

The Livinghouse Catalytic Approach to the Tandem Pauson-Khand Reaction. Entry into the Parent Ring Systems of Dicyclopenta[*a,f*]pentalene and Dicyclopenta[*a,e*]pentalene

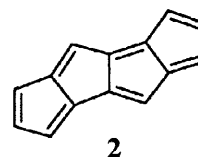
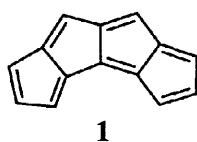
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Received 2 June 1998; revised 29 June 1998; accepted 30 June 1998

Abstract: The first photochemically-mediated catalytic tandem Pauson-Khand reaction has permitted the preparative scale synthesis of the parent ring systems **4** and **6** of dicyclopenta[*a,f*]pentalene **1** and dicyclopenta[*a,e*]pentalene **2**, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

The intramolecular Pauson-Khand reaction¹ (IPKR) has become one of the most versatile methods for the construction of bicyclo[3.3.0]octen-ones. Many natural and nonnatural products contain this substructure in their molecular framework which permits rapid synthesis *via* the IPKR. Since the discovery of the Pauson-Khand reaction,² numerous protocols have been developed to facilitate the cyclization process in a more efficient and effective manner. The modified conditions of Schreiber,³ which employ N-methylmorpholine-N-oxide (NMO), have been used to effect the cyclization under mild conditions and are more stereoselective than previous methods. Several other mediators for the IPKR include silica gel,⁴ DMSO,⁵ and sonication.⁶ Furthermore, Livinghouse⁷ has recently reported an interesting photochemically-promoted IPKR. The advantages of this method are the ability to use a catalytic amount of $\text{Co}_2(\text{CO})_8$ (i.e. 5–9 mol %) as well as ease of purification of the products which result.

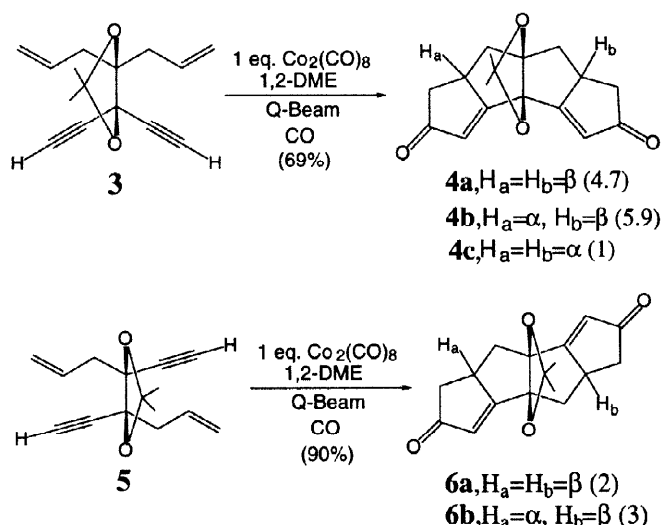
Recently the synthesis of the functionalized ring systems of dicyclopenta[*a,f*]pentalene **1** and dicyclopenta[*a,e*]pentalene **2** *via* the tandem Pauson-Khand reaction were reported.⁸ Synthesis of the target 14 π annulenes in these systems could provide important information in terms of bonding character, Hückel stabilization, aromaticity and resonance energy.



Gram quantities of the key intermediates **4** and **6** will be required to permit eventual conversion into annulenes **1** and **2**. Under the conditions of the stoichiometric Pauson-Khand reaction, transformation **3**→**4** was carried out on 3 gram scale; however, large amounts of $\text{Co}_2(\text{CO})_8$ (i.e. 13 g) and NMO were required and chromatography proved laborious (Scheme 1). Consequently, the photochemical catalytic IPKR was investigated for its applicability toward a tandem cyclization process. The constrained systems of diene-diyne **3**

and **5** were ideal candidates for this process, wherein the alkene and alkyne units are in the eclipsed conformation which should facilitate tandem cyclization. When diene-diyne **3** (300 mg) was treated with 9 mol % of $\text{Co}_2(\text{CO})_8$ followed by irradiation of the reaction mixture with a Q-Beam MAX MILLION lamp at 50–55°C,⁷ tetracycles **4a–c** were isolated in 74% yield. This constitutes a 95% yield for each of the six bonds generated in this regiospecific process. Attempts to increase the scale of diene-diyne **3** while maintaining 9 mol % catalyst resulted in prolonged reaction times (>72 h). Consequently, for preparative purposes diene-diyne **3** was stirred with 1 equivalent of $\text{Co}_2(\text{CO})_8$ on 6 gram scale and this was followed by irradiation to furnish the tetracyclic system **4** in 69% yield. All three isomers of **4** may be employed towards the synthesis of annulene **1**. The photochemical conditions were applied in similar fashion to generate the tetracyclic system **6**, as shown in Scheme 1. When diene-diyne **5** was treated with 20 mol % $\text{Co}_2(\text{CO})_8$, followed by photochemically-mediated cyclization, tetracycle **6** was obtained in 90% yield.

Scheme 1



In summary, the first photochemically-mediated tandem Pauson-Khand cyclization has permitted the synthesis of tetracyclics **4** and **6** in regiospecific fashion in 69% and 90% yield, respectively. This is much improved over the NMO procedure previously reported.⁸ Both tetracyclic systems contain the necessary functionality for further transformation into 14π annulenes **1** and **2**, respectively.

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