C–C Coupling

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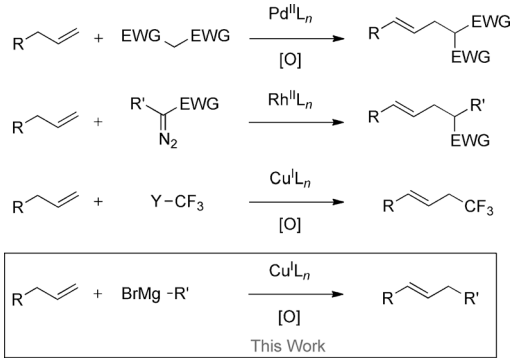
Allylic Functionalization of Unactivated Olefins with Grignard Reagents**

*Hongli Bao, Liela Bayeh, and Uttam K. Tambar**

Abstract: *New advances in the functionalization of unactivated olefins with carbon nucleophiles have provided more efficient and practical approaches to convert inexpensive starting materials into valuable products. Recent examples have been reported with stabilized carbon nucleophiles, tethered carbon nucleophiles, diazoesters, and trifluoromethane donors. A general method for functionalizing olefins with aromatic, aliphatic, and vinyl Grignard reagents was developed. In a one-pot process, olefins are oxidized by a commercially available reagent to allylic electrophiles, which undergo selective copper-catalyzed allylic alkylation with Grignard reagents. Products are formed in high yield and with high regioselectivity. This was utilized to synthesize a series of skipped dienes, a class of compounds that are prevalent in natural products and are difficult to synthesize by known allylic alkylation methods.*

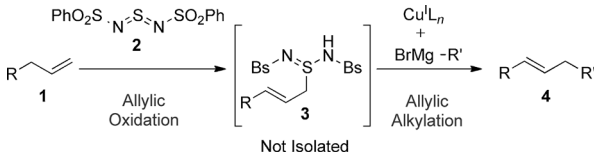
The functionalization of unactivated olefins with carbon nucleophiles is an attractive strategy for synthesizing value-added small molecules from inexpensive and abundant components of petrochemical feedstock (Scheme 1).[1,2] It is quickly becoming an alternative approach to the Heck reaction for the conversion of simple terminal olefins into more complex products.[3] Elegant examples of allylic alkylations have been reported with stabilized carbon nucleophiles,[4] tethered carbon nucleophiles,[5] diazoesters,[6] and trifluoromethane donors.[7] To complement these studies, we were interested in functionalizing unactivated olefins with Grignard reagents, which are a readily accessible and affordable class of diverse carbon nucleophiles.

Herein, we describe a general method for functionalizing unactivated olefins with aromatic, aliphatic, and vinyl Grignard reagents.[8] This one-pot process is performed by the sequential addition of a stoichiometric oxidant, copper catalyst, and a Grignard reagent to unactivated terminal olefins, which are converted into internal olefins with high *E* selectivity. In contrast to most Heck reaction protocols, our strategy exhibits broader scope in the coupling partner and does not require activated olefins for high levels of reactivity and selectivity in the formation of a single olefin isomer.[9]



Scheme 1. Allylic functionalization of unactivated olefins. EWG = electron-withdrawing group.

Allylic functionalization with carbon nucleophiles usually requires a stoichiometric oxidant to restore the starting oxidation state of the metal in the catalytic cycle. We envisioned a conceptually distinct approach, in which the stoichiometric oxidant could oxidize the unactivated olefin in the absence of a catalyst to a reactive intermediate, which would be susceptible to metal-catalyzed allylic substitution with Grignard reagents in the same reaction flask (Scheme 2).



Scheme 2. General approach to the allylic functionalization of unactivated olefins with Grignard reagents. Bs = benzenesulfonyl.

We were drawn to the metal-free allylic oxidation of unactivated olefins **1** with the commercially available sulfurdiimide reagent **2**. This chemistry was initially explored for the allylic amination of unactivated olefins through the [2,3]-rearrangement of allylic sulfinamides (**3**).[10,11] Motivated by early examples of metal-catalyzed couplings of allylic sulfides and sulfoxides with Grignard reagents,[12] we were interested in exploiting sulfinamides **3** as a new class of electrophiles for metal-catalyzed allylic substitution. Herein, we report the broad substrate scope and unique product selectivity exhibited by this novel strategy for allylic alkylation.

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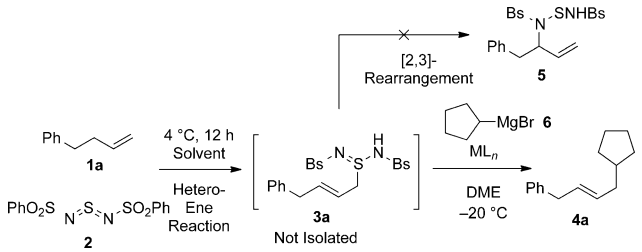
Our initial challenge in functionalizing olefins with Grignard reagents via sulfinamide **3** was the suppression of the facile [2,3]-rearrangement to allylic amines such as **5** in favor of the desired coupling with Grignard reagent **6** (Table 1). Sulfinamide **3a** was generated upon mixing olefin

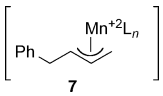
Table 1: Optimization of allylic functionalization with Grignard reagents.



Entry	ML_n	Solvent	Yield [%]
1	$[Pd_2(dba)_3]\cdot CHCl_3$[a]	Et_2O	< 5
2	$[\{Pd(C_3H_5)Cl\}_2]$[a]	Et_2O	< 5
3	$[\{Ir(cod)Cl\}_2]$[a]	Et_2O	< 5
4	$[Ir(cod)_2]BF_4$[a]	Et_2O	< 5
5	$[\{Rh(cod)Cl\}_2]$[a]	Et_2O	< 5
6	$[(C_7H_8)Mo(CO)_3]$[a,b]	Et_2O	< 5
7	CuTc	Et_2O	22
8	CuCl	Et_2O	6
9	$CuBr\cdot SMe_2$	Et_2O	25
10	$CuBr\cdot SMe_2$	DME	53
11	$CuBr\cdot SMe_2$	DME/Et_2O (1:1)	72

Reaction conditions. Step 1: Olefin **1a** (1 equiv), sulfur diimide **2** (1.2 equiv), solvent (0.3 M). Step 2: DME (0.2 M), ML_n (5 mol%), Grignard reagent **6** (4 equiv). [a] Metal complex was pretreated with 10 mol% phosphine ligands, pyridine ligands, phosphoramidite ligands, or no ligand. [b] $C_7H_8Mo(CO)_3$ = cycloheptatriene molybdenum tricarbonyl, DME = 1,2-dimethoxyethane, cod = cyclo-1,5-octadiene, dba = dibenzylidenacetone.

1a and sulfurdiimide reagent **2** for 12 h at 4 °C in various solvents. This oxidized intermediate was subsequently cooled to −20 °C and treated with several low-valent metals that typically generate electrophilic metal–allyl intermediates **7** from allylic acetates, carbonates, and halides. Palladium, iridium, rhodium, and molybdenum catalysts did not yield the internal olefin **4a** in either the presence or absence of various classes of ligands (Table 1, entries 1–6). Gratifyingly, copper(I) salts emerged as promising catalysts for this process (entries 7–11).[13] In the presence of copper(I) thiophene-2-carboxylate (CuTc), internal olefin **4a** was isolated in 22% yield (entry 7). The source of copper impacted the yield of the isolated desired product (entries 7–9). When CuTc was replaced with $CuBr\cdot SMe_2$, olefin **4a** was produced in slightly greater yield (entry 9). Given the propensity for sulfinamide **3a** to undergo a facile [2,3]-rearrangement to allylic amine **5**, we hypothesized that the proper selection of solvent for the oxidation step was essential for the efficiency of the overall process. In Et_2O, sulfurdiimide **2** and sulfinamide **3a** were largely insoluble, resulting in an inefficient oxidation reaction and subsequent allylic substitution with Grignard reagent **6**

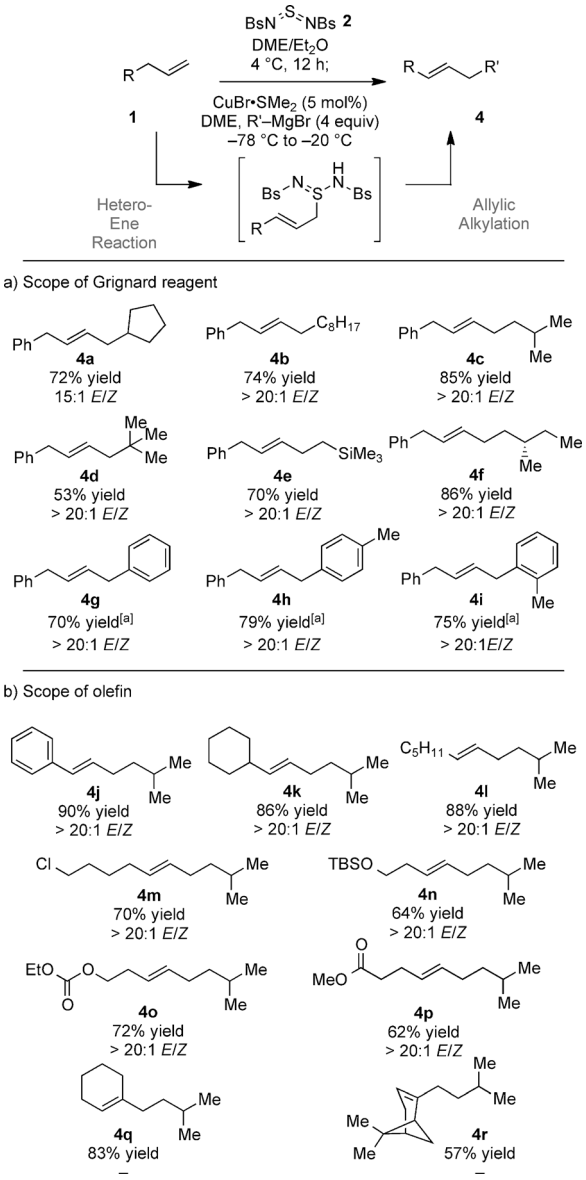


(entry 9). In DME, sulfurdiimide **2** and sulfinamide **3a** were completely soluble, which led to significant [2,3]-rearrangement to allylic amine **5** before the reaction mixture was treated with the copper and Grignard reagent (entry 10). A 1:1 mixture of DME/Et_2O produced the ideal environment for the formation and stability of sulfinamide **3a**, which was smoothly converted in situ into internal olefin **4a** (entry 11). Under these conditions, the desired product was isolated in 72% yield with high *E*-olefin selectivity (15:1) and complete regioselectivity.

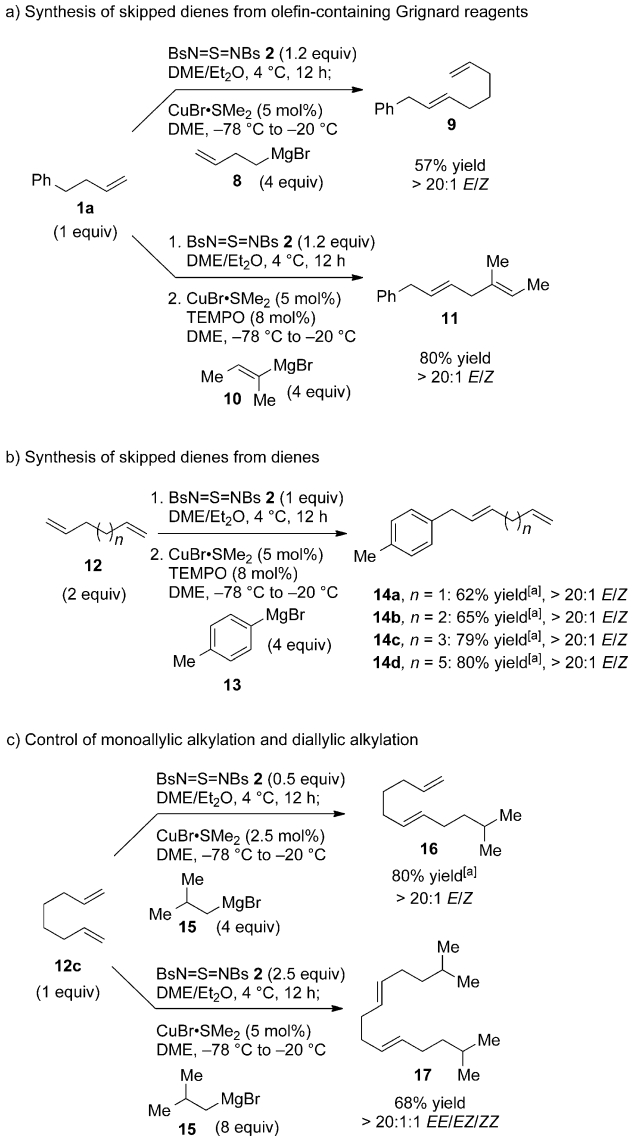
With optimal reaction conditions in hand for the functionalization of unactivated olefins with Grignard reagents, we explored the substrate scope of this process (Scheme 3). A diverse range of aliphatic Grignard reagents could be utilized in this transformation without affecting the overall efficiency of the process (Scheme 3a, **4a–f**), including Grignard reagents with trimethylsilyl groups (**4e**) and remote stereocenters (**4f**). A hindered *tert*-butyl Grignard reagent furnished the neopentyl internal olefin **4d**. When aryl Grignard reagents were employed in the reaction, the in situ conversion of sulfinamide **3a** resulted in considerably lower yields, presumably because of side reactions between the highly reactive aryl Grignard reagents and byproducts from the oxidation reaction. Optimal yields were obtained for the coupling of these aryl Grignard reagents after isolating the sulfinamide (**3a**) and adding catalytic amounts of the radical scavenger TEMPO in the second copper-catalyzed step (**4g–i**). Notably, products **4g–i** were formed with high *E*-allylic selectivity, a result distinct from both the mixture of *E*-allylic and *E*-styrenyl products typically obtained through indiscriminate β-hydride eliminations under traditional Heck conditions,[3] and the high *E*-styrenyl selectivity observed under the modified Heck conditions recently reported by the Sigman group.[14] Regardless of the Grignard reagent utilized in the reaction, we always isolated *E*-olefins as the major products (> 20:1 in most cases).

We also examined an array of terminal olefins as substrates for coupling with *iso*-butyl Grignard reagent (Scheme 3b). Unsaturated hydrocarbons furnished internal *E*-olefins in good yields (**4j–l**). This reaction was tolerant of several functional groups in the olefin substrate, including alkyl chlorides (**4m**), silyl ethers (**4n**), carbonates (**4o**), and esters (**4p**). When terminal 1,1-disubstituted exocyclic olefins were employed, we obtained trisubstituted olefins (**4q**,**r**).

To highlight the synthetic potential of the functionalization of olefins with Grignard reagents, we synthesized a series of skipped dienes (Scheme 4). Although methods have been developed for the assembly of specific classes of skipped dienes,[15] the allylic alkylation of unactivated olefins is not considered a general strategy for accessing these structures. This may be due to the difficulty in controlling the reactivity of multiple olefins in the skipped diene product towards further undesired allylic alkylations. We recognized that our strategy for functionalizing olefins is uniquely suited to synthesizing skipped dienes because we can control the reactivity of a single olefin in the presence of other unsaturated bonds through a selective oxidation reaction with sulfurdiimide **2**. We coupled terminal olefin **1a** with unsaturated Grignard reagents **8** and **10** to furnish skipped



Scheme 3. Substrate scope. Reaction conditions: 1) Olefin **1** (1 equiv), sulfurdiimide **2** (1.2 equiv), DME/Et_2O 1:1 (0.3 M). 2) DME (0.2 M), CuBr·SMe_2 (5 mol%), Grignard reagent (4 equiv). [a] Intermediary adduct was filtered and isolated before treating with copper catalyst and Grignard reagent. In addition, 8 mol% TEMPO was utilized in the second step. TBS = *tert*-butyldimethylsilyl, TEMPO = 2, 2, 6, 6-tetramethylpiperidine-*N*-oxyl.

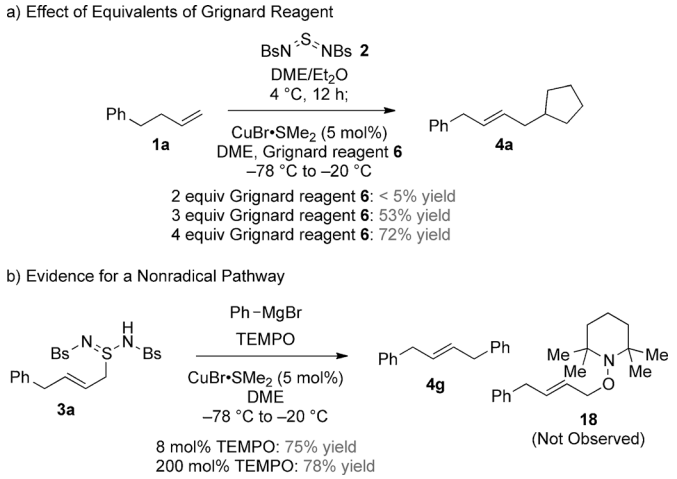


Scheme 4. Synthesis of skipped dienes. [a] Yield calculated relative to sulfurdiimide **2** as the limiting reagent.

dienes **9** and **11**, respectively (Scheme 4a). We also converted dienes **12a–d** into monoalkylation products **14a–d** by selectively controlling the monooxidation reaction of one of the olefins in the substrates with one equivalent of sulfurdiimide **2** (Scheme 4b). Finally, we controlled the mono- and dialkylation of olefin **12c** with *iso*-butyl Grignard reagent **15** by altering the relative equivalents of the two substrates, which resulted in the selective synthesis of skipped dienes **16** and **17** (Scheme 4c).

Given the distinct reactivity and product selectivity exhibited by this novel class of electrophiles, we have commenced a mechanistic examination of the copper-catalyzed functionalization of allylic sulfinamides **3** with Grignard reagents. For example, while most copper-catalyzed Grignard additions to allylic electrophiles favor the S_N2' pathway to yield branched products,[16] the allylic alkylation of sulfinamides **3** favored the S_N2 product under all the conditions we examined. In addition, the use of excess Grignard reagent was necessary to obtain a high yield of product (Scheme 5a). Most notably, in the presence of 2 equivalents of Grignard reagent **6**, we did not observe product formation, a result that suggests that Grignard reagents play a multifunctional role in the overall allylic substitution process. For example, one equivalent of Grignard reagent may initially react with the allylic sulfinamide (**3**) prior to allylic substitution.[12] Another equivalent of Grignard reagent may also react with the sulfonamide-containing byproduct produced after displacement with the first equivalent of Grignard reagent.[17]

To probe the presence of free-radical intermediates in the copper-catalyzed step, we isolated sulfinamide **3a** and sub-



Scheme 5. Mechanistic studies for the copper-catalyzed coupling of Grignard reagents and allylic sulfinamide **3a**.

jected this intermediate to the copper-catalyzed allylic substitution conditions with varying amounts of TEMPO. When sulfinamide **3a** was coupled with phenylmagnesium bromide, olefin **4g** was isolated in 78% yield even in the presence of 2 equivalents of TEMPO, with no trace of adduct **18**. This observation suggests that the productive pathway may not proceed via free-radical intermediates (Scheme 5b).[18]

In conclusion, we have developed a one-pot functionalization of unactivated olefins with Grignard reagents. We demonstrated the conversion of terminal olefins into sulfinamide intermediates that are susceptible to highly selective nucleophilic substitutions with Grignard reagents. Overall, the process exhibited a broad substrate scope for the unactivated olefins as well as the Grignard reagents. The internal olefin products were formed in high yield as predominantly single-olefin regioisomers and stereoisomers. Allylic sulfinamides **3** were unique in their ability to generate predominantly S_N2 products under all the conditions examined so far, presumably via dialkyl π-allylcopper(III) complexes, which are known to favor the formation of S_N2 products over S_N2' products.[13,19] We exploited the controlled activation of olefins in polyunsaturated structures to synthesize a variety of skipped dienes, which are prevalent in natural products and are difficult to synthesize by the known methods for allylic alkylation. We are currently expanding this strategy to include allylic functionalization with other nucleophiles to develop a diverse array of chemical transformations.

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