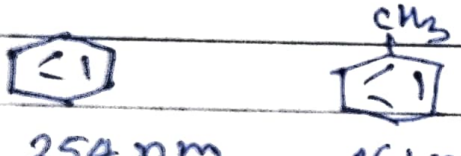
* UV spectra of aromatic compounds and heteroaromatic compounds.

Aromatic compounds :-

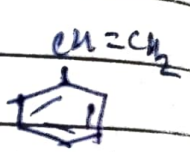
Benzene (I) shows three absorption bands at 184 nm (ϵ_{max} 60,500); 203.5 nm (ϵ_{max} 7400 often called K-band) and at 254 nm (ϵ_{max} 204, often called B-band).



254 nm

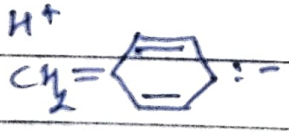
261 nm

272 nm

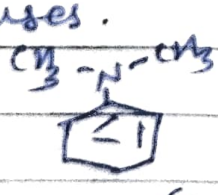


282 nm

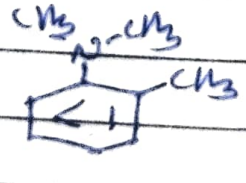
Long-wavelength electronic absorption maxima the B-band for some aromatic hydrocarbons.



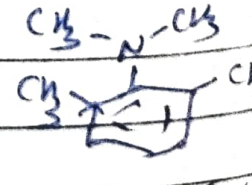
Steric effect is increases Then the wavelength is decreases.



260 (13750)
296 (2300)

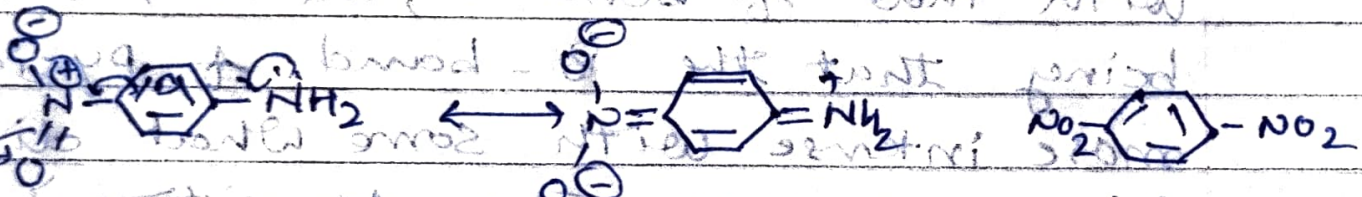


247 (6300)
288 (1200)



211 (8600)
259 (2200)

In the case of disubstituted benzenes, when an amino & a nitro are situated para to each other, a pronounced red shift in the main absorption band, i.e. K-band is observed. This effect of the presence of an electron donating & electron attracting group para to one another leads to the extension of the chromophore through the benzene ring.



λmax : 381 nm 261 nm

$\pi \rightarrow \pi^*$ Transition K band

	λmax (nm)	εmax
o-nitrophenol	279	6,600
m-NO_2 phenol	274	6000
p-NO_2 phenol	318	10,000
o-NO_2 Aniline	283	5400
m-NO_2 Aniline	280	4800
p-NO_2 Aniline	381	13500

Polycyclic - Aromatic Hydrocarbons.

λmax (nm) 254 286 375

Hetero Aromatic compounds:

λ_{max}		ε_{max}
200 nm	209 nm	6730
238 nm	240 nm	300

The spectrum of pyridine is comparable with that of benzene, the only different being that the B-band of pyridine is more intense with some what diminished fine structure. The transition is allowed for pyridine but forbidden for the more symmetrical benzene molecules.

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The Wood-Ward - fieser rules for α,β-unsaturated compounds.

(λ_{max} for $\pi \rightarrow \pi^*$ transition ε_{max} 4500 - 29,000 $\times 10^4\ m^2\ mol^{-1}$) * in ethanol

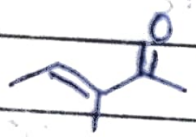
Base value for

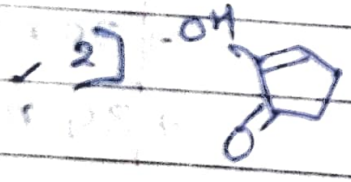
Ketone $-\overset{|}{C}=\overset{|}{C}-CO-$	acyclic or 6-ring cyclic	215 nm.
	5-ring cyclic	202 nm.
aldehydes $-\overset{|}{C}=\overset{|}{C}-CHO$		210 nm.
		207
acids and esters $-\overset{|}{C}=\overset{|}{C}CO_2H$ R		197 nm.
extended conjugation		+30 nm.
Homodiene component		+39 nm.

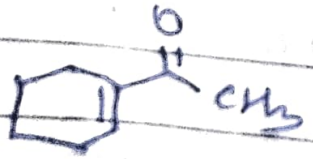
Increments for	α	β	γ	δ (nm)
-R alkyl group or ring residue	10	12	18	18
-OR	35	30	17	31
-OH	35	30	30	50
-SR	-	85	-	-
-Cl	15	12	12	12
-Br	25	30	25	25
-OCOR	6	6	6	6
$-NH_2$, $-NHR$, $-NR_2$ amino.	-	95	-	-

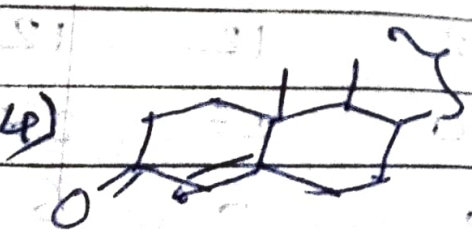
if one double bond is exocyclic to one ring
If exocyclic to two rings simultaneously

eg

1) 

2) 

3) 

4) 

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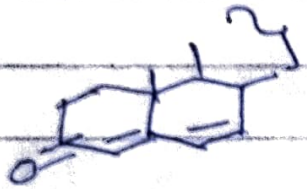
6) 

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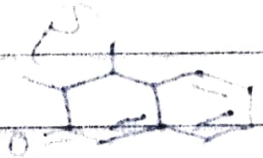
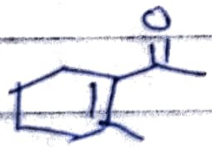
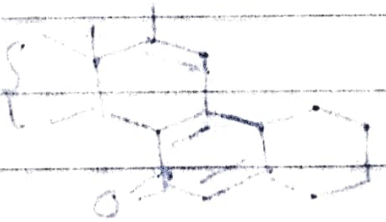


8) 



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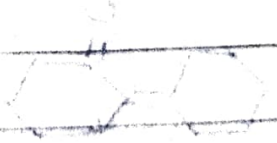

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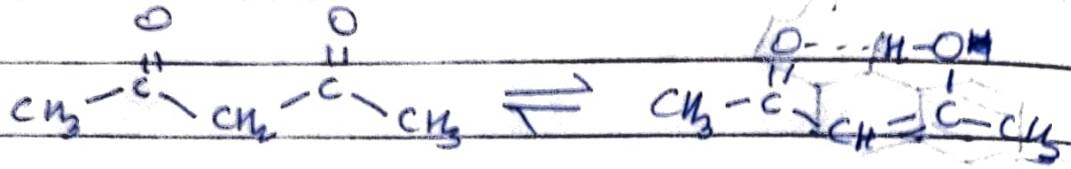
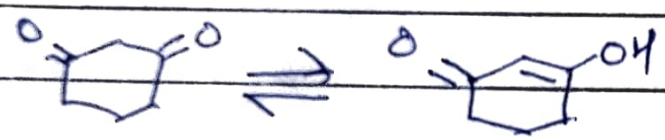
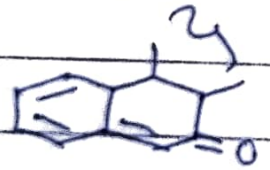
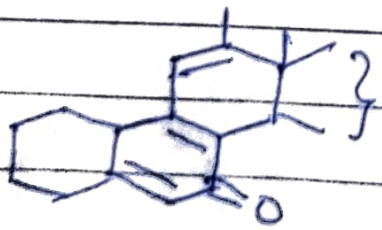
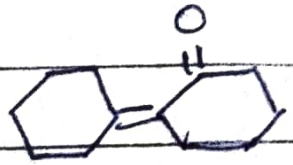
10] 

11) 

12] 

✓ 13] 

14] 

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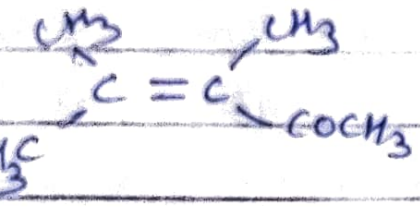

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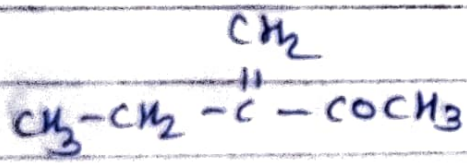

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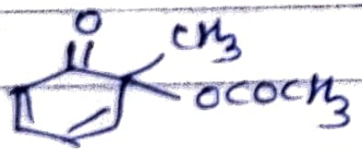

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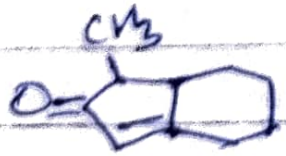

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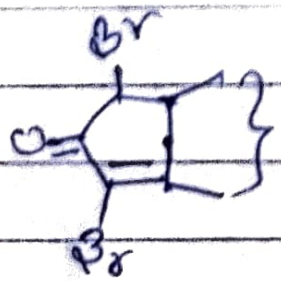

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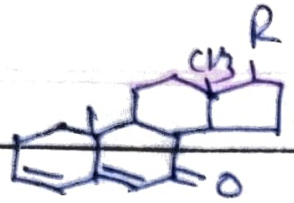
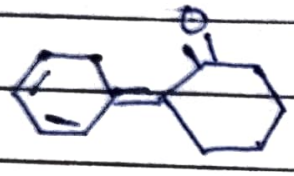
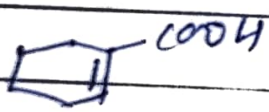
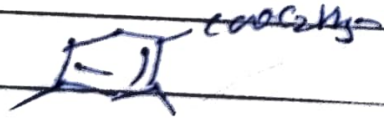
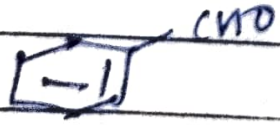
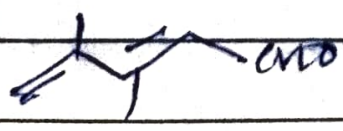
20] 

21] 

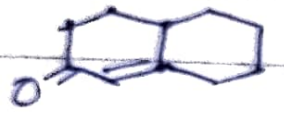
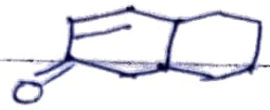
22) 

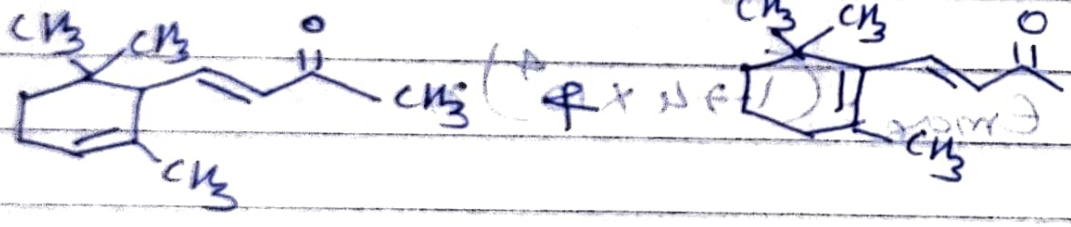
23) 

24) 

25) 

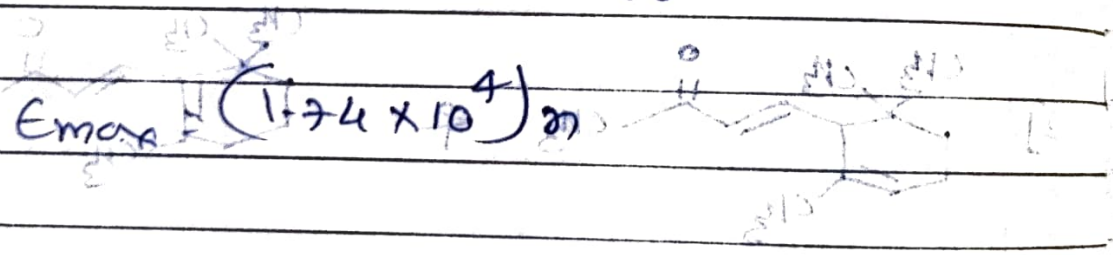
Q2 predict and explain by UV spectroscopy can be used to distinguish between the following pairs of compounds.

1)  & 

2] 

Fieser-Kuhn rules for polyenes:-

$$\lambda_{max}(hexane) = 114 + 5M + n(48.0 - 1.7n) - 16.5\ R_{endo} - 10\ R_{exo}$$



$$\epsilon_{max} = (1.74 \times 10^4)n$$

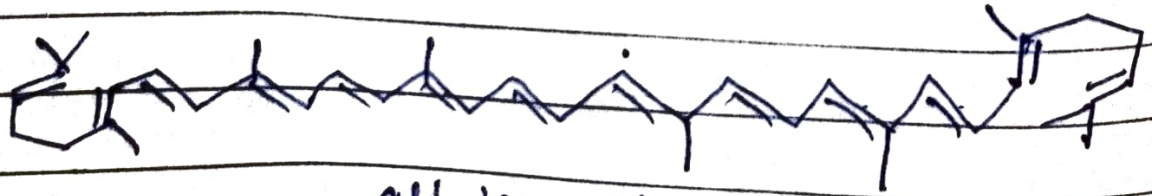
where

n = no. of conjugated double bonds.

M = no. of alkyl or aryl like substituents on the conjugated system.

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.

R_{exo} = no. of rings with exocyclic double bonds.



all-trans-lycopene

λ_{max}^{obs} = 504 (170,000) ; 474 (186,000) nm.

$\lambda_{max}^{calcu.}$ = 114 + 5(8) + 11 [48.0 − 1.7(11)] − 0 − 0

= 476 nm

λ_{max}^{obs} = 474 nm (hexane)

ε_{max}^{calc} = 1.74 × 10^4 (11) = 19.1 × 10^4

ε_{max}^{obs} = 18.6 × 10^4 (hexane)

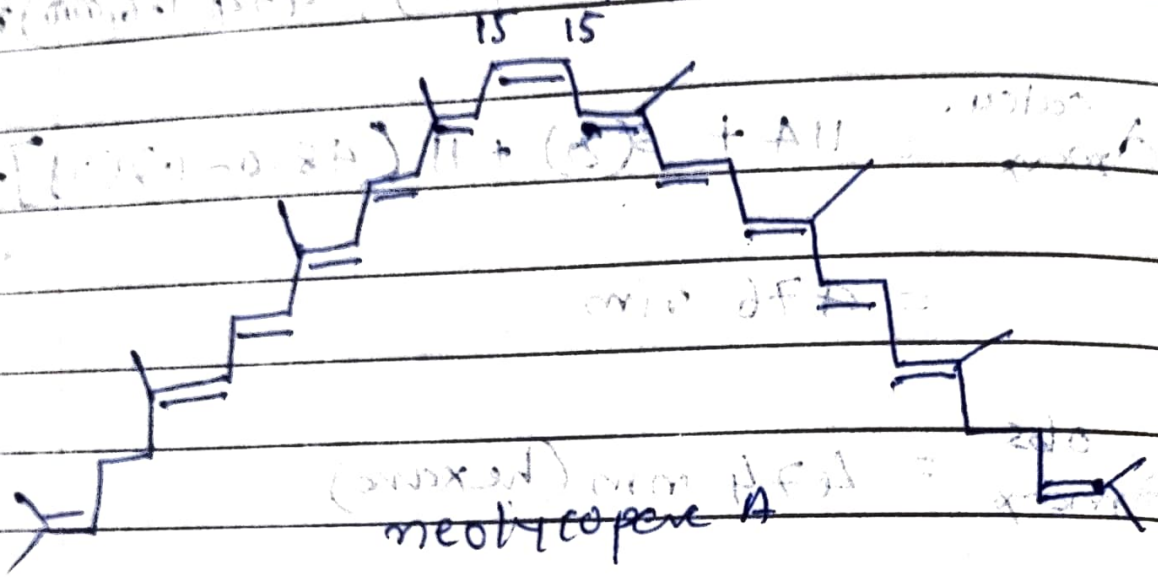
β-carotene.

λ_{max}^{cal} = 453.3 nm. ε_{max}^{calc} = 19.1 × 10^4

λ_{max}^{obs} = 452 nm (hexane) = 15.2 × 10^4.

Two endocyclic double bonds

486
−33
451

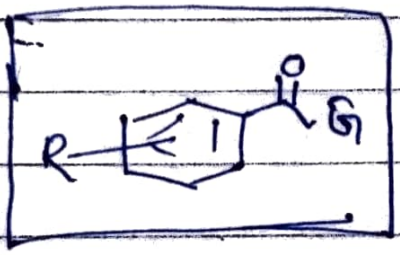


neolycopene A

λ_{max}^{obs} 500 (100,000); 470 (122,000); 361 (68,000) nm.

calculation of λ_{max} for the benzene derivatives ($R-C_6H_4-CO-G$) by A. I. Scott empricil rules :→

$R-C_6H_4-CO-G$



calc. λ_{max} nm.

parent chromophore:

G = alkyl or ring residues — 246

G = H — 250

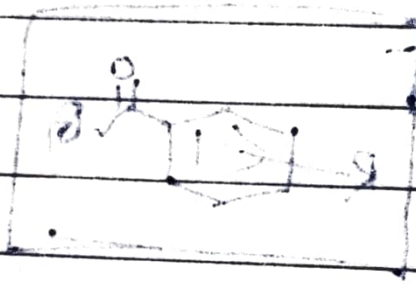
G = OH, or O Alkyl — 230

Add for R :

alkyl or ring residue	o,m	3
	p	10
-OH, -ome, -O-alkyl	o,m	7
	p	25
O^-	o	11
	m	20
	p	78
Cl	o,m	0
	p	10
Br	o,m	2
	p	15
$-NH_2$	o,m	13
	p	58
-NHAC	o,m	20
	p	45

-NMe2

o,m	20
p	85



examples

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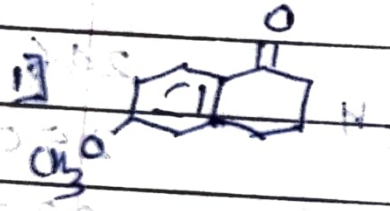

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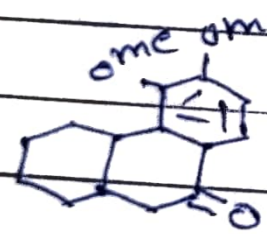

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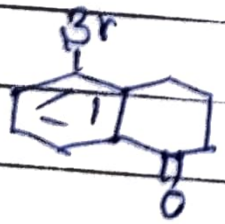

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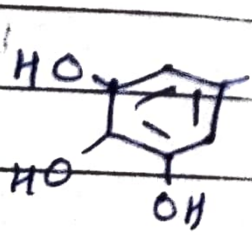

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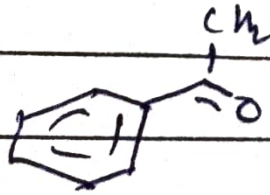
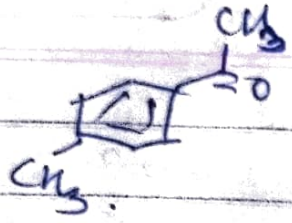
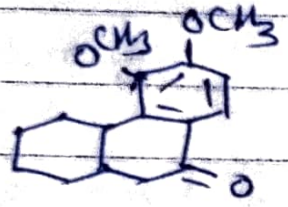
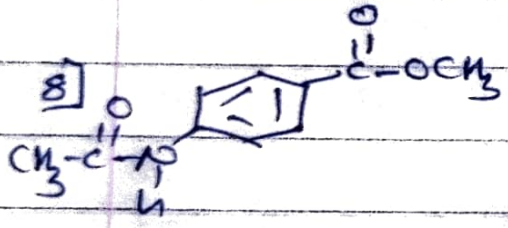


6) 

7) 

8] 

9]