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Palladium-Mediated Cyclization of 1,5-Hexadien-3-ols to 1-Methyl-1,3-cyclopentadienes

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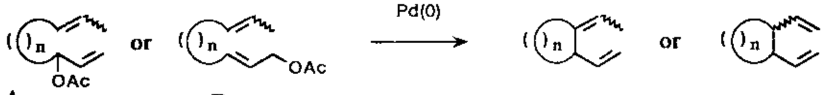
Key words : 1,3-cyclopentadienes; π-allylpalladium; cyclization.

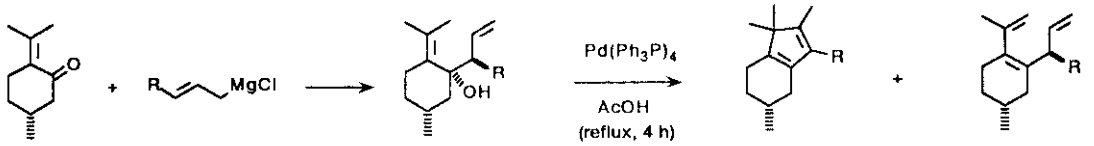
Abstract : Treatment of 1-allyl-2-alkenylidenecyclohexanols in acetic acid by the Pd(0) complex [Pd(Ph$_3$P)$_4$] led to 8-methyl bicyclo[4.3.0]nona-1(6),7-dienes. In contrast, only few examples of cyclization vs elimination were observed in acyclic 1,5-hexadien-3-ols.

The reaction of π-allylpalladium complexes with C-nucleophiles is an attractive synthetic tool.[1] In particular, the intramolecular olefin allylation of olefinic allyl acetates **A** or **B** constitutes a ring closure leading to 1-methylene-2-vinylcycloalkanes or 1,2-divinylcycloalkanes.[2-5]



A **B**

These cyclizations provide a variety of five-(six-) membered carbocyclic systems from olefinic allyl acetates with n = 3 or 4, and, to our knowledge, no report concerns the case n = 1, corresponding to 1,5-hexadien-3-ol derivatives. We have observed that 2-alkylidene-1-allyl-cyclohexanols, treated in acetic acid solution by Pd(Ph$_3$P)$_4$ (3 mole %, reflux, 4 h.), cyclized to bicyclo [4.3.0]nona-1(6),7-dienes. Allylpulegol **2a** or 3-buten-2-ylpulegol **2b**, resulting from the addition, respectively, of allyl- or crotylmagnesium chloride on (+)-(*R*)-pulegone **1**,[6] can be cyclized in cyclopentadienes **3a** or **3b**. By-products are trienes **4a** or **4b**, coming from acetic acid elimination :[7]



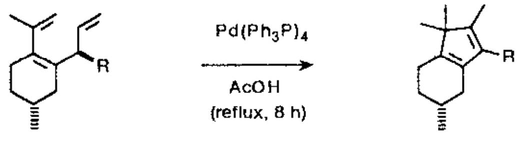
1

2a : R = H
2b : R = Me

3a : R = H (60 %)
3b : R = Me (65 %)

4a : R = H (20 %)
4b : R = Me (18 %)

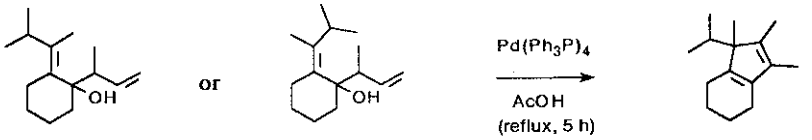
On the other hand, the isolated trienes **4a** or **4b** treated in the same conditions are cyclized in cyclopentadienes **3a** or **3b** after a longer refluxing time. So, the π-allylpalladium complex could be slowly obtained from the 1,3-diene moiety.



4a : R = H
4b : R = Me

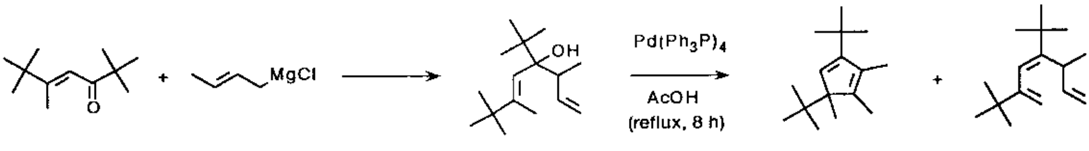
3a : R = H (75 %)
3b : R = Me (80 %)

Similar results are observed with other alkylidene-allylcyclohexanols, such as the isomeric alcohols **5a** and **5b** :



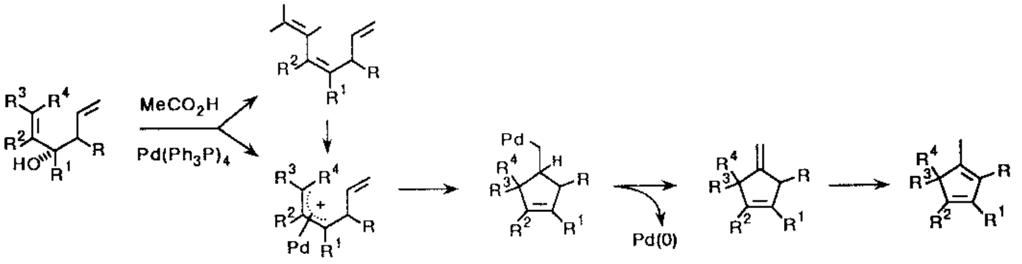
5a 5b 6 (75 - 80 %)

In contrast, acyclic 1,5-hexadien-3-ols usually lead to 1,3,6-heptatrienes as major products; only with hindered alcohols as 7, formation of cyclopentadienes is the main process :



7 8 (65 %) 9 (12 %)

This cyclization is rationalized by assuming the formation of a π-allylpalladium complex (from the allylic alcohol or the corresponding 1,3,6-heptatriene) which is then converted to a cyclopentenylmethylpalladium complex, precursor of the cyclopentadiene.



Further explorations of this new cyclization will be published in due course.

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