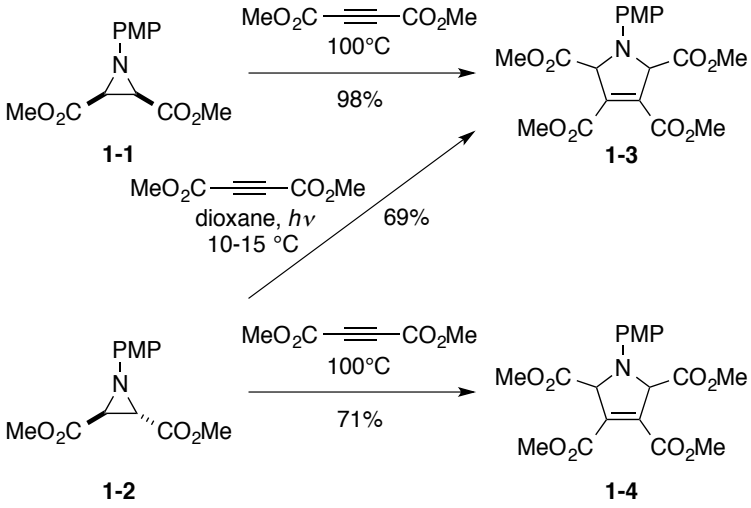
Problem Session (5)

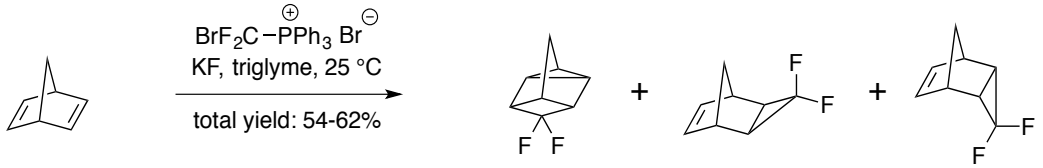
2015. 5. 9 Shunichiroh Katoh

Answer the questions below **considering orbital symmetry.**

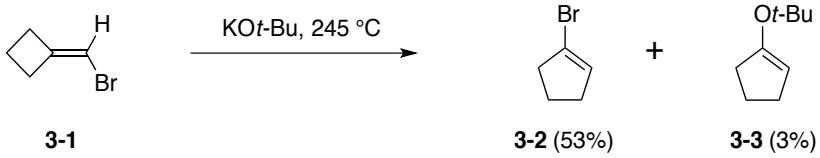
(1) Provide the reaction mechanism and predict the stereochemistries of **1-3** and **1-4**.

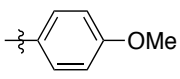


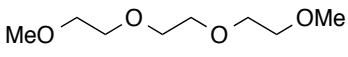
(2) Provide the reaction mechanism.



(3) Provide the reaction mechanism.



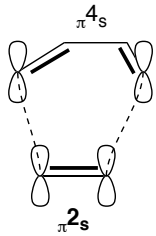
PMP = 

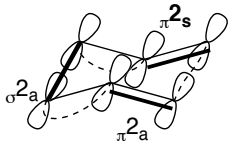
triglyme = 

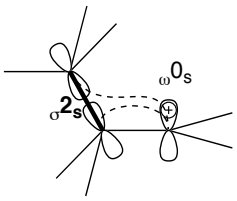
Problem Session (5) - Answer

2015. 5. 9. Shun-ichiroh Katoh

Main Topic : Orbital symmetry and Woodward-Hoffmann rules







0. Introduction

0.1. Woodward-Hoffmann rules

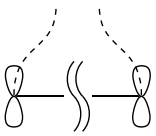
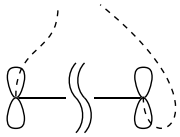
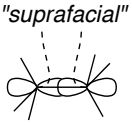
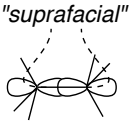
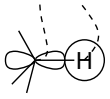
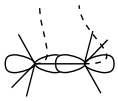
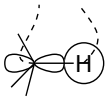
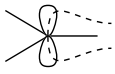
A useful rule to predict the stereochemistries of *all* pericyclic reactions, described in the following.

"A ground-state pericyclic change is symmetry-allowed when the total number of $(4q+2)_s$ *and* $(4r)_a$ *components is odd."* [1)]

⇩

And the others are allowed in exited-state pericyclic change

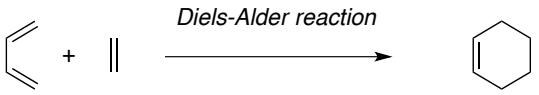
0.1.1. "Components" of pericyclic reaction:

conjugated π system	*"suprafacial"* 	*"antarafacial"* 
σ bond	*"suprafacial"*  *"suprafacial"*  *"suprafacial"* 	*"antarafacial"*  *"antarafacial"* 
non-bonding lone pare, anion or cation as "ω"	*"suprafacial"* 	 *"antarafacial"*

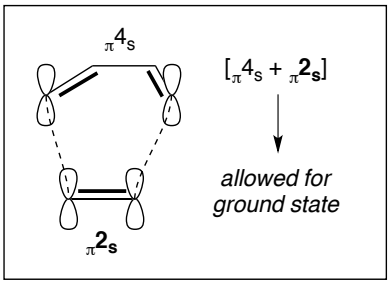
1) Woodward, R. B.; Hoffmann, R. *Angew. Chem. Int. Ed.* **1969**, *8*, 781.

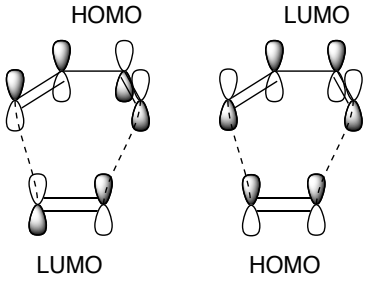
0.2. Examples of pericyclic reaction

0.2.1. Diels-Alder reaction

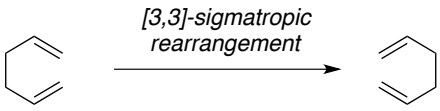


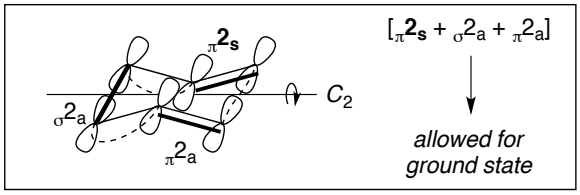
* Components which react in $(4q+2)_s$ or $(4r)_a$ manner are indicated by **boldface**.

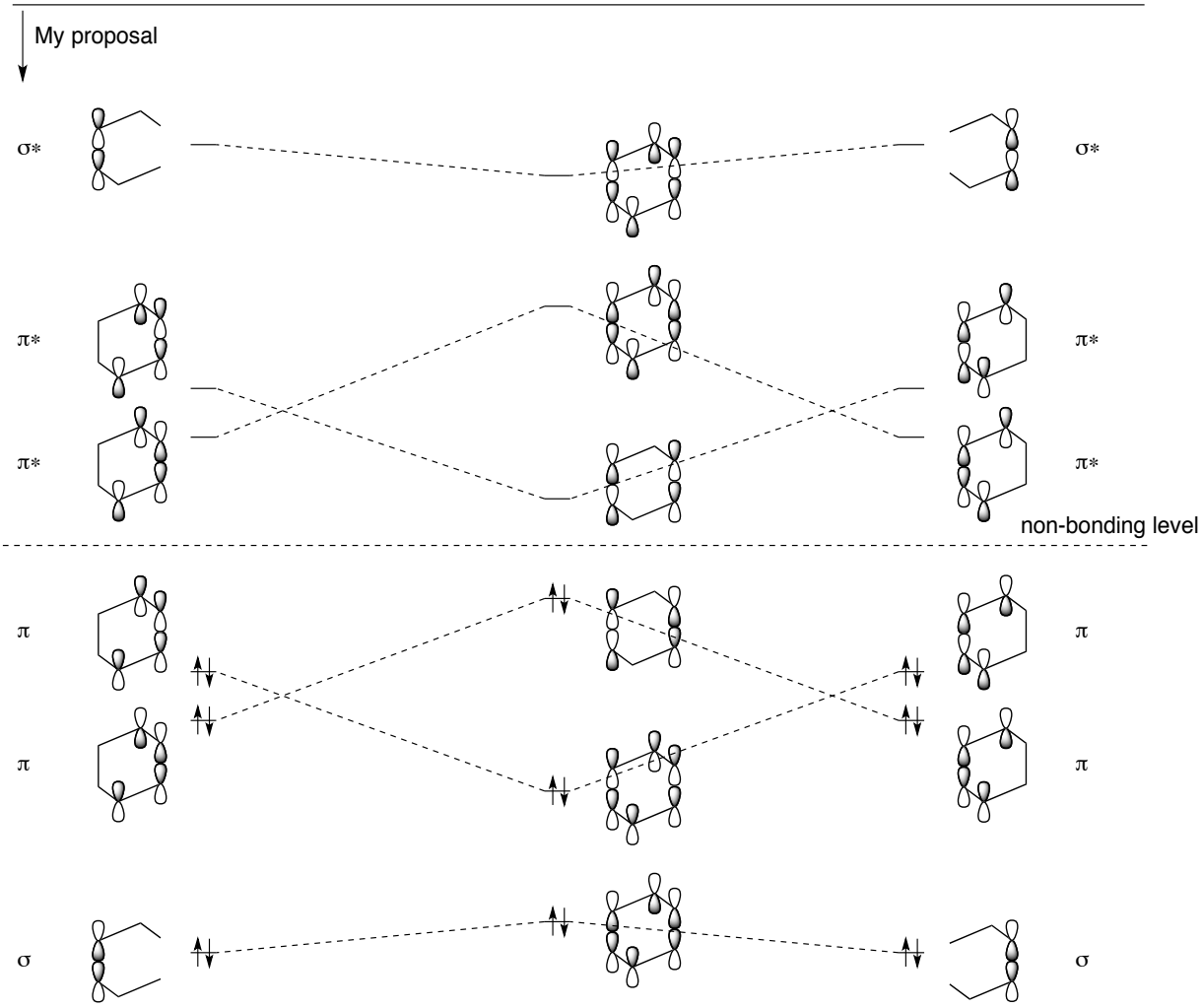




0.2.2. [3,3]-sigmatropic rearrangement

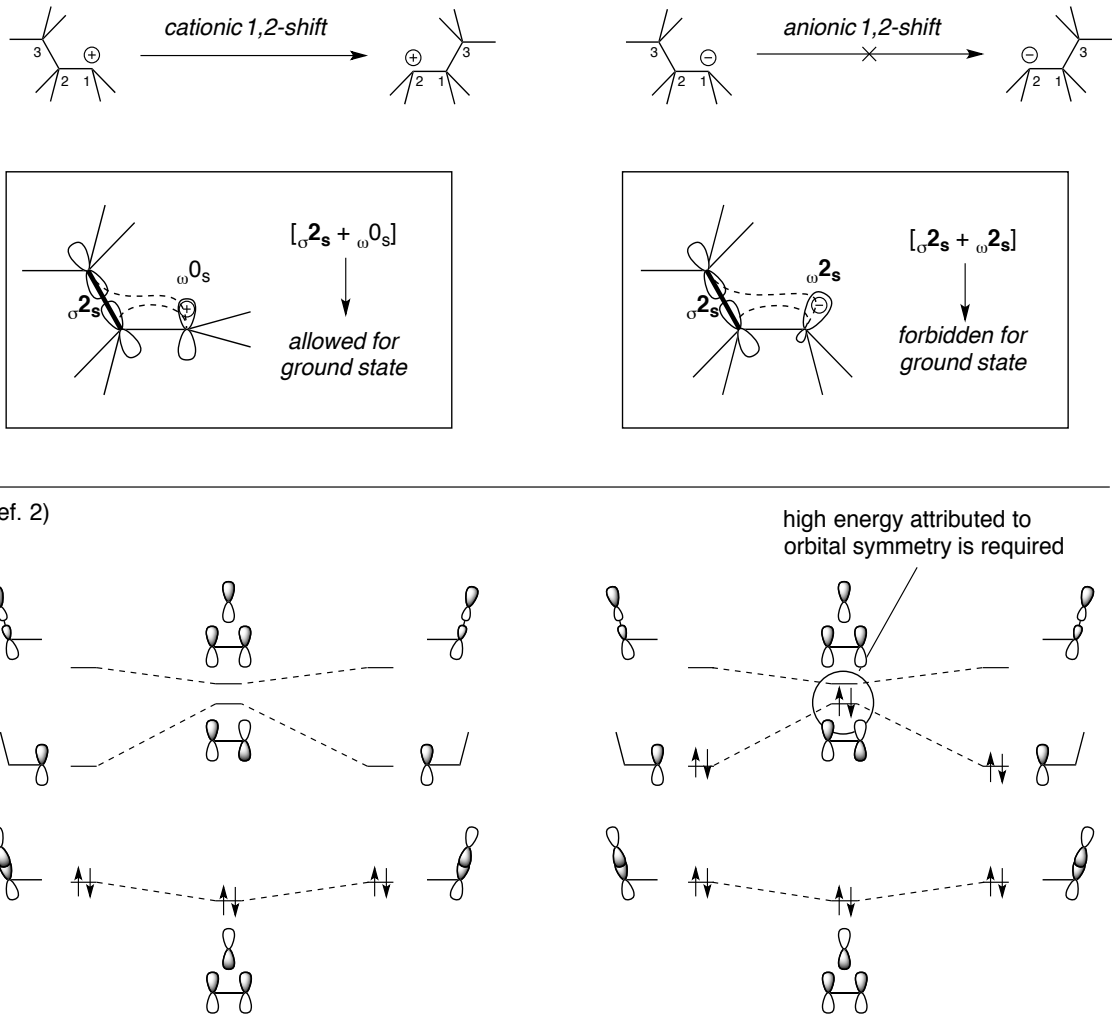






[3,3]-sigmatropic rearrangement can proceed without surpassing the non-bonding level.

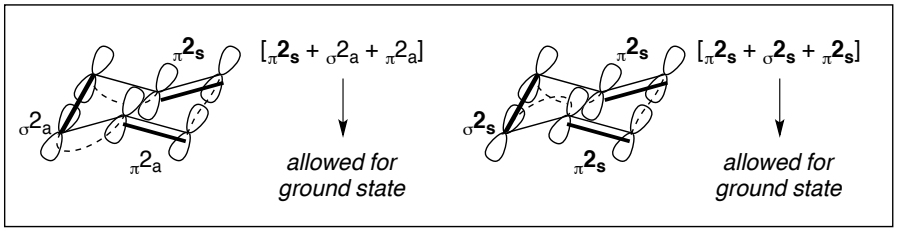
0.2.3. Cationic/anionic 1,2-shift (which are included in pericyclic reaction)



0.3. A few words of caution

a) **<u>Woodward-Hoffmann rules are applicable only for pericyclic reaction.</u>**

b) Sometimes, the same reaction can be classified in several patterns, but the result, allowed or forbidden, is always the same.



c) This rule only indicates the energy barrier attributed to orbital symmetry, not the total energy barrier.

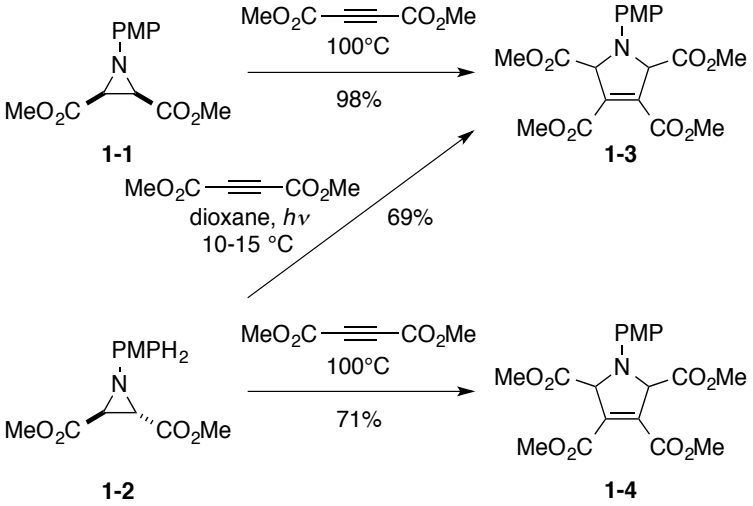
⇩

Some pericyclic reactions are *allowed* by Woodward-Hoffmann rules, but physically impossible.

d) Evin if some reaction was classified as *"allowed"*, that is not necessarily concerted reaction.

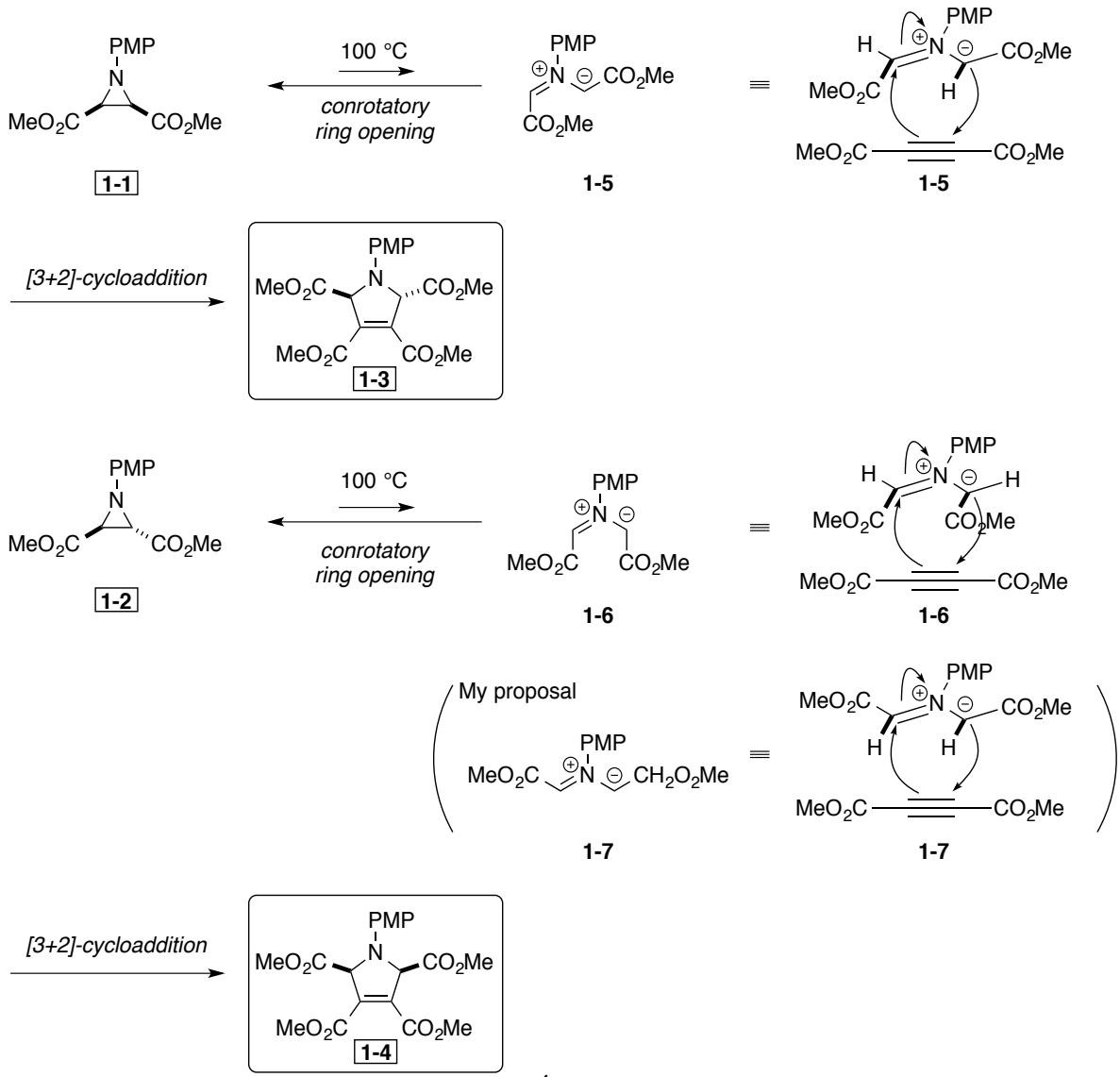
2) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393.

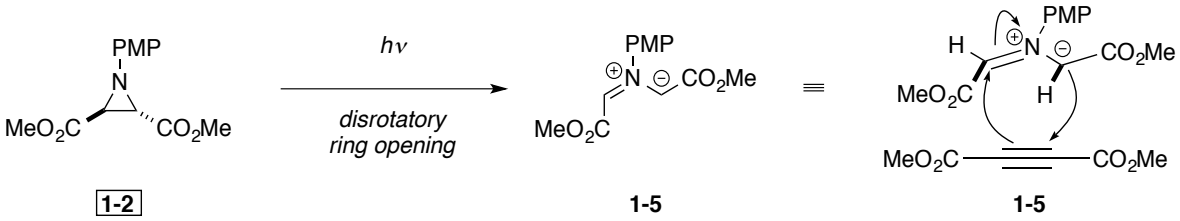
(1) Provide the reaction mechanism and predict the stereochemistries of **1-3** and **1-4**.



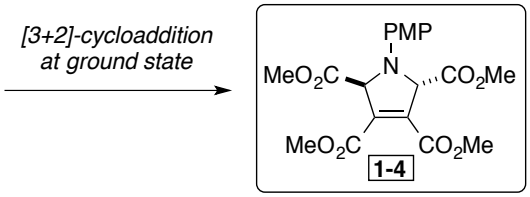
Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753.

1.1. Answer



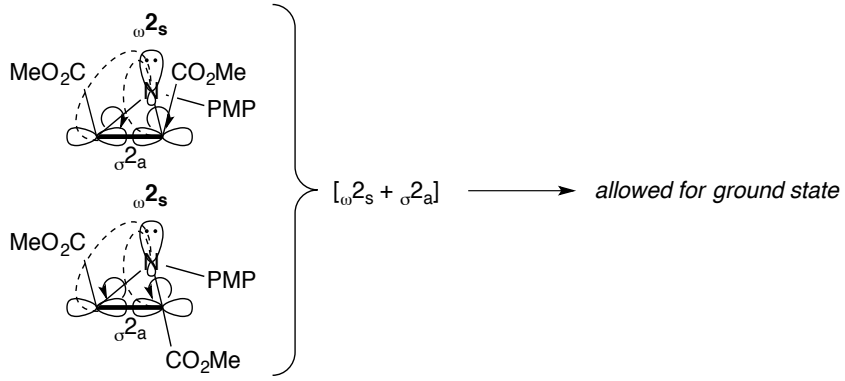


1-2 **1-5** **1-5**

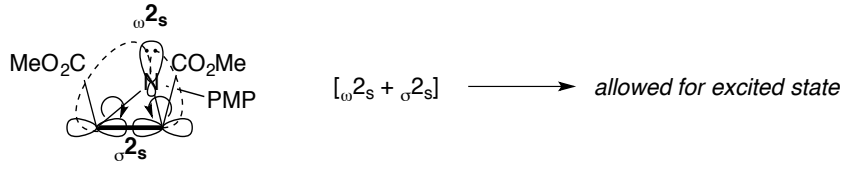


Opening of aziridine at ground state / excited state

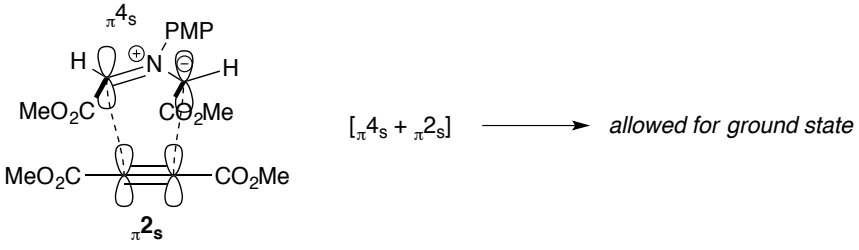
Conrotatory opening:



Disrotatory opening:

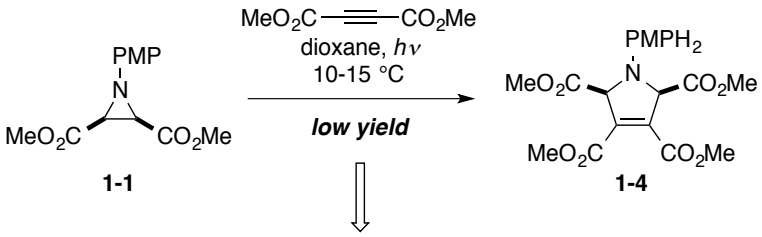


[3+2]-cycloaddition



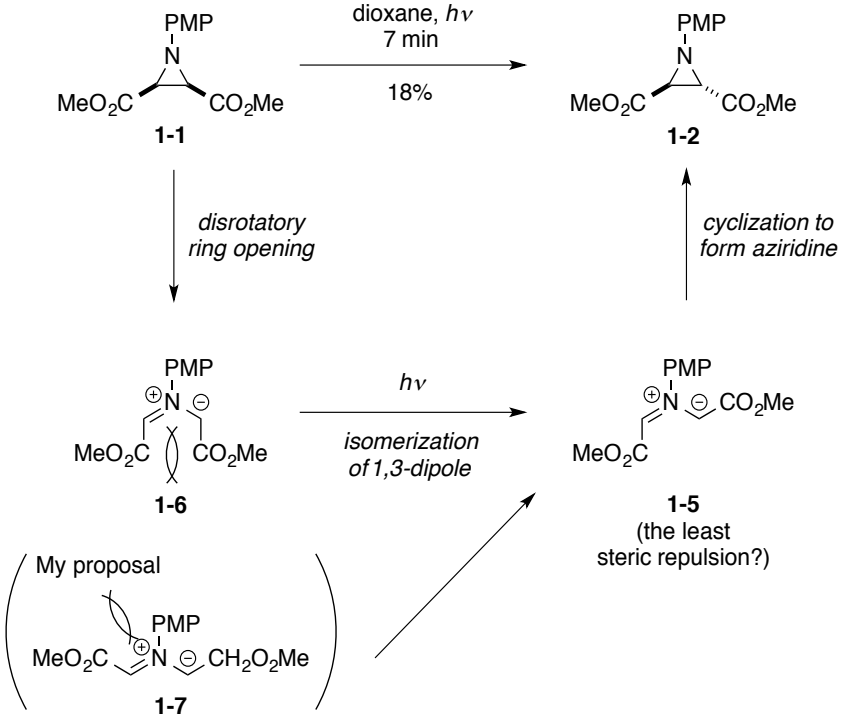
1.2. Appendix

Photoreaction of **1-2**

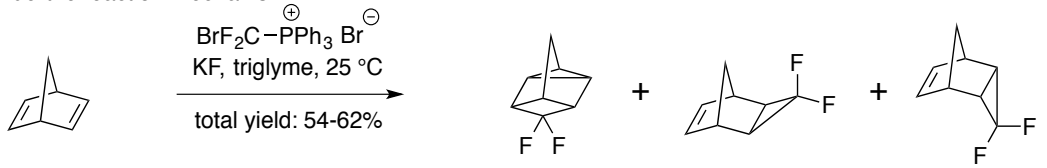


Isomerization of 1,3-dipole, shown below, or non-selective cyclization via biradical should be the reason of low yield.

Isomerization of 1,3-dipole



(2) Provide the reaction mechanism.

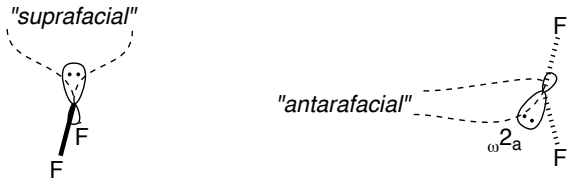


2-1 **2-2** (34%) **2-3** (55-62%) **2-4** (4-11%)

Jefford, C. W.; Mareda, J.; Gehret, J.-C. E.; Kabengele, n.; Graham, W. D.; Burger, U. *J. Am. Chem. Soc.* **1976**, *98*, 2585.

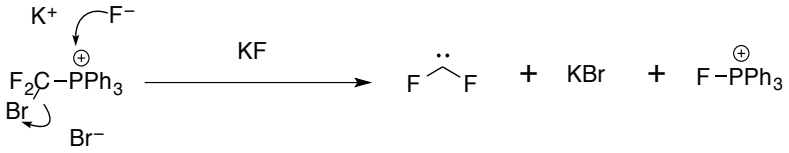
2.1. Introduction

Carbene reacts in suprafacial or antarafacial manner.

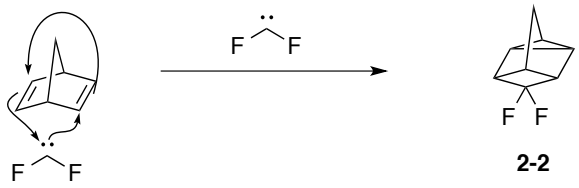


2.2. Answer

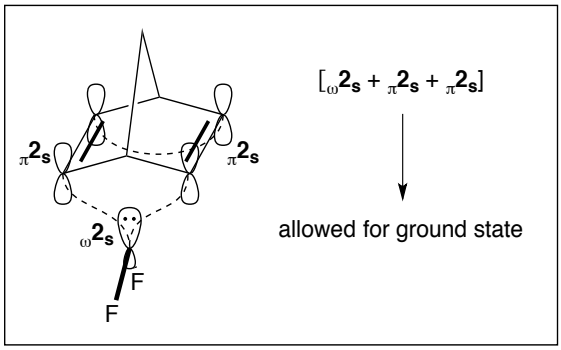
2.2.1. Generation of difluorocarbene

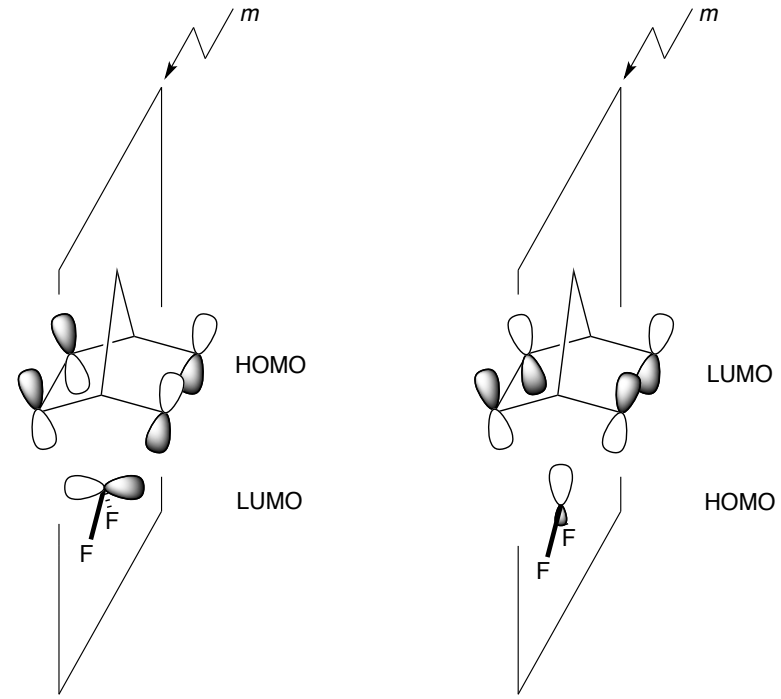


2.2.2. Mechanism for **2-2**



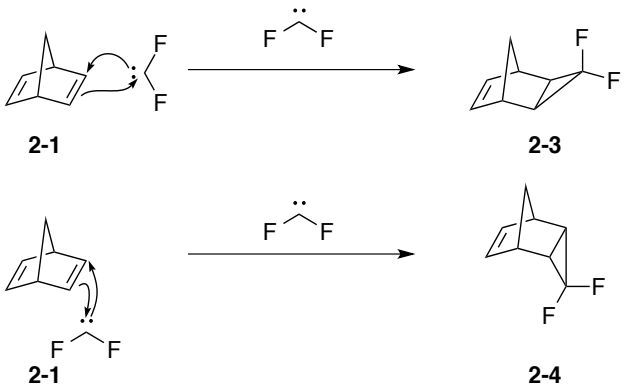
2-1 **2-2**

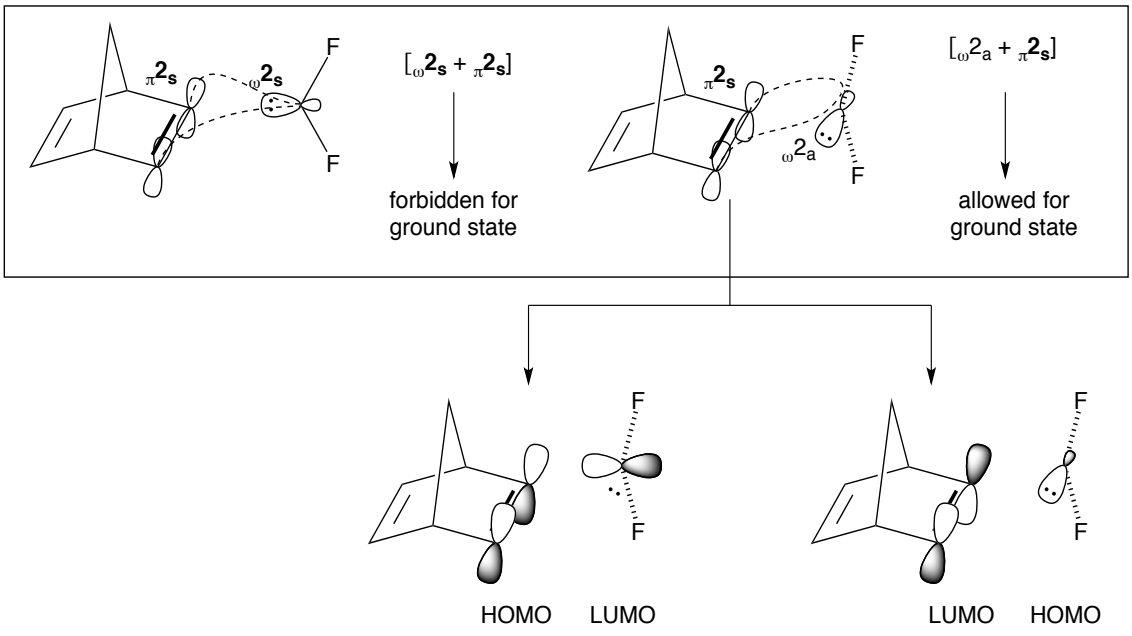




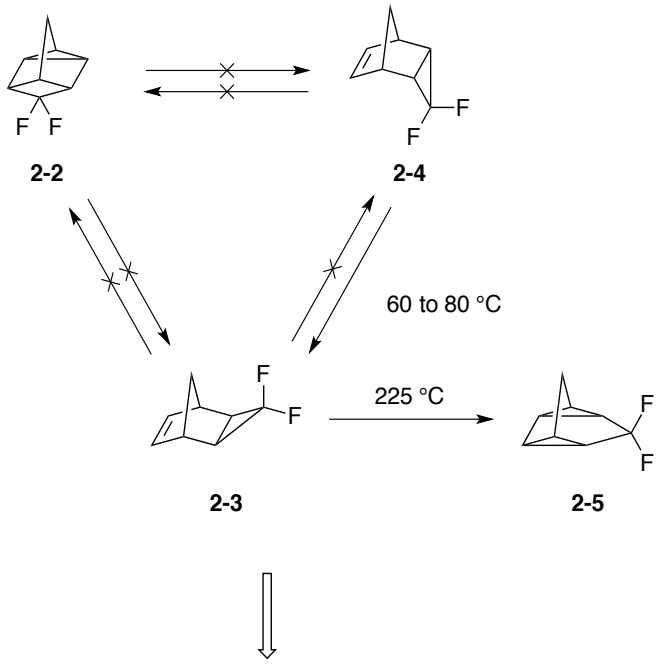
antisymmetric for "m" *symmetric for "m"*

2.2.3. Mechanism for **2-3** and **2-4**





2.2.4. Possibility of interconversion between **2-2**, **2-3** and **2-4**

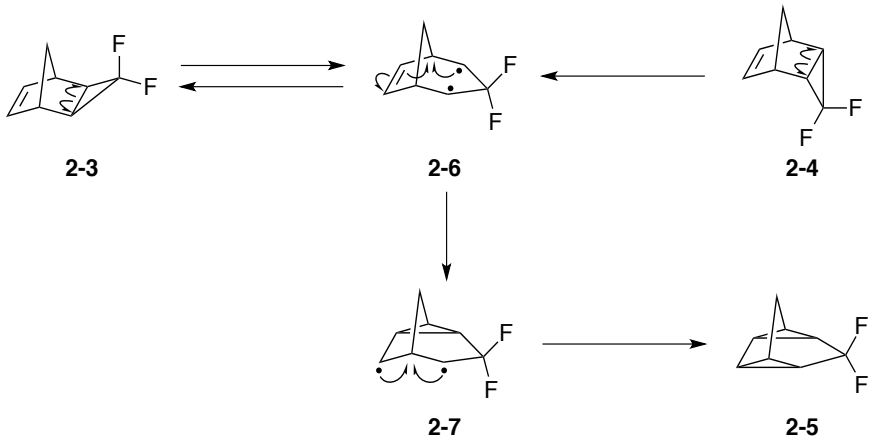


2-2 **2-4**

2-3 **2-5**

This result indicates that **2-2** and **2-4** were generated directry from **2-1**.

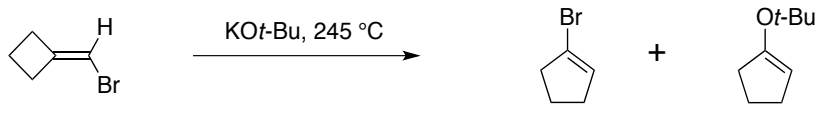
Proposed mechanism:



2-3 **2-6** **2-4**

2-7 **2-5**

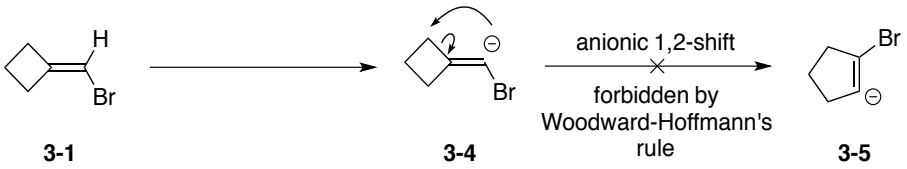
(3) Provide the reaction mechanism.



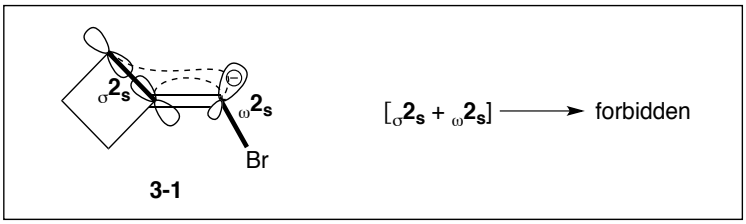
3-1 **3-2** (53%) **3-3** (3%)

Samuel, S. P.; Niu, T.-q.; Erickson, K. L. *J. Am. Chem. Soc.* **1989**, *111*, 1429.

3.1. Introduction



3-1 **3-4** **3-5**



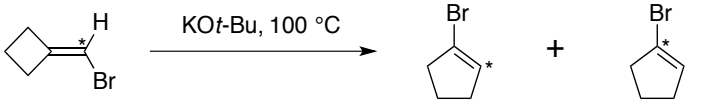
3-1

⇩

Another mechanism should be concerned.

3.2. Answer:

3.2.1. Labeling experiment

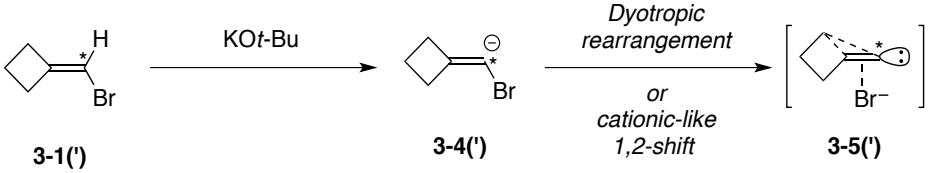


3-1' **3-2'** (14%) **3-2''** (10%)

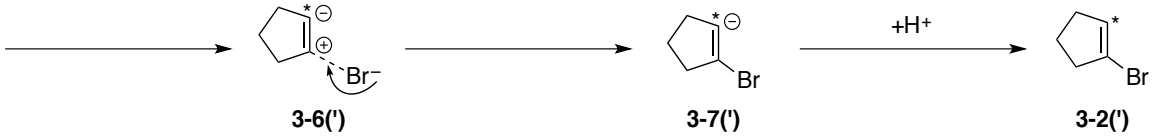
⇩

Two reaction mechanisms, "Beckmann mechanism" and "rehybridization mechanism" should be involved.

3.2.2. *"Beckmann Mechanism"*

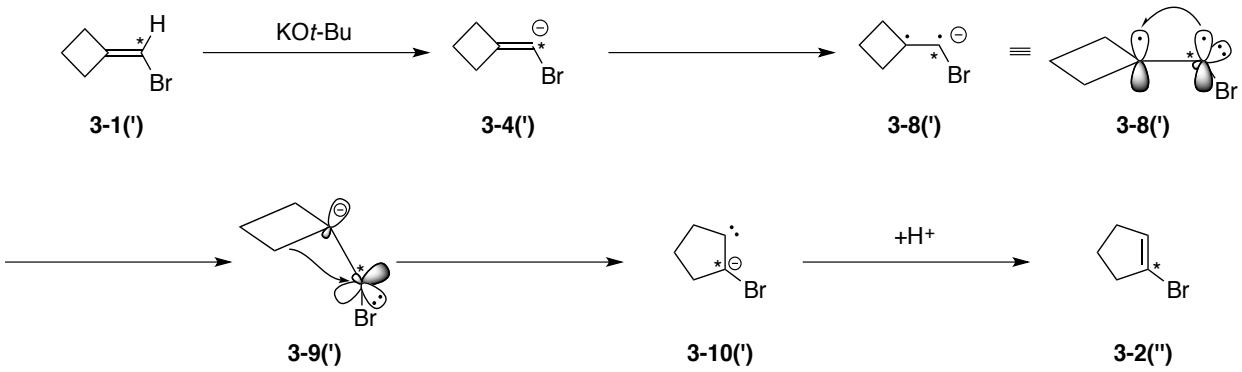


3-1(') **3-4(')** **3-5(')**



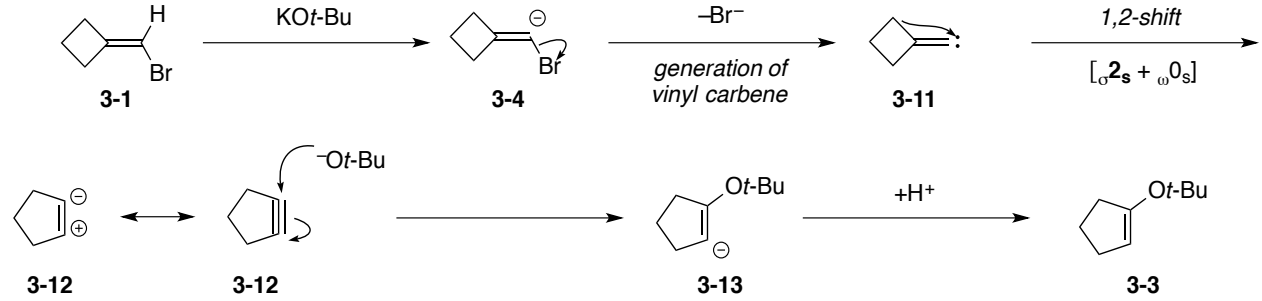
3-6(') **3-7(')** **3-2(')**

3.2.3. *"Rehybridization mechanism"*



3-1(') **3-4(')** **3-8(')** **3-8(')** **3-9(')** **3-10(')** **3-2(")**

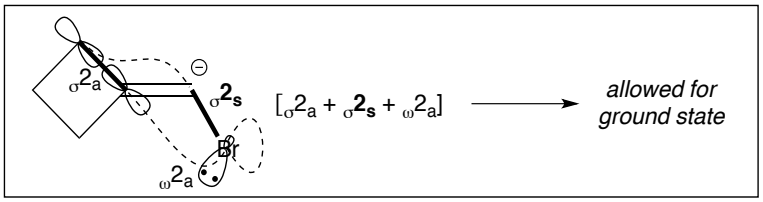
3.2.4. For by-product **3-3**

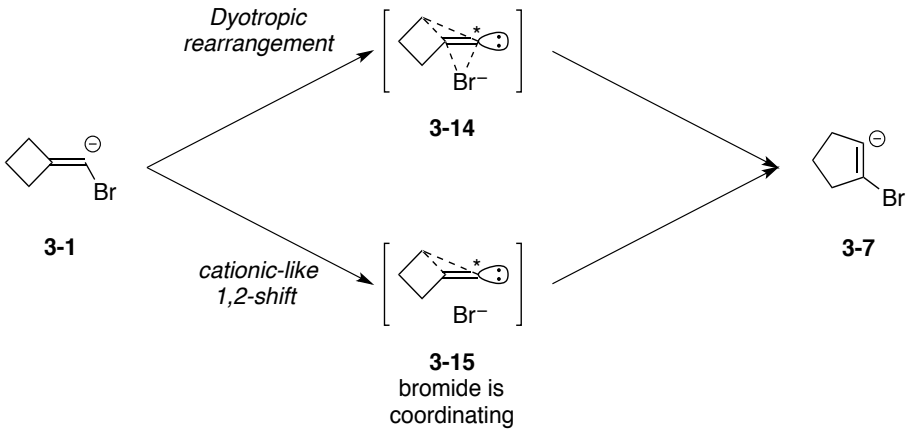


3-1 **3-4** **3-11** **3-12** **3-12** **3-13** **3-3**

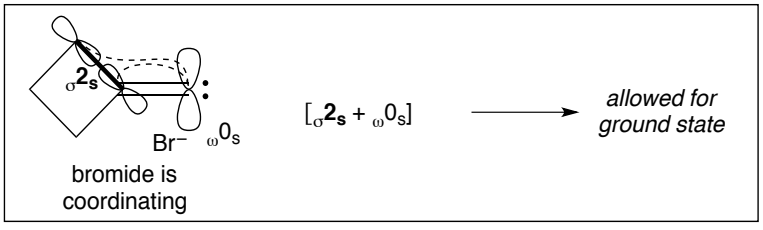
3.3. Discussion

3.3.1. "Beckmann-mechanism"

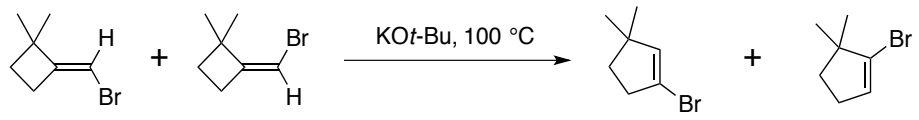




3-1 **3-14** **3-7** **3-15**
bromide is coordinating

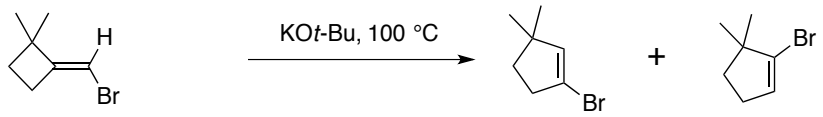


3.3.2. Complete carbene is not feasible[3)]



3-16 **3-17** **3-18** **3-19**

ratio = 1 : 1 ratio = 2.2 : 1

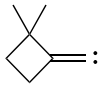


3-16 **3-18** **3-19**

ratio = 16 : 1

⇩

These results suggests that the intermediate keeps the stereochemistry. In other words, complete carbene (**3-20**) is not a feasible intermediate for cyclopentenyl bromide (**3-18** or **19**).



3-20

3) Erickson, K. L. *J. Org. Chem.* **1971**, *36*, 1031.