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BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Diastereodivergent electrophilic trapping of α-boryl lithium derivatives

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Full Research Paper

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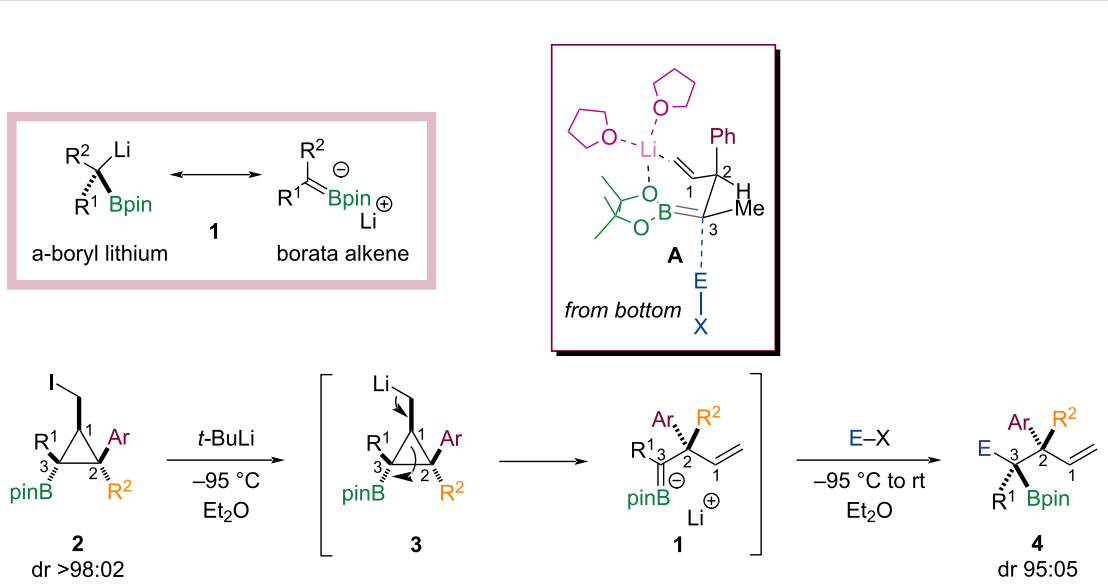
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Abstract

α-Boryl carbanions are valuable organoboron intermediates, but controlling their stereoselective reactions remains challenging. Here, we examine the diastereoselective generation and trapping of α-boryl lithium species formed by ring opening of substituted iodomethylcyclopropanes. After lithium–iodine exchange and selective C–C bond cleavage, these intermediates react with a range of electrophiles to give boronic esters bearing vicinal tri- and tetrasubstituted stereocenters in good yields and high diastereoselectivities. Notably, substrates bearing alkyl substituents display the opposite sense of diastereoselectivity to previously studied aryl-substituted analogues. The results suggest that the stereochemical outcome is independent of the initial configuration at C2 and is instead dictated by conformational preferences of the α-boryl lithium intermediate. A simplified steric model is proposed in which lithium coordination induces a pseudo-chelated structure that controls facial selectivity during electrophilic trapping. These findings expand the synthetic utility of α-boryl lithium intermediates and provide insight into the origins of their diastereoselectivity.

Introduction

α-Boryl carbanions **1** (Scheme 1), also referred to as boron alkylidenes or borata alkenes, represent a fascinating class of organoboron intermediates characterized by the delocalization of electron density from the negatively charged carbon center toward the electron-deficient boron atom. This delocalization leads to the formation of a partial π C–B bond (Scheme 1) [1,2], which provides a unique stabilization to the carbanionic center and affects its reactivity towards electrophiles. In recent years, α-boryl carbanions have attracted significant attention as highly versatile intermediates capable of engaging in diverse bond-forming processes, including C–C, C–O and C–N bond formations [3-24]. Despite their growing utility, controlling the stereoselectivity in substitution reactions of α-boryl carbanions remains a formidable task [25-27]. The electronic character of these intermediates, especially for boronic ester derivatives that allow coordination between oxygen atoms and the metal coun-



Scheme 1: Synthesis and reactivity of α-boryl lithium species.

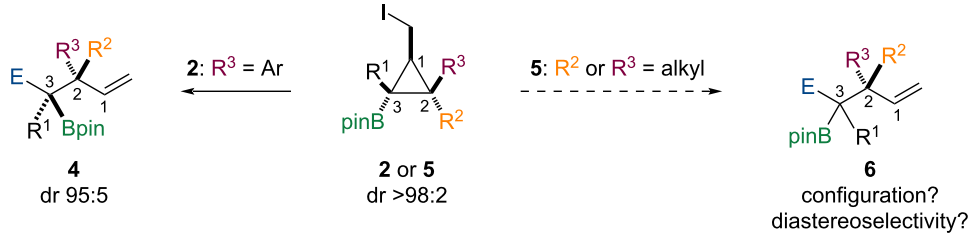
terion, complicates predictable stereochemical outcome. Developing strategies to harness the exceptional nature of these carbanions in a stereodefined manner would achieve the synthesis of polysubstituted organoboron compounds with adjacent stereocenters. The latter are highly valuable building blocks, given the pivotal role of organoboron compounds in contemporary chemistry as stable, yet reactive, intermediates that enable diverse catalytic and stereoselective transformations [28-33].

In this context, we have recently demonstrated that a broad range of arylated (iodomethyl)cyclopropylboronic ester **2** [34] undergo ring-opening reactions, followed by electrophilic trapping of the resulting α-boryl carbanion derivative **1** to afford product **4** as single diastereomers. Specifically, iodide **2** was subjected to *tert*-butyllithium (*t*-BuLi) in diethyl ether at –95 °C, efficiently generating cyclopropylmethyllithium **3** via lithium–iodine exchange. Subsequent selective C–C bond cleavage of **3**, proceeding exclusively through cleavage of the C1–C3 bond rather than the C1–C2 bond, provided direct access to α-boryl carbanion intermediate **1**. Reaction of **1** with a range of electrophiles furnished tertiary pinacol boranes with a well-defined adjacent stereocenter in excellent diastereoselectivity (Scheme 1).

Theoretical studies revealed that the electrophile preferentially approaches from the face opposite the coordinating lithium cation, with the lowest-energy transition state stabilized by a lithium cation–vinyl interaction (see **A** in Scheme 1) [34].

Results and Discussion

The intricate interplay of the coordination and steric effects suggests that the adjacent stereocenter at C2 might play a key role in the conformational stability and the stereochemical outcome. We therefore set out to extend the scope of the transformation by probing how substitution at the C2 position of precursor **2** affects the diastereoselectivity of the reaction. We were particularly interested in examining cases with alkyl (**5**) instead of aryl substituents in **2** on C2 (Scheme 2).



Scheme 2: Diastereodivergent electrophilic trapping of α-boryl lithium derivatives.

We initiated the investigation into the selectivity of the transformation with the synthesis of a library of cyclopropylmethyl iodides **5a–i**, using our previously reported methodology [35-37] (Figure 1).

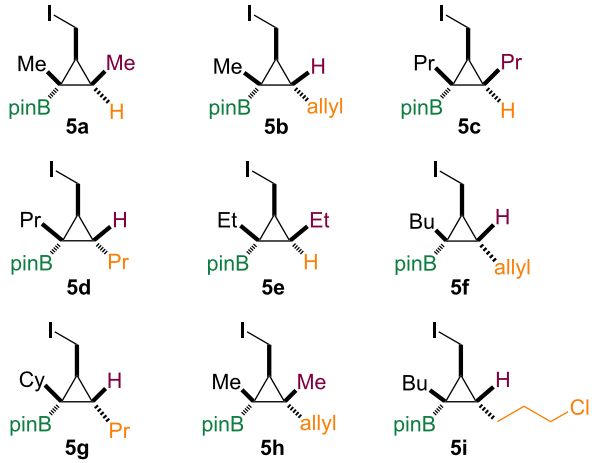
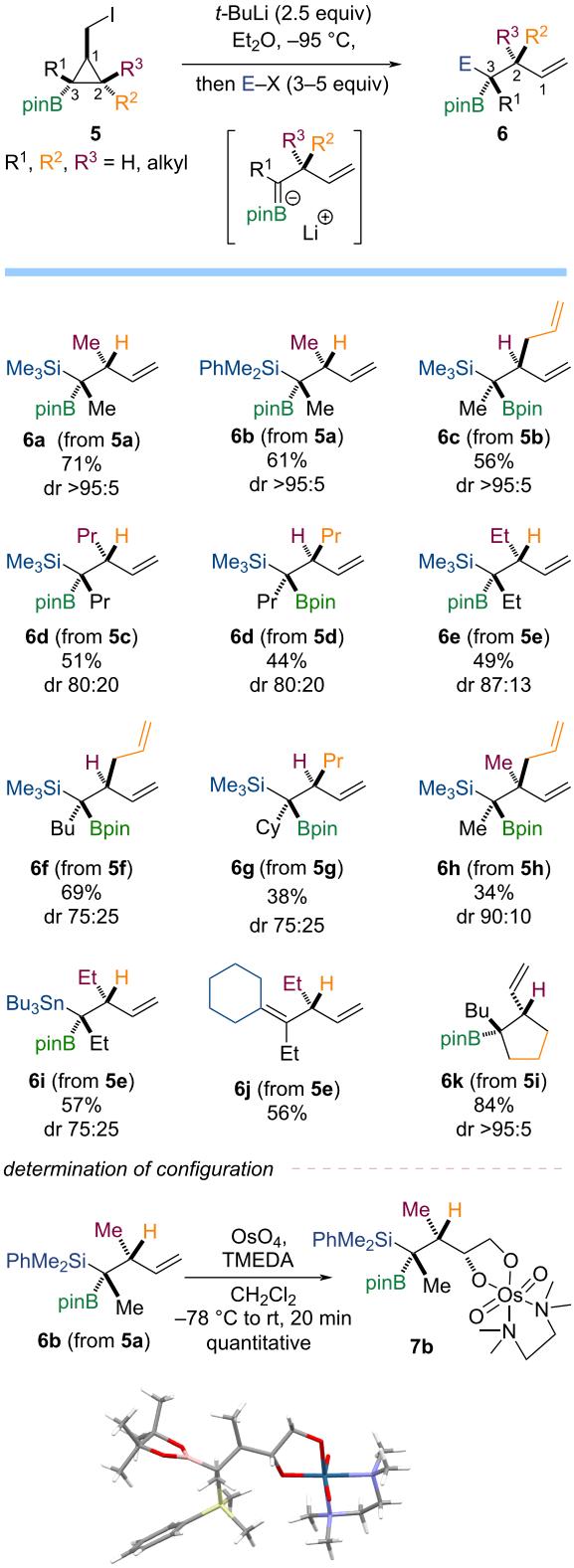


Figure 1: Cyclopropylmethyl iodide starting materials.

When the substrate **5a** (R^1 = R^3 = Me, R^2 = H) was subjected to the standard reaction conditions, the ring-opening process and trapping with Me_3SiCl occurred selectively, affording **6a** in an excellent diastereomeric ratio (Scheme 3). Replacing Me_3SiCl with the bulkier electrophile $PhMe_2SiCl$ did not alter the selectivity of the transformation, yielding **6b** as a single diastereomer (Scheme 3). The relative configuration of **6b** was determined by X-ray analysis of the osmate ester **7b**, derived from osmium-catalyzed dihydroxylation (Scheme 3) [38], and the other products were assigned by analogy. Interestingly, the relative configuration is reversed compared to the cases with aryl group as R^3 (Scheme 2) [34].

The presence of an aliphatic substituent as R^2 instead of R^3 (R^3 = H, R^2 = allyl) has no influence on the diastereoselectivity, as **6c** was obtained with high selectivity. For both **6a**/**6b** and **6c**, the alkyl substituent, whether R^3 (**6a**, **6b**) or R^2 (**6c**), has a syn-relationship with the boronic ester group. Furthermore, performing the reaction with diastereomers **5c** (R^1 = R^3 = Pr, R^2 = H) and **5d** (R^1 = R^2 = Pr, R^3 = H), produced product **6d** with the same relative configuration (described as the two enantiomers to maintain an identical configuration of C2), albeit with moderate yields and diastereoselectivities.

This observation supports the hypothesis that the reaction outcome is independent of the initial relative configuration at C2 of the starting material. Increasing the length and branching of the R^1 substituent (from Me, Et to Bu, and Cy) resulted in a slight decrease in diastereomeric ratios, providing **6e–g** in mod-

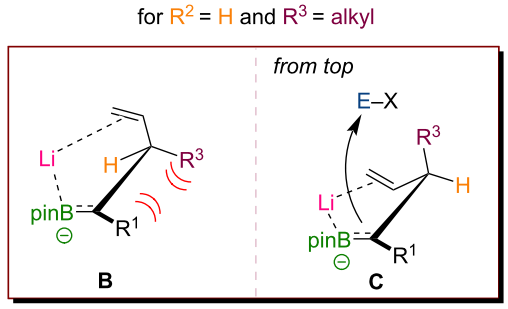


Scheme 3: Reactivity of α-boryl lithium intermediates **5** possessing alkyl substituents at the allylic position.

erate yields and selectivities. To our delight, the reaction proceeded even when three alkyl substituents were present (**5h**, $R^1 = R^3$ = Me, R^2 = allyl), providing compound **6h** bearing two adjacent fully substituted stereocenters (Scheme 3). Although the yield was relatively low (34%), the diastereomeric remained high (dr 90:10). The relative configuration of the major diastereomers of **6h** was assigned by analogy to **6c**, but it could not be definitively confirmed due to the inability to obtain suitable crystals for X-ray analysis. In addition to the nucleophilic substitution of the boryl lithium species with R_3SiCl, a small range of alternative electrophiles was examined (Scheme 3). Incorporation of a tin-based electrophile furnished stannane **6i** in moderate yields with good diastereoselectivity. Reaction with cyclohexanone led to partial elimination, which proceeded to completion upon warming the reaction mixture to room temperature, affording the bora-Wittig product **6j** in moderate yield [39]. Furthermore, an intramolecular reaction was investigated: cyclopropane **5i** possessing a chloride as a leaving group underwent highly selective cyclization to deliver the stereodefined borylated cyclopentane **6k** in high 84% yield as a single diastereomer. The relative configuration of **6k** was unambiguously established by X-ray crystallographic analysis of an osmylated derivative (see Supporting Information File 1).

As noted above, the diastereoselectivity observed for substrates bearing alkyl substituents at R^2/R^3 is opposite to that previously reported for aryl-substituted analogues (Scheme 4).

The solvent-coordinated lithium alkylidene model used to rationalize the aryl series [34] does not account for the selectivity trend in the alkyl case, indicating that different stereochemical factors dominate in the absence of an aryl substituent. We therefore propose a simplified, steric-based model to account for the observed diastereoselectivity. Based on previous theoretical calculations, this model assumes initial coordination of both the vinyl group and the Bpin moiety to the lithium counterion. Within this constrained geometry, when R^2 = H, R^3 = alkyl, the diastereocontrol is then governed by the relative steric interactions present in these two possible conformers **B** and **C**. This conformational constraint rigidifies the system through formation of a pseudo-ring, leading to potential gauche interactions between R^1 and R^3 in conformer **B** (Scheme 5).



Scheme 5: Mechanistic hypothesis to rationalize the diastereoselectivity.

In conformer **C**, however, substituents R^1 and R^3 are further apart, which expose a free diastereotopic face above the plane of the molecule and allows the electrophile to react anti to the pseudo-chelated metallacyle. When R^2 = alkyl and R^3 = H, the corresponding enantiomeric conformer leads to the same diastereomer, as expected from the enantiomeric relationship (see **6d** from **5c** and **5d**, Scheme 3).

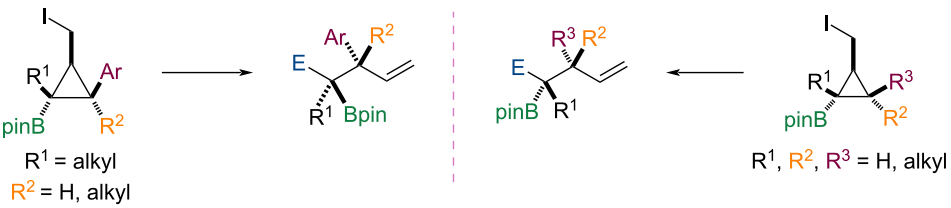
Conclusion

In conclusion, this work establishes α-boryl lithium intermediates as valuable stereogenic platforms for conducting highly diastereoselective nucleophilic transformations. The combination of the anion-stabilizing capability of boron with strain-release-driven ring fragmentation provides exceptional chemo- and regioselectivity. The use of various electrophiles enabled the synthesis of acyclic boronic esters featuring vicinal tri- and tetrasubstituted stereocenters.

Supporting Information

Supporting Information File 1

Experimental section, characterization data and copies of spectra.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-22-68-S1.pdf]



Scheme 4: Effect of the nature of the substituent R^3 on the diastereoselectivity.

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Author Contributions

Tereza Pavlíčková: conceptualization; investigation; methodology; writing – review & editing. Noam Orbach: conceptualization; investigation; methodology; writing – review & editing. Ilan Marek: conceptualization; resources; writing – original draft; writing – review & editing.

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Data Availability Statement

All data that supports the findings of this study is available in the published article and/or the supporting information of this article. The crystal data have been deposited in the Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/) deposition numbers CCDC 2537818 and 2537817.

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A study towards the undirected fluorination and chlorination of cubane 1,4-diester

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Letter

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Abstract

A study towards the undirected C–H fluorination and chlorination of cubane 1,4-diester is described using a user-friendly reagent such as Selectfluor and 1,3-dichloro-5,5-dimethylhydantoin under photoinduction. While the fluorocubane 1,4-diester is formed in low yield (8% yield) due to loss of material, the chlorocubane 1,4-diester was on the other hand prepared in 59% yield without the need for any photocatalyst. Moreover, a proof-of-concept of the chlorination of this strained scaffold was demonstrated using flow technology.

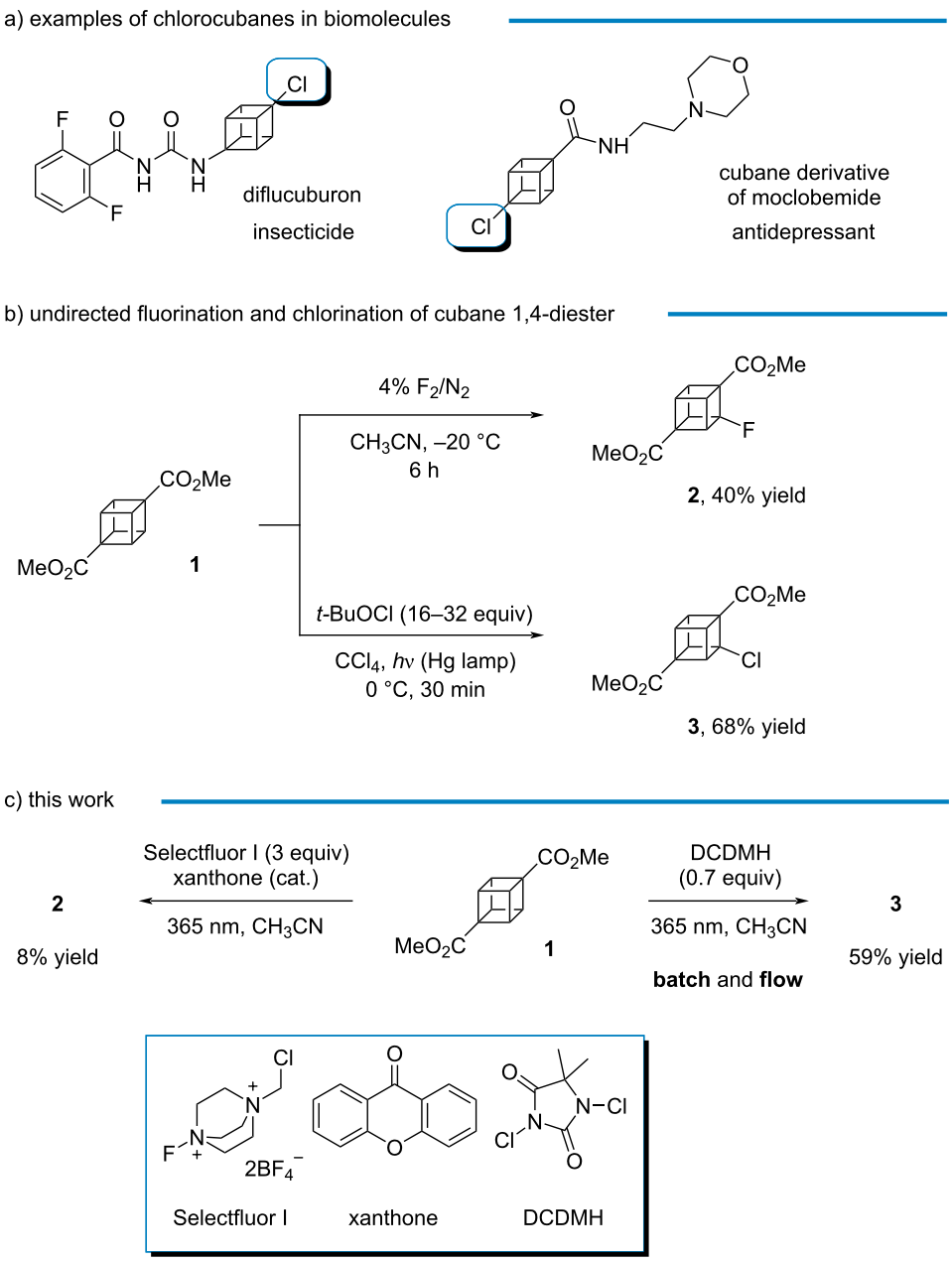
Introduction

The strained cubane scaffold serves as a three-dimensional bioisosteric alternative to benzene, sharing similar dimensions but lacking π-character [1]. Functionalization of the commercially available cubane 1,4-diester is a critical step to obtain isosteres of trisubstituted benzene rings in molecules of interest. Of note, molecules incorporating the cubane motif often exhibit enhanced solubility, metabolic stability, nonspecific binding, and biological activity compared to their aromatic counterparts [2-5].

Among the functionalization strategies, halogenation – particularly fluorination and chlorination – represents a powerful tool for modulating physicochemical properties of aromatic rings, including acidity, halogen bonding, metabolic stability, and solubility [6,7]. The chlorocubane motif can be found in biomolecules with interesting biological properties like the cubyl analogues of diflubenzuron and of moclobemide (Scheme 1a) [8].

As 1,4-disubstituted halocubane derivatives are prepared by halodecarboxylation, the synthetic routes to 1,2,4-trisubstituted halocubanes are lengthier, requiring prior carboxylation of cubane 1,4-diester [9,10].

As an alternative route, halogenation by hydrogen abstraction of cubane 1,4-diester remains difficult. The presence of ester



Scheme 1: Undirected fluorination and chlorination of cubane 1,4-diester **1**.

groups gives rise to strong C–H bonds (103 kcal·mol^{-1}) to the framework. While studying the formation of cubyl radicals, Della and Walton observed the deactivation of cubane 1,4-diester toward hydrogen abstraction compared to cubane and alkylcubane [11].

Accordingly, the undirected C–H fluorination or chlorination of cubane 1,4-diester **1** requires harsh conditions (Scheme 1b). The C–H fluorination of **1** was initially reported by Lagodzinskaya in the presence of F_2 in 40% yield [12]. Elsewhere, Kaleta disclosed the photoinduced C–H chlorination of **1** in 68% yield using an excess of *t*-BuOCl in CCl_4 [13].

When one aims to selectively monohalogenate cubane 1,4-diester, there is a threefold challenge entailing 1) incomplete conversion, leading to potentially co-eluting mixtures of starting material and halocubane 1,4-diester, 2) polyhalogenation and, 3) degradation of the strained carbon cage.

We wish to describe herein our efforts to perform the C–H fluorination and chlorination of cubane 1,4-diester under user-friendly conditions using readily available reagents and solvents (Scheme 1c).

Results and Discussion

Fluorination of cubane 1,4-diester

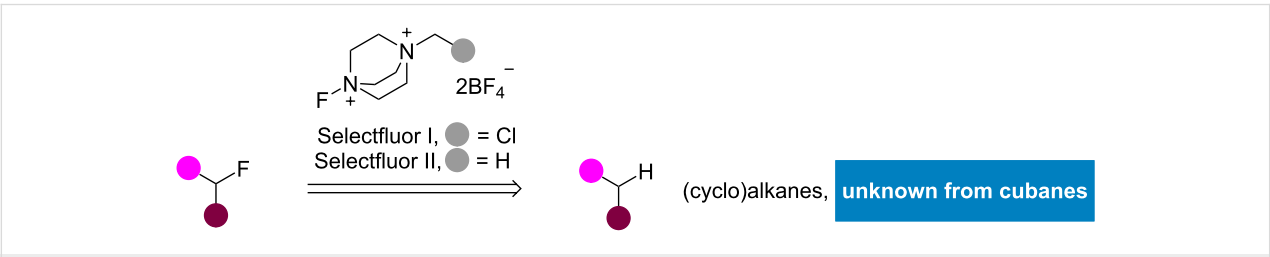
The study began with the design of a new approach to the fluorocubane 1,4-diester **2** by the undirected fluorination of the commercially available cubane 1,4-diester with Selectfluor instead of fluorine gas. Selectfluor I and II, are practical sources of electrophilic fluorine, employed in undirected C–H fluorination of (cyclo)alkanes [14] involving HAT mechanisms with [15-19] or without photocatalysts [20-22] (Scheme 2).

Exposing cubane 1,4-diester to Selectfluor I or II in the presence of peroxydisulfate salts upon heating or under photoactivation led to the isolation of a small amount of fluorocubane **2** (ca. 5% yield) alongside variable amounts of remaining starting material, an important loss of material being noted (Scheme 3).

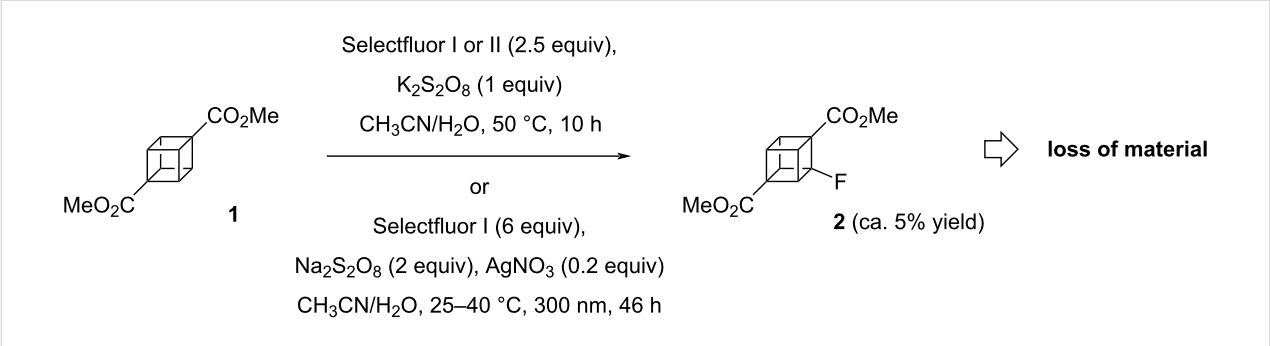
Slightly more side products were noted in the crude of the reaction with Selectfluor II. Therefore, the first generation of reagent was preferred for the rest of the study. To mitigate degradation, milder conditions were sought using photocatalysis. While attempts to perform the fluorination with tetracyanobenzene, benzophenone, or TBADT were unsuccessful [23], the photocatalyst xanthone (20 mol %) at 300 or 350 nm gave slightly better results (Table 1). In the best scenario, however, **2** was isolated in 8% yield amid partial conversion (ratio **1**:**2** = 1:6). It must be noted that the separation of **2** from the starting material is challenging and achieving higher conversion was detrimental to the mass balance.

As a possible explanation of the degradation, we isolated 2-acetylcubane 1,4-diester **4** in variable amounts (up to 8% yield), the highest amount being obtained when operating the C–H fluorination at 300 nm in CH_3CN/H_2O (Table 1, entry 1). At this wavelength, the mass balance is lower than at 365 nm. The acetylated product **4** may originate from the reaction of the cubyl radical with acetonitrile followed by hydrolysis of the resulting imine/enamine. Since acetyl, or the parent imine, can be fluorinated with Selectfluor I, it is possible that the fluorination of acetyl **4** or its imine precursor also occurred, followed by degradation. The uncontrolled C–H acetylation of fluorocubane **2** may take place as well. Note that no conversion was observed when operating in methanol instead of acetonitrile (not shown) which is consistent with previous studies on C–H fluorination using the reagent [20,21].

To understand the reaction parameters inducing the formation of **4**, cubane 1,4-diester **1** was exposed to xanthone (0.2 equiv) purposely without Selectfluor I at 365 nm (Table 1, entry 2). Acetyl **4** was observed as traces in the crude of the reaction. The compound was not detected when carrying out the same experiment at 300 nm (Table 1, entry 3).

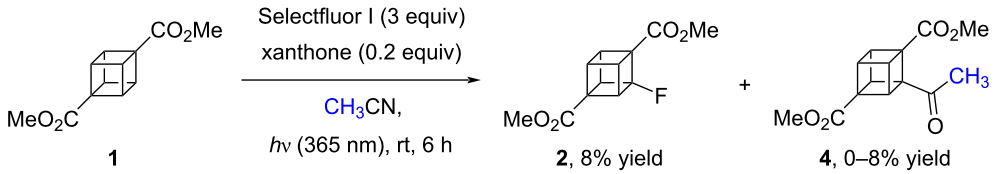


Scheme 2: Undirected fluorination of (cyclo)alkanes with Selectfluor reagents.



Scheme 3: Fluorination of **1** with Selectfluor I or II and peroxydisulfate.

Table 1: Photoinduced fluorination of **1** and deviations from these conditions.



entry	deviations	**2**	**4**
1[a]	300 nm, CH_3CN/H_2O 1:1, 16 h	8%[a]	8%[a]
2[b]	without Selectfluor I, 16 h	–	traces[b]
3	300 nm without Selectfluor I, 16 h	–	not detected[b]
4	Selectfluor I (6 equiv), 85 °C, 16 h without xanthone and *hv*	traces[b]	not detected[b]
5	Selectfluor I (6 equiv), 300 nm, CH_3CN/H_2O 1:1, 24 h without xanthone	traces[b]	traces[b]
6	300 nm in CD_3CN/H_2O 1:1, 16 h	8%[a]	**4**-d_3, 5%[a]

[a]Isolated yield; [b]inspection of the crude reaction by ^{1}H NMR spectroscopy (300 MHz).

Furthermore, attempting the C–H fluorination upon heating (Table 1, entry 4, Selectfluor I (6 equiv), CH_3CN, 85 °C, 16 h) without photocatalyst led to traces of **2** while **4** was not detected. At 300 nm and without Xanthone (Table 1, entry 5), traces of **2** and **4** were observed. Performing the C–H fluorination of **1** in CD_3CN/H_2O (Table 1, entry 6, 300 nm) confirmed that the cubane scaffold reacts to a small extend with the solvent since **4**-d_3 was isolated (5% yield) alongside **2** (8% yield).

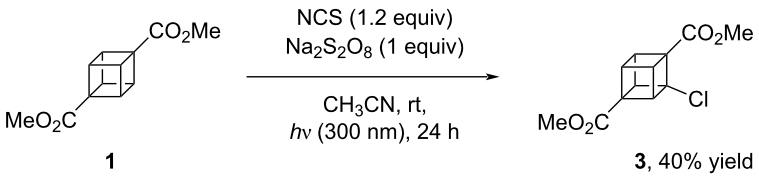
In summary, the fluorination of cubane 1,4-diester was investigated with Selectfluor I or II with or without a photocatalyst, leading to a small amount (8% yield) of fluorocubane 1,4-diester. As a possible explanation for the low mass balance, the formation of acetyl **4** hints to side reactions with the solvent. This observation motivated us to develop a strategy for the fluorodeiodination of iodocubanes with Selectfluor allowing a directed installation of the fluorine atom [24].

Chlorination of cubane 1,4-diester

Pursuing the halogenation of cubane 1,4-diester **1** with mild reagents, we sought to carry out the undirected chlorination of the material. After a screening of conditions, we identified reactions parameters inducing the smooth chlorination of **1**. As detailed in Scheme 4, *N*-chlorosuccinimide (NCS) was combined with photoexcited (300 nm) peroxydisulfate sodium salts to form chlorocubane **3** in 40% yield after 24 h of reaction (ratio **1**/**3** of 1:2.3, estimated by ^{1}H NMR spectroscopy).

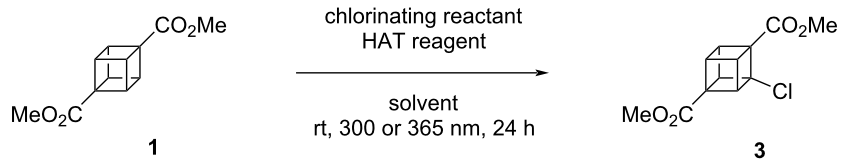
The contrast with the fluorination of **1** is noteworthy: there was no important loss of material and, probably related, the acetyl product **4** was not detected in the crude of the chlorination reaction.

From this initial result, we carried out an optimization of the reaction parameters (Table 2). Performing the experiment at 365 nm (Table 2, entry 2) was slightly better (44% yield) while increasing the concentration ([**1**] = 0.1 mol/L, Table 2, entry 3) enhanced the ratio **1**/**3** (1:2 to 1:2.6) and yield (52%). On the other hand, a higher concentration (Table 2, entry 4) was unfavorable. Unexpectedly, it was found that the use of sodium peroxydisulfate was slightly detrimental (Table 2, entry 5) and operating without the oxidant led to **3** in 57% yield (ratio **1**/**3** = 1:4.5). Solvent screening revealed that acetonitrile gave a better result than chlorinated solvents or acetone (Table 2, entries 6–9). Eventually, 1,3-dichloro-5,5-dimethylhydantoin



Scheme 4: Undirected photoinduced chlorination of **1**.

Table 2: Chlorination reaction of **1**.



entry	reactant	HAT reagent (1 equiv)	solvent	[**1**] (mol/L)	ratio **1**/**3**[a]	yield (isolated)
1[b]	NCS[c]	$Na_2S_2O_8$	CH_3CN	0.05	1:2.3	40%
2[d]	NCS[c]	$Na_2S_2O_8$	CH_3CN	0.05	1:2	44%
3[d]	NCS[c]	$Na_2S_2O_8$	CH_3CN	0.1	1:2.6	52%
4[d]	NCS[c]	$Na_2S_2O_8$	CH_3CN	0.2	1:1.9	48%
5[d]	NCS[c]	–	CH_3CN	0.1	1:4.5	57%
6[d]	NCS[c]	–	CH_2Cl_2	0.1	1:1.2	nd
7[d]	NCS[c]	–	acetone	0.1	nr	
8[d]	NCS[c]	–	DCE	0.1	nr	
9[d]	NCS[c]	–	$CHCl_3$	0.1	nr	
10[d]	DCDMH[e]	–	CH_3CN	0.1	1:3.2	59%

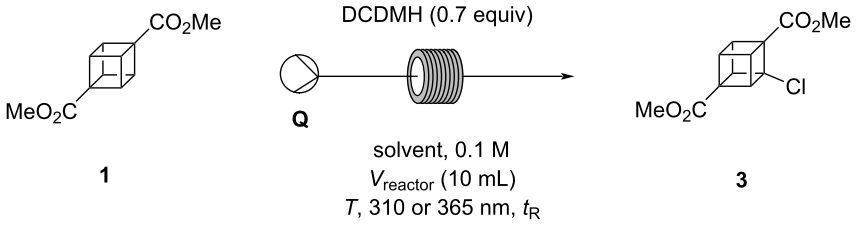
[a]Estimated by ^{1}H NMR spectroscopy. [b]300 nm; [c]1.2 equiv; [d]365 nm; [e]0.7 equiv.; nr: no reaction; nd: not determined; DCE: 1,2-dichloroethane.

(DCDMH) was found to be slightly more efficient than NCS (Table 2, entry 10), giving **3** in 59% yield (ratio **1**/**3** = 1:3.2). The separation of **3** from the starting material is challenging and attempts to achieve higher conversion resulted in negative mass balance.

We next sought to develop the chlorination reaction in flow conditions (in a Vapourtec® R-series) as a proof-of-concept with aims both to (i) scale up and (ii) to evaluate the impact of the t_R (residence time) on the amount of polychlorocubane products (Table 3). In batch, small amounts of polychlorocubanes were detected and we were curious to examine whether these products could be suppressed.

It was noted that when using CH_3CN as solvent, the substrate **1** partially precipitated in the tube (flow rate 0.4 mL/min, Table 3,

Table 3: Chlorination reaction of **1** in flow.



entry	flow rate **Q** (mL/min)	solvent	T (°C)	t_R (min)	ratio **1**/**3**[a]
1[b,c]	0.4	CH_3CN	28	25	–
2[b,c]	0.4	CH_3CN/CH_2Cl_2 10:1	28	25	1:0.42
3[b,c]	0.4	CH_3CN/CH_2Cl_2 4:1	28	25	1:0.82
4[c,d]	0.22	CH_3CN	30	45	1:1.32
5[d,e]	0.33	CH_3CN	28	30	1:1.13

[a]Estimated by ^{1}H NMR spectroscopy; [b]partial precipitation; [c]365 nm; [d]heating at 30 °C and sonication of the solution of **1** (c = 0.1 M); [e]310 nm.

entry 1). Therefore, a co-solvent CH_2Cl_2 was introduced (Table 3, entries 2 and 3) and even though partial solubilization of **1** was achieved, low amounts of **3** were formed. After 45 min of residence, chlorocubane **3** became the major product (ratio **1**/**3** = 1:1.32) when using a pre-heated and sonicated initial solution of **1** in CH_3CN (Table 3, entry 4). However, small amounts of polychlorinated cubanes were detected. A similar setting was tested at 310 nm (Table 3, entry 5) which led to the isolation of **3** in 41% yield (61% based on remaining starting material).

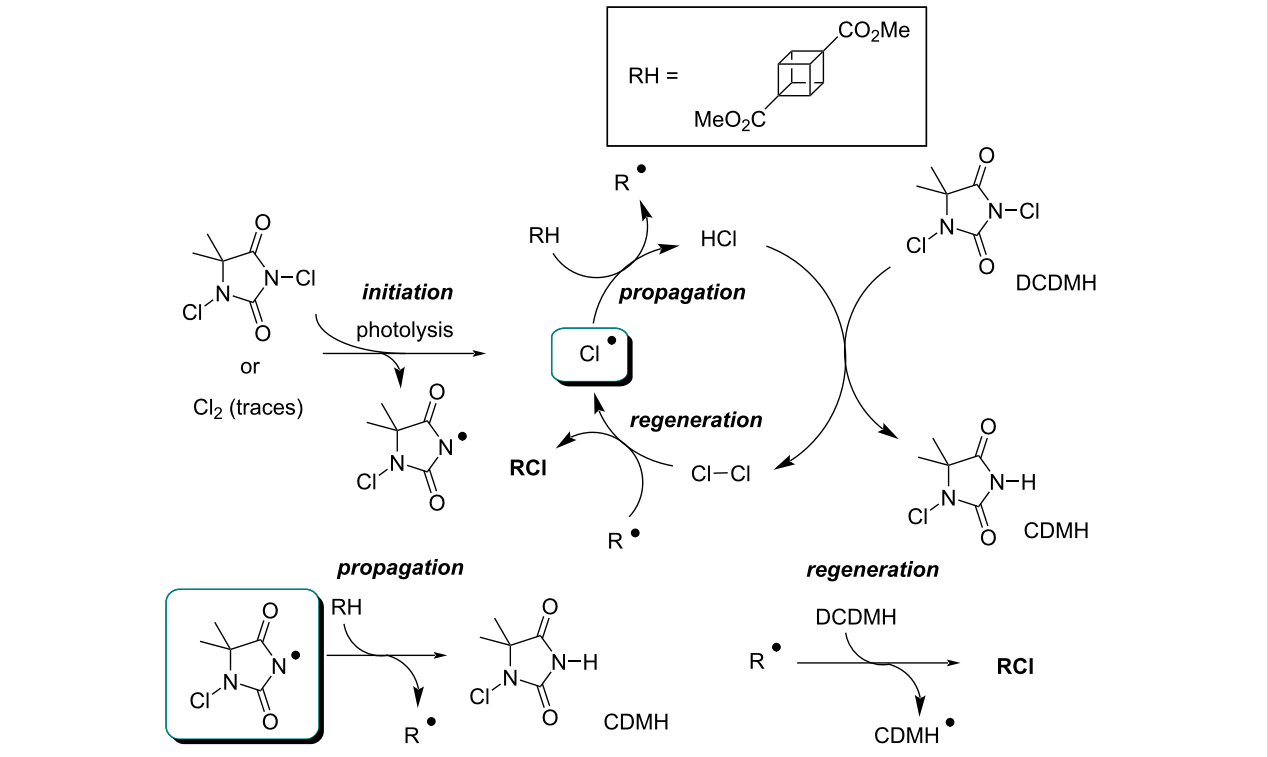
While the chlorination of **1** was achieved by Kaleta using a large excess of *t*-BuOCl (16–32 equiv) under photoactivation [13], the utility of the current method involving DCDMH (0.7 equiv) is noteworthy. Since the photolysis of NCS has been described by MacMillan at 450 nm to release chlorine radicals ($Cl^{\bullet}$) [25], a tentative mechanism proposal would imply that N-centered and chlorine radicals are similarly released by photolysis of DCDMH or of molecular chlorine contained as traces in the reagent (Scheme 5). When the experiment was conducted in the dark, no chlorination occurred. Propagating the chain, the radicals will in turn engage in cubane HAT to give HCl (BDE = 102 kcal·mol^{-1}), a process observed in other contexts [26].

Note that HAT activation of cubane is a challenging transformation (BDE = 103 kcal·mol^{-1}) performed here with stable and available reagents DCDMH or NCS. The generation of cubyl radicals from cubane 1,4-diester traditionally requires photoexcited strong and unstable oxidants, such as *t*-BuOX (X = Cl [13], I [27]), or tetra-*n*-butylammonium decatungstate (TBADT) [28-33].

The reaction of HCl with DCDMH would generate molecular chlorine [34], which by reaction with cubyl radicals may subsequently form chlorocubane and regenerate $Cl^{\bullet}$. An alternative and parallel pathway may involve the reactivity of the N-centered radical chlorodimethylhydantoin (CDMH) [35], which could form the cubyl radical by HAT and regeneration of the N-centered radical species ($CDMH^{\bullet}$) after its reaction with DCDMH [36].

Conclusion

Mild conditions were developed to perform undirected fluorination and chlorination of the commercially available cubane 1,4-diester, which will be of interest for the synthesis of substituted benzene isosteres. Whilst the fluorination protocol was limited in efficiency compared to the fluorodeiodination strategy, user-friendly reagents and solvents were successfully employed for the chlorination reaction. The transformation was performed in batch and we demonstrated a proof-of-concept flow implementation. These advances should facilitate the incorporation of chlorocubyl motifs into molecules in various



Scheme 5: Proposed mechanism.

fields of investigation spanning pharmaceuticals, functional materials, and crop science.

Supporting Information

Supporting Information File 1

Experimental section and copies of spectra.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-22-101-S1.pdf]

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Data Availability Statement

All data that supports the findings of this study is available in the published article and/or the supporting information of this article.

Preprint

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36. A comparison between 1,3-dichloro-2,2-dimethylhydantoin and 1,3-dibromo-2,2-dimethylhydantoin reveals that the reactivity of the first reactant is higher toward cubane C–H bonds under photoinduction (365 nm, CH_3CN, 16 h).

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