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Synthesis of Diindeno-Fused 4*H*-Cyclopenta[*def*]phenanthren-4-ones and Related Compounds via Benzannulated Enediynyl Propargylic Alcohols

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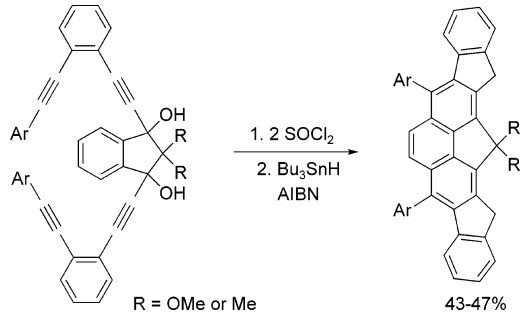

Treatment of propargylic diols **5**−**7** with thionyl chloride promoted a cascade sequence of reactions leading to dichlorides **10**−**12** and, after reduction with tributyltin hydride, the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrenes **13**−**15** in a single operation. Hydrolysis of **13** and **14** furnished 4*H*-cyclopenta[*def*]phenanthren-4-ones **16** and **17**, respectively. Air oxidation of an alkaline solution of dichloride **11** produced diketone **18**.

Benzannulated enediynyl propargylic alcohols are useful precursors of the corresponding enyne-allenes, which have found applications in the synthesis of polycyclic aromatic compounds.[1] The ability of the reaction sequence to involve an aryl ring in a formal Diels−Alder reaction under mild thermal conditions provides many opportunities for the assembly of novel aromatic structures. We have successfully employed this synthetic pathway for efficient transformations of 1,3-indandiones **1**[2] and **2**[3] to the diindeno-fused 4*H*-cyclopenta[*def*]-phenanthrene derivatives **13**−**18** (Scheme 1).

Condensation between **1** and 2 equiv of **3** led to propargylic diol **5** as a mixture of the *trans* and *cis* isomers. Treatment of *trans*-**5** with thionyl chloride then promoted a cascade sequence of reactions involving initially two S_Ni' reactions to produce in situ the benzannulated chloroenyne-allene **8** as described previously.[1b,c,e] Two subsequent formal Diels−Alder reactions, presumably with each involving a Schmittel cyclization reaction to form the corresponding biradical[1i−k] followed by an intramolecular radical−radical coupling reaction, then gave **9**, which in turn underwent two prototropic rearrangements to furnish the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrene derivative **10**. Because the relative reaction rates of the steps of the cascade sequence have not been determined, it is also possible that the first unit of the benzannulated enediynyl propargylic alcohol moiety could undergo a formal Diels−Alder reaction and a prototropic rearrangement before the second unit would begin its cyclization sequence.

Dichloride **10** is prone to hydrolysis as observed previously in related compounds.[1b,c] It was operationally convenient to reduce the crude product of **10** without further purification with tributyltin hydride to furnish **13** in 46% overall yield from *trans*-**5**. Hydrolysis of the dimethyl ketal group then gave the diindeno-fused 4*H*-cyclopenta[*def*]phenanthren-4-one **16**. Similarly, **17** bearing two additional 1,1,3,3-tetramethylbutyl (*t*-Oct) substituents was synthesized by treatment of either *trans*-**6** or *cis*-**6**, prepared from condensation between **1** and **4**, with thionyl chloride followed by reduction and hydrolysis. Compared to **16**, the presence of the two *t*-Oct substituents in **17** greatly enhances its solubility in common organic solvents. It was also possible to convert crude dichloride **11** to diketone **18** in 45% overall yield from *trans*-**6** by air oxidation of **11** in the presence of a 2 M NaOH solution. By starting from 2,2-dimethyl-1,3-indandione (**2**) for condensation with **3**, the reaction sequence likewise led to **15**.

The success in using diols **5**−**7** for two cascade reaction sequences in a single operation further demonstrates the versatility of this synthetic pathway for the construction of novel polycyclic aromatic structures. It is worth noting that the diindeno-fused 4*H*-cyclopenta[*def*]phenanthrenes **13**−**18** have a 41-carbon framework, 38 carbons on the aromatic rings and three carbons on the three five-membered rings, that is represented on the surface of C_{60}. Several synthetic methods have been reported for 4*H*-cyclopenta[*def*]phenanthrenes,[4] and a 4*H*-cyclopenta-[*def*]phenanthrene derivative was used in the first synthesis of corannulene, a bow-shaped $C_{20}H_{10}$ aromatic hydrocarbon.[4l,m]

The diacetylene 1-ethynyl-2-(phenylethynyl)benzene, for lithiation to produce **3**, was prepared as reported previously,[1d] whereas diacetylene **25** for **4** was prepared by starting from commercially available 4-*t*-Oct-phenol (**19**) (Scheme 2). Transformation of **19** to the correspond-

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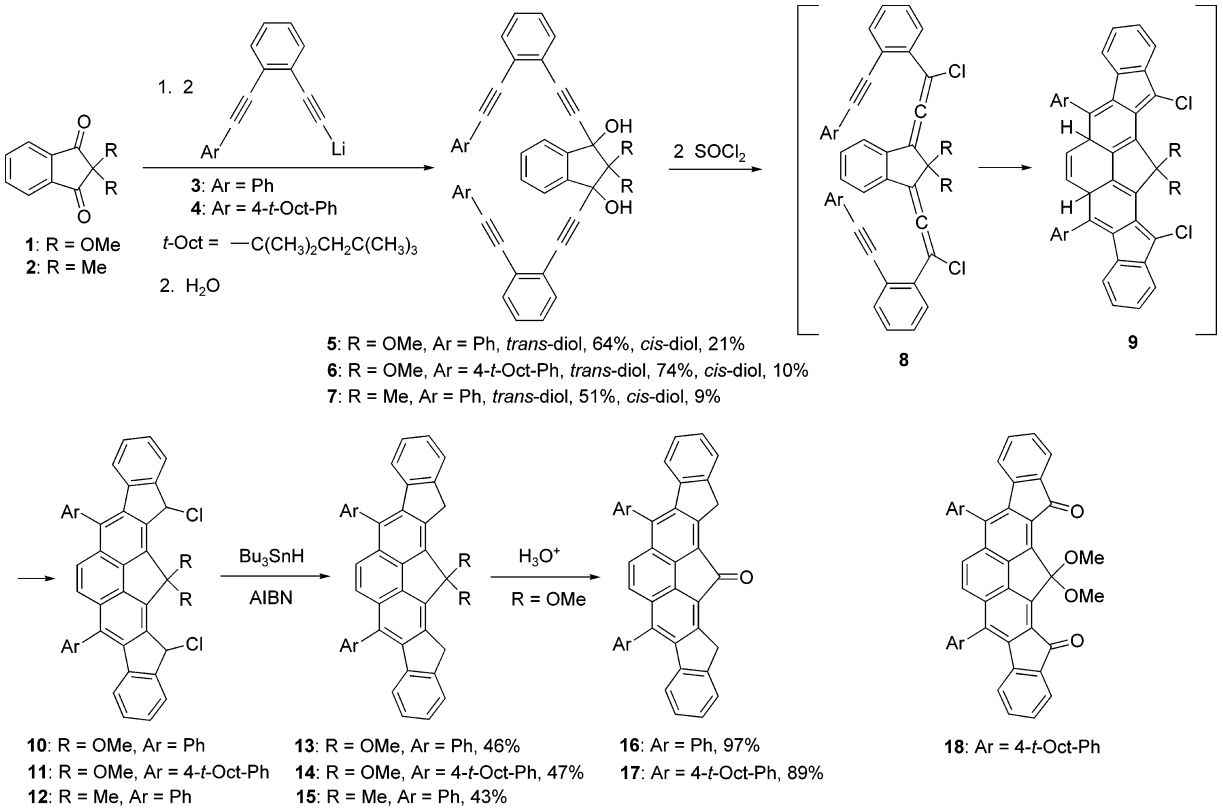
SCHEME 1

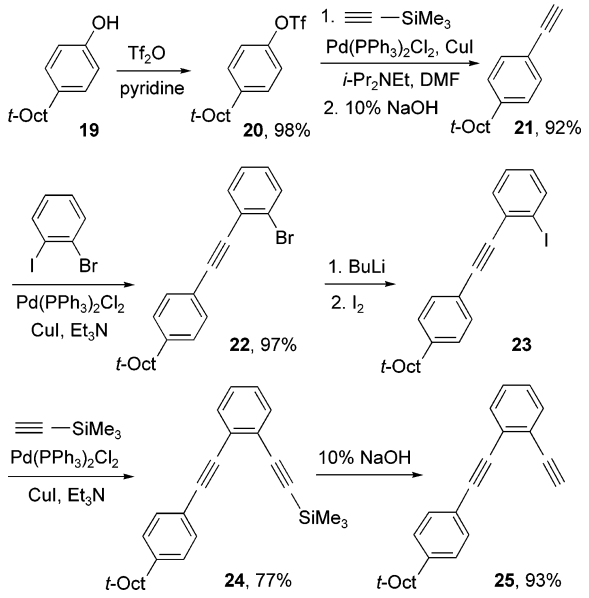


ing triflate **20** followed by a Sonogashira reaction[5] with (trimethylsilyl)acetylene and desilylation then furnished arylacetylene **21**. Coupling of **21** with 1-bromo-2-iodobenzene to form **22** followed by a bromo to iodo exchange to produce **23** for a cross-coupling reaction with (trimethylsilyl)acetylene and desilylation then produced **25**.

Experimental Section

Propargylic Diols 6. To a solution of 2.126 g of **25** (6.772 mmol) in 15 mL of THF was added 2.57 mL of a 2.5 M solution of *n*-butyllithium (6.43 mmol) in hexanes at 0 °C. The reaction mixture was then allowed to warm to room temperature. After 30 min, a solution of 0.634 g of **1** (3.078 mmol) in 10 mL of THF was added via cannula, and the mixture was stirred at room temperature for 12 h. Water (15 mL) was introduced, and the reaction mixture was concentrated to remove organic solvents. Diethyl ether (25 mL) was added, and the organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a solid residue. The residue was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to afford 1.887 g (2.263 mmol, 74%) of *trans*-diol **6** and 0.251 g (0.301 mmol, 10%) of *cis*-diol **6** as white solids. *trans*-Diol **6**: mp 136−139 °C; R_f 0.20 (hexanes/CH_2Cl_2 = 1:1); IR 3519, 2216, 834, 757 cm^{-1}; ^{1}H NMR δ 7.72−7.67 (2 H, m), 7.53−7.46 (4 H, m), 7.41−7.36 (4 H, m), 7.32−7.21 (10 H, m) 3.87 (2 H, s), 3.81 (6 H, s), 1.73 (4 H, s), 1.34 (12 H, s), 0.70 (18 H, s); ^{13}C NMR δ 150.8, 142.3, 132.2, 131.9, 131.3, 129.8, 128.3, 127.6, 126.3, 126.1, 124.7, 124.3, 119.7, 109.7, 93.7, 91.7, 87.4, 86.5, 77.1, 56.8, 53.2, 38.7, 32.3, 31.8, 31.4; MS *m/z* 857 (MNa$^+$), 817, 785; HRMS calcd for $C_{59}H_{62}O_4Na$ (MNa$^+$) 857.4546, found 857.4587. *cis*-Diol **6**: R_f 0.04 (hexanes/CH_2Cl_2 = 1:1); IR 3501, 2216, 834, 758 cm^{-1}; ^{1}H

SCHEME 2



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NMR δ 7.84−7.78 (2 H, m), 7.56−7.49 (4 H, m), 7.45−7.39 (4 H, m), 7.34−7.22 (8 H, m), 7.21−7.18 (2 H, m), 3.89 (3 H, s), 3.66 (3 H, s), 3.64 (2 H, s), 1.73 (4 H, s), 1.34 (12 H, s), 0.70 (18 H, s); ^{13}C NMR δ 150.8, 142.7, 132.1, 131.9, 131.3, 130.1, 128.4, 127.6, 126.4, 126.1, 125.0, 124.7, 119.7, 109.2, 93.8, 90.8, 87.4, 87.0, 78.1, 56.7, 53.0, 52.3, 38.7, 32.3, 31.8, 31.5, 31.4; MS *m/z* 857 (MNa^+), 817, 785; HRMS calcd for $C_{59}H_{62}O_4Na$ (MNa^+) 857.4546, found 857.4586.

4*H*-Cyclopenta[*def*]phenanthren-4-one Dimethyl Ketal 14. To 1.625 g of *trans*-**6** (1.948 mmol) in 15 mL of THF at 0 °C was added via cannula a solution of 0.781 g of thionyl chloride (6.57 mmol) and 1.058 g of anhydrous pyridine (13.38 mmol) in 10 mL of THF. The reaction mixture was then allowed to warm to room temperature. After 8 h, the reaction mixture was concentrated, and 20 mL of water and 30 mL of methylene chloride were added. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a solid residue (crude product of dichloride **11**). To a flask containing 0.030 g (0.21 mmol) of AIBN were added a solution of the crude product of **11** in 30 mL of benzene and 1.58 mL of tributyltin hydride (1.71 g, 5.94 mmol). The resulting mixture was heated at 80 °C for 18 h before it was allowed to cool to room temperature. The mixture was treated with 20 mL of a 10% aqueous KF solution, stirred for 2 h, and filtered. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated to furnish a solid residue. The residue was purified by flash column chromatography (silica gel/50% CH_2Cl_2 in hexanes) to afford 0.731 g of **14** (0.911 mmol, 47% yield from *trans*-**6**; similar result with *cis*-**6**) as a yellow solid: compound turns dark at 268 °C and becomes black without melting at 273 °C; R_f 0.23 (hexanes/CH_2Cl_2 = 1:1); IR 1104, 822, 780, 748, 715 cm^{-1}; ^{1}H NMR δ 7.66−7.58 (6 H, m), 7.40 (4 H, d, J = 8.4 Hz), 7.38 (2 H, s), 7.27 (2 H, td, J = 7.4, 1.0 Hz), 7.02 (2 H, t, J = 7.5 Hz), 6.86 (2 H, d, J = 7.9 Hz); 4.33 (4 H, s), 3.33 (6 H, s), 1.91 (4 H, s), 1.52 (12 H, s), 0.89 (18 H, s); ^{13}C NMR δ 149.7, 144.0, 141.7, 139.8, 138.0, 135.1, 134.7, 133.7, 129.1, 126.8, 126.75, 127.71, 126.3, 125.0, 123.7, 123.6, 114.7, 57.1, 52.7, 38.6, 34.6, 32.6, 31.9, 31.8.

4*H*-Cyclopenta[*def*]phenanthren-4-one 17. To a mixture of 0.705 g of **14** (0.879 mmol), 30 mL of CH_2Cl_2, and 60 mL of acetone was added 35 mL of a 5% HCl solution. The progress of hydrolysis was monitored by TLC. After 19 h, the reaction mixture was concentrated in vacuo, and 50 mL of CH_2Cl_2 was added. The organic layer was separated, washed with a saturated aqueous $NaHCO_3$ solution and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/33% hexanes in CH_2Cl_2) to afford 0.592 g (0.783 mmol, 89%) of **17** as a yellow solid: compound turns dark at 305 °C and becomes black without melting at 314 °C; R_f 0.33 (hexanes/CH_2Cl_2 = 1:2); IR (KBr) 1709, 736 cm^{-1}; ^{1}H NMR δ 7.50 (4 H, d, J = 8.2 Hz), 7.34 (2 H, d, J = 7.4 Hz), 7.27 (4 H, d, J = 8.2 Hz), 7.18 (2 H,s), 7.11 (2 H, t, J = 7.3 Hz), 6.89 (2 H, t, J = 7.4 Hz), 6.69 (2 H, d, J = 7.9 Hz), 3.99 (4 H, s), 1.88 (4 H, s), 1.49 (12 H, s), 0.88 (18 H, s); ^{13}C NMR δ 193.6, 149.9, 143.8, 141.0, 140.6, 138.3, 137.1, 134.0, 128.7, 127.3, 126.9, 126.8, 126.4, 126.1 124.9, 123.4, 57.1, 38.6, 34.5, 32.6, 31.9, 31.8; MS *m/z* 756 (M^+), 685, 570; HRMS calcd for $C_{57}H_{56}O$ 756.4331, found 756.4348.

Diketone 18. To a solution of the crude product of dichloride **11**, prepared from 0.701 g (0.841 mmol) of *trans*-**6**, in 30 mL of THF was added 8 mL of a 2 M aqueous sodium hydroxide solution at 0 °C. The resulting mixture was stirred at room temperature for 24 h with a slow stream of air bubbling into the solution. The reaction mixture was concentrated in vacuo and then extracted with methylene chloride. The organic layer was washed with a saturated NH_4Cl solution and water, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel/25% CH_2Cl_2 and 25% Et_2O in hexanes) to afford 0.315 g of **18** (0.380 mmol, 45% yield from *trans*-**6**) as a yellow solid: compound turns dark at 315 °C and becomes black without melting at 331 °C; R_f 0.14 (hexanes/CH_2Cl_2/Et_2O = 1:1:1); IR (KBr) 1715, 752 cm^{-1}; ^{1}H NMR δ 7.74 (2 H, d, J = 6.7 Hz), 7.61 (4 H, d, J = 8.4 Hz), 7.36 (2 H, s), 7.34 (2 H, d, J = 8.4 Hz), 7.22 (2 H, td, J = 7.4, 0.7 Hz), 7.10 (2 H, td, J = 7.6, 1.2 Hz), 6.55 (2 H, d, J = 7.7 Hz), 3.68 (6 H, s), 1.88 (4 H, s), 1.48 (12 H, s), 0.85 (18 H, s); ^{13}C NMR δ 191.5, 150.7, 145.2, 139.6, 139.5, 137.4, 135.7, 135.1, 134.3, 133.0, 131.9, 129.6, 128.8, 128.7, 127.2, 127.0, 124.2, 123.9, 113.6, 57.0, 53.8, 38.7, 32.6, 31.9, 31.8; MS *m/z* 853 (MNa^+), 807, 795; HRMS calcd for $C_{59}H_{58}O_4Na$ (MNa^+) 853.4233, found 853.4259.

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Supporting Information Available: Experimental procedures and spectroscopic data for **5**, **7**, **13**, **15**, **16**, **20**−**22**, **24**, and **25** and ^{1}H and/or ^{13}C NMR spectra of compounds **5**−**7**, **13**−**18**, **20**−**22**, **24**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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