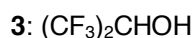
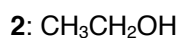
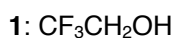
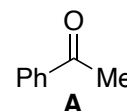
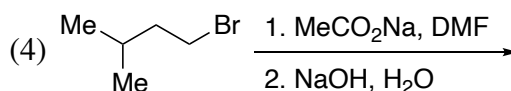
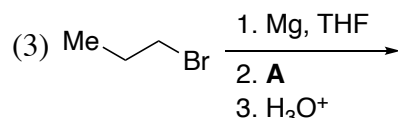
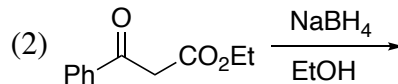
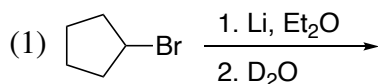


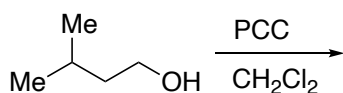
問 1. 次の化合物 1-4 について、酸性度が大きなものから順に並べよ。また、その理由を簡潔に説明せよ。



問 2. 次の反応(1)-(3)について、主生成物の構造式を示せ。



問 3. 次のアルコールの酸化について、以下の設問に答えよ。



(1) PCC の構造式を示せ。

(2) この反応の主生成物の構造式を示せ。

(3) この反応の反応機構を示せ。

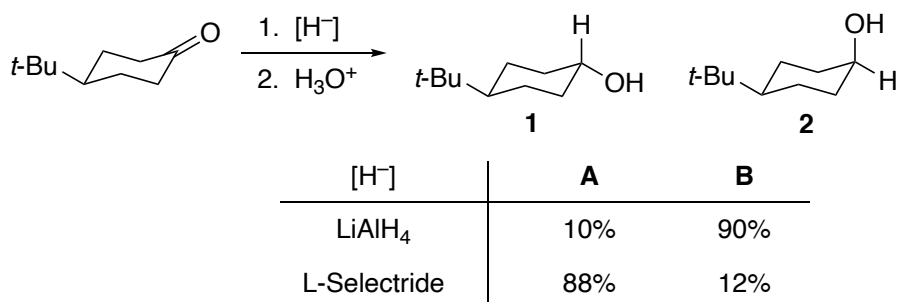
(4) PCC の代わりにクロム酸を酸化剤として用いた場合の主生成物の構造式を示せ。また、その生成物が生成する過程を説明せよ。

(5) PCC の調製法が報告されている最初の原著論文を調べ、その書誌情報(例 *Chem. Lett.* 1977, 1415-1418. (雑誌名 発行年, ページ.))を示せ。

問 4. 次の文章は、学部生向けのある有機化学の教科書に記載されている一節である。この説明を読み、以下の設問に答えよ。

When the carbonyl group is constrained within a cyclic structure, access to the carbonyl carbon atom may be more favorable from one side of the molecule than from the other. For example, the reduction of 4-*tert*-butylcyclohexanone with lithium aluminum hydride produces an unequal mixture of the *cis* and *trans* geometrical isomers of 4-*tert*-butylcyclohexanol. In this example we would not have expected optically active products because the reactants are both achiral. Furthermore, the product alcohols possess a plane of symmetry and are therefore achiral.

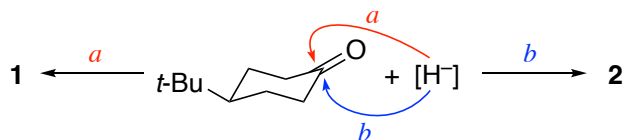
Formation of an unequal mixture of the 4-*tert*-butylcyclohexanol stereoisomers is due to a more favorable approach of hydride from one side of the ketone molecule. That can be demonstrated experimentally by carrying out the same reduction with lithium tri-*sec*-butylborohydride (L-Selectride), a considerably larger reducing agent than lithium aluminum hydride. The ratio of products changes markedly. A chemical reaction, such as that above, which leads to unequal quantities of product stereoisomers is termed stereoselective. A stereospecific reaction results when a specific reactant stereoisomer produces a specific product stereoisomer.



In the examples of the above scheme, the large *tert*-butyl group remains in the equatorial position. It acts as a conformational label which we can use to follow the reaction stereochemistry. The trans product isomer has diequatorial substituents, and the hydroxy group is axial in the cis isomer.

If the reagent approaches the molecule so as to place hydride in the axial position, the hydroxy group will be equatorial and the trans product will be formed (pathway *a*). Equatorial approach of hydride produces the cis alcohol (pathway *b*). When the larger reagent is employed, the less-hindered equatorial approach *b* is preferred and the cis isomer predominates.

The cis and trans alcohols are not equal in energy. The trans isomer with both substituents in an equatorial position is more stable. Reduction by L-Selectride provides an example of a reaction in which the more stable product is not necessarily the one formed more rapidly. That is, reaction kinetics are not always directly related to product stability. In this example the energies of the transition states reflect steric factors which are different from those of the products.



- (1) L-Selectride の調製法および L-Selectride を用いたケトンの立体選択的還元を報告した s 最初の原著論文の書誌情報を示せ。
- (2) L-Selectride の構造式を示せ。
- (3) 生成物 **A**, **B** はそれぞれ化合物 **1**, **2** のどちらに対応するか、示せ。(ヒント:最後の段落の意味をよく考えよ)
- (4) L-Selectride による還元において **A** が主生成物になる理由を考え、説明せよ。
- (5) 水素化アルミニウムリチウムによる還元において **B** が主生成物になることについて、どのような説明が提案されているかについて調査し、説明せよ。