Organic & Biomolecular Chemistry

COMMUNICATION



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Cite this: *Org. Biomol. Chem.*, 2019, **17**, 5520 Received 30th April 2019,

Accepted 18th May 2019 DOI: 10.1039/c9ob00991d

rsc.li/obc

Borylative cyclisation of diynes using BCl₃ and borocations[†]

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The borylative cyclisation of 1,2-dialkynyl benzenes with BCl₃ leads to dibenzopentalenes (*via* intramolecular S_EAr) or benzofulvenes (*via* chloride addition) depending on substituents, with stabilised vinyl cation intermediates (e.g. with a p-MeO-C₆H₄-group) favouring the latter. The use of borocations leads to more selective dibenzopentalene formation, while other diyne frameworks undergo intramolecular S_EAr selectively even with p-MeO groups.

The activation of a π nucleophile by a boron electrophile to induce cyclisation while forming C-Y (Y = C, N, S or O etc.) and C-B bonds concomitantly is an attractive method to make complex organoboranes. Termed borylative cyclisation, the catalyst-free version of this reaction^{1,2} requires sufficiently electrophilic boranes to proceed with pioneering work performed using $B(C_6F_5)_3$.³ While notable, borylative cyclisation with $B(C_6F_5)_3$ generally leads to $[RB(C_6F_5)_3]^-$ containing products (though a carboboration step also occurs in some cases generating $RB(C_6F_5)_2$ containing cyclised products).⁴ The utility of the $[RB(C_6F_5)_3]^-$ moiety is much less developed relative to RB (OR)₂ (for which there are a myriad of established functional group transformations)⁵ or $RB(Aryl)_2$ (e.g. as an acceptor for generating low LUMO energy conjugated materials).⁶ Therefore the use of alternative boron electrophiles for borylative cyclisation that form, or can be transformed readily into, RB(OR)₂ or RB(Aryl)₂ has become an area of significant activity. While we and others have utilised BCl₃,⁷ Blum and co-workers have exploited B-chloro-catecholborane (CatBCl) in borylative cyclisations,⁸ and a range of borylated systems now have been synthesised via borylative cyclisation methodologies.

In previous work of particular relevance to this study, Erker, Yamaguchi and co-workers used $B(C_6F_5)_3$, and in one example BCl_3 , for the cyclisation of 1,2-dialkynyl benzenes to form dibenzopentalenes **A** and **B** (Scheme 1 inset top right).⁹ Due to our ongoing interest in low band gap boron containing polycyclic aromatic hydrocarbons,¹⁰ we were interested in extending BCl_3 induced cyclization to related diynes substituted with donor (*e.g.* –OMe) groups. During this study certain diynes were found to form alternative borylative cyclisation products, specifically chlorinated benzofulvenes (Scheme 1, bottom). Herein we present our results into the borylative cyclisation of a range of diynes along with the development of methods to control, to some extent, the product distribution principally by varying the electrophile from BCl_3 to a borocation.

Results and discussion

The borylative cyclisation of diyne **1a**, containing two *para*methoxy groups (Fig. 1), was explored using BCl₃ in dichloro-



Scheme 1 Previous work on borylative cyclisation and bottom inset this work.

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[†]Electronic supplementary information (ESI) available: Full experimental details, NMR spectra, crystallographic data and Cartesian coordinates for all calculations. CCDC 1529716 and 1529715. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ob00991d



Fig. 1 The functionalisation of 1a using BCl_3 and subsequent pinacol protection. Inset right, solid state structure of 2-BPin, ellipsoids at the 50% probability level and hydrogens omitted for clarity. Inset left, previous work cyclising with HBr.

methane (DCM). While C-B bond formation occurred (as indicated by a δ_{11B} = 54 ppm consistent with an RBCl₂ moiety) the major product was not the expected dibenzopentalene analogue of compound A. Addition of pinacol and Et₃N followed by isolation of the pinacol boronate ester derivative enabled identification of the major product as the benzofulvene, 2-BPin, by single crystal X-ray diffraction (Fig. 1). This formulation was supported by mass and multinuclear NMR spectroscopy with 2-BPin isolated in 85% yield as a single isomer. The solid state structure of 2-BPin is unremarkable with both Ph groups and the Bpin moiety twisted out of the plane of the benzofulvene core to varying degrees to minimise steric interactions. Formation of related halogenated benzofulvenes, e.g. C (inset left Fig. 1), has been previously reported from the addition of HBr to ortho-bis(phenylethynyl)benzene, with alkyne protonation initiating the 5-endo-dig cyclisation.¹¹ In contrast to the use of HBr (or I2),12 using BCl3 as the electrophile incorporates a nucleophilic C-B site in addition to an electrophilic C-X. The formation of 2-BCl₂ presumably arises from a zwitterionic vinyl cation intermediate (Scheme 1, top middle) being trapped by chloride instead of undergoing intramolecular S_EAr. Analysis of the NMR spectra of 2-BCl₂ preparations prior to pinacol protection and for 2-BPin prior to purification revealed a second minor cyclisation product assigned as the dibenzopentalenes 3-BCl₂ and 3-BPin (the latter supported by GC-MS), respectively. The ratio of 2-BPin: 3-BPin in these mixtures from NMR spectroscopy and GC-MS is 17:1.

The borylative cyclisation of diyne **1b** using BCl₃ to form compound **A** has been previously reported.⁹ This transformation was explored again herein to determine if a borylated benzofulvene analogous to **2-BCl**₂ was present at a low percentage using identical conditions to that for the formation of **2-BCl**₂. However, only compound **A** (and **4** post pinacol protection) was observed by multinuclear NMR spectroscopy under these conditions. Compound **4** was isolated in 92% yield and its formulation further confirmed by single crystal X-ray diffraction studies (Fig. 2, inset). The solid state metrics of **4** are



Fig. 2 Borylative cyclisation of 1b. Inset right, the solid state structure of 4, ellipsoids at 50% probability level and hydrogens omitted for clarity.

unremarkable with core C–C distances comparable to that reported for compound **B** (Scheme 1).

No intermediates were observed in the borylative cyclisation reactions starting from **1a** or **1b** and leaving **2-BCl**₂ in the presence of excess BCl₃ for longer reaction times did not lead to any increase in the dibenzopentalene (disfavouring chloride abstraction from $_{vinyl}$ C–Cl in **2-BCl**₂ by BCl₃ generating the vinyl cation that subsequently undergoes S_EAr). It should also be noted that the chloride present in the benzofulvene product is derived from BCl₃ as closely comparable outcomes were observed on replacing DCM with *o*-dichlorobenzene (*o*-DCB, which is a solvent more resistant to C–Cl heterolysis).

The disparate outcomes observed commencing from diynes 1a and 1b are clearly due to the substituent electronic effects. This is attributed predominantly to the ability of the para MeO group to stabilise vinyl cation intermediates (the methoxy group will also have a small deactivating effect for S_EAr due to the σ^{+}_{meta} value of +0.05). The reduced electrophilicity of the vinyl cation derived from 1a will increase its lifetime in solution thereby enabling a reaction with a chloride source to proceed. In contrast, the vinvl cation derived from 1b will be more electrophilic than that derived from 1a, thus the S_EAr reaction will be more rapid (as found previously with related carbocations),¹³ outcompeting the chloride transfer reaction. DFT calculations at the M06-2X/6-311G(d,p) level with a polarisable continuum model (PCM) of DCM, revealed that the LUMO energies for the vinyl cations (which are dominated by $p\pi$ orbitals on the sp vinyl cation carbon and the adjacent aromatic ring in each case - see ESI⁺) vary significantly (Scheme 2). These energies will correlate with electrophilicity and the rates of reaction with π nucleophiles.¹³

Another factor that was considered in effecting the product outcome was the identity (and nucleophilicity) of the chloride donor that forms the benzofulvene. Isodesmic calculations revealed that in each case the vinyl cation (Scheme 2 top right), is more Lewis acidic towards chloride than BCl₃, thus the zwitterionic vinyl cation (Scheme 2 top left) will be favoured in solution over [vinyl-cation][BCl₄]. Though it is notable that the vinyl cation derived from **1a** and BCl₃ have similar Lewis acidity towards chloride ($\Delta G = 1.11$ kcal mol⁻¹) thus both [vinyl cation][BCl₄] and the zwitterion should be present in solution as intermediates during this reaction. Furthermore, the chloride ion affinity (CIA) of the vinyl cation



 $\label{eq:scheme 2} \begin{array}{ll} \mbox{Calculations of the energy change in chloride transfer reactions (all at the M06-2x/6-311G(d,p)/PCM (DCM) level). In the vinyl cation the anion and cation were calculated at infinite distance. \end{array}$

derived from **1a** is the lowest (of the three calculated), thus this zwitterion will be the better chloride donor and also have the highest concentration of $[BCl_4]^-$ in solution (due to the lowest ΔG). This factor coupled with the relative LUMO energies presumably explains why the benzofulvene is formed from **1a** but not **1b**. Finally, the formation of the benzofulvene from the zwitterion was found to be highly exergonic. This is consistent with the formation of the benzofulvene being irreversible under these conditions even in the presence of BCl₃ (hence there is no change in the benzofulvene/dibenzopentalene ratio from **1a** in the presence of excess BCl₃ over longer reaction times).

To probe substituent effects further and guided by these calculations three other diynes, **1c-1e** (Scheme 3), were synthesised and investigated. These were chosen to either stabilise vinyl cations to some extent or to be less Lewis acidic at boron relative to vinyl cations derived from **1b**. Compounds **1c** and **1d** have *para* F and Me substituents, respectively, while **1e** is the unsubstituted congener that was previously calculated and



Scheme 3 Product ratios from the borylative cyclisation of 1c-1e.

shown to form benzofulvene C on reaction with HBr (Fig. 1). Notably, F and Me have distinct σ^+ values (Me σ^+_{para} = $-0.31 \sigma^{+}_{meta} = -0.10$, F $\sigma^{+}_{para} = -0.07$ F $\sigma^{+}_{meta} = +0.35$), with both groups able to stabilise the vinyl cation to some extent (albeit less than MeO, $\sigma^+_{para} = -0.78$), but Me is activating while F is deactivating, with respect to S_EAr in the meta position. In each case the divne was combined with BCl₃ in DCM and after all starting divne was consumed (by in situ NMR spectroscopy) the products were converted to the pinacol boronate esters which were analysed as crude mixtures to determine the ratio of dibenzopentalene: benzofulvene by NMR spectroscopy and GC-MS. This revealed that for fluoro substituted 1c the benzofulvene 5 was the major product (ca. 90%). However, for 1d and 1e the dibenzopentalene products were the major products but were only formed in a slightly larger amount than the benzofulvene products. Combined these results indicate that deactivating the aromatic system towards S_EAr (e.g. using a meta fluorine relative to the site of S_EAr) is also an effective way to achieve preferential benzofulvene formation, more effective than vinyl cation stabilisation using a *p*-Me-C₆H₄ group in this case.

In previous work the frustrated Lewis pair (FLP) combination of $B(C_6F_5)_3/P(o-tolyl)_3$ transformed 1e selectively (97%) isolated yield) to the dibenzopentalene analogue of compound B.9 The effect of using the FLP combination of BCl₃/2,4,6tritert-butylpyridine (TBP) on product distribution was investigated as in weakly basic media the deprotonation of an arenium cation (a key step in dibenzopentalene formation) can become the rate determining step in S_EAr.¹⁴ Therefore the inclusion of TBP as a Brønsted base was hoped to favour dibenzopentalene formation. However, using BCl₃/TBP combinations led to comparable ratios of benzofulvene: dibenzopentalene starting from 1d and 1e as just using BCl₃ (>two equivalents of BCl₃ were used in these reactions as the by-product formed from S_EAr is [TBPH][BCl₄], thus use of only one equiv. BCl₃ leads to incomplete consumption of the starting divne).

With divnes 1d and 1e giving mixtures containing significant amounts of benzofulvene and dibenzopentalene products (which proved inseparable in our hands partly due to column chromatography leading to formation of protodeborylated products) alternative borylative cyclisation conditions were sought that would strongly favour formation of only one cyclised product. Considering a mechanism involving a vinyl cation intermediate two options were considered: (i) using boron electrophiles that form poorer chloride (or other anion) donors during the cyclisation process to favour dibenzopentalene formation. (ii) Increasing the concentration of chloride donor to favour benzofulvene formation, *e.g.* by adding $[BCl_4]^-$ salts. Borocations of the general formula [Y₂B(amine)]⁺ were selected for the first approach. Initial attempts focused on using borocations containing catechol (Cat) substituents, with the chelating diol disfavouring anion transfer reactions. However, [CatB (2-DMAP)[AlCl₄] (2-DMAP = 2-(N,N-dimethylamino)-pyridine) led to no reaction with 1d at room temperature or at 60 °C for 24 h. Other more electrophilic catechol based borocations,¹⁵

e.g. [CatB(NEt₃)][AlCl₄], led to very slow reactions at room temperature, with heating furnishing multiple intractable products in our hands.

From previous work, dihalo-borocations are more electrophilic than catechol derivatives thus the boronium salt [(2-DMAP)BCl₂][AlCl₄],^{7b} and the borenium salt [Cl₂B(2,6lutidine)][AlCl₄]¹⁶ were investigated. In comparison to [BCl₄]⁻ and [RBCl₃]⁻ these borocations will form weaker chloride donors during cyclisation, as loss of chloride, e.g. from compounds with the general structure D (Fig. 3, right), would lead to dications, which will have a high chloride ion affinity (this is supported by the chloride ion affinity of the dication derived from **D** by loss of chloride (and where the amine is pyridine) being 23.8 kcal mol^{-1} greater than that of BCl₃). Furthermore, the vinyl cation **D** (where the amine is pyridine) will also be more electrophilic than the comparable zwitterion (calculations support this with a LUMO energy of -4.13 eV significantly lower in energy than that for the comparable zwitterion, -3.85 eV). Finally, AlCl₃ is also a strong Lewis acid towards chloride, notably stronger than BCl_3 (by 25 kcal mol⁻¹),¹⁷ so $[AlCl_4]^-$ will also be a poor chloride donor.

Using the boronium salt [Cl₂B(2-DMAP)][AlCl₄] in the cyclisation of 1d led to more selective formation of dibenzopentalene 8, with a 1:10 ratio of 7:8 observed (by NMR spectroscopy and GC-MS). In contrast, the use of [Cl₂B(2-DMAP) [AlCl₄] in the cyclisation of **1e** led to a smaller change in the ratio of benzofulvene to dibenzopentalene (Scheme 4, inset for ratios). Therefore the borenium salt [Cl₂B(2,6lutidine) [AlCl₄] was utilised as this will form an even poorer chloride donor (as 2,6-lutidine is a poorer nucleophile than 2-DMAP). Indeed using [Cl₂B(2,6-lutidine)][AlCl₄] the selectivity for the dibenzopentalene product 10 increased, with the ratio of 9:10 now 1:7. Thus it is possible to exert significant control over the product distribution in borylative cyclisation using borocations to increase the amount of dibenzopentalene products from 1d and 1e. However, attempts to use either of the $[Cl_2B(amine)]^+$ borocations to initiate cyclisation of **1a** led to complex mixtures containing minimal dibenzopentalene, in part due to competitive ether cleavage, consistent with the reduced functional group tolerance of borocations relative to BCl₃.^{7b,15}



BCl₂

General structure D

or $R = NMe_2 R' = H$

Θ

٩ry

AICI

R = R' = Me

decreasing

chloride donor

power

FG

CI

С

Θ

BCL



Scheme 4 Change in product ratio on altering the boron electrophile or by the addition of an exogenous chloride source.

Attempts to increase the amount of benzofulvene product formed by addition of an exogenous chloride donor were partially successful. For example, while the borylative cyclisation of 1d using BCl₃ in the presence of three equivalents of [NBu₄][BCl₄] did lead to a change in the product ratio, the chlorinated benzofulvene 7: dibenzopentalene 8 ratio was only 3:2. With divne 1e a small change also was observed with the ratio of 9:10 using BCl₃/three equiv. of [NBu₄][BCl₄] being 1:1. Compound 5 was formed more selectively (with no 6 observed by NMR spectroscopy) when cyclisation using BCl₃ was repeated in the presence of 3 equiv. [NBu₄][BCl₄]. However, attempts to form the benzofulvene derived from 1b were unsuccessful using BCl₃/3 equiv. [NBu₄][BCl₄] with the dibenzopentalene product still formed in excellent conversion, presumably due to the intermediacy of a highly electrophilic vinyl cation that leads to rapid intramolecular S_EAr. Thus increasing the chloride donor concentration using [BCl₄]⁻ has only a modest effect on selectivity. The use of "better" halide donors (i.e. free halide as in previously reported systems using HBr or I_2)^{11,12} is not possible in this system as these would react with BCl_3 (to form $[X-BCl_3]^-$, X = halide). Furthermore, the use of weaker Lewis acids e.g. PhBCl2 led to complex mixtures and significant amounts of unreacted divne 1d after 18 h. Therefore the ability to access other benzofulvenes is limited via this methodology to requiring substituents that strongly stabilise the vinyl cation or significantly disfavour S_EAr.

With an understanding of substituent effects in hand for aryl substituted diynes, the heteroaromatic bis-thienyl derivative **1f**, was investigated next (Scheme 5). The 3-thienyl derivative was selected to preclude any $S \rightarrow BCl_3$ interactions directing reactivity and altering the reaction outcome.⁹ **1f** contains an electron rich thiophene heteroaromatic able to stabilise a vinyl cation to a greater extent (relative to benzene), however, the higher nucleophilicity of thiophene and its lower aromaticity (relative to benzene) will favour the S_EAr reaction. Indeed on addition of BCl₃ to **1f** the S_EAr product, **11**, was the major product with no benzofulvene product observed by NMR spectroscopy. Using other conditions discussed above

equilibrium position dependent on

relative chloride ion affinity of

BCl₃ and RBCl₂

-BCla

+ BCl₃

potential chloride donors shown in red

FG

FG

⊖BCl₃

FG



Scheme 5 Borylative cyclisation of diyne 1f.

led to no observation of a benzofulvene product by NMR spectroscopy and GC-MS.

Finally, other diynes were explored to determine if *p*-MeOphenyl substituents would again lead to a chloro incorporated product (*e.g.* inset Scheme 6) by stabilising a vinyl cation intermediate during borylative cyclisation. Compound E had been previously shown to undergo cyclisation with BCl₃ readily and was isolated as compound F post protection.^{7b} Thus the *p*-MeO analogue, **12** was synthesised, however, this underwent cyclisation to give the product from intramolecular S_EAr exclusively, with **13** isolated in 79% yield. No difference in product distribution was observed on performing the cyclisation with BCl₃ in the presence of 3 equiv. of [NBu₄][BCl₄].

Hypothesising that the absence of any vinyl chloride product derived from 12 maybe due to the flexibility in the partially saturated 12 leading to a low barrier for the intramolecular S_EAr step we investigated another fully Csp^2 based divne substituted with p-MeO-C₆H₄ groups, 14. However, addition of BCl3 to this divne also led exclusively to the SEAr product, with no chloro-vinyl product observed, even when the reaction with BCl₃ was performed in the presence of 3 equiv. of [NBu₄][BCl₄]. Compound 15 can be isolated post pinacol protection in 82% yield and is analogous to the cyclisation product derived from 14 using I_2 as the electrophile.¹⁸ Again the BCl₃ route is complementary to I₂ induced cyclisation as the former installs a C-BPin nucleophilic moiety instead of an electrophilic C-I unit. We attribute the absence of any chlorine incorporated product in the borylative cyclisation of 14 with BCl3 to a lower barrier to SEAr due to the vinyl cation intermediate containing a six membered ring (ring A, inset Fig. 4) in contrast to a five membered ring in the vinyl cation derived from 1a (ring B). The latter may result in a higher barrier for the intramolecular S_EAr step due to a less favourable geometry derived from the relative bond angles around rings A and B.



Scheme 6 Borylative cyclisation of E (previous work) and 12 (this work).



Fig. 4 Borylative cyclisation of 14. Inset right, the zwitterionic vinyl cations derived from 1a and 14 on combination with BCl₃.

Conclusions

In conclusion the product outcome from the borylative cyclisation of 1,2-dialkynylbenzenes with BCl₃ is highly dependent on substituents, with more strongly electrophilic vinyl cation intermediates favouring dibenzopentalene formation. In contrast, vinyl cations that are stabilised by donor groups (*e.g. p*-MeO-C₆H₄), or contain groups deactivating towards S_EAr lead to benzofulvene products. The product distribution can be controlled to some extent by variation in the boron electrophile and by addition of an exogenous chloride donor ([BCl₄]⁻) that does not shut down borylative cyclisation by reaction with the electrophile. However, the reaction outcome divergence could not be extended to two other diynes substituted with *p*-MeO-C₆H₄ groups presumably due to lower barriers to the S_EAr reaction in these systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The research leading to these results received funding from the ERC under framework 7 (Grant no. 305868) and the Horizon 2020 Research and Innovation Program (Grant no. 769599).

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