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Cyclopropanation of Terminal Alkenes via Sequential Atom Transfer Radical Addition/1,3-Elimination

Nicholas D. C. Tappin, Weronika Michalska, Simon Rohrbach, Philippe Renaud^{*[a]}

Abstract: An operationally simple protocol to affect an atom transfer radical addition of commercially available ICH₂Bpin to terminal alkenes has been developed. The intermediate iodide can be transformed in a one-pot process into the corresponding cyclopropane upon treatment with a fluoride source. This method is highly selective for the cyclopropanation of unactivated terminal alkenes over non-terminal alkenes and electron deficient alkenes. Due to the mildness of the procedure, a wide range of functional groups such as esters, amides, alcohols, ketones, and vinylic cyclopropanes are well tolerated.

Due to their stability and ease of handling, alkylboronic esters are extremely useful and attractive synthetic intermediates for a broad range of transformations^[1] involving carbon–heteroatom^[2] and carbon–carbon^[3–6] bond formation. Boronic esters have also been involved in a variety of radical reactions.^[7–11] They are prepared either via hydroboration,^[12,13] via reactions of organometallic species with borate esters and related reagents,^[14] via C–H activation process^[15] and more recently via radical borylation reactions.^[16] The nature of the alkyl chain at boron can be easily modified with a high level of stereocontrol by homologation reactions upon treatment with carbenoid type reagents.^[17–19]

Our long-standing interest in developing mild methods for the functionalization of alkenes via radical pathway^[20–32] incited us to investigate the iodoalkylation involving a 1-borylated alkyl radicals leading to γ -iodoalkylboronates. Based on EPR studies and calculations, Walton, Carboni, and co-workers reported that 1-borylated radicals are stabilized when the boron is sp²-hybridized, however the extent of stabilization is smaller for radicals substituted by a boronic ester substituent relative to the corresponding borinic ester or borane (Figure 1, A).^[33,34] This stabilization is the first key feature to design an iodine atom transfer process according to the pioneering work of Kharasch and Curran.^[35–41] Matching the philicities of the radicals and alkenes involved in the process is the second key feature for the success of the reaction. Strong polar effects favor an efficient and selective iodine atom transfer process over an oligomerization reaction. The resonance hybrids of the 1-borylalkyl radical suggest that the oxygen lone pairs reduce electrophilicity by the same mechanism that they decrease radical stabilization (Figure

1, B). Based on these simple considerations, it is expected that iodine atom transfer between 1-iodoalkylboronic esters and alkenes should be possible – but still challenging – due to moderate thermodynamic and polar effects.^[42] Recently, Zard and co-workers rationalized the inefficiency of the xanthate transfer mediated addition of electrophilic radicals to pinacol vinylboronate by the lack of favorable thermodynamic and polar effects.^[43–45]

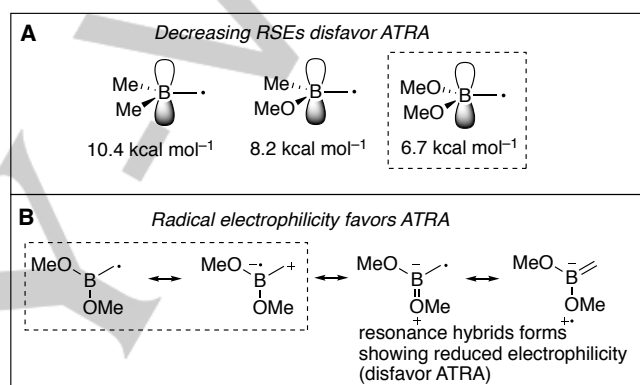


Figure 1. Radical stabilization energies (RSEs) of 1-borylated radicals and resonance hybrids of boronic esters derived radicals.^[34]

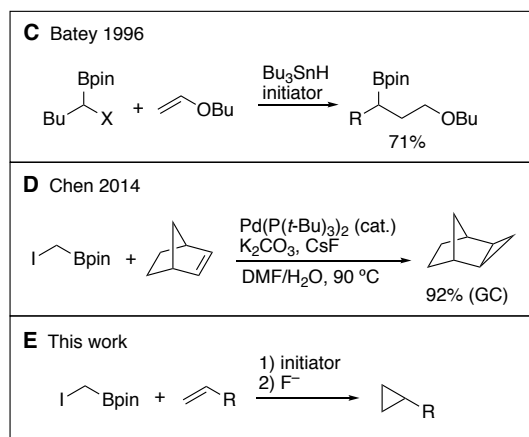
α -Haloboronic esters have been used in tin-mediated (Scheme 1, C)^[46–49] and metal-catalyzed radical processes.^[50–52] Chen reported the Pd(0) catalyzed cyclopropanation of norbornene using potassium iodomethyltrifluoroborate.^[53] Interestingly, pinacol iodomethylboronic ester could also be used for this transformation (Scheme 1, D). A mechanism involving a palladocyclobutane intermediate was proposed. Finally, 1-borylated alkyl radicals were involved in the elegant nickel-catalyzed alkylation and arylation of α -haloboronic esters developed by Fu^[54] and Martin,^[55] respectively. 1-Borylated alkyl radicals have also been generated from Barton esters^[56] and xanthates^[45] as well as through radical addition to vinylboronates.^[43,44,46,57–61] and to ate complexes of vinylboronates.^[62–64] To the best of our knowledge no halogen ATRA process involving 1-haloalkylboronates have been reported. This reaction would be highly attractive since it opens a way to prepare in a straightforward manner 3-haloalkylboronates that are potential precursors of cyclopropanes via a 1,3-elimination process.^[65–68] The stable boronic ester has not yet been used for this transformation and this attractive 1,3-cyclization has been limited to a few very simple unfunctionalized cyclopropanes since the precursors were only available by hydroboration of allylic halides. We report here, a study of the iodine atom transfer reactions between pinacol iodomethylboronate **1** and non-

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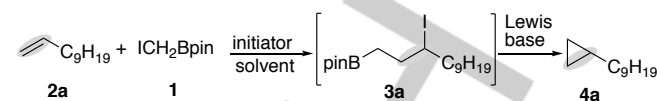
activated alkenes **2** (Scheme 1, E) that led to the development of a metal-free cyclopropanation procedure.^[69]



Scheme 1. Reaction of alkenes with 1-haloalkylboronic esters. DMF = *N,N*-Dimethylformamide. Bpin = pinacolboryl

Initial attempts to run the iodine atom transfer reaction between ICH₂Bpin **1** and 1-undecene **2a** as a substrate demonstrated that the 3-iodoalkylboronate **3a** was decomposing during purification on silica gel. Eventually, we decided not to isolate **3a** and to convert it immediately into the cyclopropane **4a**. Preliminary experiments with small amount of isolated boronic ester **3a** showed that the cyclopropane formation was possible upon treatment with a variety of nucleophiles such as HO[−], EtO[−], and F[−]. Having established that the cyclopropane formation was possible, we started to optimize the whole process as outlined in Table 1. Initiation with BEt₃ and oxygen or DTBHN were attempted first using either NaOH or LiOH to trigger the cyclopropanation but yields remained low (Table 1, entries 1–3). DLP was eventually identified as a superior initiating system and the use of one equivalent was necessary to reach the best yields (Table 1, entries 6–8).^[70] The reagent used to induce the cyclopropane formation was found to be less crucial. Good but slightly irreproducible results were obtained with the biphasic NaOH or LiOH system (Table 1, entries 3–4), higher yields and reproducibility were achieved by using LiOEt or TBAF (Table 1, entries 5, 6). The latter was finally selected for its mildness. The role of the solvent was found to be less critical. Good yields were obtained in benzene and chlorobenzene (Table 1, entries 6, 9). The reaction works also well in DCE (Table 1, entry 10) and it was found later that the reaction gave a similar yield when run in dry EtOAc (Table 1, entry 11). For the purposes of this investigation dry benzene was selected as the solvent of choice but one scale-up experiment was run in EtOAc with a more polar alkene (see below).

Table 1. Optimization of the cyclopropanation of undecene **2a** with pinacol iodomethylboronate **1**.^[a] DLP = dilauroyl peroxide; DTBHN = di-*tert*-butyl hyponitrite; TBAF = tetra-*n*-butylammonium peroxide; DCE = 1,2-dichloroethane; EtOAc = ethyl acetate.

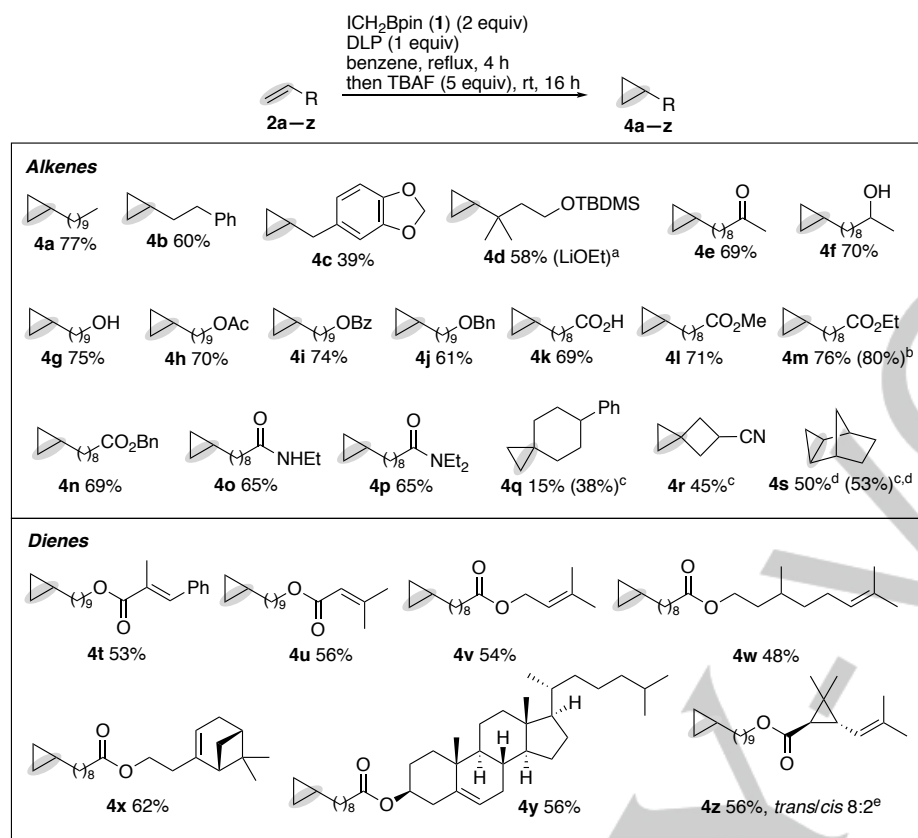


Entry	Initiator	Solvent, T	Lewis base	Yield ^[b]
1	BEt ₃ , air	CH ₂ Cl ₂ , rt	NaOH	28%
2	BEt ₃ , DTBHN	CH ₂ Cl ₂ , reflux	NaOH	21%
3	BEt ₃ , ^[c] DTBHN	CH ₂ Cl ₂ , reflux	LiOH	35%
4	DLP (1 equiv)	C ₆ H ₆ , reflux	LiOH	71%
5	DLP (1 equiv)	C ₆ H ₆ , reflux	LiOEt	75%
6	DLP (1 equiv)	C ₆ H ₆ , reflux	TBAF	73%
7	DLP (0.2 equiv)	C ₆ H ₆ , reflux	TBAF	40%
8	DLP (1.4 equiv)	C ₆ H ₆ , reflux	TBAF	71%
9	DLP (1 equiv)	ClC ₆ H ₅ , reflux	TBAF	74%
10	DLP (1 equiv)	DCE, reflux	TBAF	68%
11	DLP (1 equiv)	EtOAc, reflux	TBAF	74% ^[d]

[a] Reactions were run using **2a** (1 mmol), **1** (2 mmol) in dry benzene (3.3 mL) then the nucleophilic solution was added and the reaction mixture stirred vigorously. [b] Yields determined by GC using pentadecane as internal standard. [c] Syringe pump addition. [d] NMR yield with 1,4-dimethoxybenzene as external standard.

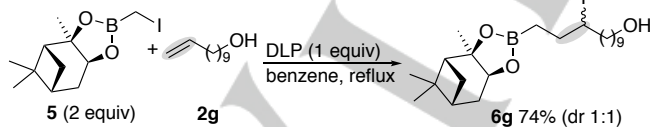
The scope of the reaction was investigated with a series of substrates (Scheme 2). Simple terminal alkenes bearing a wide range of functional group such as the electron rich aromatic ring of safrole (**2c**), the silyl ether **2d** (using LiOEt instead of TBAF to avoid cleavage of the silyl group), the ketone **2e**, the unprotected primary and secondary alcohols **2f** and **2g**, the acylated alcohols **2h** and **2i**, the benzyl ether **2j**, the free carboxylic acid **2k**, the esters **2l** and **2m**, and the secondary and tertiary amides **2n** and **2o** gave the desired products in fair to good yields (39–80%). Interestingly, the cyclopropanation of **2d** involved a neopentyl iodide showing that the cyclization mechanism is probably best described as a 1,3-elimination process in analogy to the reaction of 3-haloalkylboranes where inversion of the configuration at occurs at the halide and boron substituted carbon atoms.^[71,72] When 1,1-disubstituted alkenes were employed (such as **2q**), troubles were encountered with the stability of the intermediate iodides and a 15% yield was obtained with DLP under thermal initiation. Initiation with BEt₃/air turned out to be best since it could be performed at room temperature to give **4q** in 38% yield. Reaction with the methylenecyclobutane **2r** afforded the slightly volatile **4r** in a 45% yield. Following Chen's work,^[53] we also cyclopropanated norbornene **2s** to **4s** in 53% yield. Next, the procedure was used on diverse dienes to test the chemoselectivity. α,β -Unsaturated esters **2t** and **2u** reacted selectively at the unactivated terminal alkene. Acylated prenol, citronellol, nopanol, and cholesterol **2w–2y** were selectively cyclopropanated at the terminal non-activated alkene to give **4w–4y** in 48–62% yields. Finally, the chrysanthemic ester **2z** afforded **4z** as a single isolated regioisomer without any modification of the *trans/cis* 8:2 diastereomeric ratio demonstrating further the mildness of the reaction conditions.

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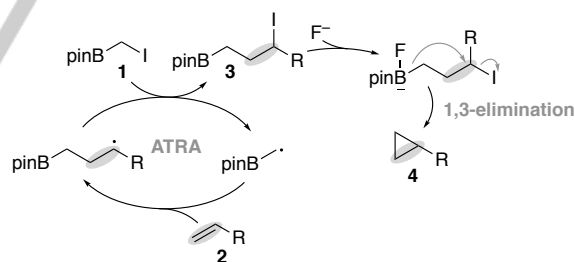
Scheme 2. Scope of the cyclopropanation. Procedure: All reactions were run on 1 mmol scale with no special precautions to remove moisture or air. Alkene (1 mmol), ICH_2Bpin (2 mmol), and DLP (1 mmol) were heated in refluxing benzene (0.3 M) under argon for 4 h; to the cooled reaction mixture was added TBAF solution (5 equiv, 1.0 M in THF) and stirred for 16 h. Each yield was determined by $^1\text{H-NMR}$ analysis of the crude product mixture after work-up using 1,4-dimethoxybenzene as reference. a) LiOEt (1.0 M in EtOH) was used instead of TBAF. b) Reaction performed in EtOAc on a 5 mmol scale. c) Initiated with BEt_3 (0.5–1.2 equiv) open to air, rt. d) Yield estimated by GC analysis using 1,5-cyclooctadiene as reference. See SI for details. e) No erosion of the *trans/cis* ratio.

The isolation of the pinacol γ -iodoalkylboronic esters **3** resulting from the reaction of ICH_2Bpin **1** over numerous alkenes was challenging due to their instability during purification by silica gel chromatography. Pinanediol boronic esters are known to be thermodynamically more stable,^[73,74] therefore we tested the reaction of iodomethylboronic ester **5** with alkene **2g**. ATRA product **6g** was stable to silica gel purification and was obtained in 74% isolated yield (Scheme 3).



Scheme 3. Isolation of a pinanediol γ -iodoalkylboronic ester.

The mechanism of the cyclopropanation reaction is depicted in Scheme 4 and corresponds to a classical radical iodine ATRA coupled with a Lewis base promoted 1,3-elimination (or intramolecular nucleophilic substitution). The radical addition to alkenes is controlled by polar and steric effects: the electron withdrawing boryl group favors the addition to electron rich alkenes and radical addition are much faster at the less hindered position. These two effects rationalize well the observed regioselectivities reported in Scheme 2.



Scheme 4. Mechanism of the cyclopropanation involving ATRA (= atom transfer radical addition) and 1,3-elimination processes.

In conclusion, we have reported here an unprecedented approach for the formation of cyclopropanes relying on a one-pot iodine atom transfer radical addition followed by an ionic intramolecular substitution process (1,3-elimination). The whole sequence is characterized by mild reaction conditions and excellent functional group tolerance. Interestingly, the high regioselectivity observed for terminal non-activated alkenes over non-terminal and electron deficient alkenes cannot be achieved easily using classical cyclopropanation methods.^[69] Finally, the possible isolation of the intermediate products of iodine atom transfer depicted in Scheme 3 open new opportunities for further synthetic applications.

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Keywords: radical reaction • organoboron • cyclopropanation • alkenes • 1-borylated radical • iodine atom transfer • ATRA • boronate complexes.

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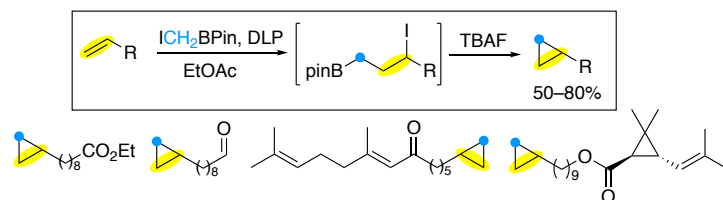
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An operationally simple protocol for the cyclopropanation of alkenes with ICH_2BPin via an iodine atom transfer radical addition followed by a fluoride promoted 1,3-elimination reaction has been developed. This procedure requires no metal and tolerates a broad range of reactive functional groups.