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# Chemistry on the rim of buckybowls: derivatization of 1,2,5,6-tetrabromocorannulene

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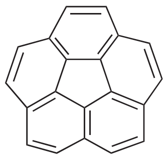
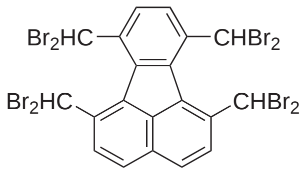
## Abstract

Synthesis of a number of substituted corannulenes and dibenzo[*a*,*g*]corannulenes starting from 1,2,5,6-tetrabromocorannulene **3** is described. Since **3** is conveniently obtained by a large scale, non-pyrolytic route, it may serve as a synthon for the further elaboration of this bowl-shaped system.

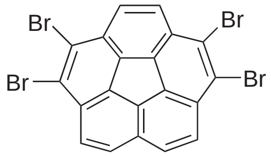
The synthesis of buckybowls, i.e. bowl-shaped, polycyclic aromatic hydrocarbons with carbon networks represented on the surface of fullerenes, has attracted significant attention.[1] The smallest member of the family, corannulene (**1**), was first synthesized by an elaborate 16 step synthesis in the 'pre-fullerene' era by Barth and Lawton.[2] A major breakthrough occurred in 1991 when the Scott group announced a much simpler route to **1** employing flash vacuum pyrolysis (FVP) in the final step.[3]



**1**



**2**



**3**

Since then several buckybowls have been obtained by FVP.[1] However, despite the great success with pyrolytic methods, the need for conventional, condensed phase protocols is critical to the further exploration of these systems since FVP suffers from problems with scale-up, low yields, and relatively non-volatile precursors being required for larger bowls. Only recently have such protocols been developed, mostly utilizing transition metal catalyzed intramolecular coupling of

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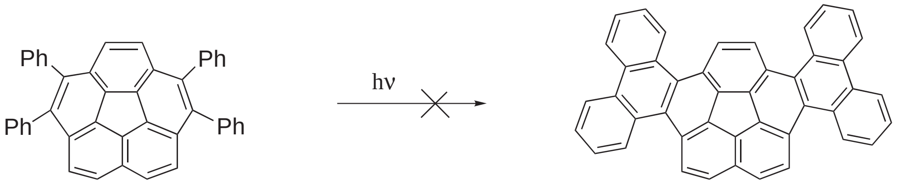
bromides.[4] However, we have just discovered that short reflux of tetrakis(dibromomethyl)-fluoranthene **2** with NaOH in dioxane/water (3:1) produces 1,2,5,6-terabromocorannulene **3** in 83% isolated yield.[5] This simple procedure offers an inexpensive, large scale synthetic route to corannulene and its derivatives. In this communication we report our recent progress in functionalization of the corannulene core utilizing **3** as a synthon. These reactions of 1,2,5,6-terabromocorannulene are depicted in Scheme 1.[6]

**Debromination**. Our original attempts to produce corannulene by the debromination of **3** met with only limited success. Treatment of **3** with *n*-butyl- or methyllithium in THF, followed by quenching with dilute HCl, produces mixtures of corannulene and mono- to tetraalkylated corannulenes even at −78°C.[5] Reduction with LiAlH$_4$ in THF gives a mixture of **3** and di- and tetrahydrocorannulenes. While this latter mixture can be converted to corannulene by DDQ, the combined yield of the two steps is only ca. 30%.[5] However, we subsequently found that refluxing **3** in ethanol for 6 h with an excess of activated zinc powder and potassium iodide produces corannulene in 90% yield.[7] This step, combined with the high yield for the formation of **3** from **2**, makes the present protocol an attractive, low-cost alternative synthesis of corannulene.

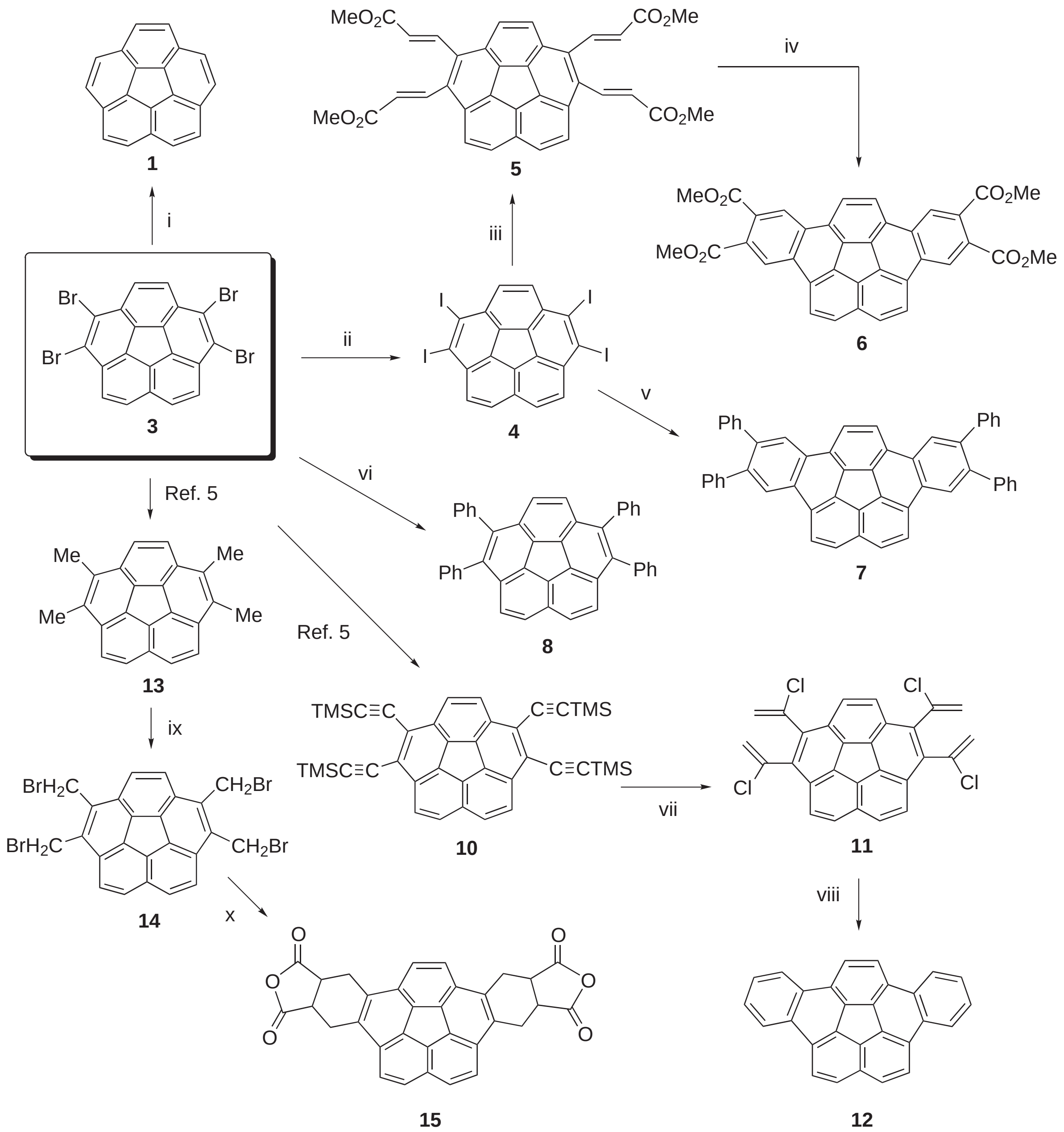
**Halogen exchange and Heck reactions**. The bromine atoms in **3** are replaced with iodine in good yield by 18 h reflux with an excess of KI in DMF. The resulting tetraiodocorannulene **4** undergoes condensation with methyl acrylate under Heck conditions[8] yielding the tetrakis-methylacrylate **5**; subsequent reflux with DDQ in *o*-xylene affords the tetrakis(methylcarboxy) derivative **6** of the known dibenzo[*a*,*g*]corannulene.[4f] Interestingly, condensation of **4** with styrene under Heck conditions leads to the formation of tetraphenyldibenzocorannulene C$_{52}$H$_{30}$ (**7**) in a single step. Notwithstanding the moderate yields of this reaction (ca. 45%, not optimized), it nonetheless has great potential for the expansion of the corannulene system to produce larger buckybowls.

**Suzuki coupling**. Coupling of **3** with phenylboronic acid was achieved under Suzuki conditions[9a] in the solvent mixture of toluene/ethanol/water (5:5:2) which has been suggested for sterically congested systems.[9b] Tetraphenylcorannulene **8** is formed in good yield (60–70%). The *ortho* orientation of the appended phenyl groups in **8** raised an interesting possibility for further reaction, given the well-known *o*-terphenyl to triphenylene cyclization, possibly affording buckybowl **9**. However, attempts at cyclization either photochemically or by oxidative coupling, have so far been unsuccessful, presumably due to the curvature of the system. We continue to explore other possibilities for cyclization, including pyrolytic methods.



**8** **9**

**Conversion of tetraacetylene**. Compound **3** couples with (TMS)acetylene to give **10** in high yield,[5] and further treatment with HCl in acetic acid[10] leads to the tetrakis(1-chlorovinyl) derivative **11**. We were interested in the latter due to the possibility of generating five-membered rings via flash vacuum pyrolysis. However, FVP of **11** at 1025°C led only to dibenzo[*a*,*g*]corannulene **12**.[4f]



Scheme 1. *Reagents and conditions*: (i) Zn/KI/EtOH, reflux 6 h, 90%. (ii) CuI/KI/DMF, reflux 18 h, 70%. (iii) $CH_2CHCOOMe/P(o\text{-tollyl})_3/Pd(OAc)_2/Bu_4NBr/K_2CO_3/DMF$, 100°C, 48 h, 43%. (iv) DDQ/*o*-xylene, reflux 4 h, 55%. (v) as (iii), styrene instead of $CH_2CHCOOMe$, 43%. (vi) $PhB(OH)_2/Pd(PPh_3)_4/PhMe/EtOH/water/Na_2CO_3$, reflux 24 h, 66%. (vii) AcOH/HCl, 80°C, 3 h, 30%. (viii) FVP, $N_2$ (1 torr), 1025°C, ca. 5%. (ix) NBS, dibenzoyl peroxide/$CCl_4$, h$\gamma$, reflux 4 h, 70%. (x) Maleic anhydride/KI/18-crown-6/toluene, reflux 24 h, 23%

**Conversion of tetramethylcorannulene**. Compound **13** is converted to **14** by bromination with NBS. Subsequent treatment of **14** with KI in the presence of excess maleic anhydride leads to the formation of the bis-anhydride **15**, presumably through the intermediacy of a reactive quinoid species. While proton and carbon NMR suggest **15** to be a single isomer, its stereochemistry could not be determined from these spectra.

In summary, the range and scope of corannulene chemistry has now been extended so that this novel aromatic hydrocarbon can be employed as the starting point for new and interesting bowl-shaped systems.

## Acknowledgements

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