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## COMMUNICATION

## Hydrosilylation of epoxides catalyzed by a cationic $\eta^1$ -silane iridium(III) complex<sup>†</sup>

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Cationic silane complex 2, catalyzes the hydrosilylation of epoxides and cyclic ethers to give the silyl-protected alcohols, regioselectively. A mechanistic study shows that the epoxide undergoes isomerization to the ketone, followed by hydrosilylation.

Epoxides<sup>1</sup> are useful precusors to a variety of materials through ring-opening under acidic or basic conditions.<sup>2</sup> Regioselectivity of the ring opening is usually observed and can be controlled by variation in reaction conditions.<sup>3</sup> The catalytic hydrosilylation of epoxides by transition metal complexes, however, has rarely been reported.<sup>3k</sup> Recently, we reported catalytic C–O bond cleavage of alkyl ethers by silanes using the highly electrophilic  $\eta^1$ -silane complex **2** generated *in situ* from the conveniently prepared acetone complex **1**.<sup>4</sup> The basic mechanism is illustrated in Scheme 1. We report here application of this chemistry to epoxides which results in regioselective ring-opening and one-pot conversion of epoxides to silyl-protected alcohols.

Hydrosilylations of epoxides were conducted either in methylene chloride or in chlorobenzene at 22 °C. Catalyst loadings of 0.25 or 0.5 mol% were generally used together with 1.5 equiv. of  $Et_3SiH$ . Slow inverse addition of the diluted



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substrate has been employed in this catalysis to prevent polymerization of the epoxide (See Supporting information). Results of typical hydrosilylations are summarized in Table 1.

**Table 1** Hydrosilylation of epoxides and cyclic ethers with  $1^a$ 

Entry	Catalyst mol (%)	Substrate	t h	Conv. <sup>b</sup> %	Products	Yield <sup>c</sup> %
	0.25	Ph Ph	1	quant.	Et₃SiO⌒ Ph	91(78)
2	0.25	<u>م</u> ر	1	quant.	Et <sub>3</sub> SiO	83 <sup>d</sup>
3	0.25	,°	1	quant.	Et₃SiO ↓	68(30)
4	0.5	~ <b>^</b>	1	quant.	Et₃SiO └	quant.
5	0.5	Ph Ph	1	quant.	Et₃SiO <sup>∕</sup> Ph Ph	>95 <sup>e</sup>
6	0.25	Bu	2.5	quant. <sup>g</sup>	Et₃SiO HBu +	54
					Et₃SiO <sup>∕∕</sup> <sup>Bu</sup>	46
7	0.5	Å	1	quant.	Et <sub>3</sub> SiO	>95(85) <sup>f</sup>
$8^h$	0.5	$\langle \bigcirc$	1	quant.	Et <sub>3</sub> SiO	quant.
$9^h$	0.5	~ <b>°</b> /	2.2	quant. <sup>i</sup>	Et <sub>3</sub> SiO	37
					Et <sub>3</sub> SiO <sup>-</sup>	63
10 <sup><i>h</i></sup>	0.5	<b>°</b>	2.5	quant. <sup>i</sup>	Et <sub>3</sub> SiO +	90 10

<sup>*a*</sup> Reaction conditions: 0.005 mmol of **1**, solvent =  $CD_2Cl_2$ , 1.5 equiv. Et<sub>3</sub>SiH, 22 °C, slow addition of the substrate (1.0 or 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) *via* syringe pump over 2 h. <sup>*b*</sup> Determined by <sup>1</sup>H NMR. <sup>*c*</sup> NMR yields based on an internal standard, and isolated yields in parentheses. <sup>*d*</sup> 8% of Dimeric product observed. <sup>*e*</sup> 2% of 1,2-Diphenylethane observed. <sup>*f*</sup> *trans*: *cis* = 59% : 41%. <sup>*g*</sup> NMR yield = 82% and isolated yield is 45%. <sup>*h*</sup> Direct addition of the substrate to the catalyst solution in C<sub>6</sub>D<sub>5</sub>Cl. <sup>*i*</sup> NMR yield = quant.

Styrene oxide smoothly undergoes hydrosilylation to give the corresponding silyl-protected primary alcohol, Et<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>Ph in 91% NMR yield (entry 1). Hydrosilylation of 1,2-epoxy-2methyl propane at 22 °C produces the silyl-protected primary alcohol and the dimeric product, Et<sub>3</sub>SiOCMe<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>-CHMe<sub>2</sub>,<sup>5</sup> in 83% and 8% NMR yields, respectively (entry 2). 2-Methyl-2,3-epoxy butane is also selectively converted to the silvl-protected secondary alcohol (entry 3). Unexpectedly, hydrosilylation of 2,3-dimethyl-2,3-epoxy butane gives only the silyl-protected secondary alcohol, not the silyl-protected tertiary alcohol, Et<sub>3</sub>SiOCMe<sub>2</sub>CMe<sub>2</sub>, indicating that methyl migration occurs following ring opening (entry 4). Similarly, trans-stilbene oxide is quantitatively hydrosilylated to produce Et<sub>3</sub>SiOCH<sub>2</sub>CHPh<sub>2</sub>, indicating a 1,2-phenyl migration (entry 5). 1,2-Epoxy hexane undergoes C-O bond cleavage at both C-O bonds of the epoxide to result in a mixture of the silylprotected primary and secondary alcohols in a ratio of 0.46:0.54 in 82% NMR yield (entry 6). Hydrosilylation of methyl-1,2-cyclopentene oxide smoothly proceeds to give 2-methyl cyclopentyl triethyl silyl ether in excellent yield with 59:41 trans/cis product ratio (entry 7). Formation of two isomers as products indicates the mechanism could be more complex than silvlation followed by ring opening with 3. Tetrahydrofuran derivatives have been examined in the hydrosilvlation reactions (entry 8-10). Tetrahydrofuran is hydrosilvlated in 1 h to produce n-butyl triethylsilvl ether in a quantitative yield (entry 8). 2,2-Dimethyl tetrahydrofuran undergoes a selective cleavage of the C-O bond at the more substituted carbon to afford the silyl-protected primary alcohol (entry 9). The silvl alkyl ether having an internal olefin (63%) is likely formed via silulation, ring opening to a tertiary carbocation and elimination to the trisubstituted alkene. In contrast, the hydrosilvlation of 2-methyl tetrahydrofuran gives the corresponding silyl-protected secondary alcohol as a main product (entry 10).

In the light of the unusual results for methyl-1,2-cyclopentene oxide (both *cis* and *trans* isomers formed),<sup>3j</sup> we initiated a mechanistic investigation of some of the hydrosilylation reactions. Hydrosilylation of styrene oxide using Et<sub>3</sub>SiD yields the corresponding silyl-protected alcohol, Et<sub>3</sub>SiOCH<sup> $\alpha$ </sup>D–CH<sub>2</sub><sup> $\beta$ </sup>Ph, in which the ratio of  $\alpha$ –H to  $\beta$ –H is confirmed to be *ca.* 1 : 2. This result suggests a quantitative isomerization *via* a hydride shift (eqn (1)).



In addition, the product obtained from the hydrosilylation of methyl-1,2-cyclopentene oxide using Et<sub>3</sub>SiD at 22 °C exhibits only two <sup>2</sup>H signals at  $\delta 3.82$  and 3.46 due to  $\alpha$ -deuterated *cis* (43%) and *trans* (57%) isomers, respectively, indicating again a quantitative D-incorporation into the  $\alpha$ -carbon of the product *via* hydride shift to form **4**, followed by hydride transfer from **3**-*d*<sub>2</sub> to the carbon  $\alpha$  to oxygen (Scheme 2). Intermediate **4**, a silylated



ketone, is analogous to the key intermediate in hydrosilylation of ketones by **2** which we previously reported.<sup>6</sup> Here, we have observed upon hydrosilylation of 2-methyl cyclopentanone at 0 °C the same isomer ratio of the product (*trans*:cis = 75:25), confirming the intermediacy of **4**. Furthermore, these experiments suggest that ketone could be intially formed *via* isomerization, then, in a second step, hydrosilylated. To probe this possibility, the reaction of **1**, Et<sub>3</sub>SiH, and methyl-1,2-cyclopentene oxide in a ratio of 1:53:27 in CD<sub>2</sub>Cl<sub>2</sub> was monitored over -60 to -20 °C by NMR spectroscopy (eqn (2)).



Rearrangement of the epoxide to the ketone occurs at -60 °C resulting in 79% conversion of the epoxide in 10 min. Upon warming to -40 °C, the remaining epoxide was consumed quantitatively over 20 min. The <sup>13</sup>C NMR spectrum at -40 °C clearly shows the six resonances of 2-methyl cyclopentanone, but, at this stage, no resonances of product 2-methyl cyclopentyl triethyl silyl ether. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows 81 mol% of several signals over  $\delta 175$  to 171, which are assignable to the cationic iridium species coordinated to 2-methyl cyclopentanone, [Ir-H][2-methyl cyclopentanone]<sup>+</sup> (5).<sup>7</sup> A <sup>31</sup>P signal at  $\delta$ 190 is assigned to [Ir–H]H<sub>2</sub><sup>+</sup> (19 mol%), is formed due to H<sub>2</sub>O (Et<sub>3</sub>SiOSiEt<sub>3</sub> also is observed to accompany formation of [Ir-H]H2<sup>+</sup>). At -20 °C, 2-methyl cyclopentanone begins to undergo hydrosilylation to afford 2-methyl cyclopentyl triethyl silyl ether as a main product in 78% : 22% trans/cis ratio (quantitative conversion in 30 min). The results of the low temperature NMR experiments confirm that the epoxide is preferentially rearranged to the ketone, prior to being hydrosilylated. Furthermore, the reaction of Lambert's reagent,  $Et_3Si^+B(C_6F_5)_4^{-8}$  (1 equiv.) with methyl-1,2-cyclopentene oxide (5 equiv.) at -40 °C gives quantitatively 2-methyl cyclopentanone in 0.5 h.9 This clearly indicates that  $Et_3Si^+$  from  $Et_3Si^+B(C_6F_5)_4^-$  can isomerize the epoxide to the ketone.<sup>10</sup>

Results obtained in this study are consistent with the proposed catalytic cycle in Scheme 3. Isomerization of the epoxide to the ketone is rapid and followed by hydrosilylation. Regioselectivity is observed when opening of silylated epoxides results in selective formation of a stabilized carbocation (tertiary (entries 2,3); benzylic (entry 1)).<sup>11</sup> The isomerization pathway may involve direct transfer of  $Et_3Si^+$  from 4 to epoxide (lower isomerization cycle, Scheme 3) or the transfer



could occur *via* the intermediacy of **2** (upper isomerization cycle). The dominant resting state in the dual cycle is  $[Ir-H][ketone]^+$ , **5**. The hydrosilylation cycle using **2** was previously described<sup>6</sup> and is similar to an earlier report by Nikonov<sup>12</sup> who established a similar mechanism of hydrosilylation of carbonyls and nitriles employing the cationic ruthenium silane complex  $[Cp(Pr^i_3P)-Ru(NCMe)(\eta^2-HSiMe_2Ph)]^+$ .

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