Pergamon

Tetrahedron 57 (2001) 3637–3644

TETRAHEDRON

'Buckybowls'—introducing curvature by solution phase synthesis

Andrzej Sygula,* Guopin Xu, Zbigniew Marcinow and Peter W. Rabideau*

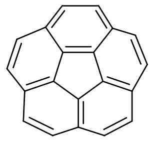
Department of Chemistry and Ames Laboratory, Iowa State University, Ames, IA 50011, USA

Received 30 September 2000; accepted 22 November 2000

Abstract—New, non-pyrolytic methods are presented for the synthesis of curved-surface, polynuclear aromatic hydrocarbons related to the fullerenes. Tetrabromocorannulene is conveniently prepared on a large scale and then converted to corannulene, and also used as a synthon for further elaboration. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

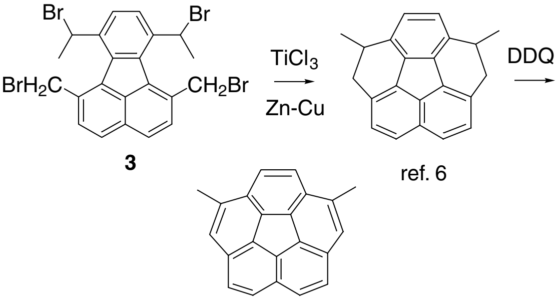
'Buckybowls' are curved-surface, polynuclear aromatic hydrocarbons with carbon frameworks that can be identified on the buckminsterfullerene (C_{60}) surface.[1] The simplest member of this family is corannulene (**1**), a $C_{20}H_{10}$ hydrocarbon representing the polar cap of C_{60}. This novel aromatic hydrocarbon was first synthesized in 1966 by Barth and Lawton in a formidable, 16-step process.[2] However, this potential new field of aromatic hydrocarbon chemistry essentially laid dormant for many years since attempts to improve the synthesis of **1** employing fluoranthene derivatives[3a,b] or naphthalenocyclophanes[3c,d] as precursors met with failure. The lack of success was attributed to the challenging task of forming the strained corannulene core from less strained or strain-free precursors. This all changed with the more recent innovations from the Scott[4] and Siegel[5] groups in 1991 and 1992, respectively, where flash vacuum pyrolysis (FVP) methods were employed for the curvature producing step. The success of the FVP method was attributed to the high temperatures employed (ca. 1100°C) as well as to the separation of the molecules in the gas phase preventing oligo- and polymerization of the precursors.



1

FVP emerged as the primary route to buckybowls, and several novel systems were produced by application of this technique.[1] However, investigations of the chemistry of these novel polycyclic aromatic hydrocarbons, as well as their use as starting materials in the synthesis of larger bowls or perhaps even buckminsterfullerene itself, are impractical by this route. The yield of buckybowls produced by FVP, especially larger systems, is often in the range of 1–5%, and this vacuum technique does not easily allow for scale-up. Moreover, higher molecular weight FVP precursors are not easily introduced into the hot tube due to volatility problems and many react thermally to afford polymers prior to vaporization. And, of course, functional groups are more or less prohibited with FVP, even if the other problems could be overcome.

As a consequence, it became clear that practical, non-pyrolytic methods would be necessary for the full development of this new field, and efforts toward this goal produced some promising results. In a groundbreaking report, the Siegel group described a non-pyrolytic route to 2,5-dimethylcorannulene **2** via reductive low-valent titanium coupling of 1,6-bis(bromomethyl)-7,10-bis(1-bromoethyl)-fluoranthene **3** followed by dehydrogenation of the dimethyltetrahydrocorannulene intermediate.[6] Despite a modest yield of 18% for the two combined steps, this work demonstrated the potential for reasonable, non-pyrolytic routes to buckybowls. It was subsequently discovered that dibromomethyl substituents are considerably more effective than bromomethyl groups, and the

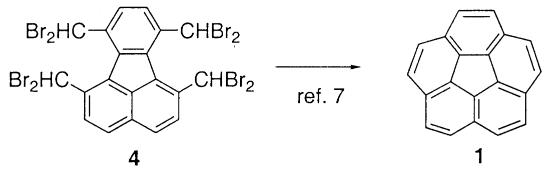


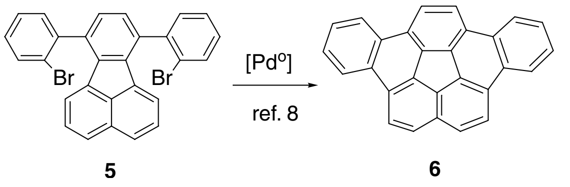
2

Keywords: bowl-shaped aromatic hydrocarbons; buckybowls; strained rings.

* Corresponding authors. Tel.: +515-294-3220; fax: +515-294-1303; e-mail: rabideau@iastate.edu

0040–4020/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(01)00251-4





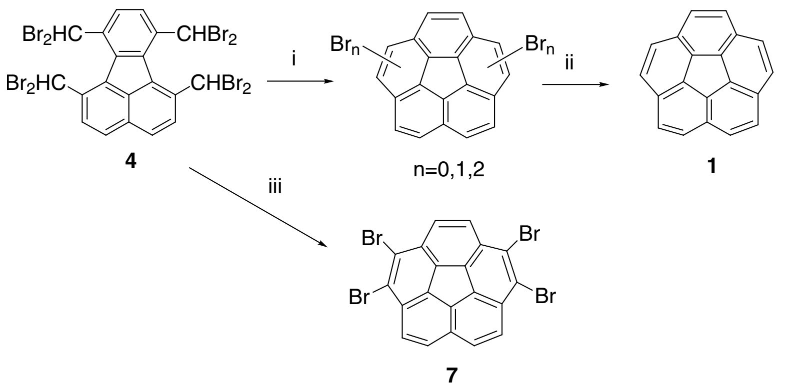
yield of corannulene in the coupling step from **4** was pushed to 70–80%.[7] In another recent approach, intramolecular palladium-catalyzed arylation was employed with 7,10-di(2-bromophenyl)fluoranthene (**5**) to produce dibenzo-[a,g]corannulene (**6**) in good yield.[8]

Herein, we describe an even simpler coupling process that is quick, inexpensive, and easy to scale-up.[9] As a result, the corannulene system is now readily available and, as we demonstrate, can serve as starting material for the synthesis of additional novel, bowl-shaped systems.

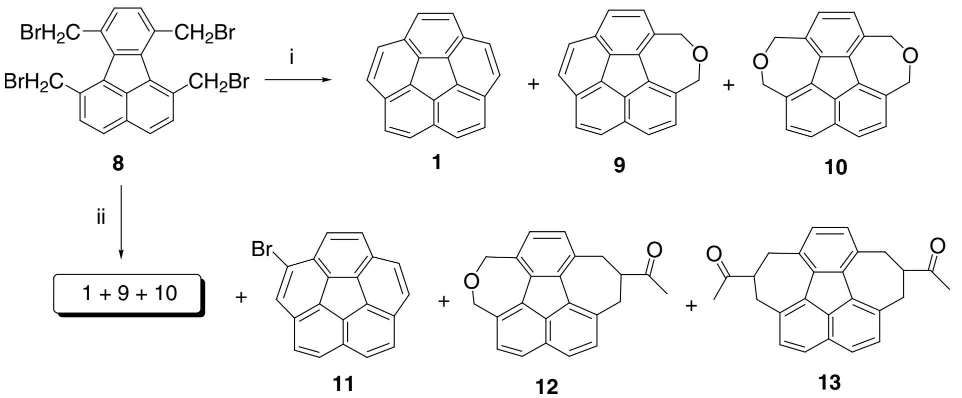
2. Results and discussion

Serendipity rules! Our continuing investigations into alternative, non-pyrolytic methods for corannulene formation led us to attempt the hydrolysis of octabromide **4** so as to generate the tetraaldehyde as a precursor for carbonyl coupling. However, reflux of **4** in acetone/water with sodium carbonate did not produce any aldehyde, but rather a mixture of products with an ^{1}H NMR spectrum exhibiting multiple signals in the range of 7.1–8.1 ppm suggesting only the presence of aryl protons. GC/MS analysis of the mixture showed dibromocorannulene with some tribromocoranulene as well as traces of monobromocorannulene! (Scheme 1). Without attempting separation of the mixture, we treated it with *n*-butyllithium in THF at −78°C and then quenched the reaction at that temperature with dilute HCl. This simple procedure yielded corannulene in 50–55% for the two steps combined. The only by-products identified were traces of *n*-butylcorannulene and ca. 5% of a hydrocarbon with a *m/e* ratio of 498, tentatively assigned as a corannulene dimer.

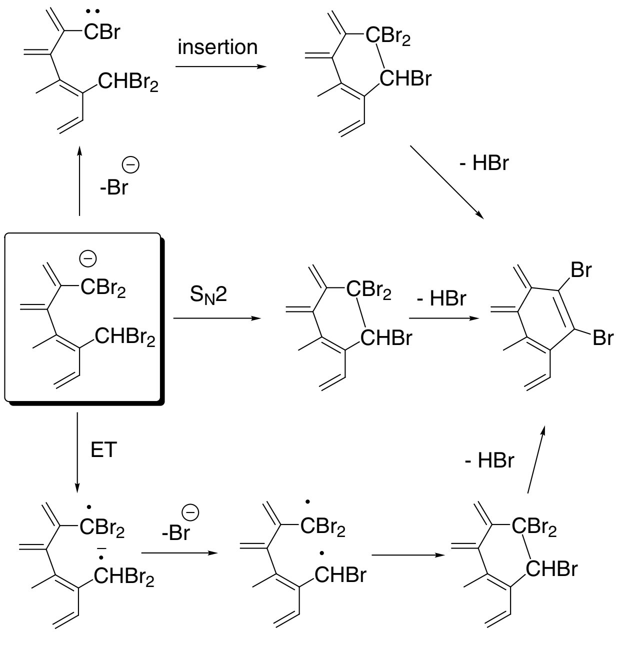
Replacement of sodium carbonate with sodium hydroxide accelerated the coupling considerably, but did not otherwise change the outcome or yield of the reaction. However, when the acetone/water solvent system was replaced by dioxane/water, a brief 15 min reflux of **4** with sodium hydroxide led to clean formation of a single product identified as 1,2,5,6-tetrabromocorannulene (**7**) in an impressive 83% isolated yield.



Scheme 1. *Reagents and conditions*: (i) acetone/water (3:1), NaOH, reflux, 1 h. (ii) *n*-BuLi, THF, −78°C min; then quench (dil. HCl), 50–55% combined yield of the two steps. (iii) dioxane/water (ca. 3:1), NaOH, reflux 15 min, 83%.



Scheme 2. *Conditions*: (i) dioxane/water (3:1), NaOH, reflux1 h. (ii) acetone/water (3:1), NaOH, reflux 1 h.



Scheme 3. Schematic representation of possible pathways from the carbanion to the new carbon–carbon bond formation.

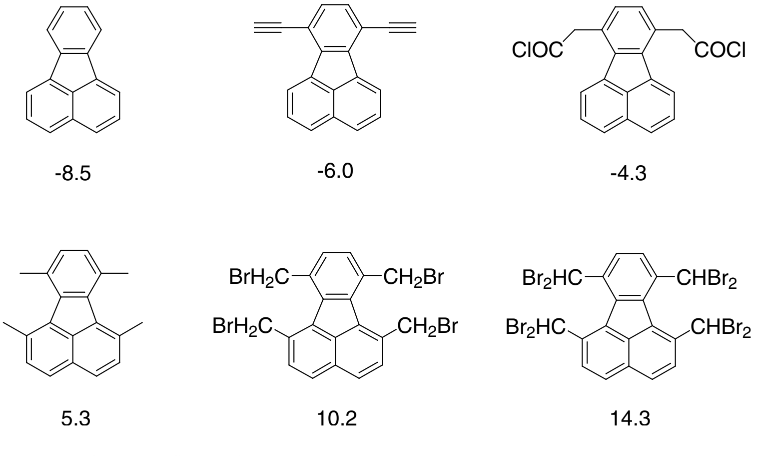
The major synthetic advantage of this transformation is its simplicity and low cost. The previously described, non-pyrolytic synthesis of corannulene from **4** was achieved by low-valent titanium or vanadium coupling.[7] This protocol, although reported to produce the parent **1** in similar yields to the present method, requires strictly anhydrous and oxygen-free conditions, as well as high-dilution techniques; i.e. slow addition of the precursor solution, typically over a period of 2 days. The present route avoids these requirements involving only brief reflux of **4** in aqueous solvent with sodium hydroxide followed by crystallization from xylenes. Moreover, the coupling in dioxane/water provides tetrabromocorannulene, an attractive starting material for further elaboration of the corannulene core.

2.1. Mechanistic considerations

To gain insight into the mechanism, we investigated the behavior of tetrakis(bromomethyl)fluoranthene **8** under similar conditions (Scheme 2). Thus brief reflux of **8** in dioxane/water (3:1) with NaOH gave a mixture of products that were identified by GC/MS and NMR as corannulene (**1**) and the cyclic ethers **9** and **10**. Apparently the latter two products result from competing hydrolysis of one of the bromomethyl groups to hydroxymethyl which subsequently substitutes the bromine atom of the neighboring bromomethyl resulting in ether formation. Reflux of **8** in acetone/water mixture with NaOH produced an even more complicated mixture of products including **1**, **9** and **10**, along with bromocorannulene (**11**), and two products resulting from the reaction of the intermediates with acetone tentatively assigned as **12** and **13**.

The different behavior of **4**, as compared to the bromomethyl analog **8**, is likely due to competition between proton abstraction and nucleophilic substitution. Deprotonation is dominant for **4** since the hydrogen atom in ArCHBr$_2$ is more acidic than ArCH$_2$Br, and hydrolysis—shown to proceed by an S$_N$1 mechanism[10]—is much slower. With **8**, on the other hand, deprotonation is slower due to the decreased acidity, and hydrolysis—expected to proceed by S$_N$2 in this case[10]—becomes competitive. Hence the plethora of products with this latter system.

The exact mechanism of the transformation of **4** to bromocorannulenes is open to speculation. The first step is certainly deprotonation of ArCHBr$_2$ since prolonged reflux of **4** in dioxane/water without base, or in presence of dilute hydrochloric acid, renders unchanged starting material. However, while the coupling of benzyl halides and related compounds by strong base is well documented in the literature (beginning with the pioneering work by Kharasch[11]) the mechanism of these transformations is a matter of controversy.[12] Usually these reactions were performed under strictly anhydrous conditions in aprotic solvents to avoid competing solvolysis reactions, and they were mostly limited to intermolecular coupling of benzyl halides and related compounds. The potential of this process for ring formation through intramolecular carbenoid coupling was only recently recognized and applied to the synthesis of [5]-helicene.[12k] Several mechanistic schemes were proposed for the carbon–carbon bond forming step including nucleophilic substitution, carbene formation by α-elimination of HX, and the intermediacy of radicals originating by electron transfer from the carbanion formed in the first step. These possible pathways are presented in Scheme 3.



Scheme 4. MM2 steric energies (kcal/mol) for some fluoranthenes.

Of course we are not able to distinguish between possible mechanisms based on product outcome since all three paths lead to the same product, 1,2,5,6-tetrabromocorannulene (**7**), which is the result in dioxane/water. However, other mechanisms are likely to be responsible for the different product distribution in acetone/water (Scheme 1) since prolonged reflux of **7** in acetone/water with NaOH affords unchanged starting material which proves that **7** is not an intermediate in this solvent system.

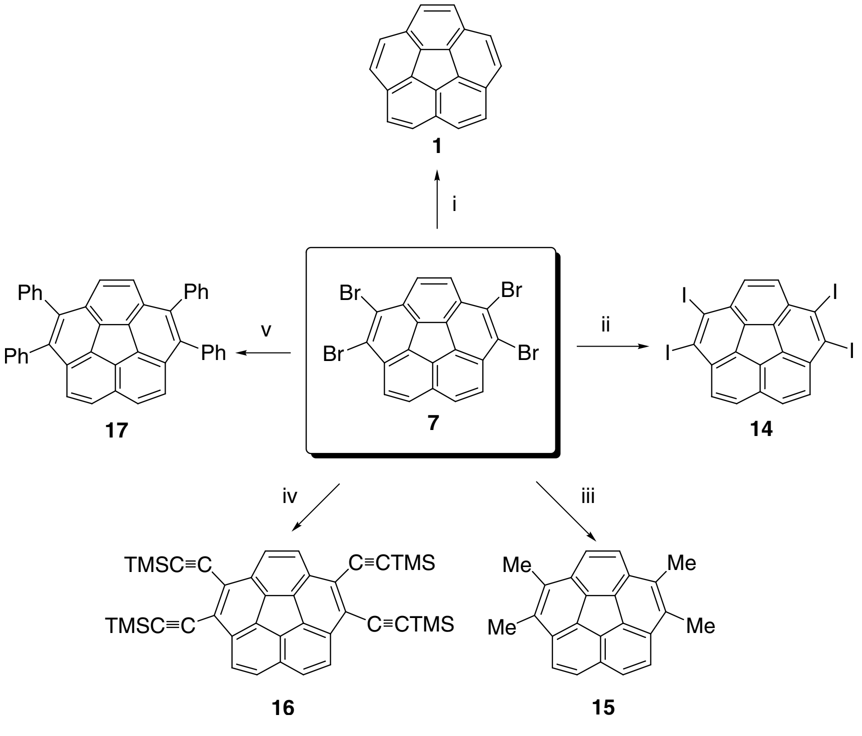
Perhaps a more interesting question lies with the fact that corannulenes can be efficiently produced by the coupling of halogenated methyl groups while other 'classical' ring closure methods using substituted fluoranthenes fail.[3a,b] While this seemed somewhat less surprising with McMurry coupling,[6,7] since this highly exothermic low-valent titanium method is known to perform well in the formation of strained rings,[13] the high yield of **7** from **4** in the presence of water as a co-solvent is quite remarkable. We believe the answer lies in the nature of the precursor rather than in the efficiency of the method. MM2 steric energies[14] are presented in Scheme 4 for some of the systems in question. The MM2 steric energy of fluoranthene is calculated to be −8.5 kcal/mol while the same method predicts 10.3 kcal/mol for corannulene. Disubstitution of fluoranthene at C7 and C10 leading to diethynyl (the precursor for pyrolytic formation of corannulene) or the bis-acetyl chloride (precursor for Friedel-Crafts type reactions) produces only modest changes in steric energy. On the other hand, 1,6,7,10-tetramethylfluoranthene exhibits steric energy exceeding the parent system by ca. 14 kcal/mol, and X-ray crystallography shows significant twisting of the fluoranthene core as a result of steric congestion of the methyl groups.[15] Of course bromination of the methyl groups causes even greater steric interactions making these systems good precursors to corannulenes due to the release of steric overcrowding.

If the efficient conversion of **4**–**7** is steric driven, other examples of dibromomethyl coupling in this system should be observable. Indeed, we found this to be the case for two other methods. Heating of **4** in DMF with sodium iodide[16] leads to a mixture of bromocorannulenes which can be converted to corannulene in ca. 40% unoptimized yield.[17] Also, heating **4** overnight in DMF with nickel powder[18] gives the same result with the yield of corannulene as ca. 75% for the two steps.

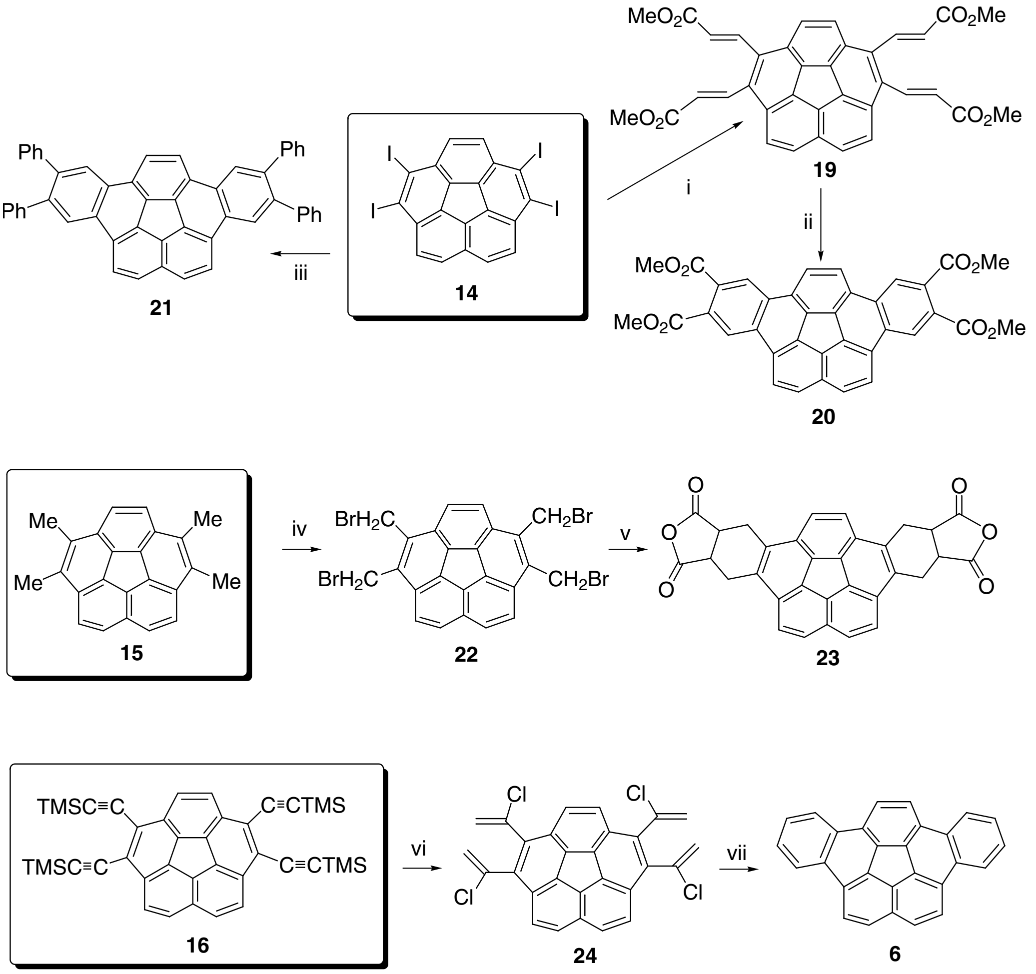
2.2. Derivatization of 1,2,5,6-tetrabromocorannulene

Having an easy and relatively low cost method for the synthesis of tetrabromocorannulene **7**, we were interested in its use as a synthon for further elaboration. Schemes 5 and 6 summarize the results.[19]

Debromination. Debromination of the mixture of bromocorannulenes obtained by carbenoid coupling of **4** in acetone/water/NaOH was achieved by low temperature metalation with *n*-BuLi in THF followed by careful quench with dilute HCl. However, this protocol failed with **7** since it produced large portions of butyl- and dibutylcorannulenes. Poor results were also obtained with methyllithium and with lithium aluminum hydride in refluxing THF which gave corannulene along with some di- and tetrahydrocorannulenes. Ultimately, we found a convenient and inexpensive method: reflux for 6 h in 95% ethanol with an excess of potassium iodide and activated zinc powder[20] to afford **1** in 90% isolated yield. Thus this inexpensive bromine



Scheme 5. Substitution reactions of **11**. *Reagents and conditions*: (i) Zn, KI, EtOH, reflux 6 h, 90%. (ii) CuI, KI, DMF, reflux 18 h, 70%. (iii) $AlMe_3$, $NiCl_2(dppp)$, DME, reflux 12 h, 76%. (iv) (TMS)acetylene, $Pd(PPh_3)_2Cl_2$, CuI, $N(Et)_3$, reflux 3 h, 86%. (v) $PhB(OH)_2$, $Pd(PPh_3)_4$, PhMe/EtOH/water, Na_2CO_3, reflux 24 h, 66%.



Scheme 6. *Reagents and conditions*: (i) $CH_2CHCOOMe$, P(*o*-tollyl)$_3$, Pd(OAc)$_2$, Bu_4NBr, K_2CO_3, DMF, 100°, 48 h, 43%. (ii) DDQ, *o*-xylene, reflux 4 h, 55%. (iii) as in (i), except styrene instead of $CH_2CHCOOMe$, 43%. (iv) NBS, dibenzoyl peroxide, CCl_4, hγ, reflux 4 h, 70%. (v) maleic anhydride, KI, 18-crown-6, toluene, reflux 24 h, 23%. (iv) AcOH/HCl, 80°, 3 h, 30%. (vii) FVP, N_2 (1 Torr), 1025°, ca. 5%.

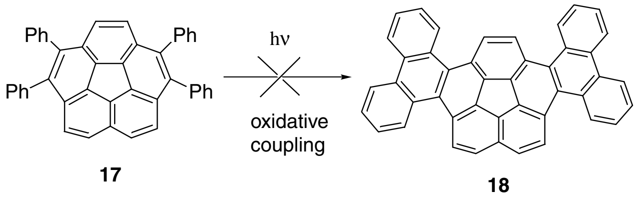
removal, when combined with the easy coupling step, offers a convenient, large-scale synthesis of **1** from **4** with a combined yield of 75% for the two steps.

Halogen exchange.[21] The four bromine atoms in **7** are replaced in good yield by iodine with 18 h reflux in DMF containing CuI and KI. The resulting tetraiodocorannulene (**14**) served as a better substrate than **7** for the Heck reaction (see below).

Methylation. Treatment of **7** with trimethylaluminum in DME with $NiCl_2$(dppp) produced 1,2,5,6-tetramethylcorannulene **15** in 76% yield. This compound was previously synthesized by McMurry coupling of 1,6,7,10-tetrakis(1-bromoethyl)fluoranthene, followed by DDQ dehydrogenation, in a low yield of 6%.[7d]

Ethynylation.[22] Similarly, 3 h reflux of **7** with trimethylsilylacetylene in triethylamine containing Pd(PPh$_3$)$_2$Cl$_2$ and CuI gave an excellent yield of the tetrakis(TMS-ethynyl) derivative **16**.

Suzuki coupling.[23a] The palladium catalyzed coupling of **7** with phenylboronic acid in toluene/ethanol/water (5:5:2), a solvent mixture that works well for sterically congested systems,[23b] provided 1,2,5,6-tetraphenylcorannulene (**17**) in 60–70% yield. The availability of **17** led us to attempt the well known *o*-terphenyl to triphenylene cyclization that would produce the novel $C_{44}H_{22}$ buckybowl (**18**). However, cyclization could not be achieved either photochemically, or by oxidative coupling, perhaps due to the curvature of **17**.



Heck reaction.[24] Palladium-catalyzed coupling of olefins to vicinal dibromoalkenes, followed by cyclization-dehydrogenation of the resulting trienes, was developed as a method for the formation of new benzene rings.[25] Application to **14** by coupling with methyl acrylate provided tetrakis-[(methoxycarbonyl)ethenyl]corannulene **19** in 45% yield (Scheme 6). Reflux of the latter in *o*-xylene with DDQ converted **19** into the tetrakis(methylcarboxy) derivative of dibenzo[a,g]corannulene (**20**). Under the same conditions, Heck coupling of **14** with styrene yielded tetraphenyldibenzo[a,g]corannulene (**21**) in one step with cyclization/dehydrogenation occurring spontaneously in this system.

From 1,2,5,6-tetramethylcorannulene. Bromination of **15** with NBS produced tetrakis(bromomethyl) derivative **22** in good yield. The *ortho* boromomethyl groups offered potential for the formation of reactive quinoid species,[26] and indeed reflux of **22** with potassium iodide and maleic anhydride in toluene produced adduct **23** in modest yield.

*From tetraacetylene (**16**)*. **16** was conveniently converted to tetrakis(1-chlorovinyl)-corannulene **24** by HCl addition in AcOH.[27] This system is of interest due to the possibility of generating additional five-membered rings on the rim of corannulene via FVP. However, the only identified product from the FVP of **24** was dibenzo[a,g]corannulene (**6**), previously synthesized by a non-pyrolytic method.[8]

3. Conclusions

The convenient, large scale synthesis of tetrabromocorannulene, and its easy conversion to corannulene itself, is expected to serve as a major step toward the further development of these novel systems. It is now possible to initiate multistep syntheses with curved-surface aromatics as reasonable starting materials.

4. Experimental

4.1. General

1,6,7,10-tetrakis(dibromomethyl)fluoranthene **4**[7c,d] and 1,6,7,10-tetrakis(bromomethyl)-fluoranthene **8**[15] were obtained by previously published methods.

4.1.1. Coupling in acetone–water. 0.6 g of sodium hydroxide pellets were added to a suspension of 1.26 g of octabromide **4** in a mixture of 120 ml of acetone and 40 ml water. The resulting mixture was refluxed for 30 min. Acetone was removed under reduced pressure, water and HCl were added, and the precipitate was filtered off and dried (magnesium sulfate). An excess of *n*-butyllithium (3 ml of 2 M solution in hexanes) was added to a solution of the above mixture in 60 ml of dry THF at −78°C. The reaction mixture was stirred for 20 min at this temperature and then carefully quenched with dilute HCl. THF was evaporated under reduced pressure, water was added, and the organic products extracted with DCM. The organic layer was dried (magnesium sulfate) and evaporated, giving 310 mg of the crude product which was chromatographed (silica gel, cyclohexane). The first fraction collected gave 187 mg of corannulene (53% of the two steps combined).

4.1.2. 1,2,5,6-Tetrabromocorannulene (7). 3 g of sodium hydroxide pellets were added to a stirred suspension of 6.5 g of octabromide **4** in 250 ml of dioxane and 100 ml of water. The reaction mixture was refluxed for 15 min (the originally formed red color faded during that time), then cooled, poured into water and acidified with HCl. The yellow precipitate was filtered and dried. Crystallization of the resulting solid from xylenes with activated charcoal gave 3.42 g of **7** (83%), mp 338–340°C (dec), as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 2H), 7.95 (d, J=8.9 Hz, 2H), 7.85 (d, J=8.9 Hz, 2H). ^{13}C NMR was not obtained due to poor solubility of **3** in common deuterated solvents. MS (EI, 70 eV) *m*/*z*, (rel. intensity >10%) 569 (13), 568 (33), 567 (36), 566 (55), 565 (47), 564 (42), 563 (40), 562 (15), 560 (19), 407 (11), 406 (14), 405 (23), 403 (14), 283 (16), 281 (17), 250(23), 246 (100), 244 (13), 203 (15), 202 (10), 162 (19), 123 (72). HRMS (EI, 70 eV) calcd for $C_{20}H_6Br_4$ (M^+) 565.7162, found 565.7165.

4.1.3. Corannulene (1). 5 ml of 4% aq. HCl was added to a suspension of 500 mg **7**, 6 g zinc powder, and 2.15 g KI in 100 ml of ethanol, and the reaction mixture was refluxed for 6 h. After removal of ethanol the product was extracted with DCM, washed with water, and filtered through a pad of silica gel. Removal of the solvent gave 202 mg (91%) of pure corannulene.

4.1.4. 1,2,5,6-Tetraiodocorannulene (14). 150 mg of **7** (0.27 mmol) was refluxed under argon for 18 h with 2.64 g of KI (6.02 mmol) and 1.01 g of CuI (5.3 mmol) in 25 ml of DMF. The reaction mixture was cooled, poured into water, and the dark precipitate was filtered off, washed with sodium thiosulfate solution, and dried (magnesium sulfate). The residue was then refluxed with 30 ml of toluene to remove soluble impurities, cooled, filtered, and dried (magnesium sulfate) to give 145 mg of a gray-yellow, very insoluble solid (72%), mp 319–321°C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J=9.0 Hz, 2H), 7.79 (s, 2H), 7.76 (d, J=9.0 Hz, 2H). Due to poor solubility, the product was not characterized by ^{13}C NMR. HRMS (EI, 70 eV) calcd for $C_{20}H_6I_4$ (M^+) 753.6649, found 753.6663.

4.1.5. 1,2,5,6-Tetramethylcorannulene (15). 6.4 ml of a 2 M solution of trimethylaluminum in ethyl ether was added dropwise under nitrogen atmosphere to a stirred and refluxing mixture of 800 mg (1.41 mmol) of **7** and 120 mg of [1,3-bis(diphenylphosphino)propane]-dichloronickel(II) in 200 ml of dry DME. After 12 h reflux, the reaction mixture was quenched with methanol followed by dilute hydrochloric acid. Benzene was added and the organic layer was separated, washed with water, dried (magnesium sulfate) and the solvents removed under reduced pressure. The resulting solid was filtered through a pad of silica gel with cyclohexane/toluene (ca. 2:1) giving 328 mg (76%) **15** (yellow solid) with spectra identical to the literature reported data.[7d]

4.1.6. 1,2,5,6-Tetrakis(trimethylsilylethynyl)corannulene (16). 200 mg (0.35 mmol) of **7** was refluxed under nitrogen for 3 h with 200 mg of trimethylsilylacetylene, 50 mg of $(PPh_3)_2PdCl_2$ and 5 mg of CuI in 30 ml of triethylamine. The solvent was then removed under reduced pressure and the crude material was chromatographed on silica gel with cyclohexane/toluene (ca. 3:1), yielding 193 mg (86%) of **16** as a yellow solid (from ethanol/benzene), changes color above 240°C; mp 277–280°C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ (strongly dependent on the concentration of the sample) 7.96 (s, 2H), 7.92 (d, J=8.8 Hz, 2H), 7.77 (d, J=8.8 Hz, 2H), 0.355 (s, 18H), 0.35 (s, 18H). ^{13}C NMR (75.44 MHz, $CDCl_3$) δ, 134.88, 134.57, 133.83, 131.57, 131.15, 130.57, 127.94, 126.52, 126.91, 125.36, 125.08, 104.79, 104.64, 101.84, 101.71, 0.45. MS (EI, 70 eV) *m/z*, (rel. intensity) 636 (18), 635 (40), 634 (100), 633 (71), 630 (10), 618 (22), 531 (21). HRMS (EI, 70 eV) calcd for $C_{40}H_{42}Si_4$ (M^+) 634.2364, found 634.2375.

4.1.7. 1,2,5,6-Tetraphenylcorannulene (17). 600 mg (1.06 mmol) **7**, 670 mg (5.3 mmol) phenylboronic acid, 42 mg (0.035 mmol) $Pd(PPh_3)_4$ and 1.66 g of Na_2CO_3 were refluxed for 24 h in a solvent mixture of toluene (50 ml), ethanol (50 ml) and water (20 ml). The solvents were removed under reduced pressure and the solid residue was treated with water, extracted with DCM, and the extracts dried (magnesium sulfate) and evaporated. The resulting crude material was crystallized from *n*-butanol/toluene to give 388 mg of **17** (66%), mp 311–312°C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J=8.8 Hz, 2H), 7.61 (d, J=8.8 Hz, 2H), 7.58 (s, 2H), 7.24–7.30 (m, 20H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.16, 138.86, 138.62, 138.57, 135.47, 135.23, 134.24, 131.72, 131.71, 130.79, 130.59, 130.21, 127.79, 127.77, 127.47, 127.40, 126.89, 126.85. HRMS (EI, 70 eV) calcd for $C_{44}H_{26}$ (M^+) 554.2035, found 554.2040.

4.1.8. 1,2,5,6-Tetrakis(2-methoxycarbonylethenyl)corannulene (19). Methyl acrylate (820 mg, 9.56 mmol) was added under argon to a suspension of **14** (350 mg, 0.46 mmol), palladium(II) acetate (11 mg, 0.05 mmol), tri-*o*-tolylphosphine (29 mg, 0.05 mmol), potassium carbonate (660 mg, 4.6 mmol) and tetrabutylammonium bromide (620 mg, 1.84 mmol) in 10 ml of DMF. The mixture was stirred at 95–100°C for 48 h, cooled to room temperature, diluted with 30 ml of DCM and filtered. The organic layer was washed three times with water, dried (magnesium sulfate) and evaporated. The crude material was purified by chromatography on silica gel with DCM/ethyl acetate (4:1) to give a yellow solid (110 mg, 45%), mp 181–182°C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J=15.9 Hz, 2H), 8.29 (d, J=15.9 Hz, 2H), 8.05 (d, J=8.7 Hz, 2H), 8.04 (s, 2H), 7.88 (d, J=8.7 Hz, 2H), 6.75 (d, J=15.9 Hz, 2H), 6.73 (d, J=15.9 Hz, 2H), 3.92 (s, 12H). ^{13}C NMR (75.4 MHz, CDCl3) δ, 166.78, 140.04, 139.97, 136.89, 135.32, 135.19, 134.65, 134.60, 131.70, 128.80, 128.75, 128.70, 127.89, 127.40, 127.33, 127.16, 52.34. HRMS (EI, 70 eV) calcd for $C_{36}H_{26}O_8$ (M^+) 586.1628, found 586.1638.

4.1.9. 4,5,10,11-Tetrakis(methoxycarbonyl)acenaphtho-[3,2,1,8-*f,g,h,i,j*]picene (20). A mixture of **19** (44 mg, 0.08 mmol) and DDQ (45 mg, 0.2 mmol) was refluxed under argon in 15 ml of dry *o*-xylene for 4 h. The solvent was evaporated and the solid residue was dissolved in DCM and filtered through a short pad of silica gel. Evaporation of the solvent gave 24 mg (55%) of a light brown solid, mp 304–306°C (dec). ^1H NMR (300 MHz, $CDCl_3$) (concentration dependent) δ, 8.73 (s, 4H), 7.93 (d, J=8.7 Hz, 2H), 7.93 (s, 2H), 7.68 (d, J=8.7 Hz, 2H), 4.08 (s, 12H). ^{13}C NMR (75.4 Hz, $CDCl_3$) δ 168.24, 168.21, 135.92, 134.38, 134.22, 134.19, 130.99, 130.15, 130.11, 128.02, 127.62, 127.23, 126.28, 126.20, 124.81, 124.70, 124.56, 53.18. HRMS (EI, 70 eV) calcd for $C_{36}H_{22}O_8$ (M^+) 582.1315, found 582.1322.

4.1.10. 4,5,10,11-Tetraphenylacenaphtho[3,2,1,8-*f,g,h,i,j*]-picene (21). This procedure was identical to the one described above for **19** except that methyl acrylate was replaced with styrene. Chromatography of the crude product (silica gel, DCM) provided 140 mg (45%) of dark solid, mp 238–240°C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 2H), 8.70 (s, 2H), 8.38 (s, 2H), 8.30 (d, J=8.7 Hz, 2H), 8.00 (d, J=8.7 Hz, 2H), 7.31–7.36 (m, 20H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.64, 141.62, 140.10, 140.01, 136.34, 135.19, 134.78, 132.57, 132.51, 130.64, 130.36, 129.10, 129.06, 128.75, 128.59, 128.31, 127.87, 127.38, 127.31, 127.06, 126.92, 124.93, 124.58. HRMS (EI, 70 eV) calcd for $C_{52}H_{30}$ (M^+) 654.2348, found 654.2356.

4.1.11. 1,2,5,6-Tetrakis(bromomethyl)corannulene (22). 110 mg of **15** (0.36 mol) was refluxed and irradiated for 6 h with a sun lamp with 260 mg (1.44 mmol) of NBS and 10 mg of dibenzoyl peroxide in 30 ml of CCl_4. The solvent was removed, the residue taken into DCM, washed well with water, dried (magnesium sulfate) and evaporated. Crystallization from toluene–ethanol provided 153 mg (68%) of **22**, mp 274–276°C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 2H), 8.00 (d, J=8.7 Hz, 2H), 7.89 (d, J=8.7 Hz, 2H), 5.18 (s, 4H), 5.15 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.07, 135.46, 135.45, 135.19, 134.85, 129.77, 129.74, 128.30, 125.40, 125.27, 25.31. HRMS (EI, 70 eV) calcd for $C_{24}H_{14}Br_4$ (M^+) 621.7788, found 621.7799.

4.1.12. Adduct 23. A mixture of **22** (155 mg, 0.25 mmol), maleic anhydride (490 mg, 5 mmol), potassium iodide (270 mg, 1.62 mmol) and dry 18-crown-6 (264 mg, 1 mmol) in 25 mL of dry toluene was refluxed for 20 h. The reaction mixture was washed with aqueous sodium thiosulfate, then water, and dried (magnesium sulfate). The purification of the residue by column chromatography on silica gel with DCM as eluent afforded **23** as a yellow solid (28 mg, 23%). ^1H NMR (300 MHz, CDCl3) δ 7.95 (s, 2H), 7.92 (d, 2H, J=9.0 Hz), 7.84 (d, 2H, J=9.0 Hz), 4.02 (m, 4H), 3.75 (m, 4H), 3.18 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 173.51, 173.42, 134.85, 134.53, 132.84, 132.65, 130.75, 130.40, 129.61, 129.29, 128.06, 124.60, 124.08, 40.92, 25.71, 25.67. MS (EI, 70 eV) *m/z* (rel. intensity) 498 (100), 470 (23), 426 (36), 351 (61), 165 (45). HRMS (EI, 70 eV) calcd for $C_{32}H_{18}O_6$ (M^+) 498.1103, found 498.1112.

4.1.13. 1,2,5,6-Tetrakis(1-chlorovinyl)corannulene (24). 320 mg (0.5 mmol) of **16** was heated to 80°C with stirring in 200 ml of acetic acid and 8 ml of concentrated HCl for 3 h. The reaction mixture was poured onto ice, the dark precipitate filtered, dried (magnesium sulfate) and chromatographed on silica gel with hot cyclohexane to give 70 mg of yellow solid (28%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.99 (d, J=8.9 Hz, 2H), 7.85 (d, J=8.9 Hz, 2H), 5.97–6.0 (m, 4H), 5.58–5.61 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.58, 135.99, 135.94, 135.10, 134.76, 134.47, 131.64, 128.77, 128.64, 128.15, 127.13, 127.05, 120.19, 120.13. HRMS (EI, 70 eV) calcd for $C_{28}H_{14}Cl_4$ (M^+) 491.9820, found 491.9827.

FVP of 24. 100 mg of **24** was pyrolyzed at 1025°C in a flow of nitrogen at 1 Torr. The red deposit (ca. 5 mg) was dissolved in DCM, filtered through a short pad of silica gel and analyzed by GC/MS and ^1H NMR indicating a single product identified as **6**.

Acknowledgements

This work was supported by the Ames Laboratory, which is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

References

1. For the recent reviews see: Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Anselms, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209–219. Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13,325–13,370. Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291–300. Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235–242.
2. Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380–381. Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730–1745.
3. (a) Craig, J. T.; Robinson, M. D. W. *Aust. J. Chem.* **1968**, *21*, 2237. (b) Jacobson, R. H. PhD Dissertation, University of California, Los Angeles, 1986. (c) Davy, J. R.; Iskander, M. N.; Reiss, J. A. *Tetrahedron Lett.* **1978**, 4085–4088. (d) Davy, J. R.; Iskander, M. N.; Reiss, J. A. *Aust. J. Chem.* **1979**, *32*, 1067–1010.
4. Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082–7084. Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920–1921. Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968.
5. Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921–1923.
6. Seiders, T. J.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754–2755.
7. (a) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1998**, *120*, 12666–12667. (b) Seiders, T. J.; Baldridge, K. K.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7439–7440. (c) Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 7800–7803. (d) Seiders, T. J.; Elliott, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804–7813.
8. Reish, H. A.; Bratcher, M. S.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1427–1430.
9. For preliminary results, see: Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **2000**, *122*, 6323–6324.
10. See for example: Salomaa, P. The Chemistry of the Carbonyl Group, Patai, S., Ed.; Wiley/Interscience: New York, 1966; Vol. 1, pp 177–210.
11. Kharasch, M. S.; Nudenberg, W.; Fields, E. K. *J. Am. Chem. Soc.* **1944**, *66*, 1276–1279.
12. (a) Hauser, C. R.; Brasen, W. R.; Skell, P. S.; Kantor, S. W.; Brodhag, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 1653–1658. (b) Ledwith, A.; Shih-Lin, Y. *Chem. Ind. (Lond)* **1964**, 1867–1868. (c) Hoeg, D. F.; Lusk, D. I. *J. Organomet. Chem.* **1996**, *5*, 1–12. (d) Hanna, S. B.; Wideman, L. G. *Chem. Ind. (Lond)* **1968**, 486. (e) Moss, R. A.; Pilkiewicz, F. G. *J. Am. Chem. Soc.* **1974**, *96*, 5632–5633. (f) Chan, K. C.; Goh, S. H.; Teoh, S. E.; Wong, W. H. *Aust. J. Chem.* **1974**, *27*, 421–423. (g) Bethell, D.; Bird, R. J. *Chem. Soc. Perkin Trans. 2* **1977**, 1856–1859. (h) Vernigor, E. M.; Shalaev, V. K.; Luk'yantes, E. A. *J. Org. Chem. USSR* **1981**, *17*, 317–321. (i) Moss, R. A.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3828–3830. (j) Huber, R. S.; Jones, G. B. *Tetrahedron Lett.* **1994**, *35*, 2655–2658. (k) Dubois, F.; Gingras, M. *Tetrahedron Lett.* **1998**, *39*, 5039–5040.
13. McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513–1524.
14. MM2 method, as a part of the CS Chem3D package (Macintosh version 5.0), was used for this study.
15. Borchardt, A.; Hardcastle, K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1993**, *34*, 273–276.
16. Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1956**, *78*, 500.
17. We thank Professor Ben Plummer for suggesting this experiment.
18. Stanger, A.; Ashkenazi, N.; Schachter, A.; Blaser, D.; Stellberg, P.; Boese, R. *J. Org. Chem.* **1996**, *61*, 2549–2552.
19. For preliminary results see: Xu, G.; Sygula, A.; Marcinow, Z.; Rabideau, P. W. *Tetrahedron Lett.* **2001**, *41*, 9931–9934.
20. Frank, R. L.; Hall, Jr., H. K. *J. Org. Chem.* **1950**, *72*, 1645–1648.
21. Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150–3152 (and references therein).
22. Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proc.* **1995**, *27*, 127–160 (and references therein).
23. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Andersen, N. G.; Maddaford, S. P.; Keay, B. A. *J. Org. Chem.* **1996**, *61*, 9556–9559.
24. Heck, R. F. *Org. React.* **1982**, *27*, 345–390.
25. Lansky, A.; Reiser, O.; de Meijere, A. *Synlett* **1990**, *1*, 405–407. Reiser, O.; Konig, B.; Meerholz, K.; Heinze, J.; Wellauer, T.; Gerson, F.; Frim, R.; Rabinovitz, M.; de Meijere, A. *J. Am. Chem. Soc.* **1993**, *115*, 3511–3518.
26. Belik, P.; Gugel, A.; Kraus, A.; Walter, M.; Mullen, K. *J. Org. Chem.* **1995**, *60*, 3307–3310. Nakamura, Y.; O-kawa, K.; Matsumoto, M.; Nishimura, J. *Tetrahedron* **2000**, *56*, 5429–5434.
27. Scott, L. T.; Necula, A. *Tetrahedron Lett.* **1997**, *38*, 1877–1880.