

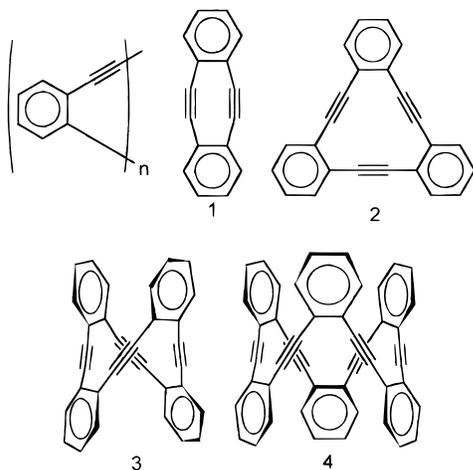
Unusual Formation of a Cyclyne Dimer and an Indenoindene Derivative

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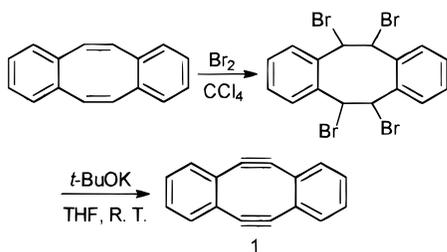
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Stephens–Castro coupling¹ and Sonogashira–Hagihara coupling² of *o*-ethynylidoaryls have been used to form cyclotriyenes such as **2**.³ The tetramer, **3**, and hexamer, **4**, are typically low-yield side products in these reactions. The formation of the dibenzocyclyne dimer **1** or substituted analogues by these types of coupling reactions has not been reported for *o*-ethynylidobenzene⁴ or *o*-ethynylidothiophenes.⁵

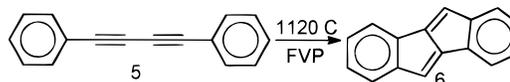


Bromination followed by dehydrobromination is the only reported route to the formation of dibenzocyclyne **1**.⁶



Flash vacuum pyrolysis of diphenylbutadiyne (**5**) gives indeno[2,1-*a*]indene (**6**) in 19% yield by an ethyne–

ethylidene rearrangement of alkynes.⁷ Indeno[2,1-*a*]indenes have been synthesized by the nucleophilic substitution of bromine from tetrabromodibenzo[*a,e*]cyclooctene by organolithium reagents.⁸ It has been reported that substitution with bulky groups⁹ or benzofusion^{10,11} gives stability to the pentalene framework.



Here we present the unusual formation of the benzocyclyne dimer (**10**) and the indeno[2,1-*a*]indene derivative (**11**) under the conditions of the Sonogashira–Hagihara reaction (Scheme 1). Desilylation of 3-iodo-5,6-dimethyl-2-(2-(trimethylsilyl)ethynyl)hydroquinone (**7**)¹² by potassium fluoride in methanol gives 5,6-dimethyl-2-ethynyl-3-iodohydroquinone (**8**) in 63% yield. The combination of **8** with *tert*-butyldimethylsilyl chloride¹³ and imidazole in dry methylene chloride under argon at room temperature for 2 days gives 5,6-dimethyl-2-ethynyl-3-iodo-1,4-bis-[(1,1-dimethylethyl)dimethylsilyl]oxy]benzene (**9**) in 43% yield. Palladium/copper-catalyzed coupling of **9** in 1:1 *i*-Pr₂NH/toluene at 90 °C for 1 day gave dimer **10** in 10% yield and 2,3,7,8-tetramethyl-1,4,6,9-tetra[(1,1-dimethylethyl)dimethylsilyl]oxy]indeno[2,1-*a*]indene (**11**) in 67% yield. The mass spectrum also revealed the presence of traces of the trimer (**12**) and higher cyclics, e.g., tetramer, pentamer, and a series of linear oligomers. No reaction was observed at room temperature when monitored by TLC.

The steric hindrance between the bulky TBDMS groups increases in going from **10** to **12**. This steric hindrance may be responsible for the preferential formation of **10** and **11**.

The high yield of the indenoindene derivative **11** may be due to the thermal rearrangement of the dimer **10** to the more stable indenoindene ring system. The yield of **11** in this case is much higher than the yield of compound **6** from FVP of **5**. This relatively high yield of 67% is also noticeable when compared to the yields of 47% for **2** and 8% for **3** isolated by Stephens–Castro coupling^{3d} and 36% for **2** from the Sonogashira–Hagihara reaction.^{3c}

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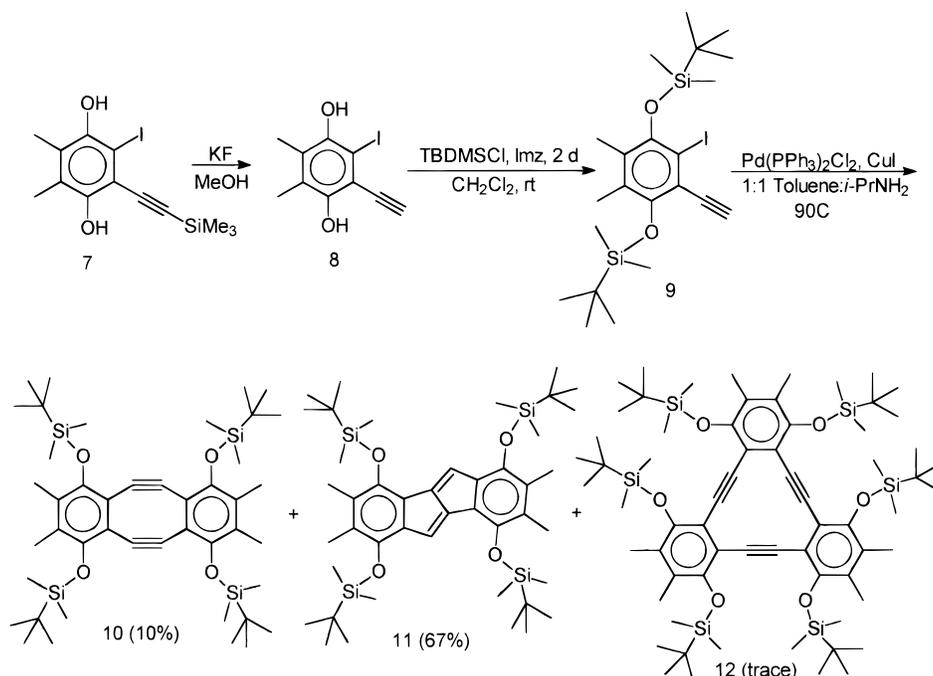
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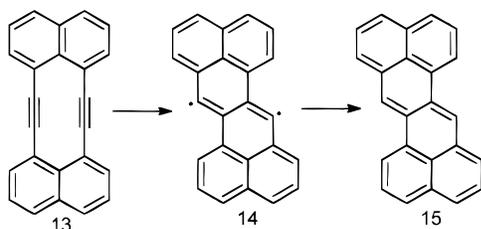
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Scheme 1

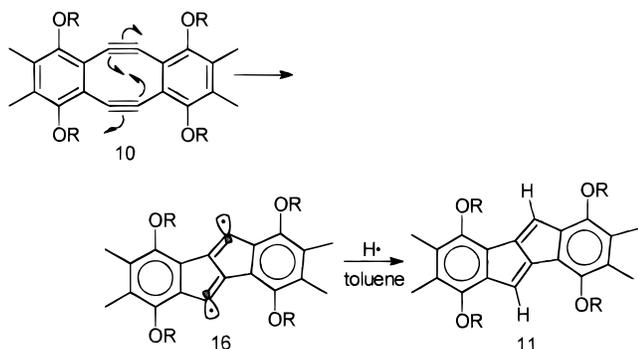


Cyclizations of cyclic aryl alkynes have been previously observed. Sondheimer¹⁴ and Staab¹⁵ synthesized hydrocarbon **15** in attempts to synthesize **13**. They proposed **14** to be the diradical intermediate in the transformation of **13** to **15**. Myers¹⁶ showed that 1,6-didehydro[10]-



annulene undergoes a facile rearrangement to a biradical 1,5-didehydronaphthalene. Compounds **2** and **3** undergo a lithium-induced cyclization to fulvalene and diindenochrysene derivatives, respectively, by a radical mechanism.¹⁷

It is reasonable to propose that indenof[2,1-*a*]indene derivative **11** is formed from cyclization of dimer **10** through the formation of a biradical **16** similar to **14**. Toluene probably serves as the hydrogen atom donor for the terminating radical recombination process.



Experimental Section

Materials. Compounds 3-iodo-5,6-dimethyl-2-(2-(trimethylsilyl)ethynyl)hydroquinone (**7**)¹² and Pd(PhCN)₂Cl₂¹⁸ were prepared according to literature procedures. Potassium fluoride, *tert*-butyldimethylsilyl chloride, calcium hydride, copper iodide, potassium hydroxide, and imidazole (Aldrich); diisopropylamine and triphenylphosphine (Janssen Chimica); methanol, hexane, toluene, carbon tetrachloride, methylene chloride, acetonitrile, and sodium sulfate (Fisher); and deuterated chloroform (Cambridge Isotope Laboratory) were used as received. Toluene was distilled from sodium and benzophenone under nitrogen. Amines and methylene chloride were distilled from KOH and calcium hydride, respectively. All reactions were monitored by thin-layer chromatography carried out on E. Merck silica gel plates (60F-254) using UV light. Flash column chromatography¹⁹ was carried out using silica gel (Baker: 40 μm).

5,6-Dimethyl-2-ethynyl-3-iodohydroquinone (8). A solution of **7** (1.359 g, 3.77 mmol), KF (263 mg, 4.53 mmol), MeOH (45 mL), and H₂O (5 mL) was stirred at room temperature for 3 h in air. The reaction mixture was quenched with H₂O (20 mL), extracted with CH₂Cl₂ (3 × 30 mL), washed with H₂O (3 × 15 mL), dried over MgSO₄, and concentrated under vacuum. Flash column chromatography of the solid crude with 7% ethyl acetate in petroleum ether gave the title compound as a white solid with a violet tint: yield 912 mg (84%); ¹H NMR (CDCl₃) δ 2.17 (s, 3 H), 2.26 (s, 3 H), 3.74 (s, 1 H), 5.03 (s, 1 H), 5.60 (s, 1 H); ¹³C NMR (CDCl₃) δ 12.53, 14.10, 81.24, 86.75, 94.60, 110.68, 125.03, 127.18, 147.26, 150.83; IR (CCl₄) ν 3306 (vw, CH bound to alkyne), 3511 (vw, OH) cm⁻¹; FDMS found for C₁₀H₉O₂I (M⁺).

5,6-Dimethyl-2-ethynyl-3-iodo-1,4-bis[(1,1-dimethylethyl)dimethylsilyloxy]benzene (9). To a mixture of **8** (991 mg,

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3.44 mmol), TBDMSCl (1.244 g, 8.25 mmol), and imidazole (562 mg, 8.25 mmol) in a Schlenk flask was added CH_2Cl_2 (60 mL). The heterogeneous mixture was stirred at room temperature for 2 d under argon, opened to air, diluted with CH_2Cl_2 (180 mL), washed with water (3×120 mL), and dried over Na_2SO_4 . Flash column chromatography of the solid crude with hexane gave the white solid **9** in 43% yield (763.2 mg): mp 94–95 °C; ^1H NMR (CDCl_3) δ 0.22 (s, 6 H), 0.28 (s, 6 H), 1.04 (s, 9 H), 1.06 (s, 9 H), 2.07 (s, 3 H), 2.16 (s, 3 H, CH_3), 3.44 (s, H); ^{13}C NMR (CDCl_3) δ -2.65, -1.50, 14.86, 16.56, 18.77, 19.02, 26.29, 26.59, 84.40, 85.18, 94.78, 119.42, 129.49, 130.49, 148.74, 150.36; IR (CCl_4) 2107 (vw, $\text{C}\equiv\text{C}$), 3311 (m, $\text{C}\equiv\text{H}$) cm^{-1} ; UV-vis (hexane) λ_{max} (log ϵ) 216 (4.68), 252 (4.06, br), 266 (3.90, br sh), 316 (3.33, br) nm; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{37}\text{Si}_2\text{O}_2\text{I}$ 516.1377, found 516.1370. Anal. Calcd for $\text{C}_{22}\text{H}_{37}\text{Si}_2\text{O}_2\text{I}$: C, 51.16; H, 7.17. Found: C, 52.41; H, 7.56.

Synthesis of Dimer (10) and 2,3,7,8-Tetramethyl-1,4,6,9-tetra((1,1-dimethylethyl)dimethylsilyloxy)indeno[2,1-a]indene (11) by Pd–Cu-Catalyzed Self-Coupling of 9. To a mixture of **9** (300 mg, 0.58 mmol), $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (0.011 g, 0.02 mmol), PPh_3 (0.018 g, 0.06 mmol), and CuI (0.018 g, 0.09 mmol) under argon was added toluene (10 mL) followed by *i*- Pr_2NH (10 mL). The reaction mixture (0.02 M with respect to **9**) was gradually heated. White insolubles formed after heating at 90 °C for 2–3 h. The color of the reaction mixture darkened from straw yellow to orange yellow after heating at 90 °C for 1 d. After 1 day, TLC showed two new spots and indicated no change when the reaction was heated at 110 °C for an additional 2 h. Volatiles were removed under vacuum, and hexane (50 mL) was added to the residue. The white insoluble solid was filtered from the orange solution and washed thoroughly with hexane (3×20 mL), and the combined orange filtrate was concentrated under vacuum to an orange solid. Flash column chromatography of the orange solid eluting with 4% CH_2Cl_2 in hexane gave the yellow solid dimer (**10**) in 10% (22.7 mg) yield and the orange solid indenoindene conjugated system (**11**) in 67% (152 mg) yield.

Characterization of **10**: mp 300 °C; ^1H NMR (CDCl_3) δ 0.23 (s, 24 H), 1.02 (s, 36 H), 1.94 (s, 12 H); ^{13}C NMR (CDCl_3) δ -3.00, 14.57, 18.56, 26.28, 109.70, 121.93, 131.44, 145.95; IR (CCl_4) 1258 (s) cm^{-1} ; UV-vis (hexane) λ_{max} (log ϵ) 214 (4.98), 242 (4.52,

sh), 270 (4.93, sh), 282 (5.15), 372 (4.26, br), 382 (4.41), 402 (4.63) nm; HRMS (EI) calcd for $\text{C}_{44}\text{H}_{72}\text{Si}_4\text{O}_4$ 776.4508, found 776.4519. Anal. Calcd for $\text{C}_{44}\text{H}_{72}\text{Si}_4\text{O}_4$: C, 67.98; H, 9.33. Found: C, 67.03; H, 9.37.

Characterization of **11**: mp 269 °C; ^1H NMR DEPT (CDCl_3) δ 0.142 (s, 12 H), 0.147 (s, 12 H), 1.04 (s, 18 H), 1.07 (s, 18 H), 1.96 (s, 12 H), 6.34 (s, 2 H indene hydrogens); ^{13}C NMR DEPT (CDCl_3) δ -3.52 (2 $\text{Si}(\text{CH}_3)_2$), -2.72 (2 $\text{Si}(\text{CH}_3)_2$), 14.52 (CH_3 on benzene rings), 14.70 (CH_3 on benzene rings), 18.50 (2 *q*-C of *tert*-butyl), 18.60 (2 *q*-C of *tert*-butyl), 26.13 (2 (CH_3)₃), 26.33 (2 (CH_3)₃), 123.27, 124.64, 129.53, 130.45, 138.57, 143.25, 144.68, 145.79; IR (CCl_4) 1264 (s); UV-vis (hexane) λ_{max} (log ϵ) 218 (4.60), 276 (4.81), 286 (4.79, sh), 430 (4.02), 456 (4.35, br), 486 (4.43) nm; HRMS (EI) calcd for $\text{C}_{44}\text{H}_{74}\text{Si}_4\text{O}_4$ 778.4644, found 778.4677. Anal. Calcd: C, 67.86; H, 9.50. Found: C, 65.94; H, 9.51.

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