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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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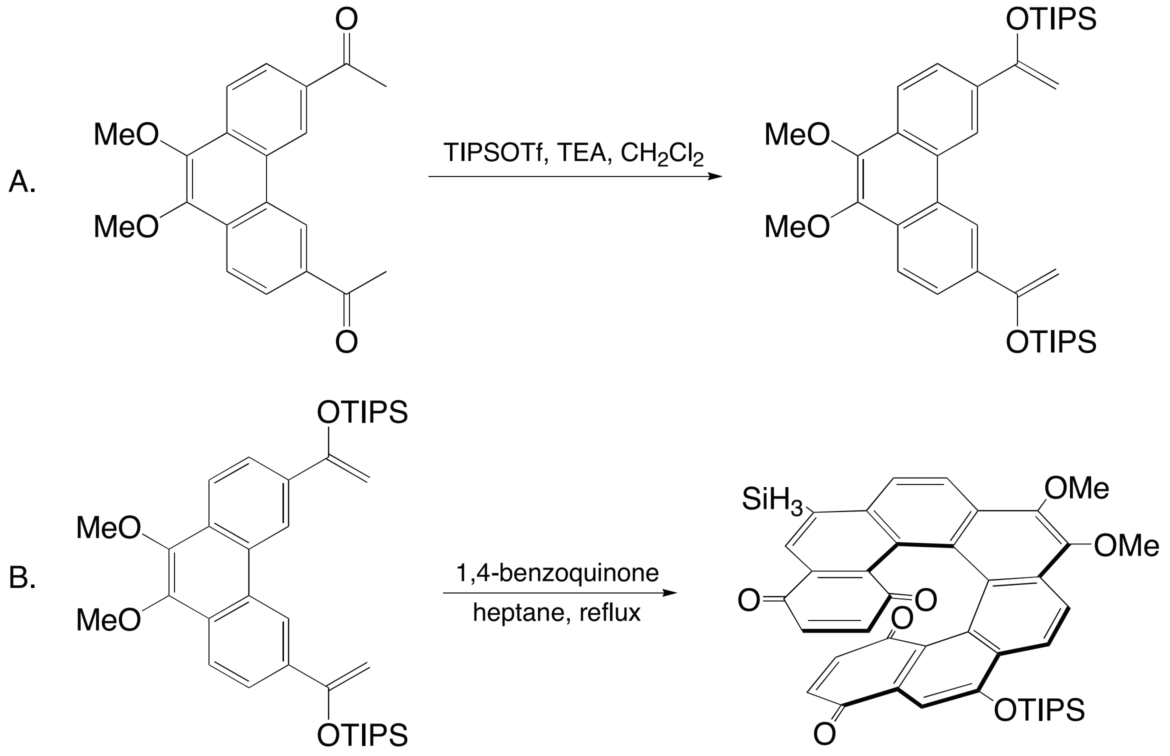
HELICENEBISQUINONES: SYNTHESIS OF A [7]HELICENEBISQUINONE

[(Dinaphtho[2,1-c:1',2'-g]phenanthrene-1,4,15,18-tetrone, 9,10-dimethoxy-6,13-bis[[tris(1-methylethyl)silyl]oxy]-)]



Submitted by Kamil Paruch, Libor Vyklicky, and Thomas J. Katz.[1]
Checked by Mitsuru Kitamura and Koichi Narasaka.

1. Procedure

A. 3,6-Bis[1-(triisopropylsiloxy)ethenyl]-9,10-dimethoxyphenanthrene. A solution of 8 g (0.025 mol) of 3,6-diacetyl-9,10-dimethoxyphenanthrene (Note 1) and 28 mL of triethylamine (Et_3N) (Note 2) in 80 mL of dry dichloromethane (CH_2Cl_2) (Note 2) is prepared under nitrogen in a 250-mL, round-bottomed flask equipped with a magnetic stir bar. The flask is cooled in an ice bath and 14 mL (0.052 mol) of triisopropylsilyl triflate (Note 3) is slowly added by syringe. The mixture is stirred for 15 min while cooling in the ice bath, then for 1 h at ambient temperature. Hexane (200 mL) is added, and the organic phase is washed twice with 100-mL portions of 1M aqueous potassium hydroxide (KOH), dried quickly over potassium carbonate (K_2CO_3), and filtered. The solvent is removed, and the oily residue is dissolved in ca. 40 mL of hexane. The solution is poured onto a 4 × 4-cm plug of neutral alumina and washed with 200 mL of hexane. The solvent is removed and the residue is dried under vacuum (0.5 torr/80 °C). 3,6-Bis[1-(triisopropylsiloxy)ethenyl]-9,10-dimethoxyphenanthrene (14.4 g, 91%) is obtained as a yellow oil (Notes 4, 5) and used in the subsequent step without further purification.

B. 6,13-Bis(triisopropylsiloxy)-9,10-dimethoxy[7]helicenebisquinone. A solution of the material obtained in Step A in 100 mL of heptane (Notes 6, 7) is added under nitrogen to a 500-mL, round-bottomed flask fitted with a reflux condenser. Thirty-four grams (0.31 mol) of 1,4-benzoquinone is added (Notes 8, 9), and the mixture is heated with an oil bath at 120 °C for 3.5 days with stirring (Note 10). The reaction mixture is then cooled to 25 °C and 25 mL of CH_2Cl_2 is added. The solids are broken into small pieces with the aid of a spatula, and the mixture is shaken for 15 min with 50 g of sand (Note 11). The supernatant liquid is decanted, the residue is extracted three times with 70-mL portions of 1:1 hexane:CH_2Cl_2, and the combined extracts are filtered through a pad of Celite. The solution is concentrated, and 1,4-benzoquinone is removed by sublimation by heating the residue to 100 °C and applying a vacuum of ca. 0.5 torr. Methanol (MeOH, 100 mL) and ca. 20 g of sand are added, and the mixture is shaken until the solids are finely suspended (ca. 30 min). Water (20 mL) is added and the mixture is shaken for 10 min. The solids are collected by filtration and washed with ca. 250 mL of 5:1 MeOH:H_2O. The powder obtained after drying under vacuum at 100 °C is dissolved in a small amount of toluene and purified by flash chromatography[2] on a 12 × 8-cm column of silica gel. A purple impurity is eluted with toluene, and the product is eluted with 1-3% tetrahydrofuran (THF) in toluene. After removal of the solvents and drying under vacuum at 100 °C, 4.5 g of the helicenebisquinone (a 25% yield based on the enol ether, 22% based on 3,6-diacetyl-9,10-dimethoxyphenanthrene) is obtained as a dark red solid (Note 12).

2. Notes

1. Prepared according to the accompanying procedure (Paruch, K.; Vyklicky, L.; Katz, T. J. *Org. Synth.* **2003**, *80*, 227).

2. Dichloromethane and triethylamine were distilled from CaH_2.

3. Triisopropyl triflate (97%) was purchased from GSF Chemicals and used as received. The checkers purchased it from Tokyo Chemical Industry.

4. The product solidifies occasionally.

5. In two runs, the checkers obtained 15.8 and 15.2 g (99% and 98% yields). The product exhibits the following properties: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.18 (d, 36 H, *J* = 7.3), 1.35 (m, 6 H), 4.11 (s, 6 H), 4.57 (d, 2 H, *J* = 1.8), 5.06 (d, 2 H, *J* = 1.8), 7.90 (dd, 2 H, *J* = 8.6, 1.6), 8.17 (d, 2 H, *J* = 8.6), 8.96 (d, 2 H, *J* = 1.5); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 12.8, 18.2, 61.0, 90.8, 119.5, 122.0, 124.3, 128.6, 129.1, 135.4, 144.1, 156.4; IR (CCl4) cm^{-1}: 2946, 2868, 1607, 1464, 1322, 1292, 1113, 1015. The checkers reported the following elemental analysis. Calcd. for $C_{30}H_{58}O_4Si_2$: C, 71.87; H, 9.21. Found: C, 71.65; H, 9.20.

6. Heptane was distilled from sodium/benzophenone.

7. The yield is lower when toluene is used as solvent.

8. 1,4-Benzoquinone (98%, Aldrich) is purified by slurrying it in CH_2Cl_2 with two times its weight of basic alumina, filtering the mixture through Celite, concentrating the filtrate, and drying the residue under vacuum.

9. When seven molar equivalents of 1,4-benzoquinone are used, the yield drops to 12%.

10. Sometimes sublimation of 1,4-benzoquinone plugs the condenser, but turning off the cooling water ameliorates the problem.

11. The 20-30 mesh sand is obtained from Fisher Scientific.

12. In two runs the checkers obtained 8.4 and 8.5 g (40% and 42% yields). They found that the product can be purified further by recrystallization from MeOH/EtOAc; mp 272-274 °C. IR (CCl_4) cm^{-1}: 2948, 2870, 1665, 1610, 1573, 1471, 1385, 1295, 1096. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.20 (d, 18 H, *J* = 7.5), 1.24 (d, 18 H, *J* = 7.5), 1.51 (m, 6 H), 4.21 (s, 6 H), 5.92 (d, 2 H, *J* = 10.1), 6.48 (d, 2 H, *J* = 10.1), 7.38 (s, 2 H), 8.40 (d, 2 H, *J* = 8.9), 8.46 (d, 2 H, *J* = 8.9); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.0,

18.1, 61.2, 107.7, 121.1, 123.3, 125.0, 126.1, 128.0, 129.6, 129.9, 133.0, 134.1, 140.4, 145.3, 157.4, 183.6, 184.6. UV-vis (CH_3CN, c = 5.50×10^{-5} M): λ_{max} nm (log ε) 241 (4.54), 285 (4.48), 342 (4.18), 417 (3.76). Anal. Calcd for $C_{50}H_{58}O_8Si_2$: C, 71.22; H, 6.93. Found: C, 70.99; H, 6.87. The checkers obtained C, 71.20; H, 6.93.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The procedure illustrates one that has been used to prepare significant quantities of a variety of helicenebisquinones.[3] The majority of helicenes have been synthesized by photocyclization of derivatives of stilbene,[4] but in most cases only small amounts can be prepared practically. Moreover, the functional groups that have been incorporated in these helicenes have not been generally useful. Using our procedure, helicenebisquinones having functional groups suitable for subsequent transformations can be prepared easily in significant amounts. Among the structures synthesized from these helicenes are helical polymers,[5] helical discotic columnar aggregates[3e,6] and liquid crystals,[7] helical ligands,[8] nonlinear optical materials,[9] asymmetric catalysts,[10] and substances that probe remote chirality.[11]

Similar procedures have been used to prepare [7]helicenes that have different side chains,[3a,b] [5]- and [6]carbohelicenes,[3c,d,e,g] and [7] heterohelicenes.[3f,h]

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

3,6-Diacetyl-9,10-dimethoxyphenanthrene: Ethanone, 1,1'-(9,10-dimethoxy-3,6-phenanthrenediyl)bis- (9); (310899-08-2)

3,6-Bis[1-(triisopropylsiloxy)ethenyl]-9,10-dimethoxyphenanthrene: Silane,[(9,10-dimethoxy-3,6-phenenthrenediyl)bis(ethenylideneoxy)]tris(1-methylethyl)- (9); (310899-13-9)

Triisopropyl triflate: Methanesulfonic acid, trifluoro-, tris(1-methylethyl)silyl ester (9); (80522-42-5)

Triethylamine: Ethanamine, *N,N*-diethyl- (9); (121-44-8)

1,4-Benzoquinone: 2,5-Cyclohexadiene-1,4-dione (9); (106-51-4)

6,13-Bis(triisopropylsiloxy)-9,10-dimethoxy[7]helicenebisquinone : Dinaphtho [2,1-c:1',2'-g]phenanthrene-1,4,15,18-tetrone, 9,10-dimethoxy-6,13-bis[[tris(1-methylethyl)silyl]oxy]- (9); (310899-14-0)