Pergamon

Tetrahedron Letters, Vol. 38, No. 21, pp. 3657-3658, 1997

0040-4039/97 $17.00 + 0.00

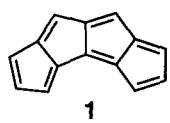
PII: S0040-4039(97)00718-1

Formation of Six Carbon-Carbon Bonds in a One Pot Process. Generation of the Dicyclopenta[a,e]pentalene Ring System *via* the Tandem Pauson-Khand Reaction

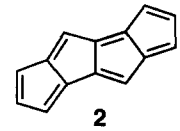
Scott G. Van Ornum and James M. Cook*
Department of Chemistry, University of Wisconsin-Milwaukee
Milwaukee, WI 53201

Abstract: *The regiospecific synthesis of the four five-membered rings of a suitably functionalized parent system **11** of dicyclopenta[a,e]pentalene **2** has been accomplished via a tandem Pauson-Khand reaction in a one pot process.* © 1997 Elsevier Science Ltd.

During the last two decades interest in the study of molecules which contain significant amounts of strain energy in their molecular structure has increased tremendously. The questions of bonding character, π overlap, homoconjugation, and Hückel stabilization are of great importance to computational and organic chemists.[1,2] Generation of molecular complexity[3] *via* the Weiss[4] reaction and the Pauson-Khand[5] reaction is similar to the level reported for the Diels-Alder cyclization for the formation of six-membered rings.[3] In this regard the tandem Pauson-Khand reaction[6,7] has provided a route for the generation of four five-membered rings contained in the dicyclopenta[a,d]pentalene system related to **1** and has now been extended to the dicyclopenta[a,e]pentalene framework contained in annulene **2**.



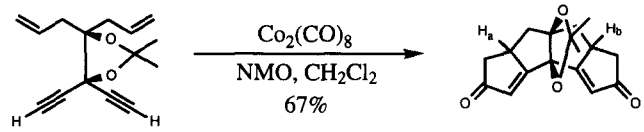
1



2

Recently the yield of the transformation of acetonide **3** into diketone **4** (Scheme 1) *via* the tandem Pauson-Khand reaction[6] has been improved to 67% which constitutes a yield of 94% in each of the six carbon-carbon bond forming steps. We now wish to report this regiospecific process has been expanded to include the synthesis of the parent ring system present in dicyclopenta[a,e]pentalene **2**.

Scheme 1



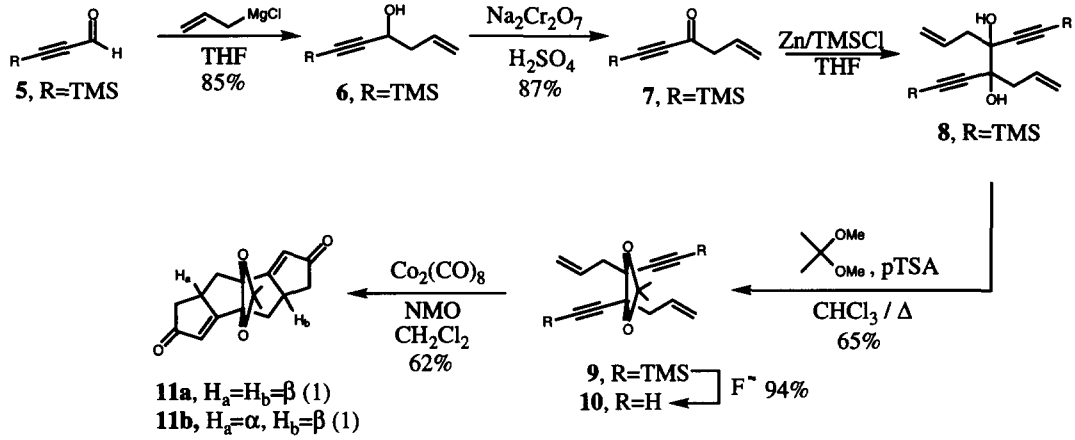
3

4a, H_a=H_b=β (3)
4b, H_a=α, H_b=β (2)

As illustrated in Scheme 2, aldehyde **5** was reacted with allyl magnesium chloride[8] [2 eq., 2M] to provide propargyl alcohol **6** in 85% yield. Oxidation of alcohol **6** with $Na_2Cr_2O_7/H_2SO_4$[9] furnished ketone **7** in 87% yield. Pinacol coupling of ketone **7** was effected with Zn/TMSCl[10] to provide a mixture of erythro and threo isomers which were separated by flash chromatography (silica gel, 3:1 hexane:EtOAc). The desired threo isomer was stirred with 2,2-dimethoxypropane in refluxing chloroform in the presence of pTSA[11] to furnish the

acetonide **9**. The silyl groups were removed from acetonide **9** on exposure to tetrabutylammonium fluoride to provide the key diene-diyne **10**. Under the modified Pauson-Khand conditions of Schreiber,[6,7,12] acetonide **10** was stirred with 3 equivalents of $Co_2(CO)_8$ in CH_2Cl_2 followed by addition of excess N-methylmorpholine N-oxide to provide the tetracyclic cyclopenta[a,e]pentalene system **11** in 62% yield. Both stereoisomers **11a** and **11b** of the tetracyclic system should serve as functionalized precursors to a planar annulene such as **2.**

Scheme 2



In summary, the tandem Pauson-Khand reaction has now been employed regiospecifically to provide entry into both the dicyclopenta[a,e]pentalene and dicyclopenta[a,d]pentalene ring systems. Six carbon-carbon bonds are formed in each case in a one pot process to provide these cyclopentapentalene systems suitably functionalized for transformation into the correponding annulenes. Further work to convert intermediates **4** and **11** into the 14π annulenes **1** and **2**, respectively, will be reported in due course.

References and Notes:

1. Hoffmann, R.; Alder, R.W.; Wilcox, C.F. *J. Am. Chem. Soc.* **1970**, *92*, 4992.
2. Streitwieser, Jr. A. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, **1961**, p.290.
3. Bertz, S.; Sommer, T. *Applications of Graph Theory to Synthesis Planning:Complexity, Reflexivity, and Vulnerability* in *Organic Synthesis: Theory and Applications,* Ed. Hudlicky, T., JAI Press Inc, Greenwich, Conn., **1993**, *2*, 67.
4. Fu, X.; Cook, J.M. *Aldrichimica Acta.* **1992**, *25*, 42.
5. Schore, N. E. *Org. React.* John Wiley & Sons, Ed. Paquette, L. A., Academic Press, N.Y. **1991**, *40*, 1.
6. Van Ornum, S.G.; Cook, J.M. *Tetrahedron Lett.*, **1996**, *37*, 7185.
7. Thommen, M.; Veretenov, A. L.; Guidetti-Grept, R.; Keese, R. *Helv. Chim. Acta.* **1996**, *79*, 461.
8. Darresh, S.; Grant, A.; MaGee, D.; Valenta, Z. *Can. J. Chem.* **1991**, *69*, 712.
9. Della, E.W.; Pigou, P. *Aust. J. Chem.* **1983**, *36*, 2261.
10. Hodge, P.; Khan, M. *J. Chem Soc., Perkin Trans I,* **1975**, *9*, 809.
11. Rosini, C.; Scamuzzi, S.; Focati, M. P.; Salvadori, P. *J. Org. Chem.* **1995**, *60*, 8289.
12. Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289.

(Received in USA 20 *March* 1997; *accepted* 3 *April* 1997)