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Organocatalysis

Lewis Base Catalyzed Synthesis of Sulfur Heterocycles via the C1-Pyridinium Enolate

Simon Cromwell[+], *Randy Sutio*[+], *Changhe Zhang, Georgina K. Such, and David W. Lupton**

Abstract: While the addition of C1-Lewis base enolates to carbonyls and related structures are well established, the related addition to thiocarbonyls compounds are unknown. Herein, we report a reaction cascade in which a C1-pyridinium enolate undergos addition to dithioesters, trithiocarbonates and xanthates. The reaction provides access to a range of dihydrothiophenes and dihydrothiopyrans (28-examples). Mechanistic investigations, including isolation of intermediates, electronic correlation, and kinetic isotope effect studies support the viability of an activated acid intermediate giving rise to the C1-pyridinium enolate which undergoes turnover limiting cyclization. Subsequent formation of a β-thiolactone regenerates the catalyst with loss of carbon oxysulfide providing the observed products.

A number of reactive intermediates are well represented in organocatalysis, transcending catalyst type, and accessible in cascades involving diverse substrates. The C1-Lewis base enolate (i.e. **1**) is one such species, featuring in a vast array of reaction designs. From early studies on the enantioselective synthesis of β-lactones by Borrmann and Wegler,[1a,b] and subsequently investigated by Wynberg,[1c] this type of intermediate has since been reported using numerous Lewis base catalysts.[2–9] Commonly ketenes, carboxylic acids, and related substrates serve as precursors to the C1-Lewis base enolate[3] which undergo annulation with ambiphilic coupling partners (i.e. **2**) (Figure 1A). While both the Lewis base catalyst and enolate precursor can be readily varied, changes to the ambiphile are more limited. Carbonyls, as foreshadowed above, remain common. For example, studies by Romo developed the in situ activation of acid **3** with Mukaiyama's reagent to provide acetyl quinidine enolate **1a** and ultimately β-lactone **4**.[4b] Electron-deficient imines as pioneered by Lectka can also be employed, allowing access to β-lactams (i.e. **5**),[5a] while conjugate acceptors serve as four atom ambiphiles, such as in Smith's synthesis of benzofurans (i.e. **6**) via isothiouronium enolate **1c** (Figure 1B).[6b] In addition to these reactions,[4–6] an array of

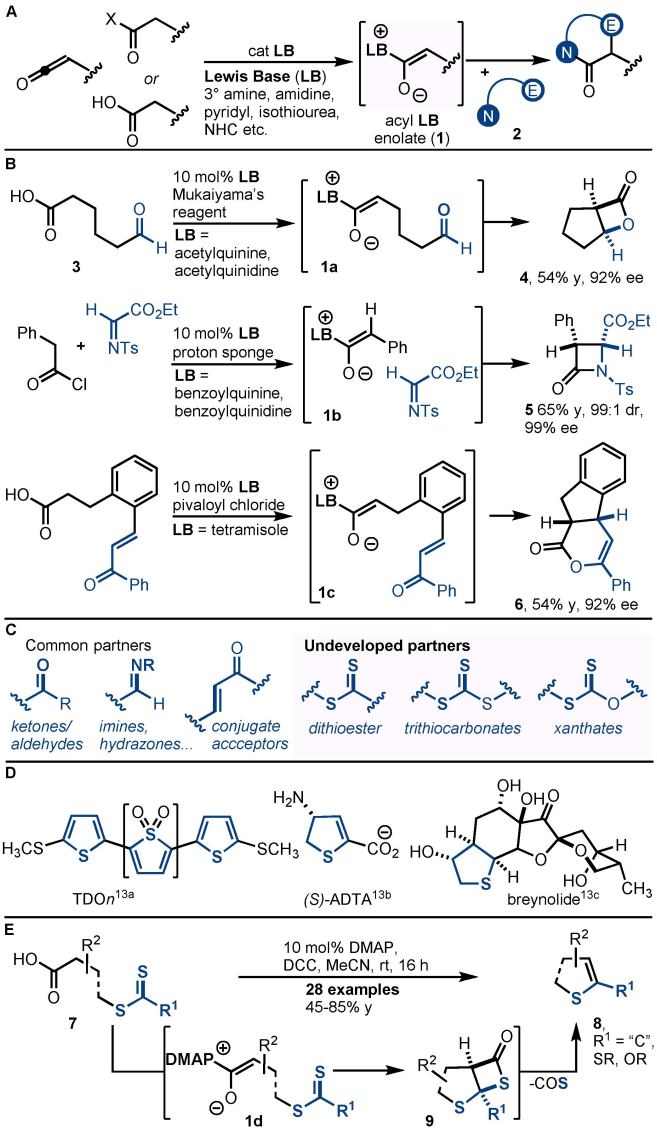


Figure 1. A) Summary of the acyl Lewis base enolate **1**. B) Representative examples of catalysis via acyl Lewis base enolate. C) Existing and undeveloped coupling partners. D) Valuable thiophenes. E) Reaction design examined herein.

[*] S. Cromwell,[+] R. Sutio,[+] Prof. Dr. D. W. Lupton
School of Chemistry, Monash University
Clayton 3800, Victoria (Australia)
E-mail: david.lupton@monash.edu
Dr. C. Zhang, Prof. Dr. G. K. Such
School of Chemistry, University of Melbourne
Parkville, Victoria (Australia)
[+] These authors contributed equally to this work.

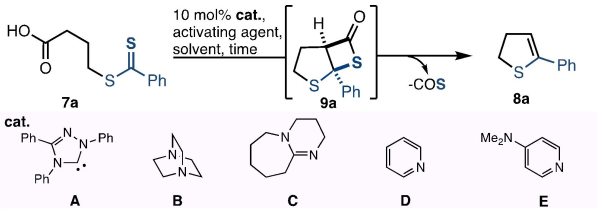
halogenations,[5g,7] alternate coupling partners[8] and dual catalytic reactions[9] have been reported.

Somewhat surprisingly, Lewis base catalysis involving the addition of C1-enolates to thiocarbonyl containing compounds are to the best of our knowledge unknown.[10] Dithioesters, trithiocarbonates, and xanthates are readily available (Figure 1C),[11] and would seem to be suitable ambiphiles for reaction discovery. The paucity of studies with such substrates may be due to reports of Claisen-type condensation between enolates and dithioesters.[12] More generally (2+2) annulations between C1-Lewis base enolates and any ester or carbonate are unknown, presumably due to the competing condensation pathway. We postulated that diversion from the Claisen-condensation pathway should be possible provided acylation is facile, thereby allowing substrates such as **7** to provide β-thiolactone fused heterocycles (i.e. **9**) via a mechanism analogous to that proposed by Romo en route to β-lactones.[4b] If viable this would define a new entry to thiophenes,[13] sulfur heterocycles found extensively (in various states of hydrogenation) in materials,[13a] medicinal[13b] and natural products chemistry[13c] (Figure 1D). Herein, we report the examination of such a reaction design. Our studies show that the C1-pyridinium enolate reacts with ester oxidation state dithioesters (**7**, R^1 = alkyl, aryl), and carbonate oxidation state trithiocarbonates (**7**, R^1 = SR) and xanthates (**7**, R^1 = OR) to give an array of dihydrothiophenes and hydrothiopyran products (i.e. **8**) (Figure 1E).

Studies commenced by exploring the cyclization of the known dithioester **7a**.[14] In situ dicyclohexyl carbodiimide (DCC) activation of **7a** was examined using *N*-heterocyclic carbene **A**, tertiary amine **B**, amidine **C**, pyridine (**D**), and dimethylaminopyridine (DMAP, **E**) as potential catalysts. While none produced the expected β-thiolactone (i.e. **9a**), all provided dihydrothiophene **8a** (Table 1, entries 1–5). The loss of carbon oxysulfide (COS), although largely unexpected,[15] likely arises due to the capacity of the sulfur and phenyl groups within thiophene **9a** to stabilize the development of radical character during elimination.[16] Although this makes enantioselective catalysis more challenging, these results demonstrate the viability of dithioesters as unreported coupling partners for C1-Lewis base enolates, thereby introducing a new approach to sulfur heterocycles. Using alternate solvents (Table 1, entries 6–8), or activating agents (Table 1, entries 9–11), failed to improve the outcome. Thus, optimal conditions with DMAP (**E**) as the catalyst to give **8a** in 67 % isolated yield after 16 hours (Table 1, entry 5) were used in subsequent studies.

The generality of the transformation was initially examined with alternate aryl dithioesters (**8a**–**h**). The reaction showed insensitivity to the electronics of the aryl group with various *para* substituted substrates (**7b**–**d**) giving the expected products with similar yields of ≥64 %. Introduction of *meta* substituents also had little impact on the outcome (**8e**, $R^3 = OCH_3$, 56 % y; **8f**, R^3 = F, 63 % y). With an *ortho* substituent the reaction remained viable, however the yield was decreased (**8g**, R^3 = 2-OCH_3, 46 %), while the 2-naphthyl substituted **8h** formed with 73 % isolated yield. Alkyl groups could replace the aryl group without impacting

Table 1: Lewis base catalyzed synthesis of dihydrothiophene **8a**.



Entry	Cat	Solvent	Activating	*t*	Yield **8a**[a]
1	A[b]	MeCN	DCC	16 h	9
2	B	MeCN	"	16 h	38
3	C	MeCN	"	16 h	26
4	D	MeCN	"	16 h	33
5	E	MeCN	"	16 h	67
6	"	THF	"	12 h	<10
7	"	CH_2Cl_2	"	"	35
8	"	$(CH_2Cl)_2$	"	"	48
9	"	MeCN	EDCI[c]	"	11
10	"	"	DIC[d]	"	37
11	"	"	HATU[e]	"	–

[a] Isolated yield. [b] TPT generated in situ by deprotonation of the azolium precursor, see Supporting Information. [c] 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide. [d] diisopropylcarbodiimide. [e] 1-[Bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-b]pyridinium 3-oxide hexafluorophosphate.

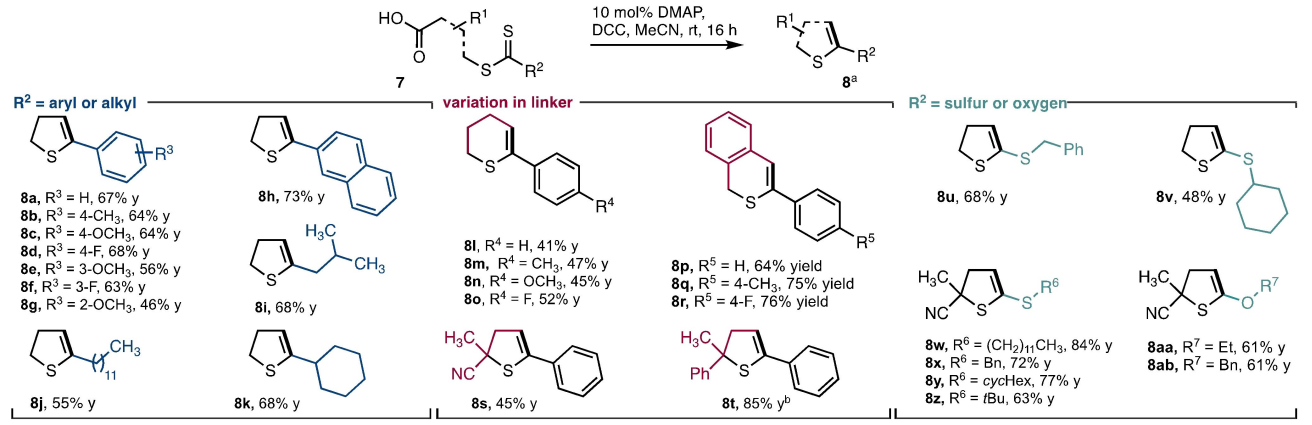
the outcome. Specifically, the primary alkyl thiophenes **8i** and **8j**, and the secondary alkyl containing **8k** were prepared in 55 to 68 % yield. The loss of COS remains facile with substrates bearing aliphatic R^2 substituents (i.e. **8i**–**k**) with no β-thiolactone observed, despite decreased capacity to stabilize radical character. This result suggests that the stabilization by the sulfur atom is sufficient to drive this process.

The linker between the carboxylic acid and the dithioester could be modified. Thus, one methylene homologated substrates produced hydrothiopyran products bearing a range of *para* substituents (**8l**–**o**) in 41 to 52 % yield. Introducing an *ortho* disubstituted phenyl linker provided the benzannulated variants (i.e. **8p**–**r**) with improved yields between 64 and 76 % yield. Quaternary carbons can also be included in the products with dihydrothiophene **8s** and **t** prepared in 45 and 85 % yield.

Trithiocarbonates (**7**, R^2 = *S*-alkyl) and xanthates (**7**, R^2 = *O*-alkyl) are common and readily accessible reagents for controlled polymerization reactions.[11] We found that trithiocarbonates engaged effectively in the DMAP-catalyzed cyclisation to give ketene dithioacetal containing products **8u**--**z** (Table 2).[17] Thus, benzysulfide substituted dihydrothiophene **8u** was prepared in 68 % yield, while the cyclohexyl analog (**8v**) was prepared in 48 % yield. Quaternary carbon containing substrates **7w**–**z** were well suited to the reaction providing the primary alkyl sulfide **8w** and **8x** (84 % and 72 % yield), the secondary alkyl sulfide **8y** (77 % yield), and the *t*-butyl sulfide **8z** (63 % yield).

Finally, xanthates **7aa** and **7ab** were prepared, and subjected to the cyclization conditions. While both cyclized effectively, giving **8aa** and **8ab** in 61 % yield, this hetero-

Table 2: Scope of the cyclization of dithioesters, trithiocarbonates and xanthates (i.e. **7a–7ab**) to give dihydrothiophenes, and dihydrothiopyrans (i.e. **8a–8ab**).



[a] Isolated yield following chromatography. [b] Prepared from partially purified **7s**, yield calculated accordingly, see Supporting Information.

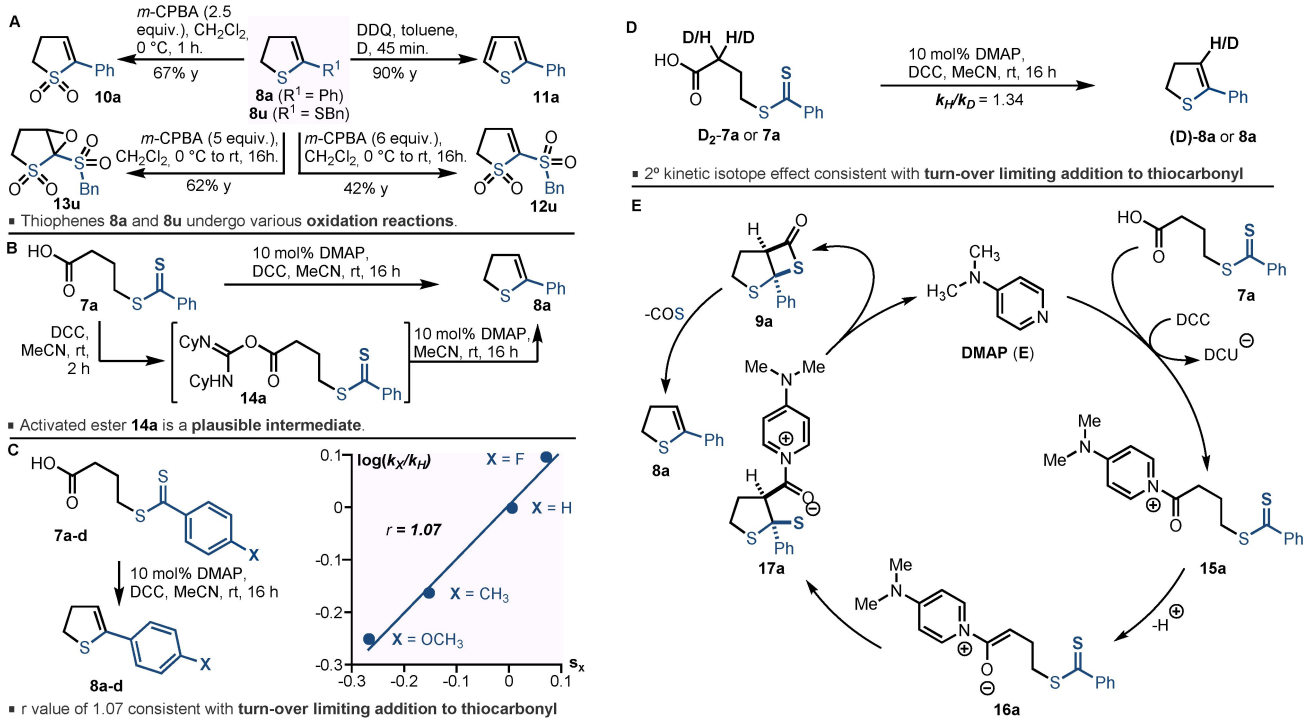


Figure 2. A) Derivatizations of thiophenes **8a** and **8u**. B) Activated acid **13a** gives dihydrothiothene **8a**. C) Electronic correlation studies. D) KIE studies. E) Plausible reaction mechanism. DCU = Dicyclohexyl urea.

cycle is yet to be reported. The uncommon ketene monothioacetal within **8aa** and **8ab** is likely less stable than the dithioacetals (i.e. **8u–8z**) leading to decomposition. Thus, even routine ^{13}C NMR characterization proved challenging, although data consistent with the structures could be obtained.

Although thioketones were not examined in this study, due to their viability in stepwise β-thiolactone preparation[15] we expect they would make suitable substrates to provide cyclopentene products, materials also accessible from the analogous ketone.

Treating dihydrothiophene **8a** to established oxidative conditions provided the expected sulfone **10a**, using *meta*-chloroperbenzoic acid (*m*-CPBA),[18a] and the aromatized 2-phenylthiophene **11a** by benzoquinone (DDQ) oxidation.[18b] The *m*-CPBA oxidation of 2-thiobenzyl thiophene **8u** gave *bis*-sulfone **12u** in 42% yield or, when performed at higher concentration, epoxide **13u** in 62% yield (Figure 2A).[18c] Mechanistic studies commenced by demonstrating the viability of the activated acid as a precursor to cyclization. Thus, **14a** was prepared and isolated by treatment of **7a** with DCC in the absence of

DMAP. When exposed to DMAP this species gave the cyclized product **8a** confirming its viability as an intermediate (Figure 2B). Next electronic correlation studies were conducted examining the rate of cyclization of four aryl dithioesters (**7a** (R = H), **7b** (R = CH_3), **7c** (R = OCH_3) and **7d** (R = F)). This study revealed a Hammett correlation with a *rho* of 1.07, consistent with turn-over limiting cyclization of the C1-pyridinium enolate to the thiocarbonyl (Figure 2C). Further supporting this are studies using **D_2-7a** and **7a** which allowed a secondary kinetic isotope effect to be identified, as expected with turn-over limiting cyclization (Figure 2D). Thus, mechanistically we propose that the reaction commences with the coupling of DCC to acid **7a** to generate the activated acid **14a**. This species, or the corresponding anhydride of **7a**, is then displaced by DMAP to give pyridinium **15a**. Deprotonation provides the C1-pyridinium enolate **16a** which undergoes turn-over limiting addition to the thiocarbonyl to yield thiolate **17a** and following loss of DMAP β-thiolactone **9a**. Ultimately, extrusion of COS gives the dihydrothiophene product **8a**.

Lewis base catalysis involving carboxylic acids and derivatives has developed into a powerful approach to reaction discovery, particularly in designs exploiting the C1-Lewis base enolate. This species can add to various coupling partners enabling numerous reactions. A limitation in this field is the array of coupling partners that are compatible. Studies reported in this manuscript introduce three thiocarbonyl containing partners and demonstrate their compatibility in annulations using a relatively common in situ activation strategy with four important classes of Lewis base catalysts. While, DMAP catalysis has been examined herein, we note that the conversion was also possible with NHC, tertiary amine, and amidine catalysts. Building upon these studies we expect that thiocarbonyls will, in time, become integral in a host of new reaction designs using the plethora of known Lewis base catalysts and C1-Lewis base enolate precursors. Finally, while ablation of point chirality in this study provides achiral products, desymmetrizing reactions, or those that produce axially chiral materials[19] may well be accessible by drawing upon the results reported herein.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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