QFL-0341 (2019)

Caracterização de compostos aromáticos

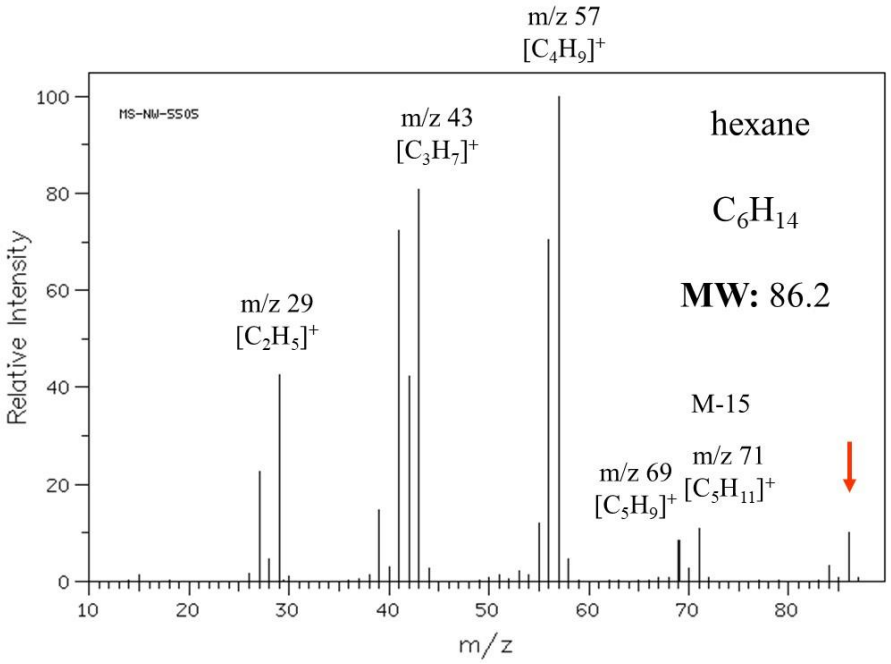
Espectrometria de massas

Espectroscopia no IV e UV

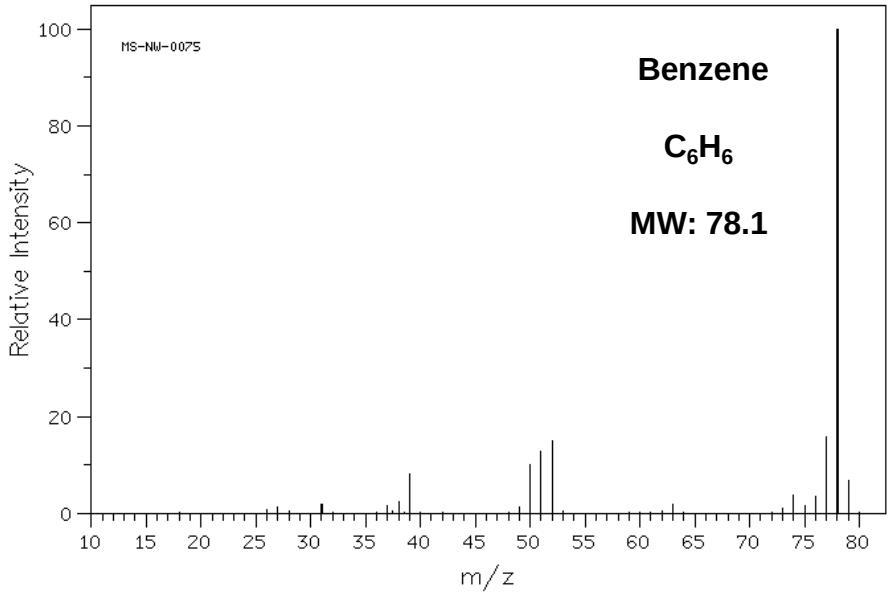
Espectroscopia de RMN de ^{1}H e ^{13}C

Espectros de massas de compostos aromáticos

(são facilmente identificados pelos intensos íons moleculares)

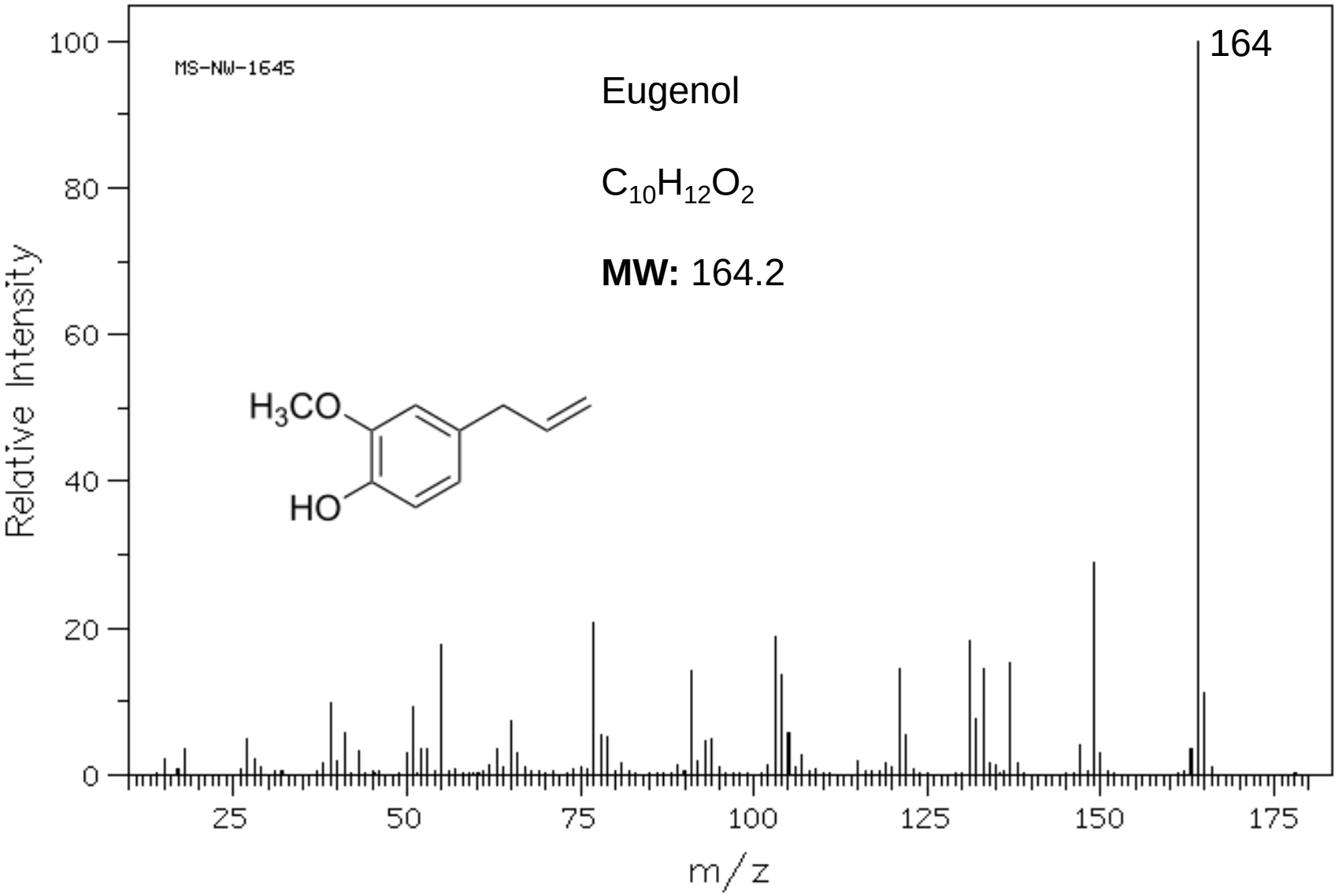


Com hidrocarbonetos alifáticos como o hexano, há Intensa fragmentação e o íon molecular não é muito intense (quanto maior o número de ramificações, menos intense será)



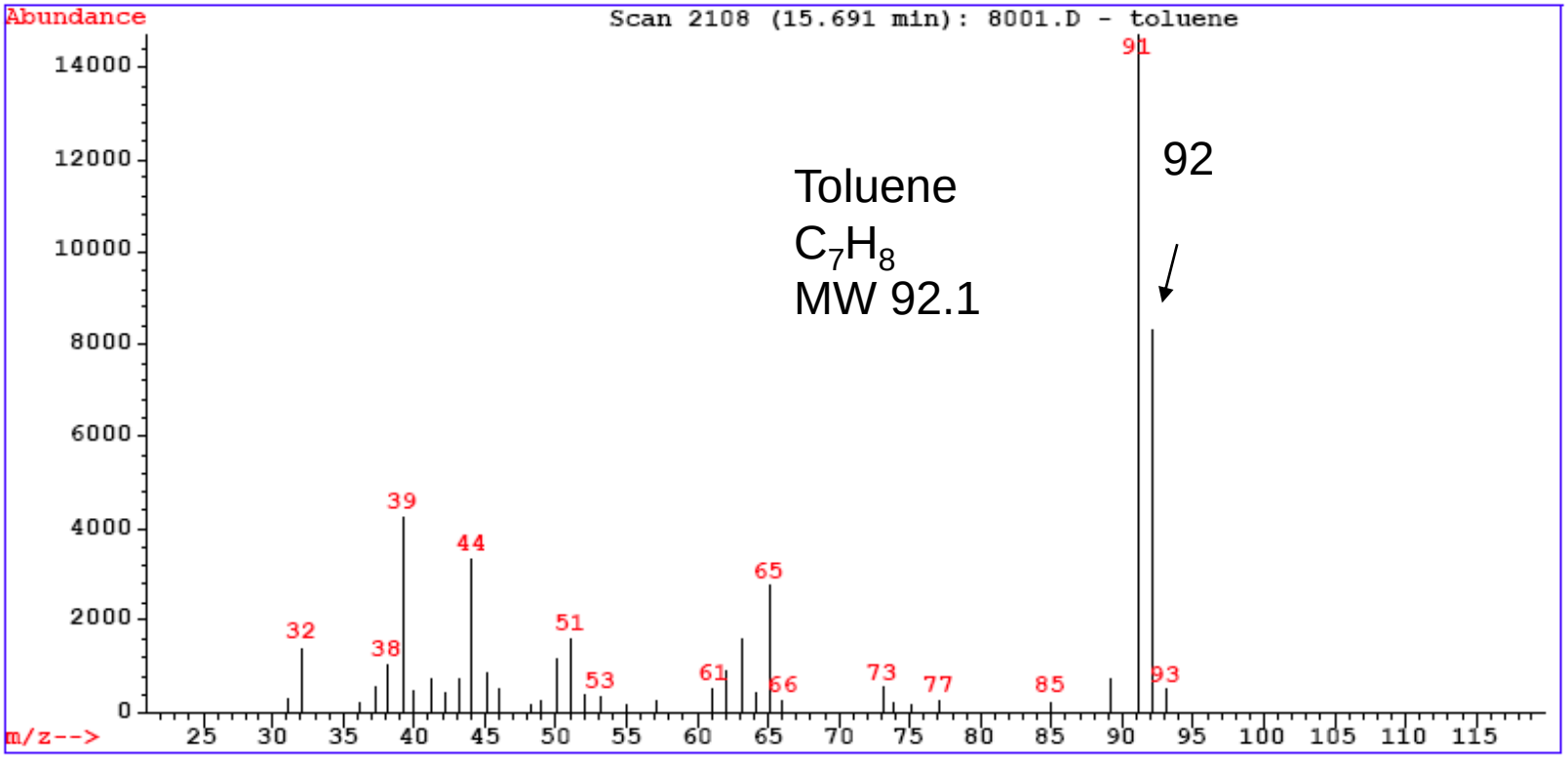
Para compostos benzenoídicos, é bastante frequente observar picos moleculares bastante intensos.

Espectro de massas do eugenol

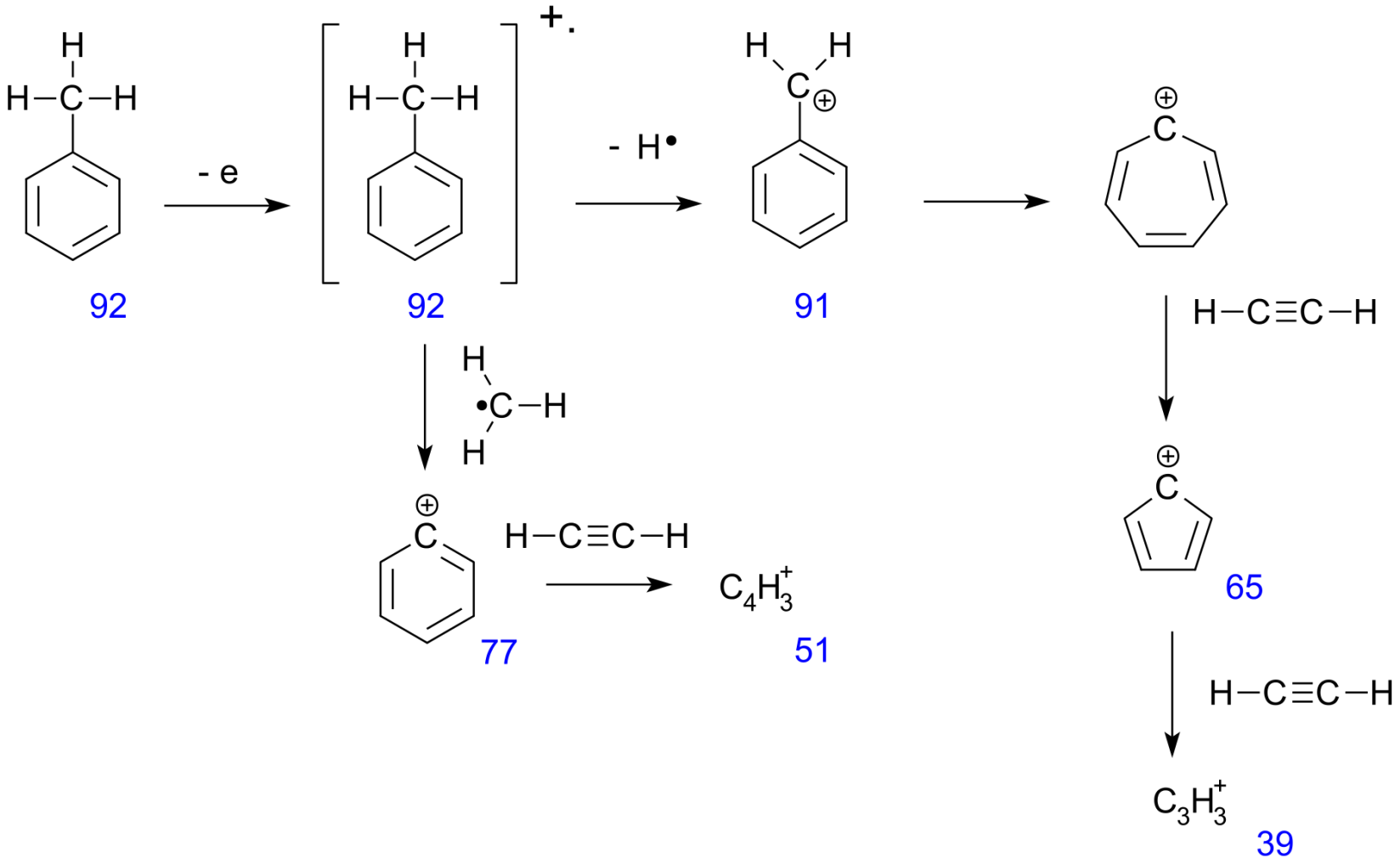


Espectros de massas de derivados do benzeno

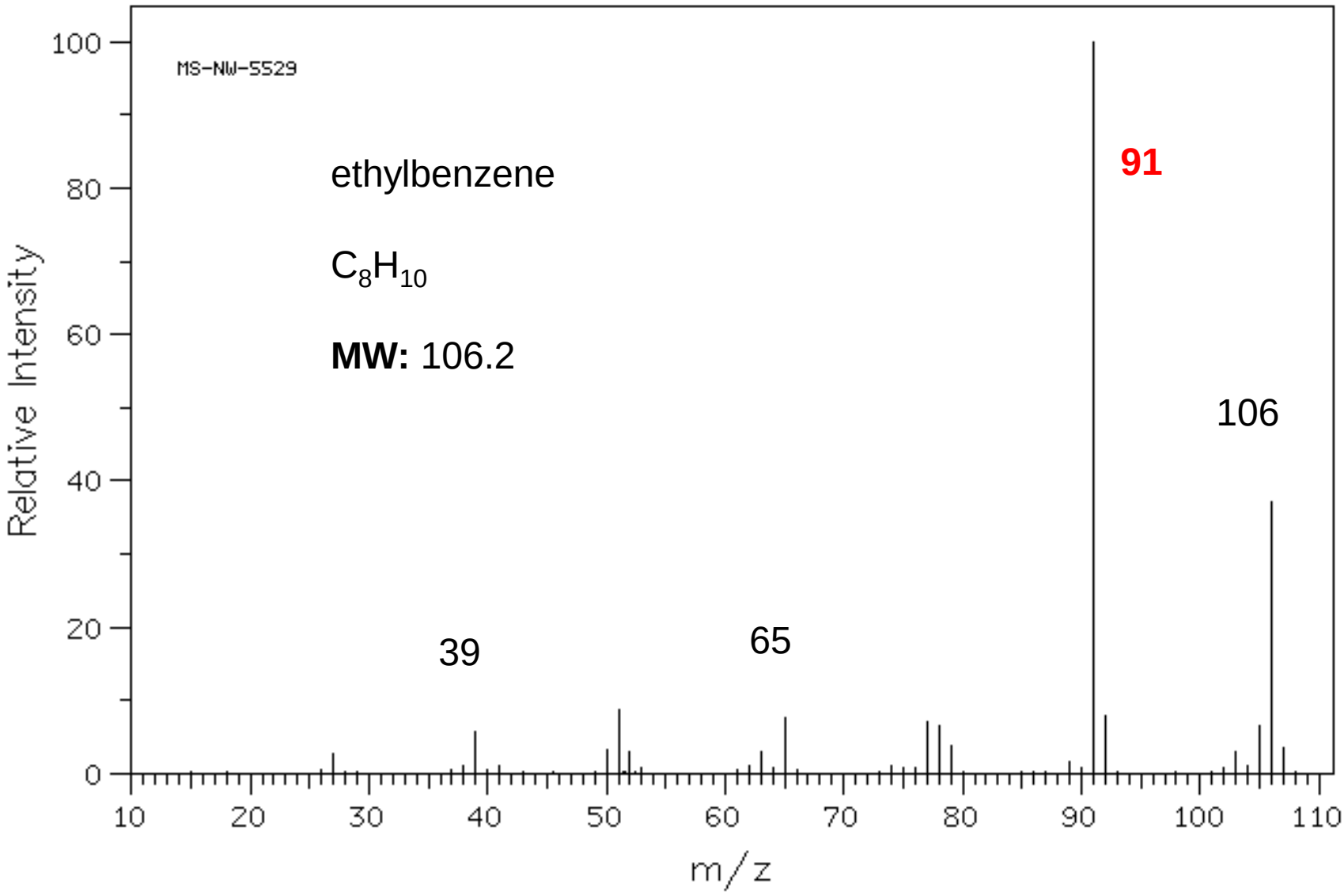
(Tolueno)



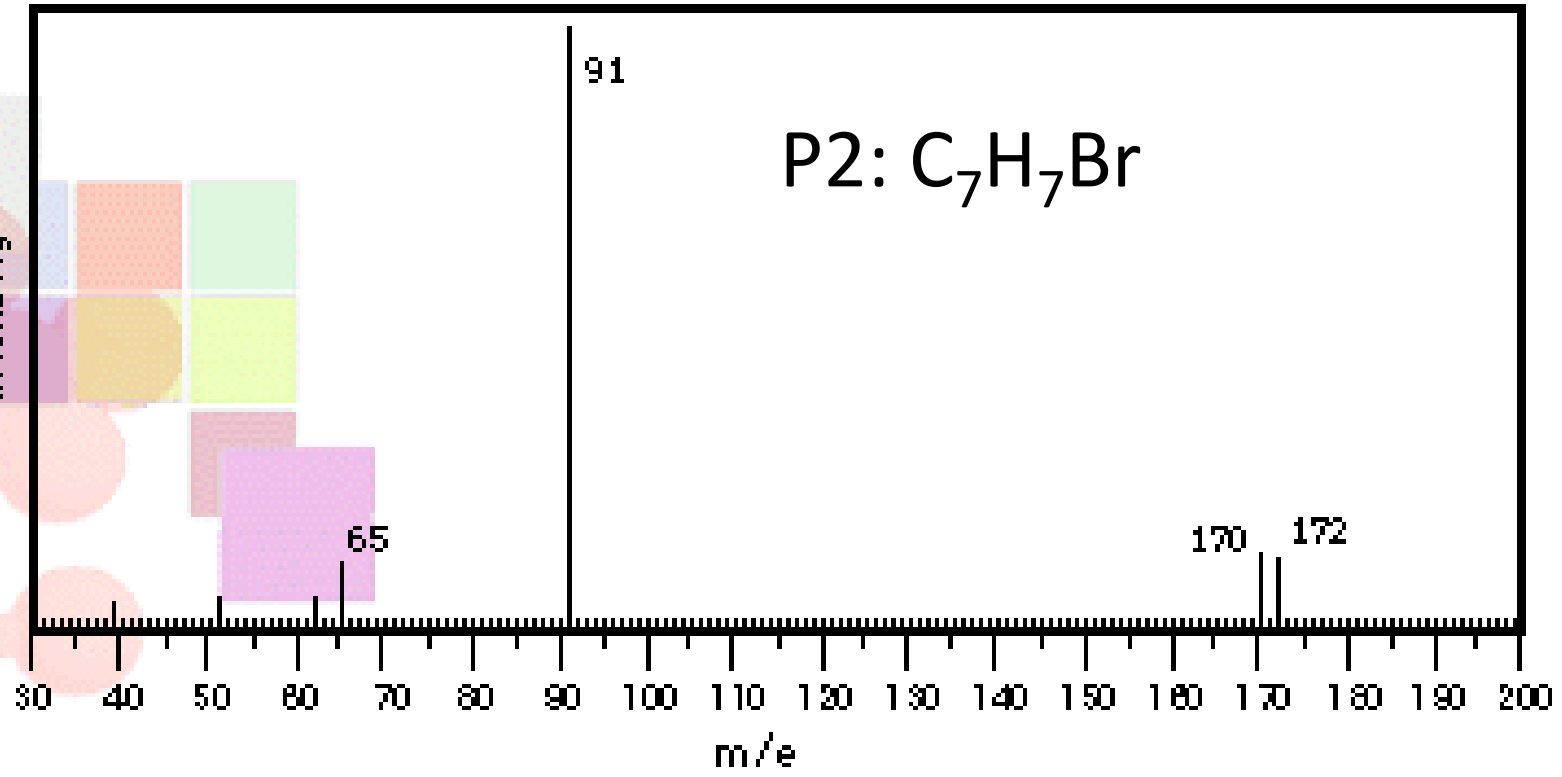
Fragmentação do toluene no espectrômetro de massas

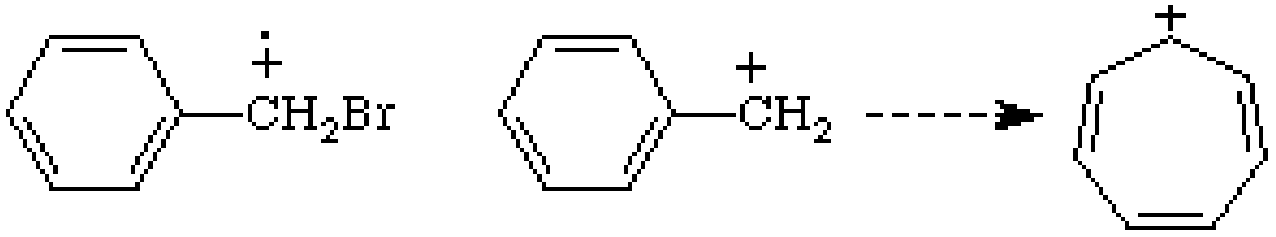


Espectros de massas de derivados do benzeno

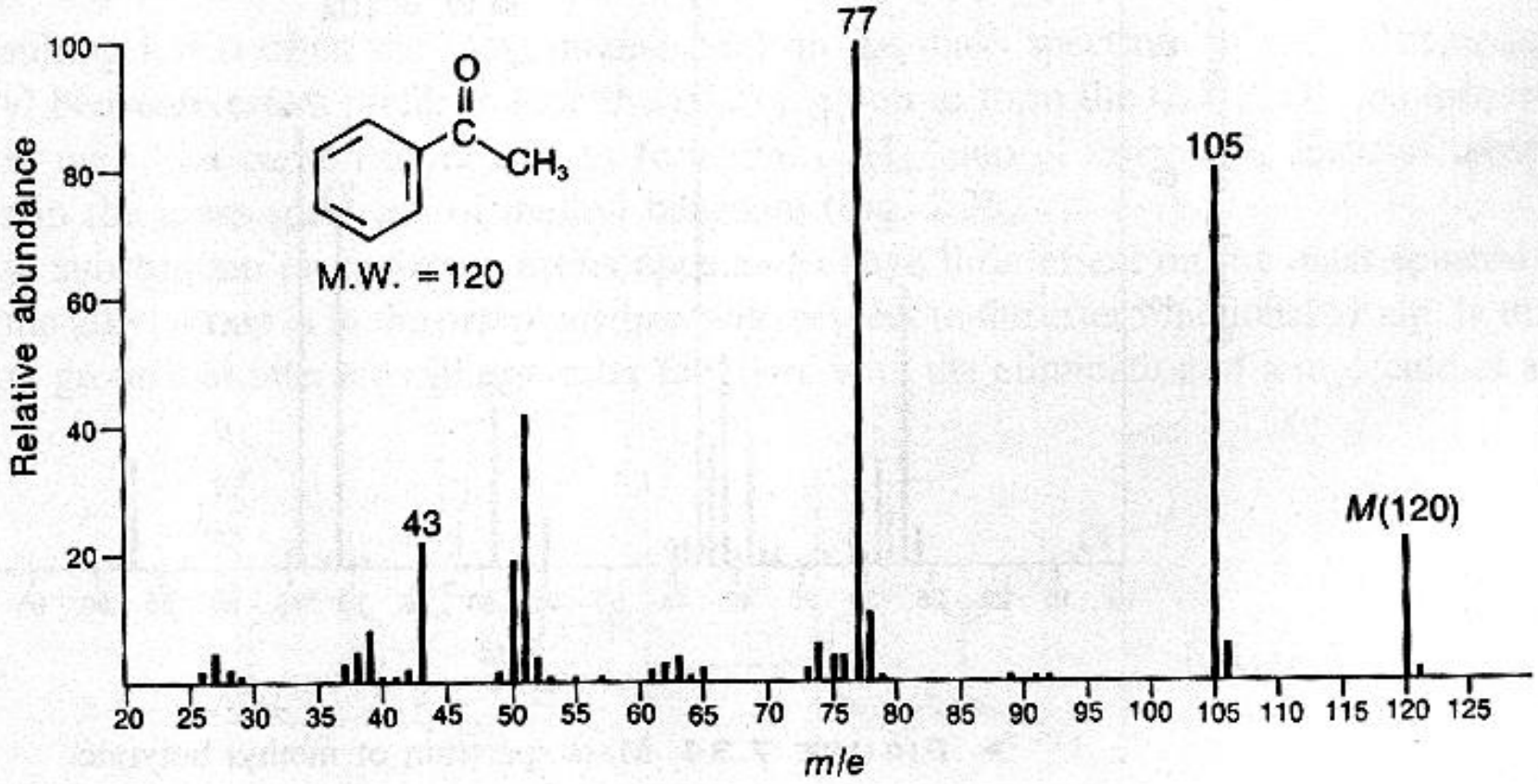


P2: C_7H_7Br



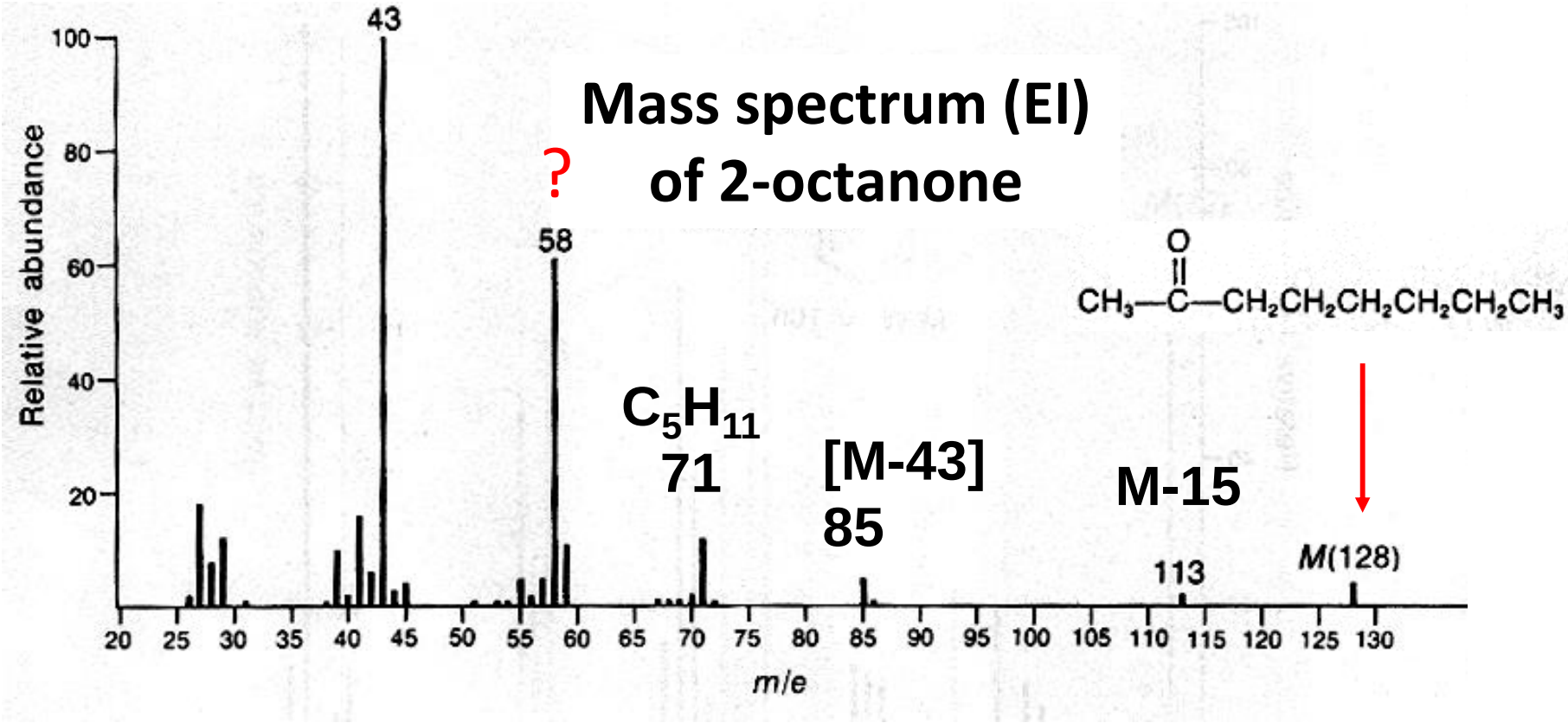


m^+ (170 and 172) m/e = 91 tropylium ion

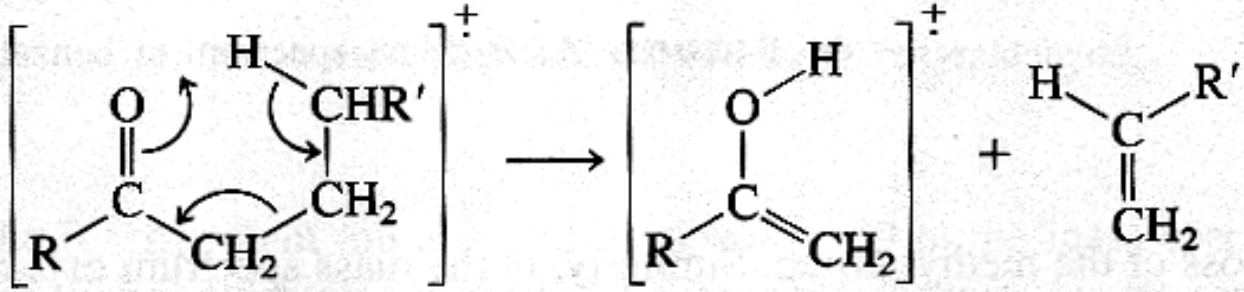


► **FIGURE 7.33** Mass spectrum of acetophenone.

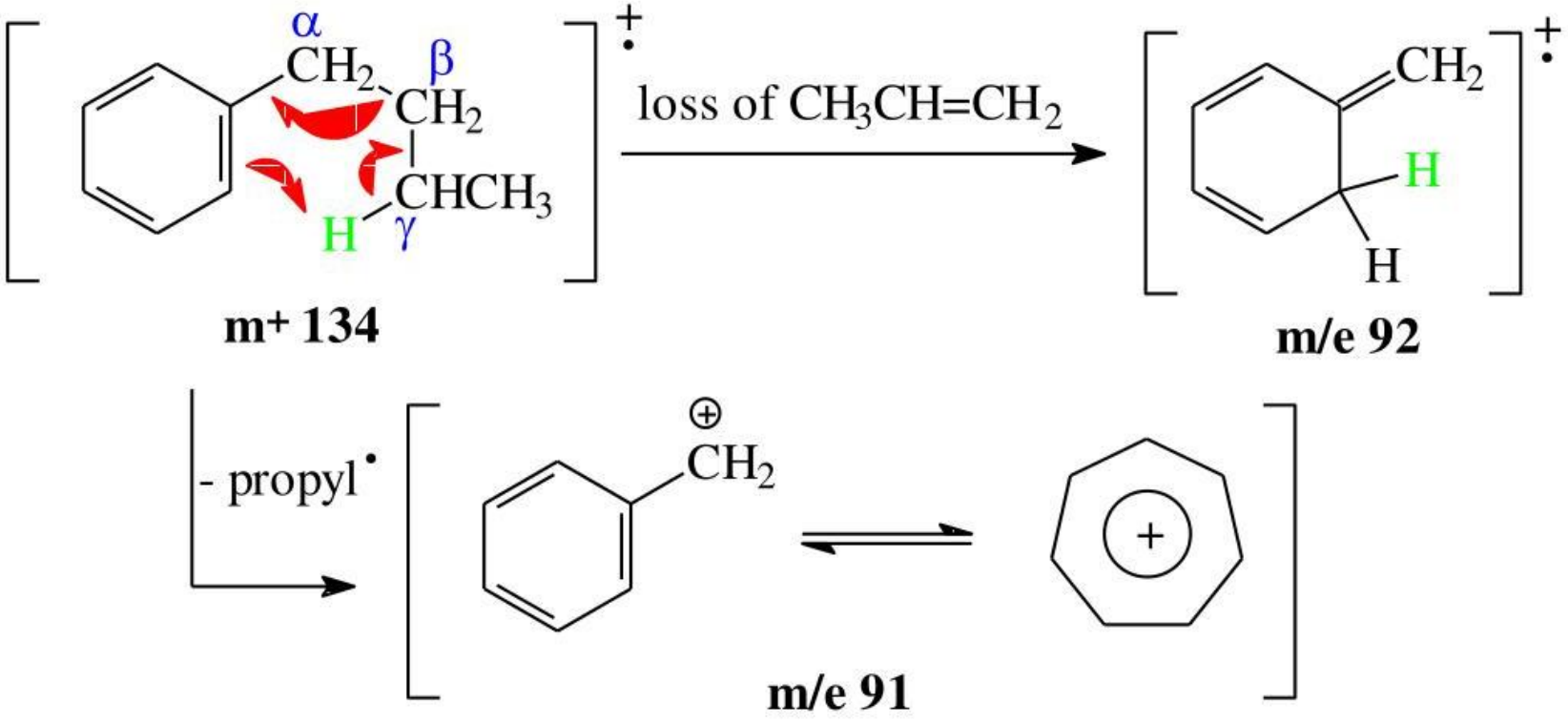
Mass spectrum (EI) of 2-octanone



McLaffert rearrangement

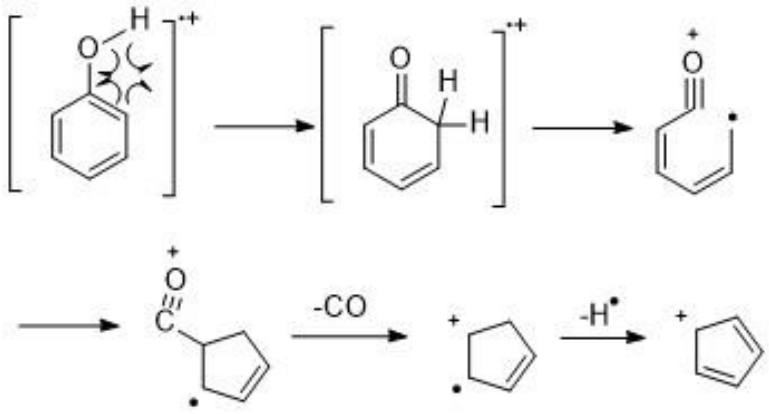


Similar McLaffert rearrangement can be observed for alkylbenzenes forming m/z 92

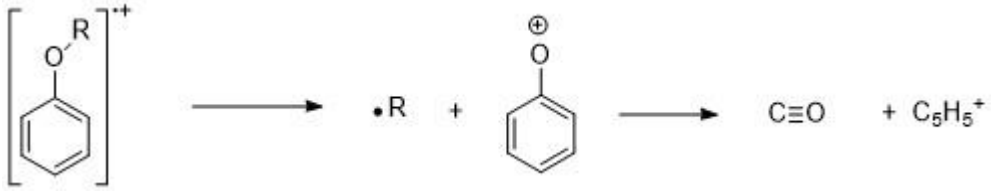


Some typical fragmentation pattern for aromatic compounds

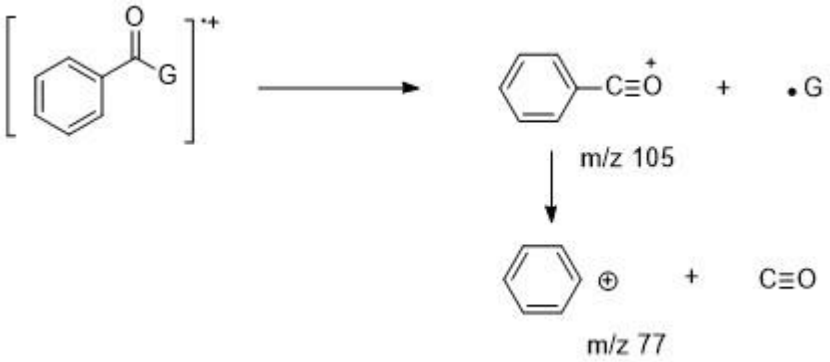
phenols



O-ethers

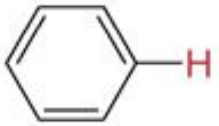
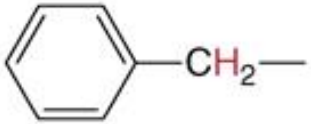


acylbenzenes



Infrared Spectroscopic of Benzenes

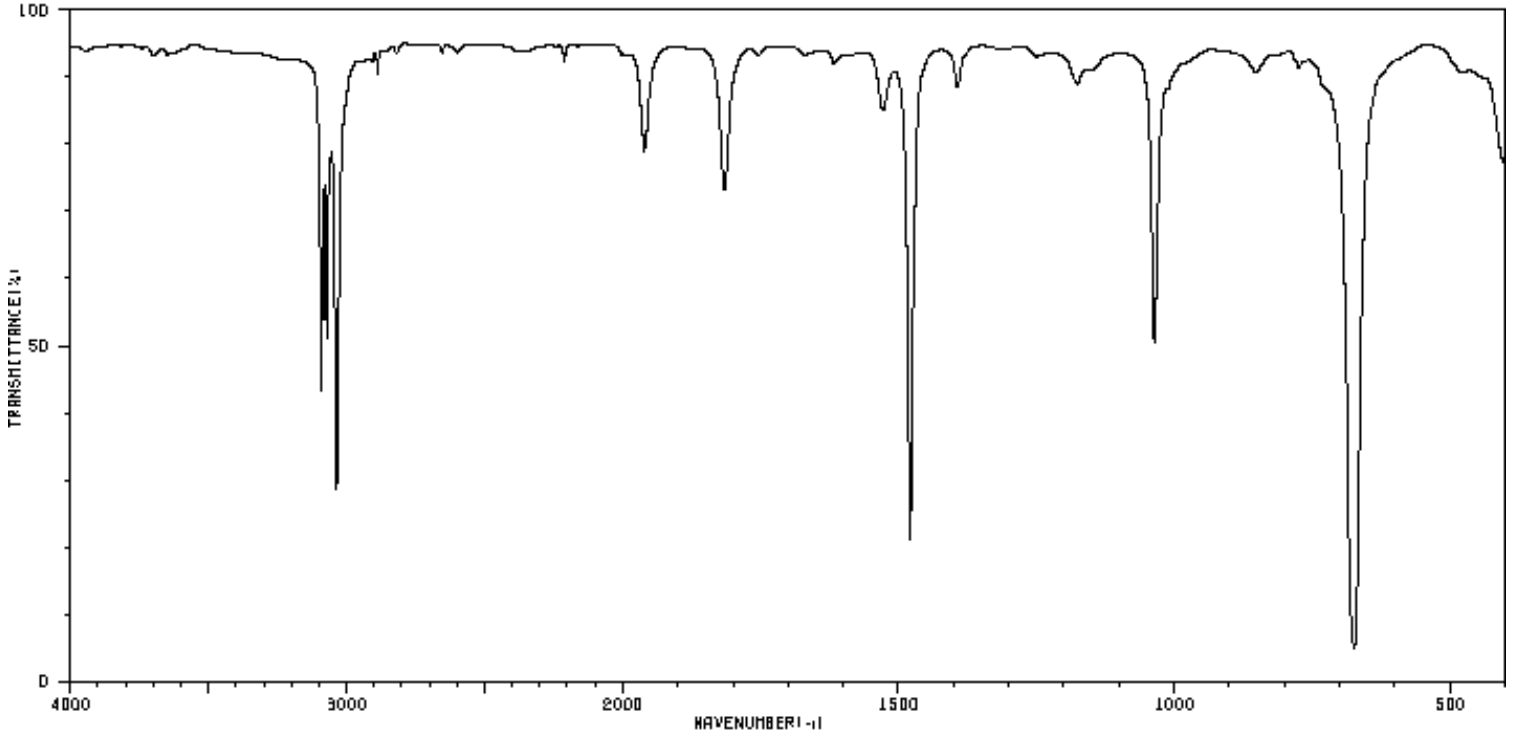
Table 17.1 Characteristic Spectroscopic Absorptions of Benzene Derivatives

IR absorptions	C_{sp^2}–H C=C (arene)	3150–3000 cm^{-1} 1600, 1500 cm^{-1}
^{1}H NMR absorptions	 (aryl H)	6.5–8 ppm (highly deshielded protons)
	 (benzylic H)	1.5–2.5 ppm (somewhat deshielded C_{sp^3}–H)
^{13}C NMR absorption	C_{sp^2} of arenes	120–150 ppm

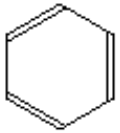
HIT-NO=1237	SCORE= ( )	SDBS-NO=898	IR-NIDA-63541 : LIQUID FILM

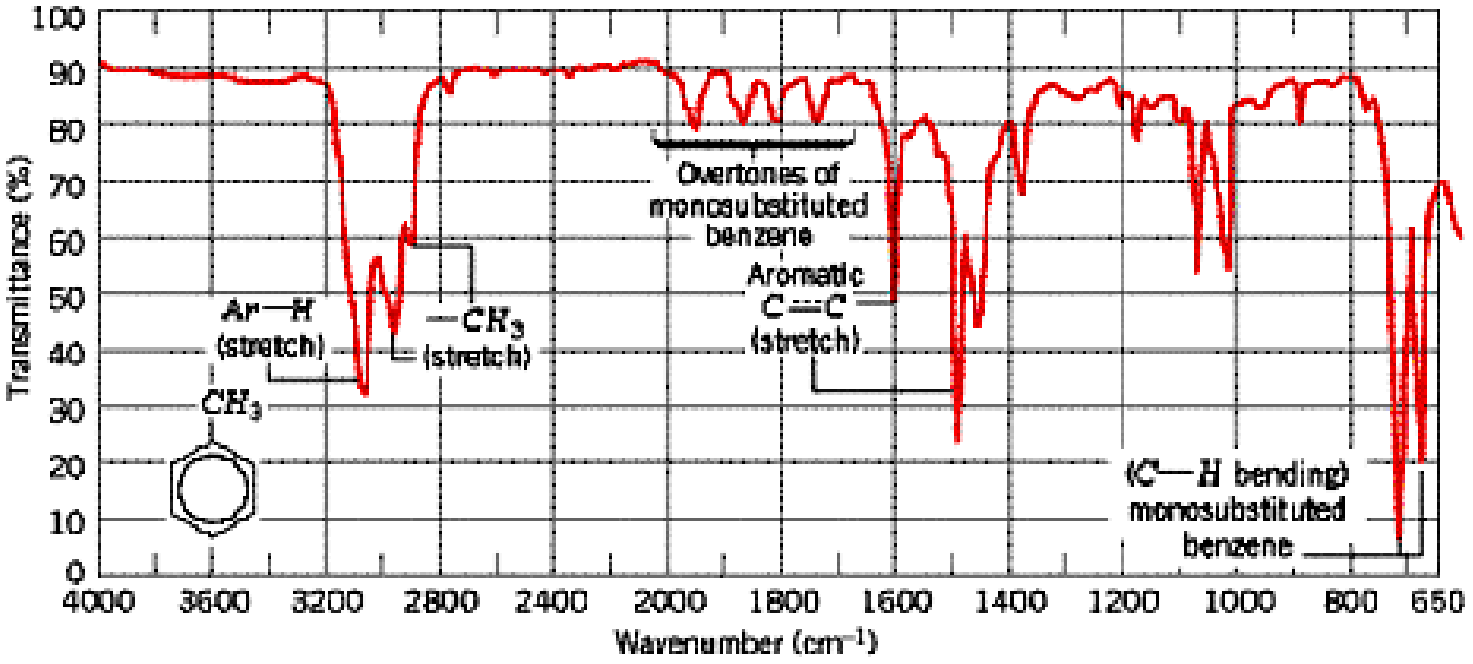
BENZENE

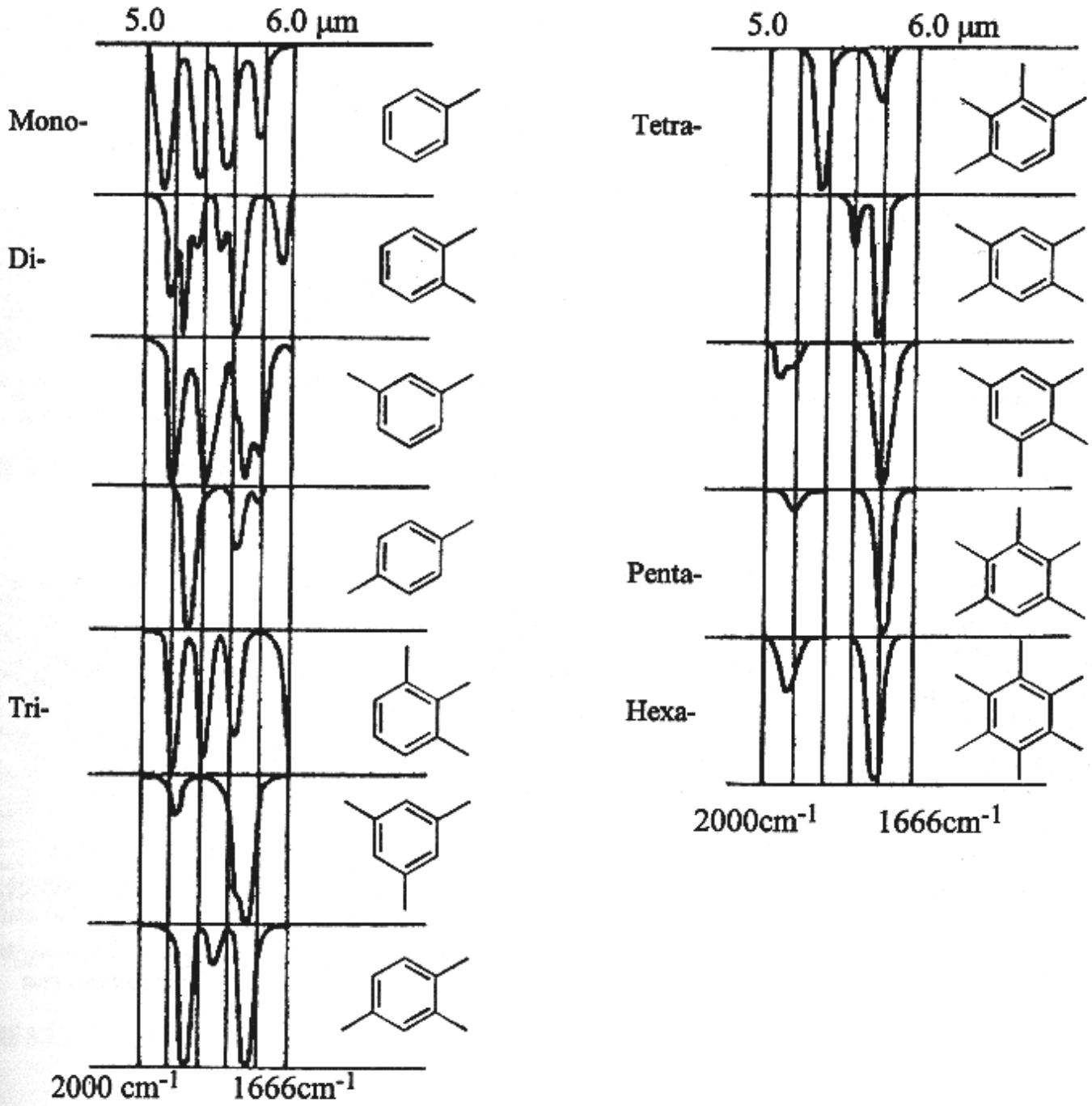
C_6H_6



3091	42	1393	84
3072	49	1176	86
3036	27	1038	49
1961	77	674	4
1815	70		
1528	81		
1479	20		




Transmittance (%)
100
90
80
70
60
50
40
30
20
10
0
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650
Wavenumber (cm⁻¹)
Ar—H (stretch)
—CH3 (stretch)
CH3
Overtones of monosubstituted benzene
Aromatic C=C (stretch)
(C—H bending) monosubstituted benzene

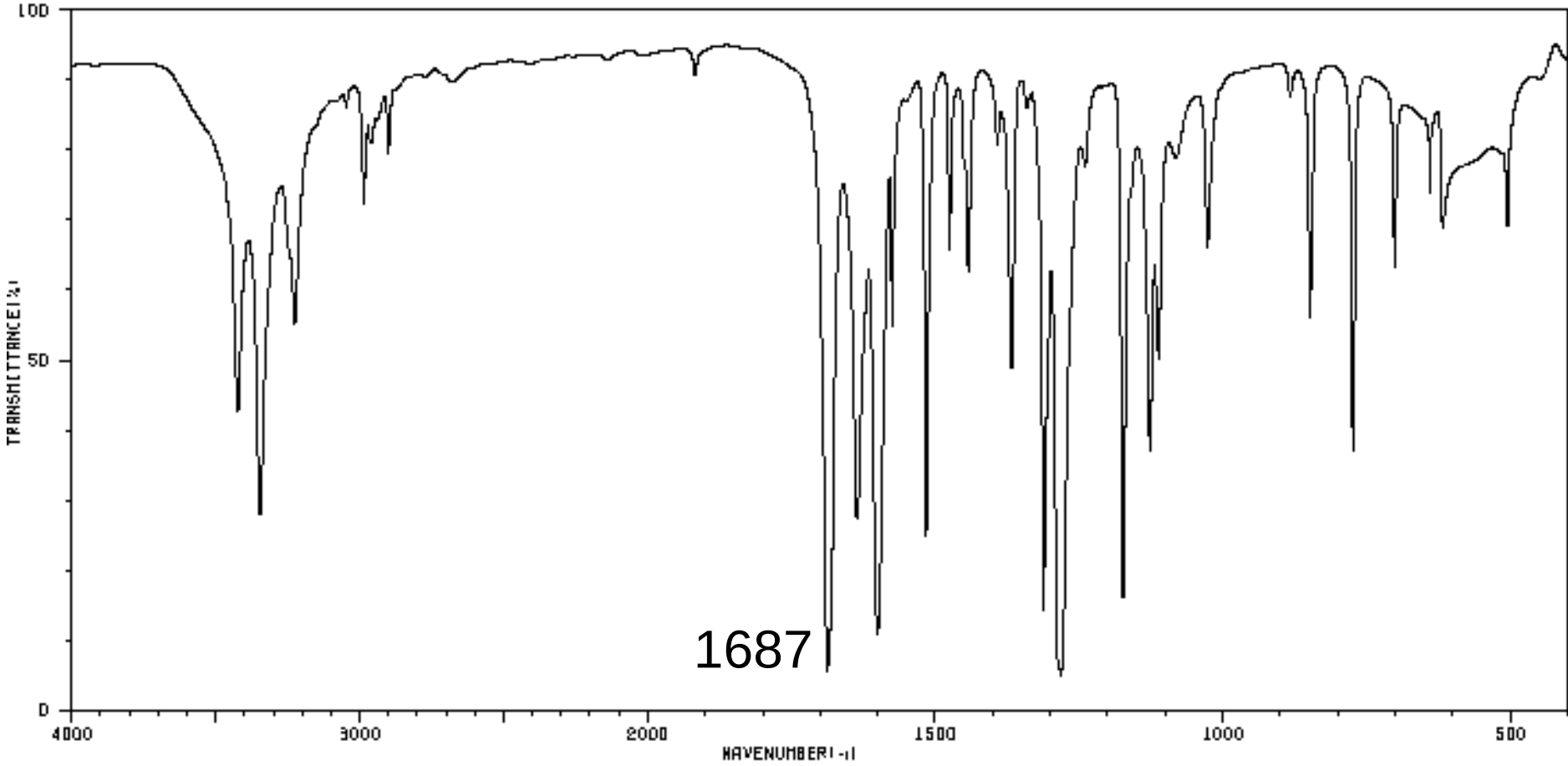

5.0
6.0 µm
Mono-
Di-
Tri-
2000 cm-1
1666cm-1
5.0
6.0 µm
Tetra-
Penta-
Hexa-
2000cm-1
1666cm-1

HIT-NO=1538 | SCORE= ( ) | SDBS-NO=1531 | IR-NIDA-04339 : KBR DISC

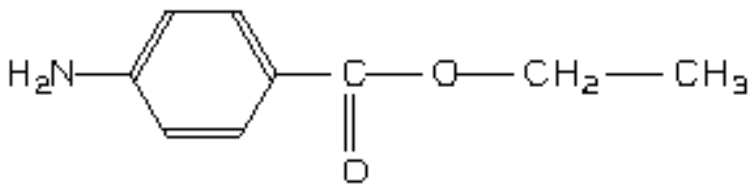
ETHYL P-AMINOBENZOATE

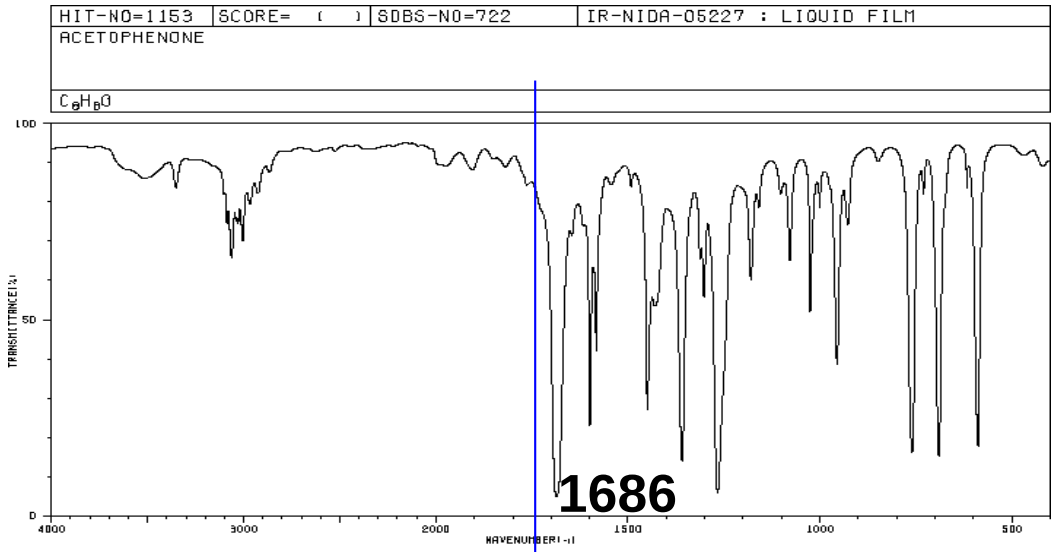
Espectro no IV da benzocaína

$C_9H_{11}NO_2$

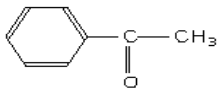


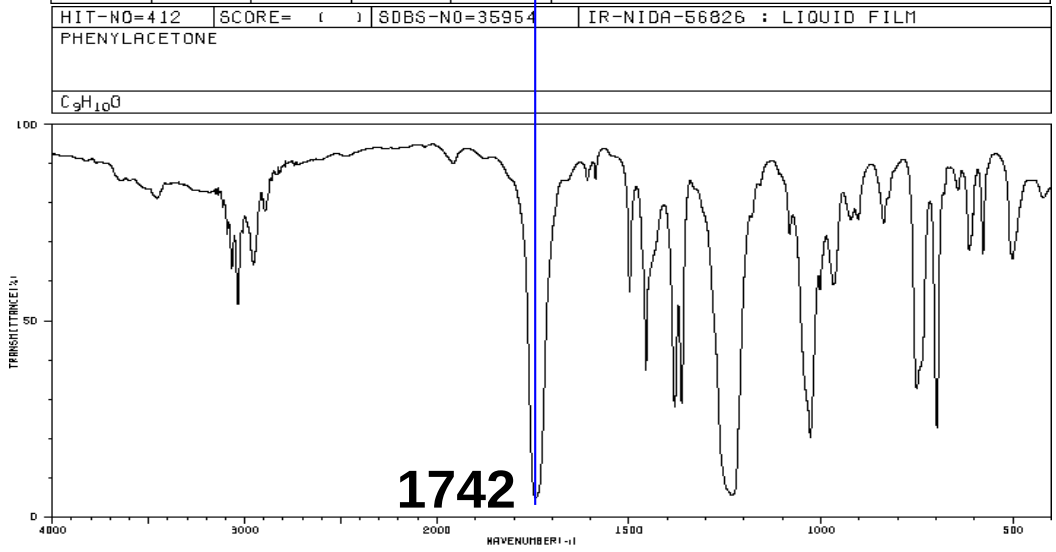
3424	41	2680	86	1460	74	1240	74	849	63
3346	26	1687	5	1443	60	1174	15	774	35
3225	53	1638	26	1393	77	1127	35	701	60
3047	81	1601	10	1367	47	1112	47	641	70
2986	70	1575	52	1342	81	1081	77	618	66
2958	77	1518	29	1312	13	1027	64	506	66
2900	77	1476	64	1282	4	883	84		



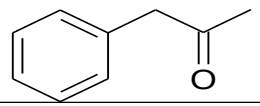


3604	84	2967	77	1645	81	1267	6	966	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1315	82	1025	50	616	61
3005	68	1583	41	1303	63	1001	74	588	17



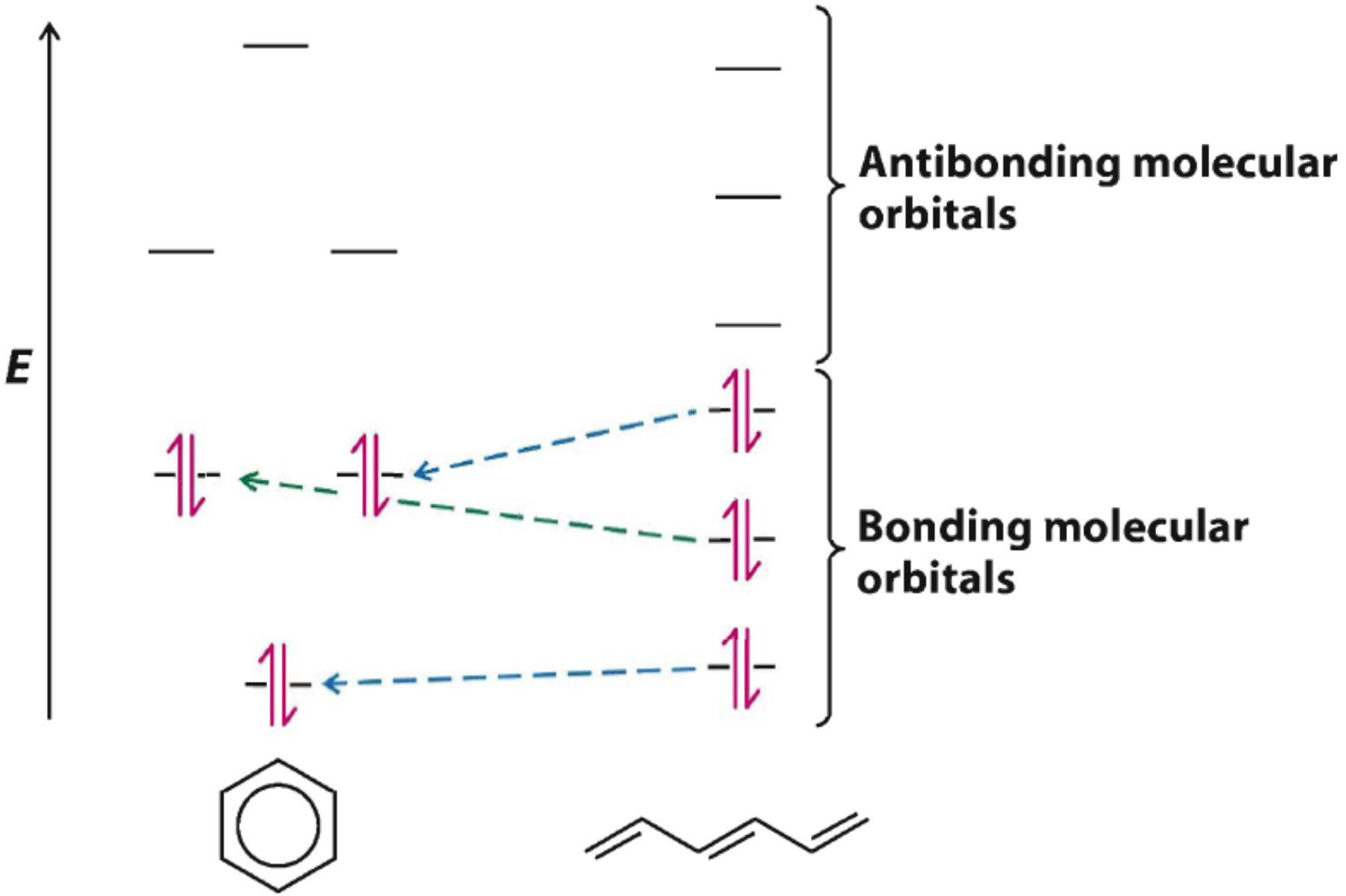


3466	79	2965	64	1381	26	922	72	699	21
3135	79	2952	62	1363	28	916	74	644	79
3114	77	2939	66	1231	5	904	72	614	66
3091	70	2894	74	1082	70	837	72	604	74
3067	60	1742	4	1028	19	826	79	578	64
3052	70	1498	55	1005	55	751	31	503	64
3036	62	1466	36	967	67	741	37	491	70



Efeito da conjugação (menor frequência para a banda da carbonila)

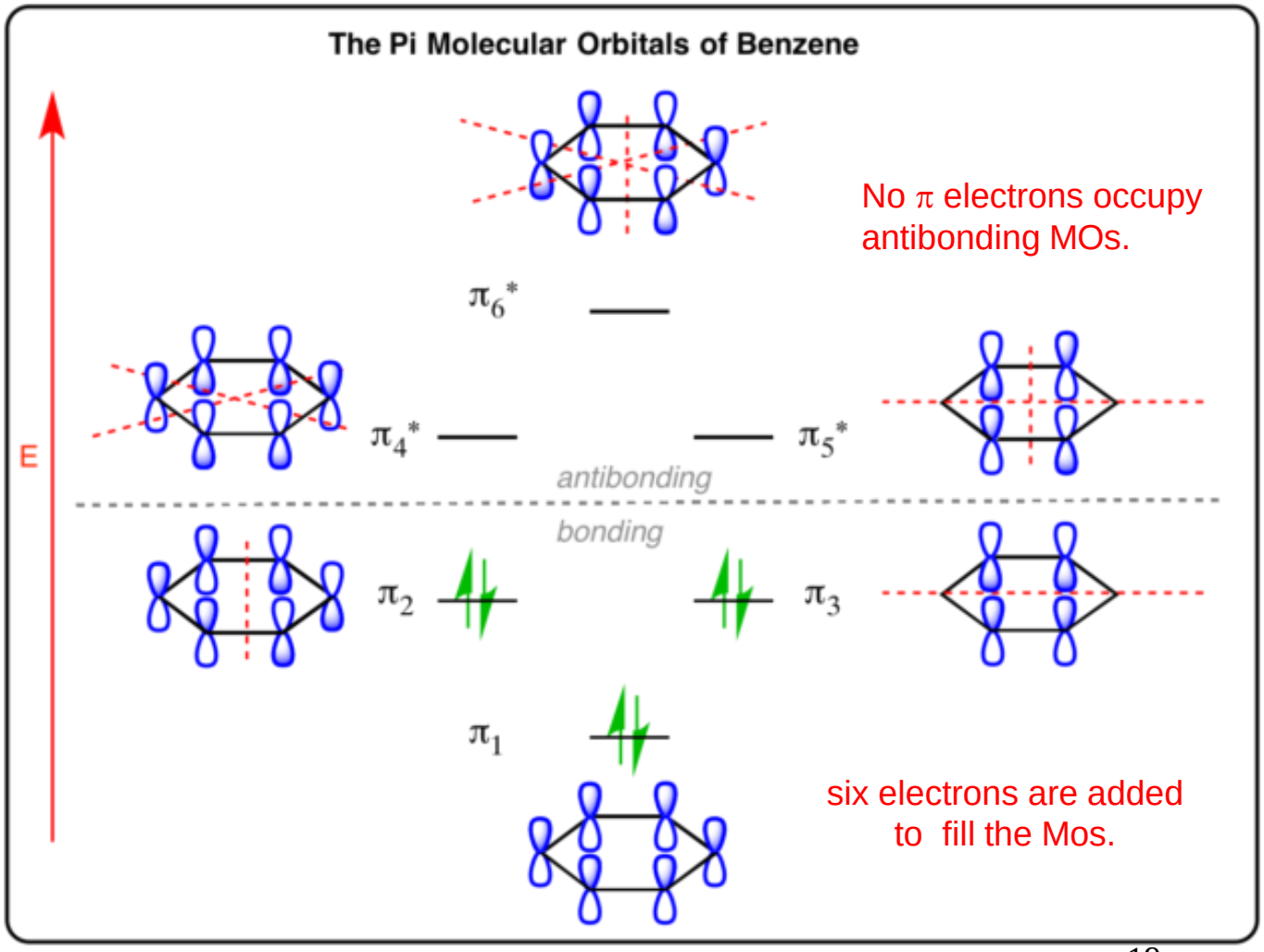
UV absorptions of Aromatic Compounds



Each of the six carbon atoms in benzene has a *p* orbital.

Six atomic *p* orbitals combine to form six π MOs.

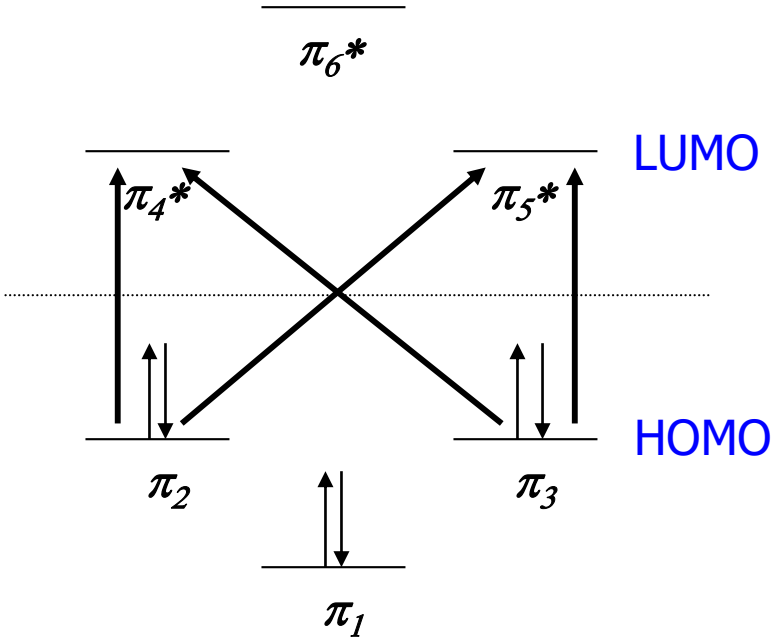
The six molecular orbitals of benzene



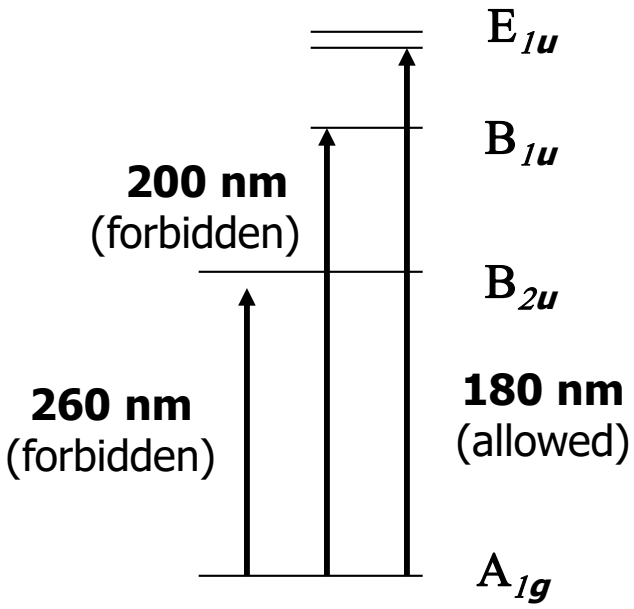
All bonding MOs (and HOMOs) are completely filled in aromatic compounds.

Aromatic Compounds

Four possible HOMO-LUMO $\pi \rightarrow \pi^*$ transitions:



Due to symmetry concerns and selection rules, the actual transition energy states of benzene are:

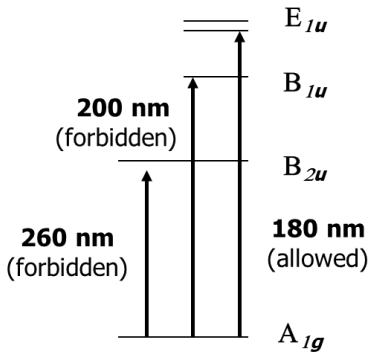


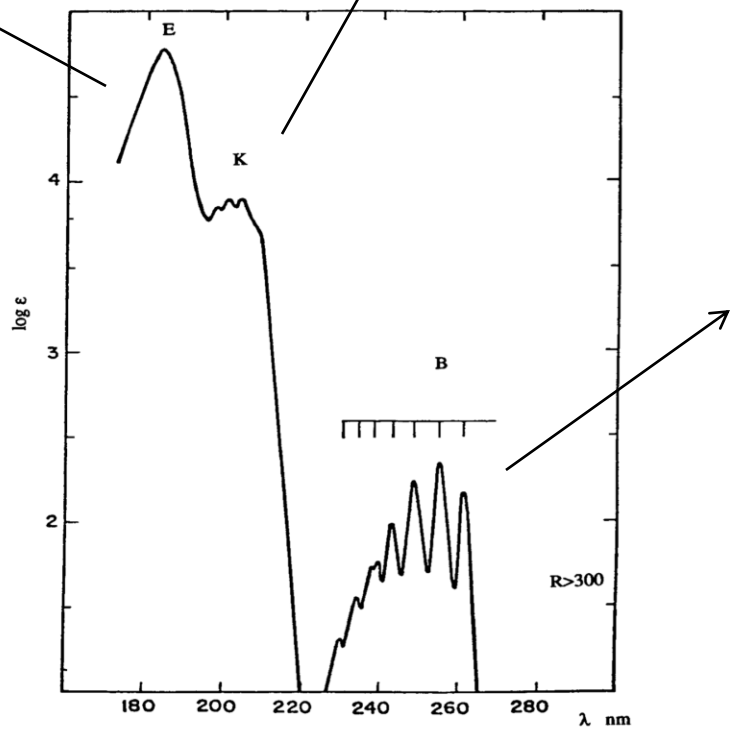
Aromatic Compounds

allowed transition
(ε = 47,000) at 180 nm:
primary band

forbidden transition at 200 nm
(ε = 7400):
second primary band

another forbidden
at 260 nm (ε = 230):
secondary band.





Mixture of limonene, other monoterpenes (C-10) and sesquiterpenes (C15)

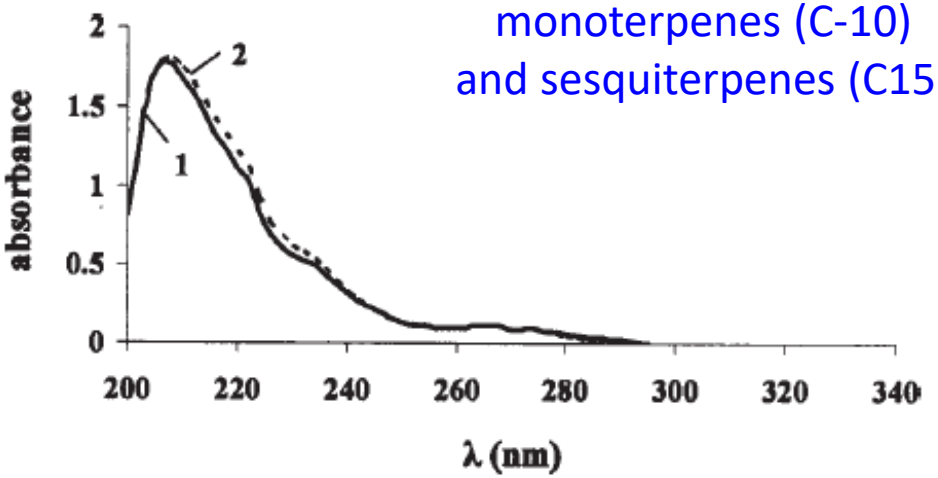
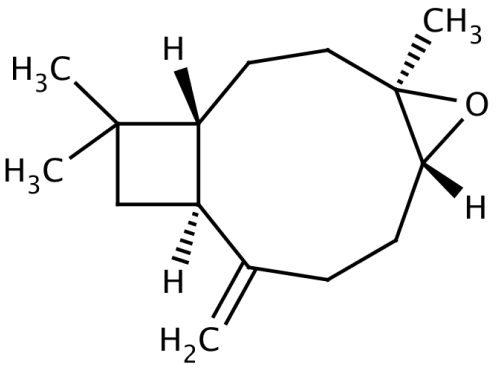
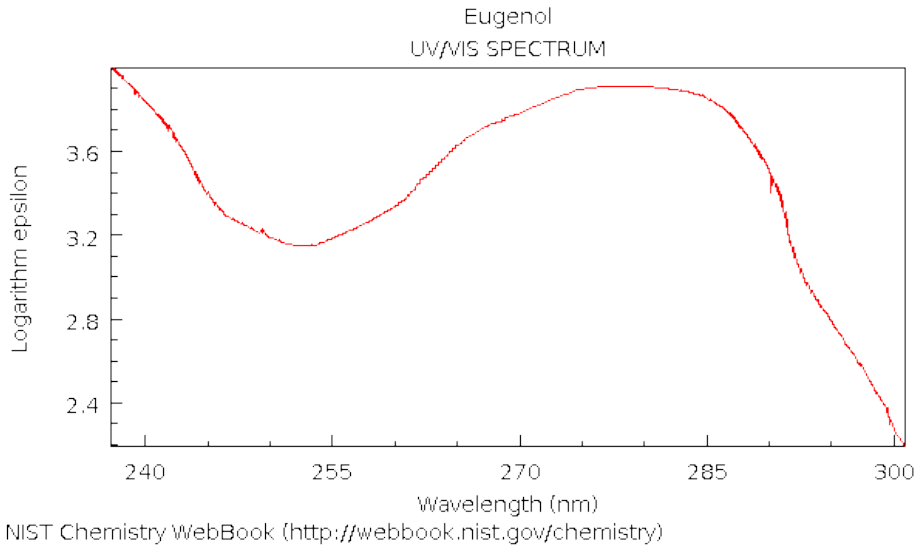
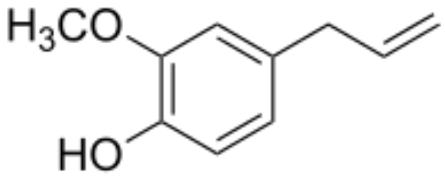


Fig. 4. Ultraviolet-visible spectra of *Eucalyptus globulus* essential oil samples: **1** – EG1; **2** – EG2

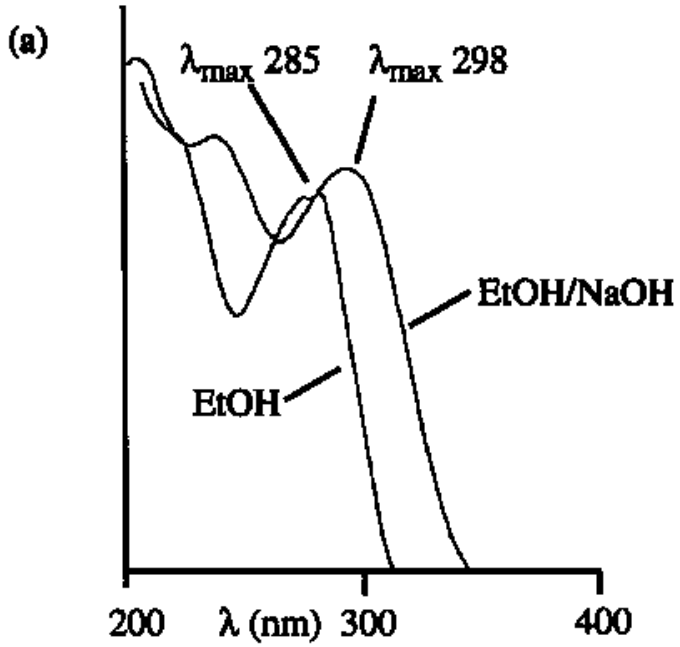


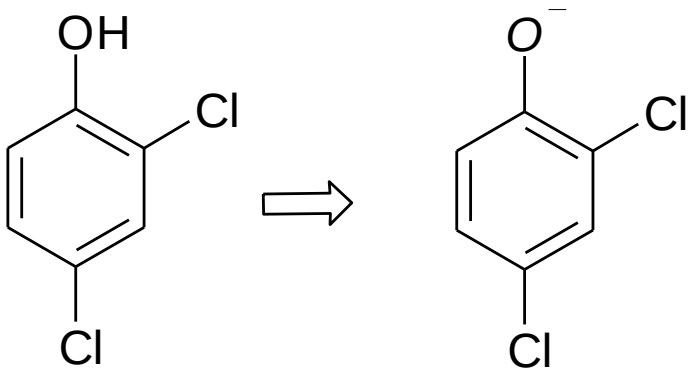




Substituent Effects on aromatic compounds

	Primary		Secondary	
Substituent	λ_{max}	ε	λ_{max}	ε
-H	203.5	7,400	254	204
-OH	211	6,200	270	1,450
$-O^-$	235	9,400	287	2,600





Bathochromic shift (increase in λ)
Hyperchromic effect (increase in absorptivity)

2,4-dichlorophenol

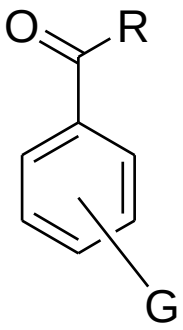
Aromatic Compounds - Substituent Effects

Electron-donating and electron-withdrawing effects

		Primary		*Secondary*	
	Substituent	λ_{max}	ε	λ_{max}	ε
	-H	203.5	7,400	254	204
Electron donating	$-CH_3$	207	7,000	261	225
	-Cl	210	7,400	264	190
	-Br	210	7,900	261	192
	-OH	211	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron withdrawing	-CN	224	13,000	271	1,000
	C(O)OH	230	11,600	273	970
	-C(O)H	250	11,400		
	$-C(O)CH_3$	224	9,800		
	$-NO_2$	269	7,800		

Aromatic Compounds
Substituent Effects; di-substituted and multiple group effects

Parent Chromophore	λ_{max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230



	Substituent increment		
G	*o*	*m*	*p*
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
$-O^-$	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHC(O)CH_3$	20	20	45
$-NHCH_3$			73
$-N(CH_3)_2$	20	20	85