

CH 310 N

T TH 2-3:30

LECTURE 7

Textbook Assignment: Chapter 15 Begin

Homework (for credit): POW 3 posted

Today's Topics:

Organometallic Reagents-Begin Aldehydes & Ketones

Notice & Announcements:

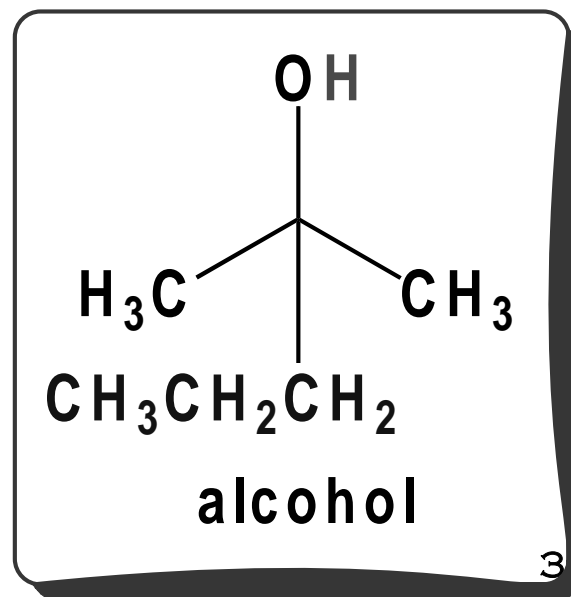
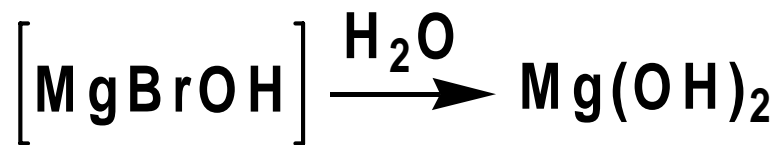
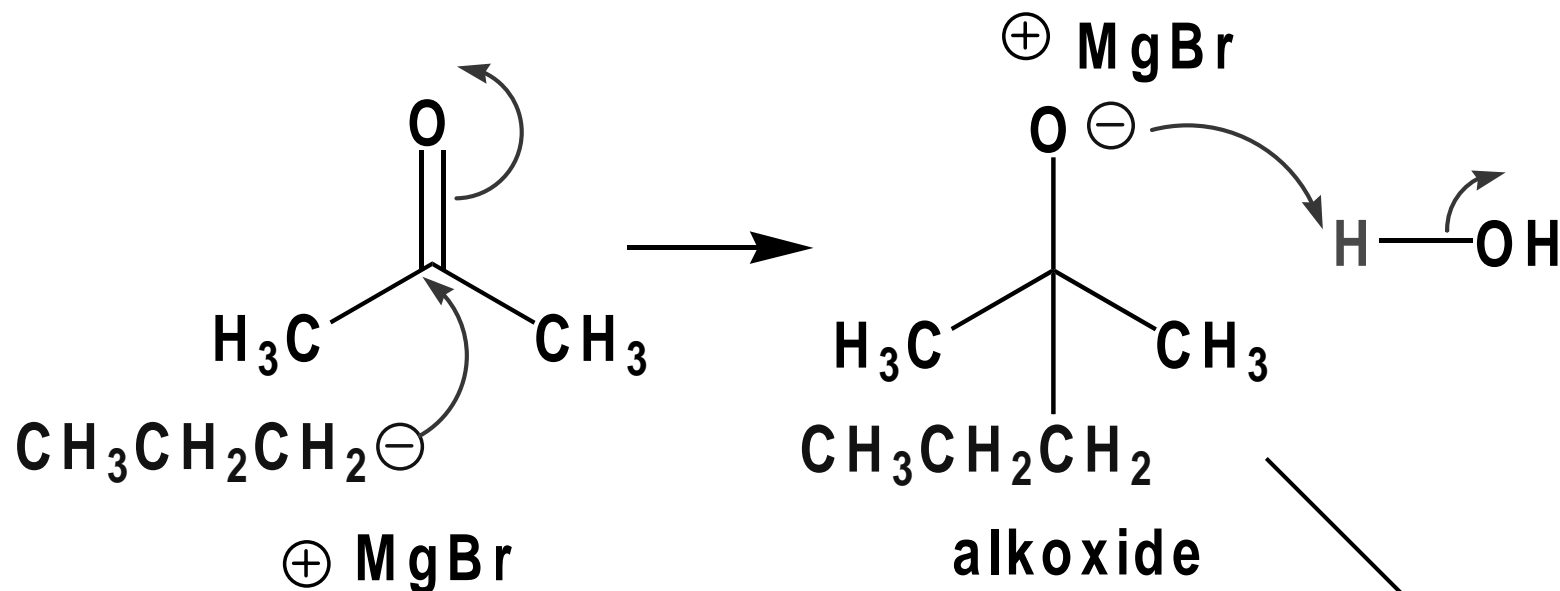
Exam I: Monday 9/21 7-9 PM

Last Name A-L: WEL 1.308

Last Name M-Z: WEL 2.224

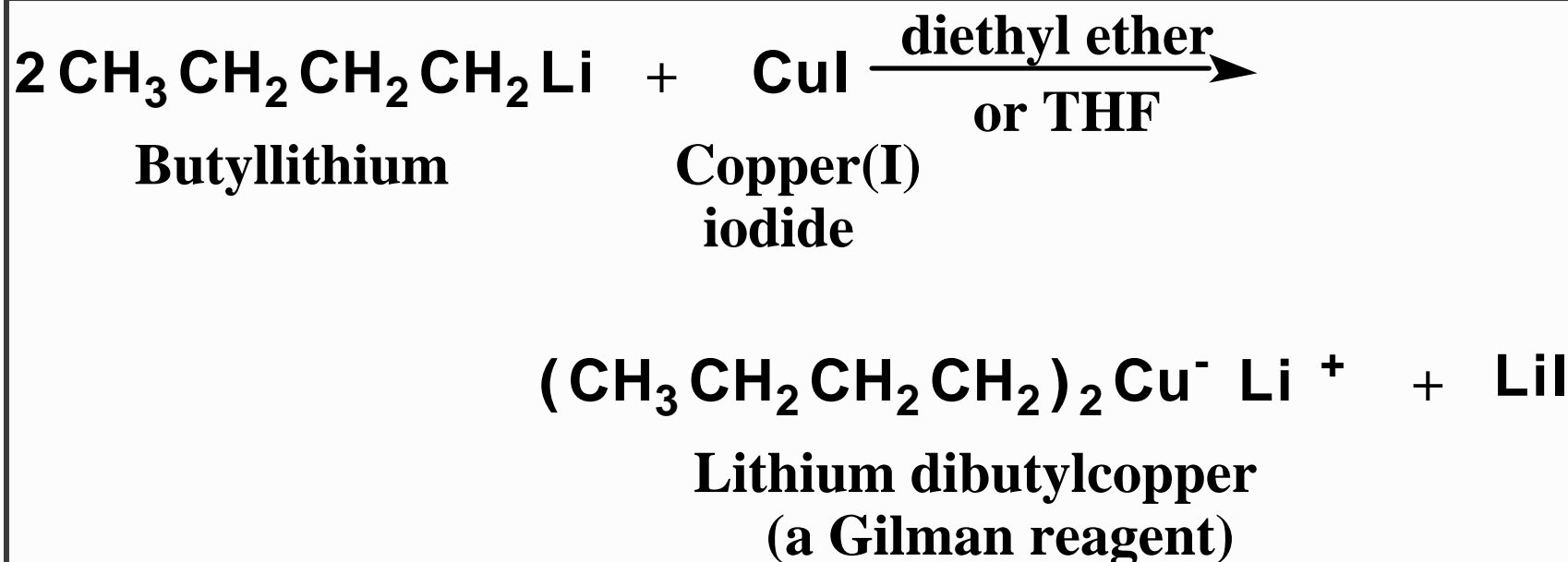
Organometallic Reagents

A Simple Example:



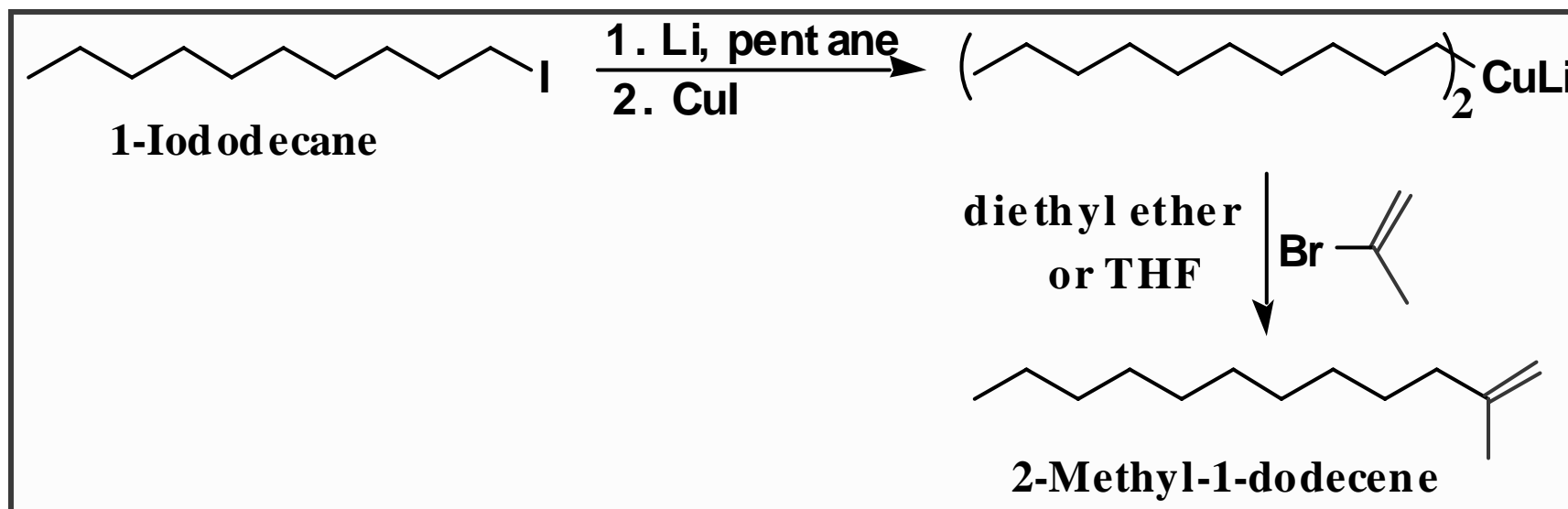
Gilman Reagents

- Lithium diorganocopper reagents, known more commonly as **Gilman reagents**
 - prepared by treating an alkyl, aryl, or alkenyl lithium compound with Cu(I) iodide



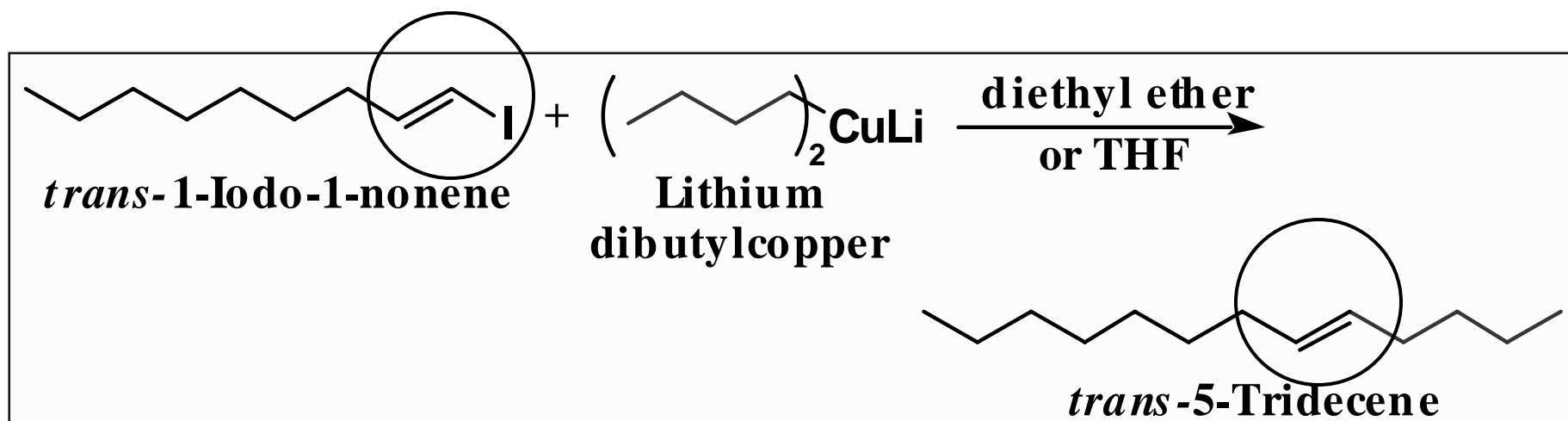
Reactions

- Coupling within organohalogen compounds
 - form new carbon-carbon bonds by coupling with alkyl and alkenyl chlorides, bromides, and iodides
 - **Example**



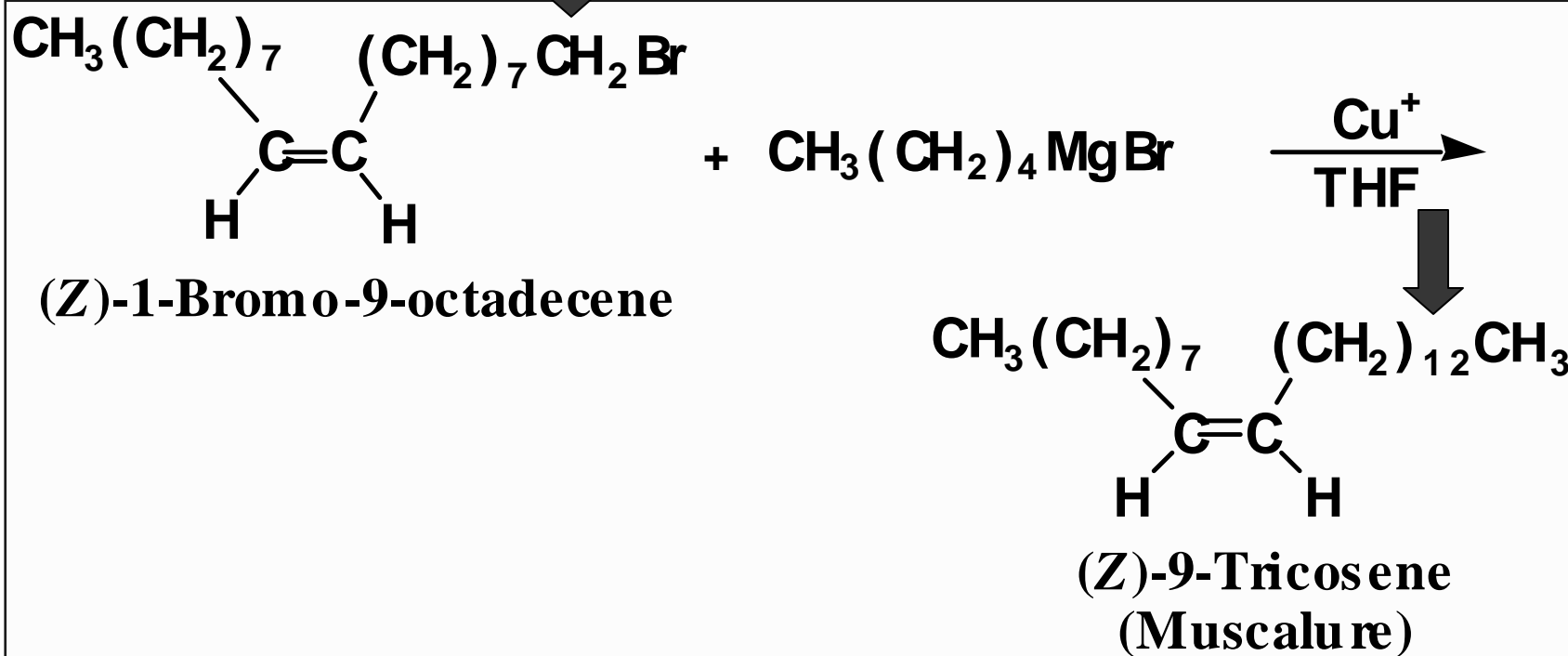
Reactions

coupling with a vinylic halide is stereospecific: the configuration of the carbon-carbon double bond is retained



Reactions

- A variation on the preparation of a Gilman reagent is to use a Grignard reagent with a catalytic amount of a copper(I) salt



Aldehydes And Ketones

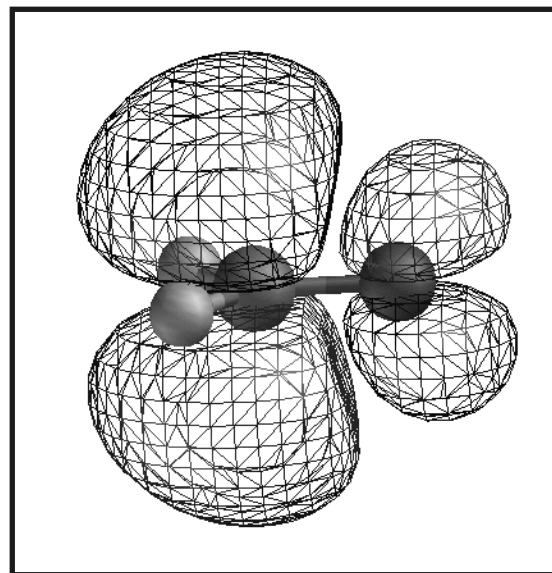
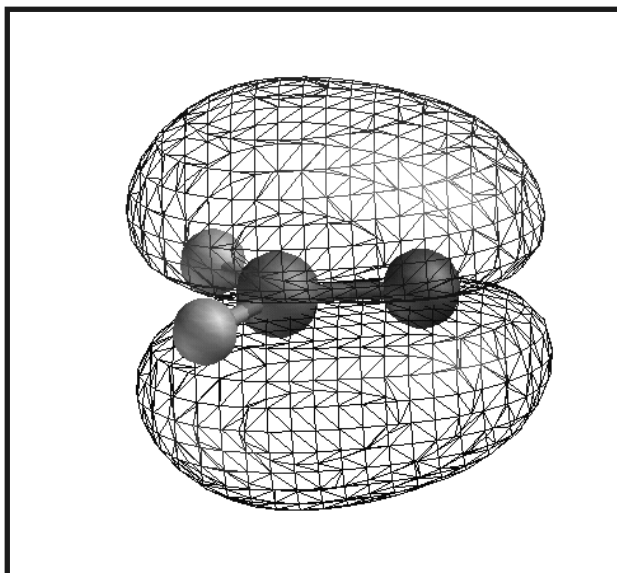
The Carbonyl Group

The next units cover the physical and chemical properties of classes of compounds containing the carbonyl group,

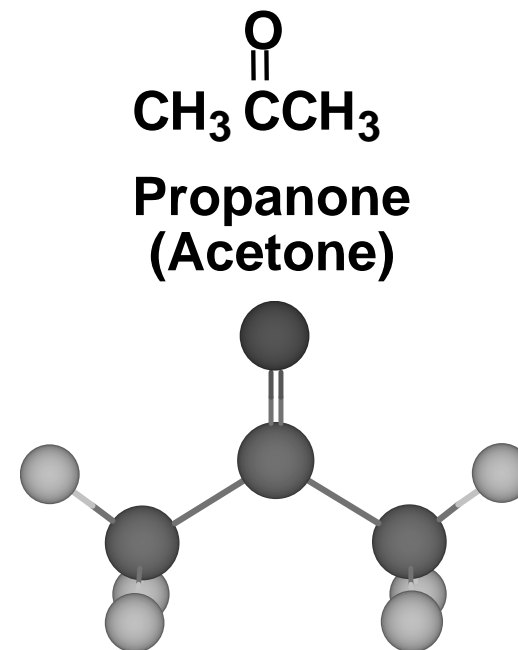
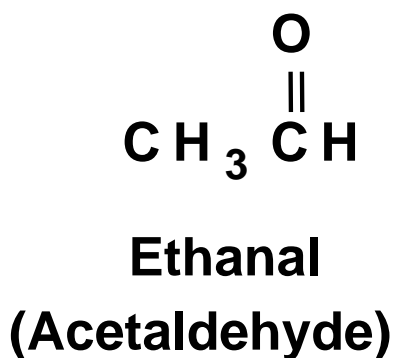
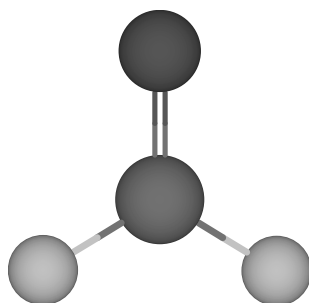
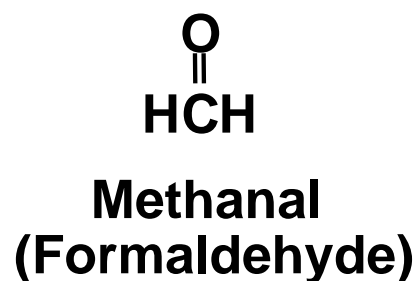


- aldehydes and ketones (Chapter 16)
- carboxylic acids (Chapter 17)
- acid halides, acid anhydrides, esters, amides (Chapter 18)
- enolate anions (Chapter 19)

- the carbonyl group consists of **one sigma bond** formed by the overlap of sp^2 hybrid orbitals and **one pi bond** formed by the overlap of parallel $2p$ orbitals
- pi bonding and pi antibonding MOs for formaldehyde



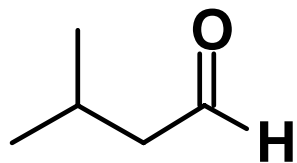
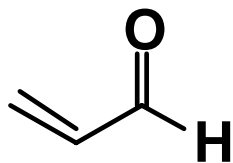
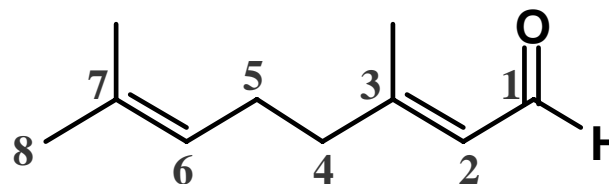
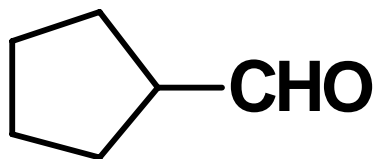
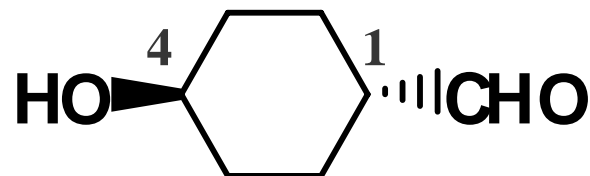
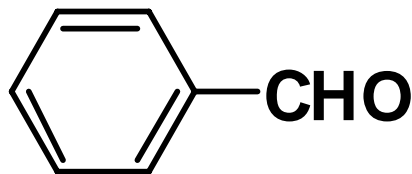
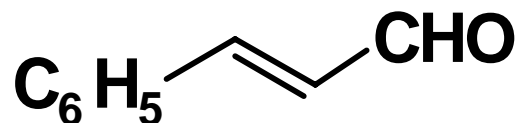
- the functional group of an **aldehyde** is a carbonyl group bonded to a H atom and a carbon atom
- the functional group of a **ketone** is a carbonyl group bonded to two carbon atoms



Nomenclature

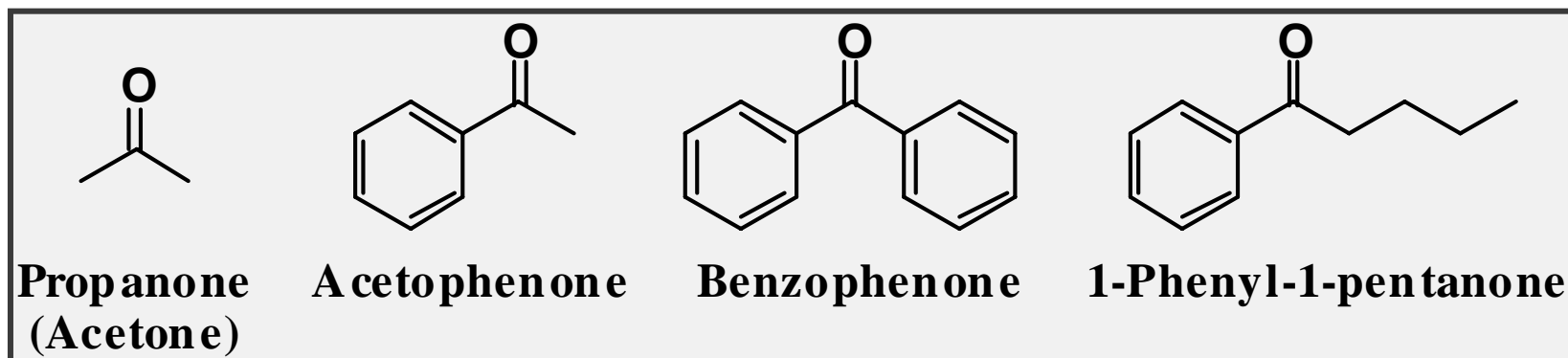
IUPAC names:

- the parent chain is the longest chain that contains the functional group
- for an aldehyde, change the suffix from -e to -al
- for an unsaturated aldehyde, change the infix from -an- to -en-; the location of the suffix determines the numbering pattern
- for a cyclic molecule in which -CHO is bonded to the ring, add the suffix -carbaldehyde

**3-Methylbutanal****2-Propenal
(Acrolein)****(2E)-3,7-Dimethyl-2,6-octadienal
(Geranial)****Cyclopentanecarbaldehyde*****trans*-4-Hydroxycyclohexanecarbaldehyde****Benzaldehyde*****trans*-3-Phenyl-2-propenal
(Cinnamaldehyde)**

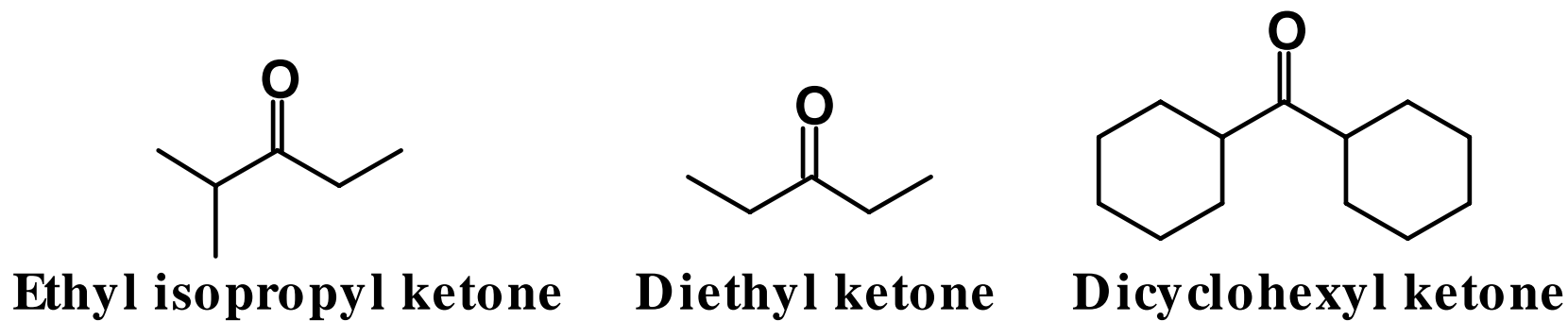
IUPAC names

- the parent alkane is the longest chain that contains the carbonyl group
- for ketones, change the suffix -e to -one
- number the chain to give C=O the smaller number
- the IUPAC retains the common names acetone, acetophenone, and benzophenone



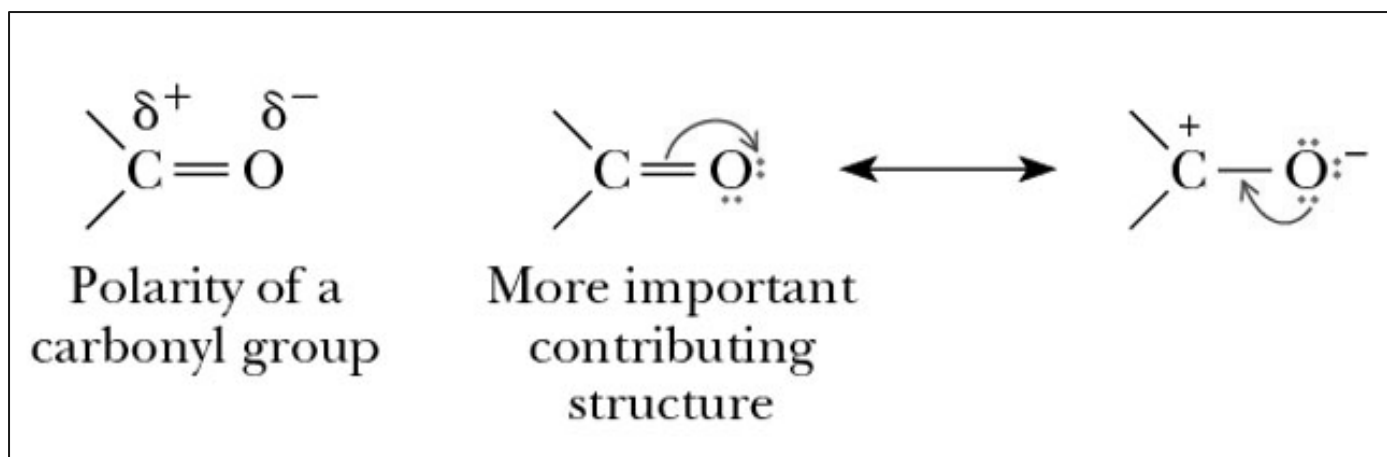
Common Names

- for an aldehyde, the common name is derived from the common name of the corresponding carboxylic acid
- for a ketone, name the two alkyl or aryl groups bonded to the carbonyl carbon and add the word ketone



Physical Properties

Oxygen is more electronegative than carbon (3.5 vs 2.5) and, therefore, a C=O group is polar

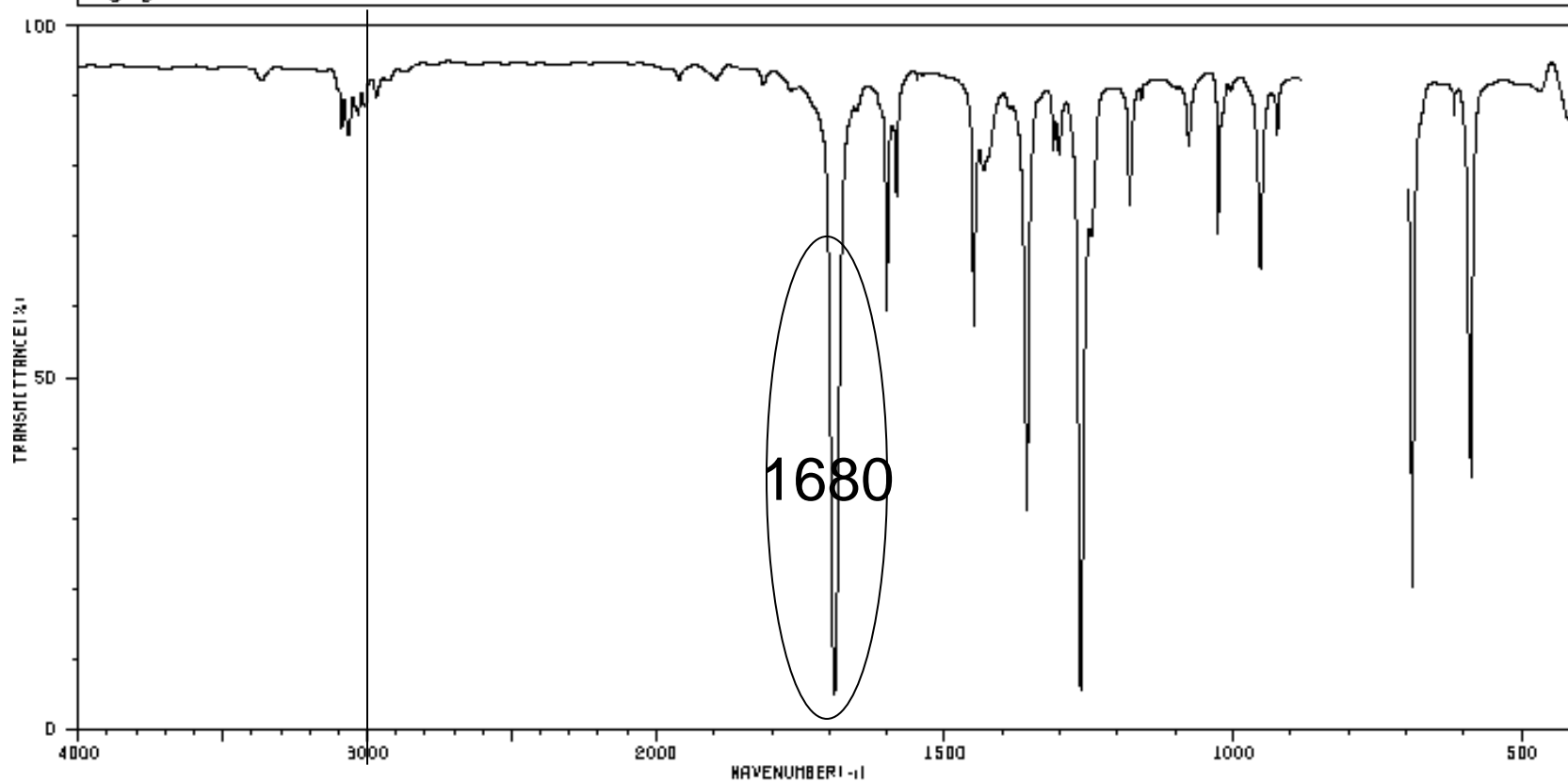


- aldehydes and ketones are **polar compounds** and interact in the pure state by dipole-dipole interaction
- they have **higher boiling points** and are more **soluble in water** than nonpolar compounds of comparable molecular weight

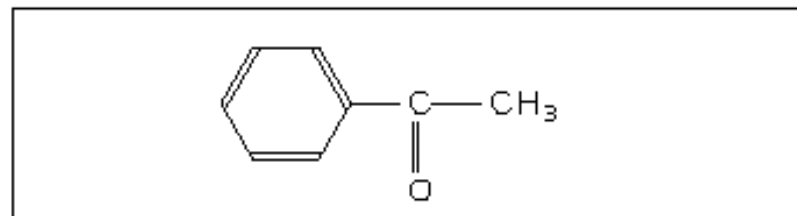
Spectral Properties

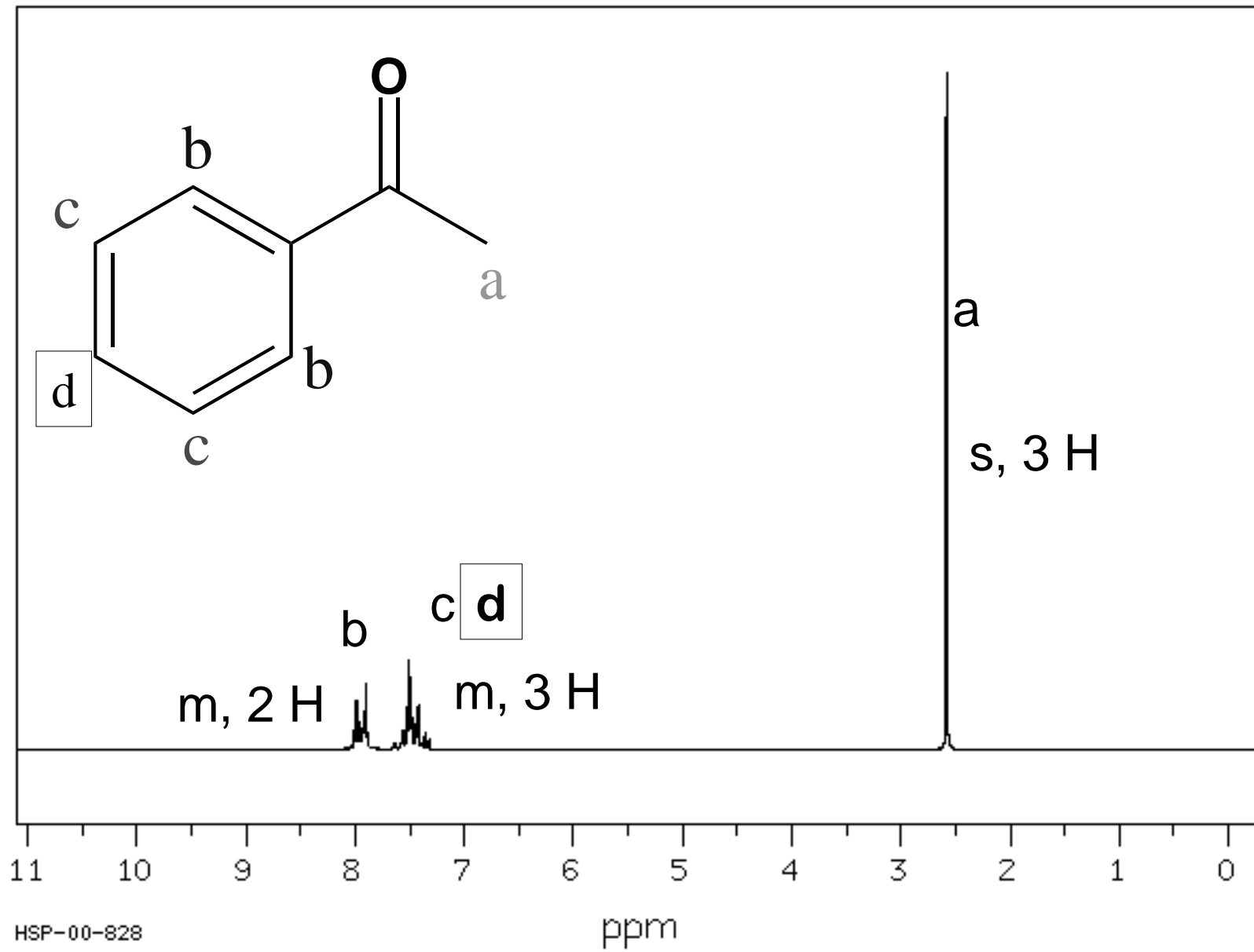
- **IR:** Carbonyl-Aldehydes 1720-1725; also show m C-H @ 2720; Ketones 1710-1715 (aryl ketones 1680)
- **NMR:** Aldehydes 9.5-10.2 (s) ketones protons α to 2.1-2.3 can be 2.2-2.6
- **^{13}C NMR:** carbonyl carbon 180-215 ppm
- **MS:** Aldehydes (M-1) loss of aldehyde H; loss of CO (M-28); both groups undergo α cleavage

HIT-NO=1117	SCORE= ()	SDBS-NO=722	IR-NIDA-08653 : CCL4 SOLUTION
ACETOPHENONE			
C ₈ H ₈ O			

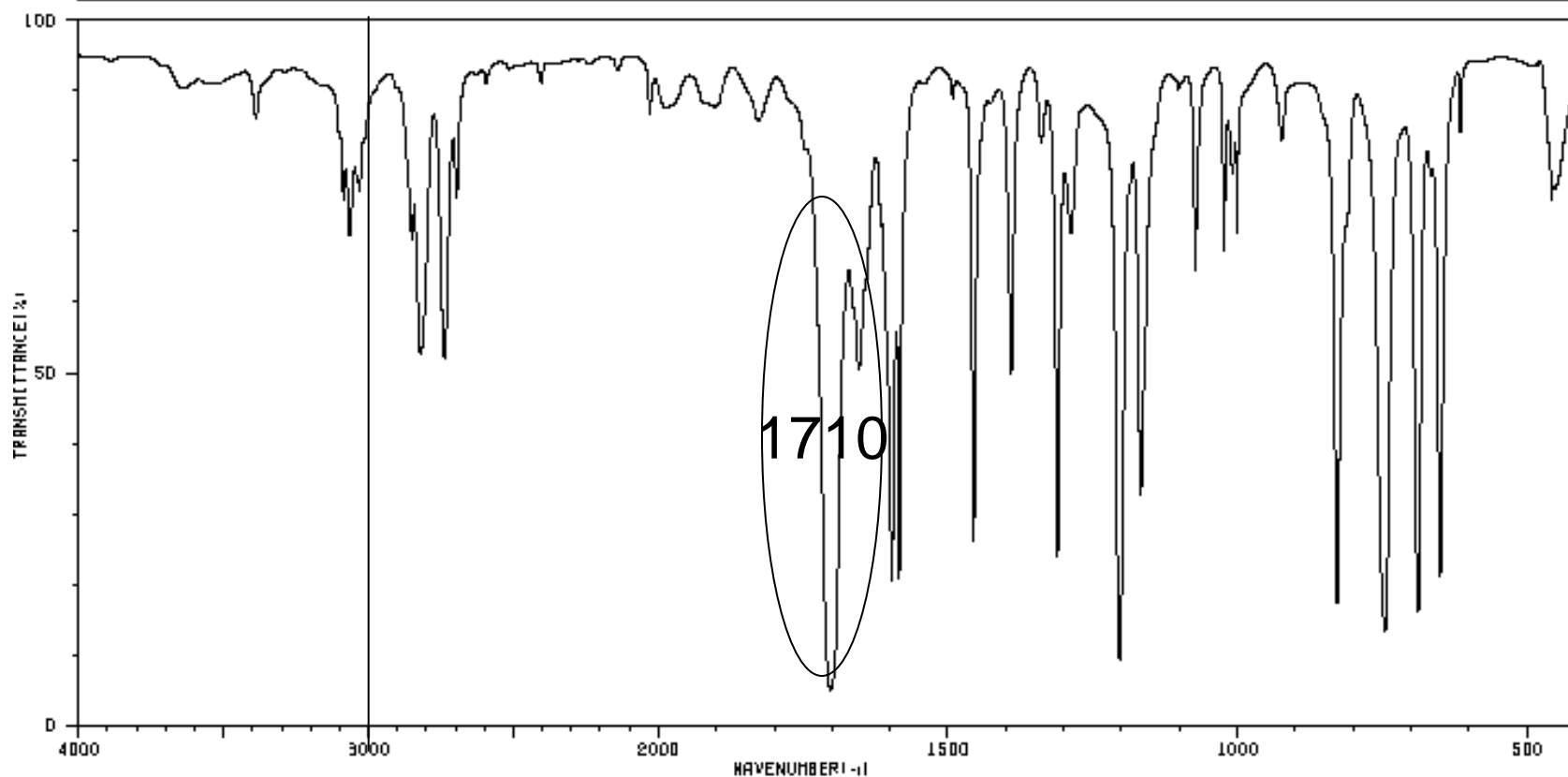


3089	81	1684	72	1246	68	690	19
3066	81	1450	55	1180	72	618	84
3031	84	1433	77	1159	86	588	34
3008	84	1368	30	1077	79		
2969	86	1312	79	1026	68		
1691	4	1302	79	953	82		
1601	67	1266	6	924	81		

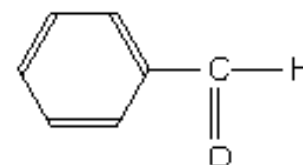


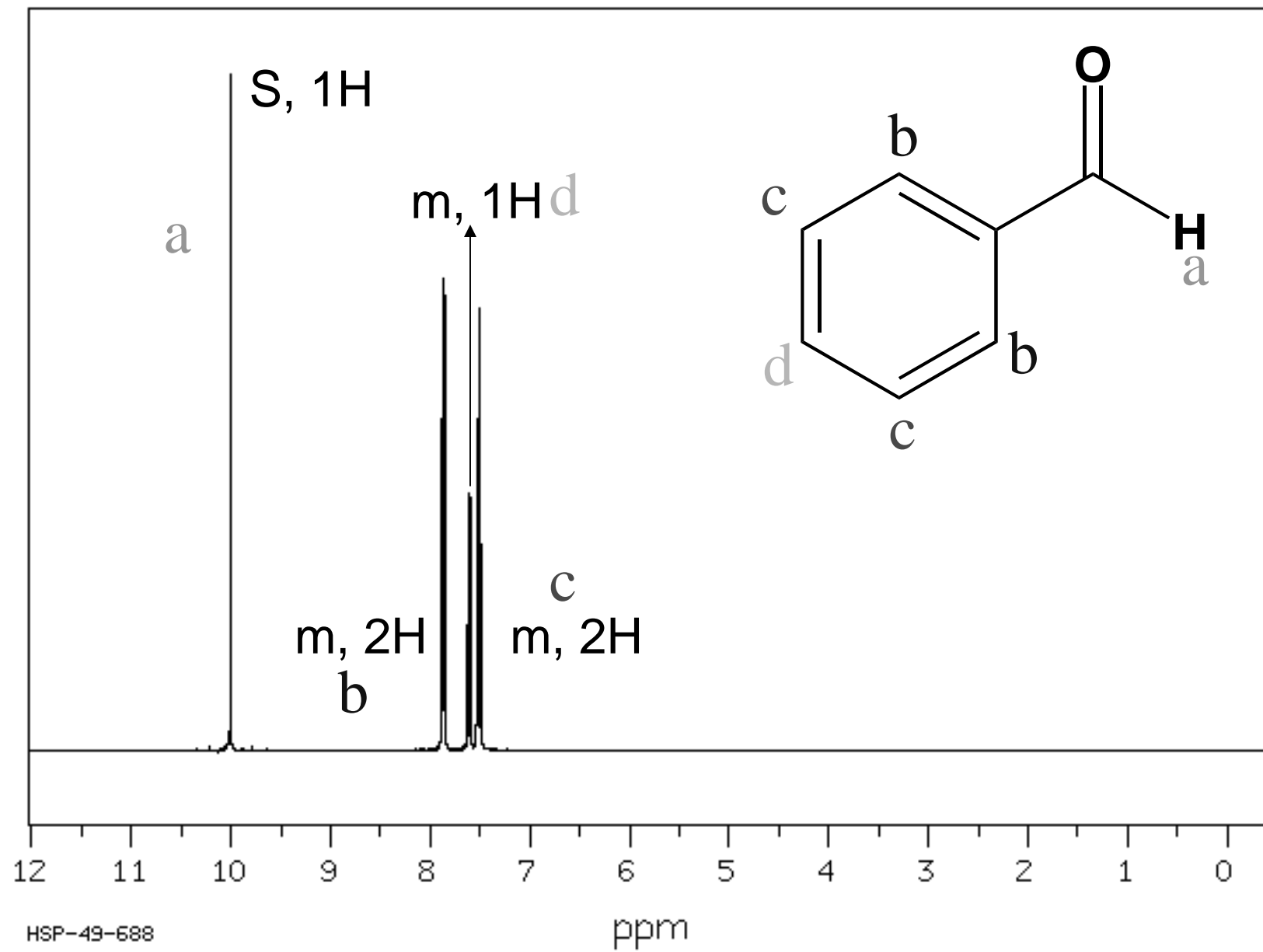


HIT-NO=1117	SCORE= ()	SDBS-NO=672	IR-NIDA-05223 : LIQUID FILM
BENZALDEHYDE			
C ₇ H ₆ O			



3086	72	1981	84	1697	20	1204	8	828	16
3065	66	1916	84	1584	20	1168	31	746	13
3031	72	1909	84	1456	25	1073	62	688	15
2860	66	1901	84	1391	47	1023	64	667	74
2820	50	1828	81	1339	79	1008	74	650	20
2736	50	1703	4	1311	23	1001	66	615	61
2696	72	1664	49	1288	68	924	79	467	72





Reaction Themes

One of the most common reaction themes of a carbonyl group is addition of a nucleophile to form a tetrahedral carbonyl addition compound (intermediate).

