$6\pi e^-$ vs $8\pi e^-$ Electrocyclization of 1-Aryl- and Heteroaryl-Substituted (1Z,3Z)-1,3,5-Hexatrienes

**Silvia García-Rubín**, Jesús A. Varela and Carlos Saá*

Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela
Av. das Ciencias s/n, CP: 15782 Santiago de Compostela, Spain
silvia.garcia@usc.es

## "Formal" Ru-Catalyzed [4+2+2] Cycloadditions of 1,6-Diynes to 1,3-Dienes

Recently, we have developed a "formal" Ru-catalyzed [4+2+2] cycloaddition of unsubstituted 1,6-diynes **1** to 1,3-dienes **2** to give 1,3,5-cyclooctatrienes **4**.[1] A plausible mechanism involves the initial Ru-catalyzed linear coupling between diynes **1** and 1,3-dienes **2** to give (3Z,5Z)-1,3,5,7-octatetraenes **3**, which undergo conrotatory $8\pi e^-$ electrocyclization to 1,3,5-cyclooctatrienes **4**.
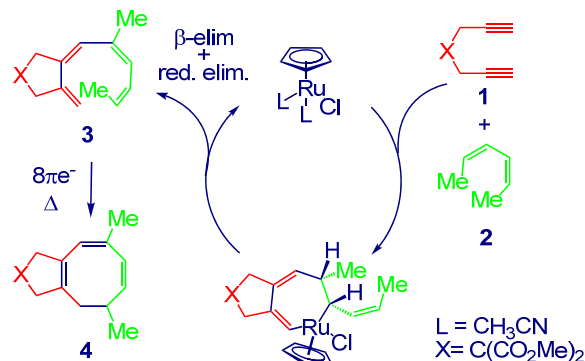
L = CH₃CN
X = C(CO₂Me)₂

Electrocyclization of 1-Aryl-and Heteroaryl Substituted (1Z,3Z)-1,3,5-Hexatrienes

1   5a   6a
X = C(CO₂Me)₂

7a 66%
8a 45%
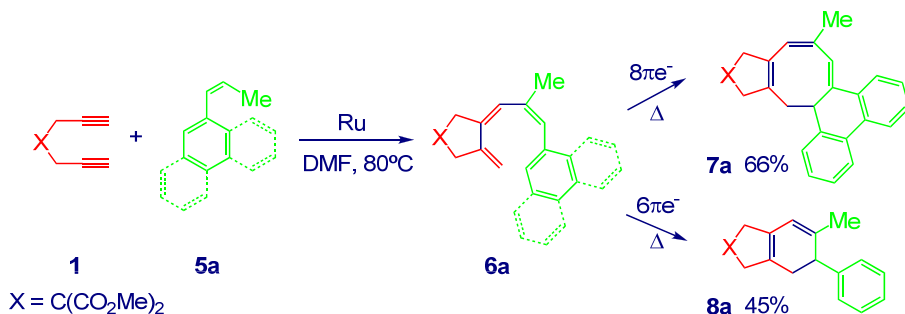
Ru = 10% [Cp*Ru(CH₃CN)₃]PF₆ / 10% Et₄NCl.
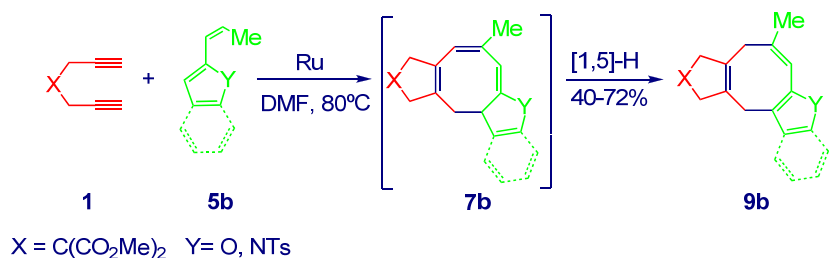
Peri selectivity of the electrocyclization of 1-aryl-substituted (1Z,3Z)-1,3,5-hexatrienes **6a**, obtained by Ru-catalyzed linear couplig of 1,6-diynes **1** to Z-propenylarenes **5a**, can be efficiently modulated depending on the aromaticity of the arene: 1,3,5-hexatrienylarenes give $8\pi e^-$ electrocyclization with exception of 1,3,5-hexatrienylbenzenes, which give $6\pi e^-$ electrocyclization.[2]

1   5b   7b   9b
X = C(CO₂Me)₂   Y= O, NTs

When the reaction was performed using Z-propenylheteroarenes such as **5b**, 1,4,6-cyclooctatrienes **9b** were obtained in quite good yields. The reaction takes place through the initial formation of 1,3,5-cyclooctatrienes **7b** by a "formal" Ru-catalyzed [4+2+2] cycloaddition reaction followed by a [1,5]-hydrogen shift.

DFT Calculations: $6\pi e^-$ vs $8\pi e^-$ Electrocyclization Reactions[3]

DFT calculations were performed for the $6\pi e^-$ and $8\pi e^-$ electrocyclizations of (1Z,3Z)-1,3,5-hexatrienes **6a´** and **6b´**. The results clearly show that $6\pi e^-$ electrocyclizations are thermodynamically favored, whereas $8\pi e^-$ electrocyclizations are kinetically favored.
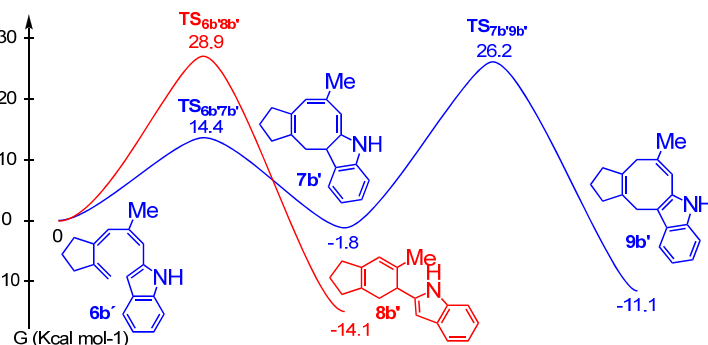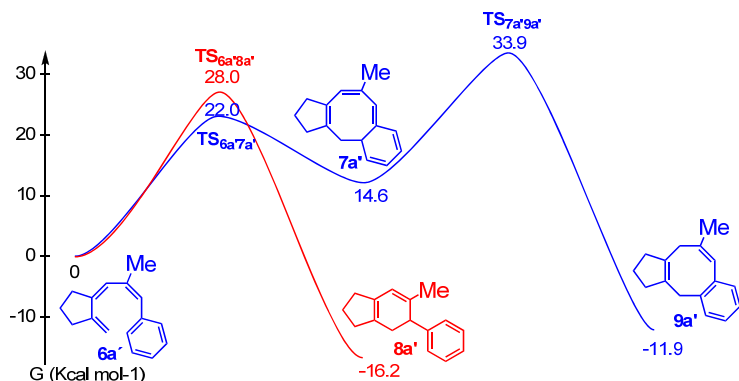
Referencias: [1] J.A. Varela, L. Castedo, C. Saá, *Org. Lett.* **2003**, *5*, 2841-2844 .
[2] García-Rubín, S.; Varela, J. A.; Castedo, L.; Saá, C. *Org. Lett.* **2009**, *11*, 983-986.
[3] Lecea, B.; Arrieta, A.; Cossio, F. P. *J. Org. Chem.* **2005**, *70*, 1035-1041