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Ytterbium Trifluoromethanesulfonate [Yb(OTf)3] Promoted Indium Mediated Allylation Reactions of Carbonyl Compounds in Aqueous Media

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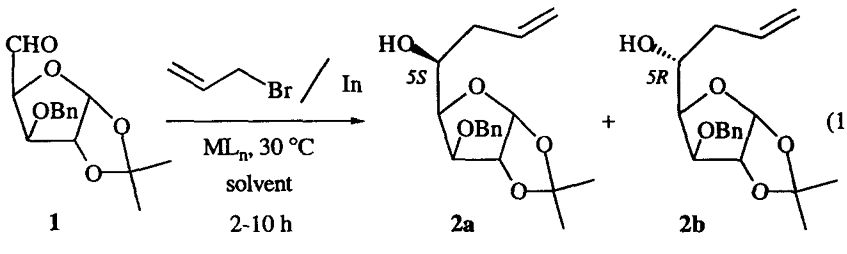
Abstract: Indium-mediated allylation reactions of the sugar derivative **1** in aqueous media have been found to proceed with high anti diastereofacial selectivity in the presence of ytterbium trifluoromethanesulfonate as Lewis acid.

The Lewis acid-catalyzed carbonyl addition reaction of allylic organometallic reagents is a versatile synthetic tool for acyclic stereocontrol.[1] Among the many organometallic reagents that have been successfully employed, allyltin, allylzinc and allylindium reagents comprise a unique group which undergo reaction with aldehydes in aqueous media.[2] In connection with our interest in developing organic reactions in aqueous media as a synthetic tool for acyclic stereocontrol[3], we have recently discovered that lanthanide triflates increase the rate and diastereofacial selectivity of allylindium addition to α-aminoaldehyde.[4] In extension of this, herein we report that the Lewis-acid promoted indium mediated allylation of a sugar derivative gives high anti-diastereofacial selectivity with the judicious choice of solvent and Lewis acid employed.

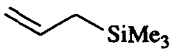
Lanthanide triflates have been reported to catalyze a range of Lewis acid promoted reactions, including the Aldol reaction, Diels-Alder reaction and Micheal addition and allyltin reactions.[5] The catalysts are readily prepared from the corresponding lanthanide oxide and triflic acid.[6] The reaction of the glucose derived aldehyde[7] (1) with allylindium is representative. To allylbromide (0.26 mL, 3 mmol), indium (114.8 mg, 1 mmol) and Yb(OTf)$_3$ (310 mg, 0.5 mmol) in the indicated solvent was added the aldehyde (0.5 mmol) at 30 °C. Commercially available indium powder (Aldrich company; 150 mesh) was used, and the suspension of the reactants was allowed to stir at room temperature until the starting materials was not observed on TLC. The yields reported in Table 1 were of isolated materials, following column chromatography over silica gel.

All the allylmetal reactions studied afforded good yields of the allylation products (Table 1).[8] It was discovered by experimentation that the use of DMF as co-solvent increases the diastereofacial selectivity (entry 3). Of special interest is the increase in reactivity and high anti-diastereofacial selectivity observed when Yb(OTf)$_3$ was added to the reaction in DMF-H_2O (entry 4). For the major diastereomer formed in each of the indium-mediated allylation reaction, the hydroxy function formed and that originally present at C-4 of the starting dialdose **1** have anti relationship. This result is in agreement with observation made by Danishefsky et al. for the non-chelation controlled reaction under aprotic conditions of similar carbohydrate containing an asymmetric center adjacent to the carbonyl function.[9b] It should be noted that the major product, *S* configuration at C-5 in **2** obtained in the reaction of **1** with allylsilane in the presence of $SnCl_4$ is opposite to our allylation reactions (entry 5).[9b, 10]



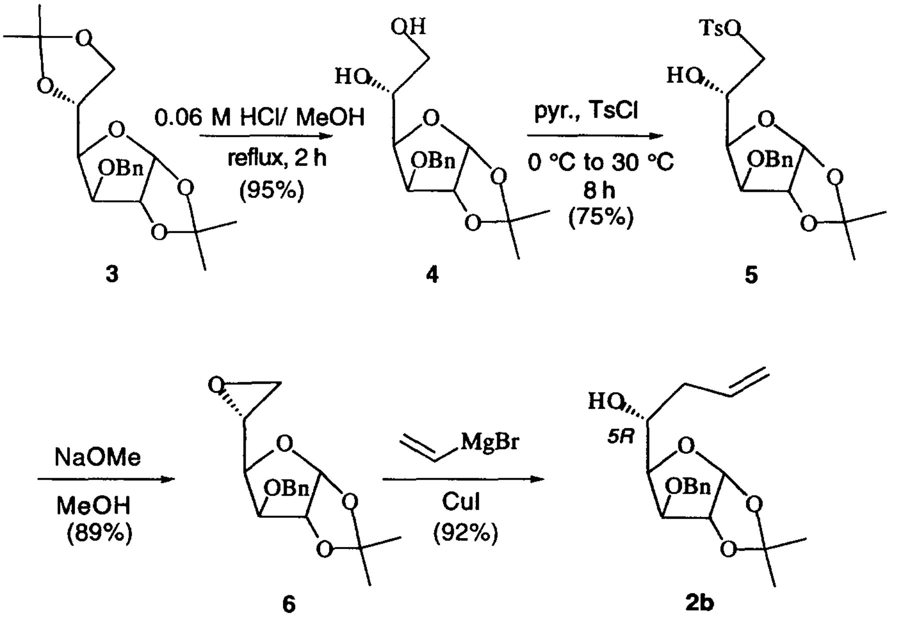
(1)

Table 1 Indium mediated allylation reactions[a]

Entry	MLn	Conditions	**2a** : **2b**[b] (%yield)[c]
1	-	H_2O (10 h)	41 : 59 (66%)
2	-	H_2O-THF: 4-1 (10 h)	24 : 76 (72%)
3	-	DMF-H_2O: 6:4 (2 h)	17 : 83 (82%)
4	Yb(OTf)$_3$	DMF-H_2O: 6:4 (1 h)	6 : 94 (88%)
5	 SiMe$_3$ SnCl$_4$	CH_2Cl_2, -78 °C	88 : 12 (76%)[d]

[a] All reactions were carried out on a 0.5-1 mmol scale. [b] The isomer ratio was determined by ^{13}C NMR and HPLC analyses. [c] Yield of isolated product after silica gel chromatography. [d] Reaction carried out under non-protic condition using allylsilane instead of allylbromide/In.

The stereochemical assignments of the allylation products **2a** and **2b** deserves comment. The stereochemistry of the new stereogenic centre (C-5) formed by addition of the allyl group was assigned on the basis of the ^1H NMR, ^{13}C NMR, t.l.c analyses as compared with authentic **2b** prepared unambiguously from D-glucose as shown in Scheme 1. Selective ketal deprotection of diacetone-D-glucose (**3**) followed by tosylation of the less steric hydroxyl group gave **5** in good yield. Treatment of **5** with sodium methoxide to yield the epoxide **6** which was selectively opened by vinylgrignard and copper halide to give **2b** in good yield.



Scheme 1

Particularly noteworthy is the effect of the solvent on the selectivity of the reaction. The choice of the solvent and Lewis acid plays an important role in the diastereofacial selectivity of the reaction. The anti-diastereofacial selectivity thus observed is reasonably explained in terms of Felkin-Anh's or Cram's model.[9] Thus, this new type of indium-mediated allylation is proved to proceed under effective nonchelation control. By contrast, the allylation reaction of 1 with allylsilane in the presence of $SnCl_4$ well reflects the cyclic chelate transition state.[10]

In conclusion, this work has demonstrated the utility of the Lewis acid-catalyzed indium mediated allylation in aqueous media as a synthetic tool for acyclic stereocontrol with the judicious choice of the solvent and Lewis acid employed. These allylation products will doubtless serve as key intermediates for the synthesis of various natural products.[11] Work is in progress to apply this methodology to more highly functionalized systems and other halide sources.

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8. Key data: (5*R*)-**2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3 (3H, s), 1.5 (3H, s), 2.2 (m, 2H), 4.0~4.1 (3H, m), 4.5~4.7 (2H, dd, *J*=11.8, 11.8 Hz), 4.62 (1H, m), 5.1 (2H, m), 5.8 (1H, m), 5.98 (1H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.4, 26.9, 38.2, 39, 68.3, 72.0, 72.3, 75.6, 78.5, 105.0, 111.7, 112.1, 118.0, 127.9, 128.2, 128.7, 134.3, 137.1; (5*S*)-**2a**: ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.4, 26.9, 37.5, 39, 68.3, 69.4, 72.3, 75.6, 78.5, 105.0, 111.7, 112.1, 118.0, 117.3, 128.2, 128.7, 134.3, 137.1.
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