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AN APPROACH TO TRICYCLO[8.4.0.0^{4,7}] TETRADECAHEPTA-1,3,5,7,9,11,13-ENE (BENZO[1,2-*a*]CYCLOBUTA [1,2-*e*]CYCLOOCTATETRAENE)

UNUSUAL THERMAL REARRANGEMENTS IN THE $C_{14}H_{10}$ MANIFOLD

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Abstract—In an attempt to prepare the title compound **2** we have discovered that the isomeric 1,2-bis(but-1-en-3-ynyl)-benzenes and some of their silylated and deuterated derivatives **6a-d** are converted to 2-(but-1-en-3-ynyl)naphthalenes **9a-d**. Deuterium and silyl labeling experiments point to the operation of at least two mechanisms in these rearrangements. Heats of formation estimates make it feasible that **2** is an intermediate in one of them.

The fusion of two $4n\pi$ electronic ring systems results in a bicyclic structure with a $4n+2\pi$ electron periphery. In such a compound the constituent rings are antiaromatic, while the π-periphery is aromatic. Which of these

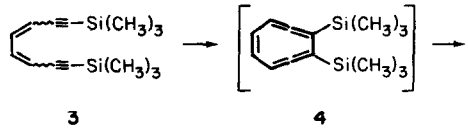
1

opposing tendencies is stronger in a prototype of this kind, bicyclo-[6.2.0]decapentaene (**1**), has been the subject of several experimental[1,2] and theoretical[3] efforts. The 9,10-diphenyl-derivative of **1** deviates from planarity[1] only by an average of 10.5° and shows slight bond alternation. Significantly, the parent compound **1** sustains an induced diamagnetic ring current causing the 9,10-protons to resonate at δ 7.32, making it seemingly aromatic.[2] Curiously, theory is at odds with this conclusion. Thus, Aihara, who disputed the validity of the ring current criterion of aromaticity as it applies to fused ring systems on theoretical grounds, calculated the resonance energy of **1** as destabilizing.[3] An HMO estimate by Gastmans *et al.*[4], using the method of Hess and Schaad,[5] reached the same conclusion, as does the graph-theoretical approach devised by Randić (89% AA).[6]

In this connection it appeared to us that a benzoderivative of **1**, tricyclo[8.4.0.0^{4,7}]tetradecahepta-1,3,5,7,9,11,13-ene (**2**), exhibited several interesting features. Although it contains an aromatic 14π electron periphery in **2a**, this structure lacks an aromatic benzene ring. In contrast, those resonance forms which contain a benzene ring (e.g. **2b**) are destabilized by cyclobutadiene components. Thus, benzofusion to **1** as in **2** may destabilize the favored dimethylenecyclobutene structure for **1**.[2] The possibility that the various Kekulé-representations for **2** may constitute valence bond tautomers such as those observed for cyclooctatetraene[7] is another intriguing feature associated with **2**.

We have estimated the potential (anti)aromaticity of **2** with contradictory results. The Hückel resonance energy[5] is 0.009 β per electron, as opposed to $-0.028\,\beta$ for **1**,[4] suggesting that **2** should be somewhat stabilized by resonance to an extent similar to that in naphtho[*b*]cyclobutadiene (0.007 β).[5] A graph-theoretical approach[6] predicts relatively strong destabilization (64% AA), although to a lesser degree than in **1**.

The only known example of a derivative of **2** is its tricarbonyl iron complex.[8] Our synthetic approach to **2** relied on our earlier observation that flash vacuum pyrolysis (FVP) of any of the three isomers of the dienediyne **3** furnished mainly **5**,[9] presumably proceeding *via* the intermediacy of bisallene **4**. Based on this prece-



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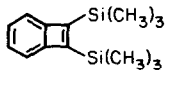

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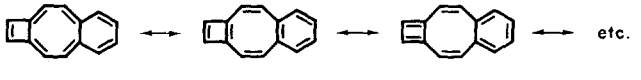
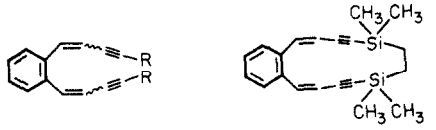


2a 2b 2c

dence, it appeared reasonable to employ the benzologous 1,2-bis(but-1-en-3-ynyl)benzenes (**6**), as potential precursors to **2**. During the course of this work we dis-



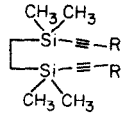
6a; R = $Si(CH_3)_3$
6b; R = H
6c; R = D

6d

covered a series of unusual rearrangements which appear to dominate the thermal chemistry of the starting materials **6**, resulting in the naphthaleneynes **9**. Although neither **2** nor any of its derivatives were detected, we believe they may be intermediates in some of the observed reactions.

RESULTS

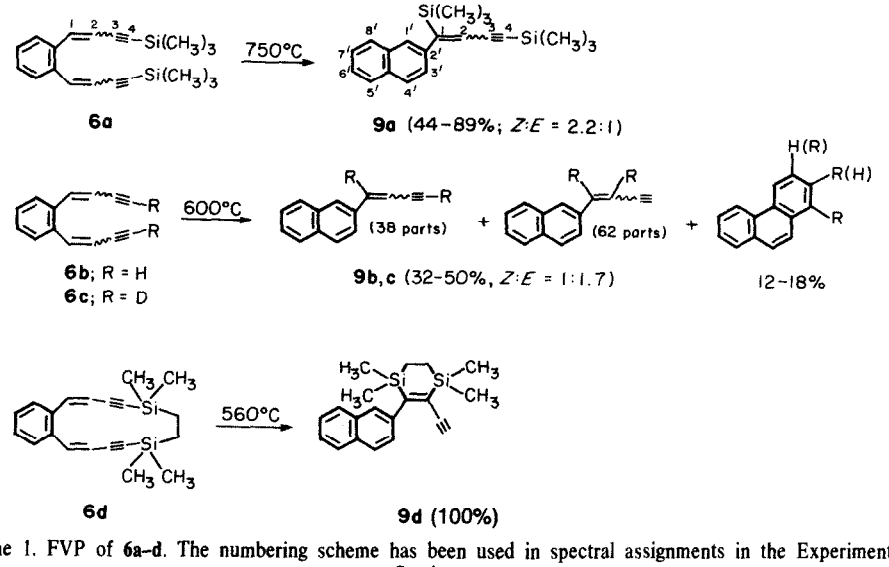
Compound **6a** was prepared by the bis-Wittig reaction[10] of *o*-xylylenebis(triphenylphosphonium bromide)[11] and trimethylsilylpropynal[12] as a partially separable mixture of all three isomers in 43% yield. Proto- and deuterio-desilylation (EtONa/EtOH(D), 81%) provided **6b** and **6c**, respectively. In order to obtain **6d**, dialdehyde **8** was synthesized as follows. Reaction of the Grignard reagent formed from ethylmagnesium bromide and propargyltetrahydropyranyl ether[13] with 1,2-



7; R = CH_2OH
8; R = CHO

bis(chlorodimethylsilyl)ethane followed by acid hydrolysis gave diol **7** in 74% yield.[12b] Oxidation[12c] of **7** provided **8** in 63% yield. The bis-Wittig reaction of **8** with *o*-xylylenebis(triphenylphosphonium bromide) gave (*Z*, *Z*)-**6d** in 1–3% yield along with other products. Compound **6d** exhibited two silylmethyl resonances (δ 0.13 and 0.10) in the ^{1}H NMR spectrum, indicative of a conformationally rigid and (according to models) tub-shaped structure. The results of the FVP reactions of **6a–d** are summarized in Scheme 1. The variations in yields were caused by differing amounts of polymer formation at the source, and in some cases by product losses in separation procedures. The ^{1}H NMR spectra of the crude pyrolysates showed that only the products indicated in Scheme 1 were present.[14] The temperatures indicated were the minima at which complete reaction of the starting compounds was observed. The products were assigned structures based on a combination of spectral and chemical methods. Compound **6a** was subjected to FVP as a 6:1 mixture of (*E*, *Z*)- and (*Z*, *Z*)-isomers and as the pure (*E*, *E*)-isomer. In both cases **9a** was the only product (*E*:*Z* = 2.2:1) obtained in 55% and 44% yield, respectively.

Examination of the ^{1}H NMR spectrum of (*E*)- and (*Z*)-**9a** revealed doublets at δ 7.56 (J = 1.2 Hz) and δ 7.65 (J = 1.2 Hz) respectively, indicative of a 2-substituted naphthalene derivative. The double bond stereochemistry was tentatively identified by comparison of the ^{1}H chemical shifts of the trimethylsilyl singlets at δ 0.27 and 0.21 in (*E*)-**9a** with those of (*Z*)-**9a** at δ 0.15 and −0.10 with the expectation that trimethylsilyl groups closer to the diatropic naphthalene ring should appear at lower field. This assignment was confirmed by selective protodesilylation of the alkynylsilyl function (Scheme 2). The alkynyl proton in (*E*)-**10** absorbed as a doublet at δ 2.85 (J = 2.6 Hz) while (*Z*)-**10** exhibited a doublet of δ 2.53 (J = 2.2 Hz). This assignment is again consistent with the anticipated effect of a proximal or distal naphthalene ring on the chemical shift of the alkyne proton. The two stereoisomers of **9b**[15] and 1-phenylbut-1-en-3-yne[16] in which the stereochemistry around the double bond was unambiguously assigned by the coupling pattern observed, show similar trends. The location of the vinyltrimethylsilyl groups in **9a** was determined by inspection of the chemical shift of the neighboring vinyl hydrogen (δ 6.13 and 6.25 for the (*Z*)- and (*E*)-isomers, respectively), consistent with similar chemical shifts for the β-vinylprotons in **9b**[15] and 1-phenylbut-1-en-3-yne.[16] This

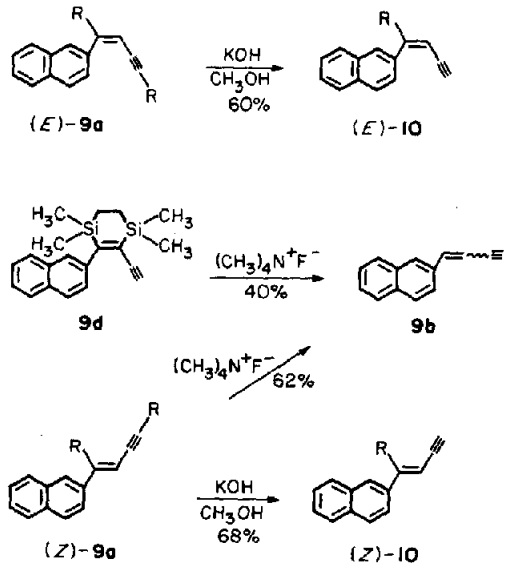


6a → **9a** (44–89%; *Z*:*E* = 2.2:1)

6b; R = H
6c; R = D → **9b,c** (32–50%, *Z*:*E* = 1:1.7)

6d → **9d** (100%)

Scheme 1. FVP of **6a–d**. The numbering scheme has been used in spectral assignments in the Experimental Section.



Scheme 2. Structure proofs of **9a–d** [R = $Si(CH_3)_3$]

is further corroborated by the observation of a relatively large (long range) coupling (J = 2.2 and 2.6 Hz) between the vinyl- and alkynyl-proton in (*E*)- and (*Z*)-**10**.[15,16] Complete protodesilylation of pure (*E*)- or (*Z*)-**9a** gave **9b** as a mixture of isomers[15], providing further structural proof.

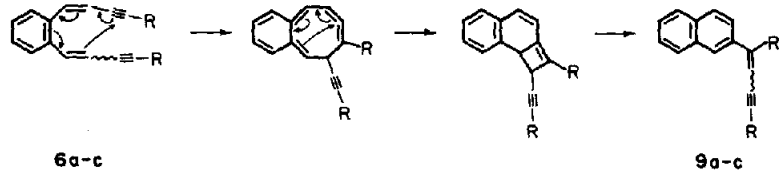
A mixture of all three isomers of **6b** was subjected to FVP to give a mixture of 1-(2-naphthyl)but-1-en-3-ynes (**9b**) in 32–50% yield (*Z*:*E* = 1.7:1). A second product was shown to be phenanthrene (12–18%) by comparison with authentic material. Independent pyrolysis (820°) of **9b** also gave phenanthrene (36%). FVP of **6c** gave the dideuterated naphthylbutenynes **9c** (Scheme 1), the deuterium appearing in all three possible locations of the butenyne substituent as determined by ^1H NMR spectroscopy: 100% at C-1, 62% at C-2 and 38% at C-4. In addition, dideuteriophenanthrene was formed labeled at C-1 (50%), C_2 and C_3 (summing to 50%).[17] The exact distribution of the label at the latter two carbons could not be quantified due to the near chemical shift isochronism of H-2 and H-3 and the degeneracy of C-2 and C-3 at the field strength at our disposal. However, the appearance of a broad singlet superimposed on a doublet (J = 8.5 Hz) of approximately equal intensity at δ 8.69 in an ^1H NMR spectrum from which the signals due to the undeuterated ring had been subtracted, indicated that extensive scrambling between C_2 and C_3 had occurred.

Finally, FVP of (*Z*, *Z*)-**6d** gave **9d** in quantitative yield. The ^1H NMR spectrum of **9d** exhibited two silylmethyl singlets (δ 0.23 and 0.03), a singlet (δ 3.30) for the alkynyl proton and no absorptions in the vinyl region, in accord with the assigned structure. Further structural proof for **9d** was obtained by fluoride mediated protodesilylation to **9b** (Scheme 2).

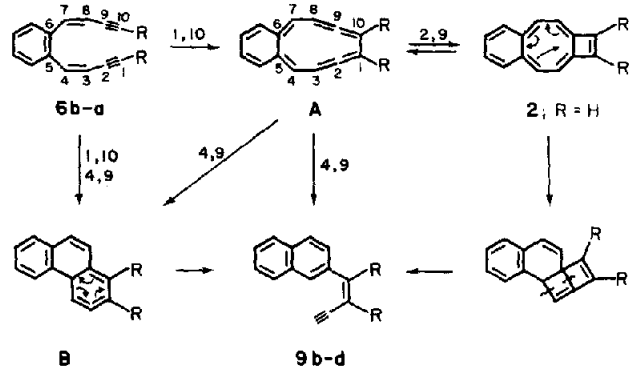
None of the pyrolytic transformations of **6** described in this section produced any detectable amount of **2** or its derivatives.

DISCUSSION

The FVP of **6** seems to uniformly lead to the naphthylbutenynes **9** in addition to phenanthrene (formed only from **6b, c**). However, the substituent labels in these products occur in three distinct patterns: either at C-1 and C-4 (**9a**), at C-1 and C-2 (**9d**), or at C-1, C-2, and C-4 (**9b, c**). This finding indicates that there must be at least two mechanistic pathways leading to products as suggested in Schemes 3 and 4. It seems reasonable to assume that under the conditions of pyrolysis relatively fast (*E*), (*Z*)-isomerization occurs in **6a–c**.[9,16,18,19] Thus, nearly identical product distributions are obtained regardless of the stereochemistry of the starting material. The mechanism depicted in Scheme 3 then provides a rationale for the products **9** bearing the label at C-14. After initial (*E*), (*Z*)-equilibration, the (*E*, *Z*)-and/or (*Z*, *Z*)-isomer undergoes an eight electron electrocyclic ring closure to an intermediate eight-membered cyclic



Scheme 3. Proposed mechanism of formation of **9a–c** from **6a–c** [R = H, D, $Si(CH_3)_3$]



Scheme 4. Proposed mechanism of formation of **9b–d** from **6b–d** [R = H, D, $(CH_3)_2SiCH_2CH_2Si(CH_3)_2$]. Numbers on arrows indicate the positions between which bond formation occurs.

allene. Electrocyclic (six-electron) closure regenerates the benzene ring and concomitantly furnishes a fused cyclobutene which would subsequently ring open to the product.

The mechanism depicted in Scheme 4 explains the formation of the products labeled at C-1,2. Electrocyclic closure of (*Z*, *Z*)-**6** (the benzologous analogy to the closure of **3** to **4**) initially forms bisallene **A**, anticipated[20] to be in equilibrium with its isomer **2** (or its derivatives), the goal of this project. Intermediate **A**, however, may go on by other pathways. Thus, electrocyclic closure involving C-4,9 to **B** followed by ring opening would give **9**. Alternatively, **A** may give **9** directly by C-4,9 bond formation and concomitant C-3,4 bond breaking. Target **2** may independently lead to **9** via a six-electron electrocyclic closure followed by a retro[2 + 2] cycloaddition (Scheme 4). Finally, another (although kinetically less likely) possibility involves a cycloaddition of one enyne unit in **6** (e.g. C-1,2,3,4) to the other alkyne (e.g. C-9,10) furnishing **B** without the intermediacy of **A**.

Pyrolysis of **6a** gives solely **9a**, indicating the exclusive operation of the mechanism elaborated in Scheme 3. Apparently, the bulk of the trimethylsilyl groups precludes a close approach between C-1 and C-10, enforcing this pathway. It may be pointed out that a similar deviation from the major mode of ring closure was observed in the pyrolysis of **3**[9] leading to a small amount of an aromatic byproduct to **5**, not observed in the analogous cyclization of protodesilyated **3** to benzocyclobutadiene dimer.[21]

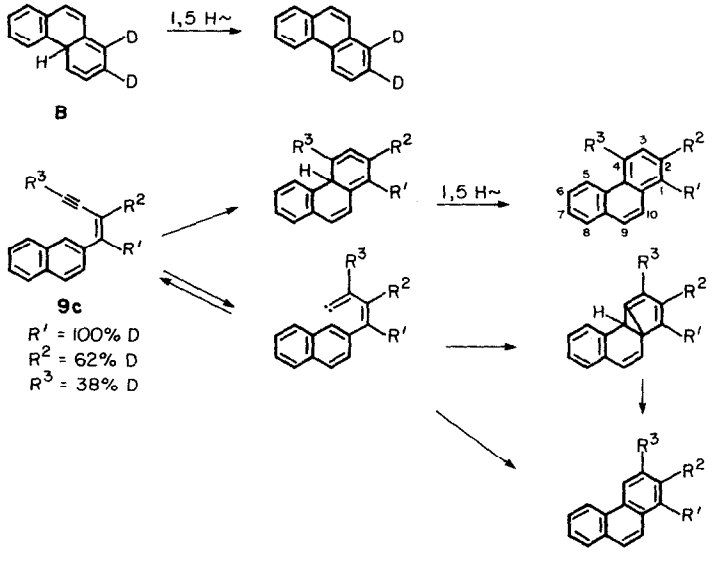
In contrast to **6a**, compound **6d**, in which the alkyne groups are being held in close proximity, chooses one or more of the pathways in Scheme 4. Models indicate that direct reaction from **6d** to **B** is unlikely in view of the excessive distance between C-4 and C-9. We therefore favor **A** as the initial intermediate en route to **9d**.

Finally, deuterium labeled **6c** forms naphthylbutenynes **9c** which exhibit deuterium at all three positions of the butenyne substituent, C-1 (Scheme 1) being completely deuterated. This is consistent with the simultaneous operation of both the mechanisms in Scheme 3 and 4. We have not excluded the possibility that the individual stereoisomers react by distinct mechanisms in this case.

In order to assess the thermodynamic feasibility of our schemes the heats of formation for various compounds were estimated using group-equivalent techniques.[22] The following results were obtained (kcal mole^{-1}): **6b** 165; **B** (Scheme 4) 141; **2** (as a polyene) ~138; **9b** 108; phenanthrene 50. Thus, **2**, if formed, would be thermodynamically unstable with respect to rearrangement to **9b**.

Several mechanisms can be envisioned for the formation of phenanthrene from **6b, c** (Scheme 5). The first constitutes a simple 1,5-hydrogen migration from **B**. The other two processes involve cyclizations of **9b**, either direct followed by a hydride shift, or through the intermediacy of a vinyl carbene. Interconversion of acetylene and vinylidene has been proposed in the pyrolysis of ethyne.[23] Wentrup and coworkers have suggested both a vinyl carbene intermediate and direct cyclization as possible mechanisms for the thermal conversion of phenylbut-1-en-3-yne to naphthalene.[19] The intermediacy of **B** appears unlikely to us since it does not account for the appearance of deuterium at C-3. Furthermore if **B** were to be a precursor to phenanthrene, then a phenanthrene derivative should have been observed in the pyrolysis of **6d**, since there is no apparent reason why an annulated disilacyclohexene should inhibit 1,5-hydride migration.

The evidence points to **9b** as the precursor to phenanthrene. Thus, **9b** furnishes the latter on independent pyrolysis. The absence of a phenanthrene derivative in the FVP of **6d** may be explained by invoking a steric barrier to coplanarity of the butenyne fragment with the naphthalene ring due to the presence of the added disilacyclohexene ring. If one postulates a vinylcarbene pathway as the mechanistic connection between **9c** and the dideuteriophenanthrenes a ready explanation for the observed deuterium labeling is found: C-1 is completely deuterated, C-2 and C-3 share the rest of the label. Direct ring closure would result in the presence of label at C-4, which is not observed



Scheme 5. Proposed mechanisms for phenanthrene formation.

(<5%). The relatively facile generation of phenanthrene from **9b, c** when the latter is formed from **6b, c** is probably due to the initial vibrationally excited nature of the intermediate. Calculations show that vinylidene is 34–40 kcal mole^{-1} more energetic than ethyne.[24] Since the conversion of **6b** to **9b** is *ca* 57 kcal mole^{-1} exothermic, the intermediate **9b** is probably sufficiently activated for further reaction.

In conclusion, we have discovered that the enynes **6a–d** undergo unusual thermal rearrangements by at least two different mechanistic modes depending on the substituents on the alkyne termini. Although the target compound **2** was not isolated it could have been an intermediate.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Varian EM-390 (90 MHz) or on home-built 200 and 250MHz instruments. Spectra are reported in δ referenced to TMS where CCl_4 was the solvent. When other solvents were used peaks were measured relative to their residual proton peak using the following chemical shifts: $CDCl_3$ δ 7.24, C_6D_6 7.15, CD_3CN 1.93. IR spectra were observed on a Perkin-Elmer 337 spectrometer and are reported in cm^{-1}, UV spectra were recorded on a Cary 219 spectrometer and are reported in nm (log ϵ). Mass spectra and elemental analyses were performed by the Mass Spectral Service and Microanalytical Laboratory of the University of California, Berkeley, California. Analyses are within 0.3% of calculated values unless otherwise noted. Mps and bps are uncorrected. Mps were determined on a Thomas-Hoover Unimelt apparatus. Column chromatography was carried out using Alfa aluminum oxide, activated, neutral, CAMAG, 95+%, −60 mesh to which 5% water was added (activity III), or EM reagents silica gel 60, 70–230 mesh ASTM. Preparative TLC was performed on plates prepared from EM reagents silica gel PF-254 with $CaSO_4 \cdot 1/2\ H_2O$ using a spinning plate, continuous elution system (Chromatotron, Harrison Research) under N_2. Anhyd ether was used as received. THF was distilled from sodium–benzophenone. DMSO was distilled from CaH_2.

3-*Trimethysilylprop-2-ynal.* The aldehyde was prepared by oxidation of 3-trimethylsilylprop-2-yn-1-ol[12b] as described[12c] except for the phase transfer catalyst employed: $(n\text{-}Pr)_4N^+HSO_4^-$. The base washing was omitted. The product was a colorless liquid bp 44–46°, 17 torr (lit.[12a] 52°, 17 torr) obtained in 70% yield.

1,2-*Bis*(4-*trimethylsilylbut*-1-*en*-3-*ynyl*)*benzene* (**6a**), The procedure for bis-Wittig reactions was adapted from Vollhardt.[10] A suspension of *o*-xylylenebis(triphenylphosphonium bromide)[11] (7.89g, 10 mmol, dried overnight at 100°, 0.1 torr) in ether (350 ml) was stirred under N_2 at RT while n-BuLi in hexane soln (1.27 M, 16 ml, 20 mmol) was added over 20 min. The color changed to deep purple-red. After stirring another 90 min a soln of 3-trimethylsilylpropropynal (2.52 g, 20 mmol) was added at RT over 2 min. The mixture turned brown. After stirring 20 hr the reaction was filtered and concentrated on the rotary evaporator leaving a dark, viscous oil (4.8g). Filtration through alumina with ether was followed by chromatography on a 30 × 1.5 cm alumina column, eluting with pentane. A yellow, fast moving band was obtained giving a yellow oil (1.39 g, 4.35 mmol, 43%) which was a mixture of (*Z, Z*)-, (*E, E*)-, and (*E, Z*)-isomers of **6a** in the ratio 1:1.7:6.0 (^{1}H NMR spectral integration). Of this, 600 mg was separated into two fractions using an Altex LC equipped with two 10 mm d × 20 cm l. Ultrasphere ODS (reverse phase) columns connected in series, eluting with CH_3CN. Fraction 1 gave a 6:1 mixture (^{1}H NMR) of (*E, Z*)- and (*Z, Z*)-**6a** (450 mg): pale yellow oil; ^{1}H NMR (90 MHz, CCl_4) δ 8.1 (m), 7.3 (m) (combined integration 4H), 7.17 [d, J = 16, (*E*)- H-1], 6.92 [d, J = 12, (*Z*)-H-1 of (*E, Z*)-isomer], 6.81 [d, J = 12, (*Z*)-H-1 of (*Z, Z*)-isomer] (combined integration 2H), 5.93 [d, J = 16, (*E*)-H-2], 5.69 [d, J = 12, (*Z*)-H-2 of (*E, Z*)-isomer, 5.64 [d, J = 12, (*Z*)-H-2 of (*Z, Z*)-isomer] (combined integration 2H), 0.25 (s), 0.24 (s), 0.22 (s) (combined integration 18H); IR (neat) 3100, 3050, 2180, 2150, 2120, 1470, 1440, 1400, 1245, 1100, 1060, 1020, 950, 850, 750, 690, 650, 635; UV (EtOH) 307 (4.42), 280 (4.35), 272 sh (4.30), 268 sh (4.27); *m/e* (rel intensity) 322 (M$^+$, 7), 307 (10), 233 (14), 219 (12), 209 (12), 155 (17), 152 (11), 149 (17), 83 (10), 73 (100); HRMS: calcd ($C_{20}H_{26}Si_2$) 322.1573. Found: 322.1564. Anal. ($C_{20}H_{26}Si_2$) C,H. Fraction 2 gave (*E, E*)-**6a** (107 mg): pale yellow oil; ^{1}H NMR (90 MHz, CCl_4) δ 7.26 (m, 4H), 7.23 (d, J = 16, 2H, H-1), 5.99 (d, J = 16, 2H, H-2), 0.20 (s, 18H); IR (neat) 3200, 2950, 2920, 2130, 1460, 1440, 1400, 1250, 1060, 950, 850, 750, 680, 640; *m/e* (rel intensity) 322 (M$^+$, 7), 307 (10), 233 (14), 219 (12), 209 (12), 155 (17), 152 (11), 149 (17), 83 (10), 73 (100); HRMS: Calc. ($C_{20}H_{26}Si_2$) 322.1573. (Found: 322.1564.) Anal. calc ($C_{20}H_{26}Si_2$) C 74.46, H 8.12. (Found: C 73.90, H 8.33.)

Pyrolysis of **6a**, *preparation of* (E)- *and* (Z)-1,4-*bis*(*trimethylsilyl*)-1-(2-*naphthyl*) *but*-1-*en*-3-*yne* (**9a**). For FVP a horizontal unpacked quartz tube (2 × 50 cm), closed at one end was used. The tube was treated with hexamethyldisilazane and dried at 150° for several h prior to use. The starting material, a 6:1 mixture of (*E, Z*)- and (*Z, Z*)-**6a** (98 mg, 0.30 mmol) was placed near the closed end. The tube was connected to a cold finger (liquid N_2) and the system was evacuated to between 5×10^{-4} torr and 10^{-5} torr. A Hoskins furnace was used to heat a *ca* 15 cm portion of the tube between the starting material and the cold zone to 740° (measured at the hottest point). Other parts of the apparatus were heated with electrical heating tape. In this way on sublimation the product collected only on the cold finger. The pyrolysate was washed off the cold finger with pentane giving 95 mg partly crystalline material exhibiting a pale violet color. ^{1}H NMR spectra and LC showed only two products. They were separated by LC (MeOH). Fraction 1 gave (*Z*)-**9a** (39 mg, 0.12 mmol, 40%): colorless crystals, m.p. 91.5–93° (from CH_3OH); ^{1}H NMR (250 MHz, CD_3CN) δ 7.85 (m, 3H, H-4',5',8'), 7.65 (d, J = 1.2, 1H, H-1'), 7.48 (m, 2H, H-6',7'), 7.33 (dd, J = 1.7, 8.5, 1H, H-3'), 6.13 (s, 1H, vinyl), 0.15 (s, 9H), −0.10 (s, 9H); IR (KBr) 3080, 2950, 2900, 2150, 1550, 1245, 1150, 900, 875, 850, 825, 750, 640; UV (EtOH) 290 (3.76), 272 (4.07), 261 (4.30), 223 (4.70), 211 (4.50); *m/e* (rel intensity) 322 (M$^+$, 59), 308 (12), 307 (37), 250 (5), 249 (19), 248 (14), 235 (6), 234 (15), 233 (22), 155 (46); HRMS calcd ($C_{20}H_{26}Si_2$): 322.1573. Found: 322.1559. Anal. ($C_{20}H_{26}Si_2$) C,H. Fraction 2 gave (*E*)-**9a** (18 mg, 0.056 mmol, 18%): colorless crystals, mp 60.2–60.7° (after two crystallizations from MeOH). ^{1}H NMR (250 MHz, CD_3CN) δ 7.83 (m, 3H, H-4',5',8'), 7.56 (d, J = 1.2), 1H, H-1'), 7.47 (m, 2H, H-6',7'), 7.25 (dd, J = 1.7, 8.5, 1H, H-3'), 6.25 (s, 1H, vinyl), 0.27 (s, 9H), 0.21 (s, 9H); IR (KBr) 3080, 2950, 2900, 2180, 2150, 1550, 1245, 1150, 900, 875, 850, 825, 750, 640; UV (EtOH) 292 sh (3.84), 273 (4.16), 264 (4.16), 221 (4.47); *m/e* same as (*Z*)-**9a**; HRMS ($C_{20}H_{26}Si_2$) Calc 322.1573. (Found 322.1567.) Anal. ($C_{20}H_{26}Si_2$) C,H.

Fluoride protodesilylation of (Z)-**9a** *to* **9b**. Compound (*Z*)-**9a** (3 mg, 9 μmol) was treated with $Me_4N^+F^- \cdot 3H_2O$ (25 mg) in DMSO (1.5 ml) with stirring under N_2 for 90 min at 55°. The cooled mixture was poured into water and pentane, the organic phase dried ($MgSO_4$), filtered and the solvent removed leaving a colorless oil (1 mg, 62%) whose ^{1}H NMR spectrum (250 MHz) was identical to **9b**[15] obtained by pyrolysis of **6b** except for the *E*:*Z* ratio (*ca.* 1:2). TLC (silica gel, pentane) showed two spots with identical R_F to cospotted **9b**.

Base catalyzed protodesilylation of (Z)-**9a** *to* (Z)-1-*trimethylsilyl*-1-(2-*naphthyl*)*but*-1-*en*-3-*yne* [(Z)-**10**] Compound (*Z*)-**9a** (30 mg, 93 μmol) was stirred in MeOH (30 ml) containing KOH (3 mg) under N_2 for 45 min. The mixture was then poured into brine and extracted with two portions of benzene (2 × 25 ml). The extracts were dried ($MgSO_4$), filtered, and the solvent removed leaving partly solid, nearly pure (*Z*)-**10** (16 mg, 64 μmol, 68%). Crystallization (CH_3OH) and sublimation (55°, 0.02 torr) gave (*Z*)-**10**: colorless crystals, mp 53–55°; ^{1}H NMR (C_6D_6, 250 MHz) δ 7.63 (m, 3H, H-4',5',8'), 7.34 (dd, J = 1.7, 8.4, 1H, H-3'), 7.23 (m, 3H, H-1',6',7'), 6.09 (d, J = 2.2, 1H, vinyl), 2.53 (d, J = 2.2, 1H, alkynyl), 0.01 (s, 9H); IR (KBr) 3300, 3050, 2950, 2900, 2100, 1590, 1500, 1375, 1250, 1100, 1000, 950, 930, 840, 820, 750, 650, 625; UV (EtOH), 281 (3.86), 268 (4.14), 257 (4.19), 221 (4.85); *m/e* (rel intensity) 250 (M$^+$, 22), 237 (6), 236 (23), 235 (100), 219 (17), 209 (14), 152 (18), 83 (72), 73 (59); HRMS Calc ($C_{17}H_{18}Si$): 250.1178. (Found: 250.1172.)

Base catalyzed protodesilylation of (E)-**9a** *to* (E)-**10**. The same procedure used for desilylation of (*Z*)-**9a** was followed to give (*E*)-**10** (60%), colorless oil: ^{1}H NMR (250 MHz, C_6D_6) δ 7.59 (m, 2H, H-5',8'), 7.51 (d, J = 8.6, 1H, H-4'), 7.40 (br s, 1H, H-1'), 7.23 (m, 2H, H-6',7'), 7.08 (dd, J = 1.6, 8.5, 1H, H-3'), 6.22 (d, J = 2.5, 1H), 2.85 (d, J = 2.6, 1H), 0.35 (s, 9H).

1,2-*Bis*(*but*-1-*en*-3-*ynyl*)*benzene* (**6b**). A mixture of the three isomers of **6a** (58 mg, 0.18 mmol) was stirred in abs. EtOH (2 ml) containing NaOEt (from ~3 mg Na) for 1 hr under N_2. The mixture was poured into water and pentane, the aqueous phase extracted with pentane, and the combined organic layers dried ($MgSO_4$), filtered and concentrated leaving 26 mg (0.15 mmol, 81%) of a colorless oil that rapidly turned yellow, orange, and then brown when concentrated. The product was a 1:1.5:3.5 mixture of (*Z*, *Z*)-, (*E*, *E*)- and (*E*, *Z*)-**6b** (by ^{1}H NMR spectral integration): ^{1}H NMR (200 MHz, C_6D_6) δ 8.21 (m), 8.06 (m), 7.0 (m), 6.50 [d, J = 11.9, H-1 of (*Z*, *Z*)-isomer], 6.42 [d, J = 11.9, (*Z*)-H-1 of (*E*, *Z*)-isomer] (combined integration 6H), 5.82 [dd, J = 16.2, 2.3, (*E*)-H-2 of (*E*, *Z*)-isomer], 5.77 [dd, J = 16.1, 2.3, H-2 of (*E*, *E*)-isomer], 5.48 [dd, J = 11.9, 2.3, H-2 of (*Z*, *Z*)-isomer], 5.39 [dd, J = 11.9, 2.3, (*Z*)-H-2 of (*E*, *Z*)-isomer] (combined integration 2H), 2.72 (m, 2H, H-4); IR ($CHCl_3$) 3285, 3060, 3010, 2280, 2100, 1475, 1450, 995, 670, 620; *m*/*e* (rel intensity) 178 (M^+, 100), 177 (30), 176 (55), 175 (14), 152 (31); HRMS Calc ($C_{14}H_{10}$); 178.0783. (Found: 178.0784.)

Pyrolysis of **6b** *to* **9b** *and phenanthrene*. The mixture of **6b** isomers (106 mg, 0.60 mmole) was pyrolyzed as for **6a** but the oven was heated to 600°. A red, brittle residue remained at the source. Only **9b** and phenanthrene were observed by ^{1}H NMR spectroscopy of the crude pyrolysate, which had a violet color. Preparative TLC (pentane) gave two bands: fraction 1 gave phenanthrene (19 mg, 0.11 mmol, 18%): colorless crystals, mp 98.5–102° (mixed with authentic material, m.p. 98.5–101.5°); the ^{1}H NMR (200 MHz) spectrum and TLC behavior (silica, pentane) were identical to authentic phenanthrene. Fraction 2 gave a 1.7:1 mixture of (*E*)- and (*Z*)-**9b** (33 mg, 0.19 mmol, 32%): pale violet crystals, m.p. 82–110° [lit.[15] m.p. 80.5–82° for (*E*)-**9b**, 108–110° for (*Z*)-**9b**]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.20 (m), 8.12 (dd, J = 8.7, 1.8), 7.79 (m), 7.51 (m) (combined integration 7H), 7.19 [d, J = 16.5, (*E*)-H-1], 6.86 [d, J = 12.0, (*Z*)-H-1] (combined integration 1H], 6.24 [dd, J = 16.3, 2.4, (*E*)-H-2], 5.75 (dd, J = 12.1, 2.7, (*Z*)-H-2] (combined integration 1H), 3.41 [dd, J = 2.7, 1.0, (*Z*)-H-4], 3.10 [dd, J = 2.4, 0.5, (*E*)-H-4] (combined integration 1H); the ^{1}H NMR data for this compound concur with the literature values;[15] IR (NaCl) 3300, 3060, 3010, 2920, 2850, 2100, 1635, 955, 895, 860, 810, 665, 640; *m*/*e* (rel intensity) 178 (M^+, 100), 177 (30), 176 (55), 175 (14), 152 (31); HRMS Calcd ($C_{14}H_{10}$): 178.0783. (Found: 178.0784.)

1,2-*Bis*(4-*deuterio*-*but*-1-*en*-3-*ynyl*)*benzene* (**6c**). The mixture of all three isomers of **6a** (116 mg, 0.36 mmol) was treated with EtOD containing NaOEt (from 10 mg Na and 5 ml EtOD, 99% D) for 3 hr. Pentane (10 ml) and D_2O (2 ml, 99.9%) were added, the organic phase dried ($MgSO_4$), and solvent removed leaving a 1:1.5:3.5 mixture of (*Z*, *Z*)-, (*E*, *E*)- and (*E*, *Z*)-**6c** (38 mg, 0.21 mmol, 59%): yellow oil; the ^{1}H NMR (200 MHz, $CDCl_3$) spectrum was the same as that of **6b** except that the H-2 resonances occur as d (J = 12.0 and 16.3) rather than dd; the integrated intensity of the alkynyl region was less than 3% than that of the H-2-resonances; *m*/*e* (rel intensity) 180 (M^+, 100), 179 (10), 178 (3), 154 (4). HRMS Calc ($C_{14}H_8D_2$) 180.0906. (Found 180.0912.)

Pyrolysis of **6c**. This experiment was carried out in the same way as the pyrolysis of **6b**. Thus, **6c** (38 mg, 0.21 mmol) yielded phenanthrene-d_2 (10 mg, 0.055 mmol, 26%): colorless crystals; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.69 (br d, J = 8.5, a broad singlet is superimposed at δ 8.69, 1.95H, H-4[17]), 7.89 (m, 1.03H, H-1), 7.74 (s, 2.05H, H-9), 7.60 (m, 2.98H, H-2,3); *m*/*e* (rel intensity) 180 (M^+, 100), 179 (12), 178 (16), 177 (8), 154 (6), 153 (7), 152 (6), 149 (8), 90 (11); HRMS calc ($C_{14}H_8D_2$): 180.0906. Found: 180.0905. The naphthylbutenynes (**9c**) were obtained in 50% yield: ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.20 (m) 8.12 (dd, J = 8.7, 1.8), 7.79 (m), 7.51 (m) (combined integration 7H), 6.25 [t, J ≅ 2, (*E*)-2-H], 5.77 [br s, (*Z*)-isomer, vinyl on C_2) (combined integration 0.38 H), 3.42 (s, 0.20H, (*Z*)-isomer, alkynyl), 3.11 (*s*, 0.34H, (*E*)-isomer, alkynyl) (combined integration 0.62H); *m*/*e* (rel intensity) 180 (M^+, 100) 179 (8), 86 (16), 84 (26). HRMS Calc ($C_{14}H_8D_2$): 180.0906. (Found: 180.0912.)

4,4,7,7-*Tetramethyl*-4,7-*disiladeca*-2,8-*diyne*-1,10-*diol* (**7**). This procedure was adapted from that used for preparation of 3-trimethylsilylprop-2-yn-ol.[12b] A soln of EtMgBr in THF (0.31 mol in 300 ml) was stirred in an ice bath while propargyltetrahydropyranyl ether (42.06 g, 0.30 mmol) in THF (50 ml) was added dropwise. The ice bath was removed and the mixture stirred at room temp for 30 min and then at reflux for 30 min. It was then cooled (ice bath) and a solution of 1,2-bis(chlorodimethylsilyl)ethane (32.1 g, 0.149 mol) in THF (70 ml) added dropwise. Stirring was continued at room temp for 18 hr and then at reflux for 1 hr. After cooling in ice, sat NH_4Cl aq (40 ml) was added dropwise. The organic phase was decanted from the granular ppt and the ppt was washed with 4 portions of ether (80 ml). The combined organic layers were concentrated on a rotary evaporator. The residue was stirred with MeOH (350 ml), ice (35 g), and conc HCl (0.5 ml) for two days, and poured into 1.5l water. This was extracted with 6 portions of ether (100 ml). The combined extracts were dried ($MgSO_4$), filtered, and concentrated on a rotary evaporator leaving a yellow oil (46 g). Distillation (b.p. 138–155°; 0.01 to 0.1 torr) gave **7** (28.1 g, 0.111 mol, 74%): viscous, nearly colorless oil; ^{1}H NMR (90 MHz, CCl_4) δ 4.21 (br s, 4H), 3.53 (br s, 2H), 0.61 (s, 4H), 0.20 (s, 12H); IR (neat) 3350, 2950, 2900, 2880, 2175, 1400, 1350, 1250; *m*/*e* (rel intensity) 254 (M^+, 1), 236 (1), 221 (9), 193 (23), 161 (14), 149 (25), 147 (11), 145 (53), 133 (34), 131 (10), 119 (20), 117 (22), 113 (34), 111 (14), 96 (72), 85 (100); HRMS Calc ($C_{12}H_{22}O_2Si_2$): 254.1158. (Found: 254.1158.)

4,4,7,7-*Tetramethyl*-4,7-*disiladeca*-2,8-*diynedial*. The procedure of Landini *et al.*[12c] was adapted. The diol **7** (509 mg, 2 mmol) in CH_2Cl_2 (10 ml) and *n*-$Pr_4N^+HSO_4^-$ (0.4 mmol from 0.81 g 10% n-$Pr_4N^+OH^-$ and 0.05 ml conc H_2SO_4) were stirred at −10° while a soln of K_2CrO_4 (513 mg, 2.64 mmol) in 32% H_2SO_4 (9 ml) was added dropwise over 40 min. The temp was maintained between −10 and 0°. After stirring another 15 min at −5°, 10% $FeSO_4$ (14 ml) was added. The mixture was poured into water and CH_2Cl_2, the aqueous phase extracted with CH_2Cl_2, and the combined organic phases were washed with water, dried ($MgSO_4$) and the solvent removed leaving nearly pure (^{1}H NMR) dialdehyde **8** (342 mg, 1.37 mmol, 68%). An attempted bulb-to-bulb distillation resulted in a violent decomposition. ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.00 (*s*, 2H), 0.53 (s, 4H), 0.12 (s, 12H); IR (neat) 2940, 2860, 2150, 1660, 1250, 1130, 1090, 1010, 850, 800; *m*/*e* (rel intensity) 250 (M^+, 3), 235 (18), 222 (12), 207 (41), 133 (63), 111 (100); HRMS Calc ($C_{12}H_{18}O_2Si_2$): 250.0845. (Found: 250.0844.)

(*Z*, *Z*)-1,12-*Disila*-6,7-*benzocyclotetradeca*-4,8-*dien*-2,10-*diyne* (**6d**). To a suspension of *o*-xylylenebis(triphenylphosphonium bromide) (10.60 g, 13.4 mmol) (dried overnight at 100°, 0.05 torr) in ether (1200 ml) was added n-BuLi in hexane solution (1.41 M, 19 ml, 26.8 mmol) with stirring at RT. After stirring for 3 hr the deep purple-red soln was cooled to −70°. A soln of **8** (3.37 g, 13.4 mmol) in ether (25 ml) was added all at once. The dry-ice bath was removed and after stirring at room temp for 20 hr sat NH_4Cl aq (5 ml) was added and the ppt allowed to settle. The supernatant soln was decanted, dried ($MgSO_4$), and concentrated leaving a dark residue. It was dissolved in a minimum of ether and pentane added. The ppt was filtered off and the filtrate concentrated to a dark oil. Filtration through 20 g alumina (pentane) gave a colorless residue that turned yellow. Chromatography on 2 mm silica preparative TLC plates eluting with 0.75% ether in pentane gave two bands. Fraction 1 was a mixture of stereoisomers of **6d** (306 mg); fraction 2 was a mixture which was not investigated. Crystallization (pentane, −80°) of fraction 1 gave (*Z*, *Z*)-**6d** (82 mg, 0.26 mmol, 1%): colorless crystals, m.p. 79–81°; (the mother liquor contains additional product, isolable by reverse-phase LC eluting with MeCN; the yield can thus be increased to about 3%); ^{1}H NMR (250 MHz, C_6D_6) δ 7.46 (AA', 2H), 7.07 (BB', 2H), 6.53 (d, J = 11.2, 2H), 5.59 (d, J = 11.3, 2H), 0.4 (m, AA'BB', 4H), 0.13 (s, 6H), 0.10 (s, 6H); IR (neat) 3000, 2140, 1610, 1250, 1050, 845, 835, 780, 750; UV (isooctane) 251 (4.19), 214 (4.14); *m*/*e* (rel intensity) 320 (M^+, 20), 305 (61), 277

(70), 245 (60), 73 (97), 71 (68), 59 (61), 57 (100); HRMS Calc: ($C_{20}H_{24}Si_2$) 320.1417. (Found: 320.1432.) Anal. ($C_{20}H_{24}Si_2$) C, H.

Pyrolysis of **6d** *to* 1-*ethynyl*-3,3,5,5-*tetramethyl*-2-(2-*naphthyl*)-3,5-*disilacyclohex*-1-*ene* (**9d**). Flash vacuum pyrolysis of **6d** (44 mg, 0.14 mmol) at 560° gave a violet pyrolysate which was nearly pure **9d** (^{1}H NMR) (44 mg, 0.14 mmol, 100%). Crystallization (MeOH) gave pure **9d**: colorless crystals, mp 87–88°; ^{1}H NMR (250 MHz, CD_3CN) δ 7.85 (m, 3H, H-4′,5′,8′), 7.47 (m, 3H, H-1′,6′,7′), 7.19 (dd, J = 8.4, 1.7, 1H, H-3′), 3.30 (s, 1H), 0.85 (AA′BB′, 4H) 0.23 (s, 6H), 0.03 (s, 6H); IR ($CHCl_3$) 3305, 3280, 2960, 2110, 1650, 1620, 1590, 1420, 1245, 830; UV (isooctane) 381 (2.49), 365 (2.60), 309 sh (4.06), 299 (4.13), 270 (4.19), 260 (4.22), 253 (4.22), 223 (4.83); *m/e* (rel intensity) 320 (M^+, 84), 305 (100), 277 (63), 245 (40), 209 (75), 149 (43), 73 (78); HRMS Calc ($C_{20}H_{24}Si_2$): 320.1417. (Found: 320.1432.) Anal. ($C_{20}H_{24}Si_2$) C, H.

Fluoride protodesilylation of **9d**. A mixture of **9d** (27 mg, 0.084 mmol) $Me_4N^+F^-$. $3H_2O$ (100 mg) and DMSO (2.4 ml) was stirred under N_2 for 2 hr at 50°. The mixture was cooled, poured into brine (30 ml), and extracted with pentane. The combined extracts were washed with water, dried ($MgSO_4$) and the solvent removed leaving a colorless oil (20 mg). This was chromatographed on a 1 mm silica preparative TLC plate (pentane). The first band was an unidentified oil (12 mg). The second band gave colorless crystals (6 mg, 0.033 mmol, 40%). The ^{1}H NMR spectrum (250 MHz) was identical to that of (**6b**) except that the ratio of *E*:*Z* was 4.3:1.

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