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One-Pot Desilylation/Dimerization of Ethynyl- and Butadiynyltrimethylsilanes. Synthesis of Tetrayne-Linked Dehydrobenzoannulenes.

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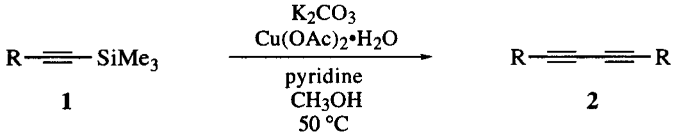
Abstract: Addition of K_2CO_3 to standard Eglinton coupling conditions effects a one-pot desilylation/dimerization reaction of alkynyltrimethylsilanes. Use of this procedure on substituted phenylbutadiynylsilanes ultimately leads to the formation of dehydrobenzoannulenes possessing an unprecedented number of acetylene linkers. © 1997 Elsevier Science Ltd.

The resurgence of dehydrobenzoannulene chemistry over the last few years has led to the synthesis and study of a large number of new macrocycles exhibiting fascinating chemical and physical properties.[1] For example, certain systems have polymerized topochemically to give polydiacetylene tubes[2a] or decomposed explosively to furnish carbon-rich residues containing "bucky" materials.[2b] All of these new examples, though, are either monoyne- or diyne-connected molecules. Surprisingly, triyne and higher polyyne-linked annulenes have proven elusive.[3] This absence can be attributed to two factors: 1) method of annulene formation and 2) instability of alkyne precursors. Traditional copper-mediated dimerization/cyclooligomerization reactions of α,ω-diacetylenes typically produce complex mixtures of diyne-linked products that are difficult to separate and often provide low isolated yields of a desired macrocycle.[4] Palladium-catalyzed alkynylation has proven effective in the preparation of monoyne-linked annulenes.[1c] Both of these routes might be effective for the production of higher polyyne-linked systems; however, a vast majority of the terminal diynes, triynes, etc., needed for synthesis are highly sensitive molecules prone to rapid decomposition.[5] We recently reported a new dehydrobenzoannulene synthesis that circumvents this problem by generating unstable phenylbutadiynes *in situ* under Pd-coupling conditions;[6] thus, it should be possible to utilize *in situ* generated alkynes in a variety of other transformations. We report herein a simple one-pot desilylation/dimerization sequence for alkynyltrimethysilanes and feature this reaction as the key step in the synthesis of the first tetrayne-linked dehydrobenzoannulenes.

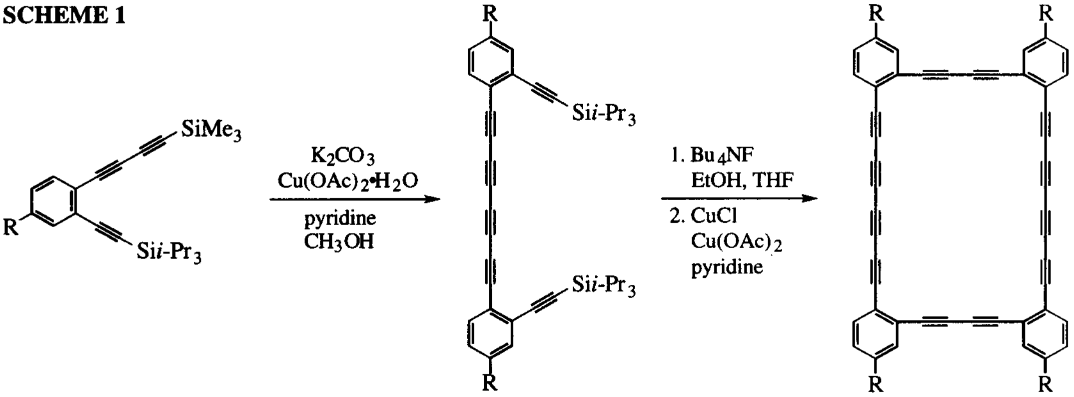
A common method for protiodesilylation of alkynyltrimethylsilanes involves K_2CO_3 in methanol.[7] We reasoned that addition of excess K_2CO_3 to standard Eglinton oxidative dimerization conditions ($Cu(OAc)_2 \cdot H_2O$, pyridine, methanol)[4c] should accomplish desilylation and alkyne dimerization in a single step; this indeed proved to be the case. Addition of ethynylsilanes **1a**-**c**[8a,b] (5 min) or butadiynylsilane **1d**[8c] (12 h)[9] to $Cu(OAc)_2 \cdot H_2O$ (40 equiv) and K_2CO_3 (30 equiv) in pyridine/methanol (1:1 v:v) at 50 °C provided dimers **2a**-**d**[10] in very good to excellent yields.



a	R = C_6H_5	98%
b	R = 2-BrC_6H_4	85%
c	R = 2,6-$Br_2C_6H_3$	92%
d	R = $C_6H_5C{\equiv}C$	82%

Formation of **2d** proved conclusively that reactive phenylbutadiynes could be utilized in this reaction sequence and then subjected to further elaboration. Exposure of substituted butadiynylsilane **3a**[6a] to the same conditions afforded tetrayne **4a**[11] as a bright yellow solid (Scheme 1). Subsequent desilylation with Bu_4NF and cyclization with CuCl/Cu$(OAc)_2$[4d] under pseudo-high dilution conditions provided the orange cyclodimer **5a**[11] as the sole product; neither higher cyclooligomers nor the highly strained macrocycle arising from intramolecular ring closure were detected. Compound **5a** proved to be only marginally soluble in common solvents. Repetition of the synthetic sequence using **3b**[6b] furnished macrocycle **5b**[11]; inclusion of the *t*-butyl substituents noticeably improved product solubility and thus the isolated yield.

SCHEME 1



3a R = H
3b R = *t*-Bu

4a R = H (61%)
4b R = *t*-Bu (70%)

5a R = H (51%)
5b R = *t*-Bu (64%)

The [32]annulene derivatives were remarkably stable, showing little or no decomposition over several weeks in solution or in the crystalline state. Onset of decomposition occurred around 125 °C. DSC analysis showed this to be an extremely exothermic process that occurred over a narrow 8-10 °C range. The spectral properties of hydrocarbons **5a-b** varied only slightly from their acyclic precursors. For example, the benzene resonances in the ^1H NMR data were shifted downfield by less than 0.10 ppm upon cyclization, which we attribute to increased conjugation. The non-planarity of the 32-membered ring precluded any upfield shifts caused by a paratropic ring current.[12]

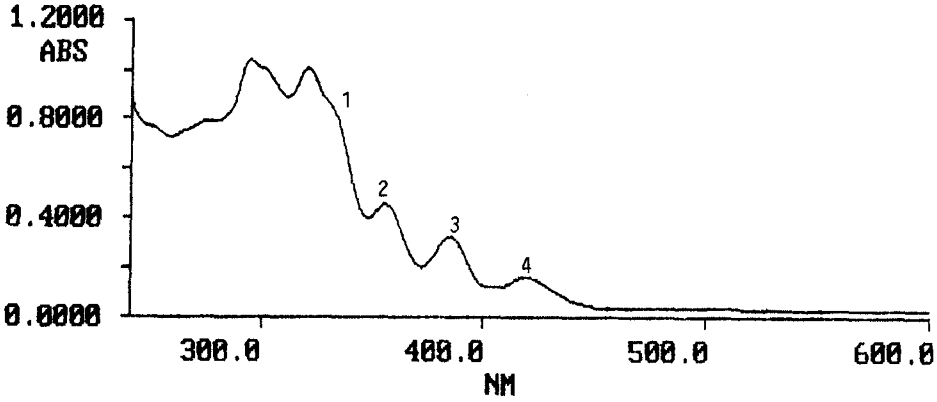


Figure 1. Electronic absorption spectrum of macrocycle **5a**.

The electronic absorption spectra of annulenes **5a-b** are dominated by the characteristic pattern of 1,8-diphenyloctatetrayne (**2d**),[13] as illustrated in Figure 1. Comparison of the assigned four diagnostic peaks in all five tetraynes is presented in Table 1. Compounds **4a-b** and **5a-b** exhibit small bathochromic shifts with respect to **2d**, *ca.* 10-20 nm. It is interesting to note that, as with the ^{1}H NMR data, the effect of cyclization on the UV data is minimal. The absorption bands at longer wavelengths are attributed to the interaction of the ^1L_a-state of the benzene nucleus with the polyacetylenic chromophore.[14]

Table 1. Selected Peaks from the Electronic Absorption Spectra of **2d**, **4a-b**, **5a-b**.[a,b]

Compd	Peak 1	Peak 2	Peak 3	Peak 4
2d[c]	318 (27,300)	342 (33,800)	367 (34,000)	397 (21,200)
4a	328 (47,300)	352 (27,800)	379 (30,200)	411 (21,100)
4b	330 (48,500)	353 (27,900)	380 (29,000)	412 (18,800)
5a	327 sh (78,000)	353 (43,800)	381 (33,400)	415 (18,600)
5b	330 sh (82,000)	356 (47,400)	385 (34,400)	419 (17,600)

[a] Peak assignments are as shown in Figure 1. [b] Spectra were obtained in CH_2Cl_2. [c] Reference 13.

In conclusion, we have developed an efficient one-pot desilylation/dimerization reaction of alkynyltrimethylsilanes and have prepared the first dehydrobenzoannulenes possessing an unprecedented number of four acetylenes between the aromatic rings. Further studies exploring the reactivity of these polyynes and other related annulenes will be reported in due course.

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9. Addition of butadiynylsilanes **1d** and **3a-b** occurred via syringe pump in order to minimize concentration and thus restrict polymerization of the reactive acetylenes.
10. **2a-b**: Reference 5, page 221; **2c**: Whitlock, B. J.; Whitlock, H. W. *J. Org. Chem.* **1972**, *37*, 3559; **2d**: Ogawa, T.; Sotelo, M.; Burillo, G.; Marvel, C. S. *J. Polym. Sci., Part C: Polym. Lett.* **1989**, *27*, 167.
11. Selected spectral data (^{1}H NMR: 300 MHz, ^{13}C NMR: 75.5 MHz, CDCl$_3$): **4a**: ^{1}H NMR δ 7.53-7.46 (m, 4H), 7.33 (dt, J = 7.8, 1.5, 2H), 7.26 (dt, J = 7.8, 1.5, 2H), 1.17 (s, 42H); ^{13}C NMR δ 133.22, 132.42, 129.37, 128.21, 128.00, 123.60, 104.17, 96.79, 78.02, 76.45, 68.08, 63.98, 18.66, 11.30; IR (CH$_2$Cl$_2$) υ 2208, 2156, 2127 cm^{-1}. **4b**: ^{1}H NMR δ 7.47 (d, J = 1.8, 2H), 7.45 (d, J = 8.2, 2H), 7.30 (dd, J = 8.2, 1.8, 4H), 1.31 (s, 18H), 1.18 (s, 42H); ^{13}C NMR δ 153.10, 133.09, 129.29, 127.85, 125.54, 120.79, 104.76, 95.90, 77.50, 76.71, 67.88, 64.06, 34.95, 30.92, 18.69, 11.34; IR (CH$_2$Cl$_2$) υ 2204, 2158 cm^{-1}. **5a**: ^{1}H NMR δ 7.58-7.51 (m, 8H), 7.38-7.35 (m, 8H); ^{13}C NMR δ 133.43, 132.48, 129.11, 128.72, 126.19, 124.90, 81.01, 79.11, 78.68, 75.18, 69.38, 63.98. **5b**: ^{1}H NMR δ 7.54 (d, J = 1.8, 4H), 7.49 (d, J = 8.5, 4H), 7.36 (dd, J = 8.5, 1.8, 4H), 1.31 (s, 36H); ^{13}C NMR δ 153.08, 133.38, 129.69, 126.52, 125.91, 121.91, 81.33, 78.27, 77.76, 75.34, 68.95, 63.83, 35.12, 30.88; MS (Pos-FAB, 121mV) *m/z* 817 (37, M$^+$+1), 816 (43, M$^+$), 154 (100).
12. To date, we have been unable to grow suitable crystals for X-ray diffraction studies. The non-planarity of **5a-b** is assumed based on the wealth of data for similar tetrabenzo-annelated structures.[2b,3,6a]
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