Diels–Alder Reactions

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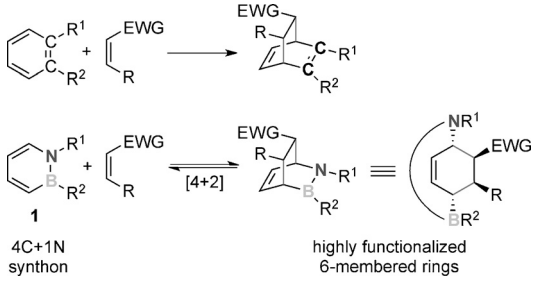
Diels–Alder Reactions of 1,2-Azaborines**

*Richard J. Burford, Bo Li, Monica Vasiliu, David A. Dixon, and Shih-Yuan Liu**

Abstract: *Diels–Alder reactions employing 1,2-azaborine heterocycles as 1,3-dienes are reported. Carbocyclic compounds with high stereochemical and functional complexity are produced, as exemplified by the straightforward two-step synthesis of an amino allyl boronic ester bearing four contiguous stereocenters as a single diastereomer. Whereas electron-deficient dienophiles undergo irreversible Diels–Alder reactions, a reversible Diels–Alder reaction with the less electron-deficient methyl acrylate is observed. Both the N and the B substituent of the 1,2-azaborine exert significant influence on the [4+2] cycloaddition reactivity as well as the aromatic character of the heterocycle. The experimentally determined thermodynamic parameters of the reversible Diels–Alder reaction between 1,2-azaborines and methyl acrylate correlate with aromaticity trends and place 1,2-azaborines approximately between furan and thiophene on the aromaticity scale.*

1,2-Azaborines are isoelectronic and isostructural analogues of benzene whereby one CC bond is replaced by a BN bond.[1] These heterocyclic aromatic compounds exhibit electronic structures that are distinct from those of benzene,[2] leading to considerable interest in their potential applications in materials science[3,4] and biomedical research.[5] We, and others, have recently evaluated the aromatic character of 1,2-azaborines against the commonly accepted criteria of aromaticity, that is, structure,[6] energy,[7] reactivity,[8] and magnetism.[1a,9] In particular, we have experimentally determined the resonance stabilization energy (RSE) of 1,2-azaborines to be approximately 17 kcal mol^{-1},[7a] which is lower than that of benzene (RSE ≈ 32 kcal mol^{-1}), but on par with other aromatic heterocycles, such as pyrrole (RSE ≈ 21 kcal mol^{-1}), thiophene (RSE ≈ 20 kcal mol^{-1}), and furan (RSE ≈ 15 kcal mol^{-1}).[10] The propensity of aromatic dienes (such as furan and thiophene) to undergo Diels–Alder reactions has been correlated with their aromaticity, that is, the more aromatic the diene, the lower the driving force (both kinetic and thermodynamic) for the cycloaddition reaction.[11] In view of the attenuated aromaticity of the 1,2-azaborine heterocycle, we wondered if it would act as a reactant in cycloaddition reactions. A successful development of such a transformation would render the 1,2-azaborine motif a potential 4C + 1N synthon[12] in organic synthesis (Scheme 1). In this Communication, we report the first examples of cycloaddition reactions of 1,2-azaborines.[13,14] We find that *N*-TBS-*B*-Me-1,2-azaborine (TBS = *tert*-butyl-dimethylsilyl) undergoes irreversible Diels–Alder reactions with electron-deficient dienophiles. However, a reversible Diels–Alder reaction with the less electron-deficient methyl acrylate is observed. We show that both the N and the B substituent of the 1,2-azaborine exert significant influence on the [4+2] cycloaddition reactivity. Furthermore, we demonstrate that our experimentally determined thermodynamic parameters of the reversible Diels–Alder reaction between 1,2-azaborines and methyl acrylate correlate with the aromatic character of the heterocycle and thus place the aromaticity of 1,2-azaborines approximately between those of furan and thiophene on the aromaticity scale of heterocycles.[15]



Scheme 1. 1,2-Azaborines as a potential 4C + 1N synthon in organic synthesis. EWG = electron withdrawing group.

In evaluating 1,2-azaborines as a potential 4C + 1N synthon, we chose first to investigate them as 1,3-dienes in [4+2] Diels–Alder (DA)[16] cycloaddition reactions with dienophiles. We found that the DA reaction of **1a** with maleic anhydride proceeded thermally to completion, albeit in 3 days (Scheme 2) and with a low yield of the isolated product (**2a** recrystallizes poorly). ^{1}H NMR spectroscopy revealed the formation of the cycloaddition adduct **2a** as a single diastereomer, which has been determined to be the *endo* diastereomer by single-crystal X-ray diffraction analysis (Scheme 2).[17]

To enhance the reaction rate, we screened a variety of Lewis acids[18] and determined that $AlCl_3$[19] was the most

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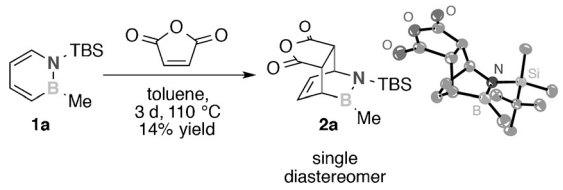
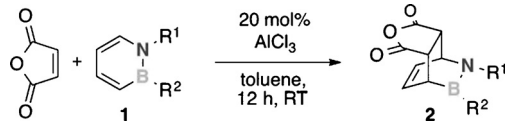


Scheme 2. Thermal Diels–Alder reaction between 1,2-azaborine **1a** and maleic anhydride. Yield given is that of the isolated product.

promising promoter for the Diels–Alder reaction between 1,2-azaborine **1** and maleic anhydride (see the Supporting Information for details). We used the $AlCl_3$-catalyzed reaction as a starting point for the survey of substituent effects. The preparation of N- and B-substituted 1,2-azaborines **1** (Table 1) for our optimization survey was straightforward

Table 1: Reaction optimization: Survey of substituent effects.



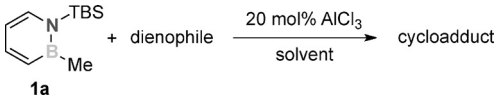
Entry	1,2-azaborine	R^1	R^2	Yield [%][a]
1	**1a**	TBS	Me	**2a**: 96
2	**1b**	Bn	Me	**2b**: 20
3	**1c**	Boc	Me	**2c**: < 5
4	**1d**	TBS	Ph	**2d**: 62
5	**1e**	TBS	≡–H	**2e**: < 5
6	**1f**	TBS	O-*i*Pr	**2f**: 94
7	**1g**	TBS	H	**2g**: < 5

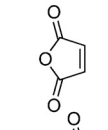
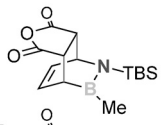
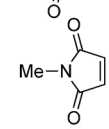
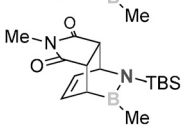
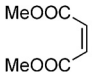
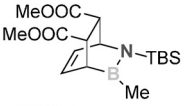
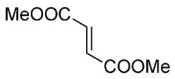
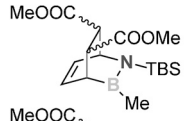
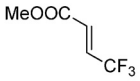
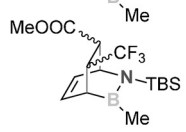
[a] Yield determined by ^{1}H NMR versus a calibrated internal standard. Abbreviations: TBS = *tert*-butyl-dimethylsilyl, Bn = benzyl, Boc = *tert*-butyloxycarbonyl.

(see the Supporting Information for details). As can be seen from Table 1, the *N*-TBS substituent is crucial for reactivity, furnishing the DA adduct **2a** in 96% observed yield (entry 1). Alkyl substituents as well as electron-withdrawing groups on nitrogen render the cycloaddition reaction significantly less effective (entries 2 and 3). The substituent on boron also plays an important role. In addition to the sp^3-hybridized methyl substituent (entry 1), the O-*i*Pr group was also effective (entry 6). On the other hand, sp-hybridized *B*-alkynyl (entry 5) and *B*-H-substituted 1,2-azaborines (entry 7) did not produce significant amounts of DA products under the screening conditions. The sp^2-hybridized *B*-Ph-substituted 1,2-azaborine was intermediate in its reactivity (entry 4).

We used 1,2-azaborine **1a** to determine the reaction scope with a number of dienophiles because of the relative ease of preparation and purification of **1a**. Table 2 shows that in addition to maleic anhydride (entry 1), *N*-methyl maleimide is also a suitable dienophile (entry 2). Noncyclic dienophiles (entries 3–5) are more sluggish in reactivity, requiring higher temperatures (50 °C instead of room temperature) for reactivity. The yields of product formation as determined by ^{1}H NMR spectroscopy range from poor to good depending on the dienophile. The isolation of the DA adducts by recrystal-

Table 2: [4+2] Cycloaddition reactions between **1a** and various dienophiles.

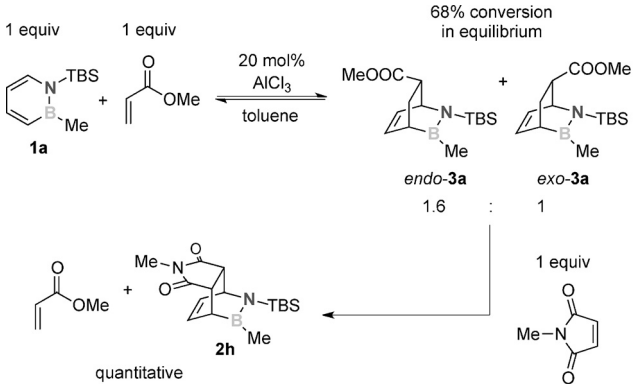


entry	dienophile	cycloadduct		yield (%)
1			**2a**	96[a] (7) >95:5 d.r.
2			**2h**	95[a] (80) >95:5 d.r.
3			**2i**	9[b] (0) >95:5 d.r.
4			**2j**	43[b] (0) 1.1:1 d.r.
5			**2k**	90[b] (37) 1.1:1 d.r. single regioisomer

Yield determined by ^{1}H NMR versus a calibrated internal standard. [a] Monitored after 12 h at room temperature in toluene. [b] Monitored after 12 h at 50 °C in CH_2Cl_2. Numbers in parentheses are yields of isolated products after recrystallization (see the Supporting Information).

lization[20] proved to be challenging, and depended on the propensity of the reaction products to recrystallize. The diastereoselectivity of the DA reaction is excellent for (*Z*)-dienophiles (entries 1–3) whereas (*E*)-dienophiles produce DA adducts in approximately 1:1 diastereoselectivity (entries 4,5). We have also obtained the crystal structure for adduct **2h** which confirms our assignment.[21] For methyl 4,4,4-trifluorocrotonate, where regiochemistry could also be an issue, we observed the formation of only one regioisomer that is consistent with the determined electronic structure of the 1,2-azaborine, that is, nucleophilic at the C3 carbon (carbon adjacent to the boron atom).[8a,22]

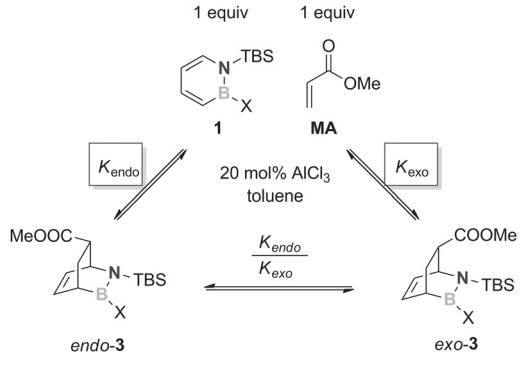
We noted that the reaction between **1a** and dimethylmaleate or dimethylfumarate (Table 2, entries 3,4) never went to completion regardless of solvent, reaction time, or reaction temperature. This observation prompted us to consider the possibility of a reversible reaction.[23] We ultimately selected methyl acrylate as a less electron-deficient dienophile to investigate the issue of reversibility. Treatment of 1,2-azaborine **1a** with one equivalent of methyl acrylate under our $AlCl_3$-catalyzed reaction conditions results in the formation of two diastereomeric cycloaddition products *endo*-**3a** and *exo*-**3a** as determined by NMR correlation experiments (HSQC, HMBC, COSY, NOESY). NOESY experiments are consistent with the *endo* product being the major isomer (Scheme 3). Although both DA products, *endo*-**3a** and *exo*-



Scheme 3. Reversible DA reaction between **1a** and methyl acrylate.

3a, were detected in situ, quantitative consumption of the starting material was never found. Upon addition of one equivalent of *N*-methylmaleimide to the reaction mixture, the ^{1}H NMR signals associated with *endo*-**3a** and *exo*-**3a** disappeared, and quantitative conversion into the *endo* DA adduct **2h** was detected, demonstrating the reversible nature of the formation of *endo*-**3a** and *exo*-**3a** (see the Supporting Information for details).

We derived the individual equilibrium constants for the formation of the *endo* (K_{endo} in Scheme 4) and *exo* (K_{exo} in Scheme 4) adducts, respectively (see the Supporting Information for details of the derivation). Consequently, the corresponding free energy ΔG values for the formation of each individual diastereomer as well as the reaction enthalpy (ΔH) and entropy (ΔS; obtained by a van't Hoff analysis) can be determined. The results for 1,2-azaborine **1a** (*B*-Me) and **1e** (*B*-CCH) are tabulated in Scheme 4 along with predicted values from quantum chemical calculations.

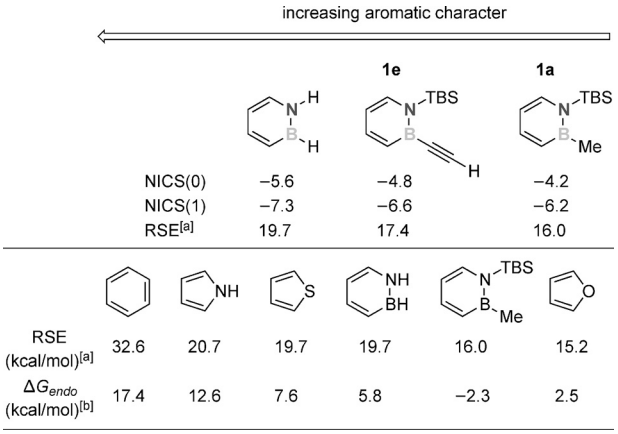


Adducts	X	ΔG_{298K} [kcal/mol][a]	K[b]	ΔH [kcal/mol][c]	ΔS [e.u.][d]
endo-**3a**	Me	–2.0 ± 0.1 (–2.3)	30.1	–13.4 ± 0.5 (–17.8)	–38 ± 2 (–44.9)
exo-**3a**	Me	–1.7 ± 0.1 (–1.4)	19.1	–14.3 ± 0.9 (–19.2)	–42 ± 3 (–51.5)
endo-**3e**	≡—H	–0.4 ± 0.1 (–0.6)	2.1	–12 ± 1 (–16.6)	–39 ± 3 (–46.4)
exo-**3e**	≡—H	–0.2 ± 0.1 (+0.2)	1.4	–15 ± 1 (–16.9)	–51 ± 4 (–49.1)

Scheme 4. Determination of thermodynamic parameters for the Diels–Alder reaction. [a] ΔG values in parentheses are predicted at the G3MP2(gas) + COSMO (G03, toluene, B3LYP/DZVP2) solvent correction level at 298 K. [b] Corresponding equilibrium constants K_{endo} or K_{exo} (M^{-1}), respectively, at 298 K. [c] ΔH values in parentheses are G3MP2 gas-phase values. [d] ΔS values in parentheses are G3MP2 gas-phase value; e.u. = cal mol^{-1} K^{-1}. MA = methyl acrylate.

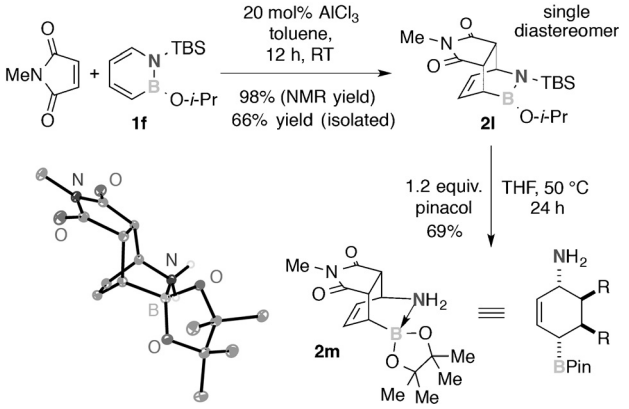
Several pieces of information can be established from the data in Scheme 4: a) There is a slightly stronger driving force (ΔG) for the formation of the *endo* diastereomer versus the *exo* diastereomer ($\Delta G_{endo} < \Delta G_{exo}$); b) the *B*-Me-substituted 1,2-azaborine **1a** has a stronger driving force for cycloadduct formation than *B*-CCH-substituted **1e** ($\Delta G_{3a} < \Delta G_{3e}$); c) although the reaction enthalpy is more negative for the formation of the *exo* diastereomer than the *endo* diastereomer ($\Delta H_{exo} < \Delta H_{endo}$), the formation of the *endo* diastereomer is ultimately slightly preferred because of entropic contributions ($\Delta S_{exo} < \Delta S_{endo}$). The trends of the experimentally determined thermodynamic parameters are consistent with those predicted by theory (see the numbers in parentheses in Scheme 4).

We wondered whether the differences in the DA reaction free energy between the *B*-Me (**1a**) and *B*-CCH-substituted 1,2-azaborine (**1e**) could be due to aromaticity. To probe this question, we calculated the nucleus independent chemical shift (NICS)[24] NICS(0) and NICS(1) values for **1a** and **1e** together with their corresponding resonance stabilization energies (RSE). Both NICS and RSE values indicate that the *B*-CCH-substituted 1,2-azaborine **1e** is more aromatic (Scheme 5, top), consistent with its decreased driving force to engage in DA reactivity. Similarly, we asked whether a heterocycle's propensity to undergo DA reactions with methyl acrylate can serve as a tool to evaluate its aromatic character. Scheme 5 (bottom) shows a general trend between the ΔG_{endo} values (predicted free energy for the formation of the *endo* cycloaddition adduct of an aromatic diene with methyl acrylate) and the RSE, placing the aromaticity of 1,2-azaborines approximately between those of furan[25] and thiophene. This analysis also highlights the tremendous influence that substituents on 1,2-azaborines exert on the RSE and the thermodynamics of the DA reaction.



Scheme 5. Correlation between DA reactivity and aromaticity. [a] See the Supporting Information for details of the prediction of the RSE value. [b] Predicted free energy at G3MP2 + COSMO/B3LYP (toluene correction) level for the formation of the *endo* cycloaddition adduct with methyl acrylate.

To demonstrate the potential utility of our DA products in organic synthesis, we sought to convert its boron component into the versatile BPin (pinacolatoboryl) functional group.[26] The formation of the DA adduct between 1,2-azaborine (**1f**; *B*-O-*i*Pr) and *N*-methylmaleimide proceeded smoothly to furnish **2l** (Scheme 6). Subsequent treatment of **2l** with



Scheme 6. Conversion of DA adducts into BPin-functionalized compounds.

pinacol (1.2 equiv) introduces the BPin functionality with concomitant removal of the *N*-TBS group to give **2m**, which we have unambiguously characterized by single-crystal X-ray diffraction analysis (Scheme 6).[27]

In summary, we have demonstrated the first example of Diels–Alder reactions of 1,2-azaborines. The reaction of *N*-TBS-*B*-Me-1,2-azaborine with a variety of electron-deficient dienophiles produces cycloadducts with high functional complexity. We determined that both the N- and the B-substituent of the 1,2-azaborine exert significant influence on the [4+2] cycloaddition reactivity and the aromatic character of the BN heterocycle. The thermodynamic parameters of the reversible Diels–Alder reaction between 1,2-azaborines and methyl acrylate correlate with aromaticity trends and thus place 1,2-azaborines between furan and thiophene on the aromaticity scale of heterocycles. This work lays the foundation for the application of 1,2-azaborines as a 4C + 1N synthon in organic synthesis, and current efforts are directed toward expanding the substrate scope of this transformation.

Keywords: aromaticity · azaborine heterocycles · boron · cycloaddition · synthetic methods

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