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Synthesis of *o*-Indan[1.1.1]cyclophane and Potential Indanyl Subunits of the Fullerenes

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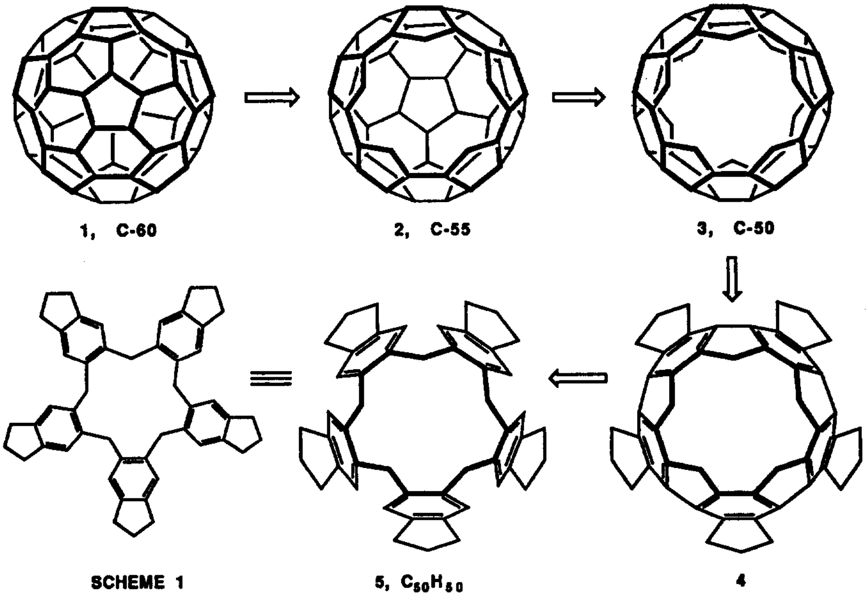
Abstract: Treatment of indane-5-carbinol with aqueous acid gave among other products the cyclic trimer cyclo[3]CH_2-[3]indane **7**, which was also formed from palladium coupling of **17** to **19**.

The recent reports by Lee[1] describing the synthesis of *ortho*-cyclophanes prompt us to describe related studies with indanyl systems and their potential relationship to the fullerenes. While research on C-60 (Buckminsterfullerene) is flourishing, it is currently restricted (by necessity) to the products obtained from the pyrolysis of graphite.[2] A more systematic and broad approach to constructing carbon allotropes is by total synthesis.[3] In particular this should allow access to compounds with an incomplete carbon sphere or ellipsoid. The overall strategy we have decided to pursue is based upon the retrosynthetic analysis in Scheme 1.



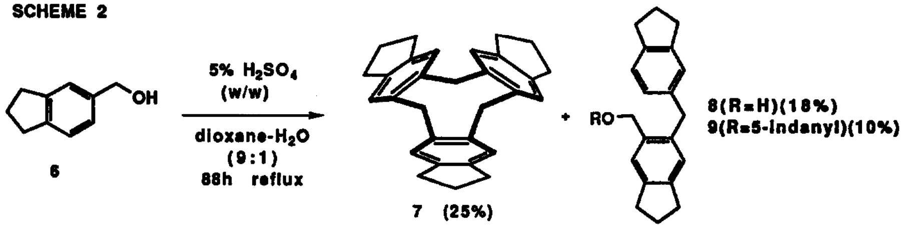
SCHEME 1

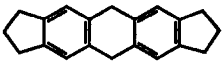
Removal of the central five-membered ring from 1 (C-60) gives 2 (C-55), and the same process leads to 3 (C-50). Breaking the C-C bonds between the consecutive five membered rings gives 4. Finally doing the same again, and of course adding the appropriate hydrogen atoms, gives the cyclo-pentamethylene-pentaindane

5, cyclo[5]CH_2-[5]indane. This is of course equally applicable to C-48 and C-72 which disconnect to four and six indane units respectively.

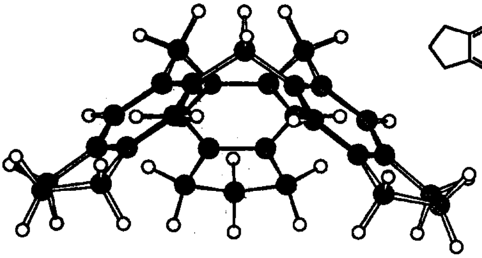
Initially we examined the acid catalyzed oligomerization of indane-5-carbinol **6**.[4] Treatment of **6** with 5% H_2SO_4(w/w)/dioxane-H_2O (9:1)/reflux 88h gave cyclo[3]CH_2-[3]indane **7**, the carbinol **8** and its indanyl ether **9**. We could detect higher molecular weight oligomers (MS) but since they were in such small amounts and as a complex mixture, they were not pursued. While we could obtain crystals of **7**, m.p. >360 °C they were not suitable for single crystal X-ray analysis. The non-equivalence of the bridging methylene hydrogens is shown by their ^{1}H NMR resonances: 3.63 and 4.80 ABq J = 13.4 Hz. MM2 energy minimization suggests that the molecule adopts a cup-like conformation where the nine-membered ring is too rigid to undergo rapid inversion. It is notable that the dimer **10** was not found among the reaction products.

SCHEME 2





10(Not observed)

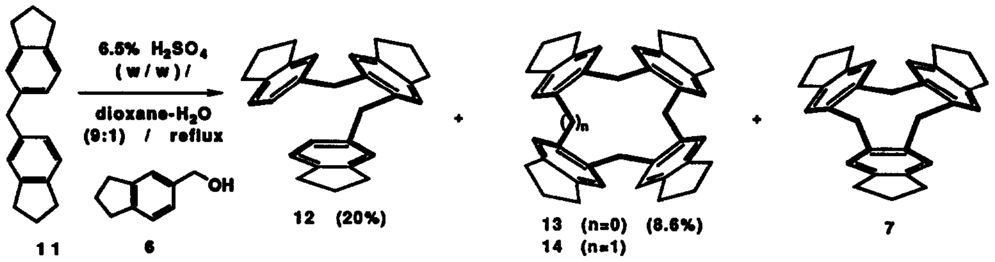


MM2 minimised Chem 3D representation of 7 (side-view) showing the non-equivalent hydrogens on the bridging methylene groups.

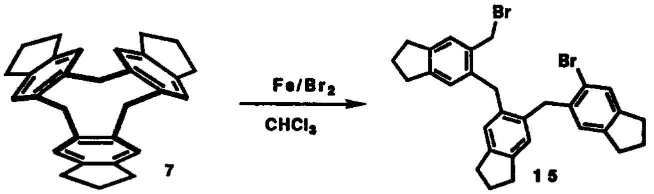
Treatment of 5,5-diindanemethane **11**[5] with **6** in 6.5% H_2SO_4 (w/w)/dioxane-H_2O (9:1)/reflux gave the linear triindanyl **12** (20%), the linear tetraindanyl **13** (8.6%) and the cyclophane **7** (traces). This last compound presumably derives only from **6**. When the linear triindanyl **9** was exposed to paraformaldehyde/H_2SO_4/ dioxane /reflux the cyclophane **7** was isolated in 17% yield. In contrast, exposure of the tetraindanyl **13** to these same conditions gave no isolable amounts of the corresponding cyclo[4]CH_2-[4]indane **14**, but we could detect trace amounts of **7** from the distinctive ^{1}H NMR AB system. The formation of **7** from **13** suggests that *ipso*-substitution is the dominant electrophilic pathway.[6]

This appears to be common to the chemistry of orthocyclophanes since we have found that treatment of cyclo[3]CH_2-[3]indane **7** with Br_2/$CHCl_3$ gave the ring-opened dibromide **15** as the major product.[7]

SCHEME 3

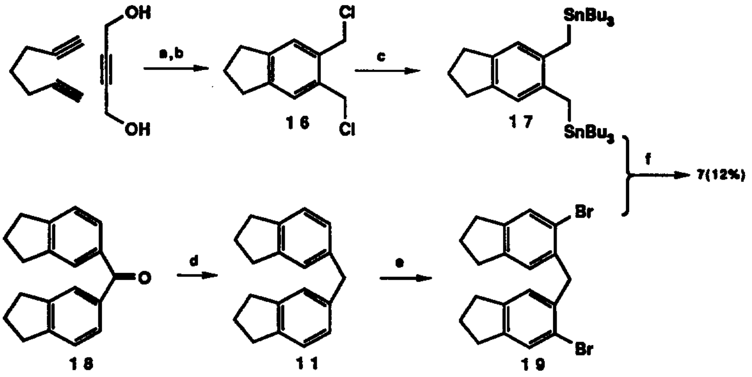


SCHEME 4



In order to avoid electrophilic aromatic substitution conditions we have examined a different strategy to synthesise **7**. Rhodium catalyzed coupling of hept-1,6-diyne and but-2-yn-1,4-diol using a minor modification of the method reported by Grigg[8], followed by treatment with thionylchloride gave **16**. Treatment of **16** with $LiSnBu_3$ gave the bis-stannane **17**.[9] The known ketone **18**[5] was reduced by ionic hydrogenation to **11** and brominated to give **19**.[10] Palladium catalyzed coupling[11] of **17** to **19** in the presence of air gave **7** albeit in low yield.

SCHEME 5



a) $Rh(PPh_3)_3Cl$ (cat), EtOH/reflux, 82%. b) $SOCl_2$, reflux, 85%. c) $LiSnBu_3$/THF/-78°-25°C, 95%. d) Et_3SiH/TFA/25°C, 95%. e) Br_2/SiO_2/0°C, 50%. f) $Pd(PPh_3)_2(CH_2Ph)Cl$ (cat)/HMPA/115°C, sealed tube in the presence of air, 12%.

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