CHEMISTRY LETTERS, pp. 2091-2094, 1990.

[2+2] Cycloaddition Reaction between Allenyl Sulfides and Electron Deficient Olefins Promoted by Lewis Acids

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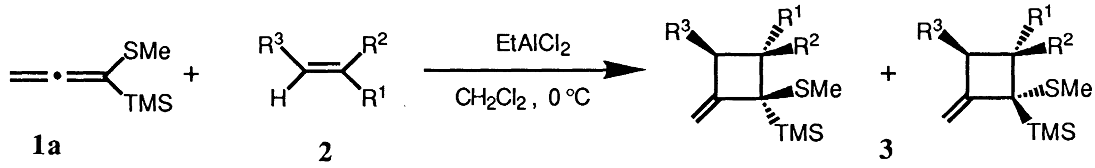
Methylenecyclobutane derivatives are prepared by the Lewis acid promoted [2+2] cycloaddition reactions of 1-substituted-1-methylthio-1,2-propadienes and electron deficient olefins. The asymmetric [2+2] cycloaddition of the allenyl sulfides also proceeds in high enantioselectivity by the use of a chiral titanium reagent.

Methylene cyclobutane derivatives are synthetically useful building blocks.1) For the construction of these compounds, [2+2] cycloaddition reactions between allenes and ethylene derivatives have been frequently employed.2) Most of the addition reactions proceeds by photochemical activation, and thermal reactions are restricted to a very limited number of examples, for instance, using the electron deficient allene derivatives3) or labile electron deficient olefins.4) Thus, scope and yields of [2+2] cycloaddition reactions using allene derivatives have not attained to the level of a practical synthetic method.

We have reported the exceptionally high reactivity of alkenyl sulfides in the [2+2] cycloaddition reaction as compared with normal alkenes and alkenyl ethers.5) Ketene dithioacetal, alkenyl and alkynyl sulfides react with α,β-unsaturated acyl derivatives in the presence of a chiral titanium reagent to afford the cyclobutane and cyclobutene derivatives in high enantioselectivity. Introduction of alkylthio group to allenes also shows a high reactivity and allenyl sulfide was employed as an ene component in the reaction with aldehydes or Schiff's bases.6) Accordingly, allenyl sulfide would be employable in [2+2] cycloaddition, and in this paper is reported the results of the reaction of allenyl sulfides **1** and electron deficient olefins.

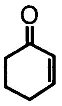
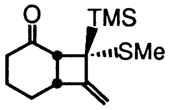
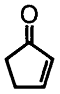
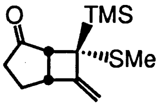
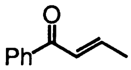
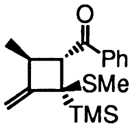
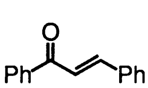
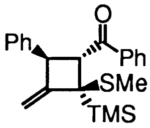
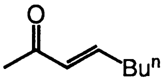
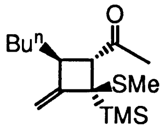
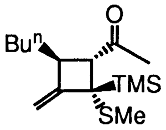
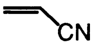
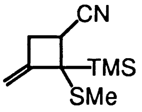
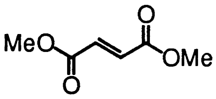
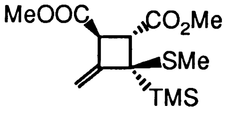
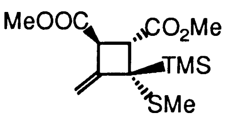
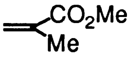
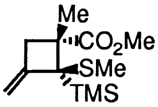
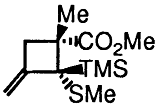
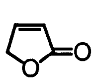
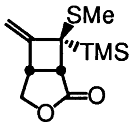
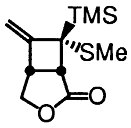


R^1 or R^2 = electron withdrawing group

The reaction of 1-trimethylsilyl-1-methylthio-1,2-propadiene **1a**7) and 2-cyclohexen-1-one **2a** was chosen as a prototypical example for the investigation and the reaction was examined under a variety of reaction conditions. In the presence of an equimolar amount of $EtAlCl_2$ at 0 °C for 3 h, bicyclo[4.2.0]octan-2-one derivative **3a** was obtained in 77% yield. When stronger Lewis acid or more than one equivalent of $EtAlCl_2$ was used, the reaction became complicated because of the decomposition of the product.

The reaction between **1a** and some electron deficient olefins were examined and the results are summarized in Table 1. There is a wide generality in this [2+2] cycloaddition reaction: Various electron deficient olefins

Table 1. [2+2] cycloaddition reaction of **1a** with electron deficient olefins

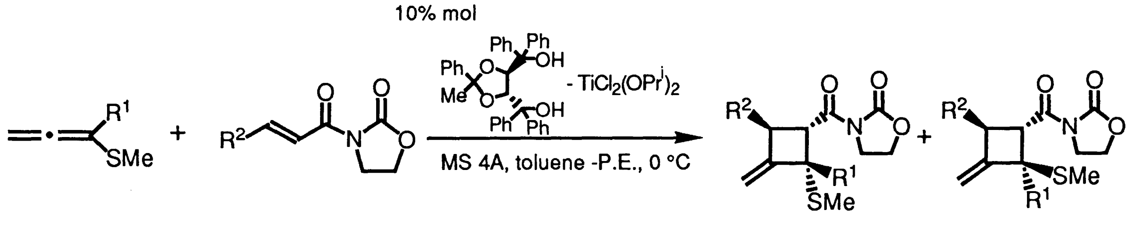
Olefin	Time, t/h	Product[a]	Yield, x/%
 **2a**	3	 **3a**	77[b]
	1.75		56[b]
	1.75		81[b]
	1.75		92[b]
	16	 	80(69:31)[c]
	1.75		75(57:43)[c,d]
	1.75	 	84(92:8)[c]
	1.5	 	91(85: 15)[c]
	72	 	54(91: 9)[c]

a) Relative stereochemistry is determined by NOESY spectrum, unless otherwise noted.
b) The other isomer is not detected.
c) The diastereomer ratio is determined by NMR.
d) Relative stereochemistry is not determined.

bearing ketone, ester or cyano functionalities are able to be employed. Moreover the reaction proceeds not only with acyclic olefins but also cyclic ones, and a variety of methylene cyclobutane derivatives are prepared from allenyl sulfide **1a**. Only C_1-C_2 double bond of the allenyl sulfide **1a** paticipates in the reaction and none of the other regio isomer is formed in all cases. The photochemical reaction between **2a** and allene gives the 8-methylene derivative as a major product.$^{8)}$ On the other hand, the reaction between **1a** and **2** affords the other regioisomer, the 7-methylene derivative **3a**. These high regioselectivities are the noteworthy character of the present Lewis acid promoted [2+2] cycloaddition of allenyl sulfides. Futhermore, no cyclopentene derivative is detected in this reaction, which is the major product of the Danheiser's [3+2] annulation reaction using allenyl silanes.$^{9)}$

The representative experimental procedure is as follows: To a dichloromethane solution (4 ml) of **1a** (1.0 mmol) and **2a** (0.73 mmol) was added $EtAlCl_2$ (0.73 mmol, 1 M hexane solution) dropwise at 0 °C. The mixture was stirred for 3 h at 0 °C, and the reaction was quenched with a few drops of NEt_3 and then with aqueous $NaHCO_3$. The crude product was purified by thin layer chromatography to afford **3a** (0.56 mmol, 77% yield).

As **1a** was found to react with α,β-unsaturated carbonyl compounds, the asymmetric version of this reaction was next investigated by using the allenyl sulfides. Since the chiral titanium reagent is known to catalyze the [2+2] cycloaddition of vinyl sulfides,$^{5)}$ the reaction between **1** and 3-acryloyl-1,3-oxazolidin-2-one derivatives **4** was investigated by the use of a catalytic amount (10% mol) of the chiral titanium reagent.$^{10)}$ The summary is shown in Table 2.



1 **4** **5** **6**

Table 2. Asymmetric [2+2] cycloaddition reaction catalyzed by the chiral titanium reagent

R^1	R^2	Yield, x/%		Opt.yield, x/%ee$^{a)}$	
		$5^{b)}$	$6^{b)}$	5	6
$SiMe_3$ (**1a**)	COOMe	quant.$^{c)}$	-	>98	-
$SnMe_3$ (**1b**)	COOMe	$93^{c)}$	-	96	-
CH_2Ph (**1c**)	COOMe	$30^{d)}$	$57^{d)}$	94	>98
$SiMe_3$ (**1a**)	H	$41^{d)}$	$21^{d)}$	>98	-

a) Optical yield is determined by measurering the 500 MHz ^{1}H-NMR spetrum of (+)-MTPA ester,$^{11)}$ which is prepared by the following sequences: 1) $Mg(OMe)_2$, 2) $LiAlH_4$, 3) (+)-MTPA-Cl, pyridine, cat.DMAP.

b) Relative stereochemistry is determined by NOESY spectrum and, in the case of entry 1, X-ray crystallographic analysis is also performed.

c) The other isomer is not detected by ^{1}H NMR.

d) **5** and **6** are separated after conversion to the corresponding methyl esters.

The reaction proceeds smoothly to give the corresponding methylenecyclobutane derivatives in good yields with very high optical purities. Allenyl sulfides having not only trimethylsilyl group (**1a**) but also trimethylstannyl (**1b**) and alkyl group (**1c**) are employed. The optical purity is very high in every case examined.[12] Only a catalytic amount of the chiral titanium reagent is required for the completion of the reactions, and the products have multi functional groups, which would be amenable to a variety of useful synthetic manipulations.

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Areas (Multiplex Organic Systems) from the Ministry of Education, Science and Culture.

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7) **1a** is prepared according to the procedure of W. H. Pearson and J. Tanaka; W. H. Pearson, K. -C. Lin, and Y. -F. Poon, *J. Org. Chem.*, **54**, 5814 (1989); J. Tanaka, S. Kanemasa, and O. Tsuge, *Bull. Chem. Soc. Jpn.*, **63**, 51 (1990).

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12) The absolute configurations of the products have not been determined. According to the previous [2+2] cycloadditions,[5] however, the *re* face of the α-carbon in the acrylic acid derivatives is supposed to be attacked when the (R, R)-1,4-diol is employed as a chiral auxilary.

(Received August 30, 1990)