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Improved Synthesis of a $C_{30}H_{12}$ Buckybowl via Benzylic Oxidation with Benzeneseleninic Anhydride

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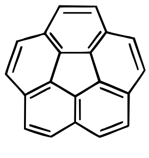
The enormous amount of attention[1] afforded to C_{60}, buckminsterfullerene or "buckyball", and its related carbon cages has generated considerable interest in curved-surface, polynuclear aromatic hydrocarbons possessing carbon frameworks that can be identified on the C_{60} surface. That is, if part of the carbon framework were removed from the buckminsterfullerene surface, and hydrogen were added to the "dangling" bonds, a fullerene-related hydrocarbon would be produced. The smallest hydrocarbon that can be generated in this way and still maintain its curvature is corannulene[2] (**1**, $C_{20}H_{10}$). While corannulene has been known for some time, similar elaboration beyond 20 carbons on the C_{60} surface has only recently been accomplished. Some examples include cyclopentacorannulene[3] (**2**) as well as two $C_{30}H_{12}$ semibuckminsterfullerenes that achieve one-half of the carbon framework of buckminsterfullerene (**3** and **4**).[4,5]

In contrast to corannulene, which undergoes rapid bowl-to-bowl inversion, the incorporation of additional five-membered rings leads to significantly more curvature and less flexibility. Hydrogenation of **2** produces a structure where bowl-to-bowl inversion becomes detectable by exchange of endo and exo hydrogens in ^{1}H NMR, and inversion was observed to proceed very slowly.[3b] As a consequence, **3** and **4** may be presumed to be rigid bowls. Because of their bowl-like structure and their relationship to the buckyball, we have referred to this class of aromatic hydrocarbons as "buckybowls".[4]



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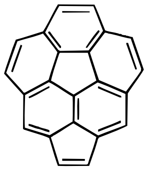

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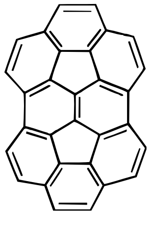

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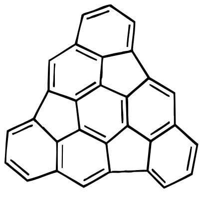

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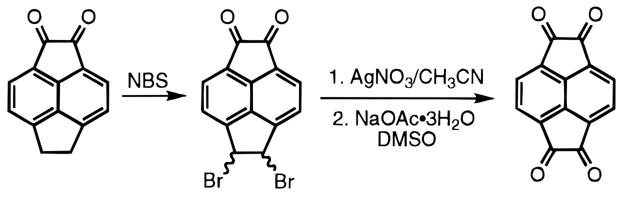
The elegant synthesis of corannulene developed by Scott and co-workers[2b] served as a basis for the synthesis of **2** and **3** as well (Scheme 1). A key step is Knoevenagel condensation of a 1,2-diketone with heptanetrione, followed by reaction with norbornadiene, to generate a diacetylated aromatic ring. After conversion to the bis(chlorovinyl) derivative by reaction with PCl_5, the final step employs a flash vacuum pyrolysis, where ring closure occurs to produce the bowl-shaped products. Scott argues that the high temperatures involved allow for drastic fluctuations from the equilibrium geometry, and this facilitates the otherwise unfavorable ring closures.

Clearly, this method provides a useful, general route to corannulene-related hydrocarbons. However, while in the case of corannulene itself acenaphthenequinone is a readily available starting material, the synthesis of 1,8-naphthoquinones presents a major problem with this route. For example, we required the previously unknown 1,2,5,6-tetraketopyracene (**6**) as an intermediate in the synthesis of **3**, but its preparation proved to be quite difficult since all of the most reasonable routes failed.[6] Ultimately, NBS bromination of **5**, followed by reaction with silver nitrate and then sodium acetate/DMSO, did produce **6** in 55−70% yield. Unfortunately, however, the reaction was not always reproducible, and our subsequent efforts to improve reproducibility as well as to discover the reasons for the inconsistency have met with failure. Given the importance of this route, not only to **3** but as a general path to buckybowls, we have explored other methods for the conversion of **5** to **6**, and herein we report our success with benzeneseleninic anhydride oxidation[7] of ethane-bridged intermediates. We have



5 **6**

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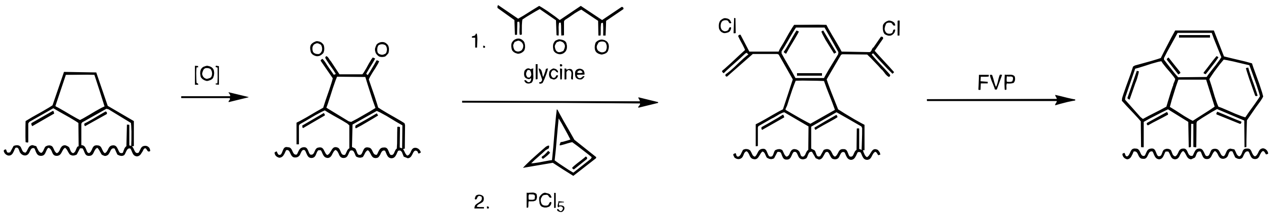
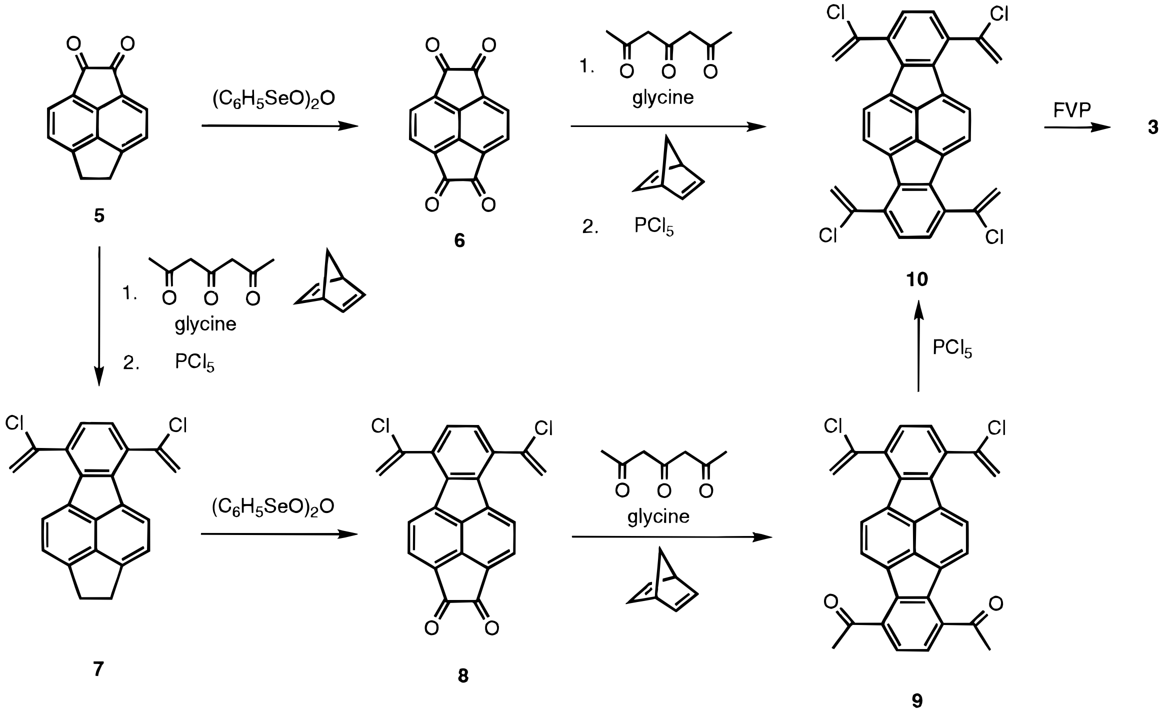
Scheme 1



Scheme 2



found that **5** is smoothly converted to **6** in good yield by reaction with benzeneseleninic anhydride in chlorobenzene.

This shorter and more reliable route to **6** greatly improves the synthetic pathway to **3**, although, even with this improvement, the yields for the conversion of **6** to **10** are still rather low (5%) due to the required, double-sided Knoevenagle condensation, aromatic ring formation, and final conversion to **10** via PCl_5.[4] Thus, we examined the possibility of using benzeneseleninic anhydride oxidation to convert **7** to **8**, since **7** can be prepared in good yield from diketone **5**.[3,4b] According to the same procedure as that used for **5**, oxidation of **7** was completed after 24 h to give **8** in 86% yield. The conversion of **8** to **10** via **9** was accomplished by reactions on only one side of the molecule; hence, the overall process was improved from 5 to 10%. Therefore, the two routes shown in Scheme 2 (upper and lower pathways) are more or less comparable, but both are greatly improved by the use of benzeneseleninic anhydride. We prefer the latter path due to much better solubility of intermediates **8** and **9**.

In conclusion, we have provided an improved synthesis of 1,2,5,6-tetraketopyracene (**6**), in that three steps have been replaced with one high-yield step. Moreover, a very unreliable step has been eliminated. In turn, this has led to an improved synthesis of buckybowl **3** using **6** as an intermediate. Alternatively, we have also provided a new route to **3** utilizing the benzeneseleninic anhydride conversion of **7** to **8**. We hope that this new route will find application in other buckybowl syntheses as well.

Experimental Section

General. ^1H (250.13 MHz) and ^{13}C (62.90 MHz) NMR spectra were recorded in $CDCl_3$ on a Bruker AC-250. Mass spectra were obtained by GC-MS. Melting points are uncorrected. Benzeneseleninic anhydride was purchased from Synmet, Inc.

1,2,5,6-Tetraketopyracene (6). A solution of **5** (832 mg, 4.0 mmol) and benzeneseleninic anhydride (2.88 g, 8.0 mmol) in 70 mL of chlorobenzene was heated at 125 °C for 72 h. After cooling, the orange precipitate was separated, washed thoroughly with aqueous $NaHCO_3$ solution, water, and dichloromethane, and then dried to give **6**: 770 mg (82%), identical (^1H NMR, ^{13}C NMR) to the previously obtained sample.[6]

7,10-Bis(1-chloroethenyl)-3,4-(dioxoethano)fluoranthene (8). A solution of **7** (1.6 g, 4.58 mmol) and benzeneseleninic anhydride (3.3 g, 9.16 mmol) in 45 mL of chlorobenzene was heated at 125 °C for 24 h. The crude product was purified by flash column chromatography on silica gel with a 1:1 mixture of hexane and CH_2Cl_2 to give 1.5 g (86%) of yellow solid **8**: mp 256−258 °C (benzene); ^1H NMR δ 5.84 (d, 2H), 6.00 (d, 2H), 7.53 (s, 2H), 8.25 (d, 2H), 8.56 (d, 2H); ^{13}C NMR δ 118.3, 120.3, 124.1, 126.4, 128.4, 130.3, 136.8, 137.4, 137.9, 139.2, 141.2, 187.0; MS m/z 376 (M^+). Anal. Calcd for $C_{22}H_{10}Cl_2O_2$: C, 70.05; H, 2.67; Cl, 18.80. Found: C, 70.37; H, 2.74; Cl, 18.65.

1,4-Bis(1-chloroethenyl)-7,10-bis(1-oxoethyl)indeno[1,2,3-*cd*]fluoranthene (9). In a 100 mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer, and a Dean−Stark receiver fitted with a condenser were heated 1.89 g (5 mmol) of **8** and 375 mg (5 mmol) of glycine in 30 mL of toluene to ~100 °C. 2,4,6-Heptanetrione (710 mg, 5 mmol) was

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then added, followed by 30 mL of norbornadiene 30 min later, and the solution was brought to reflux. After 24 h, another 710 mg (5 mmol) of 2,4,6-heptanetrione was added. The brown solution was refluxed for a total of 72 h. Toluene and excess norbornadiene were removed under reduced pressure, and the resulting mixture was extracted with CH_2Cl_2, washed with water, and dried. Flash chromatography with hexane/CH_2Cl_2 (1:1) gave 610 mg (25%) of an orange solid: mp 212−214 °C (from ethanol): ^{1}H NMR δ 2.73 (s, 6H), 5.72 (d, 2H), 5.84 (d, 2H), 7.16 (s, 1H), 7.54 (s, 2H), 7.89 (d, 2H), 8.11 (d, 2H); ^{13}C NMR δ 29.6, 117.5, 125.9, 127.7, 128.4, 129.1, 132.7, 133.5, 135.4, 136.5, 136.9, 137.6, 138.2, 139.4, 141.2, 200.8; MS m/z 480 (M^+). Anal. Calcd for $C_{30}H_{18}Cl_2O_2$: C, 74.85; H, 3.77; Cl, 14.73. Found: C, 74.97; H, 3.59; Cl, 14.62.

1,4,7,10-Tetrakis(1-chloroethenyl)indeno[1,2,3-*cd*]fluoranthene (10). A mixture of **9** (450 mg, 0.93 mmol) and 950 mg (4.56 mmol) of PCl_5 was refluxed in 15 mL of benzene for 3 h. The solvent was evaporated and the residue chromatographed on silica gel with cyclohexane to afford orange solid **10**: 190 mg (39%), identical (^{1}H NMR, ^{13}C NMR, mp) to the previously obtained sample.[4]

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