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Chemo- and Regioselective Functionalization of Polyols through Catalytic C(sp^3)−C(sp^3) Kumada-Type Coupling of Cyclic Sulfate Esters

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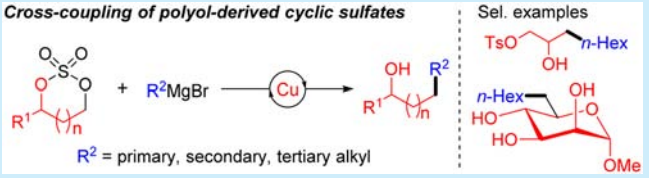
Supporting Information

ABSTRACT: This contribution describes a copper-catalyzed, C(sp^3)−C(sp^3) cross-coupling reaction of cyclic sulfate esters, a distinct class of electrophilic derivatives of polyols, with alkyl Grignard reagents to afford functionalized alcohol products in good yields. The method is operationally simple and highlights the potential of cyclic sulfate esters as highly reactive substrates in catalytic, chemoselective polyol transformations.



The selective transformation of polyol derivatives is at the frontier of our ability to transform easily accessible, biomass-derived building blocks into useful synthetic intermediates.[1] In a recent contribution, we reported the development of a catalytic reaction that addresses the challenge of regioselective deoxygenation of 1,2-diols at the primary position.[2] It was found that the siloxane intermediate involved in the transformation was endowed with unique reactivity as a result of its cyclic structure, which facilitated the reductive cleavage of the terminal C−O bond under mild conditions. The observation of high regioselectivity and enhanced reactivity of such intermediate made us consider the possibility of using the structurally analogous 1,2-cyclic sulfate esters as electrophiles in catalytic, chemoselective cross-coupling reactions of polyols.

Cyclic sulfates are a class of electrophiles that are analogous to epoxides in terms of electrophilic reactivity[3,4a] and display selectivity for nucleophilic attack at the least hindered position to yield substituted alcohols after hydrolysis.[3a] Cyclic sulfates are very versatile and useful building blocks that have found a wide variety of applications in organic synthesis,[3−6] as well as in larger scale pharmaceutical processes.[7] Cyclic sulfates provide a potential way to obtain high-value fine chemicals through selective C−O bond reductive functionalization of diols and other biomass-based platform chemicals.[8] In addition, chiral, enantioenriched 1,2-cyclic sulfates are also readily accessible through asymmetric dihydroxylation of olefins,[9] or by kinetic resolution of epoxides or diols.[10]

While cyclic sulfates have found many applications in organic synthesis, examples of their use in catalytic C−C bond-forming reactions[11] are scant.[4] Moreover, the original report of cross-coupling between (−)-diisopropyl tartrate-2,3-cyclic sulfate and benzylmagnesium chloride has been found to proceed in the absence of catalyst.[4,12] The lack of broader studies using these easily accessible electrophilic partners stands in stark contrast to the many elegant studies reported using other alcohol-derived electrophiles, such as powerful C(sp^3)−C(sp^3) Kumada-type[13] reactions using Cu and Ni catalysts and alkyl tosylates reported by the groups of Kambe,[14] Liu,[15] and Hu,[16] enantiospecific, Zn-catalyzed variant of the reaction using triflates developed by Breit,[17] and a coupling of sulfamidates very recently reported by Lee.[18] Suzuki and Negishi-type reactions of tosylates have also been reported.[19]

We envisaged that the development of metal-catalyzed cross-coupling reactions of cyclic sulfate esters would provide a conceptually new entry into the catalytic, chemoselective transformation of polyols. We started our investigations by using decane-1,2-diol cyclic sulfate (**1**) as the test substrate in control reactions with ethyl, isopropyl, and *tert*-butylmagnesium chloride in the absence of a metal salt, to find that no transformation had occurred. Once ascertained that cross-coupling with alkyl Grignard reagents requires a catalyst to occur, we proceeded to evaluate a set of metal systems that are known to catalyze cross-coupling reactions of chemically related alkyl sulfonates.[20,21] Platinum-group metal salts performed poorly, forming large amounts of decenes and no, or almost no, coupling product (Table S1). We found that a high yield of the regioselective coupling product was obtained using both Cu(I) and Cu(II) chloride salts in the absence of any additives (Table S1).[18,20] Rapid addition of 1.5 equiv of the nucleophile at room temperature is necessary in order to obtain the highest possible yield with all Grignard reagents studied (Table S2).[20] Zn(II) was also found to be a competent precatalyst, although it performed less efficiently than Cu.[17]

With a set of optimum reaction conditions in hand (1.5 equiv of RMgCl, 1% Li_2CuCl_4, overnight hydrolysis using 20% H_2SO_4), we explored the scope of Grignard reagents (Table 1). Initially, a set of simple primary alkyl Grignards were used in coupling reactions with **1**, to obtain high yields of the corresponding coupling products (entries 1−4). Next, we examined coupling reactions with nucleophiles bearing additional functionality, such as a double bond (entry 5), a trialkylsilyl

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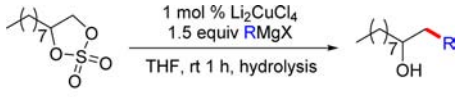
Table 1. Scope of Grignards



1

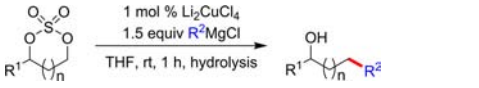
entry	R	yield (%)[a]	entry	R	yield (%)[a]
1	H_3C	85	7		40
2		84	8		85
3		80[b]	9		76
4		86	10		65
5		82	11		27
6	Si	80			

[a]Isolated yields. 1.0 mmol scale reactions. [b]Ethylmagnesium bromide was used.

group (entry 6), and an aromatic ring (entry 7), to obtain moderate to high yields of the respective products. While secondary Grignards consistently afforded good yields of the desired products (entries 8−10), *tert*-butylmagnesium chloride afforded only a low yield of the target product (entry 11), along with significant amounts of 1-decene and 2,2,3,3-tetramethylbutane. Both of these side products were detected in the reaction mixture in a 1:1 ratio.[22]

When 1,3 instead of 1,2-cyclic sulfates were used with tertiary Grignards, yields improved significantly (Table 2, entries 1 and 2). In addition, 1,3-cyclic sulfates were also efficiently coupled with a primary Grignard to give the corresponding product in high yield (Table 2, entry 3). Remarkably, a 14-membered PEG-derived macrocyclic sulfate was cross-coupled in high yield as well (Table 2, entry 4). In particular, this type of cyclic sulfates has been used in larger scales for the preparation of PEG derivatives, pointing out the possibility of using cyclic sulfates on process scales.[24] Our system also displayed good tolerance to a wide range of functional groups. Electrophilic substrates known to react with Grignard reagents were well tolerated (nitrile and ester groups, Table 2, entries 5 and 6). Moreover, substrates bearing functional groups known to be reactive under cross-coupling conditions (OTs and Cl, Table 2, entries 7 and 8), were selectively cross-coupled with the cyclic sulfate moiety at the primary position. The high reactivity of cyclic sulfate esters is demonstrated by its chemoselective cross-coupling in the presence of a tosylate group, which attests the utility of cyclic sulfates as cross-coupling partners (Table 2, entry 8). Furthermore, both unprotected hydroxyl and carboxylic acid groups were tolerated, which is an outcome that considerably improves the synthetic applicability of the protocol (Table 2, entries 9 and 10). A relevant result in the context of biomass transformation was the coupling of an acetal-protected mannopyranoside (Table 2, entry 12). In this case, a single C−O bond could be site-selectively transformed to afford a monocatenary glycolipid product that has surfactant properties[25a] and known liquid-crystalline behavior.[25b] Finally, (*R*)-decane-1,2-diol cyclic sulfate underwent cross-coupling with retention of the chiral information (Table 2, entry 13). Interestingly, substrates with double bonds two positions away from the cyclic sulfate moiety (Scheme 1, **2a** and **2b**) only afforded the corresponding parent diols **3a** and **3b**.

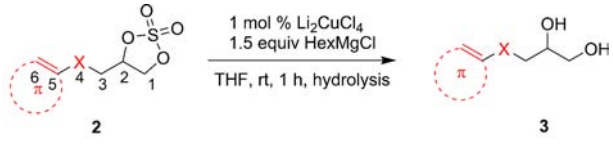
Table 2. Scope of Substrates



entry	cyclic sulfate	product	yield (%)[a]
1			66
2			71
3			87
4			71
5			50[b]
6			74
7			74
8			91
9			69[c]
10			78[c]
11			80
12			53[d]
13			81[e]

[a]Isolated yield on 1.0 mmol scale. [b]0.4 mmol scale reaction. [c]2.5 equiv of Grignard reagent used. [d]0.16 mmol scale reaction. [e]99.7% ee starting material, 96.7% ee product.[23]

Scheme 1. Observation of Desulfuration of Cyclic Sulfates Bearing 5−6 Unsaturation



2 3

a: X = O, π = Ph; **b**: X = CH_2, π = CH=CH_2

Dihexyl sulfoxide and unreacted starting material were recovered from the reaction mixture of **2b**.[20] We speculate that

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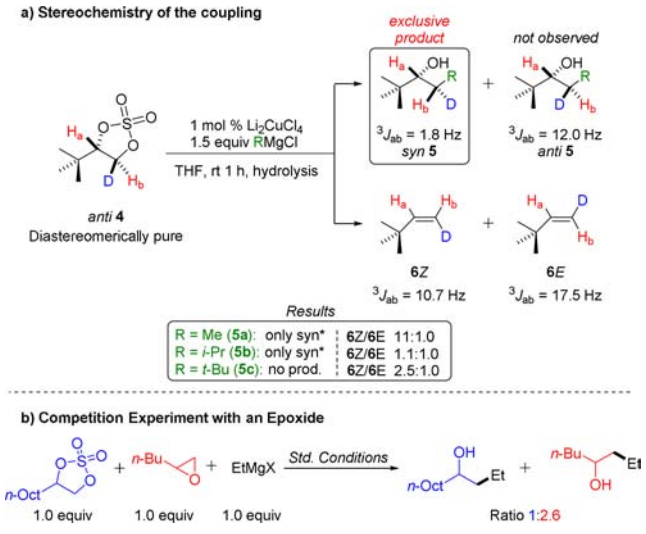
intramolecular double bonds can act as π ligands for the organocuprate catalyst and, in the case of **2a** and **2b**, this π complex can adapt a conformation that favors R group transfer to sulfur instead of carbon. Normal reactivity was observed, however, when an additional spacer was present between the site of unsaturation and the cyclic sulfate moiety (Table 2, entry 11).

Finally, we delved into the mechanism of our system. To examine the possibility of nanoparticle catalysis, excess Hg was added to a reaction of **1** with ethylmagnesium chloride, to obtain identical results as in the absence of Hg, thus rendering this possibility unlikely.[20] Next, we turned our attention to a Cu(I)−Cu(III) mediated cycle. We subjected the diastereomerically pure labeled compound **4** to our reaction conditions using primary, secondary, and tertiary Grignards. Analysis of the stereochemistry of the coupling products, directly from the crude reaction mixtures, revealed that inversion of configuration at the primary site had occurred, as evidenced by the magnitude of the $^3J_{ab}$ coupling constant of 1.8 Hz (Scheme 2a, *syn* **5a** and **5b**),[19a]

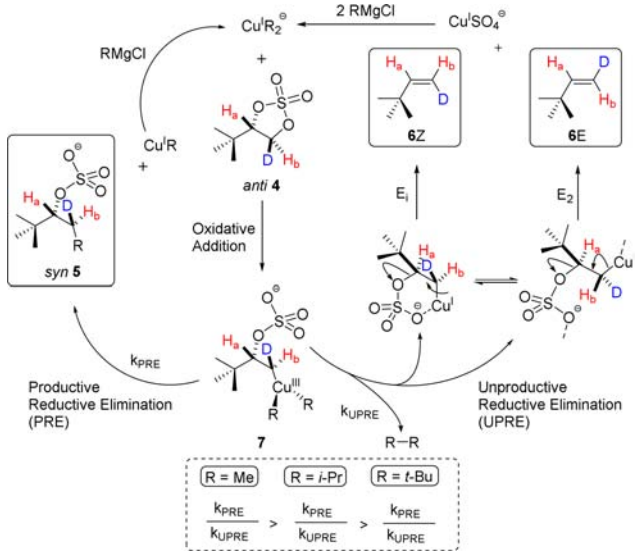
Scheme 2. Mechanistic Experiments



while no traces of *syn* **5c** were detected. In all cases, *anti* **5** products were not observed, within the NMR detection limit. This information is consistent with a catalytic cycle operating through Cu(I)−Cu(III) species.[26] Moreover, the need for quick addition of 1.5 equiv of the Grignard reagent to the reaction mixture also seems to indicate that a diorganocuprate(I) species is the active catalyst. Dropwise addition of Grignard would create a condition of constant deficiency of the reagent, which precludes formation of the catalytically active diorganocuprate.[27,28] It was also found that olefins **6***Z* and **6***E* had formed in all reactions as byproducts. These olefins are formed in a competing side reaction, where unproductive reductive elimination of the alkyl substituents takes place to form the observed homocoupling (R−R) product and the organometallic Cu(I) salt of the ring-opened sulfate,[20,22] which could then eliminate $Cu(I)SO_4^-$, by either the E_i or E_2 mechanism. Finally, although epoxides bear considerably more ring strain than 5-membered cyclic sulfate esters,[29,30] a competition experiment using a limited amount of Grignard reagent led to the formation of similar amounts of the respective coupling products. The better leaving group ability of the sulfate group, compared to that of alkoxide, appears to be sufficient to compensate for the difference in ring strain (Scheme 2b).[31]

A model for the mechanism that best fits all of the experimental data is presented in Scheme 3. We propose that

Scheme 3. Proposed Mechanism



the catalytically active diorganocuprate(I) species, most likely an oligomeric aggregate,[26] is formed in solution from either the Cu(I) or Cu(II) chloride precursor in the presence of excess Grignard. Once the diorganocuprate(I) has formed, the next step is nucleophilic attack on the cyclic sulfate at the sterically least-hindered position through one of the filled d orbitals of Cu, to form the Cu(III) organometallic intermediate **7** with inversion of configuration at the electrophilic carbon center. At this point **7** can follow a path of productive C−C bond-forming reductive elimination to yield the desired coupling product, or a path of unproductive reductive elimination to form the Grignard homocoupling product, followed by elimination of $Cu(I)SO_4^-$ to form the olefin of the respective substrate. The relative rates of the productive versus unproductive paths will be determined by the net steric bulk around **7**.

In conclusion, we have developed an operationally simple, highly chemoselective catalytic method for the $C(sp^3)$−$C(sp^3)$ cross-coupling of polyol derivatives with alkyl Grignard reagents to yield functionalized alcohols. The tolerance of our method to a broad set of functional groups, and the ability to use cyclic sulfates of various ring sizes, should allow for its implementation in target-oriented synthesis. Furthermore, the transformation reported herein highlights the potential of cyclic sulfate ester electrophiles in catalytic chemoselective transformations of polyols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01745.

Experimental details, NMR spectra, HPLC chromatographic analyses (PDF)

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Notes

The authors declare no competing financial interest.

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(20) See the Supporting Information.
(21) The reaction of **1** with benzylmagnesium chloride afforded product in the absence of catalyst.
(22) Dodecane, the homocoupling product of hexylmagnesium chloride, and 1-decene were also observed in a 1:1 ratio in reactions of **1** with HexylMgCl, although in lower quantities.
(23) A slight decrease in enantiopurity is an artifact likely due to an impurity in the chromatogram. See the Supporting Information.
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