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Formation of the Corannulene Core by Nickel-Mediated Intramolecular Coupling of Benzyl and Benzylidene Bromides: A Versatile Synthesis of Dimethyl 1,2-Corannulene Dicarboxylate

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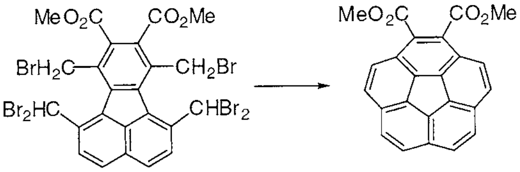
ABSTRACT



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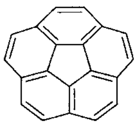
A practical synthesis of dimethyl 1,2-corannulene dicarboxylate (5) is reported, with the final ring-forming step achieved by the double intramolecular nickel powder mediated coupling of benzyl and benzylidene bromide groups with 60% isolated yield.

The synthesis of buckybowls, i.e., bowl-shaped polycyclic aromatic hydrocarbons (PAHs) with molecular networks represented on the surface of buckminsterfullerene (C_{60}), has attracted considerable interest.[1] Corannulene (**1**), the smallest member of the family, was originally synthesized by a laborious, multistep process in 1966.[2] Application of Flash Vacuum Pyrolysis (FVP) by Scott's group in the early 1990s[3] made **1** more accessible and also led to syntheses of several larger buckybowls.[1] Recently Scott, de Meijere, and others reported the formation of minute amounts of C_{60} by FVP of a $C_{60}H_{27}Cl_3$ precursor.[4] Despite its successes, FVP suffers from several disadvantages such as the following: very low yields for larger, nonvolatile systems; technical difficulties of scaling-up; and a lack of functional group tolerance. In 1996 Siegel and co-workers reported the formation of dimethylcorannulene in modest yield via low-valent titanium coupling of terabromide **2** followed by dehydrogenation of the resulting intermediate.[5] Following this report, other "wet chemistry" synthetic protocols have been developed, gener-



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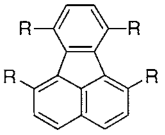
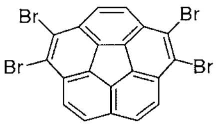


2: R = CH_2Br
3: R = $CHBr_2$



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[1] For the recent reviews see: (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (b) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (c) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (d) 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.

[2] (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380−381. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745.

[3] (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921. (c) 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.

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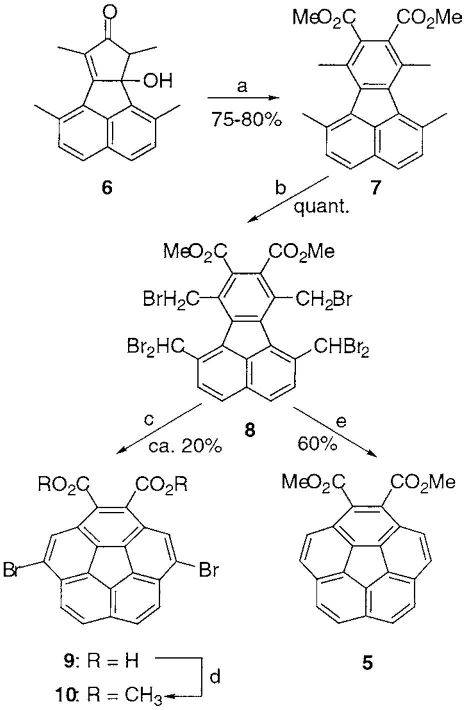
ally based on the transition metal catalyzed intramolecular coupling of aryl, benzyl or benzylidene halides.[6] Very recently we have shown that the formation of a strained curved surface aromatic network can be conveniently achieved by the intramolecular carbenoid coupling of dibromomethyl groups if enough strain is introduced into the precursor.[7] Thus, 1,2,5,6-tetrabromocorannulene **4** has been obtained with an isolated yield of 83% by simply refluxing the brominated precursor **3** in dioxane−water with sodium hydroxide.[7] In the present Letter we report a convenient condensed-phase synthesis of dimethyl 1,2-corannulene dicarboxylate (**5**) in which the final step is achieved in ca. 60% yield by nickel powder mediated intramolecular coupling of $ArCH_2Br$ with $ArCHBr_2$ groups with complete debromination of the product. This protocol provides easy and inexpensive access to 1,2-disubstituted corannulenes since the carbomethoxy groups can be converted to several substituents by standard methods.

Our synthesis, outlined in Scheme 1, starts with known carbinol **6**, easily obtainable on a large scale.[8] In a one-pot process, **6** is dehydrated at room temperature in acetic anhydride with a catalytic amount of sulfuric acid, and subsequently reacted with dimethyl acetylene dicarboxylate to give the previously reported fluoranthene **7**[8] in ca. 75−80% yield.

Bromination of the latter under standard conditions with NBS provides the hexabromide **8** in quantitative yield. Steric congestion of the methyl substituents, and the presence of two carbmethoxy groups at C8 and C9, prevents the dibromination of the proximate methyls at C7 and C10 despite prolonged reaction times and a large excess of NBS.

Brief reflux of **8** under conditions successfully applied in the synthesis of tetrabromocorannulene[7] (NaOH and aqueous dioxane) results in the formation of a sparingly soluble material that is the expected dibromo corannulene dicarboxylic acid **9**. For characterization purposes **9** was esterified to its dimethyl ester **10**.[9] Unfortunately, the yield of the two steps (ca. 20%) is rather disappointing and well below expectations for a practical synthetic route. Thus in the search for an alternative pathway, we turned our attention to the well-known and widely used nickel mediated coupling of RBr, where R is aryl or benzyl.[10] In most cases this method is used for intermolecular couplings although some intramolecular couplings leading to the formation of rings of various sizes have also been reported.[10b,f,h,i] For example, nickel-mediated intramolecular coupling of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene **11** provides 7,8-dibromocyclobutabenzene **12**,[10h] and the same procedure applied by us to the octabromide **3** produces tetrabromocoranulene **4** as a major product.[7c]

Scheme 1



[a] Conditions: (i) acetic anhydride, 1 drop of sulfuric acid, 1 h, rt, (ii) dimethyl acetylene dicarboxylate, 2 h reflux. [b]Carbon tetrachloride, NBS, dibenzoyl peroxide, $h\nu$, 2 h reflux. [c]Dioxane-water (3:1), sodium hydroxide, 30 min reflux. [d](TMS)CHN_2, benzene−methanol (7:2), 30 min, rt. [e]DMF, nickel powder, overnight, 80−90 °C.

In our hands, overnight heating of hexabromide **8** in DMF with commercial nickel powder (100 mesh) resulted in the clean formation of dimethyl 1,2-corannulenedicarboxylate **5**[11] in the respectable yield of ca. 60% (Scheme 1). The formation of two new six-membered rings is accompanied by complete debromination of the product. According to the postulated mechanism for the nickel mediated coupling of benzyl/benzylidene bromides[12] the dibromo tetrahydrocorannulene **13** should be formed under this protocol. It is possible, however, that **13** undergoes a spontaneous double elimination of HBr leading to the observed product **5**, which is stabilized

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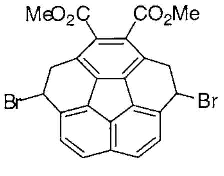
(8) Borchardt, A.; Hardcastle, K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1993**, *34*, 273−276.

(9) Yellow solid (from ethanol), mp 232−234 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ strongly dependent on concentration 4.09 (s, 6H), 7.92 (AB, $\Delta\nu = 16.4$ Hz, $J = 8.5$ Hz, 4H), 8.27 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 53.32, 123.33, 127.31, 127.59, 129.10, 129.21, 130.97, 131.14, 131.22, 134.10, 134.22, 134.37, 166.95. MS *m*/*z* (rel intensity) 527 (25), 526 (43), 525 (91), 524 (63), 523 (100), 522(29), 521 (40), 496 (20), 495 (38), 494 (78), 493 (52), 492 (69), 491 (33), 490 (30), 450 (13), 406 (24), 394 (11). HRMS (EI, 70 eV): calcd for $C_{24}H_{12}O_4Br_2$ 523.90819, found 523.90881.

by aromaticity. This obviously was not the case in the formation of **12**.



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At the moment we are not able to determine if **13** is actually an intermediate in the coupling or if a different mechanism is involved. At any rate we consider the nickel powder mediated intramolecular coupling of $ArCH_2Br$ with $ArCHBr_2$ groups as an attractive, milder alternative to the previously reported base-induced method. To our knowledge this protocol represents the first example of an efficient ring formation through an intramolecular coupling of benzyl and benzylidene bromides. Since the dibromination of sterically congested methyl groups is not possible in many instances, the nickel-mediated method may be of importance for the synthesis of other buckybowls. The protocol is simple and can easily be run on a large scale. In contrast with most of the nickel mediated protocols, our method does not require expensive Ni(0) complexes, nor in situ generated activated nickel powder, but rather utilizes commercially available, inexpensive nickel powder. Also, in view of the possibility of further transformations[13] of the carbmethoxy groups in **5**, this easy and inexpensive synthetic procedure offers an attractive route to some 1,2-disubstituted corannulenes.

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(11) Yellow solid (from ethanol), mp 149−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 4.09 (s, 6H), 7.80 (AB, $\Delta\nu = 13.2$ Hz, $J = 8.7$ Hz, 4H), 7.85 (d, $J = 8.9$ Hz, 2H), 8.07 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 53.11, 126.70, 127.01, 127.34, 128.41, 128.56, 131.16, 131.69, 131.70, 135.06, 135.85, 136.64, 167.85. MS *m*/*z* (rel intensity) 367 (18), 366 (77), 356 (24), 335 (100), 292 (24), 249 (16), 248 (28), 246 (14). HRMS (EI, 70 eV): calcd for $C_{24}H_{14}O_4$ 366.0892, found 366.0898.

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(13) To be published. Preliminary results show that, notwithstanding the unusual curvature of the corannulene moiety, the carboxylate functions appear to behave normally in chemical transformations. Base hydrolysis of **5** ($NaOH/H_2O/EtOH$) leads to the diacid that can be converted to the anhydride with acetic anhydride, or to the imide with urethane. The imide undergoes Hofmann rearrangement with hypohalite to afford the amino acid. The latter compound is being explored as a precursor to the aryne.