

The Synthesis of a Dicyclopenta[*a,e*]pentalene via a Molybdenum Hexacarbonyl-Mediated Tandem Allenic Pauson–Khand Reaction[†]

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One of the principal goals of organic chemists is to fully understand the bonding character of carbon. This interest has stimulated the synthesis of a number of highly strained molecules in the past. Among these targets, the polyquinenes, dicyclopenta[*a,e*]pentalene **1** and dicyclopenta[*a,f*]pentalene **2** (Figure 1), have not been synthesized and have been discussed only from a computational point of view. Controversy exists as to whether these 14 π parent annulenes are delocalized, exhibit aromatic Hückel-type stability, or exist as nonalternant hydrocarbons that behave as highly reactive olefins.^{2–5} Herein, we wish to report the synthesis of a 3,7-diisopropylsilyl dicyclopenta[*a,e*]pentalene, a 14 π annulene.

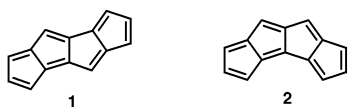
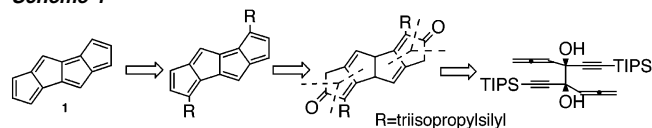


Figure 1. The structures of dicyclopenta[*a,e*]pentalene and dicyclopenta[*a,f*]pentalene.

Hafner et al. reported a 14 π system in this series related to **1**,⁶ however, this annulene was stabilized by four *tert*-butyl groups. Recently, molybdenum hexacarbonyl was reported to effect Pauson–Khand reactions by Jeong.⁷ Importantly, Brummond et al. have disclosed that alkynyl-allenes could be successfully cyclized to form cyclopentanones under these molybdenum-mediated conditions.^{8,9} In a retrosynthetic sense (Scheme 1), it was felt this molybdenum-mediated approach,^{7–10} if successful, would provide cyclopentapentalenes in regiospecific fashion (Scheme 1). Furthermore, the bulky triisopropylsilyl groups would stabilize the pentalene system.

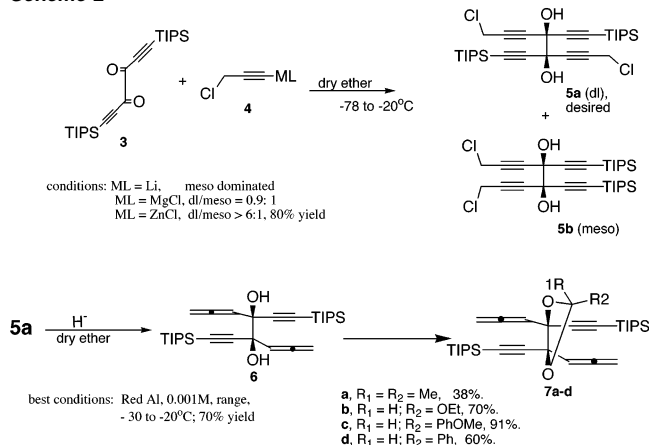
Scheme 1



Initial studies centered on an efficient method to prepare gram quantities of the bisyne-bisallene **6**. Indeed, after a few attempts, the important precursor for the tandem Pauson–Khand reaction was synthesized on gram scale (Scheme 2). The starting dialkynyl-1,2-dione **3** was prepared analogous to a reported procedure¹¹ with minor modifications to provide 30–40 g of material. The alkynilides of the propargyl chloride were generated in situ and then stirred with the dialkynyl-1,2-dione **3** at low temperature to furnish **5a** (dl) and **5b** (meso). As shown in Scheme 2, with respect to stereoselectivity and yield, zinc has proven to be the best choice as the metal counterpart of the alkynilide. In our hands, when zinc was used (formed by treating an ether solution of the lithium salt

with zinc chloride) to stabilize the carbanion, the yield was increased to over 80%, and the desired dl diastereomer **5a** became the major isomer in a ratio of 6:1 (dl:meso). These diastereomers (**5a** and **5b**) were separated by crystallization from hexanes below -30 °C. Red Al was then determined as the best source of hydride to convert the propargyl chlorides to the desired allenes. This is the first time, to our knowledge, that Red Al was successfully employed for this transformation:¹² lithium aluminum hydride¹³ produced complex mixtures with tetrayne **5a**.

Scheme 2



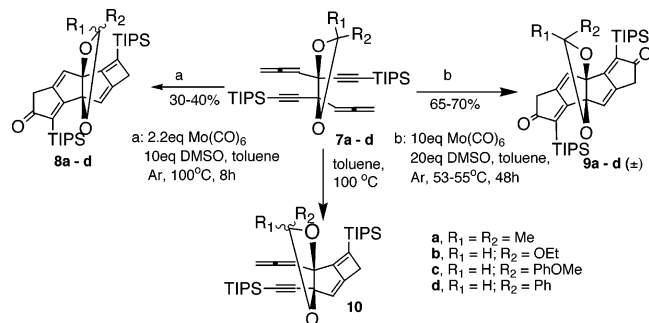
Diyne-diallene **6** was then converted into the acetal **7** (Scheme 2) to protect the hydroxyl groups while constraining the geometry to promote the tandem cyclization.¹⁴ Among the protected diols **7a–7d**, the para-methoxybenzylidene acetal **7c** was formed faster and in higher yield and was chosen to explore the tandem cyclization. When diyne-diallene **7c** was treated under the conditions reported by Jeong⁷ and Brummond⁹ (Scheme 3, condition a), the unexpected [5.5.5.4] tetracyclic systems represented by **8c** were obtained in 30–40% yield. The structure of **8c** was elucidated by single-crystal X-ray analysis of one of the two diastereomers ($R_2 = H$, $R_1 = p\text{-CH}_3\text{OC}_6\text{H}_5$).¹⁵ During preparation of this communication, this phenomenon was reported by Hammond et al. recently,¹⁶ when terminal gem-difluoroallenes were employed as substrates. However, in our hands, we observed the formation of the monocyclized [5.4] system **10¹** by proton NMR spectroscopy when the diyne-diallene **7** was heated in toluene at 100 °C in the absence of molybdenum hexacarbonyl and DMSO. This was not reported by Hammond et al.¹⁶ On the basis of these results, the cyclization was effected in a saturated solution of molybdenum hexacarbonyl/toluene at 53–55 °C (Scheme 3, condition b);¹ the desired [5.5.5.5] ring system **9** was isolated in yields ranging from 65 to 70%. The structure of **9c** was confirmed by X-ray analysis.¹⁵ This represented the regiospecific formation of six carbon–carbon

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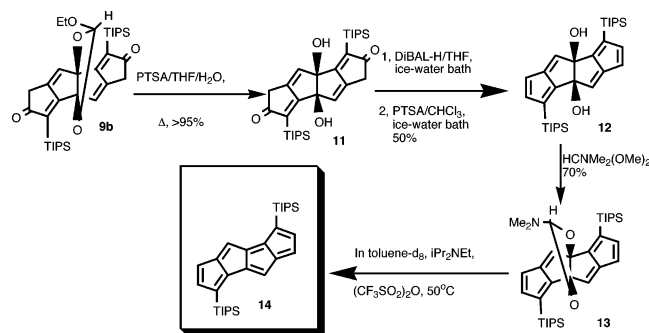
bonds in a one-pot process, where each bond formed occurred in greater than 95% yield. In this fashion, formation of the undesired [5.5.5.4] tetracycle was minimized (5–10%). The key tetracycle **9** was prepared on gram scale via this process.

Scheme 3



With this tetraene **9** in hand, introduction of the additional three units of unsaturation was explored. Attention turned to regeneration of the vicinal diol. Among the protecting groups employed (see Scheme 3, **9a–9d**), the cyclic ortho ester acetal in **9b** could be removed under the mildest conditions. The molybdenum-mediated tandem Pauson–Khand reaction in this system proceeded in 66% yield to provide the [5.5.5.5] tetracycle **9b**. The ortho ester acetal could then successfully be removed under mild conditions (in aqueous THF in the presence of a catalytic amount of PTSA) to generate the diol-diketone **11** in 95% yield. Numerous efforts were attempted to eliminate the vicinal diols at the bridgehead to form the final olefinic bond. Finally, the method reported by Yang et al.¹⁷ was employed successfully in this context. The carbonyl functions in **11** were reduced to the corresponding alcohols, and careful control of the acidity, the temperature, as well as the reaction time of the elimination step provided bisfulvene **12** (Scheme 4) in 50% yield. This material **12** was isolated as a yellow

Scheme 4



solid. The hexaene **12** was unstable and was immediately converted to the aminoketal **13** in 70% yield. Treatment of aminoketal **13** with diisopropyl ethylamine and trifluoromethane sulfonic anhydride in toluene-*d*₈ at 50 °C¹⁷ provided a purple-colored compound of low polarity. This material has been assigned a structure in agreement with the 14π annulene **14** (¹H NMR in C₆D₁₂: δ = 1.17, 1.51 (m & m, 42H), 6.60 (d, *J* = 3.2 Hz, 2H), 7.36 (s, 2H), and

7.73 (d, *J* = 3.2 Hz, 2H); ¹³C NMR δ = 13.1, 19.1, 114.1, 118.9, 122.6, 147.8, 148.3, 158.8, 165.7). To date, **14** has only survived in solution; on removal of the solvent under vacuum, a brownish-colored polymer was generated. The 1,3,5,7-tetra-*tert*-butyl-dicyclopenta[*a,e*]pentalene reported by Hafner et al. was obtained as brownish-violet crystals, and the ring-proton signals appeared at δ = 6.58 and 6.72 (in CDCl₃) in the ¹H NMR spectrum.⁶ In 14π annulene **14**, the ring-proton signals appeared at δ = 6.72 (d, *J* = 3.2 Hz), 7.43 (s), and 7.81 (d, *J* = 3.2 Hz) in CDCl₃. Obviously, the signals of the 14π annulene **14** are downfield with respect to Hafner's material. The largest difference is greater than 1 ppm (see protons 2 and 6). The differences between the proton signals of **14** and the hexaene **12** also reflect an electronic delocalization in **14**. In hexaene **12**, the corresponding signals appeared at δ = 6.15 (d, *J* = 5 Hz), 6.65 (s), and 6.77 (d, *J* = 5 Hz). This constituted a marked difference of 0.57, 0.78, and 1.04 ppm, respectively, between **12** and **14**. Furthermore, the smaller three-bond coupling constant in annulene **14** (3.2 Hz in comparison to 5 Hz in **12**) also indicated some delocalization.¹⁸ The substituent effect of the silyl group on the chemical shifts of cyclopentadiene is small (see Supporting Information). Even though 14π annulene (based on stability) behaves like a fixed alternate olefin, the chemical shifts of the protons indicate some delocalization. This was not observed in the tetra-*tert*-butyl-dicyclopenta[*a,e*]pentalene reported by Hafner,⁶ at least with respect to NMR chemical shifts.

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Supporting Information Available: The complete spectroscopic characterization of **12**, **13**, **14**, as well as attempts to trap **1** or **14**; NMR evidence for the delocalization in **14** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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