Allenylmethylsilane Derivative as a Synthetic Equivalent of 1,2,3-Butatriene: Synthesis and Reactions of Di-*exo*-methylenecyclobutanes and -cyclobutenes

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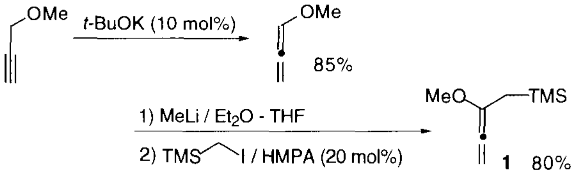
2-Methoxyallenylmethylsilane reacts with alkenes and alkynes in a [2 + 2] cycloaddition mode to give cyclobutanes and cyclobutenes, respectively. Cycloadducts are converted to di-*exo*-methylene compounds through 1,2-elimination of the methoxy and silyl groups. These di-*exo*-methylenecyclobutanes and -cyclobutenes react with alkenes and 1,3-dienes to afford fused bi- and tricyclic compounds.

Organosilicon compounds serve as synthetic equivalents of unstable active species and intermediates. Allylsilane derivatives, in particular, exhibit unique reactivities based on high nucleophilicity at the γ-carbon atom and electrophilicity at the β-carbon atom.[1] In the course of our study on the substituent effect at the β-carbon atom of allylsilanes,[2] we recently found 2-methylthio-substituted allenylmethylsilane, which has an allylsilane moiety, reacted with alkenes in a [2 + 2] cycloaddition mode[3] to afford cyclobutane derivatives that can be converted to di-*exo*-methylenecyclobutanes. [3 + 4] Cycloaddition of the di-*exo*-methylene compound was also reported.[4] Now we wish to report the [2 + 2] cycloaddition of 2-methoxyallenylmethylsilane (**1**) to alkenes and alkynes, and the use of the obtained cycloadducts for the construction of fused ring systems (Scheme 1).

Methoxy-substituted allenylmethylsilane **1** was easily prepared from propargyl methyl ether in two steps (Scheme 2).[5]

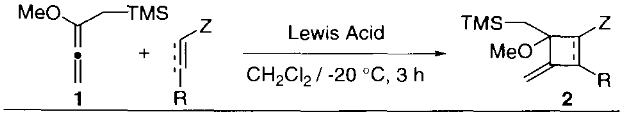


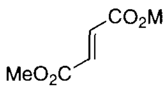
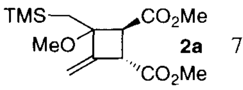
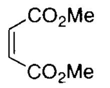
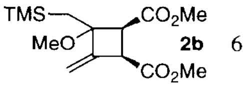
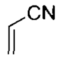
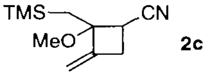
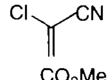
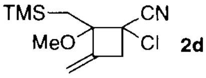
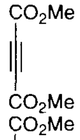
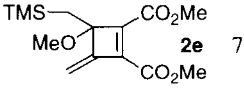
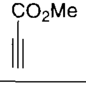
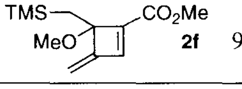
Scheme 2.

It was found that the allenylmethylsilane **1**, in the presence of a Lewis acid, reacted with electron-deficient alkenes and alkynes, as an ene in [2 + 2] cycloaddition, to give cyclobutanes **2a-d** and cyclobutenes **2e-f**, respectively (Table 1), although we previously reported that **1** reacted with carbonyl compounds as an allylsilane.[6] In the present reactions, the stereochemistry of alkenes was retained in the cycloadducts, while as for the stereochemistry around the methoxy-substituted carbon of products, no selectivity was found.

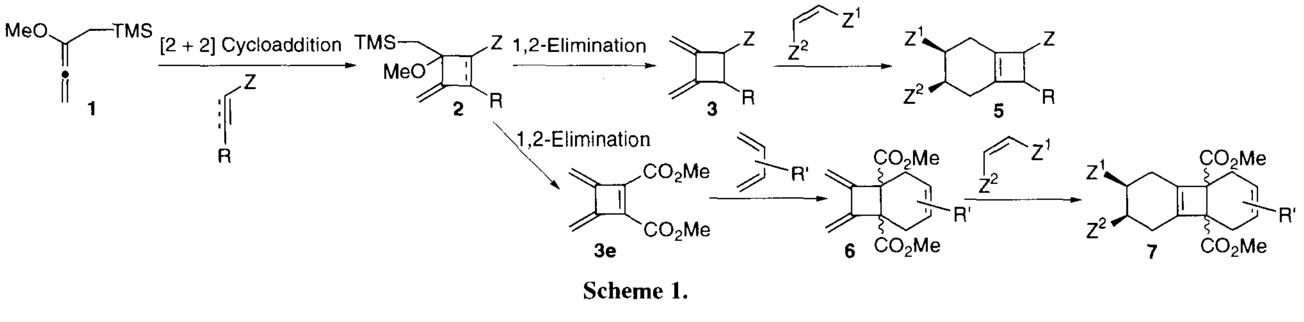
These cycloadducts were converted to the corresponding di-*exo*-methylene compounds through 1,2-elimination of the methoxy and silyl groups using only a Lewis acid as a promoter (Table 2). This is in contrast to the corresponding elimination from analogs with a methylthio-substituent, where the methylthio group must be oxidized to sulfoxide to ease the elimination, and moreover cesium fluoride was necessary together with a Lewis acid.[4]

Table 1. Cycloaddition of **1** with electron-deficient alkenes and alkynes[a]



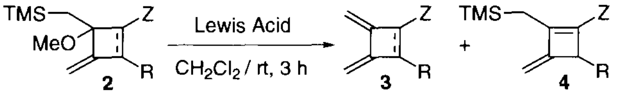
Entry	Acceptor	Lewis Acid	Product	Yield[d]/ %
1		Et_2AlCl	 **2a**	70
2		Et_2AlCl	 **2b**	69
3		Et_2AlCl	 **2c**	68
4[b]		Et_2AlCl	 **2d**	96
5		MAT[c]	 **2e**	76
6		MAT[c]	 **2f**	92

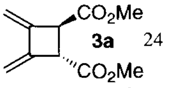
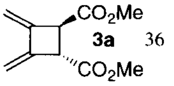
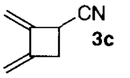
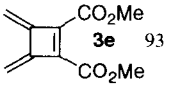
[a] All reactions were carried out using **1** (0.65 mmol), electron-deficient alkene or alkyne (0.50 mmol), and Et_2AlCl (0.50 mmol) in CH_2Cl_2. [b] The reaction was carried out at -40 °C for 3 h. [c] 2.0 equiv. of MAT[7] (Methylaluminum bis(2,4,6-tri-*tert*-butylphenoxide)) was used to an alkyne. [d] Isolated yield by column chromatography on florisil.



Scheme 1.

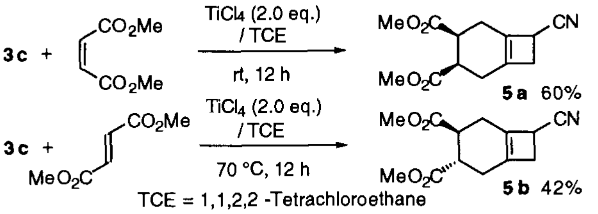
Table 2. Conversion of [2 + 2] cycloadducts **2** to di-*exo*-methylenecyclobutanes and -cyclobutene **3**^{a}



Entry	2	Lewis Acid (eq.)	Products	Yield^b / %	
			3		4
1	**2a**	TiCl$_4$ (2.0)	 **3a**	24	—^{c}
2	**2a**	BF$_3$ • Et$_2$O (3.0)	 **3a**	36	36
3	**2c**	BF$_3$ • Et$_2$O (3.0)	 **3c**	87	12
4^d	**2e**	TiCl$_4$ (2.0)	 **3e**	93	—^{c}

^{a}All reactions were carried out using **2** (0.5 mmol) and Lewis acid (1.00 mmol) at rt for 3 h, otherwise noted. ^{b}Yield was determined by ^{1}H-NMR. ^{c}Not detected. ^{d}The reaction was carried out at rt, fot 6 h.

Next we examined the reactivity of di-*exo*-methylene compounds, **3c** and **3e** (Scheme 3). Di-*exo*-methylene-cyclobutane **3c**, under the influence of a Lewis acid, reacted with methyl maleate and fumarate to afford the cycloadducts **5a** and **5b**, respectively.[8] Cyclobutene derivative **3e**,[9] as a diene, resisted the Diels-Alder reaction with maleate and fumarate, possibly because of low HOMO level of **3e** or the difficulty in the formation of the cyclobutadiene skeleton.



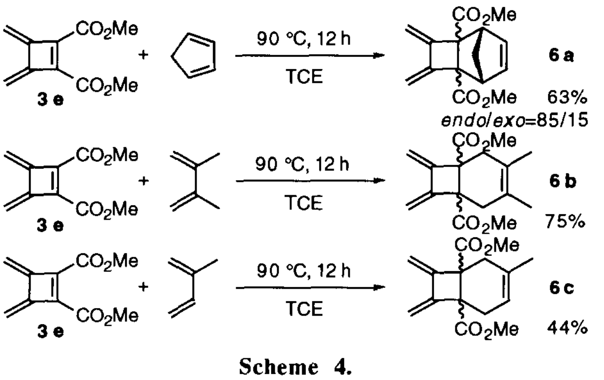
5a 60%

5b 42%

TCE = 1,1,2,2 -Tetrachloroethane

Scheme 3.

On the other hand, **3e**, as a dienophile, reacted with 1,3-dienes (Scheme 4). These reactions proceeded at 90 °C without any promoter and, with cyclopentadiene, the corresponding cycloadduct **6a** was obtained in 63% yield (*endo*/*exo*=85/15). Other 1,3-dienes also reacted with **3e** to yield **6b** and **6c**.



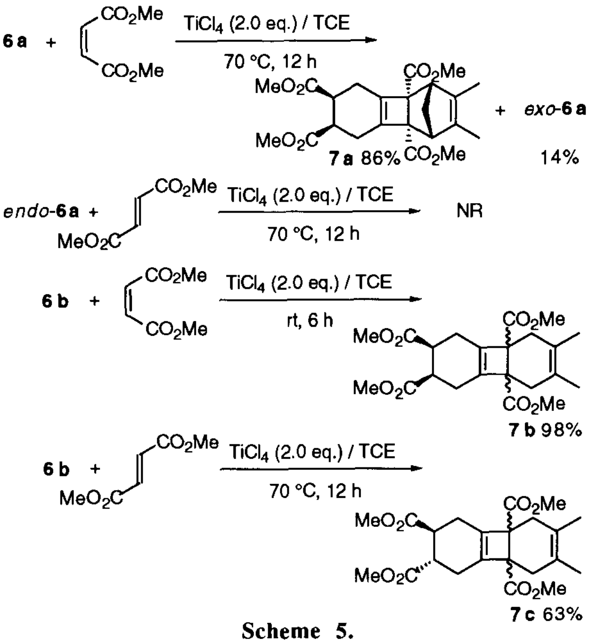
6a 63% *endo*/*exo*=85/15

6b 75%

6c 44%

Scheme 4.

Further Diels-Alder reactions of the resulting cycloadducts **6a** and **6b** were studied (Scheme 5). It is interesting that, in the reaction of **6a** as a diastereomeric mixture, only *endo*-**6a** reacts with maleate to give **7a**, and *exo*-**6a** was completely recovered, while with fumarate, even the isolated *endo*-**6a** did not react at all. On the other hand, **6b** reacts with both maleate and fumarate. These differences in reactivity of cycloadducts **6** may be attributed to the steric hindrance.



7a 86%

14%

7b 98%

7c 63%

Scheme 5.

In these reactions, the title compound synthetically serves as a 1,2,3-butatriene equivalent.

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References and Notes

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