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Iridium-Catalyzed Regioselective Silylation of Secondary Alkyl C−H Bonds for the Synthesis of 1,3-Diols

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Supporting Information

ABSTRACT: We report Ir-catalyzed intramolecular silylation of secondary alkyl C−H bonds. (Hydrido)silyl ethers, generated *in situ* by dehydrogenative coupling of a tertiary or conformationally restricted secondary alcohol with diethylsilane, undergo regioselective silylation at a secondary C−H bond γ to the hydroxyl group. Oxidation of the resulting oxasilolanes in the same vessel generates 1,3-diols. This method provides a strategy to synthesize 1,3-diols through a hydroxyl-directed, functionalization of secondary alkyl C−H bonds. Mechanistic studies suggest that the C−H bond cleavage is the turnover-limiting step of the catalytic cycle. This silylation of secondary C−H bonds is only 40−50 times slower than the analogous silylation of primary C−H bonds.

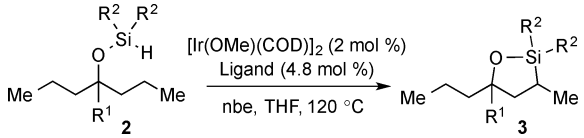
Selective functionalizations of C−H bonds by transition-metal complexes are creating new strategies for the efficient synthesis of functionalized organic molecules.[1] Among various C−H functionalization reactions, the silylation of C−H bonds is particularly valuable.[2] The organosilane products of these reactions are stable enough to be isolated readily in pure form,[3] but reactive enough to be converted to useful products through various selective transformations.[4]

Although a variety of catalysts have been developed for silylation of aromatic C−H bonds,[5−8] catalytic methods for silylation of aliphatic C−H bonds are limited.[9−14] Silylation of C−H bonds at a benzylic position[9] or adjacent to a heteroatom[10,11] occurs in the presence of a directing group, and silylation of unactivated C−H bonds at the terminal position of a triorganosilane occurs intramolecularly in the presence of catalysts containing Pt,[6a] Rh,[12] or Ir.[13] One author's group recently reported an Ir-catalyzed, hydroxyl-directed silylation of terminal alkyl C−H bonds of alcohols and ketones.[14] In this study, high-yielding reactions were limited to those functionalizing primary C−H bonds. The related silylation of secondary C−H bonds, which are sterically more demanding and less reactive than primary C−H bonds, is undeveloped.

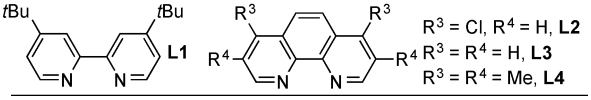
A mild, catalytic silylation of secondary C−H bonds directed by common functional groups, such as alcohols or ketones, would be synthetically useful because methylene C−H bonds are abundant in organic molecules, and the strategy of using a silyl ether derived from an alcohol or ketone for C−H bond silylation would create site-selective functionalizations of methylene C−H bonds. Oxidation of the C−H silylation product would install a secondary alcohol containing a stereogenic center. Such a process provides the opportunity to create an overall stereoselective C−H bond oxidation. However, the few examples of silylation of unactivated secondary C−H bonds have occurred in low yields under harsh reaction conditions.[11,12] Here we report that the catalyst formed from $[Ir(OMe)(COD)]_2$ and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4Phen) transforms secondary C−H bonds of tertiary and conformationally restricted secondary alcohols to secondary organosilanes in good yields with high site selectivity and stereoselectivity. This silylation reaction, along with subsequent oxidation at the C−Si bond, provides a method to convert tertiary and secondary alcohols to products in which the newly generated functionality is a secondary alcohol within a 1,3-diol. Previously reported methods for the direct conversion of alcohols to 1,3-diols based on radical reactions favor hydroxylation at benzylic and tertiary C−H bonds.[15]

To identify reaction conditions for the silylation of secondary C−H bonds, we studied reactions of alcohols containing long alkyl chains. Dehydrogenative coupling of tripropylcarbinol (**1a**) with diethylsilane catalyzed by 0.25 mol% $[Ir(OMe)(COD)]_2$

Table 1. Development of Ir-Catalyzed Hydroxyl-Directed Silylation of a Secondary C−H Bond[a]



entry	R^1	R^2	ligand	conv (%)	yield (%)
1	*n*-Pr	Et	**L1**	83	76
2	*n*-Pr	Et	**L2**	62	55
3	*n*-Pr	Et	**L3**	88	82
4	*n*-Pr	Et	**L4**	100	94
5	H	Et	**L4**	92	< 10
6	*n*-Pr	Me	**L4**	100	89
7	*n*-Pr	*i*-Pr	**L4**	12	< 10



[a]**2a** (0.5 mmol), nbe (0.6 mmol), $[Ir(OMe)(COD)]_2$ (2 mol%), and ligand (4.8 mol%) in THF at 120 °C for 24 h. Conversion and yield were determined by GC using *n*-dodecane as an internal standard. nbe = norbornene.

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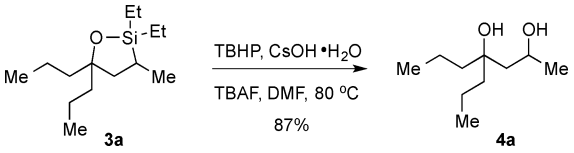
formed the (hydrido)silyl ether **2a**. In the presence of an Ir catalyst and the 4,4′-di-*tert*-butylbipyridine ligand, intramolecular cyclization provided the five-membered oxasilolane product **3a** in 76% yield (entry 1, Table 1).

The electronic properties of the ligands had a strong influence on the yield. When dichlorophenanthroline **L2** was used as a ligand, a lower yield of 55% of oxasilolane **3a** was obtained (entry 2). In contrast, when the strongly electron-donating Me_4Phen (**L4**) was used, full conversion of the substrate and a high yield of the product (94%) were observed (entry 4).

The yield of product from the silylation of a secondary C−H bond depends on the structural properties of the alcohol and the substituents on the silane. Reaction of the (hydrido)silyl ether derived from an acyclic secondary alcohol did not provide significant amounts of cyclization product (entry 5). However, reaction of a tertiary alcohol formed the oxasilole product in high yield. Further studies on secondary alcohols are discussed below. Cyclization of a (hydrido)silyl ether containing dimethyl groups on the Si was similar to cyclization of the diethyl-substituted silane (entry 6). However, the silyl ether containing bulky isopropyl groups on the Si did not react (entry 7).

After identifying an efficient catalyst and appropriate substrates for the silylation of secondary alkyl C−H bonds, we sought to identify conditions to oxidize the silylation product to form the corresponding 1,3-diol. Reaction of the secondary alkyl oxasilolanes under conditions we used previously to oxidize primary alkyl oxasilolanes did not furnish the desired diol.[14] However, heating the crude reaction mixture with *tert*-butyl hydroperoxide (TBHP), cesium hydroxide monohydrate, and tetrabutylammonium fluoride (TBAF) in a DMF solution converted the silylation product to the desired 1,3-diol (Scheme 1). These conditions were developed previously for the oxidation of sterically hindered silanes, and the reaction proceeds with retention of the configuration of the alkylsilane.[16]

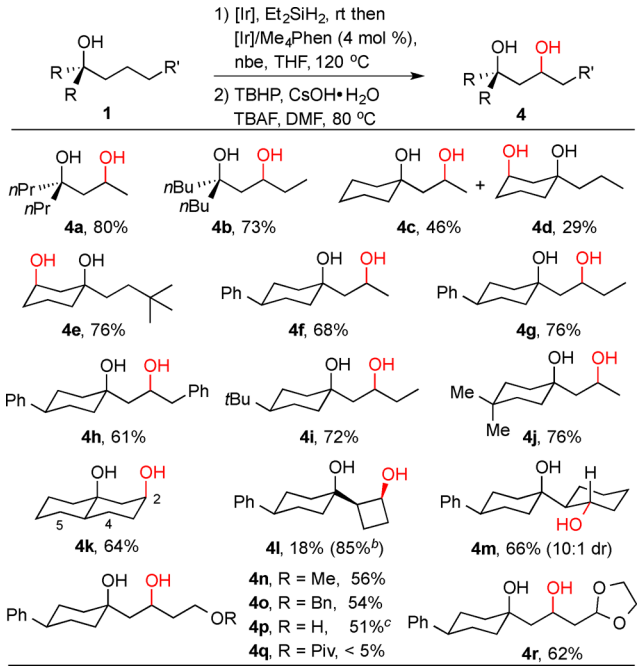
Scheme 1. Oxidation of Oxasilolane 3a



Through this sequence of silylation and oxidation, a variety of 1,3-diols were prepared from tertiary alcohols (Table 2). Tributylcarbinol underwent silylation of the secondary C−H bond (**4b**), even though the C−H bond γ to the alcohol is slightly more hindered than that in tripropylcarbinol (**4a**). In addition to acyclic tertiary alcohols, cyclic tertiary alcohols underwent silylation at a secondary C−H bond. For example, 1-propylcyclohexanol underwent hydroxylation in good yield to give two constitutional isomers (**4c**, **4d**) in a 1.6:1 ratio, resulting from hydroxylation of the side chain and hydroxylation of the axial C−H bond at the C-3 position, respectively.

Further reactions probed the effect of steric properties of the substrate on the regioselectivity of the silylation process. Reaction of a cyclohexanol containing a bulky *tert*-butyl group on the side chain led to a single product (**4e**) resulting from cleavage of the axial C−H bond on the cyclohexyl ring. In contrast, reaction of cyclohexanols containing a phenyl group on the cyclohexyl ring led to silylation of the side chains as the only product (**4f**–**4h**). In this case, the *cis* phenyl group hindered reaction at the axial C−H bonds. *tert*-Butyl and methyl groups on

Table 2. Examples of the Silylation of Secondary C−H Bonds[a]



[a]Conditions: **1** (1.0 equiv), Et_2SiH_2 (1.5 equiv), $[Ir(cod)OMe]_2$ (0.25−0.50 mol%), THF, room temperature (rt); removal of volatiles, then $[Ir(cod)OMe]_2$ (2 mol%), Me_4Phen (4.8 mol%), nbe (1.2 equiv), THF, 120 °C. Isolated yields are reported. [b]Yield for the silylation product. [c]Starting from **1p** in which R = TBS.

the cyclohexyl ring also affect the regioselectivity of the silylation reaction. The 4-*tert*-butylcyclohexanol derivative **1i** and the 4,4-dimethylcyclohexanol derivative **1j**, like the 4-phenylcyclohexanol **1f**, reacted to form **4i** and **4j** from silylation at the side chain rather than silylation at the cyclohexyl ring. Similar steric control was observed in a bicyclic system. Reaction of 9-decalinol gave a single hydroxylation product **4k** resulting from reaction at the C2 position. A methylene carbon at the C-5 position hindered reaction at the other possible silylation site (the C-4 position).

In addition to cyclohexanols containing a linear side chain, cyclohexanols bearing cyclic side chains underwent silylation in good yields (**4l**, **4m**). Reaction of cyclobutyl-substituted cyclohexanol **1l** gave a single *cis* isomer, while cyclohexyl-substituted cyclohexanol **1m** gave mainly the *trans* isomer. The relative configuration of the stereogenic centers in the major isomer of **4m** was confirmed by X-ray crystallography.

We also tested the functional group tolerance of the silylation of secondary C−H bonds. Substrates bearing methoxy, benzyloxy, siloxy, and acetal groups underwent silylation and oxidation to provide the diols in good yields (**4n**–**4p**, **4r**). The TBS group in the silylation product was cleaved during oxidation, producing the triol product (**4p**). In contrast to these silylation reactions, silylation of alcohols containing ester (**4q**) and amide groups did not occur.

In addition to the silylation of tertiary alcohols, we studied the silylation of secondary alcohols, and these results revealed the importance of conformation to the rate of C−H bond silylation. Reaction of the (hydrido)silyl ether derived from 4-heptanol did not provide significant amounts (<10%) of product (*vide supra*). To understand the origin of the lower yield of reactions of this secondary alcohol, relative to those of the reactions of the analogous tertiary alcohols, we analyzed the silylation of

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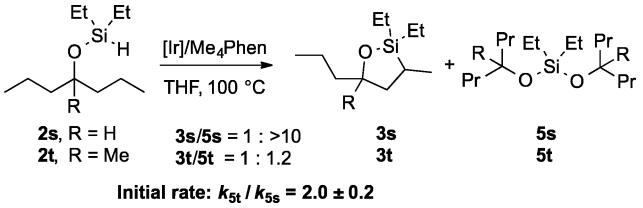
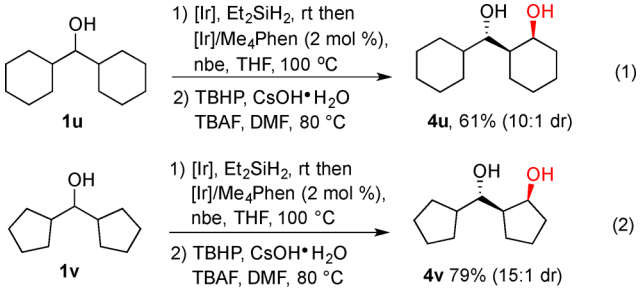
Scheme 2. Relative Rates for Silylation and Redistribution



(hydrido)silyl ethers derived from 4-heptanol and 4-methyl-4-heptanol (Scheme 2). The (hydrido)silyl ether (**2s**) derived from 4-heptanol mainly underwent silane redistribution to give the corresponding bis(alkoxy)diethylsilane.[17] The (hydrido)silyl ether (**2t**) derived from 4-methyl-4-heptanol gave products of silane redistribution and silylation in a 1.2:1 ratio. The ratio of the initial rates of formation of the product from silane redistribution of **2s** and **2t** was 1:2.0±0.2. This result shows that redistribution of the silyl ether derived from the secondary alcohol is *slower* than that of the silyl ether derived from the tertiary alcohol. Thus, the relative rates for redistribution reactions do not cause the yield for silylation of a tertiary alcohol to be higher than that for silylation of the analogous secondary alcohol; rather, it is the faster rate of C−H silylation of the tertiary alcohol that leads to the higher yield. This increased rate of reaction of the tertiary alcohol is a manifestation of the Thorpe−Ingold effect; cyclization of the *gem*-disubstituted reactant occurs faster than cyclization of the monosubstituted or unsubstituted analogues.[18] In the case of the (hydrido)silyl ether derived from a tertiary alcohol, steric repulsion between the *gem*-dialkyl groups and both the silyl ether and the third alkyl group will favor a conformation of the silyliridium intermediate in which the secondary C−H bond approaches the Ir center for C−H bond cleavage.

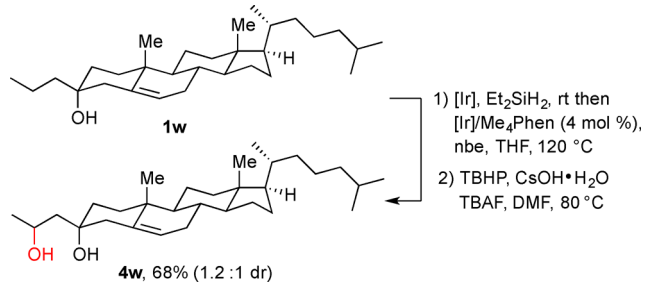
With these data in mind, we hypothesized that secondary alcohols containing substituents β to the hydroxyl groups should undergo silylation faster than secondary alcohols that have linear substituents. Consistent with this hypothesis, dicyclohexylmethanol and dicyclopentylmethanol, both of which contain substituents at the β-position of the hydroxyl groups, were converted to the corresponding diols in good yields and good diastereoselectivity by the combination of silylation and subsequent oxidation (eqs 1 and 2). The relative configuration



of the major products was determined by X-ray crystallography of their 4-nitrobenzoyl ester derivatives (see SI for details). The functionalization of secondary C−H bonds located β to a ketone also occurred after conversion of the ketone to the corresponding silyl ethers by Ir-catalyzed hydrosilylation. For example, dicyclohexyl ketone was converted to **4u** in 59% yield and 10:1 diastereoselectivity by a sequence comprising hydrosilylation, secondary C−H bond silylation, and oxidation.

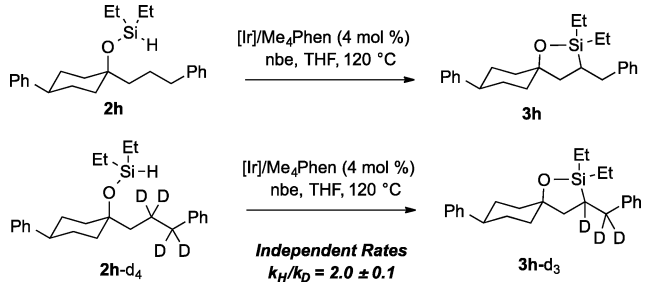
This hydroxyl-directed silylation has potential for applications to the functionalization of complex molecules. For example, the sequence of C−H silylation and oxidation was conducted with a tertiary alcohol derived from cholesterol. The hydroxyl-directed C−H functionalization reaction occurred at the side chain in good yield to afford the corresponding 1,3-diol product (Scheme 3). The high regioselectivity of this reaction should allow selective oxidation of a target C−H bond in a complex scaffold.

Scheme 3. Functionalization of a Natural Product Derivative



To gain insight into the mechanism, we measured the kinetic isotope effect (KIE). The initial rates of two separate reactions were measured with non-deuterated and deuterated substrates **2h** and **2h**-d_4. These reactions revealed a primary KIE of 2.0 ± 0.1 (Scheme 4). These data indicate that C−H cleavage is the rate-limiting step of the silylation of secondary C−H bonds.

Scheme 4. Kinetic Isotope Effect on the Silylation Reaction



In addition, we sought to obtain data on the relative rates for oxidation of primary and secondary C−H bonds in hydrosilyl ethers. Having observed the silylation of both primary and secondary C−H bonds, we could measure the relative rates for silylation at these two types of positions on an alkyl chain in separate molecules and in the same molecule. In one experiment, we measured the initial rates of silylation of silyl ethers **2x** and **2f** separately under the same conditions. Silylation at the secondary C−H bond was 49 ± 2 times slower than silylation at the primary C−H bond (Scheme 5). In a second experiment, we conducted the reaction of silyl ether **2y** containing one ethyl and two propyl substituents that would establish an intramolecular competition between primary and secondary C−H bonds. Again, the primary C−H bond underwent silylation preferentially in the presence of secondary C−H bonds (eq 3); in this case the products from the silylation of primary and secondary C−H bonds were obtained in a 41±2:1 ratio. These results suggest that silylation of a secondary C−H bond is less facile than silylation of a primary C−H bond, but only by a factor of 40−50.

In summary, we have developed an Ir-catalyzed site-selective silylation of unactivated secondary C−H bonds. After oxidation of the silylation products, 1,3-diols were obtained from the corresponding alcohols. Methods for direct conversion of alcohols to 1,3-diols are limited,[15] and previously reported

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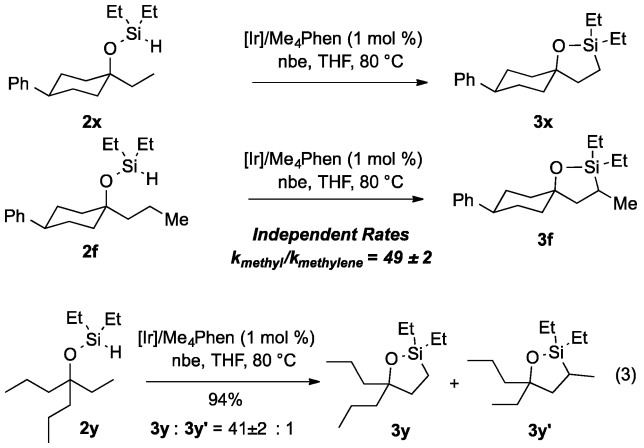
Scheme 5. Silylation of Primary and Secondary C−H Bonds



methods based on radical reactions strongly favor hydroxylation at benzylic and tertiary C−H bonds. Previously reported Ir-catalyzed silylation reactions were limited to those occurring at primary C−H bonds.[14] Now, we have shown that a secondary C−H bond can undergo hydroxylation by a sequence of C−H silylation and Tamao−Fleming oxidation reactions and that this sequence can be conducted site selectively and diastereoselectively. Moreover, the 40:1 ratio of the rate for functionalization of a primary C−H bond vs a secondary C−H bond gives rise to selective reactions at a primary position, but allows reactions to occur at a secondary position when a primary C−H bond is not located γ to the alcohol. Further studies of the reaction mechanism, functionalization of complex alcohols, and development of an asymmetric version of this reaction are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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