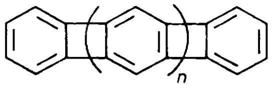
Benzo[3,4]cyclobuta[1,2-*b*]biphenylene, the First Member of a Novel Series of Linear Cyclobutadienoid Acenes

Bruce C. Berris, George H. Hovakeemian, and K. Peter C. Vollhardt*

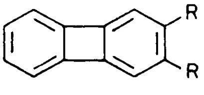
Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, U.S.A.

Palladium mediated ethynylation of iodoarenes coupled with cobalt catalysed alkyne cotrimerisations allows rapid access to benzo[3,4]cyclobuta[1,2-*b*]biphenylene, a linear biphenylenoid, and two of its trimethylsilyl derivatives.

Prompted by a recent report on the low yielding synthesis of the title compound by the vacuum pyrolysis of benzodicinnolines,[1] we report an alternative, efficient, and short iterative approach to (**1**) ($n = 1$) and its derivatives, which is potentially amenable to the preparation of higher benzocyclobutadienes (**1**) ($n > 1$) in the series. It relies on palladium to catalyse the ethynylation of iodoarenes,[2] on cobalt to effect the cotrimerisation of *o*-diethynylarenes with alkynes to give biphenylenes,[3] and on silicon to direct electrophilic aromatic *ipso*-substitutions. Compounds of type (**1**) are not only theoretically interesting in their own right but also have potential as novel materials with unusual electronic properties and metal-like conductive behaviour.[4]



(**1**)



(**2**) R = SiMe$_3$
(**3**) R = I
(**4**) R = C≡CH

2,3-Bis(trimethylsilyl)biphenylene (**2**) [prepared from *o*-diiodobenzene by trimethylsilylethynylation in the presence of palladium(II),[2] followed by desilylation and cobalt catalysed cocyclisation of the resulting *o*-diethynylbenzene with bis(trimethylsilyl)acetylene (BTMSA)[3]] was iododesilylated with ICl to give (**3**) (63%; m.p. 117—119 °C).† Renewed ethynylation [Me$_3$SiC≡CH, (PhCN)$_2$PdCl$_2$, CuI, piperidine, 80 °C,

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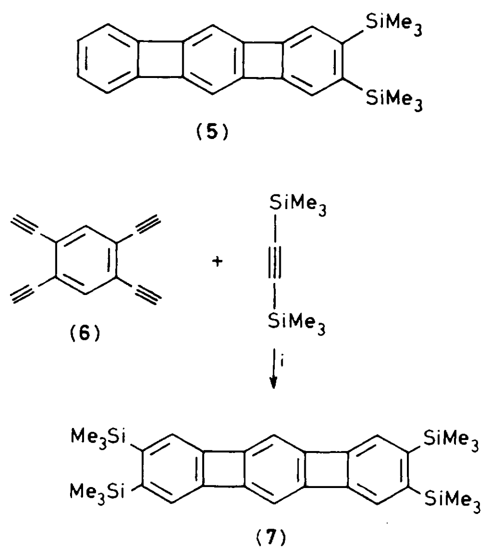
† All new compounds gave satisfactory analytical and spectral data. (**5**): ^{1}H N.m.r. (C$_6$D$_6$, 250 MHz), δ 6.84 (s, 2H), 6.45 (AA′, m, 2H), 6.19 (BB′, m, 2H), 6.07 (s, 2H), and 0.29 (s, 18H); $J_{6,7}$ 6.7 and $J_{7,8}$ 8.4 Hz; u.v., λ_{max} (iso-octane) 436 (log ε 4.46), 422 sh (4.18), 4.10 (4.24), 320 sh (3.80), 290 (5.06), and 279 nm (4.85); (**7**): ^{1}H n.m.r. (C$_6$D$_6$, 250 MHz) δ 6.94 (s, 4H), 6.31 (s, 2H), 0.38 (s, 36H); ^{13}C n.m.r. (C$_6$D$_6$) δ 153.8, 149.9, 147.7, 147.7, 121.1 (J_{CH} 158 Hz), 111.2 (J_{CH} 165 Hz), and 2.26 p.p.m.; (**1**) ($n = 1$): ^{1}H n.m.r. (C$_6$D$_6$, 250 MHz) δ 6.45 (AA′, m, 4H), 6.19 (BB′, m, 4H), and 5.92 (s, 2H); $J_{1,2}$ 6.6, $J_{2,3}$ 8.6 Hz; u.v., λ_{max} [tetrahydrofuran (THF)] 432 (log ε 4.31), 406 (4.10), 285 (4.90), and 274 nm (4.75).



Scheme 1. i, $(C_5H_5)Co(CO)_2$, dimethylformamide–toluene, heat.

75%; m.p. 110—110.5 °C], desilylation (KOH, MeOH, 100%), and cyclisation [BTMSA, $(C_5H_5)Co(CO)_2$], of the resulting diethynylbiphenylene (4) (m.p. > 270 °C decomp.) gave 2,3-bis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]biphenylene (5) (36%; red crystals, m.p. 171—174 °C).†

Alternatively, and more rapidly, the same treatment of 1,2,4,5-tetraiodobenzene[5] gave 1,2,4,5-tetrakis(ethynyl)benzene (6) (69%), and subsequently the tetrasilylbenzo[3,4]-cyclobuta[1,2-*b*]biphenylene (7)† (71%; red crystals, m.p. 238—239 °C decomp.). The cobalt mediated cyclisation of (6) to (7) is the first to construct four rings in one step[6] (Scheme 1).

Both (5) and (7) can be efficiently protodesilylated [Bu^{t}OK, Bu^{t}OH, THF, $(CH_3)_2SO$, 5 h, 80 °C] to the parent compound (1) (n = 1) the spectral analysis of which is similar to the one reported.† However, our (1) is stable to light and t.l.c. conditions, and has a higher m.p. (275—280 °C decomp.). Compounds (1), (5), and (7) are acid sensitive, being rapidly converted in chloroform, or in the presence of electrophiles, into new compounds now under investigation. The central 'benzene' ring is extraordinarily activated, undergoing 90% complete all-*cis*-hydrogenation (Pd–C, H_2, m.p. 158—160.5 °C) when cycloheptene is unaffected.

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