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$FeCl_3$-Catalyzed Nucleophilic Substitution of Propargylic Acetates with Enoxysilanes

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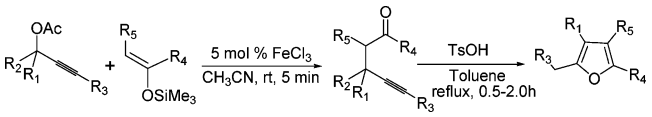

An efficient $FeCl_3$-catalyzed substitution reaction of propargylic acetates with enoxysilanes under mild conditions to afford corresponding γ-alkynyl ketones has been developed. The substitution reaction is followed by a TsOH-catalyzed cyclization without purification of the γ-alkynyl ketone intermediates, offering a straightforward synthetic route to tri- or tetrasubstituted furans.

The acetylenic carbon−carbon triple bond plays a pivotal role in a variety of functional group transformations,[1] which has resulted in the steady growth in the synthesis of propargylic derivatives. An efficient route to propargylic derivatives is through propargylic substitution reactions. Reactions of this type have been traditionally carried out by using the classical Nicholas reaction but with some drawbacks: more than a stoichiometric amount of $[Co_2(CO)_8]$ is required, and several steps are necessary to obtain propargylic products from propargylic alcohols via cationic propargylic complexes $[Co_2(CO)_6(propargyl)]^+$.[2,3] Some transition metal complexes were developed to catalyze the propargylic substitution reactions of propargylic alcohols with nucleophiles,[4,5] where most of the nucleophiles were heteroatom-centered such as alcohols, thiols, amides, and so on. However, the carbon-centered nucleophiles were unfortunately limited to allyl silanes for the construction of sp^3-sp^3 C−C bonds in the reaction.[4b,5h] Recently, Nishibayashi[6] and co-workers described an efficient coupling of propargylic alcohols with ketones for the formation of γ-alkynyl ketones and the straightforward synthesis of substituted furans in the presence of a catalytic amount of a ruthenium catalyst. Nevertheless, with this method, the substrate is generally limited to the propargylic alcohols bearing a terminal alkyne group. Matsuda's team[7] reported that iridium complex $[Ir(cod)\{P(OPh)_3\}_2]OTf$ serves as a catalyst for the transformation to γ-alkynyl ketones by the coupling of propargylic esters with enoxysilanes. However, the peculiarity and high cost of such catalysts make a barrier to their large-scale use.

We have recently developed a highly efficient iron(III)- or bismuth(III)-catalyzed propargylic substitution of propargylic alcohols or esters with various heteroatom- and carbon-centered nucleophiles.[8] Naturally, we intended to extend this method to the route to γ-alkynyl ketones. However, no propargylation occurred while using ketones as the nucleophiles under our reaction conditions, probably due to the weak nucleophilicity of the α-C of the ketones. Gratifyingly, enoxysilanes as the carbon-centered nucleophiles exhibited strong nucleophilicity. The nucleophilic substitution reaction of propargylic acetates with enoxysilanes proceeded rapidly in the presence of 5 mol % of $FeCl_3$ and efficiently afforded corresponding γ-alkynyl ketones in high yields. Herein we reported the successful results and scope of the reactions, and this iron(III)-catalyzed reaction allows for the straightforward synthesis of tri- or tetrasubstituted furans.

Reaction of propargylic acetate **1a** and enoxysilane **2a** was first carried out employing $FeCl_3$ as the catalyst. γ-Alkynyl ketone **3aa** was obtained in 83% isolated yield at room temperature within just 5 min by simple stirring of **1a** (0.5 mmol), enoxysilane **2a** (1.5 mmol), and $FeCl_3$ (0.025 mmol) in acetonitrile. With the conditions in hand, various propargylic acetates were treated with the enoxysilane **2a** in the presence of 5 mol % of $FeCl_3$and all the reactions gave the desired coupling products in moderate to high yields. Typical results are summarized in Table 1. The reaction proceeded smoothly without exclusion of moisture or air from the reaction mixture. Both electron-donating (**1m**) and electron-withdrawing (**1k, 1*l***)

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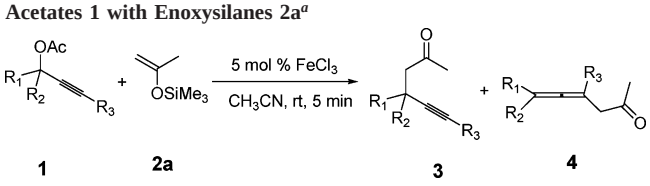
TABLE 1. $FeCl_3$-Catalyzed Substitution of Various Propargylic Acetates 1 with Enoxysilanes 2a[a]



1 2a 3 4

entry	substrate R_1; R_2; R_3	product	isolated yields of **3** (%)
1	**1a**: Ph; H; *n*-Bu	**3aa**	83
2	**1b**: Ph; H; Ph	**3ba**	95
3	**1c**: Ph; H; TMS	**3ca**	90
4[f]	**1d**: CH_3; CH_3; Ph	**3da**	92
5[f]	**1e**: $-(CH_2)_5-$; Ph	**3ea**	82
6	**1f**: Ph; CH_3; Ph	**3fa**	83
7	**1g**: Ph; H; H	**3ga**	82[b]
8[c]	**1h**: Ph; Ph; Ph	**3ha; 4ha**	53, 38(**4ha**)
9	**1i**: CH_3; H; Ph	**3ia**	0(33)[d,f]
10	**1j**: H; H; Ph	**3ja**	0(0)[d,f]
11	**1k**: 4-Cl-C_6H_4; H; *n*-Bu	**3ka**	81
12	**1*l***: 4-CN-C_6H_4; H; *n*-Bu	**3*l*a**	77[e]
13	**1m**: 2-MeO-C_6H_4; H; *n*-Bu	**3ma**	86

[a] The reactions of **1** (0.5 mmol) with enoxysilane **2a** (1.5 mmol) were carried out in the presence of $FeCl_3$ (0.025 mmol) in CH_3CN (1.0 mL) at room temperature for 5 min. [b] At 40 °C for 1 h. [c] Allenyl isomer **4ha** was concomitantly formed in the reaction. [d] The propargylic phosphate **1iP** or **1jP** was used instead of propargylic acetates as the substrate, at 60 °C for 30 min. [e] At rt, 30 min. [f] The structures of **5d**, **5e**, **1iP**, and **1jP** are the following:

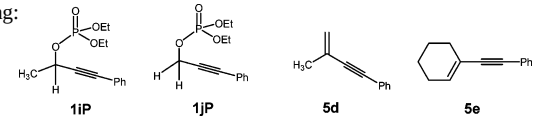


TABLE 2. $FeCl_3$-Catalyzed Substitution of Various Propargylic Acetates 1 with Nucleophiles 2[a]

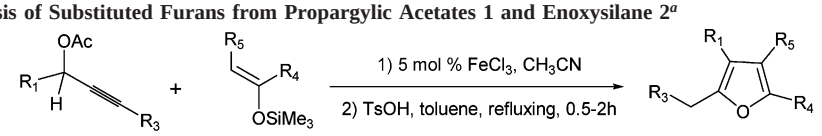
Entry	Enoxysilane	Substrate R_1; R_2; R_3	Product	Isolated yields (%) 3	4
1		**1a**, Ph; H; *n*-Bu	**ab**	83	0
2		**1b**, Ph; H; Ph	**bb**	88	0
3		**1c**, Ph; H; TMS	**cb**	91	0
4		**1d**, CH_3; CH_3; Ph	**db**	90	0
5	Ph, OSiMe3 (**2b**)	**1e**, -$(CH_2)_5$-; Ph	**eb**	83	0
6		**1f**, Ph; CH_3; Ph	**fb**	91	0
7		**1g**, Ph; H; H	**gb**	84[b]	0
8		**1h**, Ph; Ph; Ph	**hb**	42	51
9		**1i**, CH_3; H; Ph	**ib**	0(47)[c]	0
10		**1j**, H; H; Ph	**jb**	0(22)[d]	0
11		**1c**, Ph; H; TMS	**cc**	89[e]	0
12		**1d**, CH_3; CH_3; Ph	**dc**	58	24
13	OSiMe3 (**2c**)	**1e**, -$(CH_2)_5$-; Ph	**ec**	54	29
14		**1f**, Ph; CH_3; Ph	**fc**	75[f]	14
15		**1g**, Ph; H; H	**gc**	64[g]	0
16		**1h**, Ph; Ph; Ph	**hc**	0	83
17	OEt, OSiMe3 (**2d**)	**1b**, Ph; H; Ph	**bd**	60	0
18		**1h**, Ph; Ph; Ph	**hd**	47	44
19	O, O, OEt (**2e**)	**1a**, Ph; H; *n* -Bu	**ae**	70[h]	0
20		**1b**, Ph; H; Ph	**be**	87[i]	0

[a] The reactions of **1** (0.5 mmol) with enoxysilane **2** (1.5 mmol) were carried out in the presence of $FeCl_3$ (0.025 mmol) in CH_3CN (1.0 mL) at room temperature for 5 min. [b] At 40 °C for 1 h. [c] The propargylic phosphate **1iP** was used as the substrate, at 60 °C for 15 min. [d] The propargylic phosphate **1jP** was used as the substrate, at 60 °C for 3 h. [e] Two diastereoisomers were formed with the isomer ratio of 2:1. [f] Two diastereoisomers were formed with the isomer ratio of 1.3:1. [g] At 40 °C for 1 h. Two diastereoisomers were formed with the isomer ratio of 1.5:1. [h] Two diastereoisomers were formed with the isomer ratio of 1.5:1. [i] Two diastereoisomers were formed with the isomer ratio of 1.6:1.

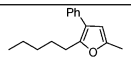
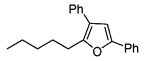
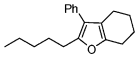
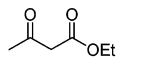
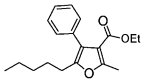
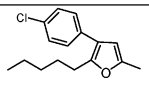
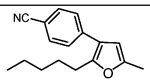
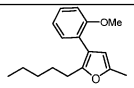
aromatic substrates reacted smoothly with enoxysilane **2a** affording the corresponding alkylated products in high yields (Table 1, entries 11−13). Functional groups such as chloro, cyano, and methoxyl in the substrates did not affect the coupling of sp^3-sp^3 C−C bonds, but the electron-withdrawing substrates require a relatively longer time for completion (Table 1, entry 12). Variation in the alkyne substituent from an aryl to an *n*-Bu, trimethylsilyl, or H (**1a**−**1c**, **1g**) is well tolerated. This is in sharp contrast to the Ru-catalyzed substitution[6] where the substrates were limited to the propargylic alcohols bearing a terminal alkyne group. Coupling of secondary benzylic propargylic acetates with **2a** was completed at room temperature within 5 min furnishing corresponding products in 77−95% yields (Table 1, entries 1−3, 7, 11−13). However, the secondary aliphatic propargylic acetate (R_1 = CH_3, R_2 = H, R_3 = Ph) **1i** did not react at all with **2a**. The starting **1i** was recovered intact. The desired transformation was accomplished by using corresponding phosphate **1iP** as the substrate under forcing conditions, with low yield (Table 1, entry 9). The primary aliphatic propargylic phosphate **1jP** did not undergo the substitution even under fierce reaction conditions (Table 1, entry 10). On the other hand, tertiary aliphatic propargylic acetates allow for the construction of sp^3-sp^3 C−C bonds in high yields (Table 1, entries 4, 5). The experimental results suggest a mechanism through the formation of a propargylic cation intermediate. Instability of the propargylic cation intermediate clearly made the substitution reaction less favorable. Unfortunately, allenyl isomer was concomitantly formed in 38% yield in the example of more hindered substrate **1h**, which has two phenyl groups on the propargylic carbon (Table 1, entry 8). This shows that an increase in steric bulk at the electrophilic site can alter the regiochemistry of the nucleophilic attack. It is noteworthy that the corresponding γ-alkynyl ketones were obtained in good yields in the examples involving the substrates **1d** and **1e** which have alkyl groups on the propargylic carbon, and the elimination product enynes **5d** and **5e** were not observed in the reaction (Table 1, entries 4, 5). This is in contrast to the Ir-catalyzed procedure of Matsuda,[7] where the enynes **5d** and **5e** were formed as the major products at 25 °C. The iron(III)-catalyzed substitution is complete in several minutes while other methodologies[6,7] require several hours. These results show the superiority of $FeCl_3$ as a catalyst for this reaction.

With these preliminary results available, the scope of the nucleophiles in this reaction was investigated (Table 2). Enoxysilanes **2b**, **2c**, and **2d** were proved to be efficient for the present transformation as well. The regioselectivity that preferred the propargylic products **3** was retained in examples involving **2b** as the nucleophile (Table 2, entries 1−7). Allenyl isomer **4hb** (**3hb**:**4hb** = 42:51**)** was concomitantly formed only in the reaction of sterically encumbered substrate **1h** (Table 2, entry 8). The primary propargylic acetate **1j** (R_1, R_2 = H) failed to give coupling product in the reaction with **2b**; the substitution was achieved by employing the corresponding phosphate **1jp** at higher temperature but lower yield (Table 2, entry 10). In the reactions involving cyclohexenoxysilane **2c**, the ratio of product **3** and **4** was obviously affected by the steric bulkiness

TABLE 3. Synthesis of Substituted Furans from Propargylic Acetates 1 and Enoxysilane 2[a]



1 **2** **6**

Entry	Substrate	Enoxysilane	Time (h)	Product	Isolated yields (%)
1	**1a** R_1=Ph R_3 = *n*-Bu	**2a,** R_4 = Me, R_5 = H	0.5	**6aa** 	81
2		**2b,** R_4 = Ph, R_5 = H	1.0	**6ab** 	65
3		**2c,** R_4=R_5= -$(CH_2)_4$-	1.0	**6ac** 	75
4		**2e** 	1.0	**6ae** 	65
5	**1k** R_1= 4-Cl-C_6H_4 R_3= *n*-Bu	**2a,** R_4 = Me, R_5 = H	0.5	**6ka** 	76
6	**1l** R_1= 4-CN-C_6H_4 R_3= *n*-Bu	**2a,** R_4 = Me, R_5 = H	2.0	**6la** 	70
7	**1m** R_1= 2-MeO-C_6H_4 R_3= *n*-Bu	**2a,** R_4 = Me, R_5 = H	0.5	**6ma** 	83
8	**1g** R_1=Ph R_3 = H	**2a,** R_4 = Me, R_5 = H	1.0	**6ga** 	73
9		**2b,** R_4 = Ph, R_5 = H	2.0	**6gb** 	80
10		**2c,** R_4=R_5= -$(CH_2)_4$-	2.0	**6gc** 	61
11	**1c** R_1=Ph R_3 = TMS	**2a,** R_4 = Me, R_5 = H	1.0	**6ga** 	75
12		**2c,** R_4=R_5= -$(CH_2)_4$-	1.0	**6gc** 	80

[a] The solution of propargylic acetates **1** (0.5 mmol), enoxysilanes **2** (1.5 mmol), and $FeCl_3$ (0.025 mmol) was stirred in CH_3CN (1.0 mL) at rt for 5 min or at 40 °C for 1 h (for substrate **1g**), or at rt for 30 min (for substrate ***1l***). Acetonitrile was then removed, followed by the addition of TsOH (0.5 mmol) and toluene (6.0 mL). Cyclization proceeded under refluxing for 0.5−2.0 h.

of the propargylic acetates **1**. γ-Alkynyl ketones **3** were the sole products in the reactions of secondary propargylic acetates **1c** and **1g**. No allenyl isomers **4** were detected (Table 2, entries 11, 15). But by changing the substrates to tertiary propargylic acetates **1d**, **1e**, and **1f**, the yields of substitution product **3** decreased and the allenyl isomer **4** was respectively obtained in 24%, 29%, and 14% yields (Table 2, entries 12−14). Especially, the allenyl isomer **4hc** was isolated as the sole product in 83% yield in the reaction of **1h** with **2c** (Table 2, entry 16). Ketene acetal **2d** retained the preferential formation of **4hd** in reaction with **1h** (Table 2, entry 18). The regioselectivity of the substitution was also affected by the steric bulkiness of the nucleophile **2**. For example, γ-alkynyl ketone **3fa** or **3fb** was the sole product in the reaction of **2a** or **2b** with **1f** (Table 1, entry 6; Table 2, entry 6). Allenyl isomer **4fc** (**3fc**: **4fc** = 75:14) was concomitantly formed in the reaction of **2c** with **1f** (Table 2, entry 14). This implies that the bulkiness at the nucleophile site affects the regioselectivity of substitution. In addition, β-diketone ester **2e** can be directly used for the propargylic substitution giving corresponding alkylated products in good yields (Table 2, entries 19, 20).

The $FeCl_3$-catalyzed propargylic substitution allows for the straightforward synthesis of tri- or tetrasubstituted furans by the sequential cyclization reaction of γ-alkynyl ketone intermediates in a one-pot procedure. The mixture of secondary propargylic acetates **1**, enoxysilanes **2**, and 5 mol % of $FeCl_3$ was simply stirred in acetonitrile. Upon reaction completion, acetonitrile was then removed in vacuo, followed by the addition of toluene and a stoichiometric amount of 4-methylbenzenesulfonic acid (TsOH). Highly substituted furans were conveniently furnished in good yields within no more than 2 h under refluxing condition[9] (Table 3). Reactions of enoxysilane **2a** with various

propargylic acetates afforded corresponding 2,3,5-trisubstituted furans in high yields (Table 3, entries 1, 5−8, 11). Functional groups such as chloro, cyano, and methoxyl in the substrates were tolerant in the TsOH-catalyzed cyclization, which allows access to other functionalized furans. The use of **2b** also gave good results under the same conditions (Table 3, entries 2, 9). Starting with cyclohexenyloxytrimethylsilane **2c** and propargylic acetates **1a**, **1g**, and **1c**, tetrasubstituted furans were isolated in 75%, 61%, and 80% yields, respectively (Table 3, entries 3, 10, 12). The trimethylsilyl group undergoes protodesilylation under the acidic cyclization conditions and so the same products were obtained in the examples involving **1g** and **1c** (Table 3, entries 8 and 11, 10 and 12). Treatment of propargylic acetate **1a** with β-diketone ester **2e** gave the 3-carboxylated tetrasubstituted **6ae** in moderate yield (Table 3, entry 4). In the sequential process, the intermediates γ-alkynyl ketones, obtained by the coupling of propargylic acetates with nucleophiles in the first step, can be directly used for the next cyclization without purification, which would lessen the yield loss of the furan products. Nishibayashi's team[6d] reported novel ruthenium- and platinum-catalyzed sequential reactions to afford the corresponding tri- and tetrasubstituted furans by the direct use of propargylic alcohols as substrates and ketones as carbon-centered nucleophiles under N_2. However, the substrates were limited to propargylic alcohols bearing a terminal alkyne group and the reaction required a rather long time for completion. In contrast, propargylic acetates bearing both a terminal alkyne group and an internal alkyne group are available, and the reaction proceeded much more rapidly without the protection inert gases. However, more active enoxysilanes of ketones as nucleophiles were required in our procedure.

In conclusion, we have developed a novel and efficient $FeCl_3$-catalyzed propargylic substitution of propargylic acetates with enoxysilanes to afford corresponding γ-alkynyl ketones in good to high yields. The reaction proceeds under mild conditions and air or moisture is tolerated. The broad scope, mild reaction conditions, short reaction time, and experimental ease of this transformation have made it a valuable alternative to current available methods for the preparation of γ-alkynyl ketones. Additionally, the $FeCl_3$-catalyzed substitution reaction can be followed by a TsOH-accelerated cyclization without purification of the γ-alkynyl ketone intermediates, offering a straightforward synthetic route to polysubstituted furans in an air atmosphere.

(9) Cyclization reaction of γ-alkynyl ketones did not proceed in acetonitrile. The $FeCl_3$-catalyzed propargylic substitution reaction also did not proceed in toluene. So it is necessary that toluene displace acetonitrile as solvent for the cyclization reaction.

Experimental Section

A typical experimental procedure for the reaction of 1-phenylhept-2-ynyl acetate (**1a**) with enoxysilane (**2a**) catalyzed by 5 mol % $FeCl_3$ is described below: To a 5-mL flask were successively added 1-phenylhept-2-ynyl acetate (**1a**, 115 mg, 0.5 mmol), enoxysilane (**2a,** 195 mg, 1.5 mmol), CH_3CN (1.0 mL), and $FeCl_3$ (4 mg, 0.025 mmol). The reaction mixture was stirred at room temperature and monitored periodically by TLC. After 5 min, the reaction was completed, the solvent was removed under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford the corresponding γ-alkynyl ketone (**3aa**) as a yellow oil (95 mg, 83% yield).

A typical experimental procedure for the synthesis of substituted furan 5-methyl-2-pentyl-3-phenylfuran **(6aa)** is described here: To a 25-mL flask were successively added 1-phenylhept-2-ynyl acetate (**1a**, 115 mg, 0.5 mmol), enoxysilane (**2a**, 195 mg, 1.5 mmol), CH_3CN (1.0 mL), and $FeCl_3$(4 mg, 0.025 mmol), then the reaction mixture was stirred at room temperature for 5 min and monitored periodically by TLC. Upon completion of the reaction, the solvent was removed under reduced pressure by an aspirator, followed by the addition of toluene (6.0 mL) and a stoichiometric amount of 4-methylbenzenesulfonic acid (86 mg, 0.5 mmol). The reaction was heated to reflux for 0.5 h and monitored by TLC. When complete, the toluene was removed under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (hexane) to afford the corresponding furan **(6aa)** as a colorless oil (92 mg, 81% yield).

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Supporting Information Available: Experimental procedures and spectra data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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