

Remarkable access to fluoroalkylated trisubstituted alkenes *via* highly stereoselective cobalt-catalyzed hydrosilylation reaction of fluoroalkylated alkynes†

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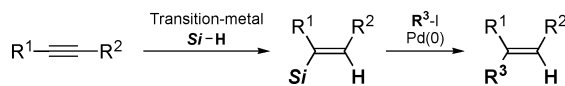
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Hydrosilylation reaction of various fluoroalkylated alkynes with Et₃SiH in the presence of a catalytic amount of Co₂(CO)₈ was investigated. The hydrosilylation of the alkynes having fluoroalkyl and aryl groups took place smoothly with good regioselectivity (*ca.* 80:20). In sharp contrast, the reaction of the alkynes having a fluoroalkyl group and a benzyl-type substituent, or various propargyl alcohols gave the corresponding vinylsilanes in an excellent regio- and stereoselective manner. Treatment of the vinylsilanes with various aldehydes in the presence of Zn(OTf)₂ and TBAF afforded the coupling products in good yields.

Introduction

The transition-metal-catalyzed hydrosilylation reaction of alkynes represents one of the most important and straightforward methods for the preparation of vinylsilanes, which can be easily converted into variously substituted ethenes with retention of configuration through the Hiyama coupling reaction (Scheme 1).^{1,2} Furthermore, the high chemoselectivity as well as mild reactivity of organosilicon compounds, as compared with other organometallic reagents, such as lithium, magnesium reagents, and so on, make the hydrosilylation and the subsequent reactions extremely valuable and applicable for preparing a wide variety of substances.



Scheme 1

Although the hydrosilylation of various alkynes has been developed and studied extensively in the *nonfluorinated chemistry*, the hydrosilylation of *fluorine-containing alkynes* has attracted little attention so far.³ Herein we wish to describe the highly regio- and stereoselective hydrosilylation reaction of fluoroalkylated internal acetylene derivatives in the presence of a catalytic amount of Co₂(CO)₈.⁴

Results and discussion

Initially, the addition of Et₃SiH to the trifluoromethylated internal alkyne **1a**⁵ was examined in the presence of 5 mol% of Co₂(CO)₈, as described in Table 1. Thus, treatment of **1a** with 1.2 equiv. of Et₃SiH in 1,2-dichloroethane at the reflux temperature for 3 h gave

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Table 1 Investigation of the reaction conditions

Entry	Si-H	Yield ^a / % of 2+3	Ratio ^a (2:3)
1	Et ₃ SiH (a)	quant. (95)	83:17
2	Et ₃ SiH ^b	70	80:20
3	Et ₃ SiH ^c	12	75:25
4	(<i>i</i> -Pr) ₃ SiH	0	—
5	Me ₂ PhSiH	84	42:58
6	Ph ₃ SiH	0	—
7	(EtO) ₃ SiH	81	29:71

^a Determined by ¹⁹F NMR. Value in parentheses is of isolated yield. ^b In the presence of 3 mol% of Co₂(CO)₈. ^c In the presence of 1 mol% of Co₂(CO)₈.

the desired vinylsilanes **2** and **3** quantitatively in a ratio of 83:17 (Entry 1). As shown in Entries 2 and 3, the use of less than 5 mol% of catalyst led to a decrease of the yield and regioselectivity. We also investigated the reaction using various silane compounds, such as triisopropylsilane, dimethylphenylsilane, triphenylsilane, and triethoxysilane, as described in Entries 4–7. As a result, the reaction with triisopropylsilane and triphenylsilane did not proceed at all, and the starting alkyne was recovered quantitatively. In sharp contrast, the use of dimethylphenylsilane and triethoxysilane caused a smooth reaction, giving the corresponding adducts in high yields, though the regioselectivity decreased significantly, as compared with that of the reaction with Et₃SiH.

Next, our attention was directed toward the hydrosilylation of various alkynes. The results are summarized in Table 2.

As shown in Entries 1–4, changing the aromatic substituent of the alkynes from *p*-ClC₆H₄ to *p*-MeOC₆H₄, *p*-MeC₆H₄, *p*-EtO₂CC₆H₄ did not significantly affect the yield and the regioselectivity, though a strongly electron-withdrawing group, such as a nitro group, disturbed the reaction, giving the corresponding product in only 16% yield (Entry 5). Additionally, a large influence of the position of the substituent on the benzene ring was not

Table 2 The hydrosilylation of various fluorinated alkynes

Entry	Rf	R	Yield ^a / % of 2+3	Ratio ^a (2:3)
1	CF ₃	<i>p</i> -ClC ₆ H ₄ (a)	quant. (95)	83:17
2	CF ₃	<i>p</i> -MeOC ₆ H ₄ (b)	(64)	84:16
3	CF ₃	<i>p</i> -MeC ₆ H ₄ (c)	62 (45)	77:23
4	CF ₃	<i>p</i> -EtO ₂ CC ₆ H ₄ (d)	80 (61)	81:19
5	CF ₃	<i>p</i> -O ₂ NC ₆ H ₄	16	N.D. ^b
6	CF ₃	<i>m</i> -ClC ₆ H ₄ (e)	77 (67)	82:18
7	CF ₃	<i>o</i> -ClC ₆ H ₄ (f)	94 (83)	71:29
8	CF ₃	Ph(CH ₂) ₃ (g)	(75)	88:12
9	CF ₃	<i>p</i> -ClC ₆ H ₄ CH ₂ (h)	89 (83)	98:2
10	CF ₃	<i>p</i> -MeOC ₆ H ₄ CH ₂ (i)	89 (84)	96:4
11	CF ₃	(j)	(86)	100:0
12	CF ₃	(k)	(74)	97:3
13	CF ₃	EtO ₂ C	37	43:57
14	CF ₃	(EtO) ₂ P(O)	0	—
15	HCF ₂	<i>p</i> -ClC ₆ H ₄ (l)	quant. (87)	97:3
16	HCF ₂	<i>p</i> -MeOC ₆ H ₄ CH ₂ (m)	(66)	95:5
17	H(CF ₂) ₃	<i>p</i> -MeOC ₆ H ₄ CH ₂ (n)	(71)	80:20

^a Determined by ¹⁹F NMR. Values in parentheses are of isolated yield.

^b Not determined.

observed (Entries 1, 6, 7), though the use of *o*-substituted phenyl group as R caused a slight decrease of the regioselectivity. The use of the alkyl group as R did not substantially change the yield and the regioselectivity (Entry 8). It is noted that the benzyl-type substituent brought about the high regioselectivity. Thus, the reaction with the alkynes having *p*-ClC₆H₄CH₂, *p*-MeOC₆H₄CH₂ group, and so on, proceeded smoothly to give the desired adducts in a highly regioselective manner (**2:3** = >96:<4) (Entries 9–12). Unfortunately, the alkynes having a CO₂Et or P(O)(OEt)₂ group did not react with Et₃SiH smoothly (Entries 13 and 14).

We also examined the reaction of the alkynes having various fluoroalkyl groups. In the case of the hydrosilylation of difluoromethylated alkynes, the high regioselectivity as well as the high yield were obtained even when the *p*-ClC₆H₄ group was used as R, in addition to the benzyl-type substituent (Entries 15 and 16). Switching a fluoroalkyl group from a CF₃ or CHF₂ group to a H(CF₂)₃ group also led to the smooth reaction, however, a slight decrease of the regioselectivity was observed (Entry 17).

We next investigated the hydrosilylation using various types of γ -fluoroalkylated propargyl alcohols **4**.⁶ The results are summarized in Table 3. As shown in Entries 1, 2, 4–6, propargyl alcohols having various substituents R², such as phenyl, 1-ethylpropyl, cyclohexyl, *t*-Bu and so on, gave the corresponding adducts **5** and **6** in high yields with high regio- and stereoselectivity. In the case of R¹ and R² ≠ H, the reaction did not take place and the starting alkyne was recovered quantitatively (Entry 7). Changing the fluoroalkyl group from a CF₃ to a HCF₂ group did not bring about any significant influence on the yield or the regioselectivity (Entry 8). However, the use of a hexafluoropropyl group as Rf led to a slight decrease of the regioselectivity (Entry 9).

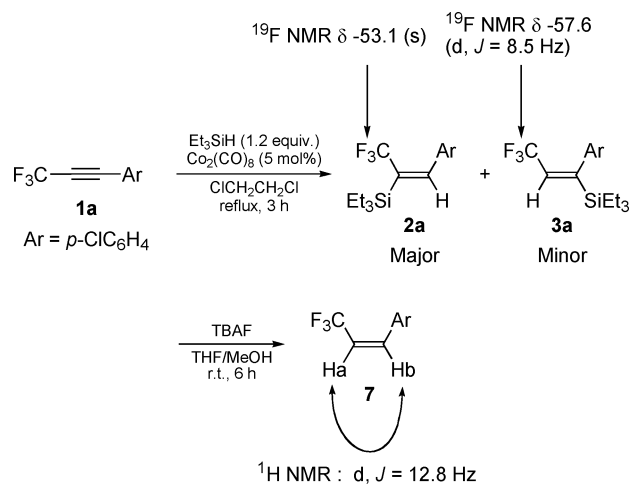
Table 3 The hydrosilylation of various fluoroalkylated propargyl alcohols

Entry	Rf	R ¹	R ²	Yield ^a / % of 5+6	Ratio ^a (5:6)
1	CF ₃	H	Ph (a)	82 (79)	99:1
2	CF ₃	H	<i>p</i> -MeOC ₆ H ₄ (b)	quant. (97)	99:1
3	CF ₃	H	Ph(CH ₂) ₂ (c)	81 (80)	76:24
4	CF ₃	H	Et ₂ CH (d)	82 (79)	100:0
5	CF ₃	H	Cy (e)	quant. (97)	99:1
6	CF ₃	H	<i>t</i> -Bu (f)	81 (80)	100:0
7	CF ₃	Me	Ph	0	—
8	HCF ₂	H	<i>p</i> -MeOC ₆ H ₄ (g)	84 (78)	96:4
9	H(CF ₂) ₃	H	<i>p</i> -MeOC ₆ H ₄ (h)	(62)	90:10

^a Determined by ¹⁹F NMR. Values in parentheses are of isolated yields.

Stereochemistry

The stereochemistry of the hydrosilylation products was determined as follows (Scheme 2). Thus, ¹⁹F NMR spectra of the major isomer **2a** in the reaction of the alkyne **1a** with Et₃SiH, showed a singlet peak, suggesting strongly that a triethylsilyl group is attached to a carbon bearing a trifluoromethyl group. On the contrary, ¹⁹F NMR spectra of the minor isomer **3a** showed a doublet peak, which means that a Et₃Si group is attached to a benzylic carbon.

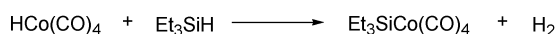
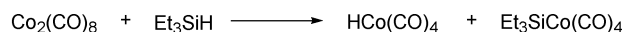
**Scheme 2**

The mixture of **2a** and **3a** was subjected to tetrabutylammonium fluoride (TBAF) in THF/H₂O to afford the disubstituted alkene **7** as a sole product. The analysis of the ¹H NMR of **7** showed the coupling constant of Ha and Hb to be 12.8 Hz, indicating that **2a** and **3a** have the *E* configuration.⁷ The stereochemistry of other hydrosilylation products was determined on the basis of the comparison with ¹⁹F NMR spectra of **2a** and **3a**.

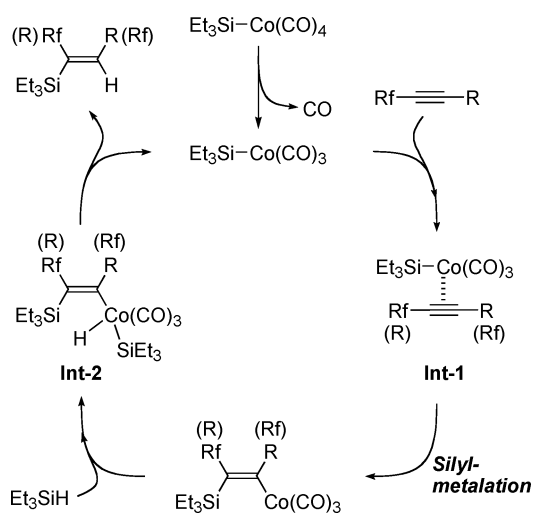
Accordingly, it was revealed that the present hydrosilylation proceeded in a highly *cis*-selective manner.

Mechanism

A plausible reaction mechanism of the reaction is outlined in Schemes 3 and 4.⁸ Thus, Et₃SiH may react with Co₂(CO)₈ even at ambient temperature to give HCo(CO)₄ and Et₃SiCo(CO)₄. HCo(CO)₄ may react with Et₃SiH again, affording Et₃SiCo(CO)₄ together with the generation of hydrogen. Elimination of CO from Et₃SiCo(CO)₄ affords Et₃SiCo(CO)₃, which may coordinate with fluoroalkylated alkynes, giving the corresponding cobalt-acetylene complex **Int-1**. The subsequent silylmatalation reaction followed by the oxidative addition of Et₃SiH into Co gives **Int-2**. Finally, the reductive elimination of Et₃Co(CO)₃ gives the desired vinylsilane.



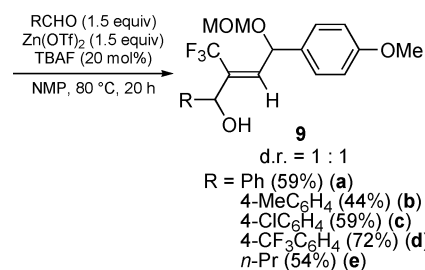
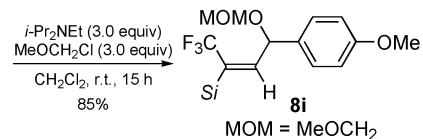
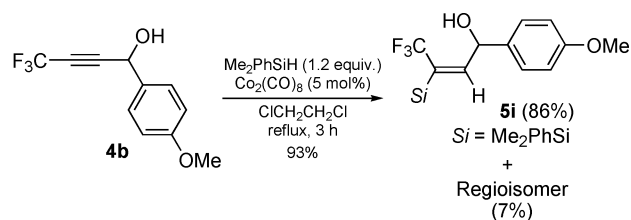
Scheme 3



Scheme 4

Synthetic application

Finally, we attempted the coupling reaction of the hydrosilylation product with various aldehydes (Scheme 5).⁹ Thus, treatment of the propargyl alcohol **4b** with 1.2 equiv. of Me₂PhSiH in the presence of 5 mol% of Co₂(CO)₈ at the reflux temperature for 3 h gave the corresponding hydrosilylation product **5i** in 86% yield, along with 7% of regioisomer. Subsequently, the protection of the hydroxy group of **5i** afforded the MOM ether **8i** in 85% yield. After several attempts at the coupling reaction of **8i** with benzaldehyde, we found that the treatment of **8i** with 1.5 equiv. each of benzaldehyde and zinc triflate in the presence of 20 mol% of TBAF in NMP at 80 °C for 20 h gave the corresponding allylic alcohol **9a** in 59% yield as a 1:1 diastereomeric mixture. Similarly, the reaction with various aldehydes, such as *p*-tolualdehyde, *p*-chlorobenzaldehyde, *p*-trifluoromethylbenzaldehyde, *n*-butyraldehyde, took place smoothly to provide the corresponding adducts in 44 ~ 72% yield as a 1:1 diastereomeric mixture.



Scheme 5

Summary

In conclusion, we have demonstrated the hydrosilylation reaction of various fluoroalkylated alkynes with Et₃SiH in the presence of a catalytic amount of Co₂(CO)₈ at the reflux temperature of dichloroethane for 3 h. The reaction proceeded smoothly to give the corresponding adducts in good to high yields. Especially, the reaction with the alkynes having benzyl-type substituents or various propargyl alcohols took place in a highly regio- and stereoselective manner. Additionally, it was revealed that the MOM ethers derived from the hydrosilylation products reacted with various aldehydes in the presence of TBAF/Zn(OTf)₂, affording the various allylic alcohols in good yields.

Experimental

General experimental procedure for the hydrosilylation and the reaction of the hydrosilylation products with various aldehydes, and characterization data for all new compounds are available via the supplementary information.†

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