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Unusual Products in Reactions Using Ethyldimesitylborane, Mesityllithium, and Carbonyl Compounds

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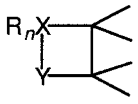
ABSTRACT: *Unusual carbonyl adducts, $Mes_2BCH=CHCHCH_3CRR^1OH$, were obtained by sequential treatment of ethyldimesitylborane with mesityllithium (<1.0 equiv.) and carbonyl compounds instead of the normal adducts, $Mes_2BCHCH_3CRR^1OH$. A mechanistic study was carried out.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:354–357, 2001

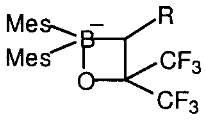
INTRODUCTION

In the course of our studies on heteracyclobutanes **1** containing a highly coordinate main group element at the position adjacent to the heteroatom [1], we have reported the synthesis of tetracoordinate 1,2-oxaboretanides **2a**, namely intermediates of the Boron–Wittig reaction under basic conditions [2,3]. During investigation on the synthesis of β-hydroxyalkyldimesitylboranes, we have found that unusual products were obtained when less than one equivalent of mesityllithium was used. We report the details of the reactions using ethyldimesitylborane and carbonyl compounds as well as the mechanistic study of the reactions.



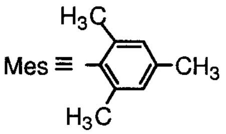
1

X= Si$^-$, Ge$^-$, Sn$^-$, P, S, Se
Y= O, N



K^+, 18-c-6

2a: R= CH_3
2b: R= H



RESULTS AND DISCUSSION

Sequential treatment of ethyldimesitylborane (**3**) with mesityllithium, carbonyl compounds such as benzophenone, 1,3-diphenyl-2-propanone, and benzaldehyde, and then aqueous NH_4Cl gave unusual adducts **4** and **5** and a diastereomeric mixture of **6a** and **6b** [4], respectively, instead of normal adducts **7**. The results are shown in Scheme 1.

^1H and ^{13}C NMR and 2D NMR spectroscopy revealed that compounds **4–6** have the $CH=CH$ group between the boron and methine carbon atoms of **7**. It is known that use of excess (1.5–2.0 equiv.) mesityllithium gave an orange solution, and the following reactions with carbonyl compounds gave usual products **7** [2,5]. On the other hand, the solution color after the reaction with less than one equivalent of mesityllithium became green or brown [6], and

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Dedicated to Prof. Naoki Inamoto on the occasion of his 72nd birthday.

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no dimesitylpropylborane was obtained when the green solution was treated with iodomethane, indicating that the expected $Mes_2BCHLiCH_3$ (**8**) does not remain in the solution [7]. In order to clarify the formation mechanism of **4**–**6**, we performed the ${}^{11}B$ NMR measurement of the green solution and quenched the reaction mixture with water.

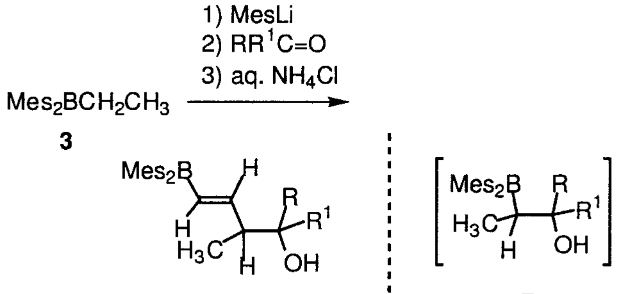
The ${}^{11}B$ NMR spectrum of the green solution showed four signals at δ −23.5 (t, ${}^{1}J_{BH}$ = 73 Hz), −12.8 (d, ${}^{1}J_{BH}$ = 78 Hz), 36 (br s), and 84 (br s), which were assigned to $[Mes_2BH_2]^-Li^+$ (**9**), $[Mes_2BHCH_2CH_3]^-Li^+$ (**10**), $[Mes_2BCH\text{-}CH\text{-}CHCH_3]^-Li^+$ (**11**), and **3**, respectively. This signal assignment was carried out by comparison with those of authentic samples, except for the signal at δ 36, as follows: borates **9** and **10** were prepared by sequential treatment of Mes_2BF with $LiAlH_4$ and then LiH, and treatment of **3** with *t*-BuLi, respectively [8,9].

As shown in Scheme 2, quenching the green solution with H_2O gave **3** (43%), **12** (5%), and **13** (20%). Although quenching with D_2O gave **12**-d_1, **3**-d_1 was not obtained, also indicating the absence of **8**. Although a borylallylic anion is known [10], its ${}^{11}B$ NMR spectrum has not been reported. It is most likely that the signal at δ 36 is attributable to **11**, which causes the change of the color, judging from the results of water-quenching experiments.

Thus, it can be concluded that the origin of the CH = CH group of **4**–**6** is the ethyl group of **3** and that the precursor of **4**–**6** is **11**. Borates **9** and **10** were treated with water to give Mes_2BH and **3**, respectively, the former of which was oxidized to afford Me_2BOH (**13**) during the workup. The addition of **11** to carbonyl compounds took place at the γ-position rather than the α-position, because of steric hindrance by bulky mesityl groups [10].

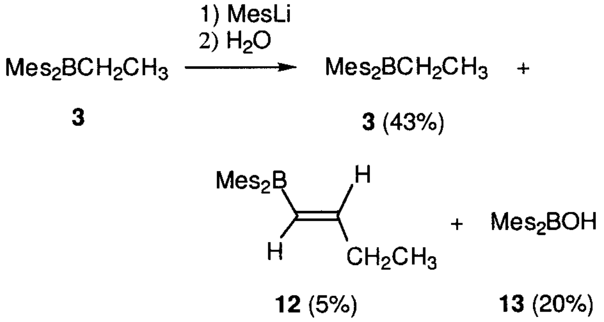
The plausible mechanism of the formation of **4**–**6** is shown in Scheme 3. The deprotonation of **3** with mesityllithium gives **8**. Hydride shift from **8** to unreacted **3** [11] affords dimesitylvinylborane (**14**) and borate **10**. Michael type addition of **8** to **14** takes place to give diborylcarbanion **15** that affords **11** with elimination of Mes_2BH (**16**) [12]. The reaction of **11** with carbonyl compounds gives **4**–**6** and **16** acts as a hydride acceptor of **8** and/or **10** to give **9**.

In summary we have demonstrated that unusual adducts are formed in the reactions using close to one equivalent of MesLi and that key steps of this reaction are a hydride shift from an α-lithioalkylborane to an unreacted alkylborane and the formation of α-borylallylic anion.

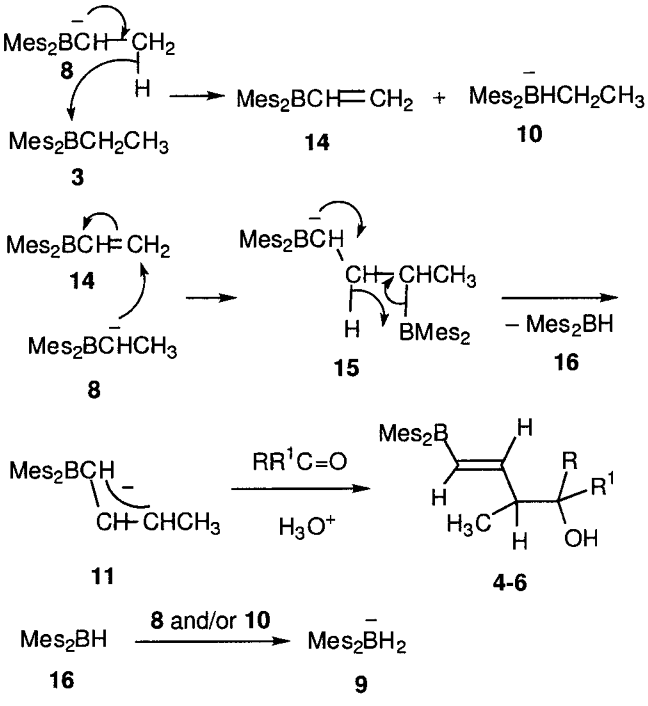


4: R, R^1= Ph (7%)
5: R, R^1= CH_2Ph (18%)
6: R, R^1= H, Ph (**a**: 22%, **b**:12%)

SCHEME 1



SCHEME 2



SCHEME 3 Plausible mechanism for the formation of **4–6** (Cation is omitted for clarity).

EXPERIMENTAL

All solvents used in the reactions were purified by the reported methods. Tetrahydrofuran (THF) was purified by distillation from diphenylketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Dry column chromatography (DCC) was performed with ICN silica DCC 60A. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAIGEL 1H + 2H columns (Japan Analytical Industry) with chloroform or toluene as solvent. ^1H NMR spectra were recorded on a JEOL JNM-A500, or a Bruker AM-500 spectrometer, operated at 500 MHz. ^{13}C NMR spectra were recorded on a Bruker AM-500 or a JEOL JNM-A500 spectrometer at 126 MHz. ^{11}B (86 MHz) NMR spectra were recorded on a JEOL EXcalibur270 spectrometer, whose chemical shifts were relative to $Et_2O \cdot BF_3$. High resolution mass spectra were obtained with a JEOL JMS-SX102L spectrometer.

*Reactions of Ethyldimesitylborane (**3**) with Mesityllithium*

With Benzophenone. To a solution of bromomesitylene (0.23 mL, 1.5 mmol) in THF (3 mL) was added *t*-BuLi (1.62 M pentane solution, 2.0 mL, 3.2 mmol) at −72°C, and the mixture was stirred for 30 minutes and then allowed to warm to room temperature. To the orange solution was added a solution of ethyldimesitylborane (**3**) (409 mg, 1.5 mmol) in THF (1.5 mL), and the reaction mixture was stirred for 1 hour. The color of the solution became brown. To the solution was added a solution of benzophenone (415 mg, 1.9 mmol) in THF (1.5 mL) at −72°C, and the mixture was stirred for 1 hour. After addition of saturated aqueous NH_4Cl, the organic layer was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After removal of the solvent, the residue was subjected to DCC (SiO_2, hexane-CH_2Cl_2 [1:1]), followed by GPLC to give $Ph_2C{=}CHCH_3$ (40%), **4** (7%), and **13** (40%). The formation of $Ph_2C{=}CHCH_3$ (40%) indicates that at least 40% of $Mes_2BCHLiCH_3$ (**8**) remained.

Compound **4**: colorless crystals, m.p. 138–139°C (hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 1.03 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.96 (s, 12H, *o*-CH_3 of Mes), 2.24 (s, 6H, *p*-CH_3 of Mes), 3.63 (dq, $^3J_{HH}$ = 6.8, 8.2 Hz, 1H, $C\underline{H}CH_3$), 6.41 (dd, $^3J_{HH}$ = 8.2, 17.5 Hz, 1H, $BCH{=}C\underline{H}$), 6.71 (d, $^3J_{HH}$ = 17.5 Hz, 1H, $BC\underline{H}{=}CH$), 6.71 (s, 4H, *m*-H of Mes), 7.11 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-H of Ph), 7.16 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-H of Ph), 7.19 (t, $^3J_{HH}$ = 7 Hz, 2H, *m*-H of Ph), 7.27 (t, $^3J_{HH}$ = 7 Hz, *m*-H of Ph), 7.40 (d, $^3J_{HH}$ = 7 Hz, 2H, *o*-H of Ph), 7.47 (d, $^3J_{HH}$ = 7 Hz, 2H, *o*-H of Ph); ^{13}C NMR ($CDCl_3$, 125 Hz) δ 14.7 (q, CH_3), 21.1 (q, *p*-CH_3 of Mes), 23.0 (q, *o*-CH_3 of Mes), 48.0 (d, $\underline{C}HCH_3$), 79.8 (s, $Ph_2\underline{C}OH$), 125.7 (d, *o*-C of Ph), 125.9 (d, *o*-C of Ph), 126.5 (d, *p*-C of Ph), 126.6 (d, *p*-C of Ph), 128.0 (d, *m*-C of Mes), 128.1 (d, *m*-C of Ph), 128.2 (d, *m*-C of Ph), 138.1 (s, *p*-C of Mes), 140.3 (s, *o*-C of Mes), 141.9 (br s, B-$\underline{C}H{=}CH$), 146.0 (s, *ipso*-C of Ph), 146.4 (s, *ipso*-C of Ph), 158.7 (d, B-$CH{=}\underline{C}H$). The signal due to *ipso*-C of Mes was not observed. HRMS (70 eV) *m/z* calcd for $C_{35}H_{37}{}^{11}B$ (M^+-H_2O) 433.2515, found 433.2493. Anal. Calcd for $C_{35}H_{39}BO \cdot 1/4\ H_2O$: C, 85.62; H, 8.11. Found: C, 85.77; H, 8.12.

With 1,3-Diphenyl-2-propanone. To a solution of bromomesitylene (0.22 mL, 1.4 mmol) in THF (3 mL) was added *t*-BuLi (1.62 M pentane solution, 1.7 mL, 2.8 mmol) at −72°C, and the mixture was stirred for 15 minutes and then allowed to warm to room temperature. To the orange solution was added a solution of ethyldimesitylborane (**3**) (409 mg, 1.5 mmol) in THF (1.5 mL), and the reaction mixture was stirred for 1 hour. The color of the solution became red brown. To the solution was added a solution of 1,3-diphenyl-2-propanone (294 mg, 1.1 mmol) in THF (1.5 mL) at −72°C, and the mixture was stirred for 1 hour. When the temperature was allowed to warm to −45°C, the color of the solution became green. After addition of saturated aqueous NH_4Cl, the organic layer was extracted with CH_2Cl_2, and the extracts were dried over $MgSO_4$. After removal of the solvent, the residue was subjected to DCC (SiO_2 and hexane–CH_2Cl_2 [1:1]) followed by GPLC to give **3** (22%), 4-benzyl-4-hydroxy-3-methyl-5-phenyl-1-pentenyldimesitylborane (**5**) (18%), and **13** (19%).

Compound **5**: colorless viscous oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 2.19 (s, 12H, *o*-CH_3 of Mes), 2.28 (s, 6H, *p*-CH_3 of Mes), 2.50 (dq, $^3J_{HH}$ = 6.9, 7.1 Hz, 1H, $C\underline{H}CH_3$), 2.61 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CHHPh), 2.69 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CHHPh), 2.74 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CHHPh), 2.87 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CHHPh), 6.61 (dd, $^3J_{HH}$ = 7.1, 17.3 Hz, 1H, $BCH{=}C\underline{H}$), 6.74 (d, $^3J_{HH}$ = 17.3 Hz, 1H, $BC\underline{H}{=}CH$), 6.81 (s, 4H, *m*-H of Mes), 7.09–7.27 (m, 10H, Ph); HRMS (70 eV) *m/z* calcd for $C_{37}H_{43}{}^{11}B$ (M^+) 514.3407, found 514.3433.

With Benzaldehyde. A similar reaction using bromomesitylene (0.11 mL, 0.7 mmol), *t*-BuLi (1.77 M pentane solution, 0.8 mL, 1.4 mmol), **3** (176 mg, 0.63 mmol), and benzaldehyde (0.1 mL, 0.98 mmol) was carried out. After addition of a solution of **3**, the color of the solution became green. Dry column chromatography of the residue gave **3** (21%), less polar diastereomer **6a** (22%), and polar diastereomer **6b** (12%) of 4-hydroxy-3-methyl-5-phenyl-1-butenyldimesitylborane.

Compound **6a**: colorless crystals: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 2.01 (s, 12H, *o*-CH_3 of Mes), 2.26 (s, 6H, *p*-CH_3 of Mes), 2.70 (ddq, $^3J_{HH}$ = 6.7, 6.8, 7.7 Hz, 1H, $C\underline{H}CH_3$), 4.56 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CHPh), 6.28 (dd, $^3J_{HH}$ = 7.7, 17.3 Hz, 1H, $BCH{=}C\underline{H}$), 6.56 (d, $^3J_{HH}$ = 17.3 Hz, 1H, $BC\underline{H}{=}CH$), 6.74 (s, 4H, *m*-H of Mes), 7.22–7.27 (m, 5H, Ph).

Compound **6b**: colorless crystals: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 2.14 (s, 12H, *o*-CH_3 of Mes), 2.28 (s, 6H, *p*-CH_3 of Mes), 2.70 (dt, $^3J_{HH}$ = 6.9, 8.1, 8.1 Hz, 1H, $C\underline{H}CH_3$), 4.47 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CHPh), 6.44 (dd, $^3J_{HH}$ = 8.1, 17.3 Hz, 1H, $BCH{=}C\underline{H}$), 6.75 (d, $^3J_{HH}$ = 17.3 Hz, 1H, $BC\underline{H}{=}CH$), 6.79 (s, 4H, *m*-H of Mes), 7.24–7.32 (m, 5H, Ph).

With Water. A similar reaction using bromomesitylene (0.06 mL, 0.36 mmol), *t*-BuLi (1.62 M pentane solution, 0.44 mL, 0.72 mmol), and **3** (101 mg, 0.36 mmol) was carried out. After addition of a solution of **3**, the color of the solution became green. After stirring was continued for 12 hours, water was added to the solution. The organic layer was extracted with hexane, and the extracts were dried over $MgSO_4$. After removal of the solvent, the residue was subjected to GPLC to **3** (43%), 1-butenyldimesitylborane (**12**) (5%), and **13** (20%).

Compound **12**: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3), 2.16 (s, 12H, *o*-CH_3 of Mes), 2.22–2.26 (m, 2H, CH_2), 2.27 (s, 6H, *p*-CH_3 of Mes), 6.51 (dt, $^3J_{HH}$ = 17.4, 5.8 Hz, 1H, $BCH{=}C\underline{H}$), 6.64 (dt, $^3J_{HH}$ = 17.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $BC\underline{H}{=}CH$), 6.79 (s, 2H, *m*-H of Mes); $^{13}C\{^1H\}$ NMR(126 MHz, $CDCl_3$) δ 12.1 (s, $CH_2\underline{C}H_3$), 21.1 (s, *p*-CH_3 of Mes), 23.2 (s, *o*-CH_3 of Mes), 29.0 (s, $\underline{C}H_2CH_3$), 128.1 (s, *m*-C of Mes), 138.1, 139.1 (br s, $B\underline{C}H{=}CH$), 140.4, 142.2 (br s, *ipso*-C of Mes), 160.6 (s, $BCH{=}\underline{C}H$); ^{11}B NMR (86 MHz, $CDCl_3$) δ 70.7. HRMS (70 eV) *m/z* calcd for $C_{22}H_{19}{}^{11}B$ (M^+) 304.2362, found 304.2366.

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