

ELECTROPHILIC REACTION OF ALLYLTRIMETHYLSILANE WITH NITRILES IN THE  
PRESENCE OF BORON TRICHLORIDE

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Allyltrimethylsilane reacted with various nitriles in the presence of boron trichloride, giving after hydrolysis  $\beta,\gamma$ -unsaturated ketones in high yields. The reactions of substituted allyltrimethylsilanes and intramolecular reaction of allylic trimethylsilane with nitrile were also studied.

Allyltrimethylsilane is a useful synthetic intermediate with a highly nucleophilic double bond. Allylic transfer takes place from allyltrimethylsilane to the electrophilic carbon center in the presence of Lewis acids.<sup>1)</sup> Acyl halide, aldehyde, and ketone have been used as the electrophile, but the electrophilic reaction of allyltrimethylsilane with nitriles has not been reported. This may be due to the relatively low electrophilicity of nitriles, which usually react with alkenes as the nucleophile in the presence of acids (Ritter reaction).<sup>2)</sup>

Recently, we have found that boron trichloride ( $\text{BCl}_3$ ) serves as a useful activator of nitriles and that in its presence, various alkenes react with electron-deficient nitriles.<sup>3)</sup> Here we report that allyltrimethylsilane 1 reacts with nitriles in the presence of  $\text{BCl}_3$ , giving after hydrolysis  $\beta,\gamma$ -unsaturated ketones 2 in high yields. This reaction proceeds smoothly not only with electron-deficient nitriles but also aliphatic nitriles. The procedure for the reaction of electron-deficient nitriles was similar to that reported for the reaction of 1-octene with trichloroacetonitrile (Method A).<sup>3)</sup> In the reaction of aliphatic nitriles, 1 was added slowly (over 3 h) to a mixture of nitrile and  $\text{BCl}_3$  at room temperature in dichloromethane under argon (Method B). As shown in Table 1, all reactions gave the products in high yields.

Table 1. The Reaction of Allyltrimethylsilane with Nitriles in the Presence of  $\text{BCl}_3$

$$\text{CH}_2=\text{CH}-\text{CH}_2-\text{SiMe}_3 + \text{RCN} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{BCl}_3} \left[ \text{R}-\text{C}(\text{N}^+\text{BCl}_3)-\text{CH}_2-\text{CH}=\text{CH}_2-\text{SiMe}_3 \right] \xrightarrow[2) \text{H}_2\text{O}]{1) -\text{Me}_3\text{SiCl}} \text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}=\text{CH}_2$$

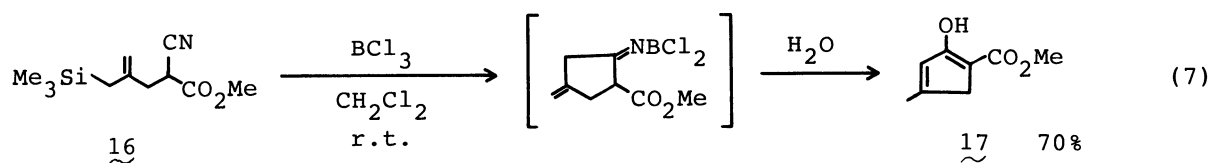
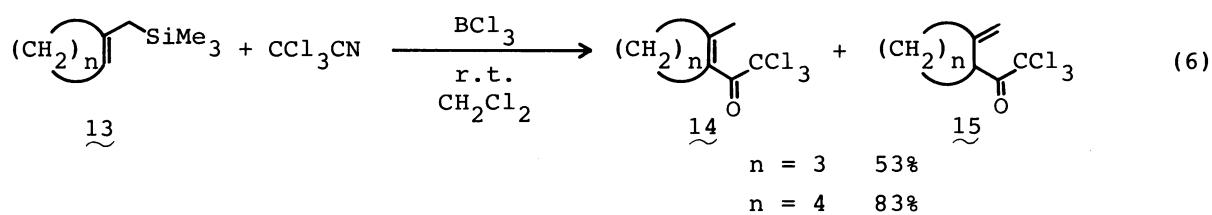
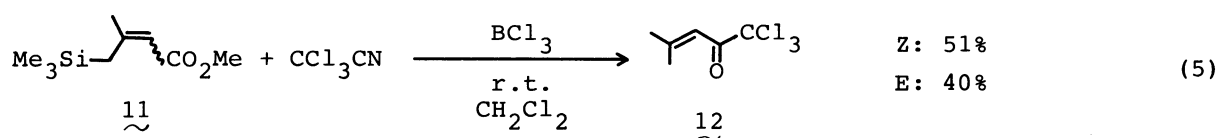
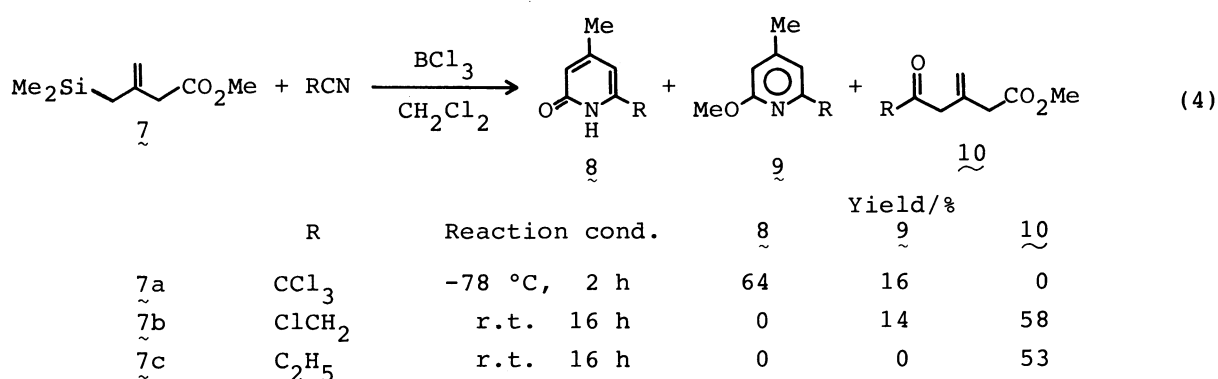
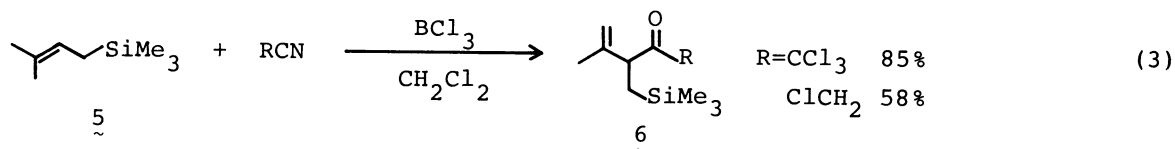
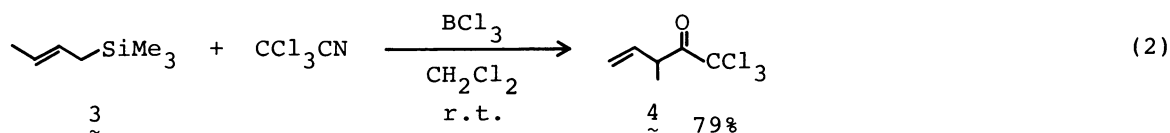
Run	R	Reaction conditions <sup>a)</sup>	Yield/% <sup>b)</sup>
1	$\text{CCl}_3$	A	76
2	$\text{CH}_2\text{Cl}$	A	86
3	$\text{CH}_3$	B	68
4	$\text{C}_2\text{H}_5$	B	69
5	$\text{CH}_2\text{CO}_2\text{Me}$	B	70
6	$(\text{CH}_2)_3\text{Cl}$	B	72
7	$(\text{CH}_2)_4\text{Br}$	B	62
8	$\text{PhCH}_2$	B	38

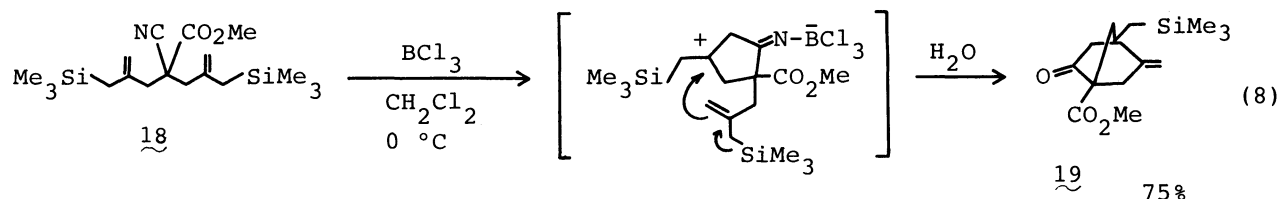
a) For conditions, see text.

b) Products were isolated by chromatography ( $\text{SiO}_2$ , 60 pre-packed column A, Merck A. G.) and identified by IR and NMR spectra.

The reactions of various substituted allyltrimethylsilane were also investigated. The substituent at the  $\gamma$ -position of allyltrimethylsilane plays an important role in the reaction because of the steric effect, while the substituent at the  $\beta$ -position does not affect it. (E)-Crotyltrimethylsilane<sup>4)</sup> 3 reacted only with trichloroacetonitrile (Eq. 2). In the case of  $\gamma,\gamma$ -dimethylallyltrimethylsilane 5,<sup>5)</sup> the reactivity with nitriles as allyltrimethylsilane was completely suppressed, and the ene reaction took place (Eq. 3). Methyl 3-(trimethylsilylmethyl)-3-butenate 7<sup>6)</sup> reacted with various nitriles (Eq. 4). In this case, the high acidity of the hydrogen at the 4-position due to the electron-withdrawing effect of the trichloromethyl or chloromethyl group caused the primary adduct to assume an enamine form, cyclization took place in the reaction with trichloroacetonitrile or chloroacetonitrile. Only trichloroacetonitrile could react at room temperature with allyltrimethylsilane 11<sup>6)</sup> and 13.<sup>7)</sup> The compound 11 gave  $\alpha,\beta$ -unsaturated ketone 12 after spontaneous decarboxylation, while isomerization of double bond took place in the case of cyclic allyltrimethylsilane 13 (Eqs. 5 and 6).

Intramolecular reaction of allylic trimethylsilane with nitrile also took place in the presence of  $\text{BCl}_3$ . Treatment of 16<sup>8)</sup> with  $\text{BCl}_3$  at room temperature in dichloromethane gave the cyclopentenone derivative 17 in 70% yield as the





enolized form (Eq. 7). When compound 18<sup>8)</sup> was treated with  $\text{BCl}_3$  at  $0\text{ }^\circ\text{C}$  in dichloromethane, tandem cyclization of intramolecular allyltrimethylsilane occurred. After the first intramolecular cyclization of allyltrimethylsilane to nitrile, another allyltrimethylsilane attacked the generated carbenium ion and [3.2.1] bicyclic compound 19 was obtained in 75% yield (Eq. 8). This tandem cyclization may be a useful and general reaction for a compound which has two allyltrimethylsilane moieties and one electrophilic carbon center.

All these reactions proceeded well only with  $\text{BCl}_3$  and not with other Lewis acids. They were all carried out in dichloromethane, while the use of other solvents did not give successful results.

#### References

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