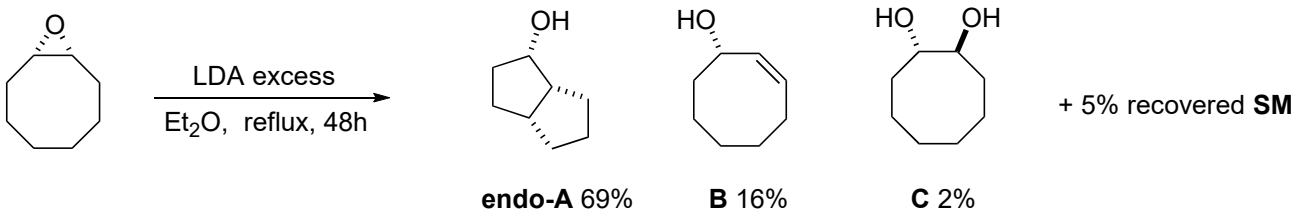
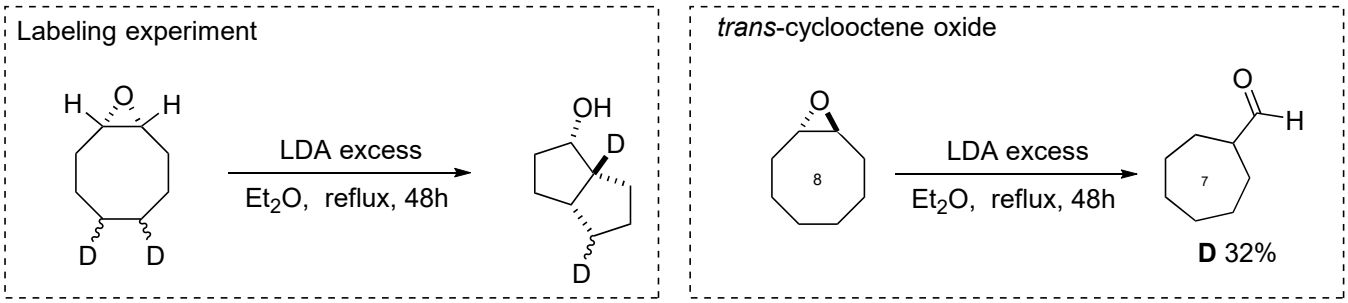
Exercice 1 : *Proximity Effect*

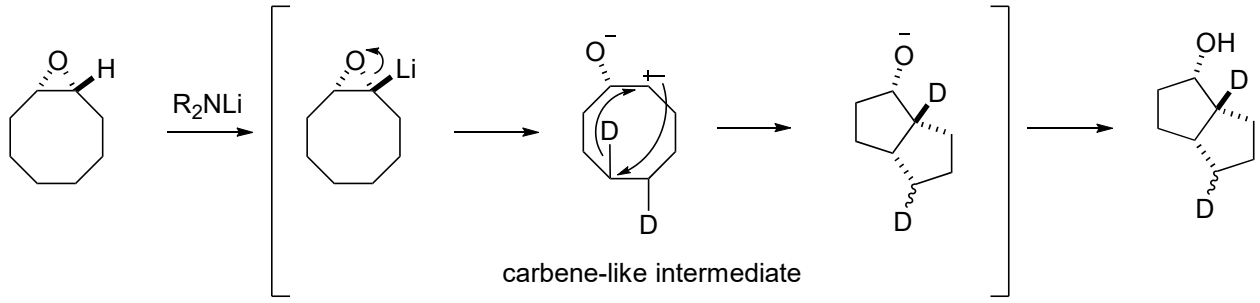
1-A) Considering the deuterium labeling experiment (*vide infra*), please provide a plausible mechanism accounting for the formation of bicyclic alcohol **A**.
1-B) Upon treatment under identical conditions, *trans*-cyclooctene oxide is converted into a mixture of cycloheptanecarboxaldehyde **7** and **exo-A.** Provide a mechanism for the formation of **7**.



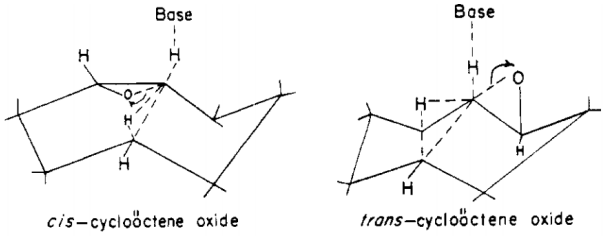


A. C. Cope, JACS **1958** 2849

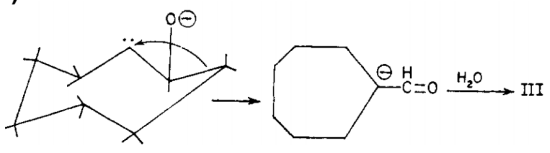
Solutions :
1-A)



Proposed transition state :



1-B)



JACS **1960** 6370 | TL **1977** 4281
JACS **1970** 2064 | CC **1996** 1015
Synthesis **1975** 602 | OL **2001** 441

Exercice 2 & 3 : See publications.
For questions regarding the mechanism of the Reformatsky reaction in Shenvi's total synthesis of Bilobalide, see :
Utimoto, *Chem. Lett.,* **1995** 463
Heathcock, *Organometallics,* **1987,** 2069
Yamamoto, *Polyhedron,* **1990,** 223
Cozzi, Adv. *Synth. Catal.,* **2008,** 975