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# A Versatile Route to Acyl (MIDA)Boronates.

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In memory of Professors Albert Eschenmoser and Bernard Bigot, and Dr. Guy Rossey

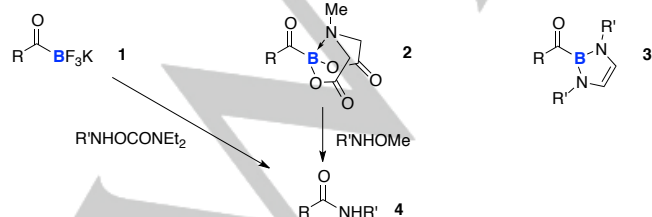
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**Abstract:** A modular approach to highly functional acyl (MIDA)boronates is described. It involves the generation of the hitherto unknown radical derived from acetyl (MIDA)boronate and its capture by various alkenes, including electronically unbiased, unactivated alkenes. In contrast to the anion of acetyl (MIDA)boronate, which has not so far been employed in synthesis, the corresponding radical is well behaved and readily produced from the novel  $\alpha$ -xanthyl acetyl (MIDA)boronate. This shelf-stable, easily prepared solid is a convenient acyl (MIDA)boronate transfer agent that provides a direct entry to numerous otherwise inaccessible structures, including latent 1,4-dicarbonyl derivatives that can be transformed into B(MIDA) substituted pyrroles and furans. A competition experiment indicated the acyl (MIDA)boronate substituted radical to be more stable than the all-carbon acetyl radical but somewhat less reactive in additions to alkenes.

## Introduction

Organoboron compounds play a major role in organic synthesis and medicinal chemistry.<sup>[1]</sup> The Suzuki-Miyaura coupling is indeed one of the most employed reactions by medicinal chemists.<sup>[2]</sup> Moreover, the number of drug substances containing a boron atom is steadily increasing.<sup>[3]</sup> Much effort has therefore been devoted to access novel organoboron derivatives. In this respect, acylborons, such as compounds **1-3** (Scheme 1), have recently emerged as a highly promising class of organoboron derivatives, exhibiting an interesting pattern of reactivity.<sup>[4]</sup> For instance, acyl(MIDA)boronates **2** react with *O*-methylhydroxylamines to furnish amides **4** at room temperature, in water, and even in a dilute medium.<sup>[5]</sup> These conditions, which further tolerate various unprotected functional groups, are ideal for accomplishing bioconjugations of proteins and other complex biomolecules. Another useful transformation is the reductive amination to give ultimately an  $\alpha$ -aminoboronic acid (not shown).<sup>[6]</sup>

**Scheme 1.** The most common acylborons.

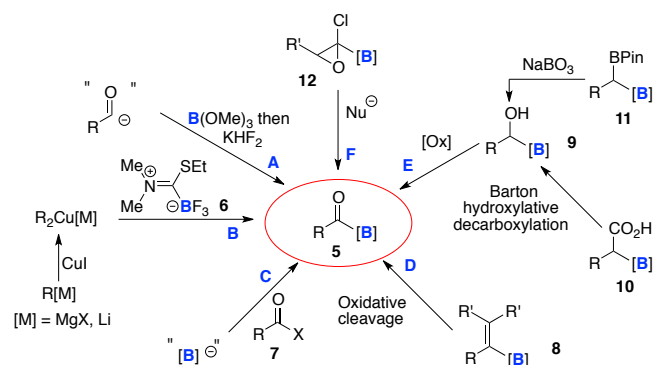


Acylborons can be isolated as stable entities when the boron atom is substituted with non-migrating groups. Most common are potassium acyltrifluoroborates **1**, acyl(MIDA)boronates **2**, and

NHC stabilized acylborons **3**, with the last being the least studied of the three. The number of routes to these compounds has however remained relatively limited. The main approaches are displayed in Scheme 2.<sup>[4]</sup>

One of the early first approaches to acylboron **5** relies on the reaction of acyl anion equivalents, such as alkoxyvinyl lithiums or organolithiums derived from Katrizky' *N*-( $\alpha$ -alkoxyalkyl)-benzotriazoles, with trimethoxyborane and *in situ* conversion into potassium acyltrifluoroborates (path **A**).<sup>[7]</sup> Dithianoyllithiums have also been used, but only one example of deprotection into the acylboron has been documented.<sup>[7d,e]</sup> Bode and coworkers devised the interesting acylboron transfer reagent **6**, which reacts with (hetero)aryllithiums or, more generally, with organocopper derivatives to give acyltrifluoroborates **1** (path **B**).<sup>[8]</sup> A third route involves the reaction of boron anion equivalents with activated carboxylic acids **7** such as acid chlorides (path **C**).<sup>[9]</sup> A more recent synthesis is based on the oxidative cleavage of alkenylborons **8**, either by ozonolysis according to the groups of Bode and Ito<sup>[10]</sup> or by OsO<sub>4</sub>/NMO dihydroxylation followed by treatment with periodate according to Perrin<sup>[11]</sup> (path **D**). The oxidation of alcohols **9** constitutes a straightforward access to acylborons **5** (path **E**). Various methods can furnish the requisite alcohols, including the reaction of aldehydes with boryl anion equivalents.<sup>[12]</sup> In an approach reported by the group of Yudin, the elegant Barton decarboxylative hydroxylation was applied to carboxylic acids **10**.<sup>[13]</sup> Selective perborate cleavage of unsymmetrical gem-diboronates **11** as described by Sharma is another route to alcohols **9**.<sup>[14]</sup> Finally, Wang disclosed that the reaction of chloroepoxides **12** (X = Cl) either with a Lewis acid or with various nucleophiles also furnishes acylborons **5** (path **F**).<sup>[15]</sup>

**Scheme 2.** Main routes to acylborons



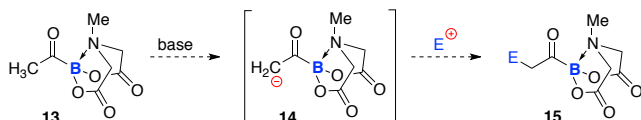
Only route **B** involves an acylboron transfer reagent **6** but requires starting with a reactive organolithium or a Grignard reagent, which in some cases must be converted into a cuprate. Remarkably, the obvious complementary approach involving the formation of an

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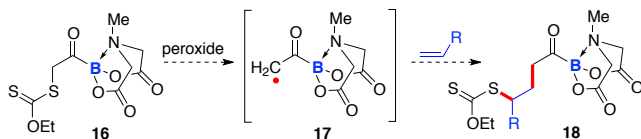
acylboron enolate such as **14** and its capture with an electrophile has not been reported, as far as we can tell (Scheme 3a). This is presumably due to the incompatibility of acylborons with the basic conditions needed to generate the corresponding enolates. In the case of acetyl (MIDA)boronate **13**, the presence of the two carboxylates in the MIDA portion is certainly a complicating factor.

**Scheme 3.** Anion and radical derived from acetyl (MIDA)boronate.

a) Alkylation of the enolate of acetyl (MIDA) boronate — So far unreported



b) Generation and capture of the acetyl (MIDA) boronate radical— This work



From our perspective, this raised the question as to the behavior of the corresponding radical **17** and whether it could be easily produced and implicated in synthetically useful transformations. We had shown that xanthates were uniquely effective as precursors for a variety of acetyl radicals, which could be readily intercepted even by unactivated alkenes.<sup>[16,17]</sup> Transposed to  $\alpha$ -xanthyl acetyl (MIDA)boronate **16**, this would furnish adduct **18** (Scheme 3b).

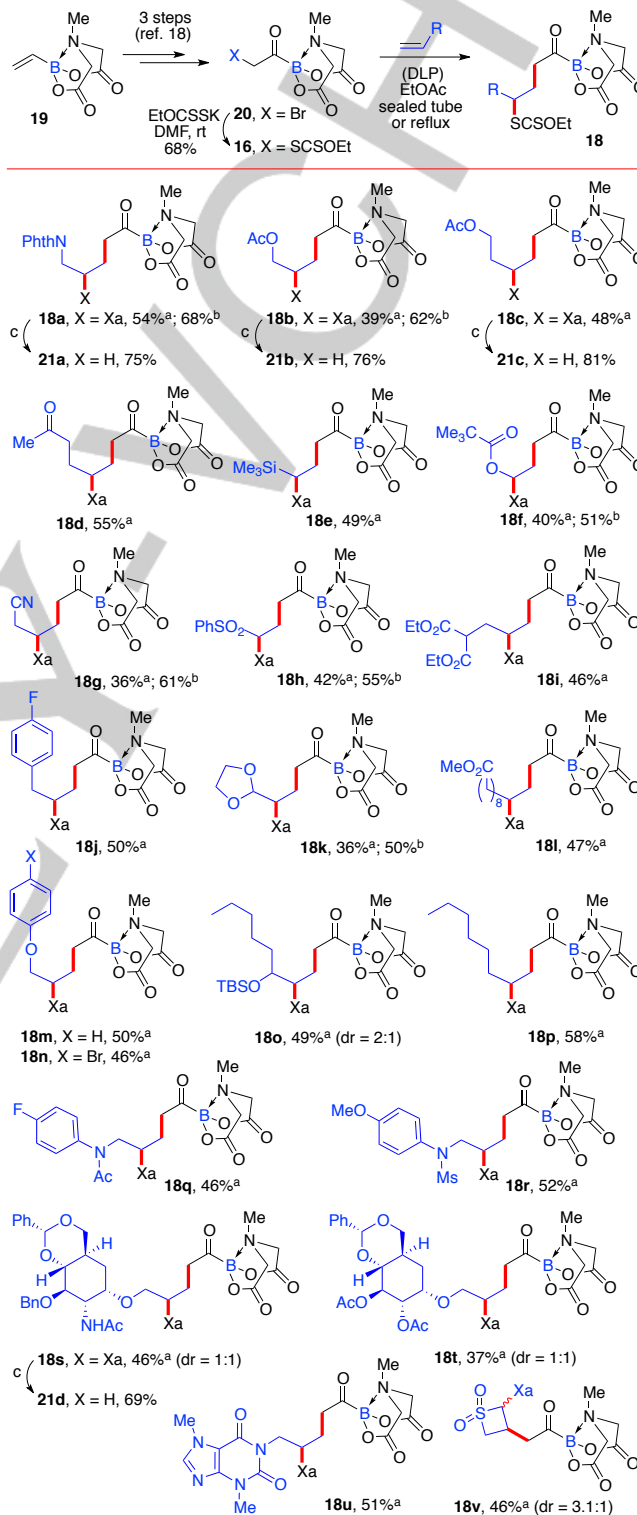
## Results and Discussion

For the synthesis of the requisite xanthate **16**, we took advantage of the accessibility of the bromide precursor **19** by the procedure described by Yudin and co-workers (Scheme 4).<sup>[18]</sup> Its reaction with potassium *O*-ethyl xanthate furnished the desired xanthate **16** as a slightly yellowish shelf-stable solid on gram scale. We were pleased to find that its addition to a broad range of alkenes proceeded as expected to give adducts **18a-18v**, as depicted in Scheme 4. The reaction was carried in ethyl acetate, either at reflux or in a closed vial at 83 °C, in the presence of dilauroyl peroxide (DLP) as initiator (procedure a). In most cases, the yields were synthetically useful and numerous functional groups were tolerated, opening in this manner access to structures not available by the existing methods summarized above in Scheme 2. In this respect, the carbohydrate examples **18s** and **18t** are particularly noteworthy. The presence of the xanthate in the adducts provides an entry into all manner of sulfur functionalities and can be exploited for the creation of further new carbon-carbon bonds. It can also be reductively removed with tris(trimethylsilyl)silane to provide simpler structures without harm to the other functional groups, and in particular to the acyl boronate motif.<sup>[19]</sup> This is illustrated by the formation in generally good yield of compounds **21a-d** in Scheme 4.

In a few cases, the yield of the xanthate adducts was disappointingly and inexplicably low under the usual reaction conditions. For example, the addition of xanthate **16** to allyl acetate and allyl cyanide furnished adducts **18b** and **18g** in 39% and 36% respectively. We therefore decided to look more carefully at the addition to *N*-allyl phthalimide, even though the

yield in this case was reasonable (54%). We hoped that the bulky phthalimide group would simplify tracking the side products and allow us to have a good mass balance for the process.

**Scheme 4.** Examples of functional acyl (MIDA)boronates [Xa = -SC(=S)OEt; NPhth = phthalimide].

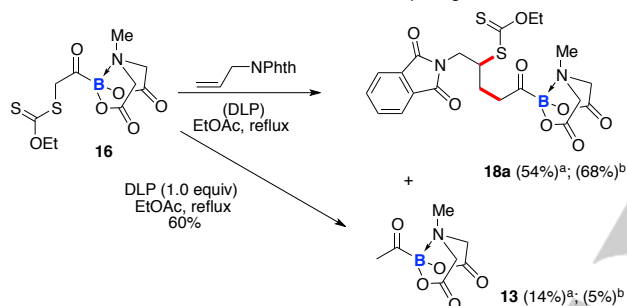


a) 0.2 equiv DLP added every 2h (0.4-0.6 equiv in total); reaction time ca 4-6h.  
 b) 0.05 equiv DLP added every hour (0.4 equiv in total); reaction time ca 9-12h.  
 c) (Me<sub>3</sub>Si)<sub>3</sub>SiH, AIBN (0.2 equiv added every hour; 0.4 equiv in total), Me<sub>3</sub>CN, reflux, 2h.

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The main side-product that we ultimately found did not contain any phthalimide group; it turned out to be the known acetylboronate **13**, isolated in 14% yield (Scheme 5). This compound is most likely derived by hydrogen atom abstraction from the solvent by intermediate radical **17** and its formation could indicate an excessively high flux of radicals as compared to the rate of addition to the alkene. This causes a rise in the concentration of radical **17** to levels leading to significant competition from hydrogen atom abstraction from the solvent. Indeed, exposing xanthate **16** in the absence of the alkene to a stoichiometric amount of DLP furnished acetylboronate **13** in 60% yield. In the light of these considerations, we reduced the flux of radicals by adding the peroxide initiator in smaller amounts over a longer reaction time (conditions **b**). Under these modified conditions, the yield of adduct **18a** increased to 68% while the yield of acetylboronate **13** decreased to 5% (Scheme 5). We noted a similar increase in the yield of adducts **18b**, **18f**, **18g**, **18h**, and **18k** from 39%, 40%, 36%, 42%, and 36% to 62%, 51%, 61%, 55%, and 50%, respectively, when the radical additions were performed under conditions **b** (Scheme 4).

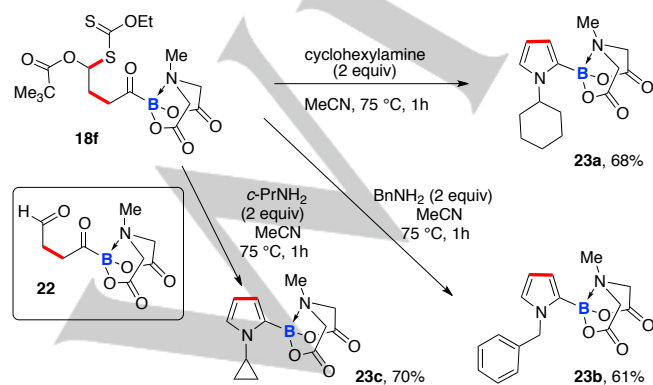
**Scheme 5.** Premature reduction as the main competing side reaction.



- a) 0.2 equiv DLP added every 2h (0.6 equiv in total); reaction time 4h.  
b) 0.05 equiv DLP added every hour (0.4 equiv in total); reaction time ca. 9-12h.

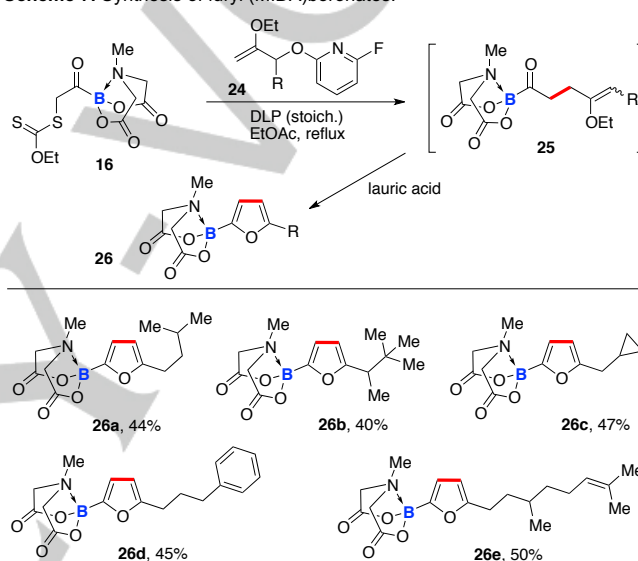
The broad functional group tolerance translates into the ability of combining the acyl (MIDA)boronate motif with various other groups, thus offering numerous opportunities for subsequent transformations. One case in point is adduct **18f**, where the xanthate and pivalate groups are on the same carbon and which can therefore be viewed as a latent form of 1,4-ketoaldehyde **22** (Scheme 6). Its condensation with primary amines leads therefore to pyrroles **23a-c** bearing a B(MIDA) group on C-2.<sup>[20]</sup> This convergent, straightforward route to such pyrroles complements previous approaches.<sup>[15, 21]</sup>

**Scheme 6.** Synthesis of 2-pyrrolyl (MIDA)boronates.



Another pathway to 1,4-dicarbonyl derivative equivalents is outlined in Scheme 7. It consists in reacting xanthate **16** with enol ethers of structure **24**.<sup>[22]</sup> The addition step is followed by  $\beta$ -scission of the fluoropyridinoxy group to give enol ethers **25**. The process requires the use of stoichiometric amounts of peroxide and generates an equivalent quantity of lauric acid. In the present case, we found that the lauric acid catalyzed *in situ* the ring-closure into furans **26** with loss of ethanol.<sup>[23]</sup> In this manner, furans **26a-e** were prepared in moderate yield. Addition of xanthates to allylic fluoropyridinyloxy derivatives is a highly versatile method to access not only 1,4-dicarbonyls but also alkenes, chloro-, fluoro-, and trifluoromethyl-alkenes; alkenyl sulfides, sulfoxides, and sulfones; and alkenyl pinacolato- and MIDA boronates.<sup>[24]</sup>

**Scheme 7.** Synthesis of furyl (MIDA)boronates.



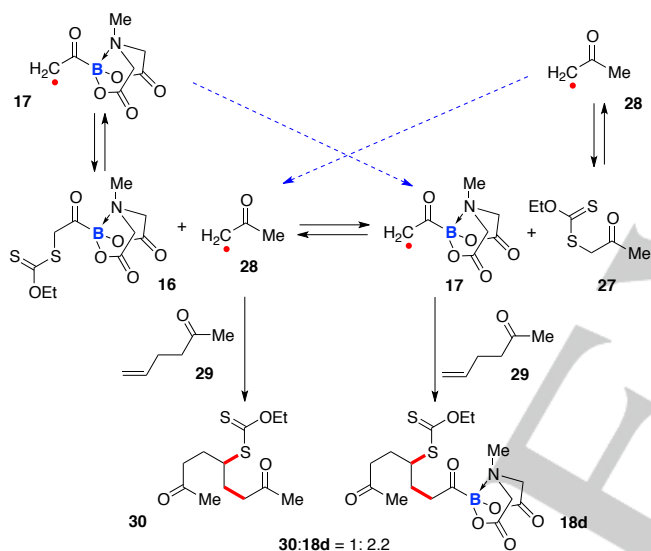
One interesting aspect concerns the reactivity of the hitherto never studied radical **17** as compared for example to the more common acetyl radicals. To shed some light on this question, we performed the competition experiment depicted in Scheme 8, whereby one equivalent each of xanthates **16** and **27** and hexenone **29** were heated in refluxing ethyl acetate in the presence of DLP as initiator. The underlying reasoning is that radicals **17** and **28**, derived respectively from xanthates **16** and **27** are in equilibrium through the fast exchange of the xanthate group, as shown in a simplified form in Scheme 8 (the xanthate exchange proceeds by a two-step addition-fragmentation process, but the intermediates involved are not shown for clarity<sup>[17]</sup>). The position of this equilibrium reflects the relative stabilities of radicals **17** and **28**. The addition of these radicals to alkene **29** is much slower than the xanthate exchange; however, it is irreversible and gives rise to adducts **18d** and **30** respectively. The reaction was not allowed to proceed to completion but stopped after 2 hours in order to limit the effect of concentration on the result.

In the event, the ratio of adduct **18d** over **30** was 2.2. This indicated that either acylboron radical **17** reacts with alkene **29** faster than acetyl radical **28** or that the equilibrium favors acylboron radical **17** over acetyl radical **28**, and the greater amount of adduct **18d** reflects in fact the higher concentration of the former species, or both. The second possibility appears to be the most likely for the following reason. In our extensive past

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studies with radical additions involving acetyl xanthates, we did not observe significant formation of prematurely reduced material (i. e., the parent ketone). This means that the rate of addition of radical **17** to the alkene is not high enough to compensate completely for the rate of production of this species, which must be particularly stabilized. Hence the observed competing hydrogen atom abstraction from the solvent. In the competition experiment, the equilibrium must therefore favor radical **17** over acetyl radical **28**. As for the irreversible addition to alkene **29**, the rates must be comparable, with the addition of radical **17** being most likely somewhat *slower* than that of acetyl radical **28**. If it were faster, then the formation of acetylboronate **13** would have been minimal because radical **17** would be consumed with lesser competition from unwanted hydrogen abstraction from the solvent. In any case, the variances are relatively modest and involve only small differences in energies. **The main stabilization of radical **17** is by spin delocalization onto the carbonyl oxygen, with the boron group appearing to play only a small indirect role.**

**Scheme 8.** Competition experiment.



## Conclusion

These preliminary results clearly underscore the value of xanthate **16** as an acylboron transfer reagent. It is a readily prepared, shelf-stable slightly yellowish crystalline solid (but preferably kept away from light) that adds to a plethora of alkenes under mild conditions tolerant of most synthetically useful functional groups. The process is easily scaled up. For example, compound **18f** that served to make the pyrroles was prepared on 5 mmoles scale without reduction in yield. Furthermore, the xanthate in the resulting products adds extra versatility, as it can in turn be converted into numerous other groups<sup>[17d]</sup> or used to create another new carbon-carbon bond by taking advantage of the ability to return to the intermediate radical.<sup>[17]</sup> It is also worth emphasizing that the B(MIDA) group can be exchanged for a trifluoroborate and other suitable boron groups (and vice-versa), so that the present approach also allows access in principle to other acylborons.<sup>[4]</sup> By providing a convenient, flexible and modular entry to a large variety of acyl (MIDA)boronates, the unique chemistry of xanthates should ultimately result in a deeper

insight into the reactivity of this emerging family of compounds and a better exploitation of their remarkable synthetic potential.

## Acknowledgements

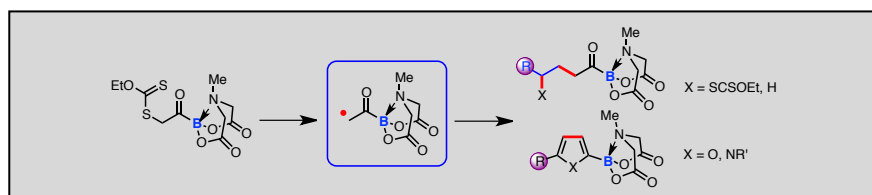
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**Keywords:** Acyl (MIDA)boronates • xanthates • radical addition • pyrroles • furans

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## Entry for the Table of Contents



Insert text for Table of Contents here. Exploiting the reactivity of the novel acetyl (MiDA)boronate radical allows access to a broad range of acyl (MIDA)boronates, which in suitable cases can be converted into B(MIDA) substituted furans and pyrroles.

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