°. IR (CCl_4):

2959, 2174, 1251, 1056. ^{1}H-NMR (200 MHz): 0.17 (*s*, 36 H); 1.18 (*t*, *J* = 7.1, 3 H); 3.79 (*q*, *J* = 7.1, 2 H); 6.05 (*s*, 1 H). ^{13}C-NMR (50 MHz): −0.45; 14.95; 59.51; 75.89; 92.88; 92.96; 98.27; 98.52; 114.97. EI-MS (70 eV): 502 (0.01, M^+), 428 (9, $[M - OCHOCH_2CH_3]^+$), 412 (2, $[M - C_3H_6O_3]^+$), 206 (100, $[(Me_3SiC{\equiv}C)_2C]^+$). Anal. calc. for $C_{25}H_{42}O_3Si_4$ (502.95): C 59.70, H 8.42; found: C 59.77, H 8.43.

2-Ethoxy-4,4,5,5-tetrakis[2-(triisopropylsilyl)ethynyl]-1,3-dioxolane (**13**). A soln. of **8** (0.22 g, 0.28 mmol), $(EtO)_3CH$ (0.5 ml, 3 mmol), and CSA (5 mg, 0.022 mmol) in CH_2Cl_2 (3 ml) was stirred for 8 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **13** (222 mg, 94%). R_f 0.6. White solid. M.p. 60–61°. IR (CCl_4): 2933, 2178, 1050. ^{1}H-NMR (200 MHz): 1.05 (*s*, 84 H); 1.18 (*t*, *J* = 7.1, 3 H); 3.86 (*q*, *J* = 7.1, 2 H); 6.13 (*s*, 1 H). ^{13}C-NMR (50 MHz): 11.18; 14.84; 18.62; 59.58; 75.75; 89.65; 90.22; 101.02 (2 ×); 114.85. FAB-MS: 766 (100, $[M - OCHOCH_2CH_3]^+$). Anal. calc. for $C_{49}H_{90}O_3Si_4$ (839.59): C 70.10, H 10.80; found: C 70.08, H 10.63.

4,4,5,5-Tetraethynyl-1,3-dioxolan-2-one (**14**). To a soln. of **9** (1.0 g, 2.1 mmol) in THF at 0° were added several drops of 1M Bu_4NF in THF, and the mixture was stirred for 3 h. Dilution with Et_2O, washing with sat. aq. NH_4Cl soln., drying ($MgSO_4$), and evaporation gave **14** (365 mg, 94%) as a clear, pale-yellow oil that darkened upon standing, but could be stored in Et_2O at −20°. IR (CCl_4): 3292, 2125, 1831, 1205, 1005. ^{1}H-NMR (200 MHz): 3.03 (*s*). ^{13}C-NMR (50 MHz): 73.78; 77.20; 80.25; 149.60. EI-MS (70 eV): 124 (3, $[C_{10}H_4]^+$), 62 (100, $[(HC{\equiv}C)_2C]^+$).

2-Methoxy-4,4,5,5-tetraethynyl-1,3-dioxolane (**15**). To a soln. of **10** (133 mg, 0.273 mmol) in MeOH (4 ml) was added K_2CO_3 (5 mg, 0.04 mmol), and the mixture was stirred at r.t. for 30 min. Dilution with Et_2O, washing with sat. aq. NH_4Cl soln., drying ($MgSO_4$), and evaporation gave **15** (54 mg, 100%) as a light-yellow oil that slowly darkened at r.t. IR (CCl_4): 3288, 2922, 2128, 1078. ^{1}H-NMR (200 MHz): 2.81 (*s*, 2 H); 2.83 (*s*, 2 H); 3.47 (*s*, 3 H); 6.07 (*s*, 1 H). ^{13}C-NMR (75 MHz): 51.87; 75.42; 76.85; 76.95; 77.04; 116.31. EI-MS (70 eV): 200 (0.2, M^+), 199 (2, $[M - 1]^+$), 169 (26, $[M - OCH_3]^+$), 122 (56, $[C_{10}H_2]^+$), 62 (100, $[(HC{\equiv}C)_2C]^+$).

2-Ethoxy-4,4,5,5-tetraethynyl-1,3-dioxolane (**16**). To a soln. of **12** (135 mg, 0.268 mmol) in MeOH (5 ml) was added K_2CO_3 (5 mg, 0.04 mmol), and the mixture was stirred at r.t. for 30 min. Dilution with Et_2O, washing with sat. aq. NH_4Cl soln., drying ($MgSO_4$), and evaporation gave **16** (56 mg, 98%) as a light-yellow oil that slowly darkened at r.t. IR (CCl_4): 3292, 2961, 2128, 1078. ^{1}H-NMR (200 MHz): 1.23 (*t*, *J* = 7.1, 3 H); 2.79 (*s*, 2 H); 2.81 (*s*, 2 H); 3.79 (*q*, *J* = 7.1, 2 H); 6.09 (*s*, 1 H). ^{13}C-NMR (50 MHz): 14.97; 61.09; 75.30; 76.74; 76.92; 77.06; 116.09. EI-MS (70 eV): 214 (0.7, M^+), 213 (5, $[M - 1]^+$), 169 (85, $[M - OCH_2CH_3]^+$), 62 (100, $[(HC{\equiv}C)_2C]^+$).

2-Methoxy-4,4,5,5-tetrakis(2-phenylethynyl)-1,3-dioxolane (**17**). To a degassed soln. of **15** (33 mg, 0.17 mmol) in Et_3N (10 ml) and dry THF (10 ml) were added PhI (0.17 g, 0.84 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.057 mmol), and CuI (20 mg, 0.11 mmol), and the mixture was stirred in the dark for 16 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **17** (41 mg, 48%) as a light-yellow oil that slowly darkened at r.t. R_f 0.3. IR (CCl_4): 3056, 2944, 2233, 1489, 1054. ^{1}H-NMR (200 MHz): 3.64 (*s*, 3 H); 6.38 (*s*, 1 H); 7.33 (*m*, 12 H); 7.52 (*d*, *J* = 6.8, 4 H); 7.54 (*d*, *J* = 6.8, 4 H). ^{13}C-NMR (50 MHz): 51.10; 77.65; 83.55; 83.78; 87.87; 87.95; 115.93; 121.51; 121.62; 128.24; 129.14; 132.11. EI-MS (70 eV): 504 (0.4, M^+), 444 (4, $[M - OCHOCH_3]^+$), 214 (100, $[(PhC{\equiv}C)_2C]^+$). HR-MS: 504.1582 (M^+, $C_{36}H_{24}O_3^+$; calc.: 504.1725).

2-Ethoxy-4,4,5,5-tetrakis(2-phenylethynyl)-1,3-dioxolane (**18**). To a degassed soln. of **16** (43 mg, 0.20 mmol) in Et_3N (10 ml) and dry THF (10 ml) were added PhI (0.20 g, 1.0 mmol), $[PdCl_2(PPh_3)_2]$ (40 mg, 0.057 mmol), and CuI (20 mg, 0.11 mmol), and the mixture was stirred in the dark for 16 h. Evaporation and chromatography (SiO_2-*H*, hexane/CH_2Cl_2 2:1) gave **18** (61 mg, 59%) as a light-yellow oil that slowly darkened at r.t. R_f 0.4. IR (CCl_4): 3058, 2928, 2233, 1490, 1052. ^{1}H-NMR (200 MHz): 1.32 (*t*, *J* = 7.1, 3 H); 4.01 (*q*, *J* = 7.1, 2 H); 6.38 (*s*, 1 H); 7.33 (*m*, 12 H); 7.50 (*m*, 8 H). ^{13}C-NMR (50 MHz): 15.22; 60.26; 77.64; 83.63; 83.84; 87.77 (2 ×); 115.82; 121.57; 121.72; 128.23; 129.08; 132.09. EI-MS (70 eV): 518 (0.4, M^+), 444 (4, $[M - OCHOCH_2CH_3]^+$), 214 (100, $[PhC{\equiv}C)_2C]^+$). HR-MS: 518.1879 (M^+, $C_{37}H_{26}O_3^+$; calc.: 518.1882).

1,6-Bis(trimethylsilyl)-3,4-bis[2-(trimethylsilyl)ethynyl]hex-3-ene-1,5-diyne (**19**) [8a] [14b]. An intimate mixture of **12** (40 mg, 0.089 mmol) and CSA (*ca.* 10 mg, 0.043 mmol) was heated in an NMR tube under vacuum (0.1 Torr), until gas no longer evolved (*ca.* 5 min). The mixture was dissolved in hexane and filtered through a short plug (SiO_2, hexane). After concentration *in vacuo*, the residual solid was dissolved in CH_2Cl_2 (1 ml), and addition of MeOH and refrigeration overnight led to precipitation of **19** (9 mg, 26%) as a white solid with spectral and physical properties identical to those reported in [8a]. M.p. 196–197 ([8a]: 199–201°).

1,6-Bis(triisopropylsilyl)-3,4-bis[2-(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne (**20**). An intimate mixture of **13** (75 mg, 0.089 mmol) and CSA (*ca.* 10 mg, 0.043 mmol) was reacted as described above for **19** to give **20** (22 mg, 33%). Off-white solid. M.p. > 240°. IR (CCl_4): 2944, 2155, 2142, 1238, 1191. ^{1}H-NMR (200 MHz): 1.06 (*s*). ^{13}C-NMR (50 MHz): 11.11; 18.55; 102.07; 103.93; 117.05. EI-MS (70 eV): 748 (100, M^+). Anal. calc. for $C_{46}H_{84}Si_4$ (749.51): C 73.72, H 11.30; found: C 73.59, H 11.40.

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