

# The Tri- $\pi$ -Methane Rearrangement

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**Zimmerman, Howard E.\***

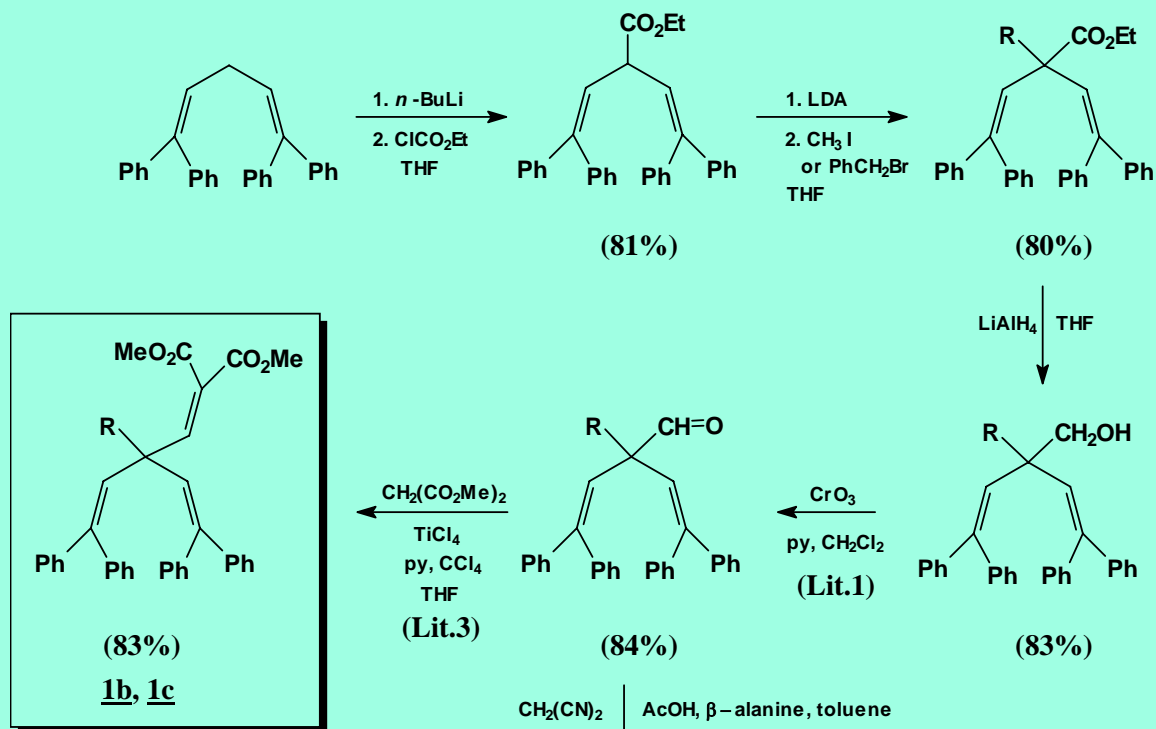
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# INTRODUCTION

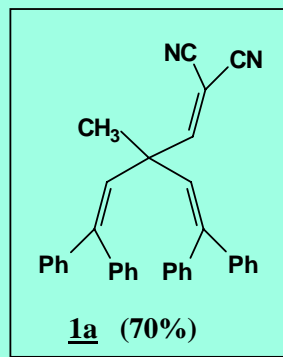
The tri- $\pi$ -methane rearrangement was discovered in 1989 (*H. E. Zimmerman, M. J. Zuraw*) when has been realized that the photolysis of reactant 1a having three vinyl moieties bonded to an  $sp^3$ -hybridized carbon led to formation of a cyclopentene 5a, but only in crystalline medium. However, in the solution photochemistry of tri- $\pi$ -methane system 1a only cyclopropanes 2a-4a as the usual di- $\pi$ -methane products were observed.

The our aims of investigation are tri- $\pi$ -methane systems 1b, 1c having a carbomethoxy unit. The present study is focussed on general photochemical and thermal reactivity of these tri- $\pi$ -methane systems.

# Syntheses of the Tri- $\pi$ -Methane Systems 1a-1c

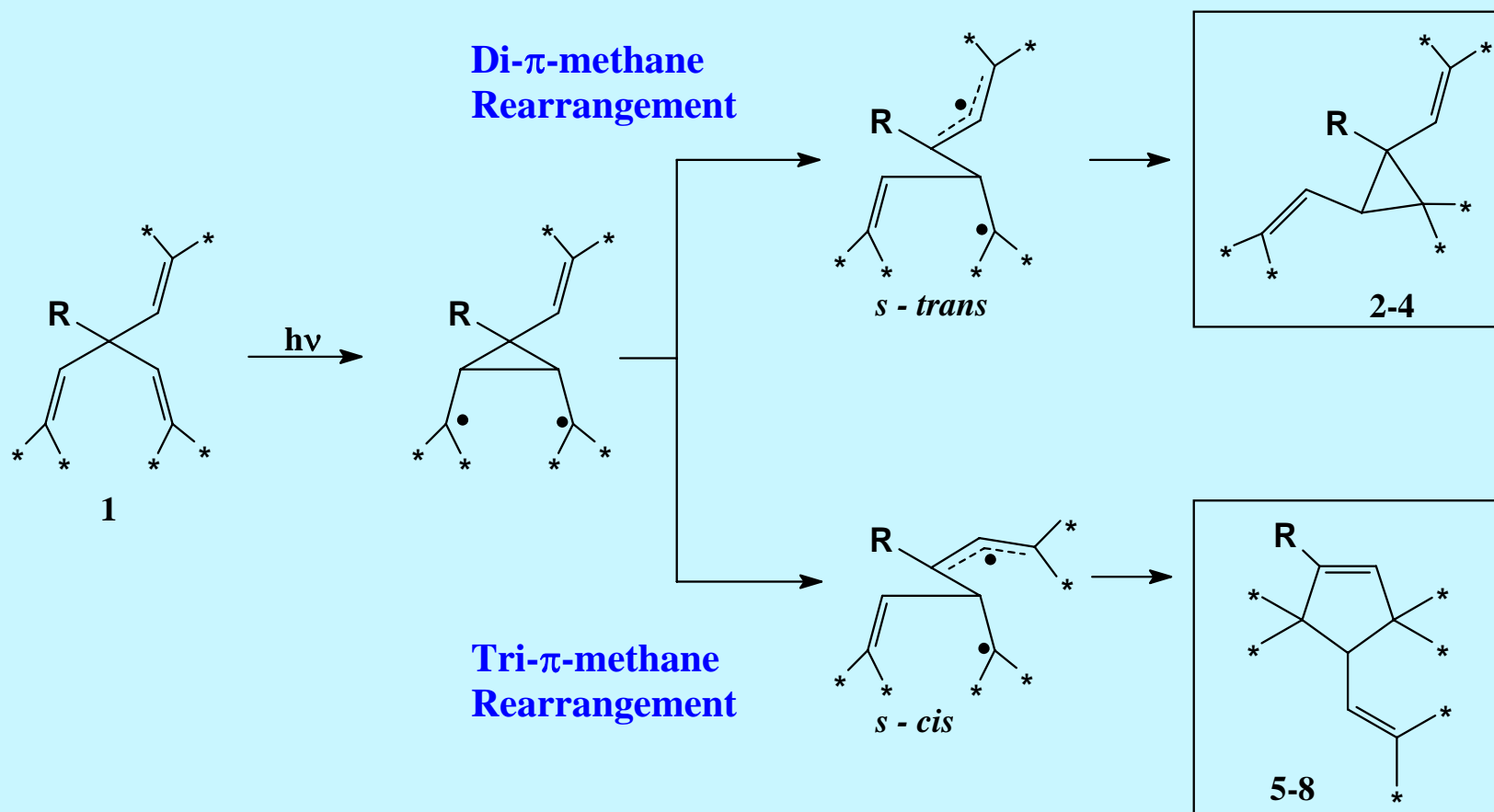


R = CH<sub>3</sub>, CH<sub>2</sub>Ph

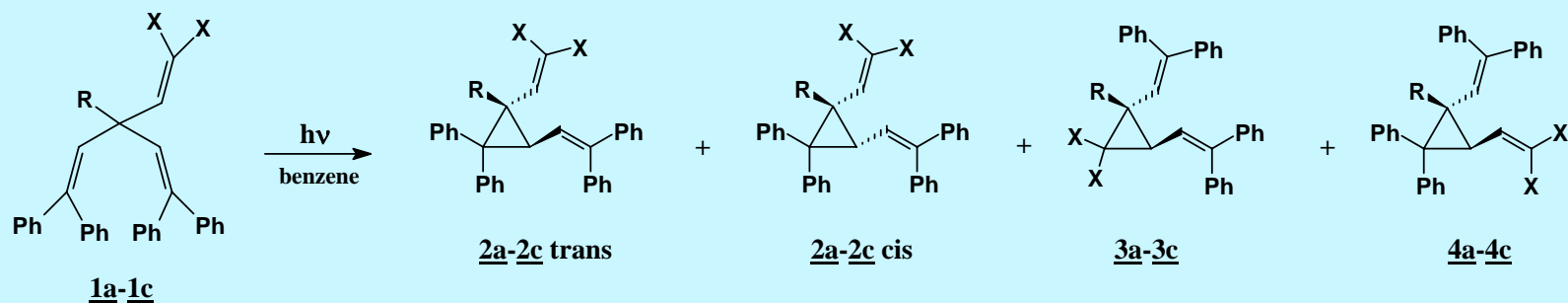


- (1) Mong, G. *MS Thesis*, UW-Madison, 1979.  
 (2) Zimmerman, H.E.; Zuraw, M.J. *J. Am. Chem. Soc.* 1989, *111*, 7974-7989.  
 (3) Lehnert, W. *Tetrahedron* 1973, *29*, 635-638.

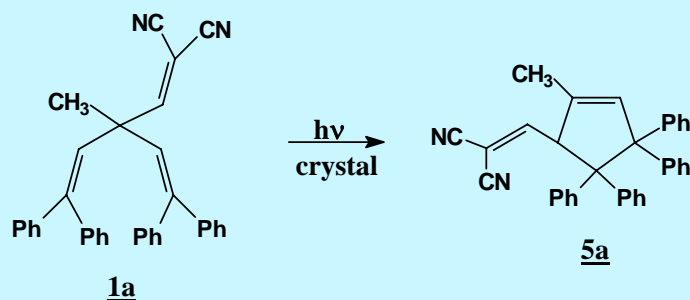
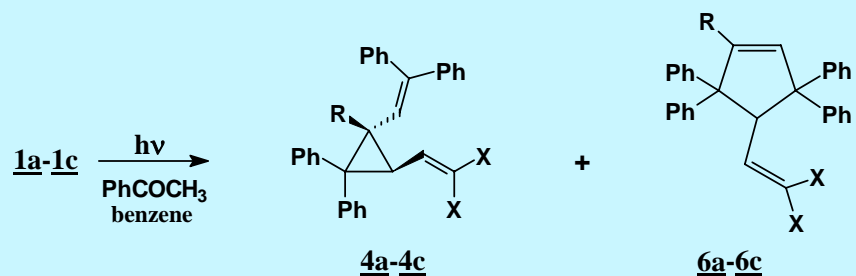
# Di- $\pi$ -Methane vs. Tri- $\pi$ -Methane Rearrangement



# Photochemical Di- $\pi$ - and Tri- $\pi$ -Methane Rearrangements

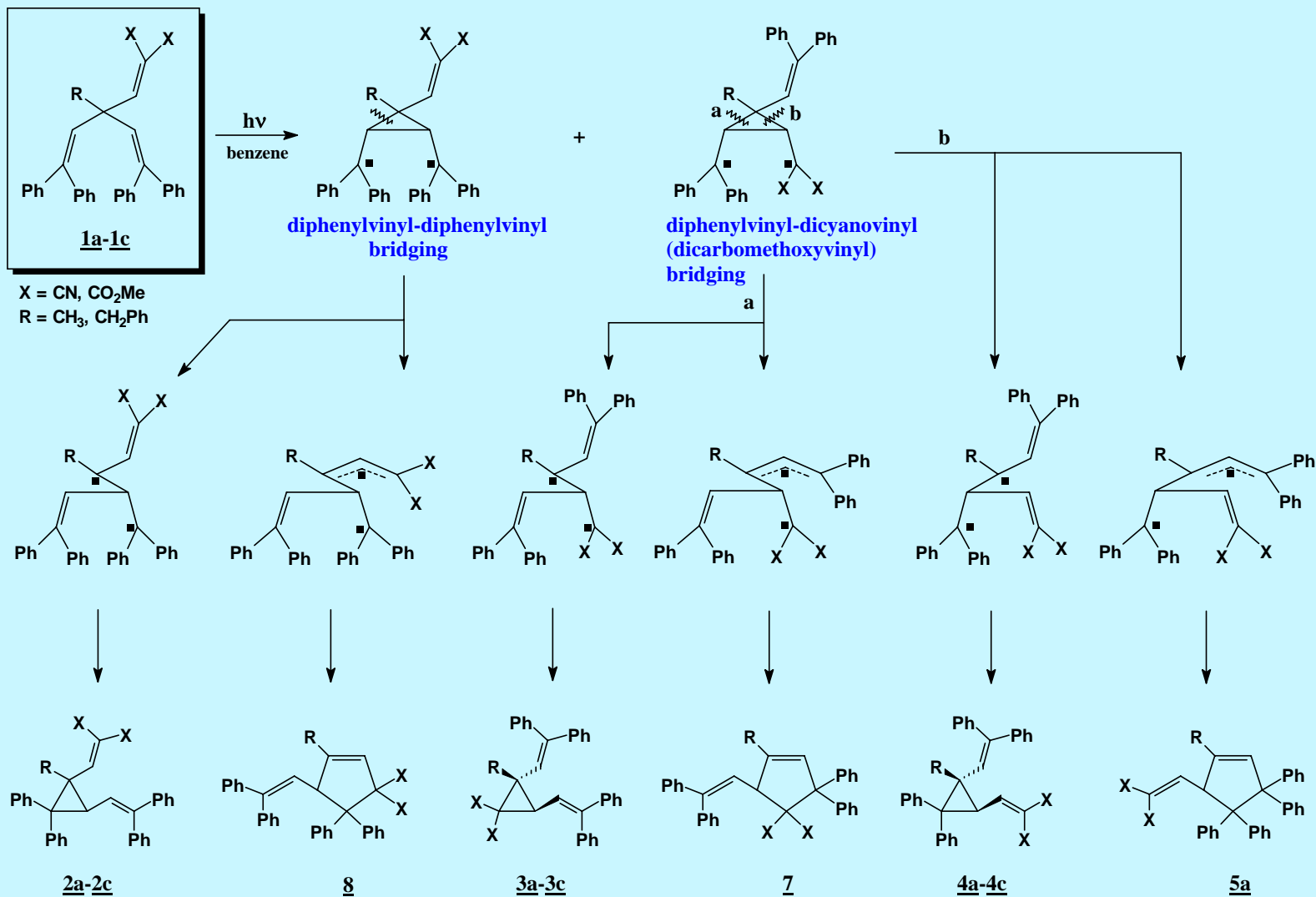


X = CN, CO<sub>2</sub>Me  
R = CH<sub>3</sub>, CH<sub>2</sub>Ph

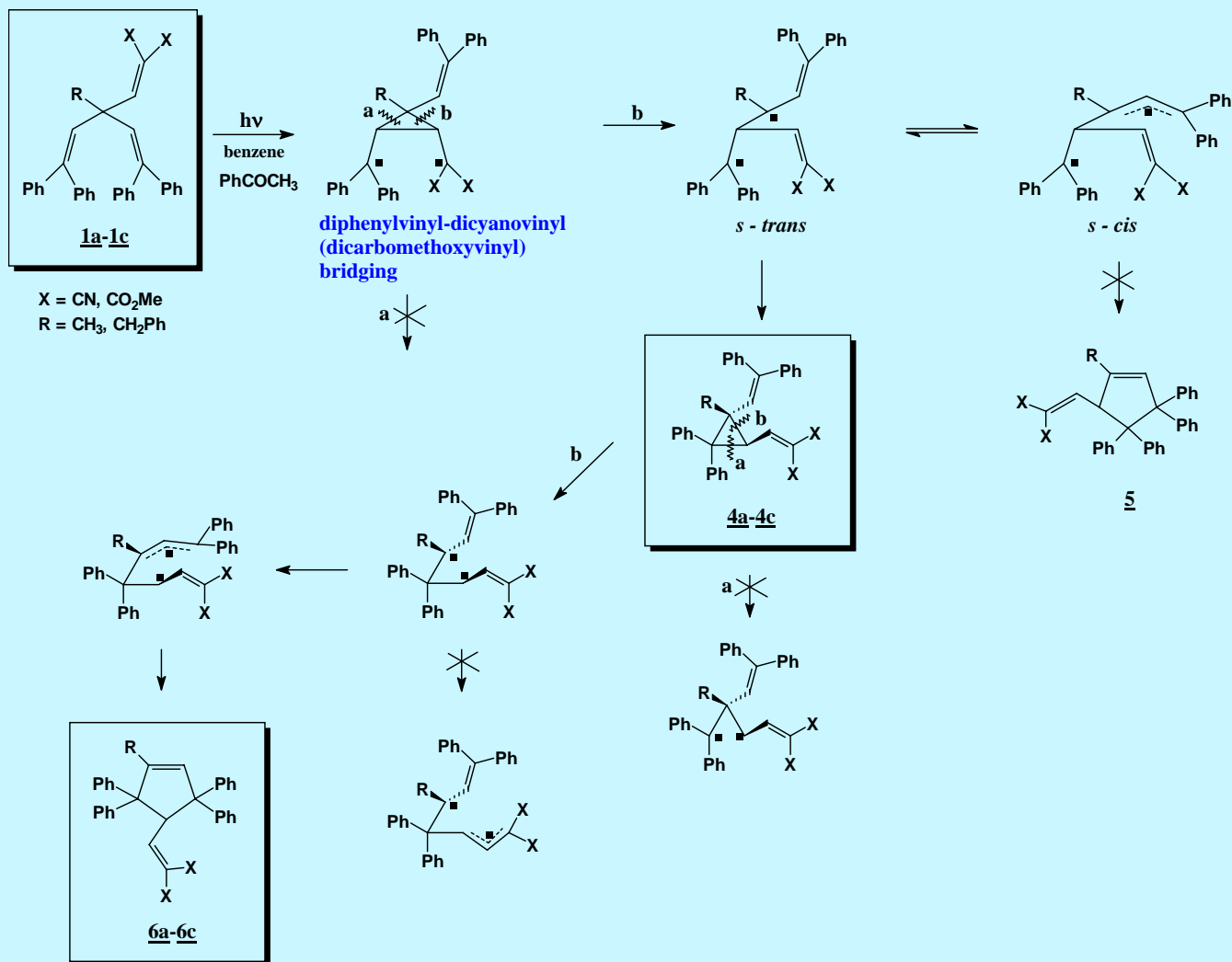


(1b - oil, 1c - unreactive)

# Mechanism of Exploratory **Direct** Photolysis of Tri- $\pi$ -Methane Systems 1a-1c

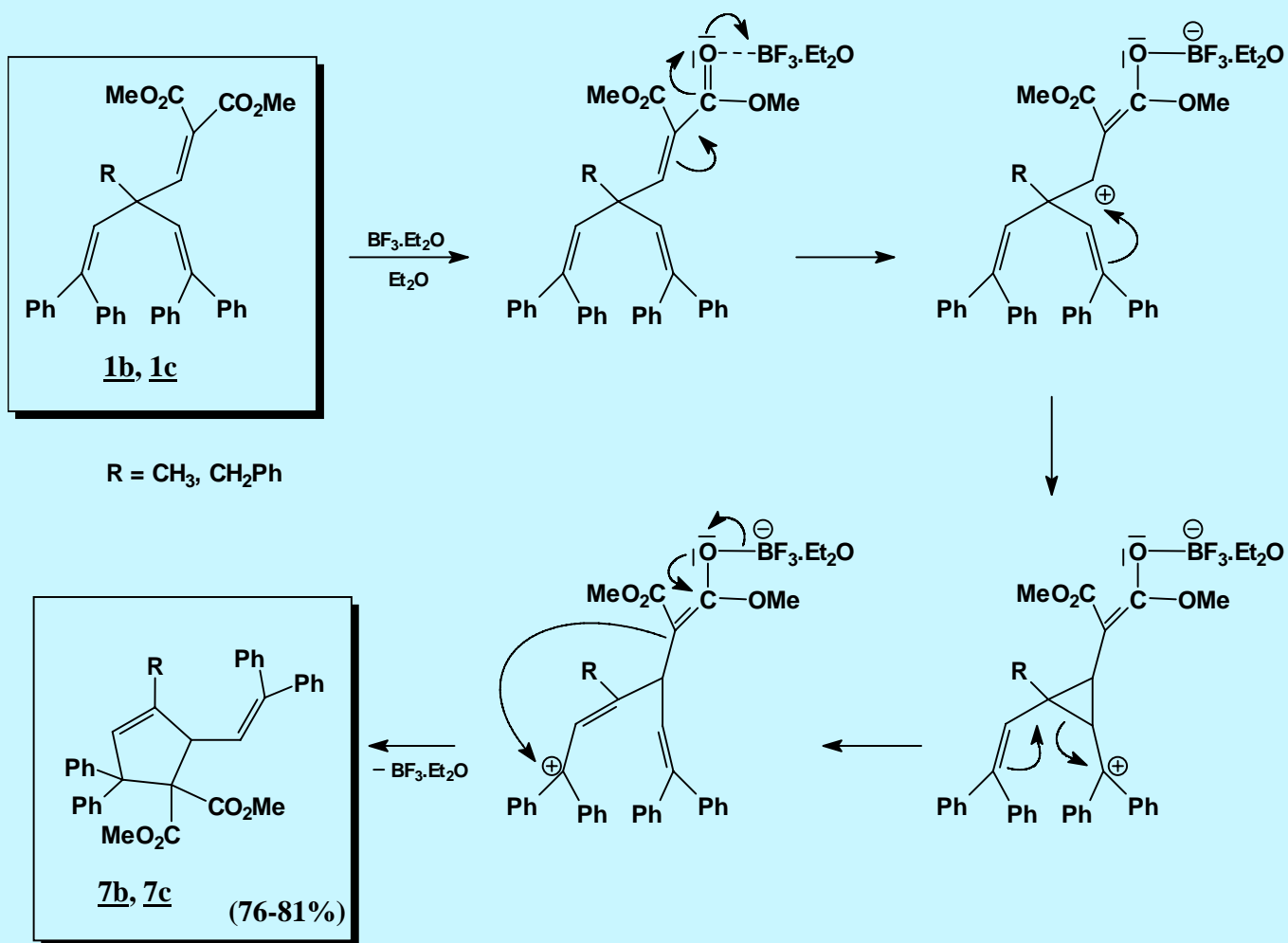


# Mechanism of Exploratory **Sensitized** Photolysis of Tri- $\pi$ -Methane Systems 1a-1c





# Tri- $\pi$ -Methane Rearrangement without Light



# CONCLUSION

- 1) The **direct solution photolysis** of tri- $\pi$ -methane systems 1a-1c led only to the vinyl cyclopropanes 2-4 as usual di- $\pi$ -methane products.
- 2) We are pursuing a search on the **photolysis in crystalline medium** for further examples of tri- $\pi$ -methane systems 1.
- 3) The **sensitized photolysis** of tri- $\pi$ -methane systems 1a-1c led to discovery of a new rearrangement of vinyl cyclopropanes 4a-4c to cyclopentenenes 6a-6c.
- 4) The tri- $\pi$ -methane rearrangement **without light** catalyzed by Lewis-acid led to another type of cyclopentenenes 7b, 7c.