SYNOPSIS
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INTRODUCTION

Tin happens to be one of the oldest metal known to man and finds mention in the early books of the old Testament. Presently in organic laboratories all over the world vast array of tin compounds are being used as substrates, reagents and catalysts to achieve synthesis of diverse nature. In organic radical chemistry organotin reagents happens to be the exclusive choice for radical ring closures, ring expansions, cascade reactions, etc.

Amongst the vast array of tin compounds, organotin hydrides have found wide range of applications in synthetic organic chemistry. Their applications include both as reagents and catalysts. They are extremely fruitful in the generation of a wide variety of molecules which are proving to be essential components of the broad class of medicinal chemistry, carbohydrate chemistry, steroid chemistry and host of bioactive molecules. They really are an automatic choice for five-membered ring closure reactions though larger rings, intricate polycyclics and a host of exotic heterocycles are also synthesized. The realms of organotin reagents are expansive.

The potential of organotin hydride need further exposition. Their use may lead to a lot of fascinating exposure of chemoselectivity, regioselectivity and stereochemistry. The horizon of organotin hydrides is so broad that their syntheses offer challenge in incorporating intramolecularly coordinating ligand, in making them environment friendly, in serving as enantioselective reagents, etc.

Objective

The present investigation was carried out with the prime objective of synthesizing a series of tin hydrides having an intramolecularly coordinating ligand. Such coordination is expected to induce a number of fascinating properties in organotin hydrides. Their properties include stereoselective hydrogen transfer, arresting spontaneous racemization at a stereogenic tin and enhancing reactivity including catalytic property.

During the present investigation a series of tin hydrides, represented by the structure given below, has been synthesized and their reactivity tested.
EXPERIMENTAL SECTION

The synthesis of the tin hydrides involved four steps:

(i) olefination of strategically substituted benzaldehydes
(ii) hydrostannation of the olefinic double bond using triphenyltin hydride
(iii) substitution of one of the phenyl groups by iodine, and
(iv) reduction of iodide to hydride by NaBH₄.

All intermediates including the stereoisomers and the tin hydrides have been characterized by m.p., IR, ¹H NMR and ¹³C NMR. In case of two of the hydrostannated products NMR spectra were not conclusive for structural elucidation and therefore single crystal XRD was utilized.

Preparations of strategically chosen olefins were carried out by either Wittig reaction or Claisen-Schmidt reaction. Eleven different olefins have been prepared and fully characterized. Olefination of both o-nitrobenzaldehyde and o-methoxybenzaldehyde were attempted.

Hydrostannation of olefinic bond by Ph₃SnH was carried out in dry benzene under reflux in the presence of AIBN as radical initiator.

Hydrostannated products were converted to corresponding tin iodide by reacting with iodine either in dichloromethane or benzene at ambient temperature. Time required for iodination varied from a few minutes to overnight.

Reduction of tin iodides with NaBH₄ finally yielded tin hydrides. Reactivity of these newly designed tin hydrides has also been tested.
RESULTS AND DISCUSSION

Wittig olefination of o-methoxybenzaldehyde, o-nitrobenzaldehyde and o-hydroxybenzaldehyde were attempted using several Wittig reagents. The olefins prepared are shown in Table 1.

Table II.1: Wittig Olefination

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehydes</th>
<th>Triphenylphosphonium salts</th>
<th>Olefins (2a-2l)</th>
<th>E/Z ratio</th>
<th>%Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>[Ph₃P′CH₃]I⁻</td>
<td>2a</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>[Ph₃P′CH₂CH₃]Br⁻</td>
<td>2b</td>
<td>65/35</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>[Ph₃P′CH₂Ph]Br⁻</td>
<td>2c</td>
<td>-</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>[Ph₃P′CH₂COOMe]Cl⁻</td>
<td>2d</td>
<td>79/21</td>
<td>87</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>[Ph₃P′CH₂COOEt]Cl⁻</td>
<td>2e</td>
<td>73/27</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>[Ph₃P′CH₂CH₃]Br⁻</td>
<td>2f</td>
<td>71/29</td>
<td>24</td>
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<tr>
<td>7</td>
<td></td>
<td>[Ph₃P′CH₂Ph]Br⁻</td>
<td>2g</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>[Ph₃P′CH₂COOEt]Cl⁻</td>
<td>2h</td>
<td>89/11</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>[Ph₃P′CH₂COOMe]Cl⁻</td>
<td>2i</td>
<td>0/100</td>
<td>20</td>
</tr>
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</table>
The two olefins prepared by utilizing the advantage of Claisen-Schmidt reaction are shown in Table 2

Table 2: Claisen-Schmidt Olefination

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Acetone</th>
<th>Olefin</th>
<th>Yield</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td>1.0 equiv.</td>
<td><img src="image2.png" alt="Image" /></td>
<td>72%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Image" /></td>
<td>0.5 equiv.</td>
<td><img src="image4.png" alt="Image" /></td>
<td>76%</td>
</tr>
</tbody>
</table>

While o-methoxybenzaldehyde and o-nitrobenzaldehyde were successfully converted to corresponding olefins, the olefination product of o-hydroxybenzaldehyde (Entry 9, Table 1) yielded coumarin.

Hydrostannation of all the olefins shown in Table 1 and 2 were attempted. But hydrostannation of only four of the o-methoxy olefins (Entry 1, 4 and 5 in Table 1 and Entry 1 in Table 2) could be achieved. Attempted hydrostannation of o-nitro olefins yielded o-amino products but no hydrostannation. Di(o-methoxybenzylidene)acetone (Entry 2, Table 2) did not yield hydrostannated product but did undergo reduction at one of the two olefinic double bonds when treated with 1.2 equivalent of Ph₃SnH under free radical condition. Olefin shown in entry 2 and 3 of Table 1 did undergo neither hydrostannation nor reduction. Only starting materials were recovered.

In hydrostannation of α,β-unsaturated esters the triphenylstannyl group is found to enter at α-position (Entry 2 and 3, Table 3) while in hydrostannation of α,β-unsaturated ketone the triphenylstannyl group enters at β-position (Entry 4, Table 3). This aspect of regioselectivity of hydrostannation differentiating between α,β-unsaturated esters and α,β-unsaturated ketone was established by single crystal XRD of the hydrostannated products shown in entry 2 and entry 4 in Table 3. ORTEP diagram of the crystals are shown in Fig. 1 and Fig. 2.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Olefin</th>
<th>Product</th>
<th>Yield(%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Olefin 1" /></td>
<td><img src="image2" alt="Product 1" /></td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Olefin 2" /></td>
<td><img src="image4" alt="Product 2" /></td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td><img src="image5" alt="Olefin 3" /></td>
<td><img src="image6" alt="Product 3" /></td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td><img src="image7" alt="Olefin 4" /></td>
<td><img src="image8" alt="Product 4" /></td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td><img src="image9" alt="Olefin 5" /></td>
<td><img src="image10" alt="Product 5" /></td>
<td>31</td>
</tr>
</tbody>
</table>
Figure 1: ORTEP representation (30% probability) of methyl 3-(o-methoxyphenyl)-2-(triphenylstannyl)propanoate

Figure 2: ORTEP representation (30% probability) of 4-(o-methoxyphenyl)-4-(triphenylstannyl)-2-butanone
Three out of the four hydrostannated products were successfully converted to the corresponding tin hydrides via tin iodides as intermediates. Tin iodides were generated in situ and converted to tin hydrides without isolation and characterization. It was interesting to note that the reactions of two of the hydrostannated products (Entry 1 and 4, Table 3) with iodine was almost instantaneous and these were completed in less than 10 minutes in dichloromethane (Entry 1, Table 3) and benzene (Entry 1 and 4, Table 3) at room temperature. But in case of other two hydrostannated products (Entry 2 and 3, Table 3) iodination did not take place in dichloromethane and in benzene overnight stirring at ambient temperature was necessary.

The Sn-H stretching frequency in the range 1830-1850 cm⁻¹ in IR is a unique feature and was helpful in identifying the tin hydrides.

The reactivity of these newly designed tin hydrides has been tested with reactions which have been reported involving other organotin hydrides.

**CONCLUSION**

Synthesis of a series of newly designed novel organotin hydrides having intramolecularly coordinating ligand, has been achieved by application of simple reactions involving easily available and cheap chemicals. All the hydrides and the intermediates involved in their synthesis have been fully characterized using IR, NMR and XRD techniques. The reactivity of the tin hydrides has also been established.