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The $EtAlCl_2$-Catalyzed Cargill Rearrangement of Bicyclo[n.2.0] Compounds Prepared by the [2+2] Cycloaddition of Cycloalkenones and 1-*t*-Butyldimethylsilyl-2-methylthioacetylene

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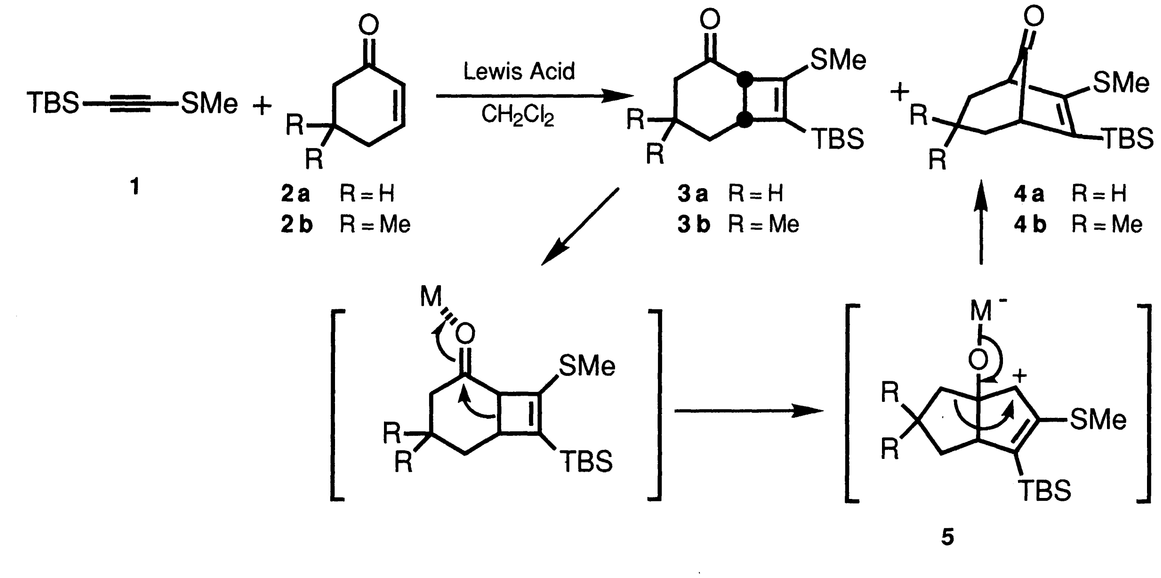
$EtAlCl_2$ catalyzes the Cargill rearrangement of bicyclo[n.2.0] compounds which were prepared by the $TiCl_4$-mediated [2+2] cycloaddition reaction of cycloalkenones and 1-*t*-butyldimethylsilyl-2-methylthioacetylene, yielding various bicyclo[n-1.2.1] compounds under mild reaction conditions.

Cyclobutene derivatives are synthetically important building blocks, which can be readily converted to various useful compounds by the rearrangement with the ring cleavage.[1] For instance, cyclobutene derivatives such as bicyclo[n.2.0] compounds are transformed into bicyclo[n-1.2.1] derivatives by the acid catalyzed Cargill rearrangement.[2,3] However, there are some drawbacks of this rearrangement: The rearrangement occurs under the harsh reaction conditions[4,5] and the yield is not generally high.[4] Moreover, there is not a reliable synthetic method for the preparation of bicyclo[n.2.0] compounds except for the photochemical [2+2] cycloaddition reaction.[6]

In the previous paper, we have reported that Lewis acid catalyzes the [2+2] cycloaddition reaction between electron deficient olefins and alkynyl sulfides to afford cyclobutene derivatives.[7] For example, the reaction between 1-*t*-butyldimethylsilyl-2-methylthioacetylene (**1**) and 2-cyclohexen-1-one (**2a**) in the presence of $SnCl_4$ or $TiCl_4$ afforded the [2+2] cycloadduct **3a** (Table 1, entries 1-3).



TBS = *tert*-Butyldimethylsilyl, M = BF_3, $EtAlCl_2$

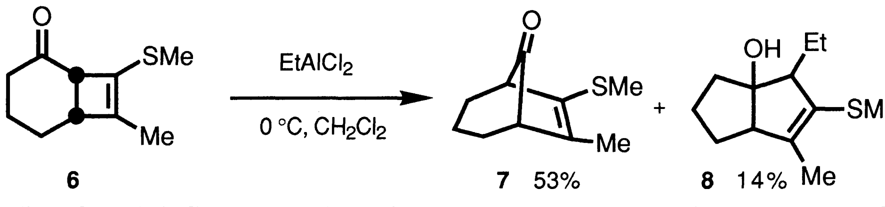
In screening the reaction conditions, when $EtAlCl_2$ or $BF_3{\bullet}OEt_2$ was used as a Lewis acid, 6-*t*-butyldimethylsilyl-7-methylthiobicyclo[3.2.1]oct-6-en-8-one (**4a**) was obtained in good yield in place of the [2+2] cycloadduct **3a** (entries 4, 5). As the treatment of the isolated cyclobutene **3a** with $EtAlCl_2$ in CH_2Cl_2 at 0 °C for 10 min resulted in the formation of **4a** in 80% yield (entry 8), the bicyclo[3.2.1]octene derivative **4a** was thought to be generated by the Cargill rearrangement of **3a**.

Although **4a** was obtained by one step procedure from **1** and cyclohexenone **2a**, the reaction of 5,5-dimethyl-2-cyclohexen-1-one (**2b**) with **1** proceeded very slowly, affording the rearranged product **4b** in low yield (40%) because of the steric hindrance caused by methyl groups (entry 7). On the other hand, the $TiCl_4$-mediated [2+2] cycloaddition reaction of **2b** proceeded smoothly to give the cyclobutene **3b** in the yield of 94% (entry 6), which rearranged to **4b** in 94% yield by the successive treatment with $EtAlCl_2$ (entry 9). These results indicate that $TiCl_4$ is the optimum Lewis acid for the [2+2] cycloaddition reaction of **1**, while $EtAlCl_2$ is suitable for the Cargill rearrangement of **3**.8)

Table 1. Effect of Lewis acids in the [2+2] cycloaddition reaction and Cargill rearrangement

Entry	Substrate	Lewis acid	Temp /°C	Time/h	Yield/% 3	4
1	**1+2a**	$TiCl_4$	-78	0.5	83 (**3a**)	0
2	**1+2a**	$TiCl_4$	0	0.3	85 (**3a**)	0
3	**1+2a**	$SnCl_4$	0	1.5	70 (**3a**)	0
4	**1+2a**	$BF_3{\bullet}OEt_2$	rt	8	0	77 (**4a**)
5	**1+2a**	$EtAlCl_2$	rt	1	0	90 (**4a**)
6	**1+2b**	$TiCl_4$	0	1	94 (**3b**)	0
7	**1+2b**	$EtAlCl_2$	rt	48	0	40 (**4b**)
8	**3a**	$EtAlCl_2$	0	0.17	0	80 (**4a**)
9	**3b**	$EtAlCl_2$	rt	0.17	0	94 (**4b**)

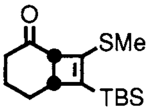
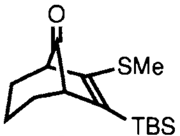
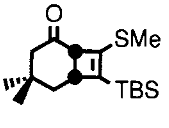
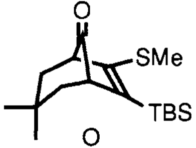
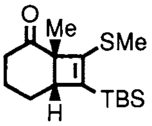
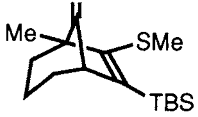
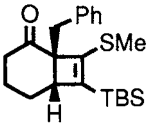
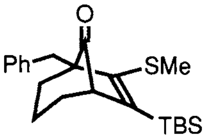
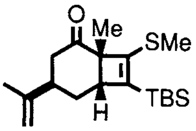
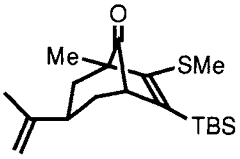
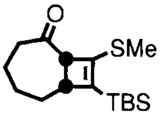
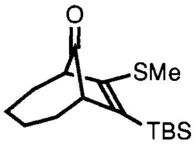
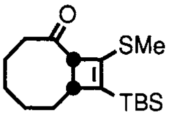
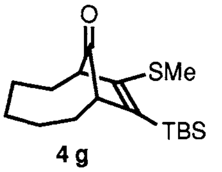
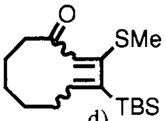
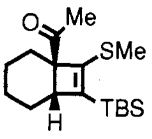
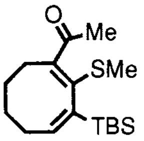
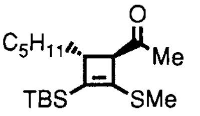
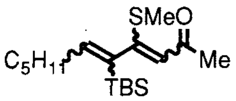
The Cargill rearrangement of bicyclo[4.2.0]oct-7-en-2-one, the fundamental structure of **3a** without methylthio and silyl substituents, occurs under severe reaction conditions (200 °C in the presence of Al_2O_3) in low yield,4) but the cyclobutene **3a** having both substituents rearranges under mild reaction conditions in good yield. Treatment of the corresponding sulfoxide and sulfone of **3a** with $EtAlCl_2$ under the same reaction conditions gave no rearranged products with the recovery of the starting materials. Thus, the facile rearrangement of **3a** is due to the introduction of methylthio group at 8 position. On the other hand, the Cargill rearrangement of 7-methyl-8-methylthiobicyclo[4.2.0]oct-7-en-2-one (**6**) having methyl substituent instead of *t*-butyldimethylsilyl (TBS) group proceeds with $EtAlCl_2$, affording the rearranged product **7** in 53% yield along with the generation of the bicyclo[3.3.0] derivative **8** in 14% yield. Accordingly, TBS group at 7 position is not essential for this rearrangement but suppresses the side reaction toward **8**.



6 **7** 53% **8** 14%

The generality of the $EtAlCl_2$-catalyzed Cargill rearrangement was examined by the use of various cyclobutene derivatives **3** prepared from the alkynylsulfide **1** and enones by the use of $TiCl_4$.9) The results are sum-

Table 2. The Cargill rearrangement catalyzed by $EtAlCl_2$[a]

Entry	Cyclobutene derivative		Rearranged product		Yield/%
1		**3a**		**4a**	80
2		**3b**		**4b**	94[b]
3		**3c**		**4c**	87
4		**3d**		**4d**	94
5		**3e**		**4e**	87
6		**3f**		**4f**	71
7		**3g**	 **4g**  **9**[d]	0 34	79 26[c]
8		**3h**		**10**	97
9		**3i**		**11**[e]	47

a) The reaction was performed in CH_2Cl_2 at 0 °C for 10 min, unless otherwise noted.
b) The reaction was performed at rt. c) The reaction time was 20 h.
d) **9** was obtained as a single isomer, the stereochemistry of which is not determined.
e) **11** was obtained as a mixture of 3 isomers, the ratio of which is 73:23:4.

marized in Table 2. The Cargill rearrangement of bicyclo[4.2.0]octene and [5.2.0]nonene derivatives **3a-f**, which were prepared from cyclohexenones and cycloheptenone, respectively, proceeded smoothly to afford bicyclo[3.2.1]octenes **4a-e** and a [4.2.1]nonene **4f** in good yield (entries 1-6). Alkyl substituent at 1 and/or 4 position(s) of bicyclo[4.2.0]oct-7-ene derivatives **3b-e** did not interfere the rearrangement (entries 2-5). The diene formation by the ring opening[10)] was not observed in the reaction of the above bicyclo[4.2.0]octene and [5.2.0]-nonene derivatives **3a-f** (entries 1-6). On the contrary, the ring opening reaction proceeded in the cases of cyclobutenes **3h, i** having acetyl group at 4-position of cyclobutenyl sulfides (entries 8, 9). Treatment of the bicyclo[6.2.0]decanone derivative **3g** for 10 min with $EtAlCl_2$ afforded the ring opening product **9** in 79% yield, but the Cargill rearrangement product **4g** was obtained in 34% yield after the prolonged (20 h) reaction time (entry 7), because of the equilibrium[11)] between **3g** and **9** under the reaction conditions. As mentioned above, the Cargill rearrangement proceeds selectively in the reaction of the bicyclo[n.2.0] derivatives (n=4, 5, 6) having oxo group at 2-position, while the diene formation occurs in the case of other types of cyclobutenes.

References

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8) After screening several Lewis acids ($TiCl_4$, $SnCl_4$, $EtAlCl_2$, Me_2AlCl, $ZnCl_2$, $BF_3{\bullet}OEt_2$) and *p*-TsOH,[3)] $EtAlCl_2$ was found to be the optimum acid catalyst in the Cargill rearrangement of **3a**.
9) The [2+2] cycloadducts **3** were prepared according to the procedure in the Ref. 7.
10) M. Hesse, "Ring Enlargement in Organic Chemistry," VCH Publishers, Inc., New York (1991); E. A. Kallel, Y. Wang, D. C. Spellmeyer, and K. N. Houk, *J. Am. Chem. Soc.*, **112**, 6759 (1990) and the references cited therein.
11) The equilibrium between **3g** and **9** is indicated by the fact that the isolated **9** was slowly converted into the mixture of **3g** and **9**.

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