# THE ORIGIN OF THE REGIOSELECTIVITIES IN 1,3-DIPOLAR CYCLOADDITION OF THIOCARBONYL YLIDES GENERATED FROM BROMO(TRIMETHYLSILYLMETHYLTHIO)-METHYLTRIMETHYLSILANE AND THE RELATED COMPOUNDS[1]

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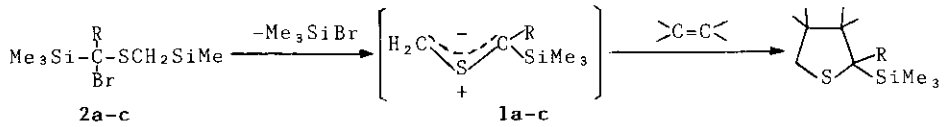
Abstract ——— The regioselectivities in 1,3-dipolar cycloaddition of thiocarbonyl ylides to methyl acrylate were found to be explained by the frontier molecular orbital theory using ab initio procedures at the STO-3G level.

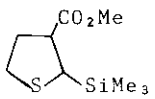
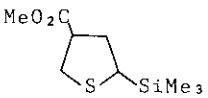
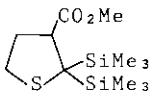
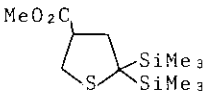
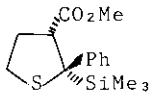
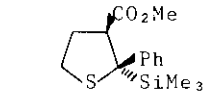
In recent years, molecular orbital calculations have been used for elucidation and prediction of organic reactions in much success. The quantitative calculations by non-empirical molecular orbital method are able to produce the reliable information for the phenomena which it is difficult to discriminate by only experiments.[2] And explaining the reactions by the qualitative modeling is also one of the effective methods.[3] The frontier molecular orbital theory is the method that represents the physical nature of molecules in organic reactions by the simplification of HOMO-LUMO interaction.[4] In previous paper, we have successfully rationalized the regio- and stereoselectivities in 1,3-dipolar cycloaddition of the intermediary azomethine ylides to conjugated dipolarophiles using the frontier molecular orbital theory from the latter viewpoint.[5]

In this paper, as a part of our continuing studies about the frontier molecular orbital consideration, we wish to discuss on the origin of the regioselectivities in 1,3-dipolar cycloaddition of the intermediary thiocarbonyl ylides (**1a-c**) generated from bromo(trimethylsilylmethylthio)methyltrimethylsilane and the related compounds (**2a-c**) as shown in Table 1.[6] This cycloaddition has just been reported by us and is a good target for molecular orbital considerations because the 1,3-dipolar cycloaddition via the simple thiocarbonyl ylides is very minor.[7] We used the geometries as shown in Table 2. The bond lengths and angles of the

Table 1. 1,3-Dipolar Cycloaddition *via* Thiocarbonyl Ylides

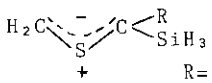


**2a-c** **1a-c**

| Substrate No. | R | Dipolarophile | Product[a] | Total yield (%) | Regioselectivity (%) |
|---|---|---|---|---|---|
| **2a** | H | $H_2C{=}CHCO_2Me$ **3** |  **4a**(3)  **4b**(1) | 52 | 75 |
| **2b** | $SiMe_3$ | **3** |  **5a**(7)  **5b**(6) | 46 | 54 |
| **2c** | Ph | **3** |  **6a**(5)  **6a'**(2) | 72 | 100 |

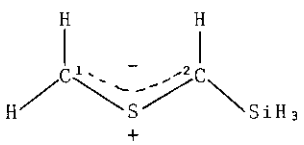
a. Ratio of the isomers is described in parentheses.

Table 2. Geometrical Parameters[a] of Thiocarbonyl Ylides

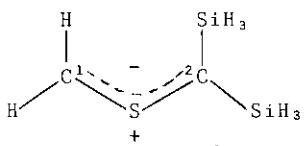
| Molecule | Bond lengths (AB, Å) | | Bond angles (ABC°) | |
|---|---|---|---|---|
|  R= H, $SiH_3$, Ph | CS 1.634 | CH 1.070 | CHS 119.8 | CSC 109.3 |
| | SiC 1.889 | SiH 1.485 | HSiH 108.3 | |

a. In other parts, the standard values were used.

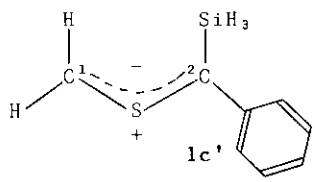
Table 3. The Energy Levels and LCAO Coefficients on the Frontier Molecular Orbitals (**1a'-c'**)



**1a'**



**1b'**



**1c'**

| Thiocarbonyl ylide No. | | Energy level (eV) | LCAO coefficients 1 | 2 |
|---|---|---|---|---|
| **1a'** | LUMO | 5.31 | 0.6261 | 0.6075 |
| | HOMO | -4.01 | 0.7085 | -0.6981 |
| **1b'** | LUMO | 5.33 | 0.6315 | 0.5805 |
| | HOMO | -3.82 | 0.7002 | -0.6919 |
| **1c'** | LUMO | 5.22 | 0.6162 | 0.6034 |
| | HOMO | -4.05 | 0.7112 | -0.6826 |

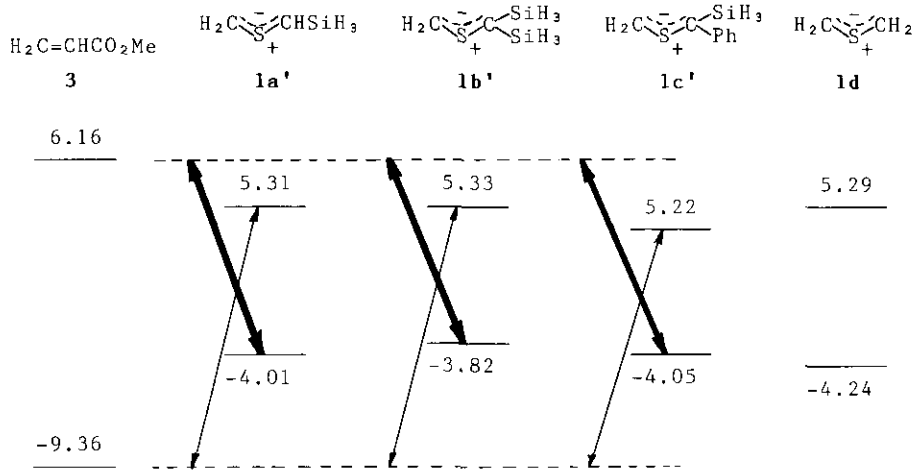



Fig. 1. The Frontier Orbital Energies of Thiocarbonyl Ylides and Methyl Acrylate. The thick arrows indicate the more favorable interactions between HOMO and LUMO.

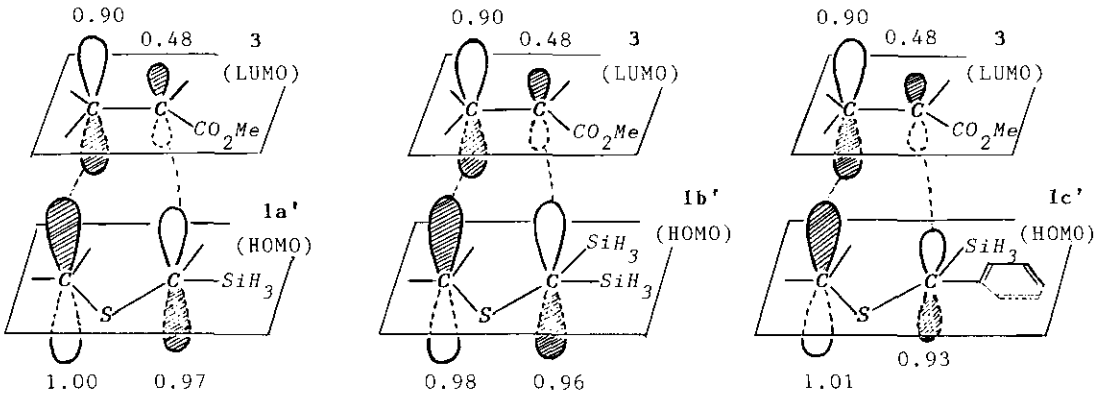



Fig. 2. The Frontier Molecular Orbital Interaction between Thiocarbonyl Ylides and Methyl Acrylate. The numerals beside the lobes indicate the frontier electron densities.

dipole part are the values optimized fully at the STO-3G level about the non-substituted thiocarbonyl ylide (**1d**) and those of the silyl group are the experimental values by microwave spectrum and electron diffraction.[8] And we adopted the STO-3G base of the minimal basis set in ab initio molecular orbital calculations.[9] The minimal basis sets are unsuitable for the quantitative calculations, but are appropriate to the frontier molecular orbital calculations.[10] The calculated results of monosilyl, disilyl, phenyl-silyl substituted thiocarbonyl ylides (**1a'**, **1b'**, **1c'**)[11] and methyl acrylate (**3**) are indicated in Table 3 and Fig. 1. All three reactions are controlled by HOMO of dipoles because of the slight instabilization of

the dipoles' HOMO energy by the electron donating silyl group and the lowering of the dipolarophiles' LUMO energy by the electron withdrawing ester group.[12] The secondary substituents, silyl and phenyl groups in **1b'** and **1c'**, respectively, have only the weak effect on the frontier molecular orbital energies. Fig. 2 shows the interaction between the dipoles **1a'-c'** and the dipolarophile **3**, and proves successfully the fact that the main product in the 1,3-dipolar cycloaddition of **1a** with **3** was 2,3-disubstituted tetrahydrothiophene. And then production of 2,4-disubstituted one as a minor product can be explained by the calculated results that the frontier electron density of the dipole carbon atom (C-2) in the silyl-substituted termini is nearly equal to that of the dipole carbon atom (C-1) in the other termini. The interactions of **1b'** with **3** and **1c'** with **3** are the same as that of **1a'** with **3**, which also proves that 2,3-disubstituted tetrahydrothiophenes (**5a**, **6a**, and **6a'**) were mainly obtained in the reactions of **1b** with **3** and **1c** with **3** (see Fig. 2). The regioselectivity in the reaction of **1b** and **3** is lower than one in the reaction of **1a** and **3** because the difference of the frontier electron densities on the two dipole termini of **1b'** is smaller than one of **1a'**. The reaction of **1c** and **3** proceeds regioselectively because the difference of the frontier electron densities on the two dipole termini of **1c'** is enough large in comparison with that of **1a'** and **1b'**.

It should be noted that the regioselectivities in 1,3-dipolar cycloaddition via the thiocarbonyl ylides (**1a-c**) is explained by the frontier molecular orbital consideration. Further investigation in this area is under way.

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