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## Lewis acid-catalyzed three-component condensation reactions of aldehydes, alkoxysilanes, and propargylsilane: synthesis of α-allenyl ethers

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Abstract—For simultaneous construction of a polyether backbone and the allenyl side chains, Lewis acid-catalyzed three-component condensation reactions of aldehydes, alkoxytrimethylsilanes, and 1-trimethylsilyl-2-butyne were studied. The reaction of these three compounds took place in the presence of a catalytic amount of TrClO<sub>4</sub> at  $-78^{\circ}$ C to yield the corresponding  $\alpha$ -allenyl ethers in good yields. This reaction was also applied to the synthesis of a polyether having allenyl side chains. © 2001 Elsevier Science Ltd. All rights reserved.

Many condensation polymers have been synthesized by the two-component polycondensation of bifunctional nucleophilic monomers and electrophilic monomers. Recently, we have reported three-component polycondensation of dialdehydes, alkylene bis(trimethylsilyl) ethers, and various silyl nucleophiles.<sup>1</sup> In these polymerizations, the use of trialkylsilanes as a silyl nucleophile gave ordinary polyethers,<sup>1a</sup> whereas the use of allyltrimethylsilane, cyanotrimethylsilane, and silyl enol ethers afforded polyethers having the allyl,<sup>1b</sup> cyano,<sup>1c</sup> and keto<sup>1d,e</sup> side chains, respectively. In the latter cases, we have demonstrated that the polyether backbone and functional side chains are simultaneously constructed in one pot. The allenyl group is also interesting as a functional side chain because allene derivatives<sup>2</sup> undergo a variety of reactions, such as cycloaddition,<sup>3a-c</sup> radical addition,<sup>3d,e</sup> photooxygenation,<sup>3f</sup> polymerization by transition metals,<sup>3g-k</sup> etc. A polymer having the allenyl side chains was synthesized by the polymerization of a monomer bearing an allenyl group,<sup>4</sup> but, to



Scheme 1.



## Scheme 2.

Keywords: propargylsilane; 1-trimethylsilyl-2-butyne; trityl perchlorate; polyether.

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Table 1.Reaction of 4a with 3

Entry	R in 3	Lewis acid (mol%)	Temp. (°C)	Time (h)	Yield (%) <sup>c</sup>			
					6	7	8	9
1 <sup>a</sup>	H: <b>3</b> a	$TrClO_4$ (5)	- 78	4.0	2	0	0	0
2 <sup>b</sup>	3a	TMSOTf (50)	-78	7.5	0	0	0	3
3 <sup>b</sup>	3a	$TiCl_{4}$ (50)	-78	1.0	14	3	1	2
4 <sup>a</sup>	Me:3b	$TrClO_4$ (5)	- 50	2.0	100 <sup>d</sup>	0	0	0

<sup>a</sup> The reaction was carried out with 5 mol% of  $TrClO_4$  in  $CH_2Cl_2$  ([4a]<sub>0</sub>=[3]<sub>0</sub>=0.5 M).

<sup>b</sup> The reaction was carried out with 50 mol% of Lewis acid in CH<sub>2</sub>Cl<sub>2</sub> ([4a]<sub>0</sub>=[3a]<sub>0</sub>=0.67 M).

<sup>c</sup> Isolated yield.

<sup>d</sup> Determined by <sup>1</sup>H NMR.

the best of our knowledge, it has not been hitherto reported that an allenyl group is directly introduced to a polymer by allenyl reagents. One might think that propargyl metallic reagents would serve as the allenyl reagents. However, the reactions of propargylmagnesium, -zinc, and -aluminum reagents with electrophiles mainly afford acetylenic derivatives.<sup>5a,b</sup> On the other hand, the reactions of propargylsilanes in the presence of Lewis acid with electrophiles such as acetals, 5a,c-e dialkyl alkylidenemalonates,5b aldehydes, ketones,5f-h and  $\alpha$ ,  $\beta$ -unsaturated acyl cyanides<sup>5i</sup> yield allenic derivatives selectively. Furthermore, trichloropropargylsilane also reacts with aldehydes in the presence of a catalytic amount of cuprous chloride to yield a-allenyl alcohols.<sup>5j,k</sup> However, the three-component reaction of propargyl silanes, aldehydes, and alkoxysilanes, where  $\alpha$ -allenyl ethers would be obtained in one pot, has not been reported. Furthermore, this reaction would be applicable to polycondensation that yields polyethers having the allenyl side chains. In this paper, we report the Lewis acid-catalyzed three-component condensation reaction of aldehydes 1, alkoxytrimethylsilanes 2, and propargylsilanes 3, and its application to polycondensation using bifunctional aldehydes and alkoxysilanes (Schemes 1 and 2).

We first studied the reaction of benzaldehyde dimethylacetal **4a** with propargylsilanes, such as 3-trimethylsilyl-1-propyne **3a**<sup>6a</sup> and 1-trimethylsilyl-2-butyne **3b**,<sup>6b</sup> because acetals were found to be an intermediate in the Lewis acid-catalyzed reactions of aldehydes, alkoxysilanes, and silyl nucleophiles.<sup>1</sup> The results are shown in Table 1. When **3a** was used, the reaction only partly proceeded with 5 mol% of triphenylmethyl perchlorate (TrClO<sub>4</sub>)<sup>7</sup> to give **6a** in very low yield and 45% recovery of **4a** (entry 1). The use of 50 mol% of trimethylsilyl trifluoromethanesulfonate (TMSOTf)<sup>8</sup> resulted in complete consumption of **4a**, but **6a** was not obtained and  $\alpha$ -propargyl ether **9** was afforded in low yield (entry 2). When 50 mol% of TiCl<sub>4</sub> was used, not only the reported<sup>4a</sup>  $\alpha$ -allenyl ether **6a** and chloroprene derivative 7 but also  $\alpha$ -propargyl ethers **8** and **9** were obtained (entry 3). Surprisingly, the reaction of **3b** with **4a** proceeded smoothly with 5 mol% of TrClO<sub>4</sub> to yield **6b** in quantitative yield (entry 4). It should be noted that the reaction of methyl-substituted **3b** with **4a** was totally different from that of unsubstituted **3a** with **4a**, and the former reaction gave selectively  $\alpha$ -allenyl ether **6b**.

Next we carried out the three-component condensation of benzaldehyde **1a**, methoxytrimethylsilane **2a**, and **3b** in the presence of 5 mol% of TrClO<sub>4</sub> or TMSOTF (Table 2). Both reactions gave **6b** in good yields; both catalysts were effective for this reaction. The fact that no  $\alpha$ -allenyl alcohol was produced as a result of a direct attack of **3b** on **1a** shows that the reaction of **3b** with an intermediate acetal, which is generated by **1a** and **2a**, proceeds selectively even in the presence of **1a** in the reaction mixture.

With the optimized conditions in hand, we carried out the reactions of a variety of 1, 2, and 3b (Table 3). Thus, a round-bottomed flask, equipped with a threeway stopcock, was charged with  $TrClO_4$  (0.025 mmol) and purged with argon. Dry dichloromethane (0.5 mL) was added to the flask, followed by cooling the solution

Table 2. Three-component condensation of 1a, 2a, and  $3b^{\rm a}$ 

Catalyst	Time (h)	Yield of <b>6b</b> (%) <sup>b</sup>
TrClO <sub>4</sub>	18	95
TMSOTf	24	97

<sup>a</sup> The reaction was carried out with 5 mol% of catalyst in  $CH_2Cl_2$  ([1a]<sub>0</sub>=[2a]<sub>0</sub>=[3b]<sub>0</sub>=0.5 M) at -78°C.

<sup>b</sup> Determined by GC.

Table 3. Three-component condensation of 1, 2, and 3b<sup>a</sup>

Entry	1	2	Temp (°C)	Time (h)	Yield of <b>5</b> (%) <sup>b</sup>
1	CHO : 1a	MeOSiMe <sub>3</sub> : <b>2a</b>	-78	18	95 <sup>c</sup>
2	СІ—	2a	-78	24	72
3	МеО-СНО	2a	-78	24	0
4	1a 🦯	OSiMe <sub>3</sub>	-78	24	86
5	1a	OSiMe <sub>3</sub>	-78	24	80
6	СНО	2a	-78 to 25	30	0
7	СНО	2a	-78 to 25	30	2
8	o	2a	-78 to -20	48	0
9	0	2a	-78	72	9

<sup>a</sup> The reaction was carried out with 5 mol% of TrClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> ([1]<sub>0</sub>=[2]<sub>0</sub>=[3b]<sub>0</sub>=0.5 M). <sup>b</sup> Isolated yield. <sup>c</sup> Determined by GC.

to  $-78^{\circ}$ C. A solution of 1 (0.5 mmol) and 2 (0.5 mmol) in dichloromethane (0.25 mL) was added at  $-78^{\circ}$ C. After 5 min, a solution of 3b (0.5 mmol) in dichloromethane (0.25 mL) was added. The solution was stirred at the indicated temperature in Table 3. The reaction mixture was quenched with a few drops of ammoniacal methanol. The solvent was evaporated and the residue was purified by column chromatography on silica gel to afford the corresponding  $\alpha$ -allenyl ethers 5. Unsubstituted 1a and an aromatic aldehyde having an electron-withdrawing group reacted with 2a and 3b to yield the corresponding 5 in high yields (entries 1 and 2). However, an aromatic aldehyde having an electrondonating group did not afford 5 in this reaction (entry 3). Although the exact structure of the obtained compound has not been revealed, the desired 5 was assumed to react with one more equivalent of highly reactive anisaldehyde on the basis of the <sup>1</sup>H NMR spectrum showing the two kinds of signals of the methoxyphenyl groups and the absence of the signal of the allenyl group. Regarding 2, not only primary 2 but also secondary 2 resulted in 5 in good yields (entries 1, 4, and 5). Compared to aromatic aldehydes, aliphatic aldehydes and ketones gave 5 in low yields. Even at higher temperatures and longer reaction times, the yields of 5 were not improved (entries 6–9).

This reaction was also applied to polycondensation. Thus, isophthalaldehyde **1b**, decamethylene bis(trimethylsilyl) ether **2b**, and **3b** were reacted with 10 mol% of TrClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at  $-50^{\circ}$ C for 24 h to yield a polyether having the allenyl side chains with the number-averaged molecular weight ( $M_n$ ) of 6600 (Scheme 2).

In summary, the present work has demonstrated that 1-trimethylsilyl-2-butyne **3b** is available for Lewis acidcatalyzed three-component condensation reactions of  $\alpha$ -allenyl ethers. Furthermore, the three-component polycondensation of dialdehydes, bifunctional silyl ethers, and **3b** yielded a functional polyether with the allenyl side chains.

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