New “Formal” Ru(II)-Catalyzed Cycloadditions of 1,6-Diynes to Alkenes, 1,3-Dienes and Arenealkylidenes

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“Formal” Ru (II)-Catalyzed [4+2+2] Cycloadditions of 1,6-Diynes to 1,3-Dienes

We recently described a new “formal” ruthenium-catalyzed [4+2+2] cycloaddition of 1,6-diynes to 1,3-di enes to give  conjugated 1,3,5-cyclooctatrienes.1 Their formation could be explained in two steps: initial formation of tetraenes 3 according to the metal-catalyzed cycle showed in Figure 1 followed by thermal conrotatory electrocyclic ring closure of 3.

Interestingly, when cis-propenylfurane 2a was used, the tricyclic cyclooctatriene 5 was obtained in acceptable yield. The reaction occurs by initial formation of 4a followed by a [1,5]-hydrogen shift. However, in the case of the styrene 2b, the opened aryltriene 3b was initially obtained, which was quantitatively cyclized to arylcyclohexadiene 6 upon heating (Scheme 1).

When cyclic alkenes 7 were used, 1,3-cyclohexadienes 8 were obtained in acceptable yields. Surprisingly, when acyclic alkenes 9 were used, isomeric 1,3-cyclohexadienes 10 were obtained in rather good yields (Scheme 2).

The likely mechanism for these processes would involve the formation of ruthenacycle intermediate V. Depending on the alkene nature, two alternatives could be envisioned from V: a) the well-established reductive elimination in the case of cyclic alkenes; b) a new β-elimination + reductive elimination to give 1,3-hexadienes 11 in the case of acyclic alkenes. Final electrocyclization of 11 gave 1,3-cyclohexadienes 10.

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