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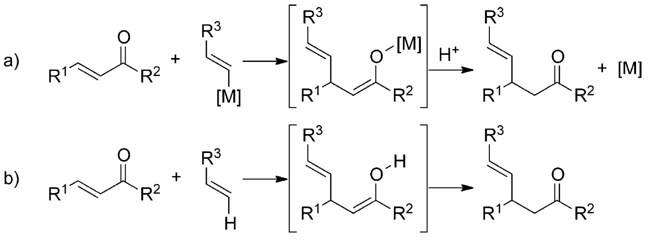
Conjugate Addition

Acid-Catalyzed Direct Conjugate Alkenylation of α,β-Unsaturated Ketones**

Kazuhiro Okamoto, Eisuke Tamura, and Kouichi Ohe**

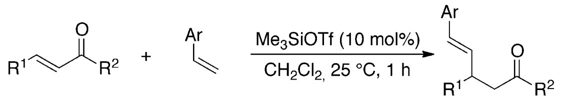
The conjugate addition reaction to α,β-unsaturated carbonyl compounds is one of the most fundamental reactions in organic chemistry. It is a powerful and reliable tool for the formation of carbon–carbon bonds.[1] Numerous C−C bond-forming conjugate addition reactions involve the nucleophilic attack of a carbanion species (known as Michael-type reactions), thus generally affording stoichiometric amounts of metal salts as waste products. Nowadays, from an environmental point of view, the reduction of waste in organic reactions is one of the most important issues to solve. For alkenylation reactions, alkenylmetal reagents are often used in the conjugate alkenylation of enones (Scheme 1 a). The direct conjugate addition of simple alkenes to enones (Scheme 1 b) is much more desirable with respect to atom efficiency. However, to date, successful examples of such a reaction have been limited to only a few transition-metal-catalyzed alkenylation reactions.[2,3]



Scheme 1. Conjugate addition of a) alkenylmetal reagents or b) simple alkenes to enones.

Meanwhile, with regard to the Lewis or Brønsted acid-promoted conjugate addition of alkenes to enones, the Mukaiyama-[4] or Sakurai–Hosomi-type[5] conjugate addition of silyl enolates or allylsilanes has been established and is widely applicable to the acetonylation or allylation of β-carbon atoms of enones. However, to date, there has been no successful approach to the acid-catalyzed alkenylation of enones with simple alkenes.[6,7] Herein, we report our findings on the acid-catalyzed alkenylation of enones with simple alkenes, the efficiency of which is strongly affected by β-silyl groups of enones or alkenes as alkenylating agent.

Our initial attempt to carry out the catalytic direct conjugate alkenylation of enones involved the use of (*E*)-1-phenyl-2-buten-1-one (**1a**) and 4-methylstyrene (**2m**) in the presence of 10 mol% of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) as a Lewis acid catalyst. Although the enone **1a** was fully converted, the target adduct **3am** was not obtained at all, and a complex mixture was obtained (Scheme 2). Interestingly, the β-silylenone **1b** underwent conjugate addition with **2m** to afford the corresponding γ,δ-unsaturated ketone **3bm** in 60% yield.



1a (R^1 = Me, R^2 = Ph) **2m** (Ar = 4-MeC_6H_4) **3am**: 0%
1b (R^1 = $SiMe_2Ph$, R^2 = Me) **3bm**: 60%

Scheme 2. Effect of silicon in the Lewis acid-catalyzed direct conjugate addition reaction. Tf = trifluoromethanesulfonyl.

Various acid catalysts[8] were examined for the conjugate addition reaction of **2m** to **1b** (Table 1). Trialkylsilyl triflates were the best catalysts for this reaction. The yield of the corresponding γ,δ-unsaturated ketone **3bm** was about 70% (entries 1–3). When other silicon Lewis acids bearing different counteranions were used, the adduct **3bm** was obtained in lower yield because the reactivity was either too high or too low (entries 4 and 5). In the reaction of **1b**, the use of trifluoromethanesulfonic acid (HOTf) afforded the product in comparable yield to that obtained with Me_3SiOTf. Other Brønsted acids or Lewis acids composed of other metals (Ti, B, Al, Ga, Sn, Sc) were ineffective in the current reaction (entries 7–15).

Various styrene derivatives were used in the present conjugate addition reaction under the most suitable reaction conditions using Me_3SiOTf (Table 2). The yields of the products in the reaction with *para-* or *ortho*-substituted styrenes were in the range of 50–66% (entries 1–6).[9] The yield was markedly increased when either 2,4,6-trimethylstyrene (**2s**) or 1,1-diphenylethylene (**2v**) was used (entries 7 and 10). α-Methylstyrene (**2t**) reacted to afford γ,δ-unsaturated ketone **3bt** as an adduct (entry 8). In contrast, the major product from α-isopropylstyrene (**2u**) was the δ,ε-unsaturated regioisomer **4** (entry 9). Although some internal olefins were generally inert in the present reaction,[10] some indene derivatives afforded adducts in good yields (entries 11–13).

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[*] Dr. K. Okamoto, E. Tamura, Prof. Dr. K. Ohe
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
E-mail: kokamoto@scl.kyoto-u.ac.jp
ohe@scl.kyoto-u.ac.jp

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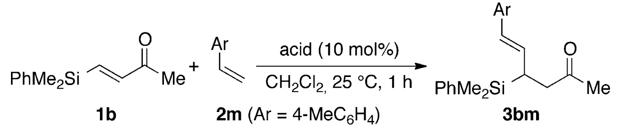
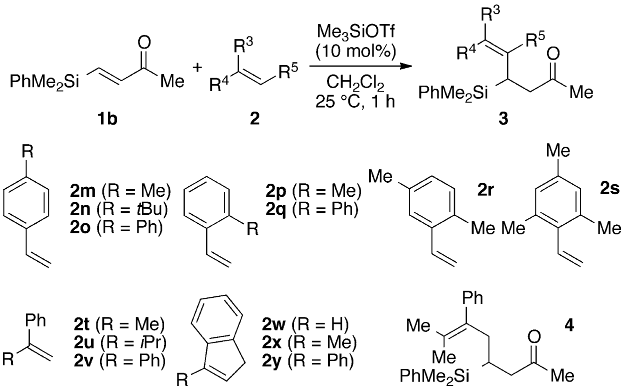
Table 1: Lewis acid- or Brønsted acid-catalyzed addition of the alkene **2m** to the silylenone **1b**.[a]



Entry	Lewis acid	**1b** Conv. [%][b]	Yield [%][b]
1	Me_3SiOTf	100	72 (60)[c]
2	$i$$Pr_3SiOTf$	100	70
3	$t$$BuMe_2SiOTf$	100	67
4	Me_3SiNTf_2	100	23
5	Me_3SiCl	0	0
6	HOTf	100	72 (60)[c]
7	$HBF_4\cdot OEt_2$	72	49
8	$HNTf_2$	72	0
9	$HOCOCF_3$	0	0
10	$TiCl_4$	100	14
11	$BF_3\cdot OEt_2$	49	26
12	$AlCl_3$	83	45
13	$GaCl_3$	56	29
14	$SnCl_4$	47	5
15[d]	$Sc(OTf)_3$	43	24

[a] The reaction was carried out with **1b** (0.20 mmol), **2m** (0.60 mmol), and acid catalyst (10 mol%) in CH_2Cl_2 (1.5 mL). [b] Conversions and yields were determined by ^1H NMR spectroscopy using $MeNO_2$ as an internal standard. [c] Yield of isolated product. [d] At 40 °C for 12 h, in 1,2-dichloroethane.

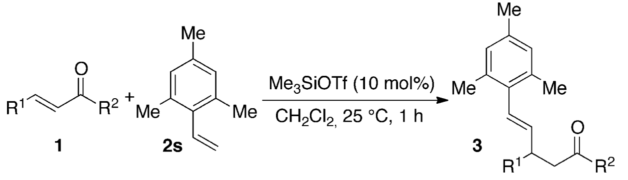
Table 2: Me_3SiOTf-catalyzed addition of the alkene **2** to the silylenone **1b**.[a]



Entry	**2**	Product	Yield [%][b]
1	**2m**	**3bm**	60 (60)[c]
2	**2n**	**3bn**	50
3	**2o**	**3bo**	58
4	**2p**	**3bp**	66 (55)[c]
5	**2q**	**3bq**	50
6	**2r**	**3br**	61
7	**2s**	**3bs**	85
8	**2t**	**3bt**	41
9	**2u**	**4**[d]	51
10	**2v**	**3bv**	91 (74)[c]
11	**2w**	**3bw**	54
12	**2x**	**3bx**	70
13	**2y**	**3by**	83

[a] The reaction was carried out with **1b** (0.20 mmol), **2** (0.60 mmol), and Me_3SiOTf (10 mol%) in CH_2Cl_2 (1.5 mL). [b] Yield of isolated product. [c] The yields in parentheses were obtained when HOTf was used as a catalyst instead of Me_3SiOTf. [d] The regioisomer **4** was obtained.

Table 3: Me_3SiOTf-catalyzed addition of 2,4,6-trimethylstyrene (**2s**) to the silylenone **1**.[a]

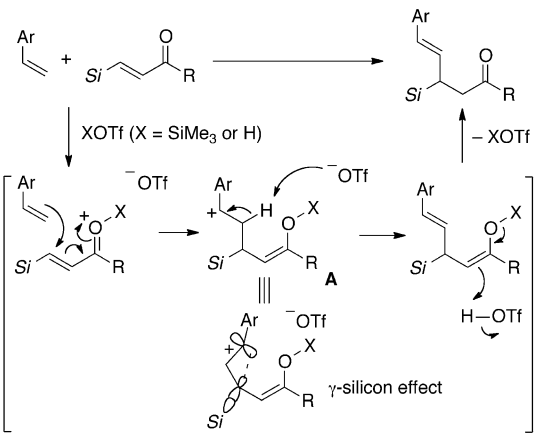


Entry	Enone	R^1	R^2	Product	Yield [%][b]
1	**1b**	$SiMe_2Ph$	Me	**3bs**	85
2[c]	**1c**	$SiMePh_2$	Me	**3cs**	79
3[d]	**1d**	$SiPh_3$	Me	**3ds**	77 (64)[f]
4[e]	**1e**	$SiMe_2Ph$	iBu	**3es**	74
5	**1f**	$SiMe_2Ph$	Ph	**3fs**	79 (55)[f]
6	**1g**	$SiMe_3$	Ph	**3gs**	79
7[e]	**1h**	$SiEt_3$	Ph	**3hs**	65
8[e]	**1i**	$SiMe_2(t\mathrm{Bu})$	Ph	**3is**	75

[a] The reaction was carried out with **1** (0.20 mmol), alkene **2s** (0.60 mmol), and Me_3SiOTf (10 mol%) in CH_2Cl_2 (1.5 mL). [b] Yield of isolated product. [c] Alkene **2s** (1.6 mmol) was used. [d] Alkene **2s** (4.0 mmol) was used. [e] Alkene **2s** (1.0 mmol) was used. [f] The yields in parentheses were obtained when HOTf was used as a catalyst instead of Me_3SiOTf.

Table 3 summarizes the scope of the silylenones **1** in the present conjugate addition reaction with the alkene **2s**. A variety of trialkylsilyl groups and substituents attached to the carbonyl group served as substituents on the enones, and the reaction proceeded selectively to afford the adducts **3** in high yield, even when enones with bulkier silyl substituents (such as Ph_3Si and $t$$BuMe_2Si$) were used.[11] As was the case with the reaction of some silylenones, when employing HOTf as a catalyst the yields were generally lower than those obtained with Me_3SiOTf as a catalyst (Table 2, entries 1, 4, and 10; Table 3, entries 3 and 5).[12]

A proposed reaction pathway of the current conjugate addition is shown in Scheme 3. First, the carbonyl oxygen atom coordinates to the acid catalyst XOTf (X = Me_3Si or H). Then, the addition of the alkene to the β-carbon atom of the activated enone generates the benzylic cation intermediate **A**, which undergoes deprotonation by the triflate anion to form the corresponding enol or silyl enolate with the generation of



Scheme 3. A proposed reaction pathway for the conjugate alkenylation.

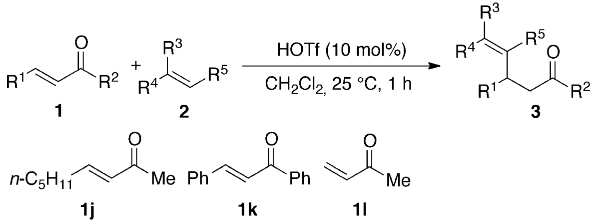
HOTf species. Finally, C protonation affords the γ,δ-unsaturated ketone as a product and regenerates the XOTf catalyst.

We are now aware that HOTf is generated even when Me_3SiOTf is used as a catalyst precursor ($X = Me_3Si$). Because the use of both Me_3SiOTf and HOTf showed similarly high catalytic activity toward the alkenylation, HOTf might serve as the true alkenylation catalyst. In fact, HOTf-catalyzed reactions using some combination of substrates reduced the yield. This result can be explained if we assume that side reactions take place. It is well known that superacids such as HOTf readily cause the scission of a $C(sp^2)-Si$ bond, which is known as protodesilylation. A HOTf-catalyzed reaction would cause the relatively faster decomposition of the starting silylenone or the adduct by protodesilylation, hence reducing the yield of the adduct. In the case of Me_3SiOTf, in contrast, a much lower concentration of HOTf exists as a reaction intermediate, and thus substrate decomposition would be avoided.

The stabilizing effects of the carbocation intermediate play a crucial role in the selectivity and efficiency of the present reaction. One of the effects is kinetic stabilization by steric hindrance on the aryl groups, and is known to suppress the oligomerization of styrenes initiated by the carbocation intermediate. Thus, favorable deprotonation from the intermediate takes place.[13] The resonance stabilization by the arene moieties of styrenes is also important. The most important stabilizing effect in the current case is the hyperconjugation caused by the silicon substituents at the γ position to the carbocation.[14,15] Based on the results of the substrate scope, the yields of the adducts seem to be in order of the degree of stabilization in the carbocation intermediate **A** (Table 2, entries 1, 4, 7, and 10). 1,1-Diphenylethylene (**2v**), in particular, will generate a strongly stabilized diphenylmethyl cation intermediate. We then anticipated that simple enones (without silicon substituents) could be used as reaction partners with 1,1-diphenylethylene.

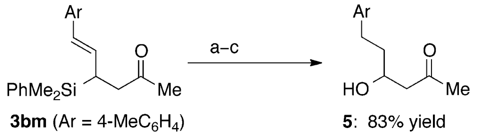
We therefore investigated the acid-catalyzed conjugate alkenylation of simple enones (Table 4). The HOTf-catalyzed reaction of **1a** with 4-methylstyrene (**2m**) did not afford the conjugate addition product (entry 1), but the reaction with the sterically congested styrenes **2p** and **2s** afforded the corresponding adducts much more selectively, in yields of 22% and 53%, respectively (entries 2 and 3). The reaction with 1,1-diphenylethylene (**2v**) was the most selective among the various alkenes (98% yield; entry 4). The simple linear enone **1j** afforded the corresponding adduct in 96% yield (entry 5). Chalcone (**1k**) was the least reactive among the enones examined, but the reaction in which 20 mol% of HOTf was used afforded the adduct in 78% yield (entry 6). In the case of methyl vinyl ketone **1l**, the use of an excess amount of enone relative to alkene increased the yield to 85% (entry 7).[16]

Table 4: HOTf-catalyzed addition of **2** with the simple enone **1**.[a]



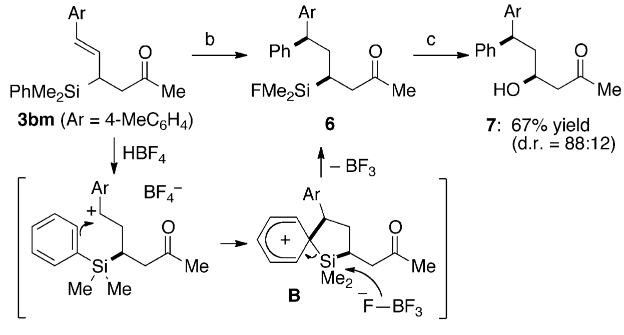
Entry	1	2	Product	Yield [%][b]
1	**1a**	**2m**	–	–[c]
2	**1a**	**2p**	**3ap**	22[d]
3	**1a**	**2s**	**3as**	53[d]
4[e]	**1a**	**2v**	**3av**	98 (89)[f]
5[e]	**1j**	**2v**	**3jv**	96 (91)[f]
6[e,g]	**1k**	**2v**	**3kv**	78
7[e,h]	**1l**	**2v**	**3lv**	85

[a] The reaction was carried out with **1** (0.20 mmol), **2** (0.60 mmol), and HOTf (10 mol%) in CH_2Cl_2 (1.5 mL). [b] Yield of isolated product. [c] Complex mixture. [d] The yields were determined by ^1H NMR spectroscopy using $MeNO_2$ as an internal standard. [e] 0.24 mmol of **2v** was used. [f] The yields in parentheses were obtained when Me_3SiOTf was used as a catalyst instead of HOTf. [g] HOTf (20 mol%) was used. [h] The enone **1l** (0.40 mmol) and **2v** (0.20 mmol) were used.



Scheme 4. Transformation of the adduct **3bm** into β-hydroxyketone **5**. Reaction conditions: a) Pd/C (10 wt%), under 1 atm H_2, CH_2Cl_2, RT. b) $HBF_4{\cdot}Et_2O$ (2.5 equiv), CH_2Cl_2, 0°C. c) 30% H_2O_2 aq. (excess), KF (2.0 equiv), $KHCO_3$ (10 equiv), THF/MeOH (1:1), RT.

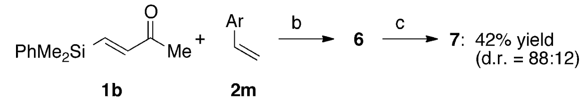
The adduct **3bm** was successfully converted into the β-hydroxyketone **5** in 83% yield by catalytic hydrogenation, a pretreatment of fluoroboric acid (HBF_4), and Tamao–Fleming oxidation (Scheme 4).[17,18] Our next aim was the direct transformation of the **3bm** alkene moiety. Generally, the oxidation of allyldimethylphenylsilane moieties is unsuccessful because of the inevitable cleavage of the allyl carbon–silicon bond in the protodesilylation step.[19] Surprisingly, however, the direct treatment of **3bm** with HBF_4 caused a 1,4-phenyl shift from the silicon atom to the δ-carbon atom,[20] and afforded the fluorosilane **6** (Scheme 5).[21] To our knowledge, a 1,4-aryl shift from silicon to a carbocation starting from allylsilane moieties has not been reported to date. The compound **6** was successfully subjected to Tamao–Fleming oxidation to afford the δ,δ-diaryl-β-hydroxyketone **7** in 67%



Scheme 5. Diastereoselective 1,4-phenyl migration for **3bm** upon treatment with HBF_4 and subsequent Tamao–Fleming oxidation. For reaction conditions b and c see Scheme 4.

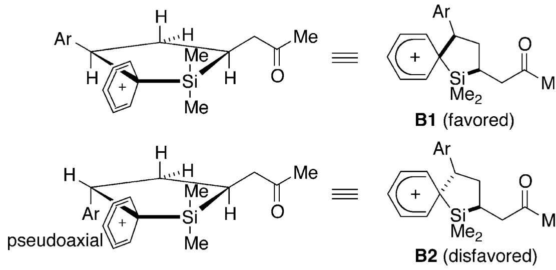
yield (d.r. = 88:12), the major diastereomer of which was identified by X-ray crystallographic analysis.[22]

At this stage, both the conjugate alkenylation step (**1**+**2**→**3**) and concomitant fluorosilane formation with 1,4-phenyl shift (**3**→**6**) involve a proton-mediated process. Therefore, we aimed to achieve the one-step preparation of **6** from **1b**. This was successful, and the reaction of **1b** with **2m** in the presence of a stoichiometric amount of $HBF_4\cdot OEt_2$ afforded, as expected, the product **6** (Scheme 6). After oxidation of **6**, the hydroxyketone **7** was obtained in an overall yield of 42%, which was almost same as that achieved in the stepwise process (60% from **1a**→**3bm** and 67% from **3bm**→**7**).



Scheme 6. One-step transformation of **1b** into **6**. For reaction conditions b and c see Scheme 4.

In our working hypothesis, 1,4-phenyl migration proceeds by initial protonation of the γ-carbon atom, the formation of the arenium-bridged spirocyclic intermediate **B**, and the attack of the fluoroborate anion on the silicon atom (Scheme 5). The high diastereoselectivity is attributed to the rigid conformation of the spirocyclic arenium intermediate **B**. Assuming that **B** favors the envelope conformation as shown in Scheme 7, both the aryl group (Ar) and the acetonyl group ($-CH_2COMe$) in the intermediate **B1** (leading to the major diastereomer) should be located in the pseudoequatorial position. In the case of intermediate **B2** (leading to the minor diastereomer), however, at least one substituent should be in the pseudoaxial position.



Scheme 7. Explanation for the origin of diastereoselectivity.

In conclusion, we have developed the acid-catalyzed direct conjugate addition of styrene derivatives to enones under simple and mild reaction conditions. The thermodynamically and kinetically controlled stability of the carbocation intermediates led to the Me_3SiOTf-catalyzed simple conjugate addition reaction of styrenes to β-silylenones. This experimental finding and mechanistic considerations further paved the way for conjugate addition reactions of styrene derivatives, catalyzed by HOTf, to simple enones. Moreover, the addition products were diastereoselectively converted into the corresponding δ,δ-diaryl-β-hydroxyketone by the previously unknown 1,4-aryl shift in the allylsilane moiety with subsequent Tamao–Fleming oxidation.

Overall, these observations provide us not only with an efficient synthetic method for alkenylated products but also with new fundamental knowledge of chemistry. Further mechanistic investigations involving computational methods about both alkenylation and 1,4-aryl migration are underway.

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[8] For a review, see: *Acid Catalysis in Modern Organic Synthesis* (Eds.: H. Yamamoto, K. Ishihara), Wiley-VCH, Weinheim, **2008**.

[9] Heteroatom-substituted styrenes such as 4-methoxystyrene or 4-trifluoromethylstyrene, and aliphatic alkenes did not react under the present reaction conditions.

[10] β-Methylstyrene, (*E*)-/(*Z*)-stilbene, and triphenylethylene were not reactive.

[11] In some cases, a large excess of the alkene **2s** was required because of the slower reaction rate compared to the dimerization of alkene **2s** as a side reaction.

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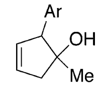

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[22] The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 949383) which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.