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Synthesis of 7,10-Bis(2-halophenyl)tribenzo[*c,f,k*]fluoranthene as a Potential Buckybowl Precursor

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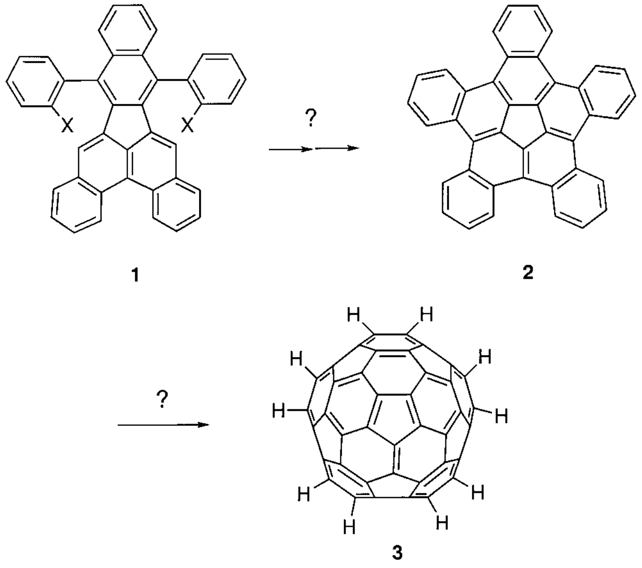
Introduction

We and others have been involved in the synthesis of polynuclear aromatic hydrocarbons having carbon frameworks that can be identified on the buckminsterfullerene surface (geodesic polyarenes or "buckybowls").[1,2] The largest of these fullerene fragments known to date is a $C_{36}H_{12}$ hydrocarbon—constituting 60% of C_{60}—by flash vacuum pyrolysis (FVP) of 1,7,13-trichloro-decacyclene.[2] While the pyrolysis route has produced some interesting buckybowls, it is clear that a limit will be reached where the pyrolysis precursor will no longer be sufficiently volatile to go through the hot zone. This has led to efforts to develop new methods for the conversion of these systems to buckybowls without the need for pyrolysis. Recent examples include the syntheses of dibenzocorannulene and benzo[ghi]fluoranthenes by Scott and Reisch,[3] and by Wang and Shevlin,[4] respectively, based on palladium-catalyzed intramolecular coupling.

Results and Discussion

Herein we report the preparation of 7,10-bis(2-halophenyl)tribenzo[*b*,*e*,*k*]fluoranthene (**1**) as a potential precursor for pentabenzocorannulene (**2**), itself a potential precursor for $C_{40}H_{10}$ buckybowl **3**; the carbon framework of the latter would constitute two-thirds of the buckminsterfullerene structure. Our synthesis of **1** involved benz[*a*]acephenanthrylene (**4**) as a key intermediate. Earlier approaches to the synthesis of this system involved syntheses with quite a number of steps and low yields,[5a] and the newer preparation by Magnus and co-workers represented a considerable improvement.[5b] Herein we describe our own route that involves fewer steps than the latter procedure, albeit with a flash vacuum pyrolysis.



Wittig type condensation between 3-bromo-2-naphthaldehyde[6] and benzyltriphenylphosphonium bromide produced the phenyl(bromonaphthyl)ethylene (**6a**) in 84% yield. Pd-catalyzed coupling with trimethylsilylacetylene[7] followed by photocyclization gave the 6-substituted benz[*c*]phenanthrene (**7a**) in 95% yield. Exposure to concentrated HCl in glacial acetic acid at 80 °C yielded 6-(1-chlorovinyl)benz[*c*]phenanthrene (**7b**) in 82% yield. Finally FVP at 920 °C furnished the key intermediate **4** (70%) (Scheme 1).

Benzeneseleninic anhydride (BSA) oxidation of the ethylene bridge of **4** by a procedure we developed earlier[8] proceeded in good yield (80%) to give diketone **8**. Knoevenagel condensation between the diketone and **9** (X = Br or Cl) afforded almost quantitatively cyclopentadienone **10** which was subjected without purification to Diels−Alder reaction with benzyne formed in situ from anthranilic acid and isoamyl nitrite to give **1** (X = Br or Cl) in good yield (80%).

In conclusion, we have provided a potentially useful route to larger fullerene fragments. While we have yet to discover a FVP procedure to convert **1** to the $C_{40}H_{10}$ buckybowl, some of the newer non-pyrolytic routes may ultimately be successful with **1** or with other related precursors that might be prepared by the methods described above.

Experimental Section

Methods and Materials. ^{1}H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were recorded in $CDC1_3$; mass spectra were obtained by GC−MS. The flash vacuum pyrolysis apparatus was purchased from Kontes Glass, Inc., and the following procedure was employed. The sample is dissolved in CH_2C1_2 and transferred to a small glass boat filled with glass wool. The solvent is evaporated and the boat is placed in the inlet chamber wrapped with a heating mantle that allows sublimation of the substrate under vacuum with a small flow of nitrogen. The pyrolysate condenses on the sidearm of the quartz tube exiting the chamber which is cooled with dry ice and acetone. Benzeneseleninic anhydride, bis(triphenylphosphine) palladium dichloride, and (trimethylsilyl)acetylene were purchased from Aldrich

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(1) (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (b) Scott, L. T. *Pure App. Chem.* **1996**, *68*, 291−300. (c) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370.

(2) (a) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R.B. M.; Brachter, M. S.; Hagen, S. *Pure App. Chem.* **1999**, *71*, 209−219. (b) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719.

(3) (a) Scott, L. T,; Reisch, H. A. Abstract No. 515. 219th National ACS Meeting, San Francisco, 2000. (b) Mehta, G.; Sarma, P. V. V. S. *Chem. Commun.* **2000**, 19.

(4) Wang, L.; Shevlin, P. B. *Tetrahedron Lett.* **2000**, *41*, 285.

(5) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1996; p 417. (b) Magnus, P.; Moris, J. C.; Lynd, V. *Synthesis* **1997**, 506.

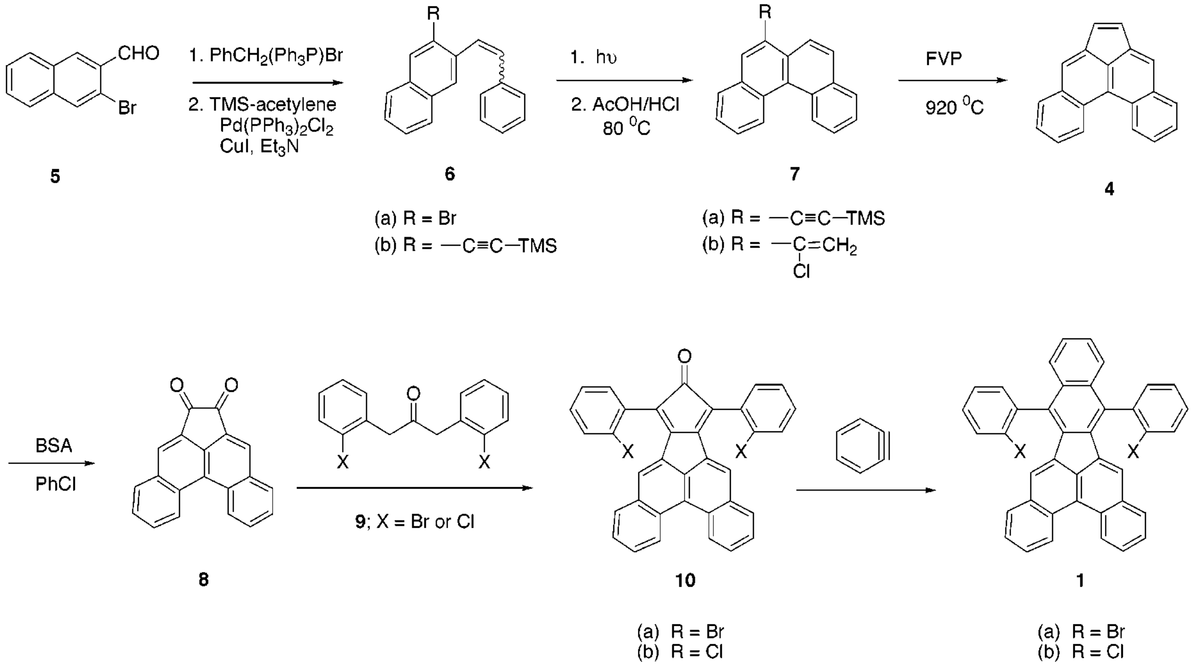
(6) Smith, J. G.; Dibble, P. W.; Sandborn, R.E. *J. Org. Chem.* **1986**, *51*, 3762

(7) Sakamato, T.; Shiraiwa, M.; Kondo, Y,; Yamanaka, H. *Synthesis* **1983**, 312.

(8) Clayton, M. D.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron Lett.* **1998**, *39*, 9127.

10.1021/jo0003798 CCC: $19.00

Scheme 1



Chemical Co., Inc. 3-Bromo-2-naphthaldehyde (**5**),[6] 1,3-bis(2-halophenyl)propanone (**9**),[9] and 3-bromo-2-styrylnaphthalene (**6a**)[10] were synthesized by published procedures.

3-Trimethylsilylethynyl-2-styrylnaphthalene (**6b**). 3-bromo-2-styrylnaphthalene (**6a**) (8.8 g, 28.7 mmol, cis/trans mixture), bis(triphenylphosphine)palladium dichloride (0.76 g, 1.06 mmol), copper(I)iodide (0.38 g, 1.98 mmol), and (trimethylsilyl)-acetylene (2.94. g, 30 mmol) in 250 mL of triethylamine were refluxed under argon. The solution turned black immediately. After stirring 20 h, the reaction mixture was quenched with water and the product was extracted with CH_2C1_2. The organic layer was dried over $MgS0_4$, filtered and evaporated. The crude material was flash chromatographed on silica gel to give an oily mixture of cis and trans isomers of **6b** (7.98 g, 86%) which was used in the next photocyclization step; separation of the mixture was not attempted.

6-(Trimethylsilylethynyl)benzo[*c*]phenanthrene (**7a**). A solution of **6b** (650 mg, 2 mmol) and 20 mg of iodine in cyclohexane (300 mL) was irradiated with a 450-W high pressure quartz Hg-vapor lamp for 2 h. Evaporation of the solvent provided a yellow oil which slowly solidified. The nearly pure **7a** (614 mg, 95%) was recrystallized from hexane to give yellow needles: mp 113–114 °C; ^1H NMR (250 MHz, $CDC1_3$) δ 9.06 (m, 2H), 8.48 (d, $J = 8.8$ Hz, 1H), 8.20 (s, 1H), 8.02–7.96 (m, 3H), 7.70–7.63 (m, 4H), 0.43 (s, 9H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 133.71, 132.82, 132.66, 130.42, 130.38,130.24, 128.41, 128.51, 128.25, 128.20, 128.07, 127.82, 127.15, 126.45, 126.40, 126.34, 124.75, 119.59, 103.73, 99.45, 0.38; MS (*m*/*e*, rel intensity) 324 (M^+, 100), 309 (195), 226 (85); HRMS calcd for $C_{23}H_{20}Si$ 324.1334, found 324.1342.

6-(L-Chlorovinyl)benzo[*c*]phenanthrene (**7b**). To a solution of 800 mg (2.47 mmol) of **7a** in 800 mL of glacial acetic acid was added 2 mL of concentrated hydrochloric acid. The solution was stirred at 80 °C for 3 h, then quenched with water and extracted with CH_2C1_2 (three times). The organic layer was washed with aq. sodium bicarbonate and water. The crude product was purified by column chromatography with hexane to give 584 mg (82%) of a white solid: mp 59–61 °C (hexane); ^1H NMR (250 MHz, $CDC1_3$) δ 9.08 (d, $J = 7.6$ Hz, 2H), 8.19 (d, $J = 8.8$ Hz, 1H), 8.20 8.01(m, 3H), 7.94 (s, 1H), 7.71–7.65 (m, 4H), 5.92 (s, 1H), 5.69 (s, 1H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 139.36, 135.52, 133.55, 132.54, 130.74, 130.36, 129.04, 128.59, 128.47, 128.30, 128.25, 128.01, 127.85, 127.76, 127.11, 126.49, 126.51, 126.41, 124.03, 118.45. MS (*m*/*e*, rel intensity); 288 (M^+, 25), 253 (100), 126 (44); HRMS calcd for $C_{20}H_{13}C1$ 288.0706, found 288.0711.

Benz[*a*]acephenanthrylene (**4**). Flash vacuum pyrolysis of 200 mg of **7b** at 920 °C under vacuum with a slow nitrogen bleed (~1 mmHg) over a period of 2 h produced 140 mg of pyrolysate which was recrystallized from hexane to give **4** as yellow needles (122 mg, 70%): identical ^1H NMR, ^{13}C NMR, and mp with previously described material.[5]

Benz[*a*]acephenanthrylene-4,5-dione (**8**). A solution of **4** (1.01 g, 4 mmol) and benzeneseleninic anhydride (1.65 g, 4.6 mmol) in 100 mL of chlorobenzene was heated for 5 h at 110 °C. The crude product was purified by flash column chromatography on silica gel with a 1:1 mixture of hexane and CH_2C1_2 to give 0.91 g (80%) of a yellow solid: mp 279–280 °C (ethanol); ^1H NMR (250 MHz, $CDC1_3$) δ 9.24 (d, $J = 8.5$ Hz, 2H), 8.50 (s, 2H), 8.27 (d, $J = 8.0$ Hz, 2H), 8.00–7.75 (m, 4H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 189.14, 139.10, 133.53, 133.23, 130.73, 127.72, 127.01, 126.81, 125.87, 125.09 (one quaternary carbon not observed); MS (*m*/*e*, rel intensity) 282 (M^+, 47), 254 (100), 226 (85); HRMS calcd for $C_{20}H_{10}O_2$ 282.0681, found 282.0688.

7,10-Bis(2-bromophenyl)tribenzo[*b,e,k*]fluoranthene (**la**). To a suspension of 510 mg (1.8l mmol) of **8** and 670 mg (1.82 mmol) of 1,3-bis(2-bromophenyl)propanone in 25 mL of methanol was added a methanolic solution of sodium hydroxide (1.82 mmol of NaOH in 20 mL of methanol). The suspension was allowed to stir at 25 °C overnight, and then the dark brown precipitate was separated, washed with methanol and dried to yield almost quantitatively (1.10 g) cyclopentadienone **10** which was used in the next step without further purification: mp 313–315 °C; ^1H NMR (250 MHz, $CDC1_3$) δ 9.22 (d, $J = 8.5$ Hz, 2H), 8.08–7.33 (m,16H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 198.21, 134.99, 133.65, 133.59, 133.13, 133.01, 132.47, 131.98, 131.79, 131.28, 130.06, 128.99, 128.55, 127.49, 127.07, 126.92, 126.78, 126.56, 124.49. Anal. Calcd for $C_{35}H_{18}Br_2O$: C, 68.43; H, 2.95. Found: C, 68.61; H, 2.87.

Solutions of anthranilic acid (685 mg, 5 mmol) in DME (20 mL) and isopentyl nitrite (860 mg, 7.4 mmol) in DME (10 mL) were added simultaneously from two dropping funnels to a boiling solution of crude **10** (500 mg, 0.83 mmol) in 20 mL of DME. The mixture was stirred at reflux for another 1 h, DME was removed under reduced pressure, and the resulting mixture was extracted with CH_2C1_2, washed with water and dried. The residue was recrystallized from ethanol to afford 430 mg (80%) of **la** (X = Br) as a pale yellow solid: mp = 390–392 °C; ^1H NMR (250 MHz, $CDC1_3$) δ 9.21 (d, $J = 8.5$ Hz, 2H), 8.01 (d, $J = 7.6$

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(9) Bennet, M. A.; Neumann, H. *Aust. J. Chem.* **1980**, *33*, 1251.

(10) (a) Martin, R. H.; Baes, M. *Tetrahedron* **1975**, *31*, 2135. (b) Stammel, C.; Fröhlich, R.; Wolff, C.; Wenck, H.; de Meijere, A.; Mattay, J. *Eur. J. Org. Chem.* **1999**, 1709.

Hz, 2H), 7.74−7.49 (m, 16H), 6.94 (s, 2H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 139.81, 135.32, 135.09, 134.45, 134.38, 133.75, 132.52, 132.42, 131.10, 130.76, 130.49, 130.17, 128.67, 127.06, 126.93, 126.60, 126.57, 125.93, 125.01, 124.44, 123.88; MALDI MS 662, 582, 502. Anal. Calcd for $C_{40}H_{22}Br_2$: C, 72.53; H, 3.35. Found; C, 72.58; H, 3.41.

Following the same two-step procedure using 1,3-bis(2-chlorophenyl)propanone, **1b** (X = C1) was obtained in 78% as a pale yellow solid: mp = 348−350 °C; ^{1}H NMR (250 MHz, $CDC1_3$) δ 9.22 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.74−7.40 (m, 16H), 6.96 (s, 2H); ^{13}C NMR (62.9 MHz, $CDC1_3$) δ 137.77, 135.29, 135.03, 134.47, 132.71, 132.67, 132.47, 132.26, 131.08, 130.77, 130.62, 130.55, 130.05, 128.05, 127.99, 127.05, 126.93, 126.61, 126.51, 125.92, 123.80; MALDI MS 572, 535, 500. Anal. Calcd for $C_{40}H_{22}C1_2$: C, 83.77; H, 3.87. Found: C, 83.83 H, 3.93

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