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Ring Opening of Epoxides by Pendant Silanols

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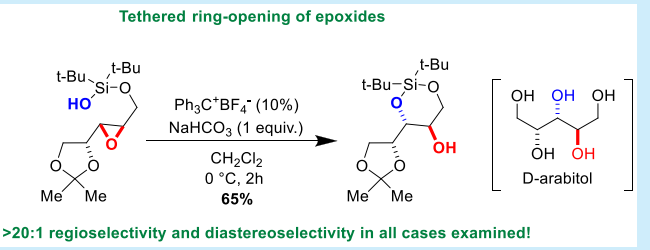
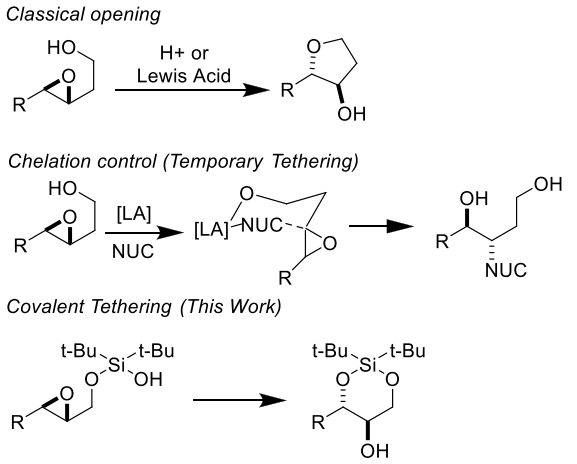
ABSTRACT: We present a new ring-opening reaction of epoxides by pendant silanols, catalyzed by either $Ph_3C^+BF_4^-$ or BINOL-phosphoric acid. Silanol epoxides derived from *trans*-allylic alcohols, *cis*-allylic alcohols, *trans*-homoallylic alcohols, and *cis*-homoallylic alcohols were all compatible and gave products from either *endo*- or *exo*-ring opening. With silanol epoxides derived from 4-alkenyl silanols, an unusual rearrangement to tetrahydrofuran products was observed. The utility of this methodology was demonstrated in a short preparation of protected D-arabitol.



Epoxides are some of the most versatile functional groups in synthetic chemistry, and their cleavage has been investigated in a variety of contexts (Scheme 1).[1−4]

Scheme 1. Previous Efforts with Ring Cleavage of Epoxides Inspire our Silanoxy-Tethered Ring-Opening Approach



Nucleophilic opening of epoxides can be broadly characterized as either intermolecular or intramolecular. Intramolecular opening of epoxides by pendant alcohols is a known route to a variety of oxygen heterocycles, including furans, pyrans, and medium-sized rings,[5,6] and this strategy has been applied on numerous occasions in natural product synthesis.[7−10] Several laboratories have established that "temporary tethering" is an effective strategy for regiocontrol in intermolecular ring-opening reactions of epoxides.[11−16] In such reactions, a Lewis acid or organocatalyst noncovalently binds to both the substrate and the nucleophile and templates attack at a single site of the epoxide. In contrast to these two areas, the use of covalent tethers for epoxide opening is much less established, and most explorations have focused on carbonates,[17−20] carbamates,[21−23] and trichloroacetamidates.[24] Of these tethers, only carbonates cleave epoxides with a masked hydroxy group.

Our laboratory is deeply invested in exploring di-*tert*-butylsilanols as covalent tethers for the intramolecular installation of hydroxy groups.[25−28] The triol motif is prevalent in a variety of carbohydrate and polyketide natural products with attractive biological activity (Figure 1). We envisioned a ring-opening reaction of epoxides by pendant di-*tert*-butylsilanols, which would form a variety of protected triols in a single transformation. While triols can be synthesized by

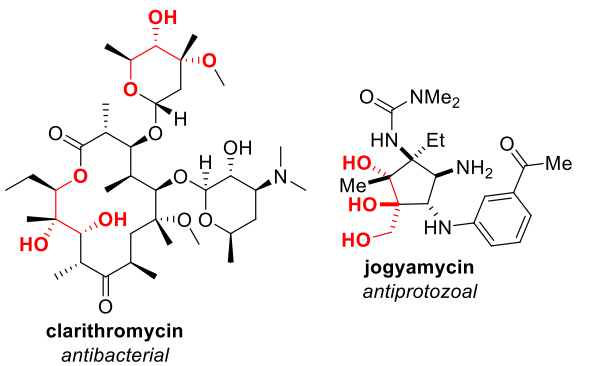


Figure 1. Triol motif that is prevalent in natural products with potent biological activity.

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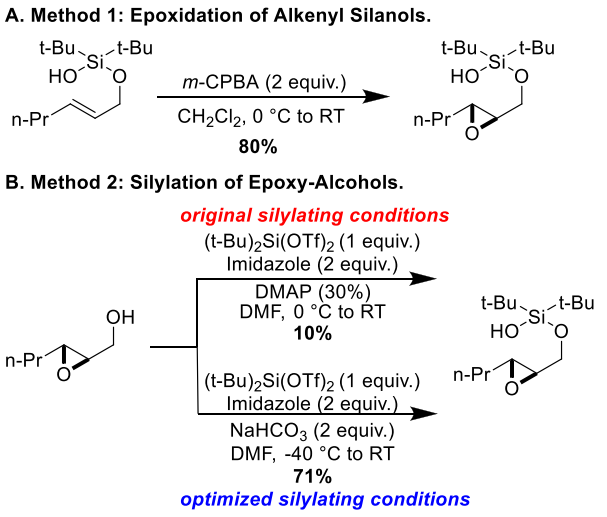
other methods, such as dihydroxylation of allylic alcohols, differential protection of the resulting hydroxyl groups can be a major challenge.[29−32] Due to geometric constraints on the transition states of these intramolecular reactions, we reasoned that such openings were likely to be highly regioselective and diastereoselective. Here, we describe our efforts to reduce this concept to practice.

The substrate silanol epoxides could be conveniently prepared using one of two methods (Scheme 2). *m*-CPBA

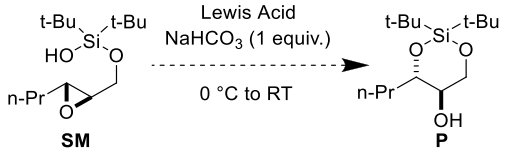
Scheme 2. Two Methods for Synthesizing Silanol Epoxides



oxidation of the alkenyl silanol[26] afforded the silanol epoxide in good yields, and in our hands, this proved to be a very general procedure (Scheme 2A). As there is much technology[33−35] for the stereocontrolled synthesis of epoxides from alkenyl alcohols, we reasoned that developing a method for attaching the silanol auxiliary directly to epoxy alcohols would be particularly impactful. Our standard silylating conditions[26] failed to deliver the product in reasonable yields with these particularly delicate substrates (Scheme 2B). We found that replacing DMAP with 2 equiv of $NaHCO_3$ and decreasing the initial reaction temperature to −40 °C allowed for silanol epoxide formation reproducibly and in much better yields (Scheme 2B).

With two protocols allowing reliable access to silanol epoxides, we began optimizing our envisioned ring-opening reaction. Treatment of di-*tert*-butyl(3-propyloxiran-2-yl)-(methoxy)silanol with 5 mol % $Sc(OTf)_3$ and 1 equiv of $NaHCO_3$ in CH_2Cl_2 for 3 h gave 20% of the desired product (Table 1, entry 1). Increasing the reaction time to 14 h led to complete consumption of the starting material with 65% product formation (Table 1, entry 2). In both cases, a major side product was di-*tert*-butylsilanediol, suggesting that starting material was fragmenting unproductively in the presence of $Sc(OTf)_3$. Switching the solvent to benzene, dichloroethane, chloroform, and ethyl acetate (Table 1, entries 3−6, respectively) was markedly deleterious. We thus decided to try different Lewis acids with the goal of reducing the extent of di-*tert*-butylsilanediol formation. While triflate salts of zinc, indium, and ytterbium (Table 1, entries 7−9, respectively) did not help reaction performance, with 10 mol % of the unusual Lewis acid triphenylcarbenium tetrafluoroborate[36] (Table 1, entry 10), product formation was excellent with no discernible starting material fragmentation.

Table 1. Optimization of Epoxide Opening by Pendant Silanols



	Lewis acid (equiv)	solvent	time (h)	P/SM[a]
1	$Sc(OTf)_3$ (5%)	CH_2Cl_2	3	20/65
2	$Sc(OTf)_3$ (5%)	CH_2Cl_2	14	65/0
3	$Sc(OTf)_3$ (5%)	C_6H_6	14	0/100
4	$Sc(OTf)_3$ (5%)	$C_2H_4Cl_2$	14	27/49
5	$Sc(OTf)_3$ (5%)	$CHCl_3$	14	10/84
6	$Sc(OTf)_3$ (5%)	EtOAc	14	0/100
7	$Zn(OTf)_3$ (5%)	CH_2Cl_2	14	0/100
8	$In(OTf)_3$ (5%)	CH_2Cl_2	14	45/25
9	$Yb(OTf)_3$ (5%)	CH_2Cl_2	14	0/100
10	$Ph_3C^+BF_4^-$ (10%)	CH_2Cl_2	2	80/0

[a]Yield estimated from ^1H NMR integration with 4-nitrotoluene as an internal standard.

Encouraged by this very positive result, we next began to explore the substrate scope (Scheme 3). Our optimized conditions proved to be general for a variety of silanol epoxides, including those with branched alkyl chains (Scheme 3, entries 1 and 2), substituted aryl rings (Scheme 3, entries 3 and 4), and heteroaryl rings (Scheme 3, entry 5). Importantly, we were not limited to disubstituted *trans*-epoxides derived from allylic silanols. Epoxides prepared from trisubstituted allylic silanols (Scheme 3, entry 6), *trans*-homoallylic silanols (Scheme 3, entry 7), and *cis*-homoallylic silanols (Scheme 3, entry 8) were all compatible with our optimized conditions. Epoxides derived from *cis*-allylic silanols were particularly problematic, likely due to unfavorable 1,3-allylic strain[37] during the cyclization event. However, we were pleased to find that maintaining the reaction temperature at −10 °C delivered the desired cyclized product in a respectable 40% yield (Scheme 3, entry 9).

When treated with $Ph_3C^+BF_4^-$, epoxides derived from aryl alkenes failed to cyclize cleanly and, in all cases examined, gave intractable mixtures of products (Table 2, entry 1). Use of $Bi(OTf)_3$ as a Lewis acid (Table 2, entry 2) or HFIP as the solvent (Table 2, entry 3) did little to improve reaction performance, but a more positive result was realized with treatment of 10-CSA[5,6] (Table 2, entries 4 and 5). We hypothesized that a milder Bronsted acid would lead to a cleaner reaction and were pleased to see that with BINOL-phosphoric acid, cyclization proceeded smoothly and with no discernible side products (Table 2, entry 6).

These conditions proved to be excellent for cyclization of aryl epoxide substrates, and a variety of substitution patterns on the aromatic ring were well tolerated (Scheme 4, entry 1). Furthermore, several substrates that failed to cyclize with $Ph_3C^+BF_4^-/NaHCO_3$ reacted cleanly under these alternate conditions (Scheme 4, entries 2 and 3). In all cases (Schemes 3 and 4), the cyclization reactions were perfectly regioselective and diastereoselective, attesting to the utility of our protocols. A crystal structure of **41** (CCDC 2126173) enabled us to unambiguously establish its relative stereochemistry, and we have assigned the stereochemistry of other products by analogy.

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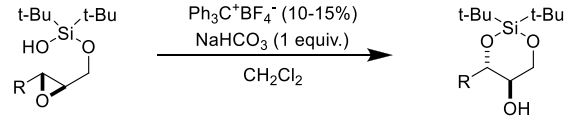
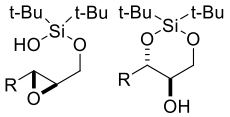
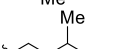
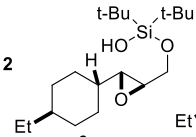
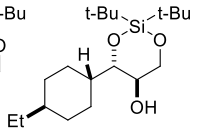
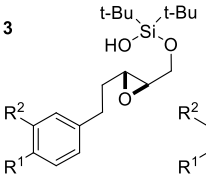
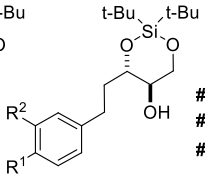
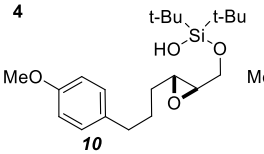
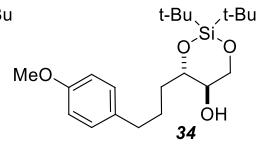
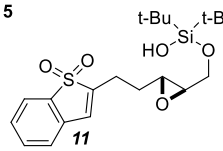
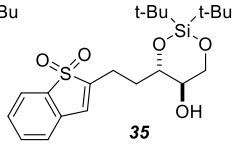
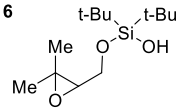
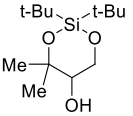
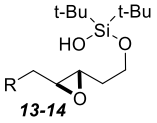
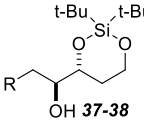
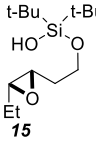
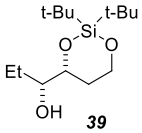
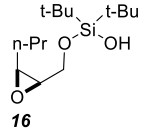
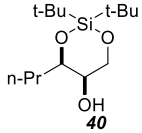
Scheme 3. Substrate Scope with Alkyl Epoxides

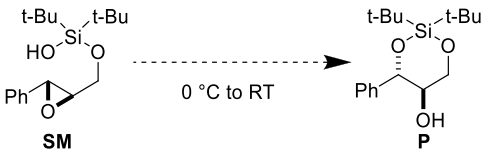


entry	substrate	product		isolated yield
1			#1, 25 R = n-Pr	80%
			#2, 26 R = 	74%
			#3, 27 R = 	83%
			#4, 28 R = i-Pr	71%
			#5, 29 R = 	52%
	1-5	25-29		
2				71%
	6	30		
3			#7, 31 R1 = F, R2 = H	72%
			#8, 32 R1 = Br, R2 = H	70%
			#9, 33 R1 = H, R2 = CF3	87%
	7-9	31-33		
4				70%
	10	34		
5				81%
	11	35		
6				74%
	12	36		
7			#13, 37 R = Me	65%
			#14, 38 R = c-Hex	50%
	13-14	OH 37-38		
8				60%
	15	39		
9				40%
	16	40		

Note: Starting material is often fully consumed with few side products. At present, we are unable to account for the decreased mass balance in some cases.

Our success with both allylic and homoallylic silanols prompted us to test our reaction with more remote silanol

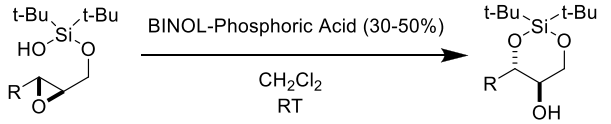
Table 2. Aryl Epoxide Opening by Pendant Silanols

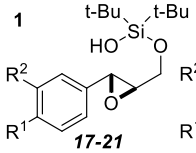
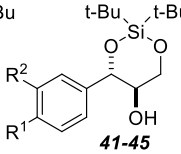
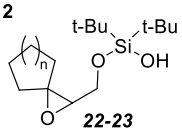
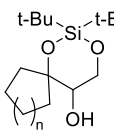
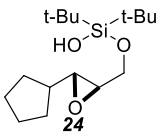
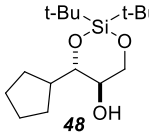


	additive	solvent	time (h)	P/SM[a]
1	$Ph_3C^+BF_4^-$ (10%), $NaHCO_3$ (1 equiv)	CH_2Cl_2	2	40/0[b]
2	$Bi(OTf)_3$ (5%), $NaHCO_3$ (1 equiv)	CH_2Cl_2	2	30/0[b]
3	none	HFIP	6	0/40[b]
4	10-CSA (1 equiv)	CH_2Cl_2	1	50/0[b]
5	10-CSA (0.25 equiv)	CH_2Cl_2	1	50/0[b]
6	BINOL-phosphoric acid (30%)[c]	CH_2Cl_2	14	80/0

[a]Yield estimated from ^{1}H NMR integration with 4-nitrotoluene as an internal standard. [b]Mixture of side products. [c](*R*)-(−)-1,1′-Binaphthyl-2,2′-diyl hydrogen phosphate, arbitrarily chosen.

Scheme 4. Substrate Scope with BINOL-Phosphoric Acid Conditions



entry	substrate	product		isolated yield
1			#17, 41 R1 = H, R2 = H	80%
			#18, 42 R1 = F, R2 = H	63%
			#19, 43 R1 = Br, R2 = H	85%
			#20, 44 R1 = Cl, R2 = H	82%
			#21, 45 R1 = H, R2 = Br	85%
	17-21	41-45		
2			#22, 46 n = 1	54%
			#23, 47 n= 2	60%
	22-23	46-47		
3			with 10-CSA	43%
			with BINOL-PA	50%[a]
	24	48		

epoxides (Scheme 5). We simply expected the product of either 7-*exo* or 8-*endo* cyclization. What we found, however, was very unexpected and much more interesting. When *trans*-epoxide **49** was treated with our optimized protocol of $Ph_3C^+BF_4^-$ (15 mol %) and $NaHCO_3$ (1 equiv) in CH_2Cl_2, tetrahydrofuran **50** formed in 60% yield (Scheme 5A)! We hypothesize that two tandem cyclizations took place. The first was the expected 8-*endo* cyclization, which was followed by an unexpected 5-*exo* ring opening. We were pleased to find that with *cis*-epoxide **51**, diastereomeric tetrahydrofuran **52** formed in similar yields (Scheme 5B). These reactions were scaled 5−7-fold, with no degradation in yield or selectivity.

We envisioned a short preparation of protected D-arabitol utilizing our ring-opening reaction as a key step (Scheme 6). With our laboratory's standard silylating conditions,[26] enantiopure silanol (+)-**54** was prepared from known chiron (+)-**53**.[38] *m*-CPBA epoxidation of (+)-**53** proceeded in

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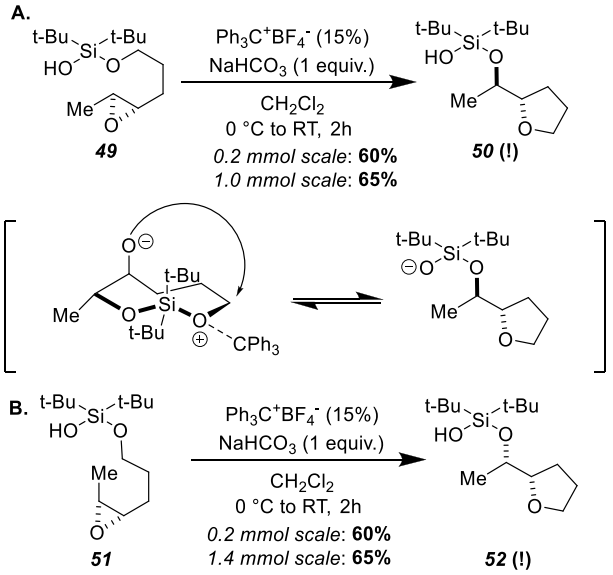
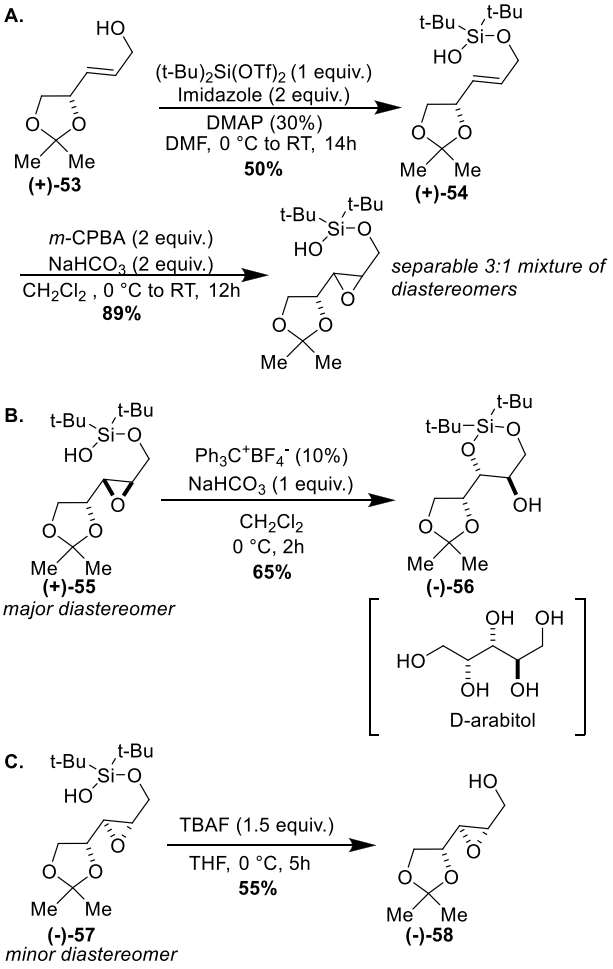
Scheme 5. An Unexpected Rearrangement with Silanol Epoxides Derived from 4-Alkenyl Silanols



Scheme 6. A Short Prepartion of Protected D-Arabitol



excellent yield to give a separable mixture of (+)-**55** and (−)-**57** (Scheme 6A). When major diastereomer (+)-**55** was treated with $Ph_3C^+BF_4^-$ (10 mol %) and $NaHCO_3$ (1 equiv), cyclized product (−)-**56** (protected D-arabitol) formed in a 65% yield (Scheme 6B). Minor diastereomer (−)-**57** was desilylated using TBAF (1.5 equiv) in THF to yield known alcohol (−)-**58**,[38,39] allowing us to assign the absolute stereochemistry of diastereomers (+)-**55** and (−)-**57** (Scheme 6C).

In summary, we present a new ring opening of epoxides by pendant silanols.[40] In all cases examined, the reaction is perfectly regioselective and diastereoselective. Silanol epoxides derived from *trans*-allylic alcohols, *cis*-allylic alcohols, *trans*-homoallylic alcohols, and *cis*-homoallylic alcohols were all compatible and gave products from either *endo*- or *exo*-ring opening. With silanol epoxides derived from 4-alkenyl silanols, an unusual rearrangement to tetrahydrofuran products was observed, which is likely the result of tandem nucleophilic attacks. The utility of this reaction was demonstrated in a short preparation of protected D-arabitol. We are optimistic that this methodology will enjoy much use in the pursuit of complex, polyhydroxylated molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c04310.

Experimental procedures, reasoning for structural assignments, and NMR spectra (PDF)

Accession Codes

CCDC 2126173 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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