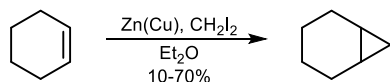
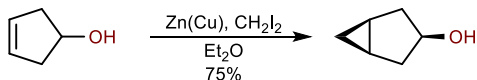


Historical Development

- Simmons and Smith (1958)

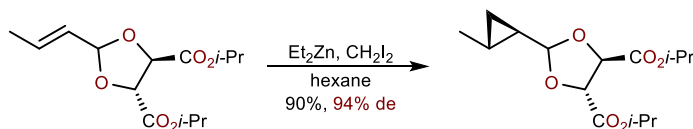


- Winstein and Sonnenburg (1961)



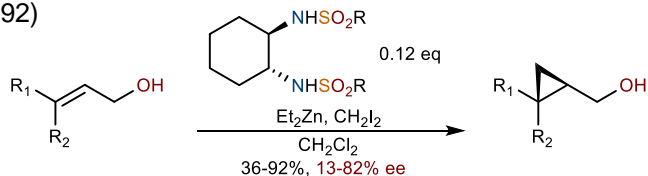
- Furukawa (1966) used CH_2I_2 and Et_2Zn , easier operationally

- Yamamoto (1985)



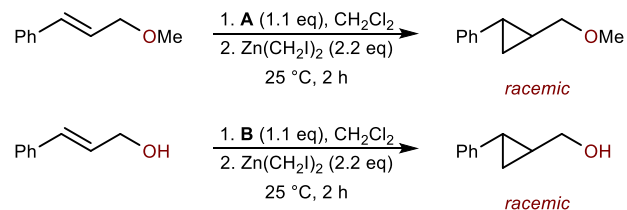
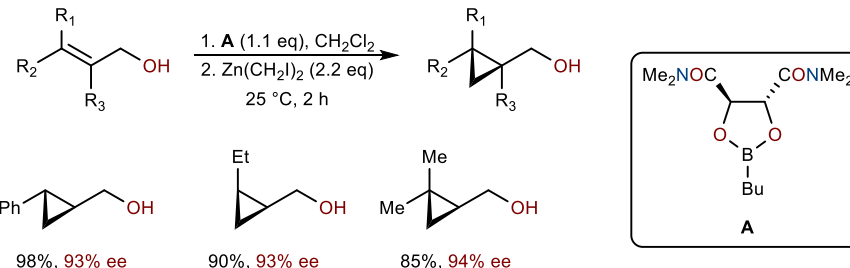
- Denmark (1991) used CH_2I_2 and DCE, better reactivity

- Kobayashi (1992)



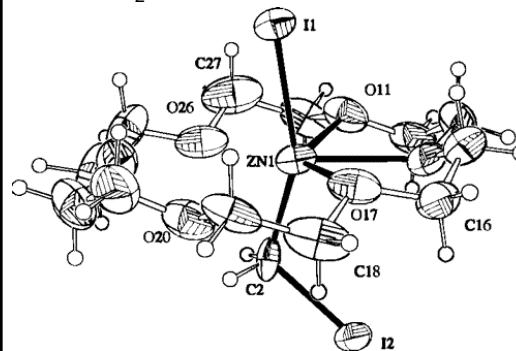
Enantioselective Simmons-Smith Cyclopropanation

- Original Report:



Charette, A. B. *J. Am. Chem. Soc.* **1994**, *116*, 2651. <https://doi.org/10.1021/ja00085a068>

- X-ray crystal structure of $\text{IZnCH}_2\text{I} \cdot 18\text{-crown-6}$:



"On a larger scale (8 mmol), this procedure sometimes led to violent explosions, due to the exothermicity of the formation of $\text{Zn}(\text{CH}_2\text{I})_2$ or of the zinc alkoxide without a complexing additive"

- Homogenous $\text{Zn}(\text{CH}_2\text{I})_2 \cdot \text{DME}$ is a safer alternative for scale-up

Charette, A. B. *J. Am. Chem. Soc.* **1996**, *118*, 28, 6792. <https://doi.org/10.1021/ja953816m>

Charette, A. B. *C&EN* **1995**, *73*, February 6, 2.

Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 5323. <https://doi.org/10.1021/ja01552a080>

Winstein, S.; Sonnenberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3235. <https://doi.org/10.1021/ja01476a016>

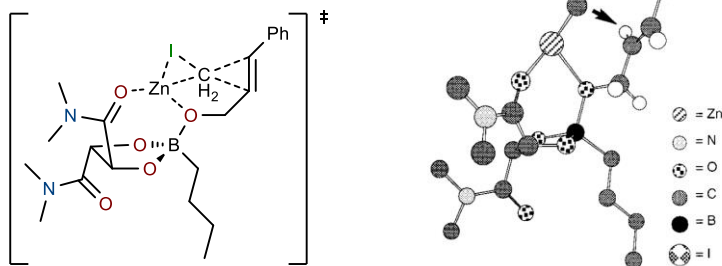
Furukawa, J. *Tetrahedron Lett.* **1966**, *28*, 3353. [https://doi.org/10.1016/S0040-4039\(01\)82791-X](https://doi.org/10.1016/S0040-4039(01)82791-X)

Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 8254. <https://doi.org/10.1021/ja00312a072>

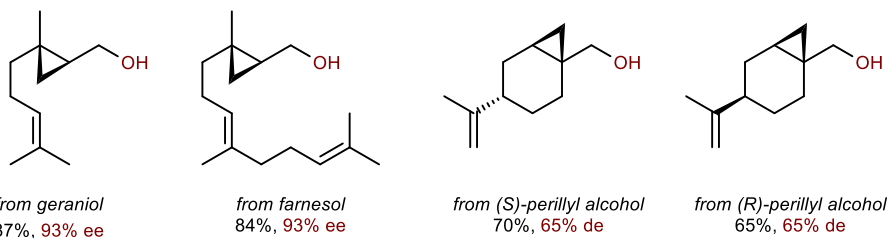
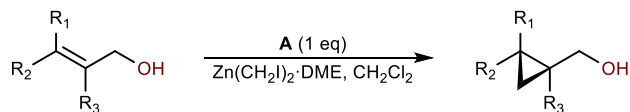
Denmark, S. E. *J. Org. Chem.* **1991**, *56*, 6974. <https://doi.org/10.1021/jo00025a007>

Kobayashi, S. *Tetrahedron Lett.* **1992**, *33*, 2575. [https://doi.org/10.1016/S0040-4039\(00\)92246-9](https://doi.org/10.1016/S0040-4039(00)92246-9)

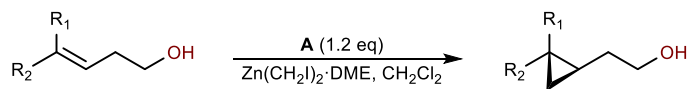
- Proposed Transition State:



- Site Selective Asymmetric Cyclopropanation of Polyenes:

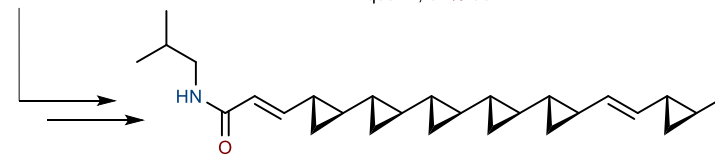
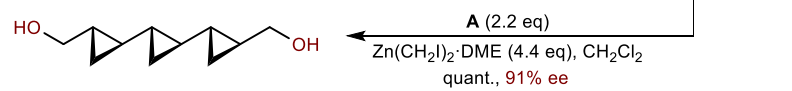
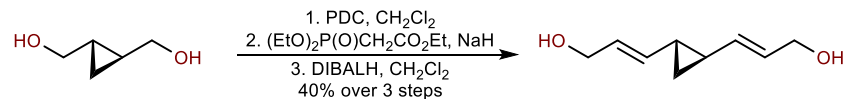


- Asymmetric Cyclopropanation of Homoallylic Alcohols



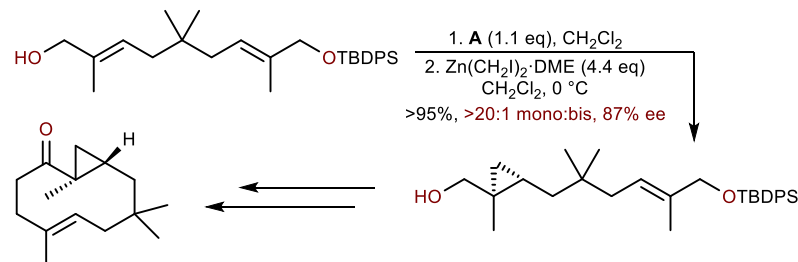
Charette, A. B. *J. Am. Chem. Soc.* **1998**, *120*, 11943. <https://doi.org/10.1021/ja982055v>

Applications in Total Synthesis



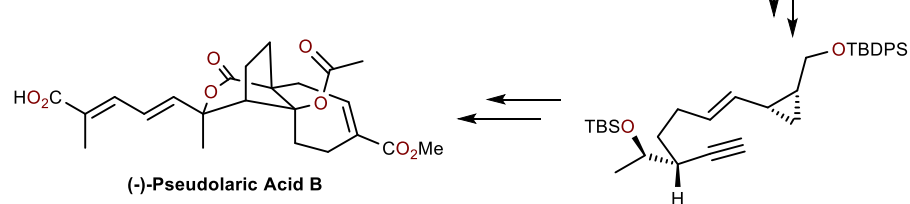
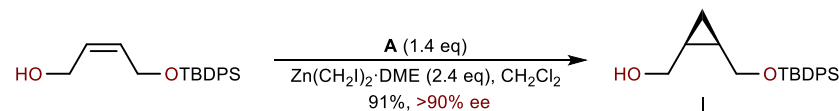
(+)-U-106305

Charette, A. B. *J. Am. Chem. Soc.* **1996**, *118*, 10327. <https://doi.org/10.1021/ja9619420>



(+)-Bicyclohumulene

Charette, A. B. *Tetrahedron* **1997**, *53*, 16277. [https://doi.org/10.1016/S0040-4020\(97\)01014-4](https://doi.org/10.1016/S0040-4020(97)01014-4)



Trost, B. M. *J. Am. Chem. Soc.* **2007**, *129*, 14556. <https://doi.org/10.1021/ja076165q>