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In-mediated synthesis of 2-(2-hydroxyethyl)homoallenylsilanes

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Abstract

Indium-mediated homoallenylation of aldehydes with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene in DMF afforded 2-(2-hydroxyethyl)homoallenylsilanes at room temperature in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: indium; homoallenylation; 2-(2-hydroxyethyl)homoallenylsilanes.

Allyl metal-mediated carbon–carbon bond formation is one of the fundamental processes in organic synthesis.[1] Although allyl metal-mediated allylation of a variety of aldehydes and ketones has received much attention, less attention has been paid to homoallenylation of the carbonyl compounds. As part of our continuing effort to synthesize 2-methyl-3-trimethylsilylmethyl dihydrofuran derivatives from homoallenyl alcohols, we needed a versatile method to prepare 2-(2-hydroxyethyl)homoallenylsilanes. Generally, 2-(2-hydroxyethyl)allylsilanes can be prepared by lithiation followed by silylation of 3-methylhomoallylic alcohols,[2] by ring opening reactions of epoxides with organometallic reagents derived from 2-haloallylsilanes[3] and by indium-mediated allylsilylation of carbonyl compounds.[4] To the best of our knowledge none of these methods has been applied to the synthesis of 2-(2-hydroxyethyl)homoallenylsilanes. The addition of organometallic reagents derived from the halomethylhomoallenylsilanes on aldehydes or ketones could be used to produce 2-(2-hydroxyethyl)homoallenylsilane. However, we could not effectively prepare the corresponding Grignard reagents from the halomethylhomoallenylsilanes. In addition Grignard reagents must be employed in excess in reactions with electrophiles having any acidic hydrogens to obtain the desired products in good yields. Therefore, we turned our attention to other organometallic reagents to synthesize 2-(2-hydroxyethyl)homoallenylsilanes. Of all the metals, indium has been employed frequently in numerous

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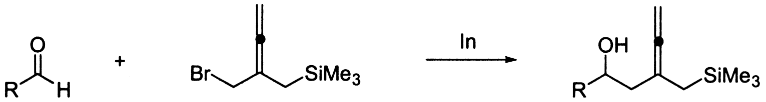
organic conversions especially in recent years because it has some prominent advantages such as easy handling, high reactivity and selectivity, and low toxicity.[5] Indeed, it has been shown to be effective in the allylation of carbonyl compounds[6] and aldimines,[7] in ring expansion reaction,[8] in Prins type cyclization,[9] and in intramolecular carbocyclizations.[10] We tried to take advantage of indium-promoted allylations and here we report our initial results on the indium-mediated homoallenylation of aldehydes (Scheme 1).



Scheme 1.

To find optimum conditions for indium-mediated homoallenylation, benzaldehyde was initially reacted with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene (**1**)[11] in the presence of indium in various solvents. Of the solvents tested such as H_2O, THF, CH_2Cl_2 and DMF, the best results were obtained in DMF. The indium-mediated reaction of benzaldehyde with homoallenyl bromide **1** in DMF afforded the homoallenylated product **5** in 92% yield (entry 4).[12] The same reaction in other solvents, however, gave lower yields as well as a longer reaction time.

As can be seen in Table 1, various aliphatic aldehydes (entries 1∼3) gave the desired compounds **2**, **3** and **4** in good yields.[13] For the aromatic aldehydes, the presence of various substituents, such as methyl (entry 5), bromo (entry 6), chloro (entry 7), nitro (entry 8), monomethoxy (entry 9), or dimethoxy (entry 10) on the aromatic ring showed little effects on either the reaction rate or yields of the reaction. It is especially noteworthy that a substrate having an acidic hydrogen such as 4-formylbenzoic acid was also reacted to produce the corresponding homoallenyl alcohol **12** in 88% yield (entry 11). The present method reaches a limit with ketones. Acetophenone did not react with 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene under the identical conditions while an indium reagent derived from 3-iodo-2-(trimethylsilylmethyl)propene reacted with acetophenone.

In summary, indium-mediated homoallenylation of aldehydes with 4-bromo-3[(trimethylsilyl)methyl]-1,2-butadiene in DMF afforded 2-(2-hydroxyethyl)homoallenylsilanes in good to excellent yields under mild conditions. Because synthetic methods for the preparation of 2-(2-hydroxyethyl)allylsilanes were reported mainly in previous works, the present method complements the existing synthetic methods. Further studies on the synthesis of 2-methyl-3-trimethylsilylmethyl dihydrofurans using 2-(2-hydroxyethyl)homoallenylsilanes are now in progress.

Acknowledgements

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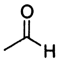
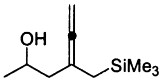
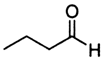
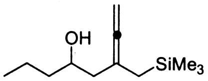
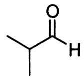
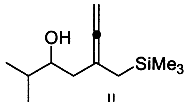
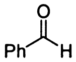
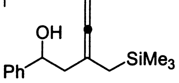
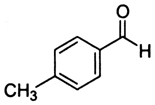
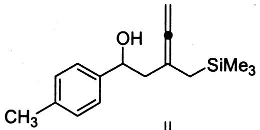
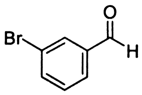
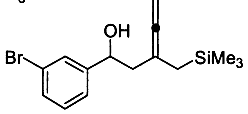
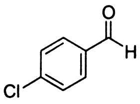
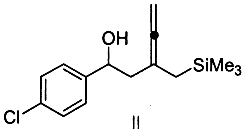
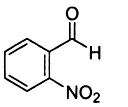
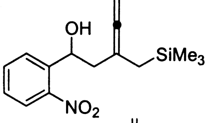
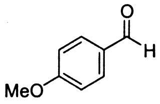
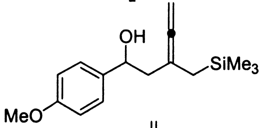
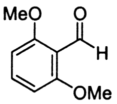
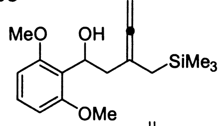
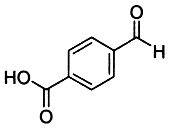
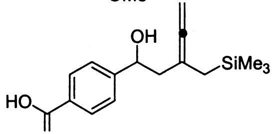
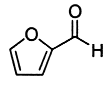
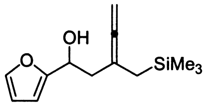
Table 1
Indium-mediated homoallenylation of aldehydes

Entry	Starting Materials	Products		Isolated Yield / %[a]
1			**2**	88
2			**3**	89
3			**4**	87
4			**5**	92 88[b] 11[c] 0[d]
5			**6**	73
6			**7**	89
7			**8**	93
8			**9**	90
9			**10**	80
10			**11**	83
11			**12**	88
12			**13**	83

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[a] All reactions were carried out with indium reagent derived from an equimolar mixture of indium and homoallenylsilane in DMF at room temperature.
[b] solvent : H_2O, [c] solvent : THF, [d] solvent : CH_2Cl_2.

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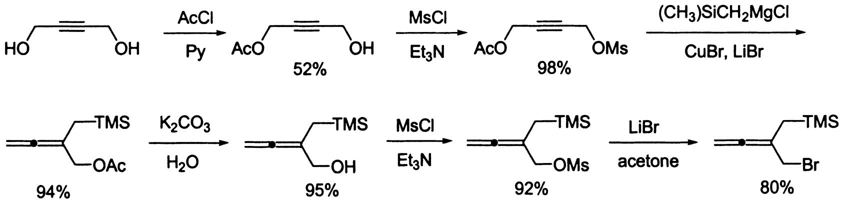
11. 4-Bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene was prepared from 2-butyn-1,4-diol as in the following scheme.



12. To a solution of indium [indium powder (99.99%) purchased from Aldrich Chem. Co.; 58 mg, 0.5 mmol) in DMF (0.6 mL) was added 4-bromo-3-[(trimethylsilyl)methyl]-1,2-butadiene (110 mg, 0.5 mmol) in DMF (0.6 mL). After the reaction mixture was stirred for 30 min at room temperature, benzaldehyde (37 mg, 0.35 mmol) was added. After 40 min at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether (3×25 mL), and the combined organic layers were washed with water (20 mL), brine (20 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane:EtOAc = 20:1) leading to 1-phenyl-3-trimethylsilylmethyl-3,4-pentadien-l-ol (80 mg, 92%).
13. All new compounds have satisfactory analytical data including ^{1}H, ^{13}C NMR, MS and IR spectroscopy.