Synthesis of Cyclopentenones with Reverse Pauson-Khand Regiocontrol via Ni-Catalyzed C–C Activation of Cyclopropanone

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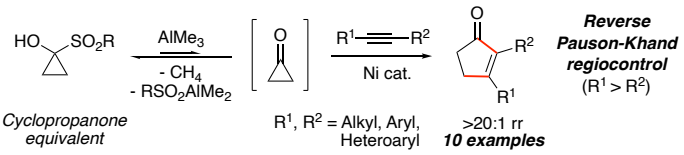
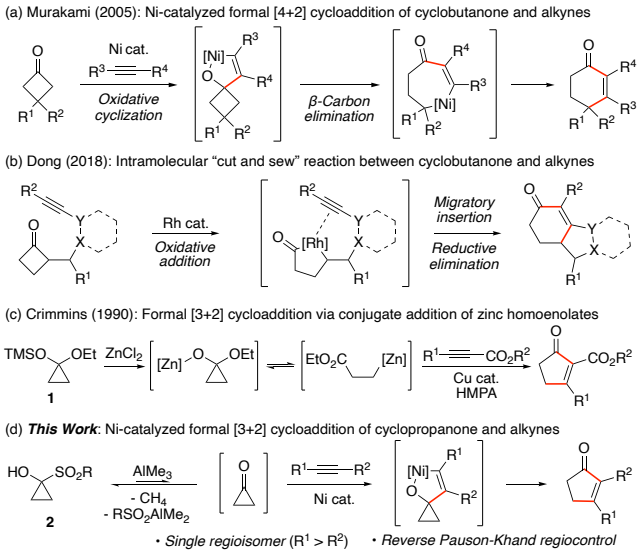
Supporting Information Placeholder



ABSTRACT: A formal [3+2] cycloaddition between cyclopropanone and alkynes via Ni-catalyzed C–C bond activation has been developed, where 1-sulfonylcyclopropanols are employed as key precursors of cyclopropanone in the presence of trimethylaluminum. The transformation provides access to 2,3-disubstituted cyclopentenones with complete regiocontrol, favoring reverse Pauson-Khand products where the large substituent is located at the 3-position of the ring. In the process, the trimethylaluminum additive is thought to play multiple roles, including as a Brønsted base triggering the equilibration to cyclopropanone and liberation of methane, as well as a source of Lewis acid to activate the carbonyl group toward Ni-catalyzed C–C activation.

Transition metal-catalyzed C–C bond activation of strained organic compounds constitutes an elegant and synthetically valuable approach to the elaboration of complex molecules.[1] In the case of small ring systems, the inherent strain energy[2] of the substrate plays a key role as a driving force to facilitate the C–C activation process. Such a bond-cleaving event is typically achieved via two distinct mechanistic pathways depending on the reaction conditions and specific substrates used, the first of which involves the direct oxidative addition of one of the C–C bonds of the ring to an electron-rich transition metal complex.[1a] Alternatively, a β-carbon elimination of an *O*-bound cycloalkanol-metal complex, as commonly encountered in metal-homoenolate chemistry when starting from cyclopropanols,[3] is also possible and leads to ring-opened carbonyl-containing nucleophilic species capable of further reactivity.[1g,4] The catalytic formation of organometallic intermediates resulting from such C–C bond activation has found widespread use in the development of ring-expansion methodologies, typically by reaction with π systems such as alkenes, alkynes and arenes.[1] In the past decades, numerous strained ring systems such as vinylcyclopropanes,[5] alkylidenecyclopropanes,[6] cyclopropenes[7] and cyclobutanes[1g,8] have been extensively studied in this regard. Mainly owing to the work of the Dong[9] and Murakami[10] groups, strained ketones such as cyclobutanones have recently emerged as particularly versatile substrates for such formal cycloadditions to afford ring-enlarged cyclic ketones with defined substitution patterns. Specifically, Murakami and co-workers reported a nickel(0)-catalyzed formal cycloaddition of cyclobutanones and alkynes via an oxidative cyclization / β-carbon elimination pathway, eventually leading to 2,3-disubstituted cyclohexenone derivatives (Scheme 1a).[9a] A distinct approach was disclosed by Dong and coworkers, where a rhodium(I) catalyst was employed to activate the C(1)–C(2) bond of cyclobutanone via direct oxidative addition (Scheme 1b).[10a] Despite these considerable advances, the analogous use of cyclopropanone derivatives for such a process remains unknown, likely due to the inherent kinetic instability of these highly strained substrates.[2,11] Indeed, while cyclopropanone itself can be synthesized by reaction of diazomethane with ketene at –78°C followed by distillation at the same temperature,[12] its widespread adoption in organic synthesis has been precluded by the difficulties associated with its preparation and storage, as it cannot be isolated in pure form and rapidly polymerizes at room temperature.

Scheme 1. Formal Cycloadditions of Strained Rings with Alkynes

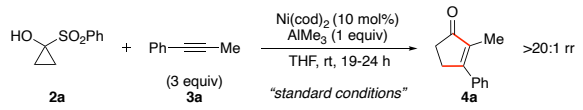


As a result, the vast majority of disconnections involving cyclopropanone building blocks utilize synthetic equivalents such as their ketal or hemiketal forms to generate the corresponding ketone in situ via α-elimination (e.g. **1**), though these unstable precursors typically require harsh conditions to react, often leading to low yields of desired product.[11d,13] Moreover, these same cyclopropanone equivalents are more commonly known to competitively equilibrate to β-nucleophilic esters in basic conditions,[3,14] thus often reacting more like cyclopropanols rather than cyclopropanones. For example, Crimmins and co-workers reported a formal [3+2] cycloaddition of silyl ethyl ketal **1** with acetylenic esters in the presence of $ZnCl_2$, leading to 2-carbalkoxycyclopentenones via zinc-homoenolate formation and conjugate addition chemistry (Scheme 1c).[15] Due to the absence of robust precursors capable of smoothly equilibrating to cyclopropanone in mild conditions, a number of potential disconnections including the transition metal catalyzed C–C activation of cyclopropanones are still inaccessible. Recently, our group reported the synthesis of a variety of crystalline 1-sulfonylcyclopropanols **2** and their application as stable yet highly reactive and modular precursors of cyclopropanones in basic conditions.[16,17] With these substrates in hand, we hypothesized that such well-behaved precursors might be key to unlock the C–C activation chemistry of cyclopropanones. Herein, we report a nickel-catalyzed formal [3+2] cycloaddition of cyclopropanone and internal alkynes using 1-sulfonylcyclopropanols as precursors in the presence of trimethylaluminum, leading to a variety of 2,3-disubstituted cyclopentenones (Scheme 1d). Notably, the products formed are analogous to the ones obtained in the classical Pauson-Khand reaction[18] but with reverse regiocontrol, with the largest substituent located at C(3), consistent with an oxidative cyclization / β-carbon elimination mechanism. Considering the relevance of substituted cyclopentenones as building blocks in numerous organic transformations,[19] this reaction should find utility in the elaboration of biologically relevant molecules.

To evaluate the viability of the proposed formal cycloaddition, 1-phenylsulfonylcyclopropanol **2a** was elected as model substrate and initially subjected to Murakami's conditions in the presence of an excess 1-phenylpropyne **3a**, $Ni(cod)_2$ and PCy_3 in toluene at 100 °C.[9a,20] Unfortunately, the desired 2,3-disubstituted cyclopentenone was not observed and most of the starting materials were recovered under these conditions. Evaluation of various reagents that could potentially promote cyclopropanone formation without negatively interfering in the catalysis identified trimethylaluminum as a key additive,[21] leading to cyclopentenone **4a** in 21% yield as a single regioisomer when the reaction was run at room temperature without added ligand (Table 1, entry 1). As the role of the trimethylaluminum remained unclear at that point, several Lewis acids such as $TiCl_4$, $SnCl_4$, $BF_3{\cdot}OEt_2$ and organometallic reagents analogous to $AlMe_3$ such as Et_2Zn were also evaluated, but none afforded the cyclopentenone product.[20] Performing the reaction in the absence of this additive or with $AlMe_2Cl$[21] instead led to no detectable yield of product, presumably due to the absence of base capable of triggering equilibration of **2a** toward cyclopropanone (entries 2-3). Notably, either increasing or lowering the temperature were both deleterious to the reaction efficiency, as we observed oligomerization of the alkyne substrate and decomposition of both the 1-sulfonylcyclopropanol **2a** and cyclopentenone **4a** when performing the reaction at 50 °C.[20] Although the presence of a Ni(0) catalyst proved essential to the desired reactivity (entry 4), the transformation was found to be more efficient when such a species was generated in situ from $NiBr_2$ and Zn(0), with an optimal loading of 30 mol% each (entries 5-8).

Interestingly, we serendipitously found that the efficiency of the reaction was significantly reduced when it was carried out with 99.9% pure $NiBr_2$ rather than 98% pure (entry 9). A survey of various metal bromide salts suspected to act as beneficial impurities in the 98% pure $NiBr_2$ was thus performed, identifying $CuBr_2$ as a competent catalytic additive (entry 10). While its exact mechanistic role in the transformation remains unknown, omission of $NiBr_2$ from the reaction conditions led to no product formation (entry 11), confirming that $CuBr_2$ alone in the presence of Zn(0) does not act as a competent catalyst in the formal cycloaddition.

Table 1. Optimization of the formal cycloaddition using substrate 2a



2a **3a** **4a**

entry	deviation from standard conditions	yield (%)[a]
1	none	21
2	$AlMe_2Cl$ instead of $AlMe_3$	<5
3	without $AlMe_3$	<5
4	without $Ni(cod)_2$	<5
5[b]	$NiBr_2/Zn^0$ (10 mol% each) instead of $Ni(cod)_2$	35
6[b]	$NiBr_2/Zn^0$ (20 mol% each) instead of $Ni(cod)_2$	40
7[b,c]	$NiBr_2/Zn^0$ (20 mol% each) instead of $Ni(cod)_2$	42
8[b,c]	$NiBr_2/Zn^0$ (30 mol% each) instead of $Ni(cod)_2$	46[d]
9[e,c]	$NiBr_2/Zn^0$ (30 mol% each) instead of $Ni(cod)_2$	29
10[e,f]	**$NiBr_2/Zn^0$ (30 mol% each), $CuBr_2$ (3 mol%)**	**48**[d,g]
11[c]	$CuBr_2$ (5 mol%), Zn^0 (30 mol%)	<5

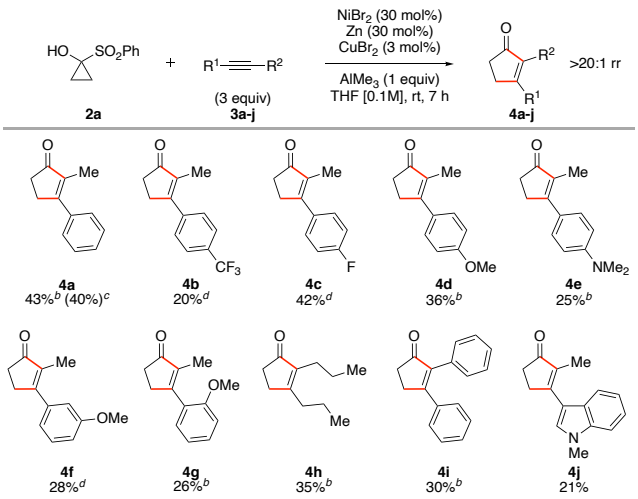
[a]Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as standard unless otherwise noted. [b]$NiBr_2$ (98% pure) was used. [c]The reaction was performed for 5 h. [d]Displayed yields are the average of three runs. [e]$NiBr_2$ (99.9%) was used. [f]The reaction was performed for 7 h. [g]Isolated yield = 43%.

Submission of various other internal alkynes **3a-j** to these optimized conditions in presence of cyclopropanone precursor **2a** afforded a number of sterically and electronically distinct 2,3-disubstituted cyclopentenones, with complete regiocontrol in all cases (Scheme 2). Substitution at the *ortho*, *meta* or *para* positions of 1-arylpropynes was found to be tolerated, with considerable variability with regards to the electronics of the arene moiety (**4a-g**). Importantly, both symmetrical dialkyl- and diarylacetylenes were shown to be compatible in the reaction (**4h-i**), as well as a 3-indolyl-substituted alkyne (**4j**). It should be noted that even after extensive investigation, the use of 2-substituted chiral cyclopropanone precursors was found to be incompatible in the reaction (not shown),[16a] thus precluding the use of this method for the direct production of chiral cyclopentenones. Although the yields observed for **4a-j** remain modest, the elaboration of such 2,3-disubstituted cyclopentenones in a regiocontrolled manner typically requires multiple synthetic steps,[19] which can be streamlined here in a single step using a novel synthetic disconnection, starting from a readily accessible stable and crystalline precursor (**2a**).

Compared with the analogous formal [4+2] cycloaddition of cyclobutanones,[9,10] an additional challenge in the developed reaction consists of controlling the initial equilibrium leading to cyclopropanone as the effective substrate. Indeed, its concentration must remain low

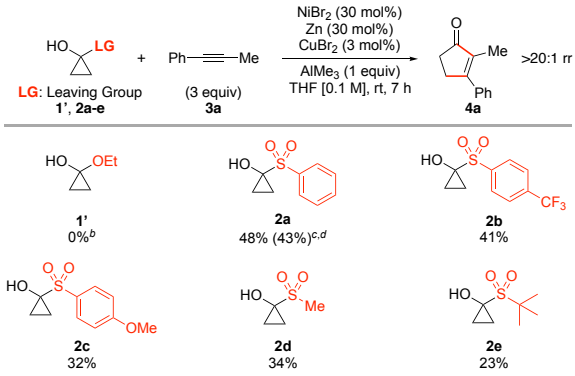
at all times in order to avoid undesired oligomerization, a common decomposition pathway in cyclopropanone chemistry.[11] To further investigate the modular character of 1-sulfonylcyclopropanols as cyclopropanone equivalents[16a] and to compare their reactivity with more established precursors,[11d] we also deemed valuable to evaluate other substrates with different leaving groups at C(1) (Scheme 3). Interestingly, while all sulfonylcyclopropanols **2a-e** evaluated led to cyclopentenone **4a** with varying efficiency, the classical precursor **1'** did not afford any product in our reaction conditions, again highlighting the poor reactivity and generality of such an unstable and volatile hemi-ketal as cyclopropanone equivalent.

Scheme 2. Scope of accessible 2,3-disubstituted cyclopentenones[a]



[a]All yields correspond to yields of isolated product on 0.25 mmol scale of **2a** unless otherwise noted. [b]Displayed yields are the average of three runs. [c]Isolated yield on 1 mmol scale of **2a** in parentheses. [d]Displayed yields are the average of two runs.

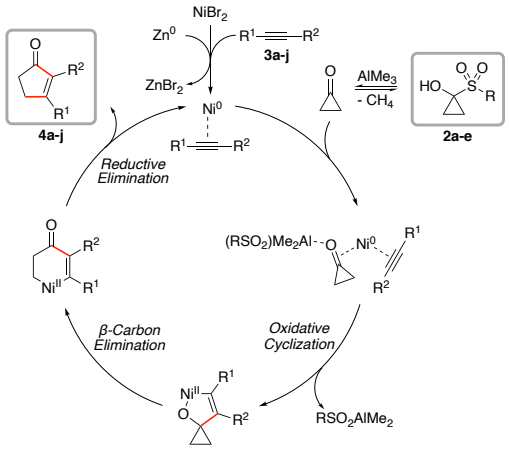
Scheme 3. Effect of the cyclopropanone precursor used[a]



[a]Yield determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as standard unless otherwise noted. [b]Reaction was performed using 10 mol% Ni(cod)$_2$ and 1 equiv. of AlMe$_3$ (25% w/w in hexane) in THF at rt for 21 h. [c]Isolated yield in parentheses. [d]Displayed yields are the average of three runs.

A plausible mechanism for the developed formal [3+2] cycloaddition is shown in Scheme 4. Considering precedents in the literature for the Ni-catalyzed C–C activation of strained ketones[1,9] as well as the complete regiocontrol observed in our reaction, a direct oxidative addition of the ring to a Ni(0) catalyst, as commonly seen with Rh(I) catalysts, was quickly ruled out as the effective mechanism. Thus, it is proposed that following reduction of NiBr$_2$ and AlMe$_3$-mediated formation of cyclopropanone, oxidative cyclization can occur leading to the corresponding oxanickelacyclopentene, which undergoes β-carbon elimination and reductive elimination. In the process, the aluminum salt (RSO_2AlMe_2) liberated in the first step likely activates cyclopropanone toward the subsequent oxidative cyclization by enhancing the π-coordination effect of the carbonyl group towards the Ni(0) metal center, in analogy to Ogoshi's Ni-catalyzed formal cycloaddition of cyclopropylketones and alkynes.[21]

Scheme 4. Postulated mechanism for the Ni-catalyzed formal [3+2] cycloaddition of cyclopropanone and alkynes



While this mechanism is consistent with analogous literature precedents,[9a,21] it is also known that Ni(II)-homoenolates can be generated from cyclopropanols in the presence of Zn(II) salts.[22] Thus, a mechanism akin to the one observed by Crimmins (see Scheme 1c), involving a carbometallation of the alkyne followed by Claisen-type condensation, must also be considered. Indeed, substrate **2a** is also technically a cyclopropanol derivative, and its direct equilibration to a metal-homoenolate species is a reasonable consideration. However, different observations led us to discard this hypothesis, including the fact that the reaction was shown to be productive with Ni(cod)$_2$ in the absence of zinc salts (see Table 1, entry 1), which are conditions unlikely to generate metal-homoenolates.[3] Moreover, the observed regioselectivity of the transformation is inconsistent with such a mechanism, as it was previously shown that metal-homoenolates typically react with alkynes such as **3a** with opposite selectivity,[23] generating a more stable 1-arylalkenyl-metal intermediate following carbometallation.

In summary, we describe the first formal [3+2] cycloaddition of cyclopropanone and alkynes, providing access to 2,3-disubstituted cyclopentenones with complete regiocontrol, favoring products with reverse Pauson-Khand selectivity. To the best of our knowledge, this work constitutes the only example of a Ni-catalyzed C–C activation of cyclopropanone, where the use of 1-sulfonylcyclopropanols as well-behaved cyclopropanone precursors was found to be essential to achieve the desired reactivity. A key trimethylaluminum additive is thought to play multiple roles in the process, including as a Brønsted base triggering the equilibration to cyclopropanone as well as a source of Lewis acid to activate the cyclopropanone towards Ni-catalyzed C–C activation via oxidative cyclization and β-carbon elimination. Considering the relevance of transition metal catalyzed C–C activation in the elaboration of complex scaffolds[1] and the ubiquity of substituted cyclopentenones in organic synthesis,[19] this work should find broad utility in the construction of biologically relevant molecules.

ASSOCIATED CONTENT

Supporting Information

Experimental details and spectroscopic data. The Supporting Information is available free of charge [redacted]

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Notes

The authors declare no competing financial interest.

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(20) See the Supporting Information for details.

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