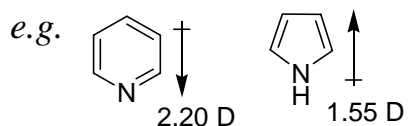


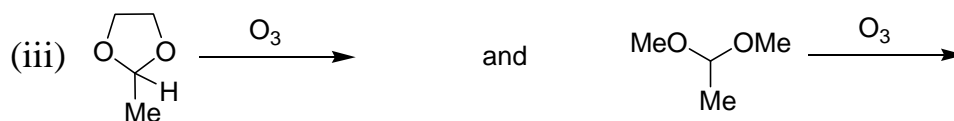
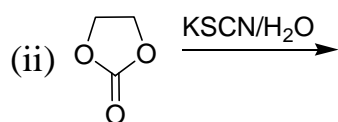
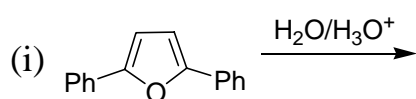
Problem set for Monday group meeting

Sec. I. Easy start: recall memory and pushing arrows

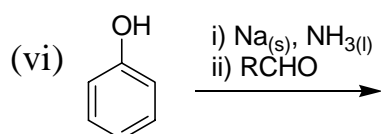
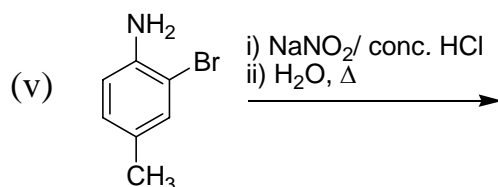
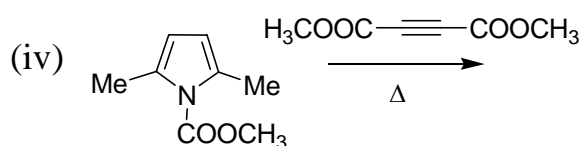
- Please explain the dipole moments of pyrrole and pyridine are in different direction?

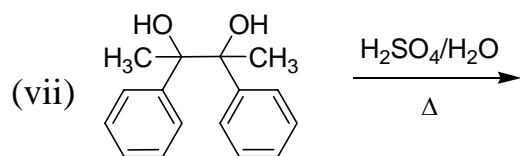


- Please complete the following reactions and provide a reasonable reaction mechanism for each transformation.



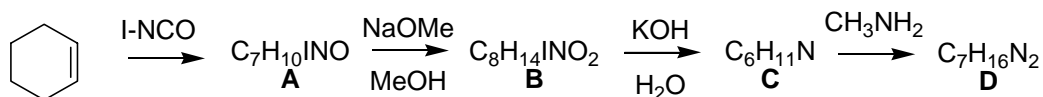
Explain why the cyclic acetal reacts with ozone faster than the acyclic acetal does?



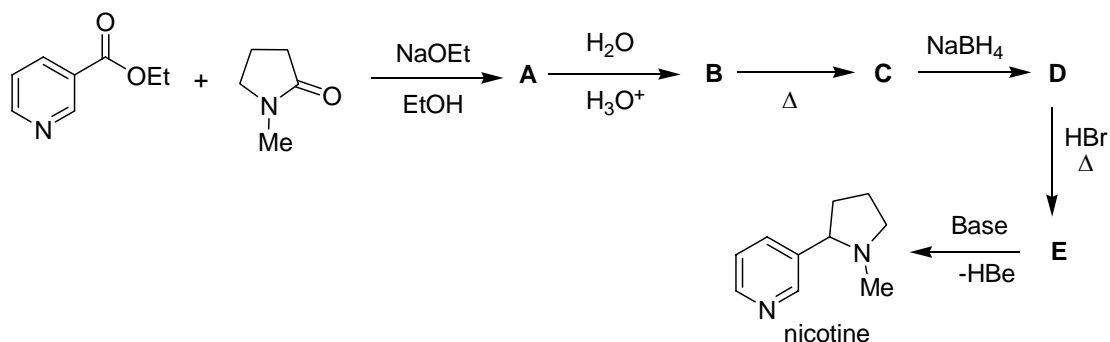


What is the name of this reaction?

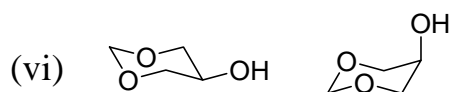
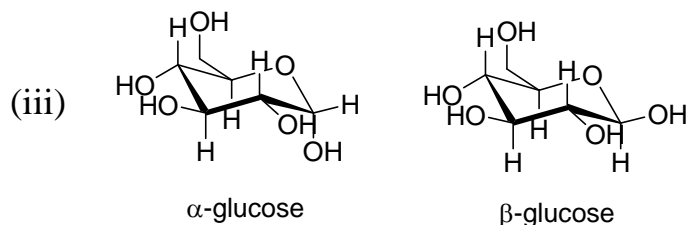
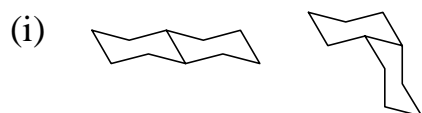
3. Please finish the transformations given below, provide structures for compound **A-D** and reaction mechanisms.



4. Nicotine can be synthesised *via* the following processes, please give the structure of products for each step (compound **A-E**).



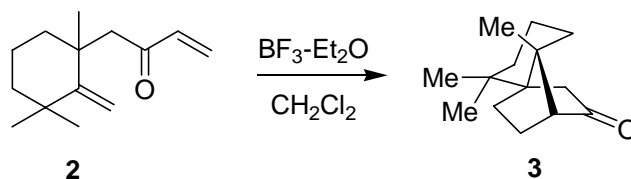
5. Consider the following conformation or isomers in each pair, which one is more thermodynamically stable than the other and why?



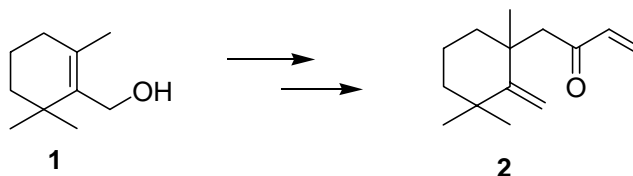
Problem set for Monday group meeting

Sec. II Moderate: reaction, synthesis and spectrum

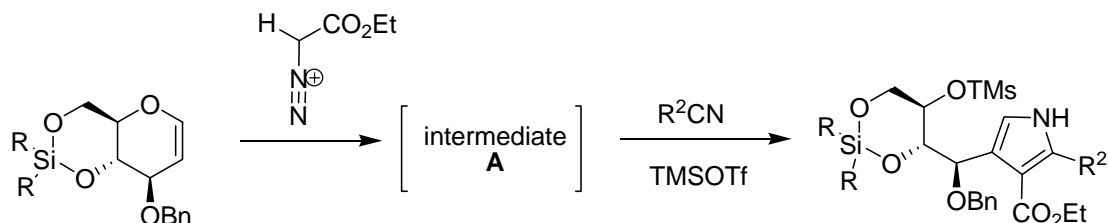
6. Normyltayl-4-one **3** has been prepared in good yield by subjecting dienone **2** with $\text{BF}_3\text{-Et}_2\text{O}$ in CH_2Cl_2 . Could you provide a reaction mechanism for this rearrangement (*hint: through carbocation intermediate*)?



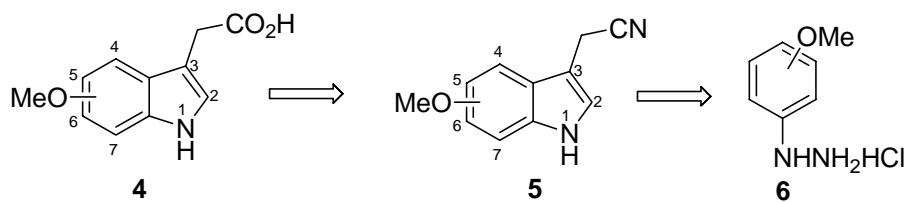
How do you prepare the dienone **2** from cyclogeraniol **1** (*hint: Claisen rearrangement to install the carbonyl group*)?



7. A novel procedure towards the synthesis of highly functionalised pyrrole from carbohydrate skeletons was illustrated below. Please provide the structure of intermediate **A** in this transformation and a reasonable mechanism (*hint: the Ritter-like reaction*).



8. Melatonin is a hormone of the vertebrate pineal containing an indole skeleton and is secreted mainly during darkness. It is well recognised that it has hypnotic action in animals and humans. Based on the indole skeleton of melatonin, an analogue **4** was synthesised for the study of its bioactivity.
- (a) Please give a synthetic route from giving hydrazine hydrochloride **6** as starting material to the melatonin analogue **4**.



(b) The NMR spectra of melatonin analogue **4** was shown as below.
Please assign the position of the methoxyl group (Fig. 1).

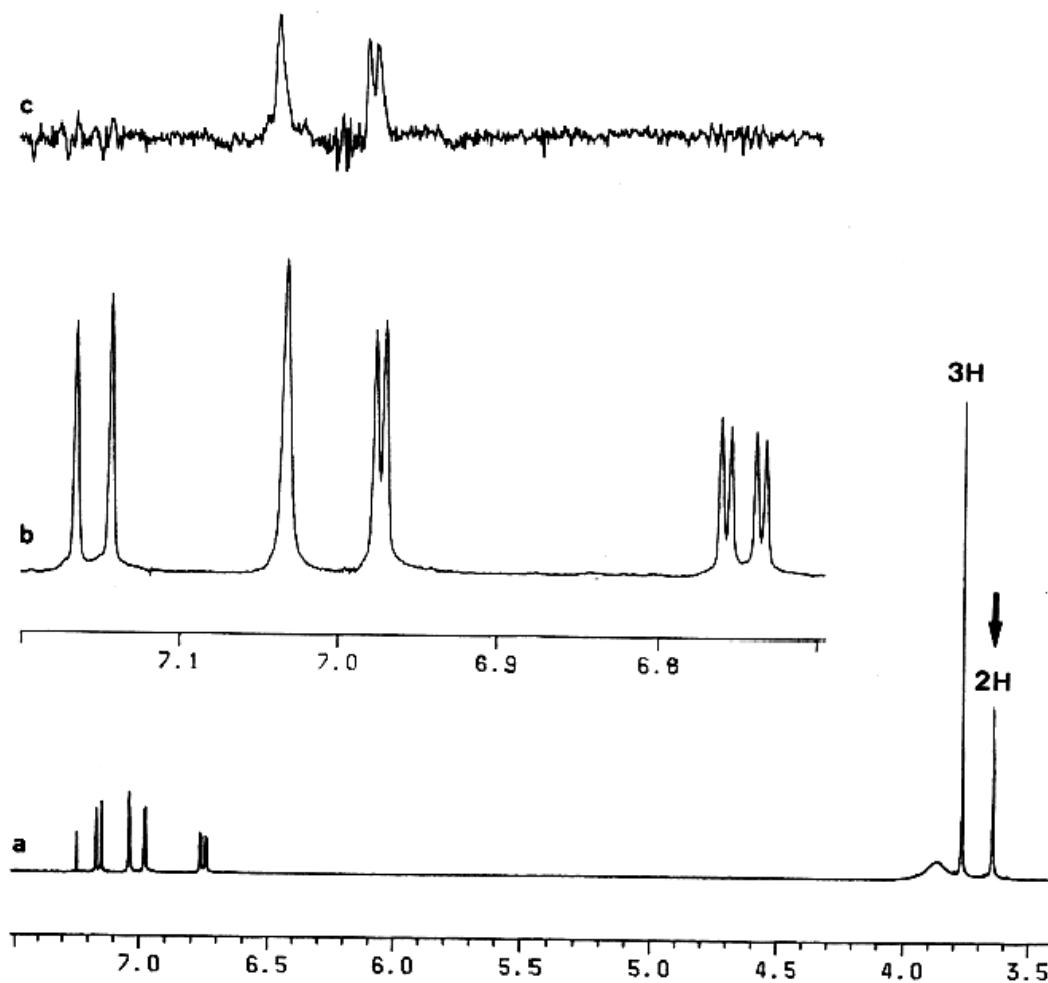


Fig. 1 400 MHz ¹H NMR spectrum of the melatonin analogue **4** in a mixture of CDCl₃ and CD₃OD. (a) Full spectrum; (b) expanded section of the aromatic proton signals; (c) ¹H NOE difference spectrum, same section as in irradiation position at δ = 3.64

(c) Based on the structure you obtained above, please assign the ^{13}C signals as far as possible using ^1H - ^{13}C HETCOR spectrum provide below (Fig. 2).

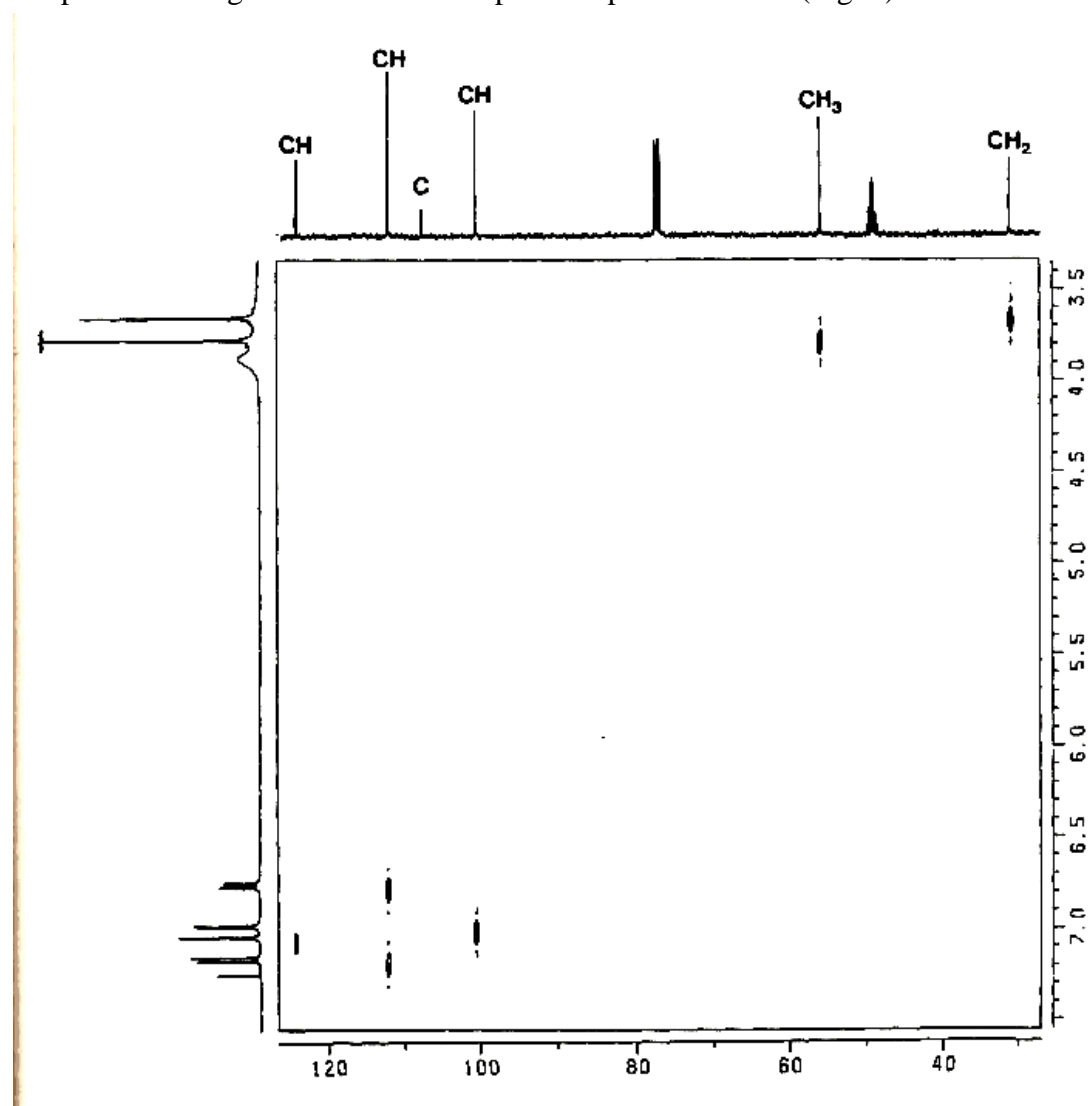


Fig. 2