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Metal-Free Catalytic Reductive Cleavage of Enol Ethers

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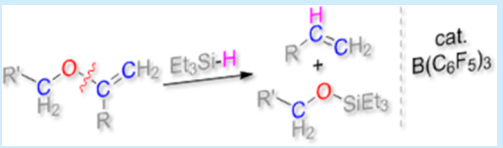
Supporting Information

ABSTRACT: In contrast to the well-known reductive cleavage of the alkyl−O bond, the cleavage of the alkenyl−O bond is much more challenging especially using metal-free approaches. Unexpectedly, alkenyl−O bonds were reductively cleaved when enol ethers were reacted with Et_3SiH and a catalytic amount of $B(C_6F_5)_3$. Supposedly, this reaction is the result of a $B(C_6F_5)_3$-catalyzed tandem hydrosilylation reaction and a silicon-assisted β-elimination. A mechanism for this cleavage reaction is proposed based on experiments and density functional theory (DFT) calculations.



The activation of alkenyl−O bonds is of great interest in synthetic organic chemistry, where it is often used in cross-coupling reactions.[1] The reductive cleavage of enol ethers has also garnered attention due to their presence in crude oil distillates and potential biofuels such as lignin.[2] Since the seminal work of Wenkert in 1979, in which the alkenyl group was reductively cleaved from enol ethers by *i*-PrMgBr in the presence of Ni-based catalysts (Figure 1A),[3] few other Ni-based catalysts have been found to activate these bonds.[1] Remarkably, Johnson very recently reported a Ni hydride complex, which was capable of dismantling vinyl ethers.[4] *In contrast, the catalytic reductive cleavage of an alkenyl group from enol ethers, using a main group based catalyst, has never been reported.* Alkyl−O bonds, however, are readily cleaved by catalytic metal-free methods. In 2000, Gevorgyan reported the $B(C_6F_5)_3$ (**1**) catalyzed cleavage of dialkyl ethers by hydrosilanes.[5] Later, this chemistry was used in the deoxygenation of carbohydrates and polyols[6] and in functional group manipulations.[7] We recently reported selective chlorination of Si−H bonds using this reactivity.[8]

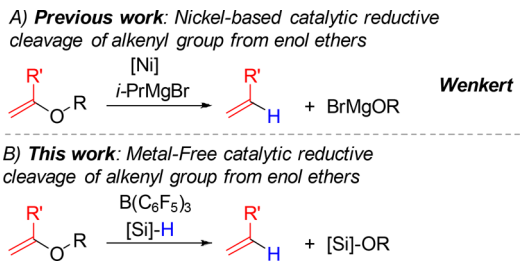
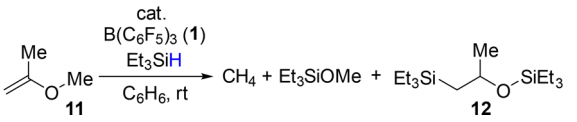


Figure 1. Catalytic reductive cleavage of enol ethers.

Herein we report the $B(C_6F_5)_3$-catalyzed reductive cleavage of an alkenyl group from enol ethers using Et_3SiH (Figure 1, B). A mechanism for this cleavage is proposed based on experiments and DFT calculations that involves an unprecedented $B(C_6F_5)_3$-catalyzed silicon-assisted β-elimination[9] of an alkoxysilane from the ether adducts with a silyl substituent β to oxygen.

We first reacted $EtOC(H)=CH_2$ (**2**) with Et_3SiH and **1** (1 mol %) in C_6H_6 at rt. Almost immediately gas formation was observed. ^1H NMR analysis revealed clean formation of Et_3SiOEt and $H_2C=CH_2$ (**3**) (Table 1, entry 1). The formation of these products was rather surprising since it implied that the reductive cleavage of a more robust vinyl group had occurred and not the expected cleavage of the ethyl group.[5−8]

To study this reactivity further, we tried other alkyl enol ethers in this reaction. Thus, reactions of $ROC(H)=CH_2$ (R = *i*-Bu (**4**), Cy (**5**), Ph (**6**), $Cl(CH_2)_2$ (**7**), and $Me_3SiO(CH_2)_2O(CH_2)_2$ (**8**)) all led to cleavage of the vinyl group (Table 1, entry 1). In $EtOC(Me)=CH_2$ (**9**) the cleavage of the propenyl group (**10**) occurred (Table 1, entry 2). The cleavage of $MeOC(Me)=CH_2$ (**11**) was not as selective and yielded CH_4, $MeOSiEt_3$, and $Et_3SiOCH(CH_3)CH_2SiEt_3$ (**12**) as the major products (eq 1).



(1)

The formation of these products could be explained by a number of processes taking place simultaneously, such as methyl and propenyl group cleavage and hydrosilylation of the C=C double bond in **11**. The difference in the reactivity between **9** and **11** is not surprising since the cleavage of dialkyl ethers is strongly influenced by sterics.[5,6]

However, when **11** was reacted with 2 equiv of Et_3SiH and **1** (1 mol %) in C_6H_6, **12** was formed cleanly and, after heating, gave propylene and $(Et_3Si)_2O$ (Table 1, entry 2). Interestingly, the same reaction in CH_2Cl_2 led to the cleavage products directly without heating. Silyl enol ethers were also tested in this reaction. Thus, the reaction with 1-(trimethylsilyloxy)-cyclopentene (**13**) led to cleavage of the cyclopentenyl group

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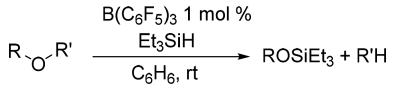
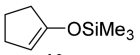
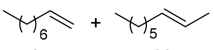
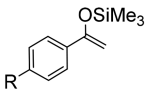
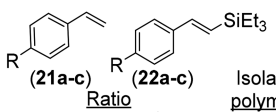
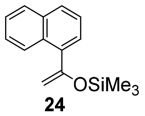
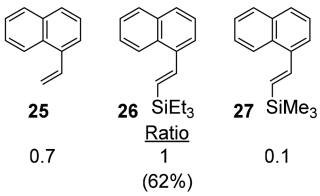
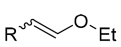
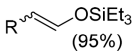
Table 1. $B(C_6F_5)_3$-Catalyzed Cleavage of the Alkyl/Silyl Enol Ethers



entry	ROR'	Olefin product (yield)
1	 R = Et (**2**), *i*-Bu (**4**), Cy (**5**), Ph (**6**),[a] $Cl(CH_2)_2$ (**7**), $Me_3Si(CH_2)_2O(CH_2)_2$ (**8**)	 **3** (70 - 95%)[b]
2	 R = Et (**9**) Me (**11**)[c]	 **10** (90-95%)[b]
3[d]	 **13**	 **14** (55%)
4	 R = Cy (**15**), Oc (**16**)	 **17** + **18** (<20%)  **19** (<20%)
5	 R = H (**20a**) Me (**20b**) F (**20c**)	 **21a-c** / **22a-c** Ratio: R = H 1 : 1; Me 1 : 0.8; F 1 : traces. Isolated polymers: **23a** (66%), **23b** (75%), **23c** (59%)
6	 **24**	 **25** 0.7; **26** SiEt3 Ratio 1 (62%); **27** $SiMe_3$ 0.1
7	 R = Me (**28**) Et (**29**)	 (95%) R = Me (**30**), Et (**31**)

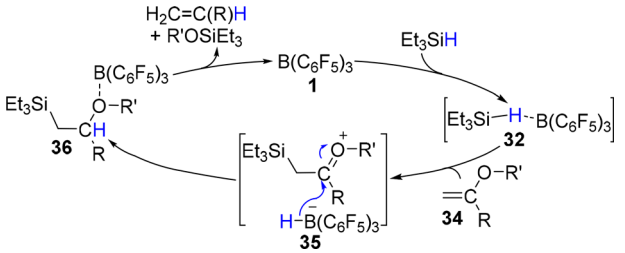
[a]Reaction works better in CH_2Cl_2. [b]NMR yields. [c]2 equiv of Et_3SiH was used. [d]Works better with 5% of **1**.

(**14**) (Table 1, entry 3). Alkenyl groups in silyl enol ethers bearing bulky alkyl groups (R = Cy (**15**), Oc (**16**)) were also cleaved, but much less efficiently (Table 1, entry 4). The terminal C=C double bond in the cleavage product of **16** partially isomerized to an internal position. Interestingly, the cleavage of silyl enol ethers substituted by aryls led not only to olefins but also to vinylsilanes (Table 1, entries 5 and 6). In the case of **20a**, **20b**, and **20c** (Table 1, entry 5), polymerization of the obtained olefins occurred. Noteworthy, in large-scale experiments, the polymerization process was even more pronounced, and the formation of vinylsilanes was diminished. EtOC(H)=C(H)Me (**28**) and EtOC(H)=C(H)Et (**29**) reacted with Et_3SiH and **1** (1 mol %) differently than **2**–**9**, giving solely the cleavage of the Et–O bond (Table 1, entry 7). The difference in the reactivity between **28**, **29**, and **2**–**11** means that the substitution at the terminal position of the C=C double bond plays a crucial role in the outcome of the reaction (alkenyl vs alkyl cleavage).

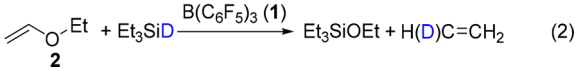
The accepted mechanism for ether cleavage by hydrosilanes in the presence of **1** relies on the formation of a $R_3Si{-}H{-}B(C_6F_5)_3$ intermediate (**32**).[10] The silicon center in **32** is then attacked by the oxygen of the R'_2O leading to $[R'_2OSiR_3]$-$[HB(C_6F_5)_3]$ salt (**33**).[5,6] Afterward, the hydride of the $HB(C_6F_5)_3$ in **33** substitutes the R′ group at the oxygen center via an S_N2-type reaction giving the ether cleavage products.[5,6] While this mechanism can explain the alkyl–O bond cleavage,[5,6] it does not, however, explain the cleavages of the alkenyl groups (Table 1, entries 1–6). An S_N2 reaction in the last step of this mechanism is hardly possible in these cases due to the development of δ^+ at the sp^2 carbon, which is strongly disfavored.

Therefore, based on the experimental findings, we propose a different mechanism for the alkenyl group cleavage. We believe that in our case the nucleophilic C=C double bond of **34** attacks the Si center in **32**, and dissociation of the Si–H bond leads to a $[Et_3SiCH_2C(R){=}O{-}R'][HB(C_6F_5)_3]$ salt (**35**). Intermediate **35** then reacts further through the delivery of the hydride from $HB(C_6F_5)_3$ to the electrophilic $C{=}O^+{-}Et$ moiety of the cation in **35** giving the hydrosilylation product, $Et_3SiCH_2CH(R)OR'$ (**36**). This step is supported by the fact that we see the formation of **12** in the reaction of **11** (see eq 1). Noteworthy, hydrosilylation of silyl enol ethers was previously reported.[11] We believe that the last step is the silicon-assisted β-elimination, promoted by **1**, that leads to the reaction products, $H_2C{=}C(R)H$ and $R'OSiEt_3$ (Scheme 1).

Scheme 1. Proposed Mechanism for $B(C_6F_5)_3$-Catalyzed Reductive Cleavage of Enol Ethers by Et_3SiH



Overall, our proposed mechanism (Scheme 1) involves a sequence of addition/elimination reactions, which resembles the nucleophilic vinylic substitution (S_NV) type reaction,[12] where the EtO^- is the nucleofuge and H^- is the nucleophile. However, unlike typical S_NV reactions that work on electron-poor C=C double bonds,[12] in our case the electron-rich C=C double bond reacts to give the substitution products. To support this hypothesis, Et_3SiD, **2**, and **1** (1 mol %) were reacted and led to $H_2C{=}C(D)H$ and Et_3SiOEt (eq 2). This supports our suggestion that the EtO^- group is replaced by H^-/D^- originating from Et_3SiH/D.



(2)

To support the last step of the proposed mechanism, the silicon-assisted β-elimination, we independently synthesized $Me_3SiCH_2CH_2OR$ (R = Et (**37**),[13] Me_3Si (**38**)[14]) which are the analogs of **36** and **12**, respectively. Heating both **37** and **38** did not result in any reactivity. However, when **37** and **38** were mixed with 1 equiv of **1** in C_6H_6 the olefination reaction took place immediately leading to Me_3SiOR (R = Et or $SiMe_3$,

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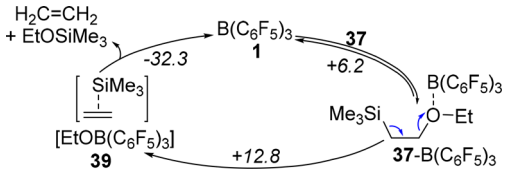
respectively) and ethylene (**3**) (eq 3), supporting our suggestion regarding the last step of the proposed mechanism (Scheme 1). The same reaction with a catalytic amount of **1** also works but requires heating to 80 °C.

(3)

To understand this silicon-assisted β-elimination we performed a DFT calculation at the BP86(D3)/def2-SVP[15] level of theory of the reaction shown in eq 3 in C_6H_6 using a polarizable continuum model (PCM).[16] Based on these calculations, we believe that this elimination proceeds in a two-step mechanism. The first step is the cleavage of the C−O bond in **37**−$B(C_6F_5)_3$, which leads to salt **39** (Scheme 2) with

Scheme 2. Calculated Mechanism for the $B(C_6F_5)_3$-Catalyzed Silicon-Assisted β-Elimination in C_6H_6 Using PCM[16a]



[a]ΔG is presented on the arrows in kcal mol^{-1}.

the ΔG = +12.8 kcal mol^{-1}. Notably, β-silyl-substituted carbocations (analogous to **39**) were synthesized previously.[17] In addition, the fact that the cleavage of **9** (Table 1, entry 8) in CH_2Cl_2 proceeds directly without heating also supports the assumption that an intermediate ion pair of type **39** is formed in this reaction. Noteworthy, a similar reactivity is obtained for **38**, which in CH_2Cl_2 undergoes olefination at rt in the presence of **1** (10 mol %). The calculated energy barrier for the cleavage of $[EtOB(C_6F_5)_3]^-$ anion from **37**−$B(C_6F_5)_3$ (**TS5**) is +21.0 kcal mol^{-1} (Figure 2). The last step of the proposed mechanism is the release of ethylene, formation of Me_3SiOEt, and regeneration of **1** and is an irreversible and strongly exergonic step (ΔG = −32.3 kcal mol^{-1}).

Accordingly, the formation of an intermediate of type **39′** also explains the formation of vinylsilanes in the reactions of aryl-substituted silyl enol ethers (Table 1, entries 5 and 6). For example, the formation of **22a** in the reaction of **20a** (Table 1, entry 5) could be explained by the reaction of the anion $[Me_3SiOB(C_6F_5)_3]^-$ in **39′**, which could act either as a nucleophile leading to styrene and $Et_3SiOSiMe_3$ via desilylation reaction (Scheme 3, path a) or as a base, abstracting the proton from the carbon α to the carbocation leading to **22a** (Scheme 3, path b).

Finally, to compare the cleavages of the alkyl group vs alkenyl group in alkyl enol ethers, we performed a DFT calculation using the same level of theory on both possible reactions of ethyl vinyl ether (**2**) with Me_3SiH and **1** in C_6H_6 using PCM.[16] According to these calculations, the formation of adduct **32** is exergonic (ΔG = −3.1 kcal mol^{-1}). The first pathway (Figure 2, blue), the attack of the nucleophilic oxygen atom of **2** at the silicon center in **32** producing $[Et(CH_2CH)OSiMe_3][HB(C_6F_5)_3]$ (**33′**), is endergonic (ΔG = +14.0 kcal mol^{-1}) with an energy barrier of +20.6 kcal mol^{-1} (**TS1**). The reaction of the hydride in $[HB(C_6F_5)_3]^-$ with $[Et(CH_2CH)$-

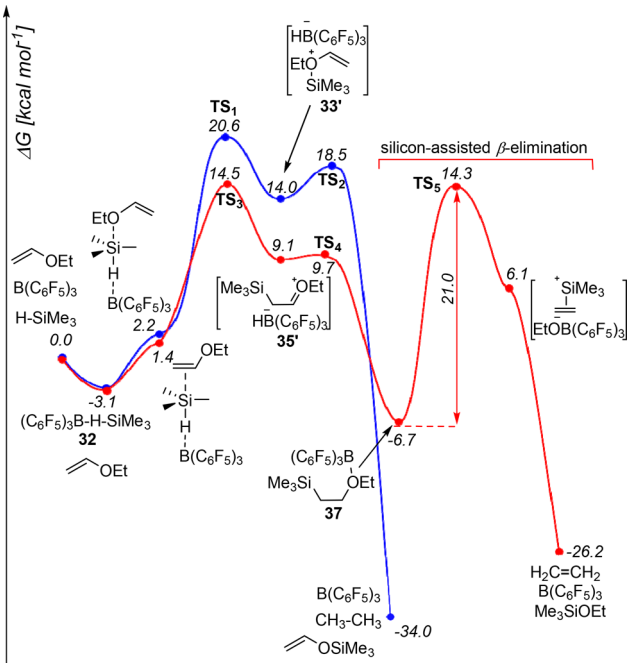
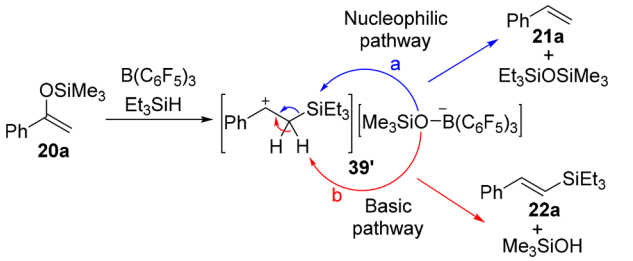


Figure 2. DFT calculation of the two possible reaction profiles for ethyl vinyl ether cleavage (ethyl group cleavage (blue) and vinyl group cleavage (red)) in C_6H_6 using PCM.[16] Gibbs free energies are given in kcal mol^{-1} relative to the starting materials.

Scheme 3. Possible Two Mechanistic Paths for the Cleavage of 14 by Et_3SiH



$OSiMe_3]^+$ in **33′** leading to the formation of ethane, vinyl silyl ether, and regeneration of **1** is exergonic with ΔG of −34.0 kcal mol^{-1}, and the $\Delta G^{\ddagger}$ for this step is 18.5 kcal mol^{-1} (**TS2**). In the second pathway (Figure 2, red), the nucleophilic attack of the silicon center in **32** by C=C double bond of **2** leading to $[EtO{=}CHCH_2SiMe_3][HB(C_6F_5)_3]$ (**35′**) is endergonic with ΔG = 9.1 kcal mol^{-1}, and $\Delta G^{\ddagger}$ for this step is 14.5 kcal mol^{-1} (**TS3**). The delivery of hydride from $[HB(C_6F_5)_3]^-$ to $[EtO{=}CHCH_2SiMe_3]^+$ in **35′** leading to a hydrosilylation product **37**−$B(C_6F_5)_3$ is exergonic (ΔG = −6.7 kcal mol^{-1}) with no activation barrier (**TS4**). The olefination, from **37**−$B(C_6F_5)_3$, occurs in a two-step reaction via intermediate **39**, as was shown previously (Scheme 2), with ΔG = −26.2 kcal mol^{-1}.

Overall, the cleavage of the vinyl group (Figure 2, red) is less exergonic than the cleavage of the ethyl group (Figure 2, blue) (−26.2 vs −34.0 kcal mol^{-1}, respectively). However, the rate-determining state (RDS)[18] **TS3** (Figure 2, red) is 6.1 kcal mol^{-1} lower than **TS1** (Figure 2, blue). We, therefore, believe that the cleavage of the vinyl group is a kinetically driven process. This also explains the reactivity of **28** and **29** (Table 1, entry 7) where the thermodynamic process took over the kinetic one, i.e., Et−O bond cleavage (Figure 2, blue), due to

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steric hindrance that prevented the hydrosilylation in the first step of the alkenyl cleavage reaction (Figure 2, red).

To conclude, we showed here that an alkenyl group can be reductively cleaved from alkyl/silyl enol ethers catalytically by hydrosilanes and catalytic amounts of $B(C_6F_5)_3$. We suggest that this cleavage is a result of a $B(C_6F_5)_3$-catalyzed two-step reaction, hydrosilylation of the alkenyl group followed by a silicon-assisted β-elimination of the $ROSiEt_3$. This reactivity shows that in principle alkenyl−O bonds can be formally cleaved, and the alkoxy/siloxy group on the C=C double bond can be substituted by a metal-free methodology. Further studies of this reaction are currently in progress in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02932.

Full experimental data, including synthetic procedures, characterization data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Doug Stephan on the occasion of his 65th birthday.

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