Reductive 1-mono- and 1,3-diallylation of isoquinoline with allylboranes

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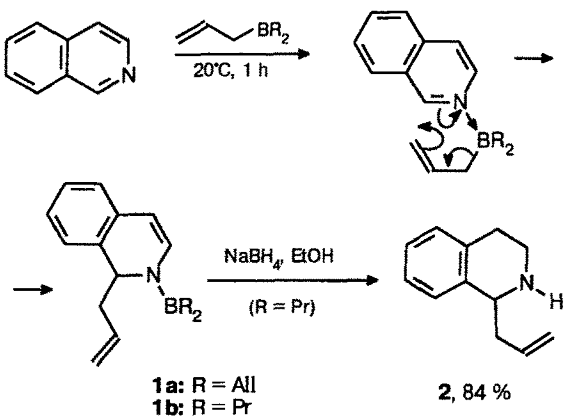
Treatment of the triallylborane-pyridine complex with alcohols leads to the complete reconstruction of the initial compound giving *trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine with a yield of up to 97 %.[1] Quinoline, 4-methylquinoline and phenantridine react with triallylborane at 20—80 °C yielding the products of 1,2-addition to C=N bond. Deboration of the latter gives the corresponding α-allylated dihydro heterocycles in more than 90 % yields.[2]

Scheme 1

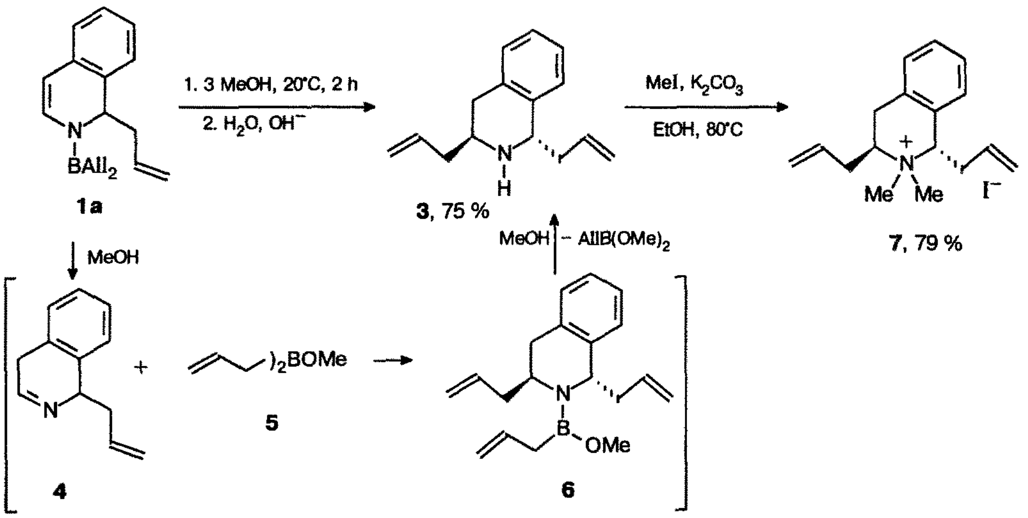


Continuing our study of nitrogen heterocycle transformations under treatment with allylic derivatives of boron, we have studied the reactions of isoquinoline with allyl(dipropyl)- and triallylborane. These reactions allowed us to obtain the products of reductive 1-monoallylation (**2**) and *trans*-1,3-diallylation (**3**). Both reactions proceed at 0—20 °C as «thermal addition» of the boron-allylic fragment to the N=C-1 bond leading correspondingly to the aminoboranes **1a** (δ^{11}B 47.4 ppm) and **1b** (b.p. 120 °C (1 Torr), δ^{11}B 51.6 ppm). The further transformations of compounds **1a** and **1b** depend on the work-up conditions (Scheme 1).

On treatment with methanol (3 equ., 20 °C, 2 h), aminoborane **1a** gives *trans*-1,3-diallyl compound **3** in 75 % yield (b.p. 103—104°C (2 Torr), n_D^{20} 1.5442). The actual mechanism of its formation is given in Scheme 2.

The protolytic deboration of compound **1a** with methanol proceeds with a double bond shift (the proton adds to the C-4 atom of the heterocycle) and leads to imine **4** and methoxy(diallyl)borane **5**. The latter quickly reacts

Scheme 2



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with **4** giving compound **6**, in which the second allylic fragment is *trans*-oriented with respect to the already present allylic group. Immediately after formation, borane **6** is split by the excess methanol present in the reaction mixture. From compound **3**, *N,N*-dimethyl salt **7** (m.p. 203—203.5 °C) and hydrochloride **3**·HCl (m.p. 139.5—140 °C), were synthesized. The *trans*-stereochemistry of the latter compound was confirmed by X-ray analysis.*

Treatment of borane **1b** with $NaBH_4$ in ethanol (20 °C, 2 h) leads to 1-allyl-1,2,3,4-tetrahydroisoquinoline **2** (84 %, n_D^{20} 1.5493; **2**·HCl, m.p. 161—162 °C). Here the reduction of imine **4** formed by the alcoholysis of **1b** takes place.

The structures of the compounds obtained were proven by instrumental methods (^{1}H, ^{13}C, ^{11}B NMR; IR; MS) and elemental analysis.

The reaction of allylmagnesium halides with isoquinoline yields 1-allylisoquinoline.[3] Ethyl-, phenyl- and benzylmagnesium halides react with isoquinoline only at 140—160 °C to give the corresponding 1-R-isoquinolines.[4]

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* X-Ray analysis was carried out at the A. N. Nesmeyanov Institute of organoelement compounds by Yu. T. Struchkov and M. O. Dekaprilevich.

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Reductive monoallylation and *trans*-2,5-diallylation of pyrrole and indole with allylboranes

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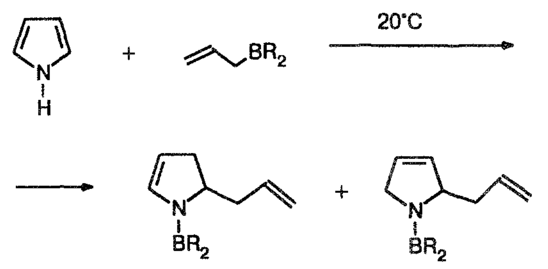
Recently, reductive *trans*-α,α'-diallylation of pyridine[1] and isoquinoline,[2] and reductive monoallylation of quinolines, phenantridine,[3] and isoquinoline[2] by treatment with allylboranes have been found in our laboratory. These amazing reactions proceed with the destruction of the aromatic system of the nitrogen heterocycles.

To continue our research in this direction we have studied the transformations of indole and pyrrole under treatment with allylic type organoboranes.

It appears that triallylborane and allyl(dipropyl)borane react with pyrrole to yield two addition products (**1a**, **2a** and **1b**, **2b**) differing in the location of the cyclic double bond (Scheme 1).

Scheme 1



1a, R = All (65 %) **2a**, R = All (35 %)
1b, R = Pr (78 %) **2b**, R = Pr (22 %)

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