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A Novel [3+2] Annelation between *ortho*-Carboranyltrimethylsilane and Conjugated Carbonyl Compounds

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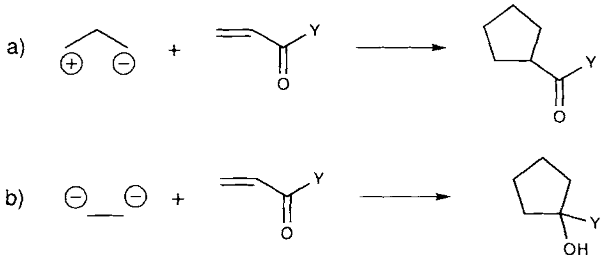
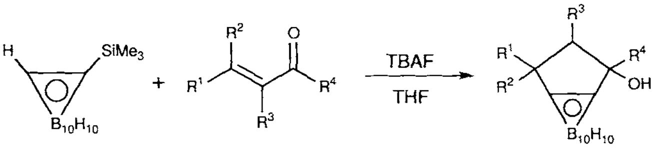
Bakthan Singaram, Jianping Cai, Hisao Nemoto, and
Yoshinori Yamamoto*

The most efficient method for the construction of five-membered carbocyclic rings is a [3+2] annulation process.[1] Perhaps the most widely utilized strategy in this regard is one in which dipolar C_3 units are utilized in conjunction with electron-deficient olefins (dipolar C_2 synthons) to achieve [3+2] annulation (Scheme 1a).[1,2] However, [3+2] annulation between dianionic C_2 and dicationic C_3 building blocks are less common than dipolar annulations.[3] This approach has been used to investigate the coupling of the 1,3-dihalides or β-haloesters with the doubly charged succinate anions[4] or tetraethoxycarbonylethyl anions.[5] We report here that [3+2] annulation between dianionic C_2 units and α,β-unsaturated ketones and aldehydes (dicationic C_3 synthons) gives the corresponding five-membered carbocycles (Scheme 1b).



Scheme 1. [2+3] annulation of dipolar C_3 and C_2 building blocks (a) and of dianionic C_2 and dicationic C_3 building blocks (b).

The TBAF-mediated (TBAF = tetrabutylammonium fluoride) reaction of 1,2-dicarba-*closo*-dodecaboran(12)-1-trimethylsilane (**1**)[6] with enones and enals **2** gave the five-membered carbocyclic compounds **3** in good yields (Tables 1 and 2).[7,8] The cycloaddition of **1** to form crotonaldehyde **2a** proceeded smoothly at 25 °C in the presence of three equivalents of TBAF, giving **3a** in 83% yield with a 58:42 mixture of *syn* and *anti* diastereoisomers (entry 1, Table 1). The use of catalytic amounts of TBAF gave a lower chemical yield. The *syn* configuration of the major diastereoisomer of **3a** was confirmed unambiguously by X-ray analysis (Figure 1). The reaction of 2-methylpropenal **2b** gave **3b** in 48% yield with a *syn/anti* ratio of 17/83 (entry 2). The stereochemistry of the major isomer of **3b**



1 **2** **3**

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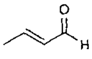
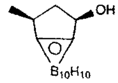
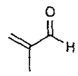
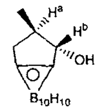
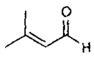
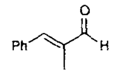
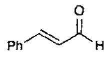
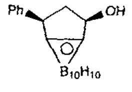
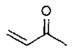
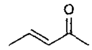
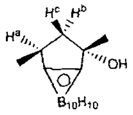
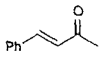
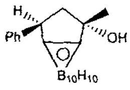
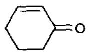
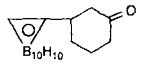
Table 1. Reaction of **1** with **2** [a].

Entry	Enones and Enals		Product [b]		Yield [%]	d.r. [c] (*syn*:*anti*)
1		**2a**		**3a**	83	58:42
2		**2b**		**3b**	48	17:83
3		**2c**		**3c**	77	–
4		**2d**		**3d**	81	[d]
5		**2e**		**3e**	76 [e]	56:44
6		**2f**		**3f**	74	–
7		**2g**		**3g**	52	40:60
8		**2h**		**3h**	35 [f]	21:79
9		**2i**		**4**	39	–

[a] Typical method: To a solution of **1** (1 equiv) and **2a** (1.1 equiv) in THF was added TBAF (3 equiv) at room temperature under argon, and the mixture was stirred for 10 min. The reaction was stopped by addition of water, and the solution extracted with diethyl ether. The solvent was removed under vacuum, and the residue purified by column chromatography over silica gel (hexane/AcOEt, 10/1). [b] For compounds for which the configuration could be determined without doubt the major diastereomer is shown. [c] The diastereomer ratio was determined by ^{1}H NMR spectroscopy, and the configuration of the products by X-ray crystallography (**3a**), NOE NMR spectroscopy (**3b** and **3g**), or by comparison with the configurations of **3a** (**3e**) and **3g** (**3h**). [d] Three diastereomers were obtained in the ratio 55:34:11; their configurations were not determined. [e] Duration of the reaction: 35 min. [f] The reaction was sluggish, and after 16 h the product was obtained in 35% yield.

Table 2. Spectroscopic data for the carboracyclopentanes **3** as well as for **4**.

3a: white solid; IR (KBr): $\tilde{\nu}$ = 3325, 2976, 2586, 1458, 1384, 1342, 1166, 731 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(*syn* isomer) = 4.72 (m, 1H), 2.82 (m, 2H), 2.24 (d, J = 5.5 Hz, 1H), 1.71 (m, 1H), 1.17 (d, J = 6.0 Hz, 3H); δ(*anti* isomer) = 4.65 (m, 1H), 3.01 (m, 1H), 2.36 (m, 1H), 2.25 (m, 1H), 2.05 (d, J = 5.0 Hz, 1H), 1.13 (d, J = 6.0 Hz, 3H); elemental analysis: calcd for $C_6H_{18}OB_{10}$: C 33.63, H 8.47; found: C 33.98, H 8.41

3b: white solid; IR (CCl$_4$): $\tilde{\nu}$ = 3583, 3363, 2970, 2588, 665 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(*anti* isomer) = 4.31 (t, J = 6.0 Hz, 1H), 2.60 (m, 2H), 2.28 (d, J = 5.6 Hz, 1H), 2.06 (dd, J = 12.8, 8.8 Hz, 1H), 1.20 (d, J = 7.2 Hz, 3H); δ(*syn* isomer) = 4.55 (dd, J = 7.6, 6.0 Hz, 1H), 3.01 (m, 1H), 2.60 (m, 1H), 2.18 (d, J = 6.0 Hz, 1H), 2.13 (dd, J = 13.6, 9.2 Hz, 1H), 1.05 (d, J = 7.2 Hz, 3H); elemental analysis: calcd for $C_6H_{18}OB_{10}$: C 33.63, H 8.47; found: C 33.36, H 8.47

3c: white solid; IR (KBr): $\tilde{\nu}$ = 3367, 2978, 2596, 1334, 1074 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 4.67 (ddd, J = 8.0, 5.1, 5.0 Hz, 1H), 2.54 (dd, J = 14.8, 8.0 Hz, 2H), 2.18 (d, J = 5.0 Hz, 1H), 2.02 (dd, J = 14.8, 5.1 Hz, 1H), 1.37 (d, J = 5.0 Hz, 3H), 1.32 (d, J = 5.0 Hz, 3H); HR-MS (EI): *m*/*z* calcd for $C_7H_{20}OB_{10}$: 230.2445; found: 230.2443; elemental analysis: calcd for $C_7H_{20}OB_{10}$: C 36.82, H 8.83; found: C 36.45, H 8.95

3d: white solid; IR (CCl$_4$): $\tilde{\nu}$ = 3853, 3448, 3066, 2968, 2588, 1498, 1149 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(α isomer) = 7.42–7.23 (m, 5H), 4.43 (dd, J = 7.0, 5.5 Hz, 1H), 3.53 (d, 10.5 Hz, 1H), 2.83–2.67 (m, 1H), 2.43 (d, J = 5.5 Hz, 1H), 1.14 (d, J = 7.0 Hz, 3H); δ(β isomer) = 7.42–7.23 (m, 5H), 4.67 (dd, J = 8.0, 5.5 Hz, 1H), 3.61 (d, 10.5 Hz, 1H), 3.19–3.08 (m, 1H), 2.25 (d, J = 5.5 Hz, 1H), 0.98 (d, J = 7.0 Hz, 3H); δ(γ isomer) = 7.42–7.23 (m, 5H), 4.52 (dd, J = 7.0, 5.5 Hz, 1H), 4.04 (d, 10.5 Hz, 1H), 3.07–2.97 (m, 1H), 2.30 (d, J = 5.5 Hz, 1H), 1.06 (d, J = 7.0 Hz, 3H); elemental analysis: calcd for $C_{12}H_{22}OB_{10}$: C 49.63, H 7.64; found: C 49.34, H 7.60

3e: white solid; IR (CCl$_4$): $\tilde{\nu}$ = 3583, 3413, 2586, 1748, 1074, 794 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(*syn* isomer) = 7.15–7.34 (m, 5H), 4.82 (m, 1H), 4.16 (dd, J = 9.5, 9.0 Hz, 1H), 2.83–3.05 (m, 1H), 2.39–2.53 (m, 1H), 2.10 (d, J = 3.0 Hz, 1H); δ(*anti* isomer) = 7.15–7.34 (m, 5H), 4.82 (m, 1H), 3.92 (dd, J = 9.0, 8.5 Hz, 1H), 2.83–3.05 (m, 1H), 2.39–2.53 (m, 1H), 2.10 (d, J = 3.0 Hz, 1H); HR-MS (EI): *m*/*z*: calcd for $C_{11}H_{20}OB_{10}$: 278.2452; found 278.2452

3f: white solid; IR (KBr): $\tilde{\nu}$ = 3583, 3467, 2991, 2956, 2592, 1452, 1379 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 2.33–2.63 (m, 4H), 2.08 (s, 1H), 1.62 (s, 1H); elemental analysis: calcd for $C_6H_{18}OB_{10}$: C 33.63, H 8.47; found: C 33.50, H 8.81

3g: white solid; IR (KBr): $\tilde{\nu}$ = 3565, 3487, 2856, 2594, 1452, 1385 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(*anti* isomer) = 3.08–2.93 (m, 1H), 2.45 (dd, J = 14.5, 7.7 Hz, 1H), 2.05 (s, 1H), 1.95 (dd, J = 14.5, 10.0 Hz, 1H), 1.55 (s, 3H), 1.11 (d, J = 6.5 Hz, 3H); δ(*syn* isomer) = 2.87–2.77 (m, 1H), 2.60 (dd, J = 14.5, 8.5 Hz, 1H), 2.00 (m, 1H), 1.62 (s, 3H), 1.18 (d, J = 6.5 Hz, 3H); elemental analysis: calcd for $C_7H_{26}OB_{10}$: C 36.82, H 8.83; found: C 36.81, H 8.85

3h: white solid; IR (CCl$_4$): $\tilde{\nu}$ = 3583, 3467, 2580, 2310, 2343, 665 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ(*anti* isomer) = 7.24–7.41 (m, 5H), 4.21 (dd, J = 10.5, 8.0 Hz, 1H), 2.75 (dd, J = 14.0, 10.5 Hz, 1H), 2.67 (dd, J = 14.0, 8.0 Hz, 1H), 2.13 (s, 1H), 1.69 (s, 3H); δ(*syn* isomer) = 7.24–7.41 (m, 5H), 4.04 (t, J = 8.0 Hz, 1H), 2.77 (m, 2H), 2.17 (s, 1H), 1.74 (s, 3H); elemental analysis: calcd for $C_{12}H_{21}OB_{10}$: C 49.80, H 7.31; found: C 49.57, H 7.28

4: yellow liquid; IR (neat): $\tilde{\nu}$ = 3781, 3085, 3060, 2933, 2586, 1716 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 3.66 (s, 1H), 1.20–2.66 (m, 9H); HR-MS (EI): *m*/*z*: calcd for $C_8H_{20}OB_{10}$: 242.2445; found 242.2452

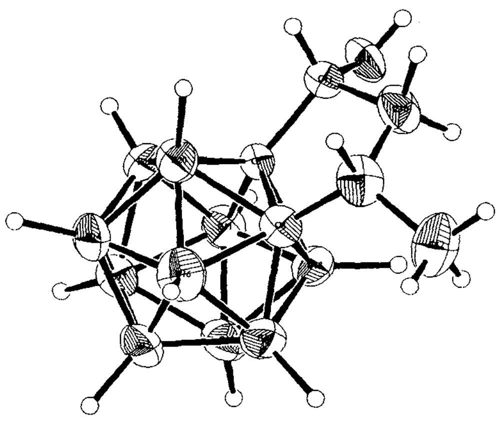


Figure 1. Crystal structure of the cyclic adduct **3a**.

was determined by NOE experiments. Since NOEs were observed between CH$_3$ protons and H^b but not between H^b and H^a, the configuration of the major isomer was *anti*. The stereochemistry of the minor isomer (*syn*) was also determined by NOE experiments. The yields in the reactions with 3-substituted aldehydes (**2a** and **2c–e**) were higher than those with 3-unsubstituted aldehyde (**2b**), as shown in Table 1 entries 1–5. The diastereoisomer ratio of **3d** was determined by 400 Hz ^{1}H NMR spectroscopy, but the stereochemistry of those isomers was not determined. Even α,β-unsaturated ketones reacted with **1** under the same reaction conditions as above to afford the cyclic adducts in good to acceptable yields (entries 6-8). The reaction of **1** with **2g** gave **3g** in 52% yield with a *syn*/*anti* ratio of 40/60. NOEs were observed between H^a and H^b, and between H^c and protons of CH$_3$ attached to the OH-substituted C atom of **3g**, thus indicating that the configuration of the major isomer was *anti* (see **3g**). However, a phenyl group at the γ-position of the enone led to higher diastereoselectivity (*syn*/*anti* = 21/79, entry 8), although the substituent groups at the γ-position of enals did not affect the diastereoselectivity (entries 1 and 5). Cyclohexenone **2i**, which has a fixed s-*trans* enone configuration, gave the corresponding 1,4-addition compound **4** in 39% yield instead of affording the expected annulation product (entry 9).

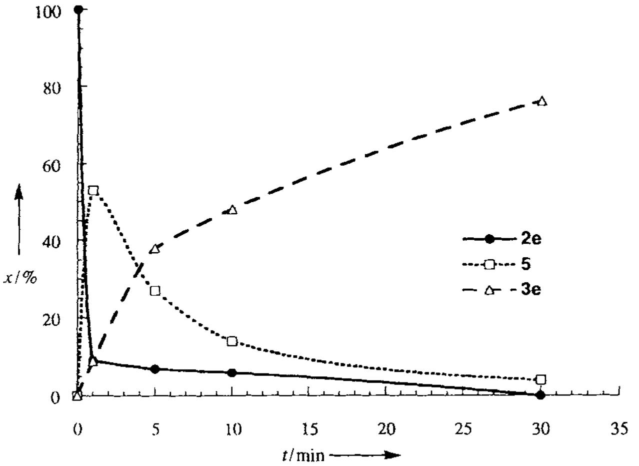
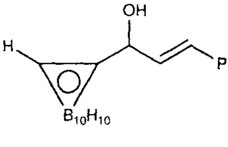


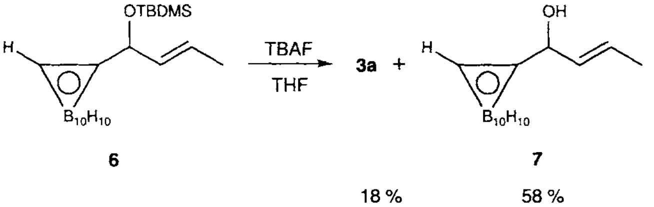
Figure 2. Concentrations of **3e** and **5** with time during the reaction of **1** and **2e** catalyzed by TBAF in THF. The amount of product x (yields) were determined by ^{1}H NMR spectroscopy.



5

To clarify the mechanism of this unique annulation reaction, we monitored the reaction of **1** with cinnamaldehyde **2e** (Figure 2). Within a minute after the addition of TBAF, the 1,2-adduct **5** and the cyclic adduct **3e** were produced in 53% and 9% yield, respectively. The yield of **5** gradually decreased and the yield of **3e** increased as the reaction progressed. After 30 min, the yield of the cyclic product **3e** was 76%, the starting enal **2e** was consumed completely, and very small amounts of the 1,2-adduct **5** were present.

Based upon this observation, it was thought that the [3+2] annulation proceeded through kinetically controlled 1,2-addition followed by the cyclization process. Actually, when **6**[9] was treated with TBAF, **3a** was obtained in 18% yield along with the formation of desilylated product **7** in 58% yield. According to



a possible mechanism for this unprecedented annulation reaction (Scheme 2), the reaction of **1** with TBAF gives an anionic intermediate **8**, which undergoes addition to **2** either in 1,2- or 1,4-manner to give the 1,2-adduct **9** or 1,4-adduct **10** that are in equilibrium. The formation of **9** is postulated to be a kinetically controlled process, as is apparent from the result of Figure 2. The thermodynamically favored **10** undergoes proton exchange to afford the 1,2-carborane anion **11**, which gives **3** by intramolecular ring closure.[10] In the case of cyclohexenone, the enolate generated by the 1,4-addition may abstract a proton from the carborane cage, but the carbonyl group cannot approach the resulting carboranyl anion for geometric reasons, and thus no annulation takes place with **2i**.

We are actively investigating the scope and limitation of this novel annulation reaction, which is synthetically useful for providing biologically active carborane derivatives for boron neutron capture therapy.[11]

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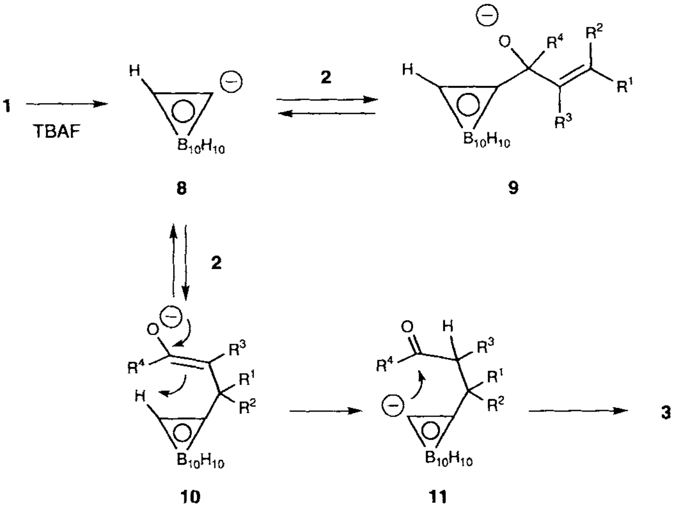

Scheme 2. Mechanism of the [2+3] annulation of **1** and **2**.

Keywords: aldehydes · annulation · carboranes · ketones

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