CARBON-CARBON BOND FORMATION VIA EPITITANATION AND AROMATIZATION OF ACETYLENES

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INTRODUCTION
The epititination process involves the oxidative addition of subvalent transition metal reagents (M^II,III) to various C=C, C=C, C=O or C=N linkages with the formation of three-membered metallacycles (3).

\[
\begin{align*}
M^{II,III} + & \quad \text{C=C} \\ 1 & \quad \text{E = C=O, N} \\ 2 & \quad \text{M}^2 = \text{Ti: Epititination process} \\
\end{align*}
\]

The bonding character of the metallacyclic adduct can range from metallacyclopropenyl ring having π-like C-M bonds (3) and a higher oxidation number for the metal center, M^III, to a π-complex (4) having little change in the M oxidation number.

Protolysis of 3 yields the monoreduction products while insertion of various unsaturated addends yields oligomers or polymers as well as cyclic compounds.

In this work, use of different acetylenes has lead to the formation of 1,2,4,5-tetrasubstituted benzenes. One such product, 1,2,4,5-tetraphenylbenzene has its applications in Molecular Tectonics.

OBJECTIVES
• To prepare dibutyltitaniunum(VI) disopropoxide complexes and apply them in the synthesis of carbon-boron bonds from different acetylenes
• To isolate and characterize such aromatic products using various laboratory and instrumental techniques

EXPERIMENTAL
All procedures involved in this work were carried out under an atmosphere of dry, deoxygenated argon.

The dibutyltitaniunum(VI) disopropoxide, Bu₂Ti(OPr')₂ was prepared from Ti(OPr')₄ and anhydrous BuLi at low temperatures (-78°C) in THF

\[
\begin{align*}
2 \text{BuLi} + \text{Ti(OPr')}_4 & \quad \text{THF} \\ -78^\circ \text{C} & \quad -2\text{Bu} \\
\end{align*}
\]

The prepared Bu₂Ti(OPr')₂ was allowed to react first with RC≡CR followed by RC≡CH in a ratio of 1:2 at -78°C and then at RT for 3h.

All the products were analyzed using 'H and 'C NMR techniques.

RESULTS

<table>
<thead>
<tr>
<th>RC≡CR</th>
<th>RC≡CH</th>
<th>Product</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=Ph</td>
<td>R=Ph</td>
<td>1,2,4,5-tetraphenylbenzene</td>
<td>90%</td>
</tr>
<tr>
<td>R=Ph</td>
<td>R=SiMe₃</td>
<td>1,2,4,5-tetraphenylsilane</td>
<td>70%</td>
</tr>
<tr>
<td>R=P₅</td>
<td>R=Ph</td>
<td>1,2,4,5-tetraphenylpentane</td>
<td>89%</td>
</tr>
</tbody>
</table>

PRODUCT ANALYSIS

'¹H and '¹³C NMR spectra of 1,2,4,5-tetraphenylbenzene

PROPOSED MECHANISM

CONCLUSIONS AND FUTURE WORK
The current work successfully demonstrates the formation of carbon-carbon bonds from different acetylenes in the formation of 1,2,4,5-tetrasubstituted benzenes

Further studies of these novel reactions are being expanded towards the use of other different unsaturated compounds in an effort to prepare linear, cyclic and/or heterocyclic compounds.

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