Non-Pyrolytic Syntheses of Buckybowls: Corannulene, Cyclopentacorannulene, and a Semibuckminsterfullerene

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Abstract: Corannulene (**1**), cyclopentacorannulene (**2**), and a $C_{30}H_{12}$ semibuckminsterfullerene (**3**) have been prepared by non-pyrolytic methods employing bromomethyl/dibromomethyl and/or dibromomethyl/dibromomethyl coupling with low-valent titanium or vanadium. Reductive coupling of tetrakis(dibromomethyl)-fluoranthene (**8**) with vanadium(III) chloride and lithium aluminum hydride affords corannulene in 70−75% yield. Similarly, hexakis(dibromomethyl)fluoranthene (**13**) leads to cyclopentacorannulene in 20−30% yield, and dodecabromo(octamethyl)indenofluoranthene (**6**) affords semibuckminsterfullerene (**3**) in 20% yield.

Introduction

Fullerene fragments, or "buckybowls", are curved-surface, polynuclear aromatic hydrocarbons with carbon frameworks that can be identified on the surface of C_{60} or other fullerenes.[1] While these hydrocarbons are quite interesting in themselves, they also have the potential to serve as synthetic intermediates for the total synthesis of fullerenes and as end-caps for carbon nanotubes. While the carbon framework of many aromatics can be identified on fullerene surfaces, $C_{20}H_{10}$ corannulene (**1**), the polar cap of C_{60}, is the simplest example of a fullerene fragment that exhibits curvature. This novel hydrocarbon was first synthesized in 1966 by Barth and Lawton,[2] but the formidable, 16-step process was too daunting to foster more than a minimal investigation of its chemistry and attempts to improve the synthesis met with failure[3] until the recent innovations from the Scott[4] and Siegel[5] groups. The flash vacuum pyrolysis method (FVP) developed by the Scott group has since served as the basis for the synthesis of several important fullerene fragments including the first "locked" bowl, cyclopentacorannulene[6] (**2**), and the first semibuckminsterfullerene (**3**).[7]

1   2   3

While FVP methods have provided routes to a number of novel buckybowls,[1] the method suffers from several disadvantages. Although corannulene is formed in 30−40% yield by FVP,[4c] the yields of other, more highly strained buckybowls are significantly lower, usually below 5%, and sometimes even below 1%.[1] Moreover, larger buckybowls become quite difficult to prepare by this method due to the lack of volatility of precursors that comes with increasing molecular weights. And, of course, vacuum processes by their nature do not lend themselves well to the large-scale production needed to effectively provide intermediates for multistep processes or possible commercial applications. Clearly, alternative routes that can provide significant quantities of these novel buckybowls will be necessary for a thorough investigation of their chemistry as well as for their use as synthetic intermediates. Presumably, these routes will involve non-pyrolytic, solution-phase processes.

Results and Discussion

Our approach to the solution-phase production of fullerene fragments[8] was developed from a report by Seiders et al., who described a non-pyrolytic route to dimethylcorannulene via reductive low-valent titanium coupling of tetrabromide **4** followed by dehydrogenation of the dimethyltetrahydrocorannulene intermediate.[9] Despite the modest yield of 18% for the two combined steps, McMurry coupling appeared to be a potential alternative to the FVP route.

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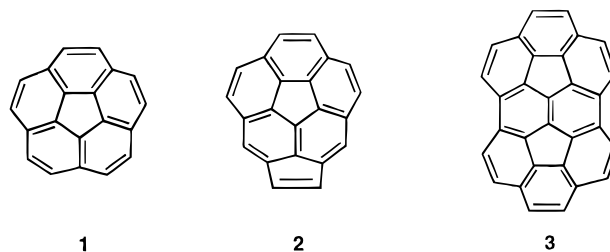
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In an attempt to explore this methodology for the preparation of semibuckminsterfullerene (**3**), we developed a synthesis of the octamethyl derivative **5**,[8b] from the known 2,3,6,7-tetram-

5

ethylnaphthalene, since **5** could, in principle, be converted to **3** by appropriate coupling of the methyls. Reaction of **5** with NBS afforded octakis(bromomethyl)indenofluoranthene (**6**), which was subjected to McMurry coupling. Unfortunately, despite several attempts employing various reductive systems in both THF and DME, this failed to produce any isolable amounts of semibuckminsterfullerene (**3**) or its octahydro derivative. Given the effort to prepare **5**, we decided to examine its bromination behavior in more detail and found that with a large excess of NBS, it produced dodecabromo derivative **7**. Reaction of the

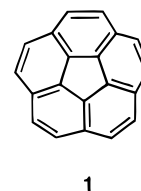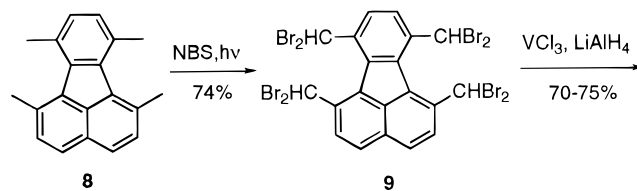| | | |
| **6** | **3** | **7** |

X = CH₂Br

Y = CHBr₂
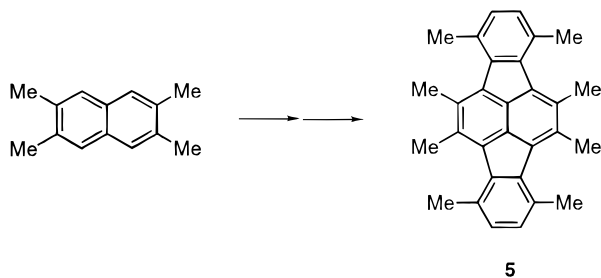
latter with low-valent titanium or vanadium did lead to semibuckminsterfullerene (**3**) albeit in modest yields of ca. 20%. However, this result suggested that dibromomethyl groups may be more reactive than the bromomethyl alternatives toward intramolecular McMurry coupling, a factor that could be especially important for the production of strained rings. In addition, the major product of the above reaction is **3**, not its octahydro derivative as would be expected if bromomethyl groups were employed. Clearly any octahydrotetrabromo intermediate that might be formed rapidly loses HBr under the reaction conditions. Formation of fully aromatized product is advantageous since it avoids a separate rearomatization step which proves to be a low-yield process with polyhydrogenated corannulenes.[2,9]
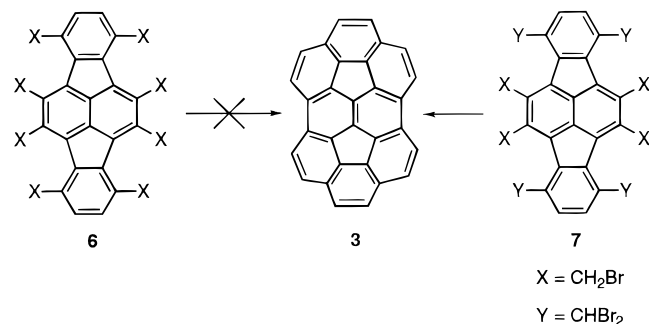
These results immediately raised a question as to whether this approach might lead to an improved solution-phase synthesis of corannulene itself. To this end, we brominated tetrameth-ylfluoranthene (**8**)[10] with 8.8 equiv of NBS in refluxing benzene

with a catalytic amount of dibenzoyl peroxide under sun lamp irradiation to produce tetrakis(dibromomethyl) derivative **9**. The

| | |
| **8** | **9** |

1

solution of **9** in DME was then added slowly through a syringe pump to a refluxing suspension of VCl₃/LiAlH₄ in the same solvent. Corannulene was formed in an impressive yield of 70–75% by this protocol! The only byproduct identified was bromocorannulene (ca. 5%), which can be separated by column chromatography (silica gel, cyclohexane) or converted to corannulene in situ by treatment with *n*-butyllithium in THF at −78 °C followed by quenching with water.

Encouraged by this success, we decided to investigate the analogous solution synthesis of cyclopentacorannulene (**2**) since we expect it to be more valuable than corannulene as a synthetic intermediate, and the extra strain present from the additional five-membered ring would also test the limits of this method. Previously we obtained **2** in rather low yield (ca. 10%) by FVP of a bis(chlorovinyl)cyclopentafluoranthene precursor.[6] More-over, corannulene was also formed as a byproduct of the pyrolysis and separation of the two hydrocarbons proved to be difficult. Our non-pyrolytic route started with 1,3,6,8-tetram-ethylnaphthalene (**10**),[11] which was doubly acylated with oxalyl chloride/aluminum chloride in dichloroethane to give diketone **11**. Condensation of **11** with 3-pentanone in methanol/KOH produced an isomeric mixture of the keto alcohol **12**, which was converted to the hexamethylfluoranthene **13** by reflux with

| | | |
| **10** | **11** | **12** |

| | | |
| **2** | **14** | **13** |
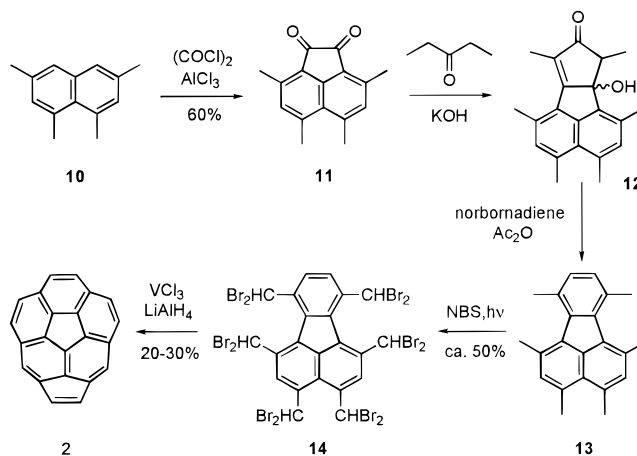
norbornadiene in acetic anhydride. Again, bromination of **13** under conditions described above with 13 equiv of NBS provided the desired hexakis(dibromomethyl)fluoranthene (**14**). Low-valent vanadium produced by reduction of vanadium trichloride by lithium aluminum hydride in DME/THF converted

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14 to cyclopentacorannulene (**2**) in moderate yields of 20−30%. Occasionally, ca. 1−2% of dihydrocyclopentacorannulene was also formed.

Conclusion

In conclusion, we have demonstrated that fullerene fragments can be prepared by solution-phase chemistry in good to modest yields by McMurry coupling. Of special significance is the success of bromomethyl/dibromomethyl and dibromomethyl/dibromomethyl coupling since at least in one case that we examined (i.e., **3**) the usual route involving bromomethyl/bromomethyl coupling failed completely. The question of whether dibromomethyl coupling may also be more facile in planar systems as well remains unanswered at this point. However, this route is definitely superior in these highly strained systems leading to curved aromatics, and we expect that a number of unusual systems will be accessible by this approach.

Perhaps of greatest significance is that this method can be scaled-up to provide sufficient quantities of these novel materials for use as intermediates in the synthesis of larger fullerene fragments. We are currently exploring these possibilities.

Experimental Section

Methods and Materials. 1,4,5,6,7,10,11,12-Octamethyl[1,2,3-*cd*]-fluoranthene (**5**),[8b] 1,6,7,10-tetramethylfluoranthene (**8**),[10] and 1,3,6,8-tetramethylnaphthalene (**10**)[11] were synthesized according to published procedures. THF was freshly distilled from benzophenone/sodium before use. Titanium powder (100-mesh) and anhydrous DME were purchased from Aldrich Chemical Co. and used without further purification. Solutions for the reductive couplings were prepared and handled under dry argon atmosphere using flame-dried glassware. Elemental analyses were carried out by Quantitative Technologies Inc.

1,4,5,6,7,10,11,12-Octakis(bromomethyl)[1,2,3-*cd*]fluoranthene (6). A solution of **5** (300 mg, 0.77 mmol), NBS (1.11 g, 6.25 mmol) and 50 mg of dibenzoyl peroxide was refluxed in 45 mL of benzene for 2 h with irradiation by a 150 W sun lamp. The solvent was evaporated under reduced pressure, and the orange solid was washed well with water, then methanol, and dried. The crude product was crystallized twice from benzene. Yield: 460 mg (58%) of a yellow powder that darkens gradually above 250 °C and melts with decomposition at 278−280 °C (sealed capillary). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.7 (v br, 4H), 5.0 (v br, 4H), 5.3 (br m, 8H), 7.51 (s, 4H). The broad C**H$_2$**Br signals sharpen into two singlets at 5.02 and 5.44 (intensity 1:1) in nitrobenzene-d_5 above 70 °C. ^{13}C NMR was not obtained due to very limited solubility of **6** in common deuterated solvents. MALDI MS: 1019, 939, 860, 780, 700, 620, 540, 460, 380.

5,6,11,12-Tetrakis(bromomethyl)-1,4,7,10-tetrakis(dibromomethyl)-[1,2,3-*cd*]fluoranthene (7). A solution of of **5** (1 g, 2.57 mmol), NBS (6.6 g, 37 mmol), and 50 mg of dibenzoyl peroxide was refluxed in 150 mL of benzene for 8 h with irradiation by a 150 W sun lamp. The solvent was evaporated under reduced pressure, and the orange solid was washed well with water, then methanol, and dried. The crude product was refluxed with ca. 50 mL of toluene, cooled, filtered, and dried. Yield: 3.25 g (83%) of the toluene solvated **7** that was sufficiently pure for use in the next step. Subsequent crystallization from toluene gave orange crystals of **7**·2C$_6$H$_5$CH$_3$ which darkens and decomposes, but does not melt below 350 °C. ^{1}H NMR (THF-d_8, 250 MHz): δ 5.1 (v br, 4H), 5.5 (v br, 4H), 7.50 (br, 4H), 8.16 (s, 4H), toluene peaks at 2.31 (s) and 7.05−7.20 (m). ^{13}C NMR (CDCl$_3$, 50.3 MHz): broad peaks δ 30.52, 40.37, 133.87, 135.03, 135.53, 139.9, $\alpha\nu\delta$ 139.86 and sharp toluene peaks at δ 21.69, 125.53, 128.45, 129.27, and 137.37. Final structure proof for **7**·2C$_6$H$_5$CH$_3$ was provided by X-ray crystal structure determination.[8b]

Formation of Semibuckminsterfullerene (3). Titanium powder (100 mesh, 2.7 g) was refluxed with trimethylsilyl chloride (6.2 g, 57 mmol) in 30 mL of dry DME under argon for 64 h. A solution of **7**·2C$_6$H$_5$CH$_3$ complex (450 mg, 0.30 mmol) in 65 mL of dry THF was added through a syringe pump to the refluxing suspension of the activated titanium[12] at a rate of ca. 3 mL per hour. After the addition was complete the mixture was refluxed for an additional 24 h. The resulting black suspension was diluted with toluene and filtered through a pad of Florosil. After evaporation of the solvent under reduced pressure, the yellow solid was refluxed with 30 mg of DDQ in 10 mL of toluene for 2 h. The solvent was removed under reduced pressure and the dark red solid was chromatographed on silica gel with cyclohexane to yield 25 mg of **3** (22%).

1,6,7,10-Tetrakis(dibromomethyl)fluoranthene (9). A mixture of **7** (2.6 g, 10 mmol), NBS (15.0 g, 84 mmol), and 150 mg of dibenzoyl peroxide was refluxed in 200 mL of benzene for 24 h with irradiation by a 150 W sun lamp. The solvent was removed under reduced pressure and the resulting dark solid was washed well with water and ethanol. Crystallization from ethanol/chloroform gave 6.6 g (74%) of a yellow solid that darkens above 250 °C (sealed capillary) and melts at 274−276 °C dec. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.09 (s, 4H), 7.21 (s, 4H), 7.98 (d, J = 8.7 Hz, 2H), 8.20 (s, 2H), 8.27 (d, J = 8.7 Hz). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 38.60, 39.20, 127.96,129.42, 130.36, 130.45, 131.88, 132.15, 132.64, 136.86, 138.25. Anal. Calcd for C$_{20}$H$_{10}$-Br$_8$: C, 27.01; H, 1.13. Found: C, 26.69; H, 1.14.

Corannulene (1). A solution of **9** (2.29 g) in 100 mL of dry DME was added through a syringe pump to a refluxing suspension of 8.4 g of vanadium(III) chloride and 0.76 g of lithium aluminum hydride at a rate of ca. 1 mL per hour. After the addition was complete, the mixture was refluxed for an additional 8 h. The reaction mixture was then diluted with benzene and filtered through a pad of Florosil. The solvents were removed under reduced pressure and the crude product was recrystallized from ethanol giving 152 mg of pure **1**. The mother liquor was evaporated under reduced pressure and the resulting solid was chromatographed on silica gel with cyclohexane. The first fraction collected gave 44 mg (5%) of bromocorannulene, and the second fraction gave an additional 320 mg of corannulene for a total yield of 472 mg (73%).

3,5,6,8-Tetramethyl-1,2-acenaphthenedione (11). A solution of **9** (5.72 g, 31 mmol) in 320 mL of 1,2-dichloroethane was added dropwise to a stirred suspension of AlCl$_3$ (18.3 g, 113 mmol) and oxalyl chloride (3.94 g, 31 mmol) in 320 mL of the same solvent at 0 °C. Stirring was continued for 6 h at the same temperature. The reaction mixture was quenched with water, the organic layer washed with diluted sodium carbonate solution and water and dried, and the solvent removed at reduced pressure. Crystallization of the crude product from toluene and chromatography of the mother liquor (silica gel, DCM) gave 4.4 g (60%) of the diketone **11** as a yellow solid that darkens and softens above 270 °C (sealed capillary), and melts at 303−306 °C dec. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 2.74 (s, 6H), 2.93 (s, 6H), 7.16 (s, 2H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 17.94, 25.28, 123.99, 127.66, 133.42, 137.40, 143.04, 149.47, 189.51. MS (*m/e*, rel intensity) 238 (62), 210 (100), 195 (20), 167 (22), 165 (55), 152 (36), 76 (20). Anal. Calcd for C$_{16}$H$_{14}$O$_2$: C, 80.65; H, 5.92. Found: C, 80.34; H, 5.97.

1,3,4,6,7,10-Hexamethylfluoranthene (13). A suspension of **10** (3.5 g, 14.7 mmol) in 40 mL of methanol with 4 mL of 3-pentanone and 2 mL of a 20% solution of potassium hydroxide in methanol was stirred at room temperature for 2 days. The yellow suspension was poured into water and acidified with dilute HCl, and the solid was filtered and dried. The crude keto alcohols **12** were refluxed for 36 h in a mixture of 100 mL of acetic anhydride and 20 mL of norbornadiene. The excess norbornadiene was distilled off and the dark solution was poured into water and stirred until most of the acetic anhydride hydrolyzed. The dark solid was separated and dried. Chromatography (silica gel, toluene/hexane) gave 2.95 g (70%) of **13** as a pale yellow solid. Mp 138−139 °C (from EtOH). ^{1}H NMR (CDCl$_3$, 250 MHz): δ 2.77 (s, 6H), 2.80 (s, 6H), 2.91 (s, 6H), 7.14 (s, 2H), 7.17 (s, 2H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 24.34, 24.42, 24.79, 126.56, 129.09, 130.30, 131.60, 133.87, 134.52, 135.43, 135.75, 139.64. MS (*m/e*, rel intensity) 286 (100), 271 (30), 239 (18), 143 (20), 128 (22), 126 (23), 120 (15). Anal. Calcd for C$_{22}$H$_{22}$: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.76.

1,3,4,6,7,10-Hexakis(dibromomethyl)fluoranthene (14). A mixture of **13** (1.7 g, 5.9 mmol), NBS (14.0 g, 78.7 mmol), and 150 mg of dibenzoyl peroxide was refluxed in 100 mL of benzene with irradiation

(12) Fürstner, A.; Huppertz, A. *J. Am. Chem. Soc.* **1995**, *117*, 4468−4475.

by a 150 W sun lamp for 2 days. The reaction mixture was diluted with benzene, washed with water, and dried, and the solvent was removed under reduced pressure. Chromatography on silica gel with cyclohexane gave 4.1 g of **14** (56%) as a bright yellow solid. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 6.98 (s, 2H), 7.05 (s, 2H), 7.58 (s, 2H), 8.20 (s, 2H), 9.19 (s, 2H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 37.24, 37.50, 37.63, 129.94, 131.50, 133.46, 137.01, 138.76, 140.10. Anal. Calcd for C$_{22}$H$_{10}$-Br$_{12}$: C, 21.43; H, 0.82. Found: C, 21.12; H, 1.07.

Cyclopentacorannulene (**2**). A solution of **13** (1.31 g, 1.06 mmol) in a mixture of 35 mL of dry THF and 15 mL of dry DME was added through a syringe pump at a rate of ca. 1 mL per hour to a refluxing suspension of 3.2 g of vanadium(III) chloride and 0.32 g of lithium aluminum hydride in 30 mL of DME and 20 mL of THF. After the addition was complete, the mixture was refluxed for an additional 8 h. The reaction mixture was then diluted with toluene and filtered through a pad of florosil. The solvents were removed under reduced pressure

and the crude product was chromatographed on silica gel with cyclohexane/benzene (20:1). The first fraction collected gave 60 mg (21%) of cyclopentacorannulene (**3**). Yields of subsequent trials under similar conditions varied in the range of 20−30%. Occasionally, ca. 1−2% of dihydrocyclopentacorannulene was also formed.

Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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