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Received September 24, 1996;
in revised form December 25, 1996

Reaction of trimethallylborane with bromopyridine — the first example of reversible 1,2-allylboration of pyridines

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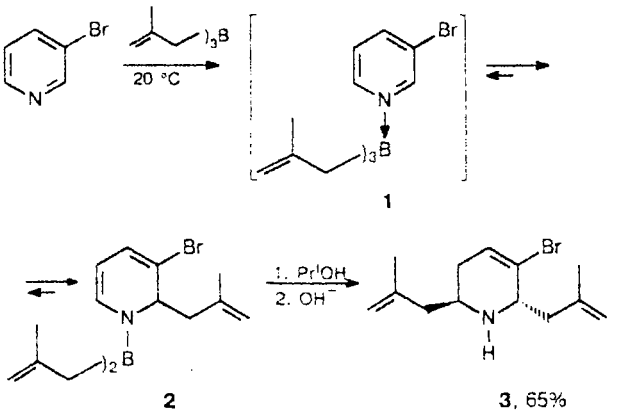
Triallyl- [1–3] and trimethallylborane[3,4] are strong Lewis acids and readily form 1 : 1 complexes with pyridine and its different derivatives. As a rule, these adducts are thermally stable but undergo complete rearrangement under the action of alcohols to give the corresponding *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridines in 70—97% yields.[5,6]

We observed that trimethallylborane (but not triallylborane) reacts with 3-bromopyridine at room temperature to give the product of 1,2-addition (**2**). The reaction proceeds so rapidly that complex **1** has not been detected (^{1}H NMR) at 20 °C (Scheme 1).

Scheme 1



This reaction is the first example of 1,2-allylboration of a pyridine compound and is of basic significance for interpretation of the mechanism of the reductive *trans*-2,6-diallylation of pyridines. Previously,[5,6] this addition has been only postulated as one of the key stages of this multistage process. It is noteworthy that 1,2-addition of organometallic compounds, *e.g.*, RLi, to pyridine was known long ago[7] and is widely used in organic synthesis.

Subsequent treatment of compound **2** with propan-2-ol (−40—20 °C) and an alkali solution resulted in the formation of amine **3** with the *trans*-arrangement of methallyl groups (yield 65%).

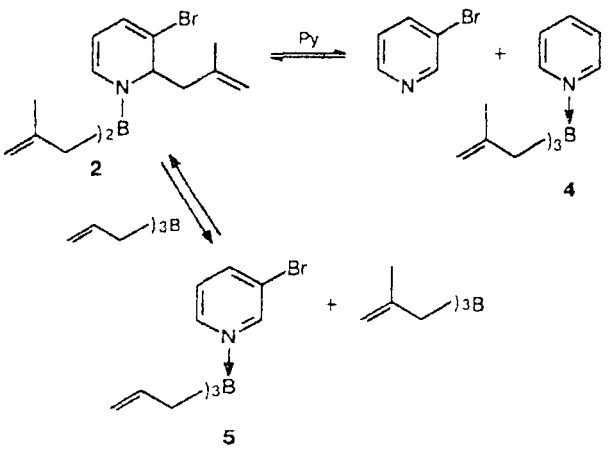
Studying the properties of dienaminoborane **2**, we also established for the first time that 1,2-allylboration of at least 3-bromopyridine is a reversible process. This is confirmed by the following data. The treatment of compound **2** with pyridine (1 : 1) gives free 3-bromopyridine and pyridine adduct **4** (46%, ^{1}H NMR). The reaction of **2** with triallylborane results in the formation of trimethallylborane and complex **5**, which, as has been shown previously,[5,6] does not give the corresponding product of 1,2-addition even after long heating at 160 °C.

The processes presented in Scheme 2 are equilibrium processes and do not proceed to completeness, since the basicity of the pyridines involved in the reaction and the Lewis acidity of the two allylboranes differ insignificantly.

Compound **2**, b.p. 90—92 °C (1 Torr), $n_D^{20.5}$=1.5365, δ^{11}B 50.2. IR (thin layer), ν/cm^{-1}: 1564, 1632, 1640, 2968, 3072. Found (%): C, 61.36; H, 7.56;

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 627—628, March, 1997.

Scheme 2



B, 3.04; Br, 23.45. $C_{17}H_{25}BBrN$. Calculated (%): C, 61.11; H, 7.54; B, 3.23; Br, 23.92.

^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.60—2.00 (m, 13 H, 3 CH_3 and 2 CH_2—B); δ_A 2.35 and δ_B 2.20 (AB-part of ABX spectrum, $^3J_{AB}$ = 13.0, $^3J_{AX}$ = 9.1, $^3J_{BX}$ = 4.4 Hz, 2 H, CH_2 of methallyl group (Met) bound to heterocycle); 4.50—4.90 (7 H, C(2)—H and CH_2=C); 5.32 (dd, 1 H, C(5)—H, $^3J_{6,5}$ = 7.4 Hz, $^3J_{4,5}$ = 5.8 Hz); 6.24 (d, 1 H, C(4)—H, $^3J_{5,4}$ = 5.8 Hz); 6.66 (d, 1 H, C(6)—H, $^3J_{5,6}$ = 7.4 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$), δ: 22.8 (q, CH_3, ^1J = 127 Hz), 37.9 (t, CH_2, ^1J = 130), 59.4 (d, C(2), ^1J = 147 Hz), 115.2 (t, CH_2=, ^1J = 157 Hz), 140 (s, =C−) are signals of methallyl group bound to the ring; 25.1 and 25.3 (q, CH_3 in B—Met, ^1J = 126 Hz); 29.7 br (t, B—CH_2, ^1J = 115 Hz); 108.0 (d, C(5), ^1J = 167 Hz); 110.9 and 111.1 (t, CH_2= in B—Met, ^1J = 153 Hz); 116.0 (s, C(3)); 123.8 (d, C(4), ^1J = 167); 129.1 (d, C(6), ^1J = 179 Hz); 144.1 and 144.5 (s, =C— in B—Met).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32555).

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Received December 25, 1996

The formation of 3-ethoxy-6-(2-hydroxyphenyl)isoxazolo[3,4-*d*]pyrimidine in the photolysis of 4-azido-5-ethoxycarbonyl-2-(2-hydroxyphenyl)pyrimidine

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Annelation of an isoxazole ring to a (hetero)aromatic ring by photolytic decomposition of *ortho*-azidoesters has not so far been reported. Irradiation of *ortho*-azidobenzoates in alcohols affords 2-alkoxy-3-methoxycarbonyl-3*H*-azepines.[1,2] After the photolysis of methyl *ortho*-azidobenzoate in an Ar-matrix at 10 K, *ortho*-2-methoxycarbonylphenylnitrene is detected; this product either undergoes ring expansion to give 3-(methoxycarbonyl)azacyclohepta-1,2,4,6-tetraene or is converted into iminoketene through a 1,4-C→N-shift of the MeO

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 629—630, March, 1997.

1066-5285/97/4603-0607 $18.00