Novel Synthesis of 2,3-Bisboryl-1,3-dienes from 1-Bromo-1-lithioethene and 1,1-Bisborylalkenes

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This paper is dedicated to Professor Ryoji Noyori on the occasion of his retirement of Nagoya University, Japan

Abstract: Treatment of 1,1-[bis(pinacolato)boryl]alkenes with excess of 1-bromo-1-lithioethene was found to give 2,3-bis-[pinacolato]boryl]-1,3-dienes in moderate to good yields. Synthetic applications of 2,3-[bis(pinacolato)boryl]-1,3-butadiene were also demonstrated.

Key words: boron, lithium, carbenoids, insertion, alkenes

Alkenylboron compounds are readily accessible and extremely useful reagents in organic synthesis.¹ In contrast, bis(alkenylboron) compounds have attracted less attention probably because their facile syntheses are quite limited,² though bis(alkenylboron) compounds would be employed for an efficient synthesis of polysubstituted olefins through double carbon-carbon bond formation with retention of configuration by a simple experimental operation. Very recently, we found that treatment of bis(pina-

Treatment of 1-bromo-1-lithioethene (1 mol), generated from vinyl bromide and lithium 2,2,6,6-tetramethylpiperidine (LiTMP) in THF- Et₂O (2:1) at -110 °C, with 1,1-bis[(pinacolato)boryl]ethene 2a (1 mol) at -110 °C gave 2,3-bisboryl-1,3-butenediene 5a in 7% yield (Scheme 2). In view that diboron 1 reacts with an equimolar amount of 1-bromo-1-lithioethene to give 2a in 91% yield,³ the low yield indicates that the reaction of the carbenoid with 2a is slower than with 1 and apparently competes with the decomposition of the lithium carbenoid. Then, we increased the amount of the carbenoid reagent, and observed that 72% yield was achieved when 5 molar equivalents of vinyl bromide and LiTMP were employed as shown in Scheme 2.⁶,⁷ Noteworthy is that 5a can be purified by column chromatography on silica gel since 2-boryl-1,3-diene is reported to be highly susceptible to dimerization.⁸ Carbenoid generation carried out in the presence of 2a gave 5a in lower yield (59%), while reaction of 2-substituted 1-bromo-1-lithioethene with 2a did not proceed at all.

The optimized conditions were applied to 2-monosubstituted bisborylalkenes 2b and 2c. The corresponding conjugated triene 5b as an E/Z mixture (73:27) and dienene 5c as the only E-isomer were respectively isolated in 74% and 38% yields.⁹ The stereochemical outcome indicates that 1-bromo-1-lithioethene preferentially attacks the

E R' \[ \text{LiBr} \]

Scheme 2. Synthesis of 2,3-bisboryl-1,3-diene 5a

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sterically less hindered boron atom of 2. Reaction of 2,2-disubstituted-1,1-diborylethenes 2d and 2e also took place smoothly, giving rise to 5d and 5e in good yields.

Scheme 3 Synthesis of 2,3-bisboryl-1,3-diene 5

One-pot synthesis of 5a from 1 is possible. As shown in Scheme 4, treatment of vinyl bromide (5 mol) with LiTMP (5 mol) followed by the addition of diboron 1 produced 5a in 82% yield.

Scheme 4 One-pot synthesis of 5a from 1

Synthetic utility of 2,3-bisboryl-1,3-butadiene 5a is demonstrated in Scheme 5. Diels–Alder reaction of 5a is particularly accelerated by the two boryl groups and indeed proceeded with maleimide even at room temperature to give 1,2-bisborylated cyclohexene 6 in 93% yield. Cross-coupling reaction with iodobenzene catalyzed by Pd(PPh3)4 allowed us to prepare 2,3-diphenyl-1,3-butadiene 7.11 1,2,3,4-Tetramethyl-2-butenes 8 or 1-silyl-2,3,4-tris(boryl)-2-butenes 9 was synthesized as a single diastereomer by Pt-catalyzed 1,4-addition reaction with bis(pinacolato)boron 1 or (dimethylphenylsilyl)(pinacolato)boron 3.12 The highly borylated compounds 8 and 9 contain both alkenyl- and allylmetal moieties and thus may serve as valuable synthetic reagents.

Scheme 5 Synthetic applications of 2,3-diboryl-1,3-butadiene

In summary, we have established a novel synthesis of 2,3-bisboryl-1,3-dienes from 1-bromo-1-lithioethene and 1,1-bisborylalkenes. We can transform 2,3-bisboryl-1,3-dienes into various types of complex molecules using the boron functionality as a key element before/after unique reactions of 1,3-dienes. Further studies based on 2,3-bisboryl-1,3-dienes are in progress in our laboratory.

Acknowledgement

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References and Notes


Representative procedure of further insertion of the carbenoid reagent appears to be a) Oppolzer, W. In Hata, T.; Kitagawa, H.; Masai, H.; Kurahashi, T.; Shimizu, M.; Shimizu et al. Bisboryl-1,3-dienes: a) Zweifel, G.; Polston, N. L. added a THF solution of vinyl bromide (1.0 M, 500 NH₄Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The reaction mixture was quenched with three drops of sat. aq MgSO₄ and the resulting mixture was gradually allowed to warm up to room temperature and stirred for 12 h. (1) Bisborylation of 1,3-dienes: Ishiyama, T.; Yamamoto, M.; Miyaura, N., Suzuki, A. Alder reaction of 1,3,-dienes: Ishiyama, T.; Yamamoto, M.; Miyaura, N. 2,2,6,6-tetramethylpiperidine (84 mmol) at 0 °C for 5 min. To this solution was added a THF solution of vinyl bromide (1.0 M, 500 mmol) at −110 °C and 1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (2a) (25 mg, 0.10 mmol) in THF (0.1 mL) successively. The resulting mixture was gradually allowed to warm up to room temperature and stirred for 12 h. The reaction mixture was quenched with three drops of sat. aq NH₄Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200 mesh silica gel, ethyl acetate-hexane = 1:10) to give 5a (22 mg, 72% yield). Mp: 140 °C (dec). TLC: R = 0.33 (hexane-ethyl acetate = 10:1). ¹H NMR (200 MHz, CDCl₃) δ 1.28 (s, 24H), 5.85 (d, J = 3.9 Hz, 2H), 5.96 (d, J = 3.9 Hz, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 24.8, 83.5, 130.6. IR (nujol) 1460, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm⁻¹; MS (70 eV) m/z 307 (M⁺+1, 7.0), 306 (M⁺, 40.0), 305 (M⁺-1, 19.6), 291 (M⁺-Me, 8.5), 165 (100). Anal. Calcd for C₂₄H₂₇B₂O₃: C, 62.80; H, 8.52. Found: C, 62.53; H, 9.42.

Further insertion of the carbenoid reagent appears to be inhibited; a reason is unclear at present.

Representative procedure of 5a: Butyllithium in hexane (1.56 M, 321 μL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (84 μL, 0.50 mmol) in a mixture of THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. To this solution was added a THF solution of vinyl bromide (1.0 M, 500 mmol, 0.50 mmol) at −110 °C and 1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (2a) (25 mg, 0.10 mmol) in THF (0.1 mL) successively. The resulting mixture was gradually allowed to warm up to room temperature and stirred for 12 h. The reaction mixture was quenched with three drops of sat. aq NH₄Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200 mesh silica gel, ethyl acetate-hexane = 1:10) to give 5a (22 mg, 72% yield). Mp: 140 °C (dec). TLC: R = 0.33 (hexane-ethyl acetate = 10:1). ¹H NMR (200 MHz, CDCl₃) δ 1.28 (s, 24H), 5.85 (d, J = 3.9 Hz, 2H), 5.96 (d, J = 3.9 Hz, 2H). ¹³C NMR (50 MHz, CDCl₃) δ 24.8, 83.5, 130.6. IR (nujol) 1460, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm⁻¹; MS (70 eV) m/z 307 (M⁺+1, 7.0), 306 (M⁺, 40.0), 305 (M⁺-1, 19.6), 291 (M⁺-Me, 8.5), 165 (100). Anal. Calcd for C₂₄H₂₇B₂O₃: C, 62.80; H, 8.52. Found: C, 62.53; H, 9.42.

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(10) The detail of Diels–Alder reaction of 5a will be reported in due course.


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