

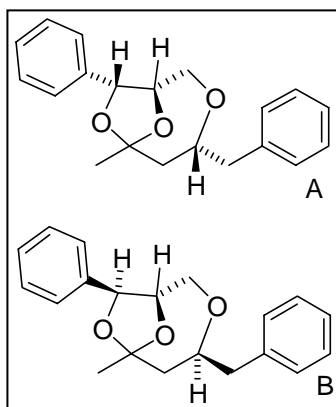
## Chem 535 Synthetic Organic Chemistry

DATE of ISSUE: Wednesday, March 24, 2004

DATE DUE: Thursday, March 31, 2004

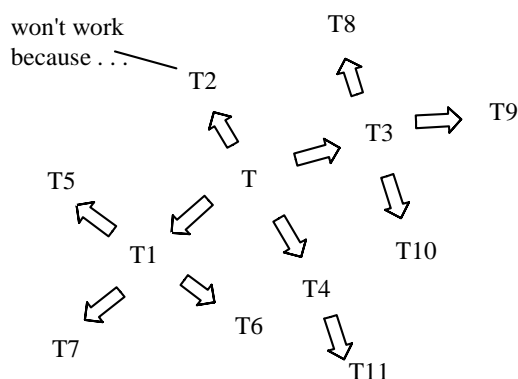
## Problem Assignment TWO

- **You must work alone.** Put your student number on the upper right-hand corner of each page. Number every page. Do not put your name on the material you turn in. I would rather grade your work without knowing who you are.
- **Type your Assignment on a computer; draw your molecular structures with a computer drawing program.**
- **List and draw exact structures and reactions of the closest precedent to your proposed synthetic operations for every step you reference.** I will take off points for steps for which there is no literature reference. **Do not cite text books; do not cite patents that do not explicitly define procedures and molecules!**
- Photocopy important pages (not the whole paper) from journals and attach them to your homework. Make sure that the reference (author, journal, vol, page number) is on the page. If need be, write it at the top of the photocopy. Put a page number on the photocopied page. Refer to the photocopied page in your text. **Don't make it difficult for the grader to conclude that someone can do the synthesis. Use a highlighter or circle the pertinent sections of the work you photocopy. Do not use a red pen.**



Consider molecules A and B and answer the following questions.

- 1 (8 pts) Which bond(s) is(are) the strategic bond(s) to disconnect first? Why?
- 2 (4 pts) Where is the molecular complexity in these two structures?
- 3 (4 pts) What is the word we use to describe how A and B are structurally related to one another. How many stereogenic atoms does A have?
- 4 (4 pts) Which if any molecule should be more difficult to synthesize? Why? To answer this you might want to make a model.
- 5 (15 pts) After reading the references given on the next page, show a retrosynthetic analysis of A and B showing 3 or 4 major routes. Remember that retrosynthetic analyses start from target molecules and show more than one way to simplify the target (example below).



- 6 (15 pts) Formulate enantiospecific forward syntheses for both molecules using the best example from your answer to number 5. How do the synthetic approaches differ as a function of stereochemistry? Include references for the non-trivial steps.

Suggestions for Bibliography (you will need to find more):

- (1) "Chemical And Biological Synthesis Of Chiral Epoxides" Besse, P.; Veschambre, H. *Tetrahedron* **1994**, 50, 8885-8927.
- (2) "Base-Promoted Isomerisations of Epoxides" Crandall, J. K.; Apparau, M. *Org. React. (N.Y.)* **1983**, 29, 345.
- (3) "Enantioselective epoxidation with peroxidic oxygen" Hoft, E. *Top. Curr. Chem.* **1993**, 164, 63.
- (4) "Rearrangements of epoxy alcohols and related compounds" Magnusson, G. *Org. Prep. Proced. Int.* **1990**, 22, 547.
- (5) "Asymmetric Epoxidation of Allylic Alcohols: The Sharpless Epoxidation" Pfenniger, A. *Synthesis* **1986**, 89.
- (6) "Synthetically Useful Reactions of Epoxides" Smith, J. G. *Synthesis* **1984**, 627.
- (7) "Catalytic Asymmetric Dihydroxylation" Kolb, H. C.; Vannieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, 94, 2483-2547.
- (8) "Synthesis of (+)-parviflorin" Hoye, T.R.; Ye, Z. *J. Am. Chem. Soc.* **1996**, 118, 1801-02. (and references therein)