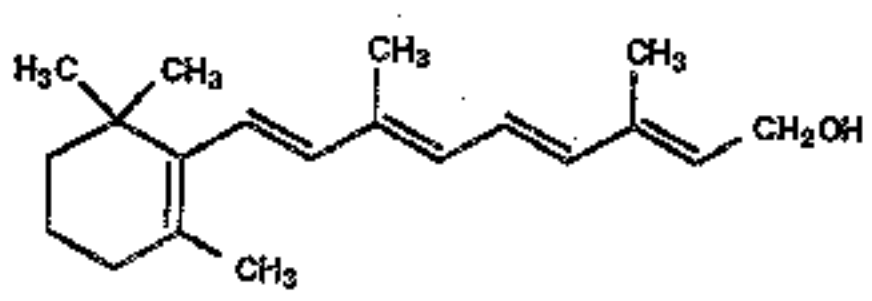
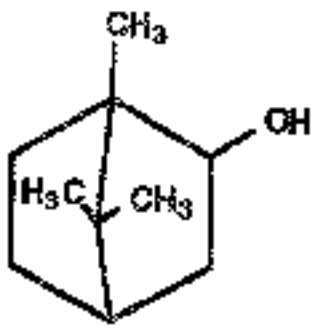
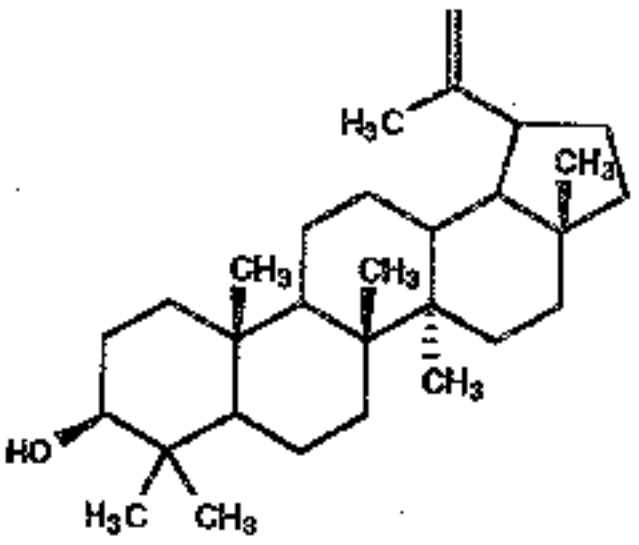
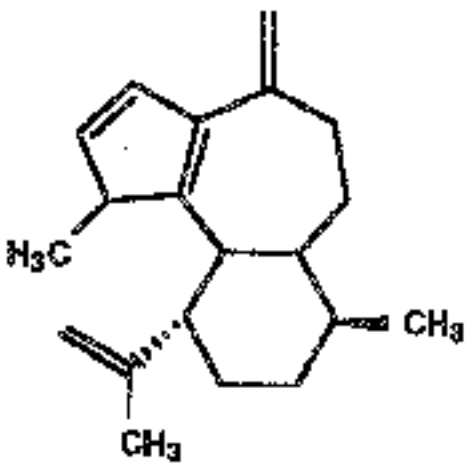
1. What is the structure of isoprene, an important building block in natural product biosynthesis? Please mark the isoprene units in each of the following compounds. (5 %)







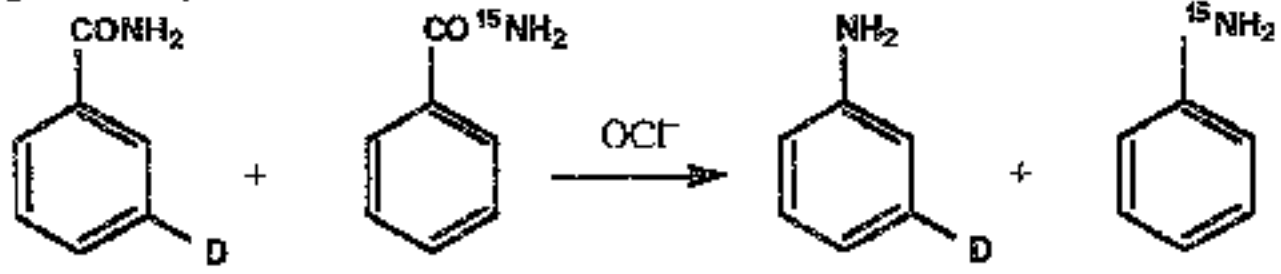


2. The sex pheromone of the silkworm moth, bombykol, has been synthesized in the following way. What is the structure of compound **A** to **F** as well as bombykol? (The biologically active form is the 10*E* isomer) (7 %)

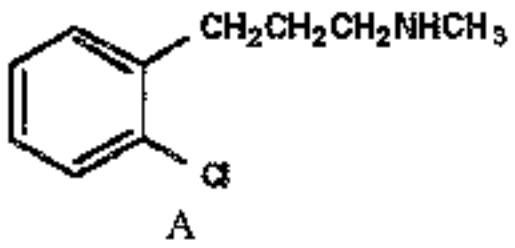
1-Pentyne + *n*-C_4H_9MgBr → **A** (C_5H_7MgBr)
A + HCHO, H^+ → **B** ($C_6H_{10}O$)
B + PBr_3 → **C** (C_6H_9Br)
C + Ph_3P, base → **D** ($C_{24}H_{23}P$)
D + Ethyl 10-oxodecanoate → **E** ($C_{18}H_{30}O_2$)
E + H_2, Lindlar catalyst → **F** ($C_{18}H_{32}O_2$)
F + $LiAlH_4$ → **Bombykol** ($C_{16}H_{30}O$)

3. Please rationalize the following reactions and propose a **mechanism** for each. (24 %)

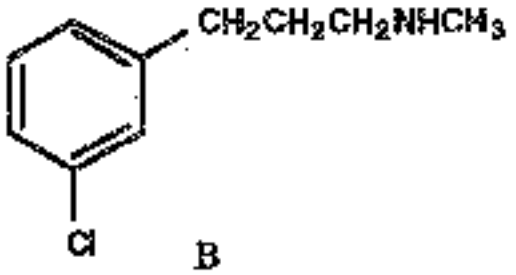
(a) Degradation of a mixture of *m*-deuteriobenzamide and benzamide-^{15}N gives only *m*-deuterioaniline and aniline-^{15}N.



(b) When either compound A or B is treated with $KN(C_2H_5)_2/HN(C_2H_5)_2$, a good yield of the same product of formula $C_{11}H_{13}N$ is obtained. Include the structure of the product.



A

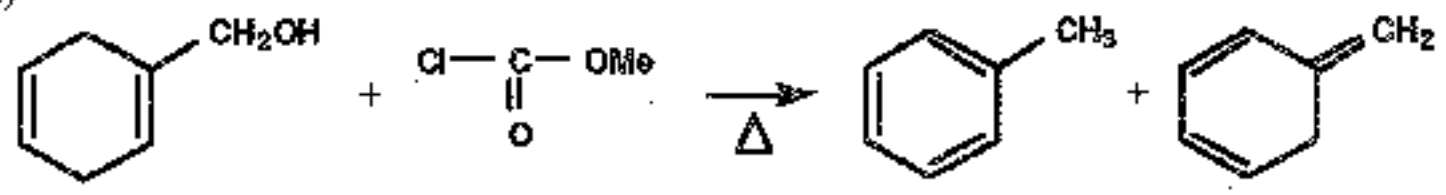


B

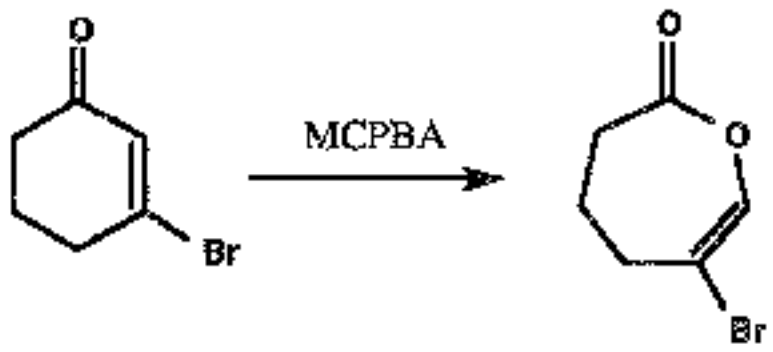
(c) Sodium α–bromopropionate undergoes hydrolysis with retention of configuration.

$$CH_3CHBrCOO^-Na^+ \xrightarrow[H_2O]{OH^-} CH_3CHOHCOO^-Na^+$$

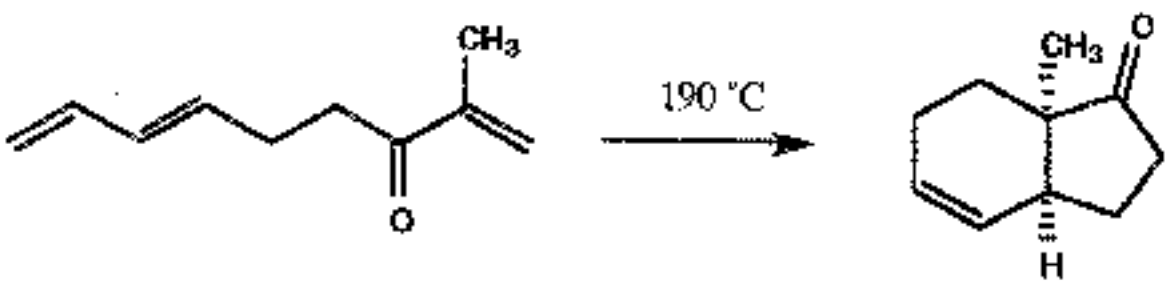
(d)



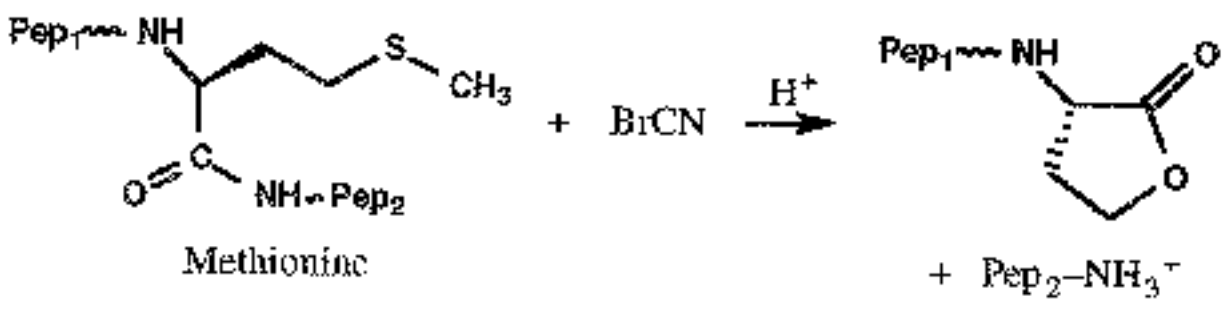
(e)



(f)

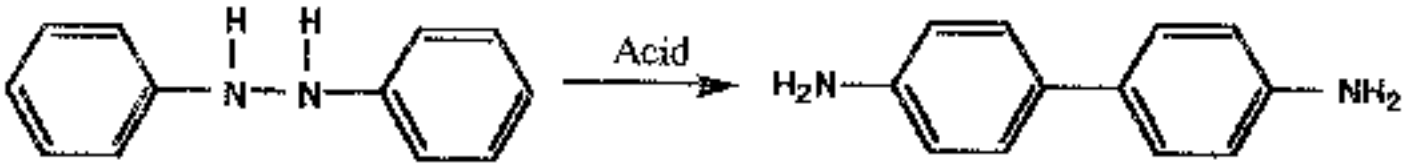


(g)



Methionine

(h)



4. Please outline a synthetic pathway less than **five steps** to make the following compounds from benzene, toluene, any needed aliphatic (**≤ 4 carbons**) and inorganic reagents. (**20 %**)
   (a) 1,5–Dibromotoluene
   (b) *p*–Nitrodiphenylmethane
   (c) *p*–Iodobenzoic acid
   (d) 2–Pentenoic acid
   (e) [1–^{14}C]–2–Methyl–1–propanol (start with $^{14}CH_3OH$)

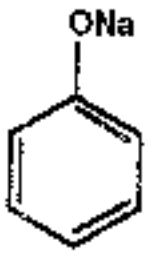
5. For the reactive carbon intermediates carbocation, carbanion, radical, singlet carbene, triplet carbene, and radical cation, show the shape and draw the hybridization orbital diagram of each. (**12 %**)

6. Give structure of the major product (include stereochemistry, if any) in each of the following reactions. (20 %)

(a)

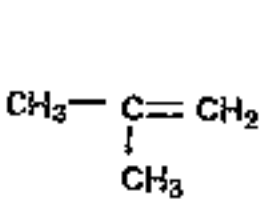
(*S*)(*Z*)-3-Hexen-2-ol + HCO_2OH ⟶ **1** + **2**

(b)



+ CO_2 ⟶ (125 °C, 5 atm) ⟶ (H^+) **3**

(c)

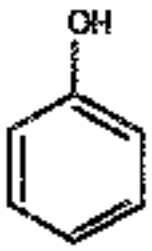


+

9-BBN

⟶ ($BrCH_2COCH_3$) **4**

(d)

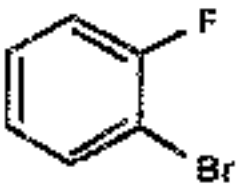


⟶ ($CHCl_3$, $NaOH_{(aq)}$, 70 °C) ⟶ (H^+) **5**

(e)

Methyl vinyl ketone + cyclohexanone ⟶ (Base) **6**

(f)



+

+ Li ⟶ **7**.

(g)

trans,*trans*-2,4-Hexadiene + ethylene ⟶ **8**

(h)

(*R*)-$HOCH_2CHOHCH{=}CH_2$ ⟶ (cold alkaline $KMnO_4$) **9** (optically active) + **10** (optically inactive)

7. Give a structure of compound $C_{10}H_{18}O$ on the basis of its IR, CMR, and HNMR spectra. **(12 %)**