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Transfer of alk-1-enyl group from boron to aluminium: a novel way to prepare (*E*)-alk-1-enyldiisobutylalanes

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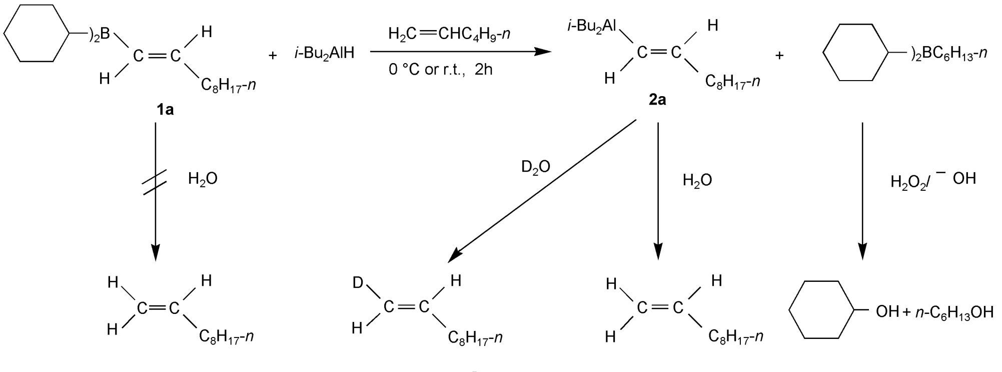
Treatment of (*E*)-alk-1-enyldicyclohexylboranes 1 with diisobutylaluminium hydride (DIBAL-H) in the presence of hex-1-ene at room temperature results in transfer of the alk-1-enyl group from boron to aluminium to give (*E*)-alk-1-enyldiisobutylalanes 2 with retention of configuration at the double bond.

Alkenylaluminium compounds are useful intermediates in organic synthesis.[1] For example, halogenation of (*E*)-alk-1-enyldiisobutylalane **2** results in the preferential cleavage of the alkenyl carbon–aluminium bond under neutral conditions to give (*E*)-1-haloalk-1-ene stereoselectively.[2] This reaction is a characteristic of **2**; however, full advantage of this feature cannot be made due to the difficulty of preparing **2** exclusively. Thus, hydroalumination of alk-1-yne with diisobutylaluminium hydride (DIBAL-H) yields the desired product **2**, accompanied by alk-1-ynyldiisobutylalane and alk-1-ene, the former of which results from metallation of alk-1-yne and the latter results from protonolysis of **2** with unreacted alk-1-yne. In particular, the undesired products increase significantly in conjugated alk-1-ynes such as phenylethyne.[1*a*]

We recently reported that treatment of (*E*)-alk-1-enyldicyclohexylboranes **1** with a slight excess of *B*-methoxy-9-borabicyclo[3.3.1]nonane (*B*-MeO-9-BBN) at 0 °C results in transfer of the (*E*)-alk-1-enyl group from boron to boron, leading to an efficient and stereoselective preparation of *B*-[(*E*)-alk-1-enyl]-9-BBN.[3] This transfer reaction contrasts with hydroboration of a 100% excess of alk-1-yne with 9-BBN from the viewpoint of efficient conversion of alk-1-yne into *B*-[(*E*)-alk-1-enyl]-9-BBN. It is more likely that such transfer reactions will provide an alternative to hydrometallation of alkynes due to the high regio- and stereo-selectivity of hydroboration. We now report here a novel preparation of (*E*)-alk-1-enyldiisobutylalanes **2** *via* treatment of (*E*)-alk-1-enyldicyclohexylboranes **1** with DIBAL-H in the presence of hex-1-ene at room temperature (Scheme 1).

In an effort to achieve transfer of the alk-1-enyl group from boron to other metals, the use of DIBAL-H as the exchange partner was investigated. It was found that when the reaction of (*E*)-dec-1-enyldicyclohexylborane (**1a**) with an equimolar amount of DIBAL-H was carried out at 0 °C or room temperature for 2 h in the presence of 2 equiv. of hex-1-ene, and the reaction mixture was hydrolyzed at room temperature for 2 h, dec-1-ene was obtained in a yield of 82–86%. Alkenyldialkylboranes, in general, do not react with water under these conditions,[4] whereas alkenyldiisobutylalanes undergo smooth hydrolysis to yield the corresponding alkene.[1] Accordingly, the formation of dec-1-ene upon hydrolysis indicated that an alkenyl carbon–aluminium bond was formed by the above reaction. To clarify the structure of decenyl group on aluminium, deuteration with deuterium oxide was run under the same conditions. After usual work-up and isolation by column chromatography on silica gel, the isolated product was analysed by ^{1}H and ^{13}C NMR spectroscopy. In the alkenyl region of the ^{1}H NMR spectrum, only one pair of signals appeared at δ 4.98 (dt, *J* 17.1, 1.5 Hz) and 5.81 (dtt, *J* 17.1, 6.7, 1.5 Hz), suggesting that the product has *trans* alkenyl protons. The ^{13}C NMR spectrum showed that two sp^2 carbon atoms of the alkene appeared at δ 113.8 (t, J_{CH} 24 Hz) and 139.1 (s), supporting that the deuterium is on the terminal sp^2 carbon atom. These results indicated that (*E*)-1-deuteriumdec-1-ene had been formed in a stereoselective manner. Thus, the (*E*)-dec-1-enyl group transferred from the boron atom of **1a** to the aluminium atom of DIBAL-H with complete retention of stereochemistry to provide (*E*)-dec-1-enyldiisobutylalane (**2a**). Moreover, we observed that the same reaction mixture was oxidized with alkaline hydrogen peroxide, instead of hydrolyzing, at 0 °C for 1 h to yield hexan-1-ol as well as cyclohexanol, the ratio of hexan-1-ol to cyclohexanol being *ca.* 0.9 to 2. This result suggests that the hydride transferred from the aluminium atom of DIBAL-H to the boron atom of **1a**, accompanied by transfer of the (*E*)-dec-1-enyl group, to generate dicyclohexylborane, which hydroborated with hex-1-ene immediately to form hex-1-yldicyclohexylborane. In the absence of hex-1-ene the formation of **2a** was hampered noticeably. Hex-1-ene gave superior results in comparison with other terminal alkenes such as 3,3-dimethylbut-1-ene and methylenecyclohexane. Thus the use of hex-1-ene is essential to the success of the transfer using DIBAL-H.

We next examined transformation of **1** into **2** followed by halogenation in order to demonstrate the scope and applicability of this method (Scheme 2). In initial experiments, successive reaction of **1a** with DIBAL-H and iodine was investigated. It was found that the use of 1.2 equiv. of DIBAL-H at room



Scheme 1

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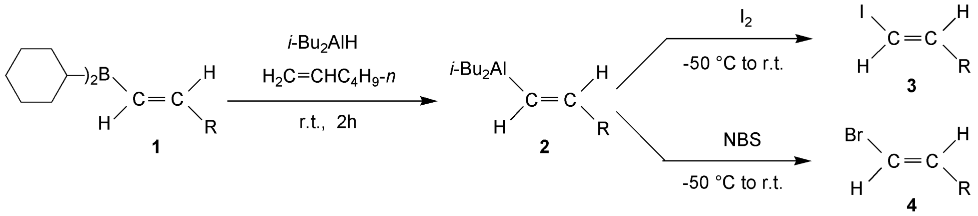

Scheme 2

temperature and the use of 1.3 equiv. of iodine under similar conditions to the literature[2] gave the best result in which the desired product (*E*)-1-iododec-1-ene (**3a**) was obtained in 78% yield based on the starting amount of dec-1-yne. The ^{1}H NMR spectrum of **3a** revealed that only one pair of signals appeared at δ 5.97 (dt, *J* 14.3, 1.5 Hz) and 6.51 (dt, *J* 14.3, 7.0 Hz) in the alkenyl region, hence the geometry of the product was assigned to be *E*-configuration. Although it is well known that treatment of **1a** with iodine produces not **3a** but rather (*Z*)-1-cyclohexyldec-1-ene *via* a sequence of addition–migration–elimination reactions,[5] this product was not observed in the reaction mixture. Bromination of **2a** derived from **1a** was also explored and, in consequence, *N*-bromosuccinimide (NBS) proved to be more selective and efficient than bromine which brought about the cleavage not only of alkenyl carbon–aluminium bond but of the isobutyl carbon–aluminium bond.[2] Thus, consecutive reaction of **1a** with 1.2 equiv. of DIBAL-H and 1.1 equiv. of NBS under the same conditions as described above afforded (*E*)-1-bromodec-1-ene (**4a**) in 82% yield based on the starting amount of dec-1-yne. The geometry of **4a** was assigned to be *E*-configuration by its ^{1}H NMR spectrum where siganls at δ 6.01 (d, *J* 13.4 Hz) and 6.15 (dt, *J* 13.4 and 6.4 Hz) were observed.

Table 1 shows the results of iodination and bromination of **2** prepared *via* transfer reaction of **1** derived from alkynes with substituents, including bulky alkyl, phenyl, alkenyl and chloroalkyl groups. Halogenations proceeded smoothly to provide the corresponding (*E*)-1-haloalk-1-enes in good yields. The process tolerates such functional groups as alkenyl and chloroalkyl. It is noteworthy that transformation of conjugated alk-1-ynes such as phenylethyne and cyclohexenylethyne into (*E*)-1-haloalk-1-enes through alkenylalane intermediates has been realised with satisfactory results.

Table 1 Iodination and bromination of (*E*)-alk-1-enyldiisobutylalanes **2** derived from (*E*)-alk-1-enyldicyclohexylboranes **1**[a]

		Yield of products[b] (%)	
R		**3**	**4**
n-C_8H_{17}	**a**	78	82
t-C_4H_9	**b**	81	
Ph	**c**	80	82
Cyclohexenyl	**d**	83	87
$Cl(CH_2)_3$	**e**	72	

[a] Both iodination and bromination were carried out at −50 °C to room temperature using 1.3 equiv. of iodine or 1.1 equiv. of NBS. [b] GLC yields based on alk-1-yne employed.

It is well known that the reaction of boron compounds with organometallic compounds, where the metal is significantly more electropositive than boron, results in transmetallation to give organoboranes.[4] As an example of transmetallation of alkenyl groups, alkenyldialkylboranes can be obtained by treatment of alkenylalanes with *B*-methoxydialkylboranes.[6] On the other hand, when the electronegativity of the metal is close to that of boron, the direction of transmetallation can be reversed under appropriate conditions. Organomercury compounds are typical of those having such reversibility. For example, treatment of alkenylboranes with mercury(II) acetate followed by sodium chloride yields alkenylmercuric chloride with retention of configuration.[7] The present reaction is, to the best of our knowledge, the first case of the transfer of an alk-1-enyl group from boron to aluminium.

In conclusion, we have successfully developed a novel pathway to (*E*)-alk-1-enyldiisobutylalanes **2** *via* the reaction of (*E*)-alk-1-enyldicyclohexylboranes **1** with DIBAL-H in the presence of hex-1-ene. This transfer of an alk-1-enyl group is achieved with complete retention of configuration at the double bond under very mild conditions. The preparation of **2** from conjugated alk-1-ynes can be performed efficiently, making this a superior method to the hydroalumination reaction.[1] We are currently investigating the scope and limitations of this reaction.

Notes and references

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