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Palladium-Catalyzed Synthesis of Tetraethynyl and Tetraethenyl Biphenyls: Elongated Tetrahedral Tectons

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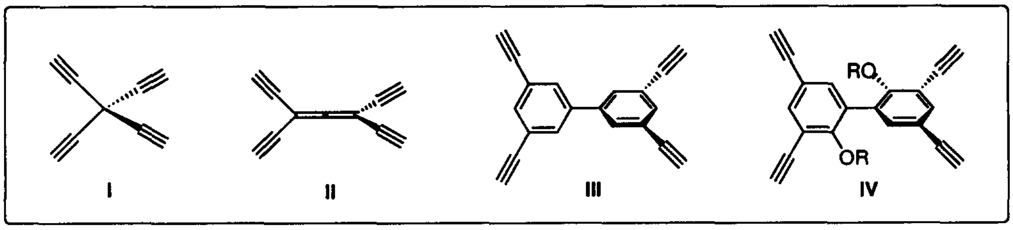
Abstract: The palladium-catalyzed coupling of O-acylated 3,3',5, 5'-tetrabromo-2,2'-biphenols with the corresponding stannanes furnishes tetraethenyl and tetraethynyl derivatives which.topologically can be considered as elongated tetrahedra. © 1997 Elsevier Science Ltd.

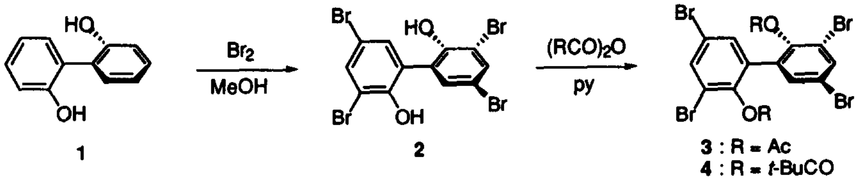
The assembly of carbon-rich two- or three dimensional nanomaterials from ethynylated scaffolds has attracted great attention.[1] Major achievements in this field are the preparation of tetraethynylmethane (I),[2] tetraethynylethene,[3] hexaethynylbenzene,[4] and π-metal complexes of tetraethynylcyclobutadiene,[5] and pentaethynylcyclopentadiene.[6] Tetraethynylallene (II), topologically related to tetraalkyne I, still remains as an elusive target.[1] Biphenyl III,[7] which displays the four alkynes in a flexible elongated tetrahedral arrangement, could offer a potential alternative to I and II.



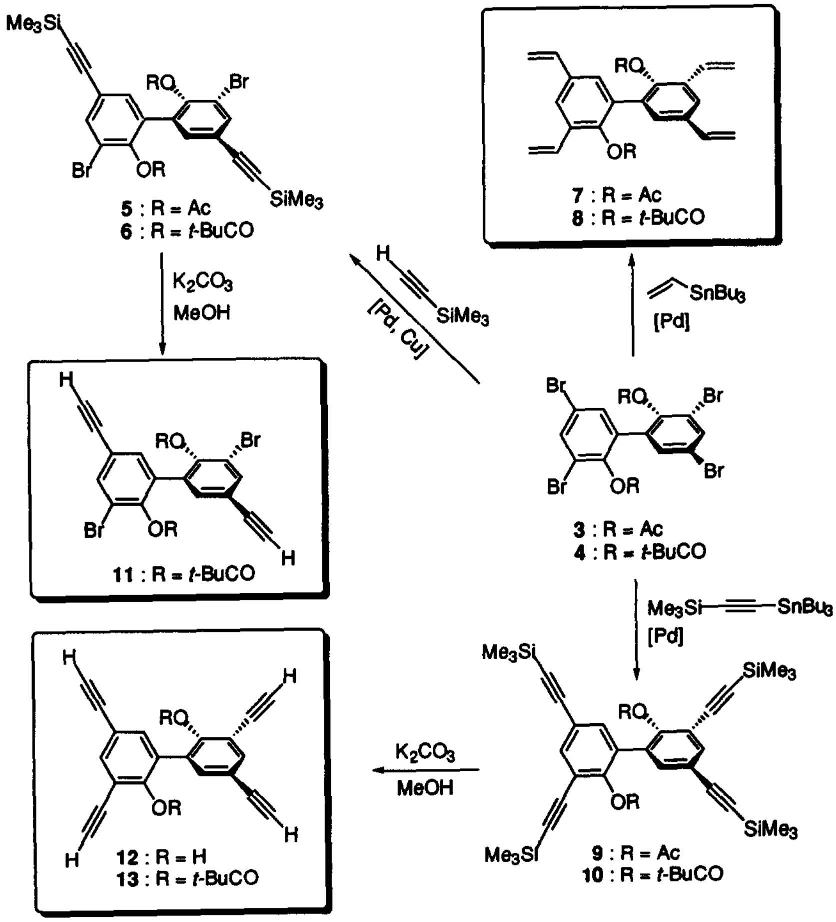
I II III IV

Herein we report a highly efficient synthesis of 2,2-dihydroxyderivatives **IV** by using the Stille cross-coupling of stannanes as the key step.[8] Biphenyls **IV** could undergo self-condensation by copper or palladium alkyne-alkyne coupling[1] to furnish three dimensional polymers bearing hydrophilic cavities. Two tetraethenylbiphenyl analogues (**7** and **8**) were also prepared by using the Stille coupling reaction. These compounds could be use as cross-linkers during polymerizations of styrenes and related monomers.[9] Additionally, biphenyls **7**-**8** could be use as core tectons for the synthesis of dendrimers.[10]

Biphenol (**1**) was efficiently tetrabrominated with excess bromine in methanol at 23 °C to give **2** in quantitative yield.[11] Acylation of **2** with acetic or trimethylacetic (pivalic) anhydride afforded **3** (97%) and **4** (95%).

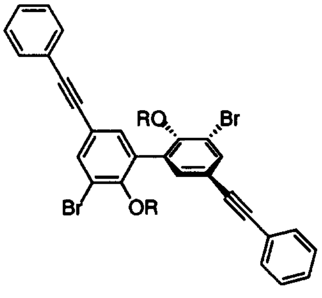


Sonogashira coupling[12] of 3 and 4 with excess trimethylsilylacetylene [$Pd(PPh_3)_2Cl_2$ and CuI catalysts (20 mol% each), Et_3N, 70 °C, 48 h] led selectively to dialkynes 5 (59%) and 6 (89%), respectively. No further coupling between 5 or 6 and trimethylsilylacetylene took place through the more hindered *o*-bromides by using this coupling procedure, even under more severe conditions. Similar results were obtained in the couplings 3 and 4 with excess 2-methyl-3-butyn-2-ol [$Pd(PPh_3)_2Cl_2$ and CuI catalysts (20 mol% each, Et_3N, reflux, 12 h]

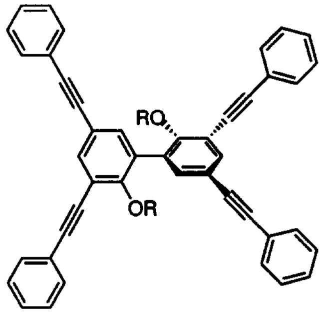


However, by using the Stille coupling of stannanes[7] the four bromides could be efficiently replaced in one step. Thus, reaction of ethenyltributylstannane with 3 and 4 in the presence of $Pd(PPh_3)_4$ as the catalyst (20 mol%, toluene, reflux, 4 h)[13] furnished 7 (73%) and 8 (85%), respectively. These tetraethynyl biphenyl derivatives were obtained as colorless oils.[14] Similarly, coupling of 3 and 4 with (trimethylsilylethynyl)tributylstannane[15] [20 mol% $Pd(PPh_3)_4$, toluene, reflux, 4 h] smoothly gave tetraalkynyl derivatives **9** (93%) and **10** (90%) as stable colorless oils.[16] Biphenyl **10** could also be obtained by coupling of dibromide **6** with the alkynyl stannane under the same conditions (92%). Deprotection of the silyl groups of **6**, **9**, and **10** under standard basic conditions (K_2CO_3, MeOH, 23 °C, 30 min) afforded **11** (96%), **12** (98%), and **13** (95%).[17]

While **11** and **13** are stable compounds, solid **12** undergoes slow decomposition as a solid. However, **12** can be easily manipulated and stored in the dark without significant decomposition. The potential utility of these tetraethynylbiphenyls as tectons for the building of more complex structures relies upon their ability to couple with the appropriate electrophiles. Interestingly, **11**, which bears both electrophilic aryl bromides and nucleophilic terminal alkynes, could be selectively coupled with iodobenzene (2 equiv) in the presence of $Pd(PPh_3)_4$ and CuI catalysts (10 mol% each) (piperidine, 23 °C, 3 h) to give **14** (88%). Additionally, coupling of **13** with iodobenzene (4 equiv) afforded **15** [$Pd(PPh_3)_4$ and CuI (20 mol% each), piperidine, 23 °C, 3 h, 83%].[18]



14 : R = *t*-BuCO



15 : R = *t*-BuCO

In summary, alkynylbiphenyls **11-13** can be readily prepared from commercially available **1** in just four steps in good overall yields (81-87%) by using the Stille cross-coupling reaction as the key step. Furthermore, tetravinylbiphenyls **7-8** have been prepared from **1** in three steps in 71% and 81% overal yields, respectively. These elongated tetrahedral tectons can be further elaborated by palladium-catalyzed reactions with aryl halides by alkyne-alkyne couplings or Heck insertion reactions. The synthesis of **14** from **11** suggests that two different alkynes could be coupled sequentially on the 2,2'-dihydroxybiphenyl core. Synthesis of more complex substrates based on these tectons is in progress.

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14. Characterization data for **8**: colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.57 (d, J = 2.1 Hz, 2H), 7.23 (d, J = 2.1 Hz, 2H), 6.77-6.58 (m, 4H), 5.82-5.68 (m, 4H), 5.37-5.23 (m, 4H), 1.03 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 176.03, 145.66, 135.73, 135.21, 131.50, 131.02, 130.25, 128.09, 123.77, 116.77, 114.54, 38.91, 26.73; EI-MS *m/z* 458 (M$^+$, 17), 374 (72), 290 (100).

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16. Characterization data for **9**: white solid, mp 185-186 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.63 (d, J = 2.1 Hz, 2H), 7.30 (d, J = 2.1 Hz, 2H), 2.10 (s, 6H), 0.22 (s, 36H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.60, 149.40, 136.43, 134.44, 130.32, 121.20, 118.44, 102.68, 100.51, 98.75, 95.57, 20.42, -17.71; EI-MS *m/z* 639 (M$^+$-16, 8), 612 (46), 570 (88), 467 (29), 73 (100).

17. (a) Characterization data for **12**: (decomposes without melting; Differential Thermal Analysis shows two exotherms at 115 and 196°C); ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.59 (d, J = 2.0 Hz, 2H), 7.43 (d, J = 2.0 Hz, 2H), 3.49 (s, 2H), 3.01 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 154.72, 136.23, 135.96, 123.54, 114.73, 109.89, 84.81, 82.07, 77.36, 76.75; MS *m/z* 282 (M$^+$, 100), 253 (23), 224 (32). (b) Characterization data for **13**: colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.66 (d, J = 2.0 Hz, 2H), 7.30 (d, J = 2.0 Hz, 2H), 3.21 (s, 2H), 3.08 (s, 2H), 1.11 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 175.34, 150.12, 136.93, 134.79, 130.46, 120.09, 117.74, 82.61, 81.38, 78.50, 77.58, 38.93, 26.74; EI-MS *m/z* 450 (M$^+$, 7), 366 (37), 282 (100).

18. Characterization data for **15**: colorless oil; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.78 (d, J = 2.1 Hz, 2H), 7.55-7.45 (m, 10H), 7.39-7.27 (m, 12H), 1.17 (s, 18H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 175.56, 148.93, 135.90, 133.79, 131.67, 131.61, 130.76, 128.74, 128.53, 128.40, 122.82, 122.68, 121.27, 118.78, 94.22, 90.36, 87.51, 83.67, 39.08, 26.92; EI-MS *m/z* 754 (M$^+$, 8), 670 (25), 586 (62), 57 (100).

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