Haloalkanes, Alcohols and Amines. Problem Sheet 3

(Alcohols)

- 1. (a) By using models and then drawing clear diagrams, show the possible chair conformations for *cis*-1,3-cyclohexanediol.
- (b) On the basis solely of 1,3-interactions, which would you expect to be the more stable conformation and why?
- (c) Infrared evidence indicates intramolecular hydrogen bonding in this diol. How would the infrared data show this? Which conformation in (a) in indicated by this evidence and where is the intramolecular H-bond?
- 2. Synthesis of the important β -blocker drug propranolol (**A**), used for the treatment of high blood pressure, was achieved according to the scheme below. Propose structures for the compounds **A-D** and mechanisms for the reactions.

OMe
$$HI \qquad (B) \qquad NaH \text{ then} \qquad (C) \qquad mCPBA \qquad (D) \qquad Propranolol (A) \\ C_{16}H_{21}NO_2$$

3. An insect pheromone has been made the following way:

HO OH HBr A
$$(C_8H_{17}OBr)$$
 B $(C_{13}H_{25}O_2Br)$

E $(C_{12}H_{22}O)$ D $(C_{17}H_{30}O_2)$ 1. LiNH₂
2. EtBr C $(C_{15}H_{26}O_2)$

MeCOCI

F $(C_{14}H_{24}O_2)$ G $(C_{14}H_{26}O_2)$

Lindlar catalyst

- (a) Give the structure of the pheromone and all intermediates including mechanisms
- (b) For maximum biological activity of the pheromone there should be 4% of it geometrical isomer present. How could you modify the above synthesis to obtain this isomer?

- 4. Propene oxide can be converted into 1,2-propanediol by the action of either dilute aqueous acid or dilute aqueous base. When optically active propene oxide is used, the 1,2-diol obtained from acidic hydrolysis has a rotation opposite to that obtained from alkaline hydrolysis. What is the most likely interpretation of these facts?
- 5. Show clearly all the mechanistic steps in the following acid catalysed transformations.