Objective 6. Identify an aromatic compound and apply substitution, elimination, and oxidation-reduction principles to aromatic side chain reactions.

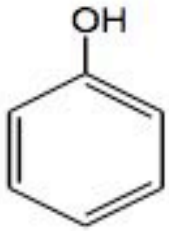
Skills: Draw structure
ID structural features and reactive sites (alpha C, beta C, LG, etc.)
ID Nu^- and E^+
use curved arrows to show bonds breaking and forming
show delocalized electrons with resonance structures.

Key ideas:
Aromatic compounds are more stable than conjugated dienes because of delocalization (draw resonance). See criteria for aromaticity.

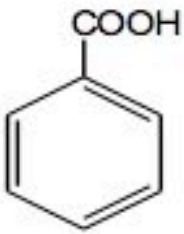
New reaction is oxidation of R for form acid.

Many Compounds Contain Arenes and Aromatics

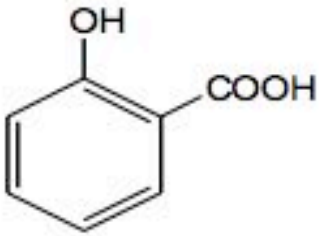
benzene



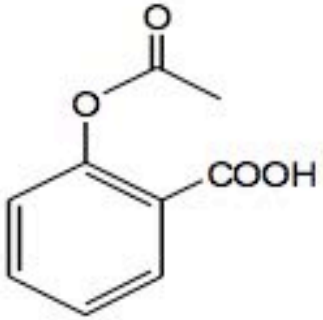
phenol



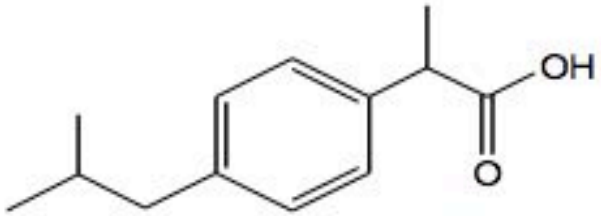
benzoic acid



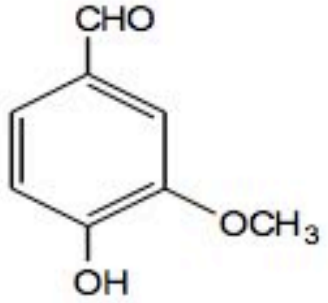
salicylic acid



aspirin



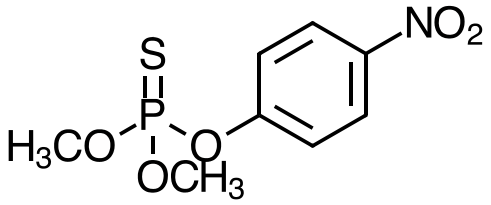
Ibuprofen



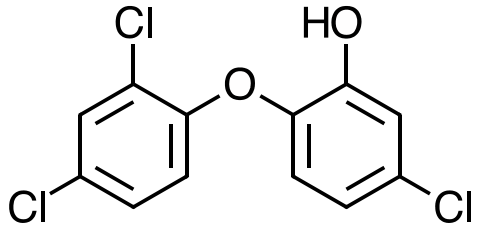
vanillan

Arene is an aromatic hydrocarbon

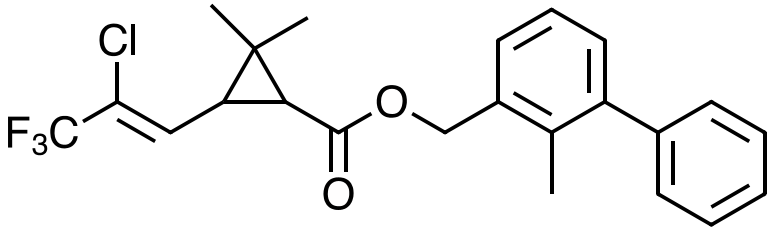
Insecticides, pesticides, and germicides contain benzene



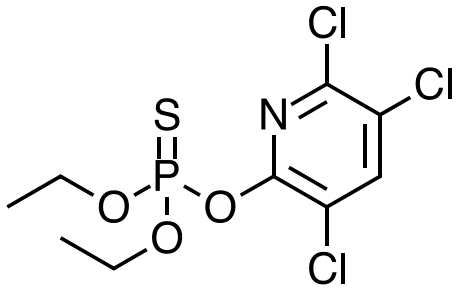
methyl parathion



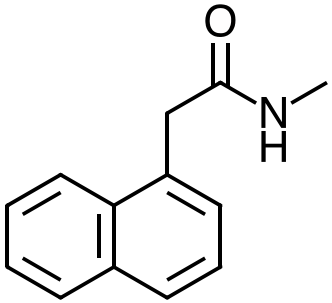
triclosan



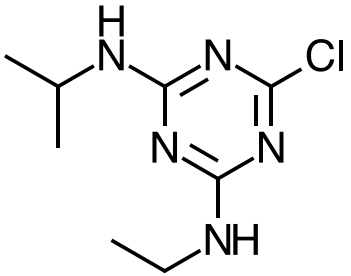
bifenthrin



chlorpyrifos



carbaryl

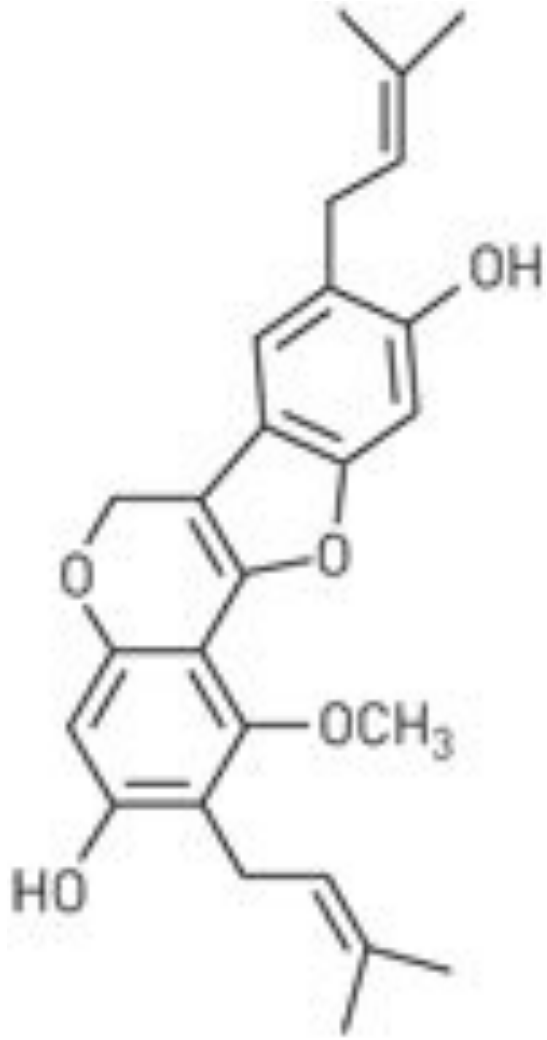


atrazine

Licorice may aid battle against dental cavities (CEN, 2/6/06, p. 25)

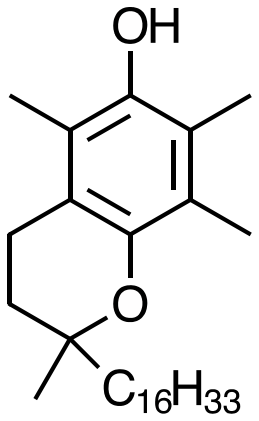
Licorice is an important herb in Chinese medicine, and its derivatives are used worldwide as flavoring and sweetening agents in tobacco, gum, candy, and beverages.

Compounds isolated from licorice root (Glycyrrhiza uralensis) exhibit potent antibacterial activity against Streptococcus mutans, an oral pathogen that causes tooth decay (J. Nat. Prod. 2006, 69, 121). Toothpaste companies are interested in the new compounds.

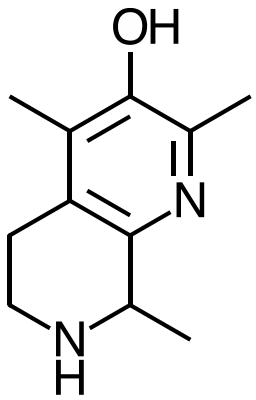


CEN, 9/27/03, p. 24 α -tocopherol (form of Vitamin E) is nature's most potent phenol antioxidant (effective radical scavengers that inhibit oxidation of lipids that contribute to atherosclerosis and Alzheimer's disease).

Incorporate N in ring = 100x more effective radical scavenger. Why do you think this compound works better?



α-tocopherol

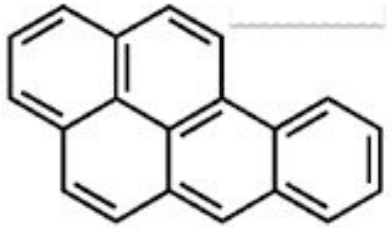


100x more effective radical scavenger than α-tocopherol

Phenolic H atom transferred to lipid peroxyl radical terminates chain reaction.

Grilling and BBQ

https://barbecuebible.com/wp-content/uploads/2013/05/0R7U0718-1.jpg



Benzo[A]Pyrene = PAH

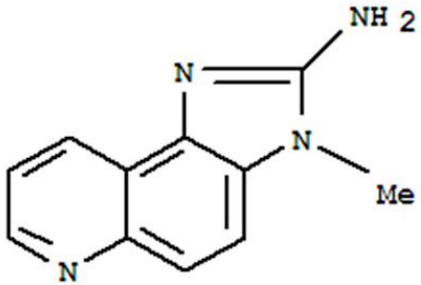
https://sciencemodalities.files.wordpress.com/2013/07/bap.jpg

Char: Heterocyclic Amines (HCA)

Smoke: Polycyclic Aromatic Hydrocarbons (PAH)

Harmful Byproducts: Advanced Glycation Endproducts (AGE)

See http://blog.doctoroz.com/oz-experts/the-hidden-dangers-of-grilling

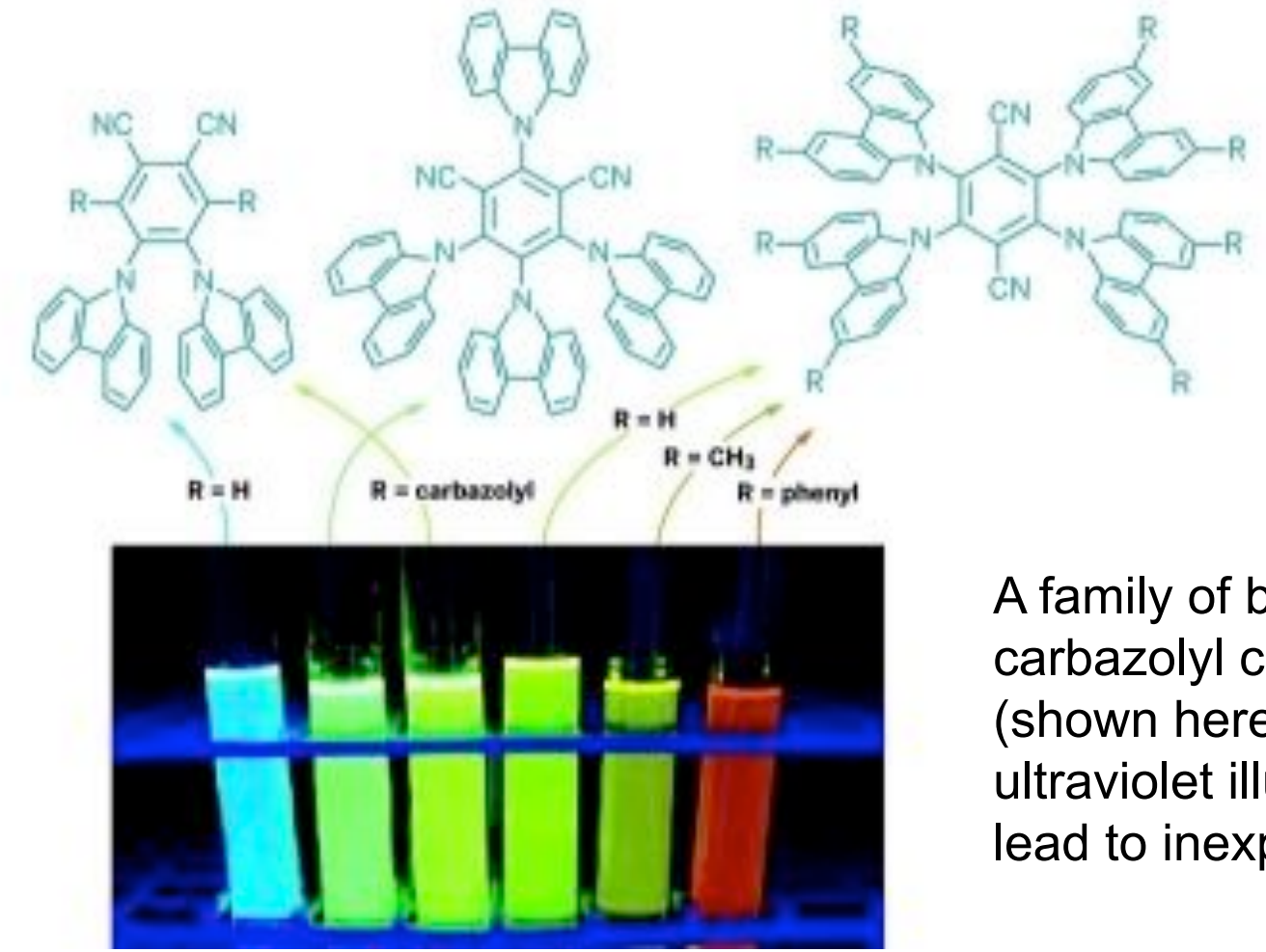


2-Amino-3-methylimidazo[4,5-f]quinoline (IQ) = HCA

https://file1.lookchem.com/300w/2010/0624/76180_96_6.jpg

http://cen.acs.org/articles/90/i51/Brighter-Organics-Display.html

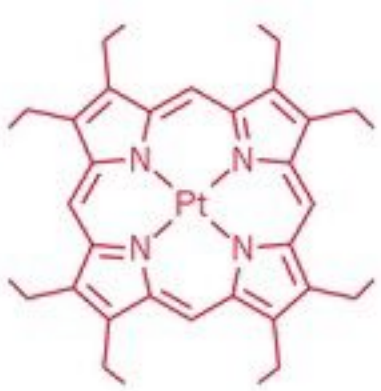
12/17/12, CEN, p. 9 “Brighter Organics On Display Electronics: Family of aromatic compounds may mean cheaper, flexible OLED screens”



A family of broadly emitting carbazolyl compounds (shown here under ultraviolet illumination) may lead to inexpensive OLEDs.

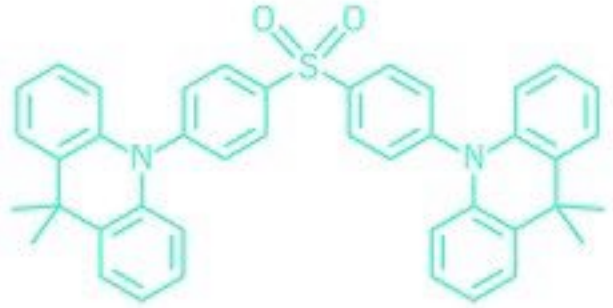
OLEDs need colored compounds

http://cen.acs.org/articles/94/i28/rise-OLED-displays.html

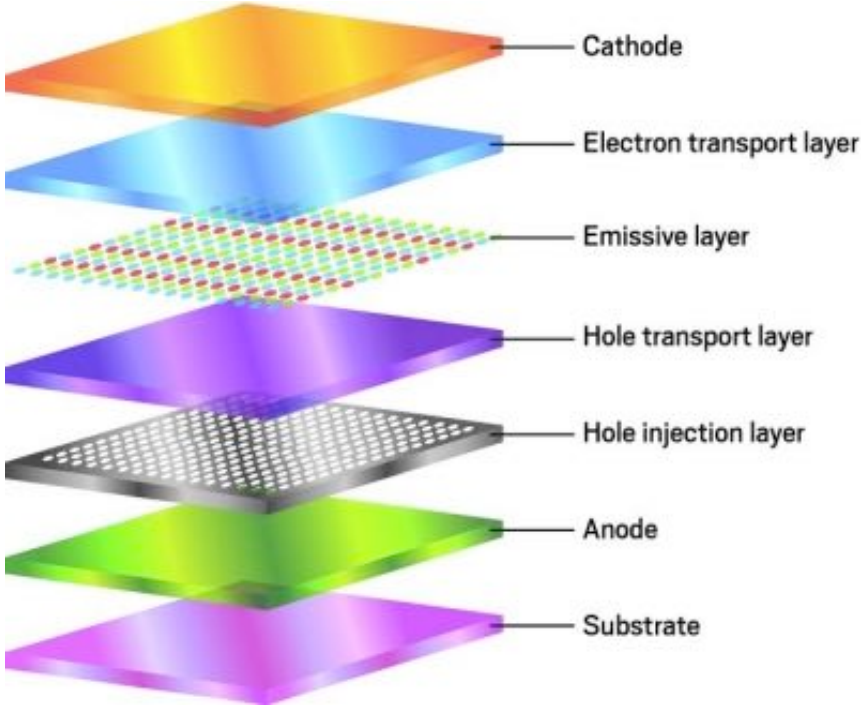


Platinum octaethylporphyrin

Tris[2-phenylpyridinato-C^2,*N*]iridium(III)



Diphenylsulfone dimethyldihydroacridine

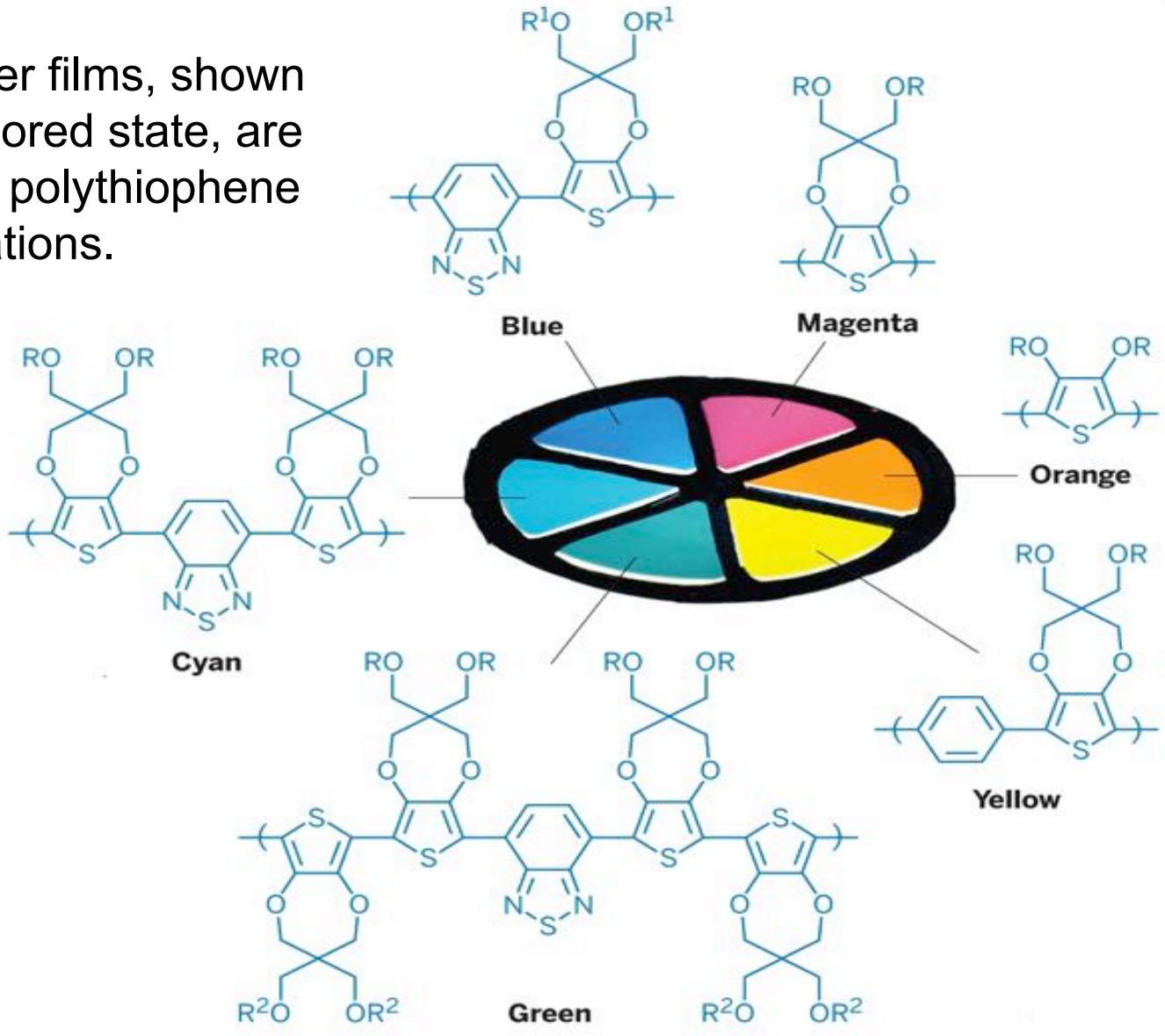


How OLEDs work

An OLED can be manufactured using a variety of substrates, including glass, plastic, and metal. It consists of several layers of organic materials sandwiched between two electrodes. When a voltage is applied across the OLED, a current of electrons flows from the cathode to the anode, adding electrons to the emissive layer and taking them away—or creating electron holes—at the anode. At the boundary between these layers, electrons find holes, fall in, and give up a photon of light. The color of the light depends on the type of organic molecule in the emissive layer. The most advanced OLEDs use electron and hole injection and transport layers to modulate electron movement.

COLOR WHEEL (http://cen.acs.org/articles/89/i24/Electrochromics-Hit-Color-Milestone.html)

Spray-cast polymer films, shown in their neutral colored state, are made possible by polythiophene synthetic modifications.
R = 2-ethylhexyl,
R1 = octyl, and
R2 = ethyl.

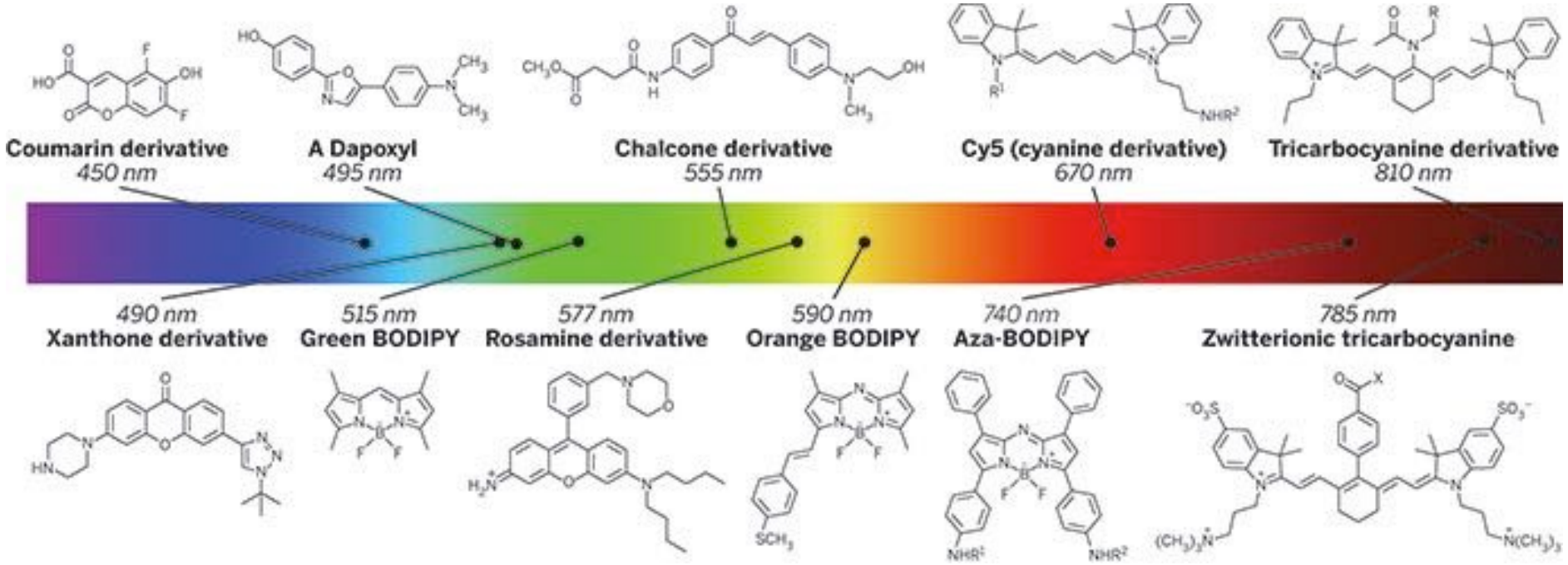


http://cen.acs.org/content/cen/articles/93/i12/Library-Bright-Ideas.html

3/23/15, CEN, p. 39 “A Library of Bright Ideas”

Fluorescent molecules to:

- stain specific cell types (biology),
- monitor enzyme activity (biochem),
- detect molecules in environment (chem)

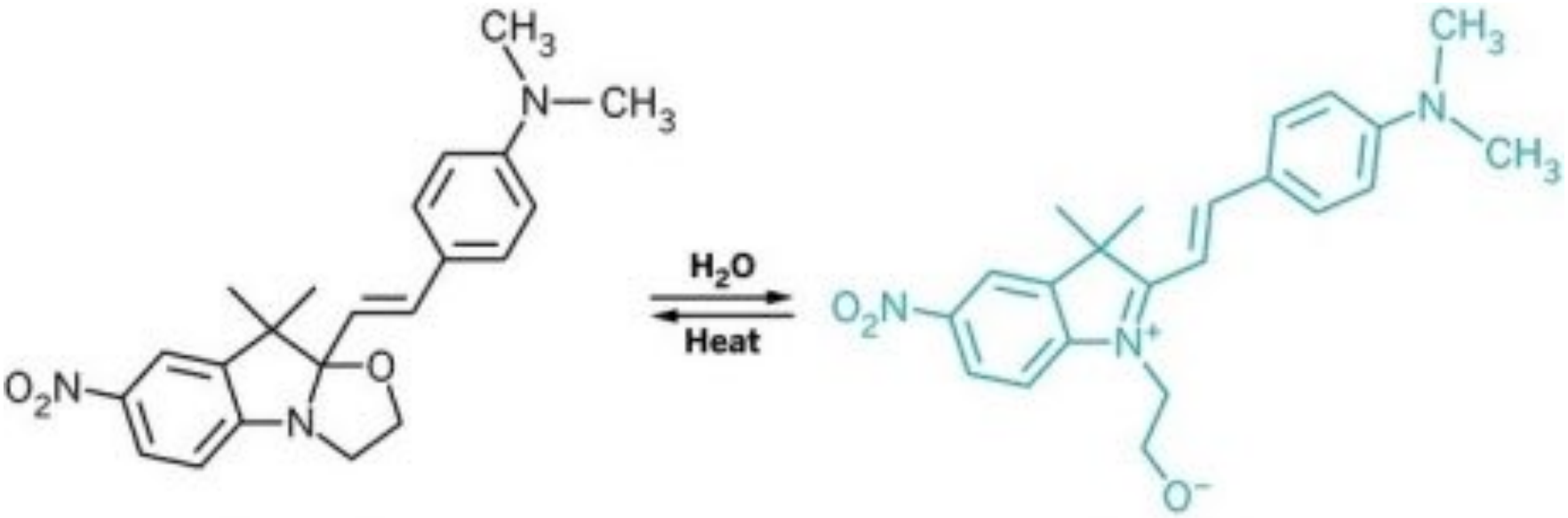


Are these compounds conjugated?

Are these compounds aromatic?

http://cen.acs.org/articles/92/i5/Rewritable-Printer-Paper-Replace-Ink.html

2/3/14, C&EN, p. 25 A new rewritable paper contains ***hydrochromic*** molecules—dyes that turn colors when exposed to water. Pages impregnated with the dyes can be printed using ordinary ink-jet printer technology by replacing the ink in cartridges with water.

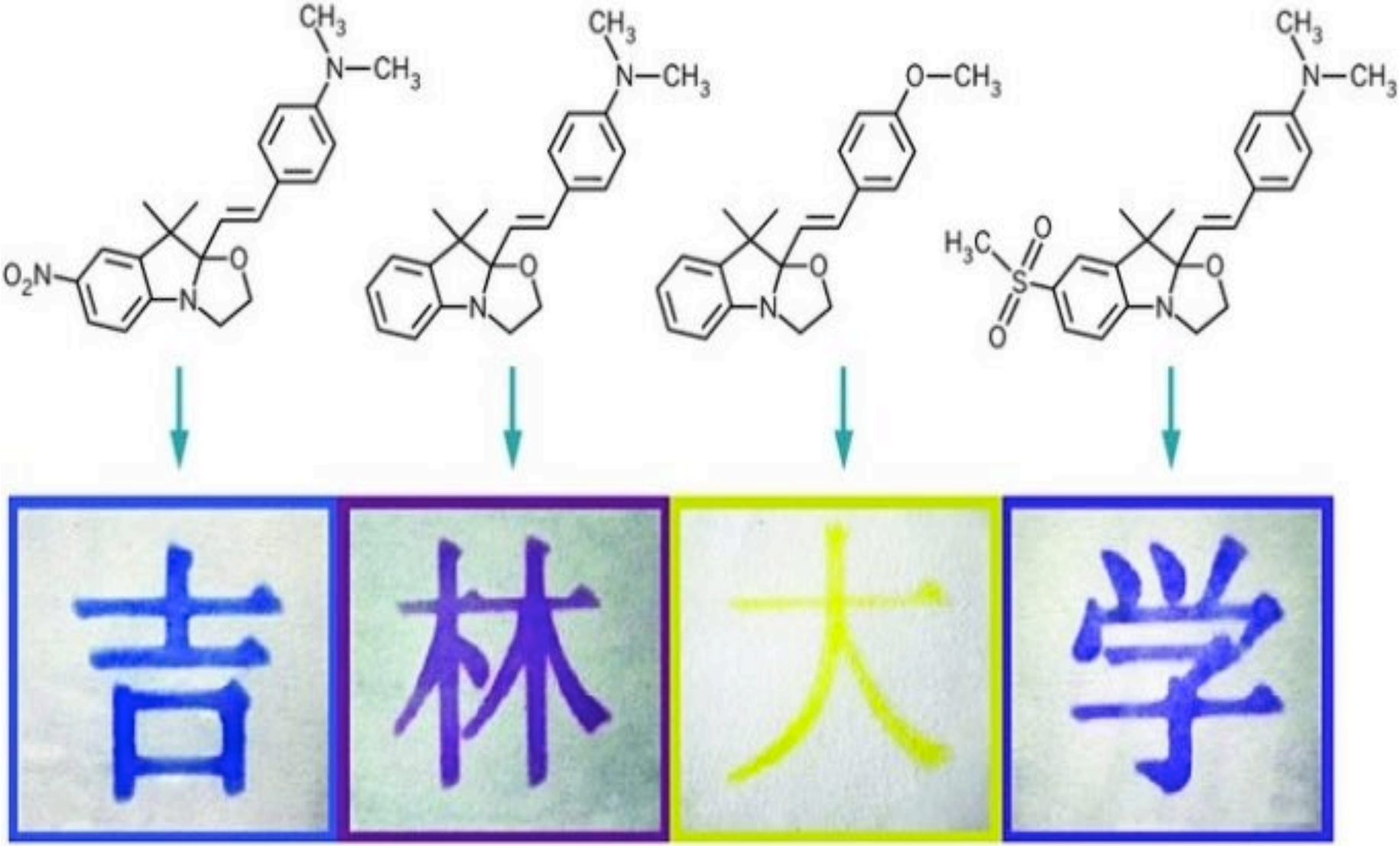


Closed form colorless

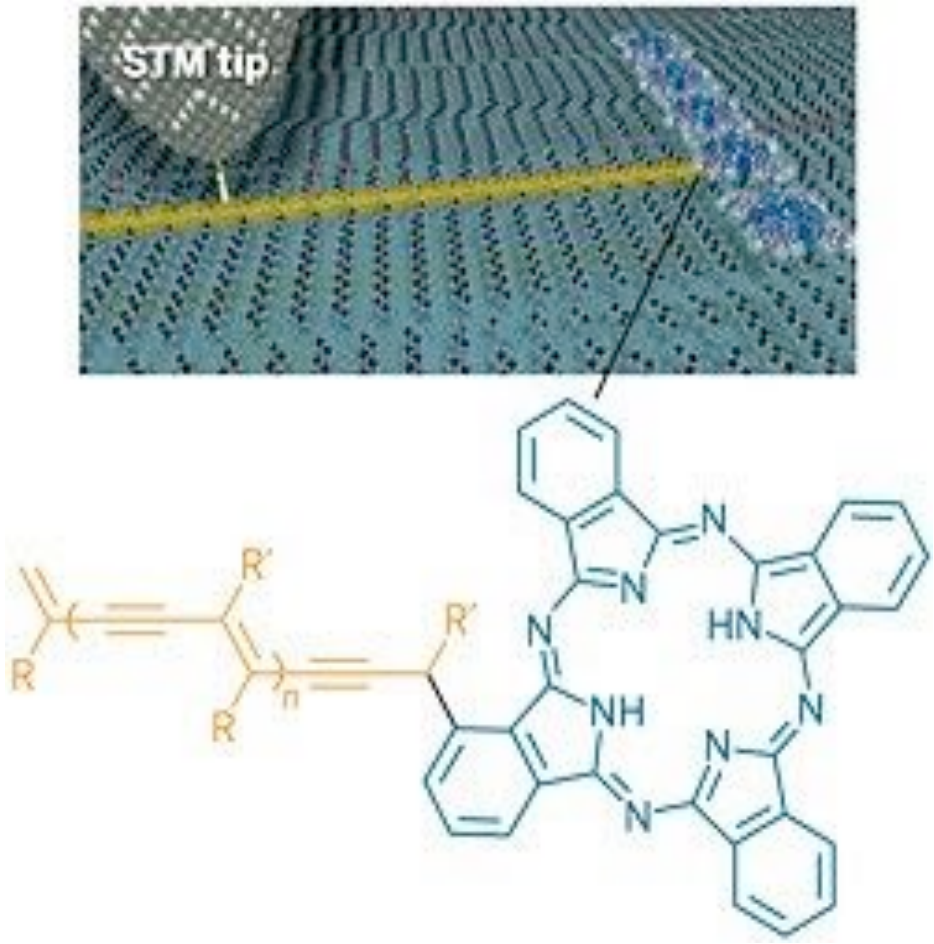
Open form blue

http://cen.acs.org/articles/92/i5/Rewritable-Printer-Paper-Replace-Ink.html

Various hydrochromic molecules switch to colorful isomers when exposed to water.



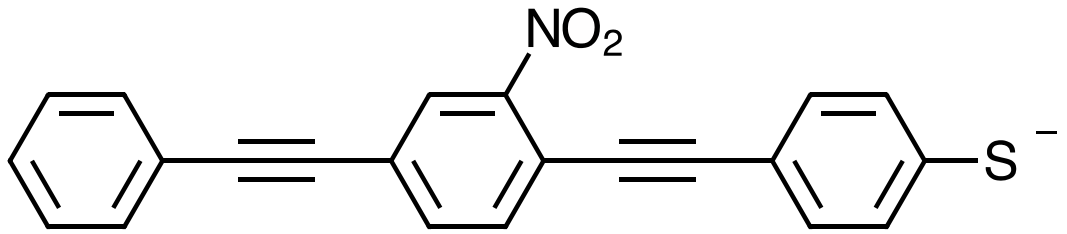
"Wiring A Single-Molecule Circuit", CEN, 5/16/11, p. 7
Organic compounds substituting for components such as wires, transistors, and rectifiers are all covalently bonded.



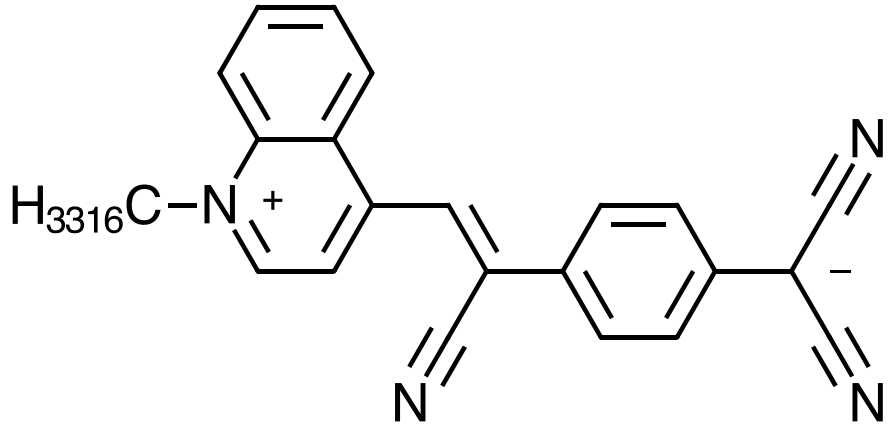
An STM tip initiates polymerization of the diacetylene groups in long-chain carboxylic acid molecules on a surface to form a wire (yellow) that then forms a bond to the single phthalocyanine molecule (blue).
R=$CH_3(CH_2)_{15}$ and R ´=$HOOC(CH_2)_8$.

http://cen.acs.org/articles/89/i20/Wiring-Single-Molecule-Circuit.html

Aromatic compounds have many applications



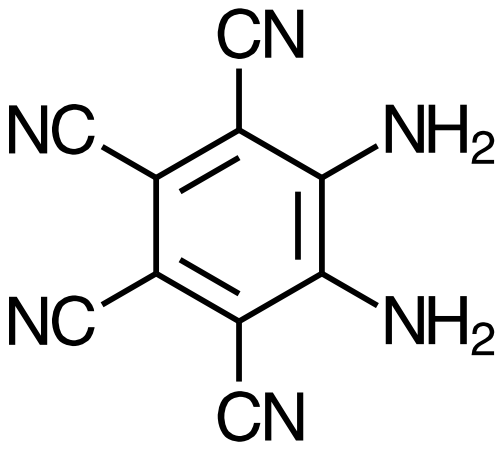
CEN, 6/25/01, p. 11 molecules that act as switches



CEN, 1/3/00, p. 22 molecular rectifier used in nanowires

C&EN, 2/15/16, *Organic molecule more polar than NaCl*
5,6-diaminobenzene-1,2,3,4-tetracarbonitrile = 14.1 Debye
NaCl = 9 Debye

Explain why this compound is so polar.



"Organic molecules with large dipole moments are desirable for their ability to enhance the efficiency of polymer films in electronic devices such as lasers, microchips for smart cards, and solar cells."

CEN, 2/25/13, p. 28 Science and Technology Concentrates

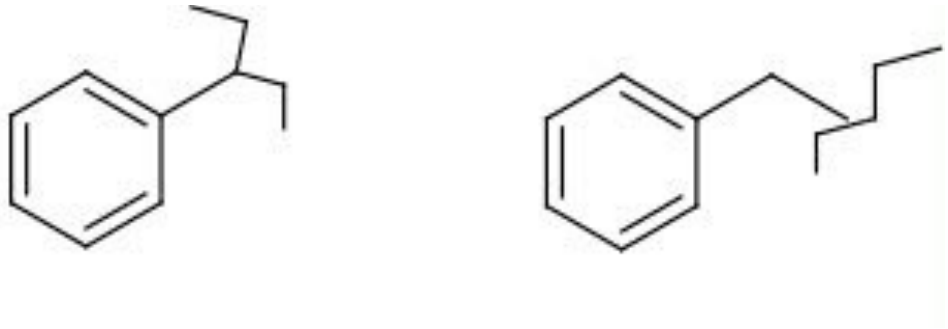
Molecular Wire Conducts Easily

Viologen-based wire

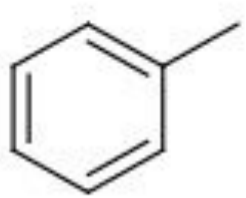
Wire tethered to gold substrate.
Wire lengths range from 1 to 6 repeating units (2.4 nm to 11.0 nm).
Longest wire has conductance of 2.9 nanosiemens (3 orders of magnitude higher than other carbon based wires of comparable length.

Naming Arenes

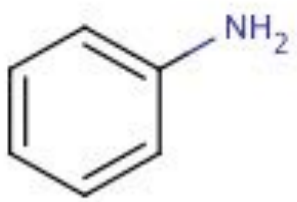
R groups: Phenyl group and benzyl group



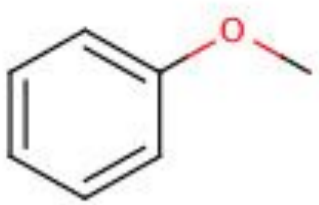
Common Names for Substituted benzenes: Table 11.1, p. 436



toluene



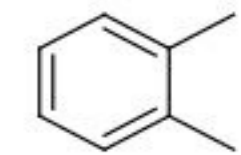
aniline



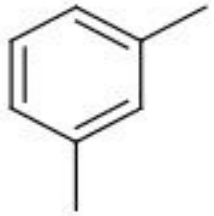
anisole

Disubstituted benzenes are named ortho, meta, and para:

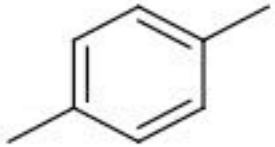
1,2 = Ortho 1,3 = meta 1,4 = para



ortho-xylene

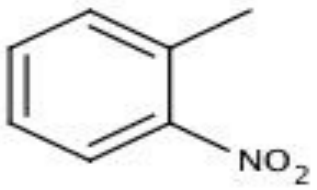


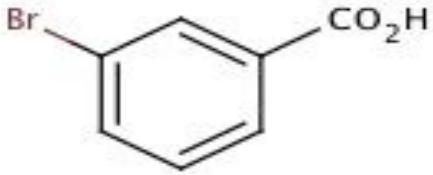
meta-xylene

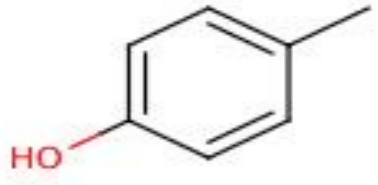


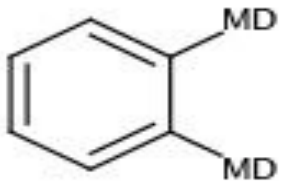
para-xylene

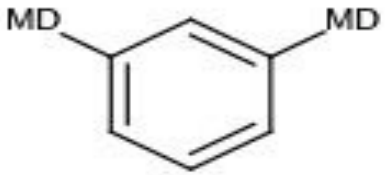
Name the following compounds. Use common name to start.

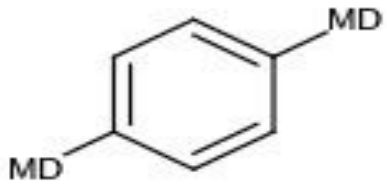




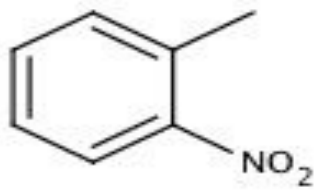




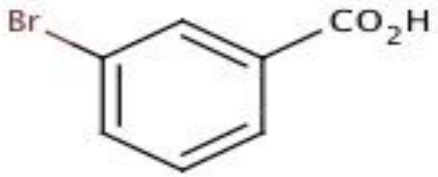




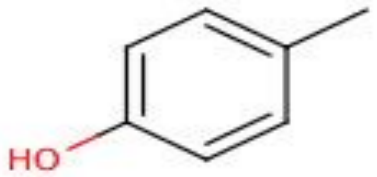
Name the following compounds. Use common name to start.



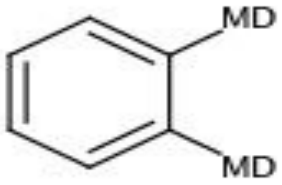
Ortho-nitro toluene



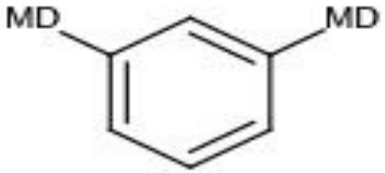
meta-bromobenzoic acid



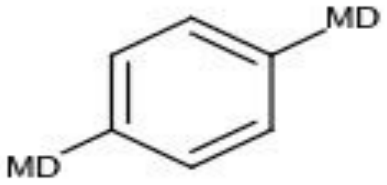
para-hydroxytoluene



Orthodox

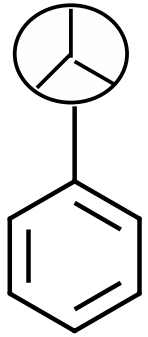


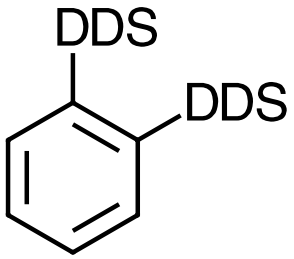
metaphysician



paradox

What is the name of these compounds?





Aromatic Means Extra Stability

Criteria:

1. Conjugated (alternating C-C and C=C bonds)
2. Ring
3. Planar
4. Huckel Rule: 4n + 2 π electrons = 2, 6, 10, .. π e^-.

π electrons are <u>delocalized</u>.

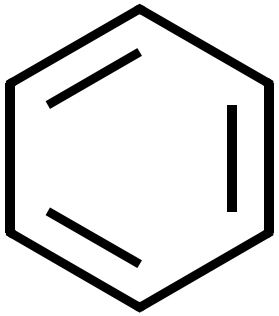
5.Smells (aroma)?

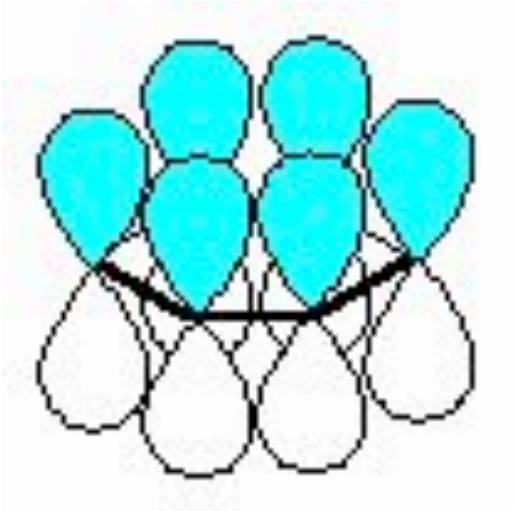
<u>Antiaromatic</u> compounds have 4n π electrons.

Are antiaromatic compounds as stable as aromatic compounds?

Benzene is Aromatic

1. Conjugated (alternating C-C and C=C bonds)
2. Ring
3. Planar
4. 6 π electrons = fits Huckel Rule (4n + 2)



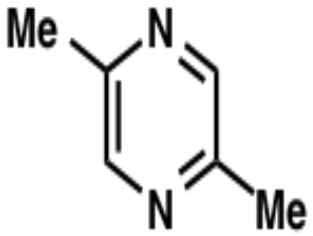


Why is each C-C the same length?

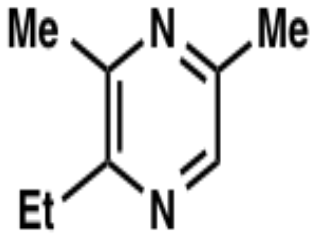
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch11/ch11-3.html

http://cen.acs.org/articles/89/i46/Switching-Off-Aromaticity.html
Scientists use laser pulse to switch off aromaticity.

The smell of BACON is aromatic (from LearnBacon.com)



2,5-dimethylpyrazine

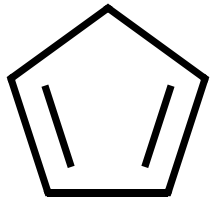


2-ethyl-3,5-dimethylpyrazine

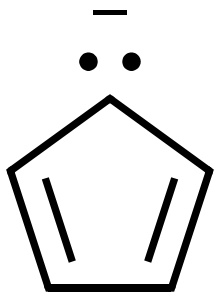
Apply the 4 rules to show these 2 compounds are aromatic.

1. Conjugated?
2. Ring?
3. Planar?
4. fits Huckel Rule (4n + 2 pi electrons)?

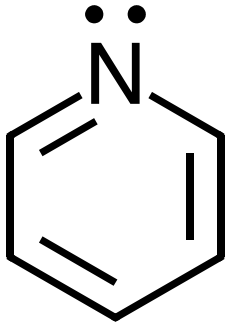
Objective: Identify the aromatic compound



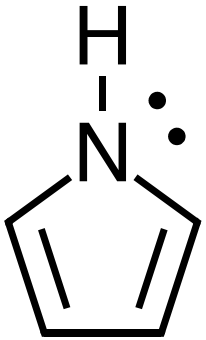
cyclopentadiene



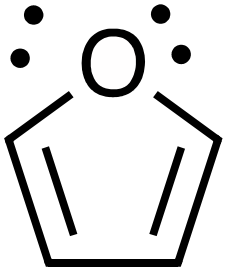
cyclopentadiene anion



pyridine



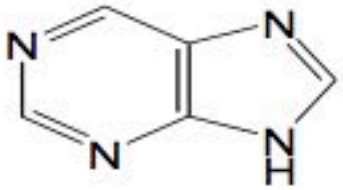
pyrrole



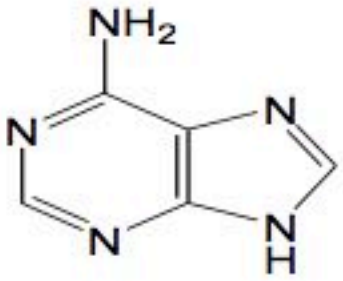
furan

DNA Bases are Aromatic

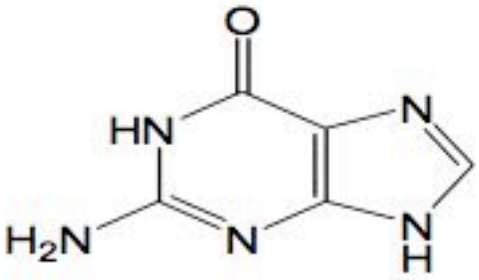
How many π electrons does each base have?



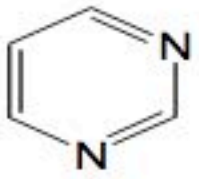
Purine



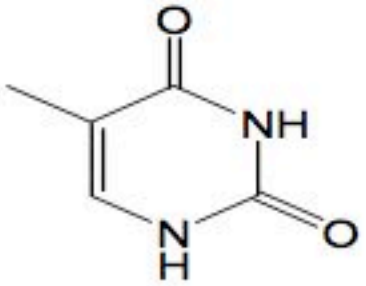
Adenine



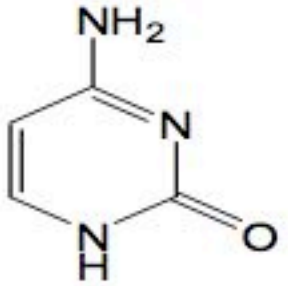
Guanine



Pyrimidine

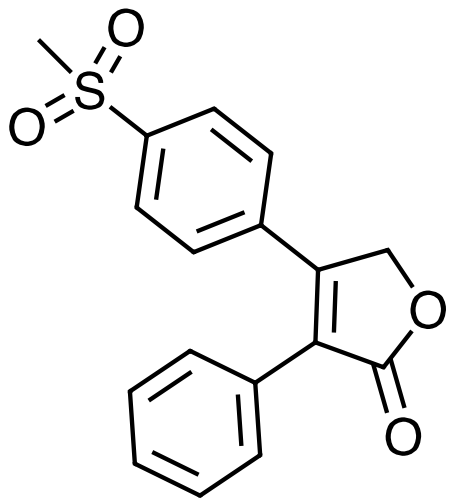


Thymine

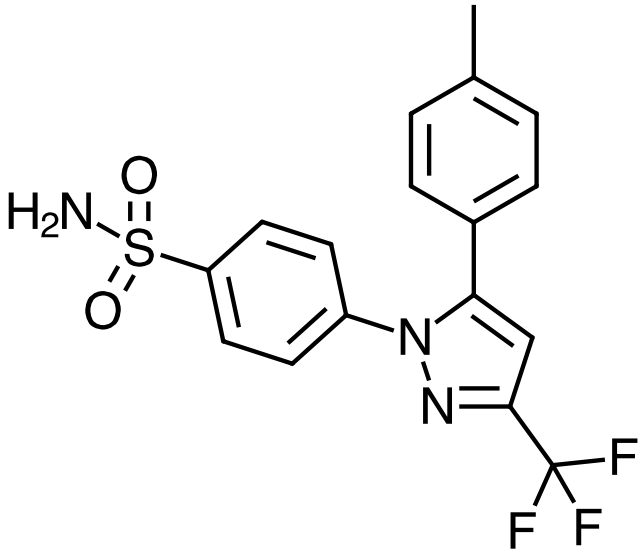


Cytosine

Non-Steroidal Anti-Inflammatory Drugs (NSAID)



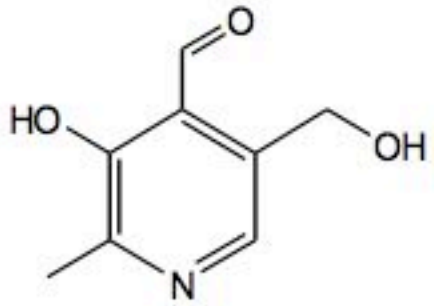
Vioxx



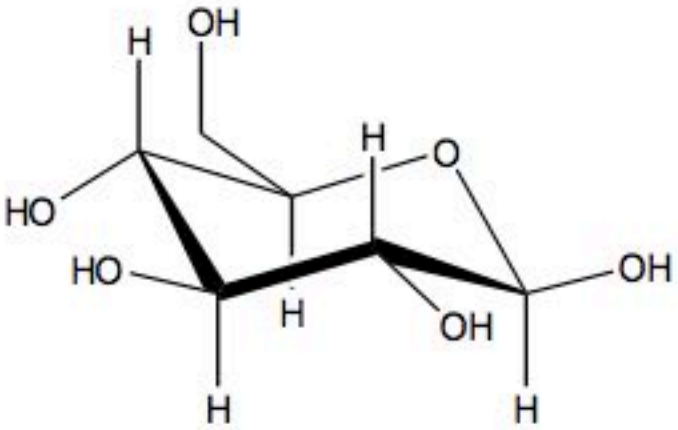
Celebrex

Which ring is NOT aromatic?

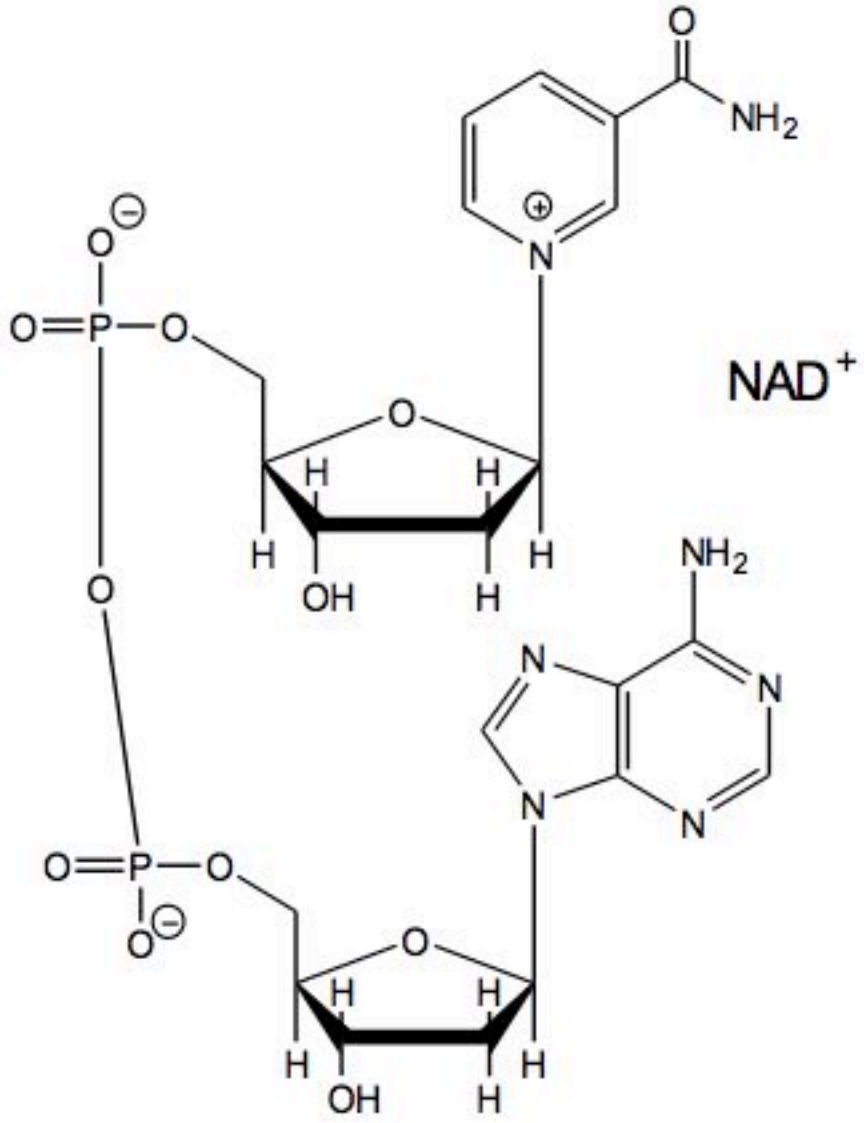
Which Biomolecule Is Aromatic?



pyridoxyl
Vitamin B_6



glucose

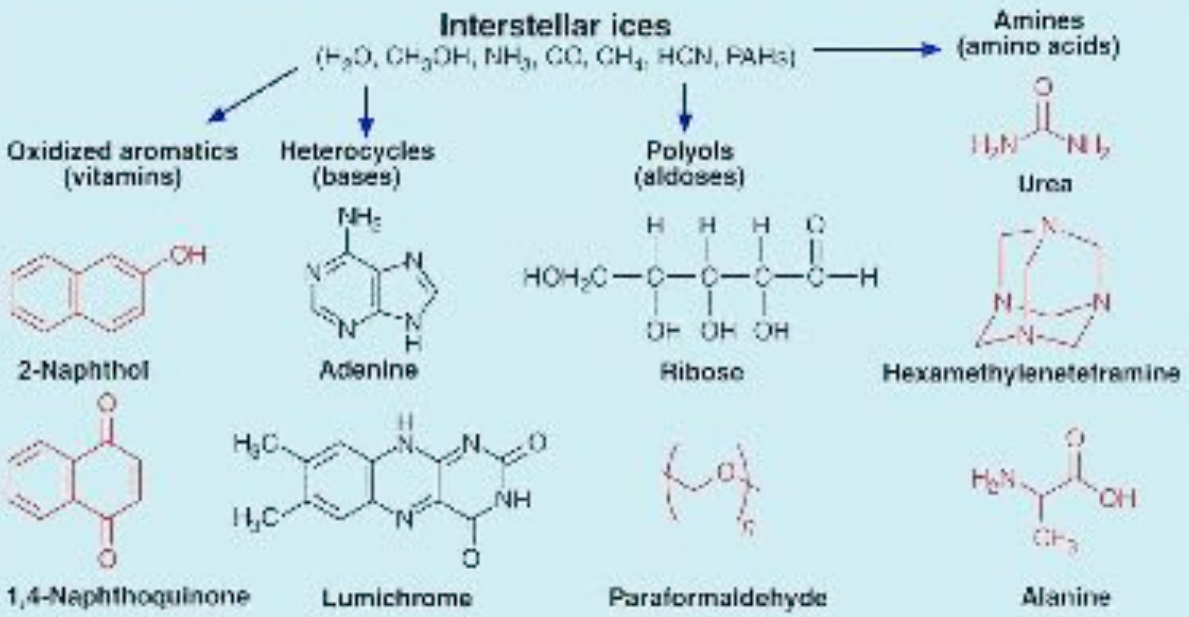


NAD^+

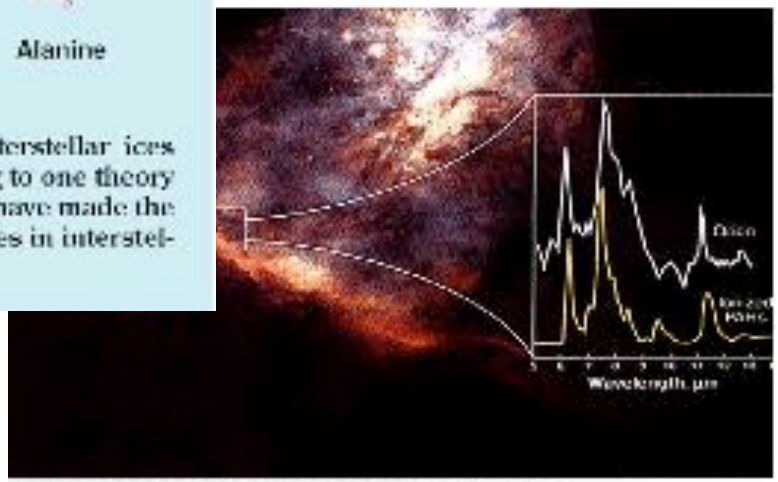
At Ames Research Center, NASA chemists search for clues to life

CENEAR 77 51 pp. 29-32, December 20, 1999

Interstellar ices may spawn biologically important molecules



Polycyclic aromatic hydrocarbons and simpler molecules that make up interstellar ices could be the source of many types of biologically relevant molecules, according to one theory being investigated in the Ames astrochemistry laboratory. So far, the chemists have made the molecules shown in red in experiments that simulate the conditions of these ices in interstellar space. The rest, reasonable in theory, are on their "wish list."

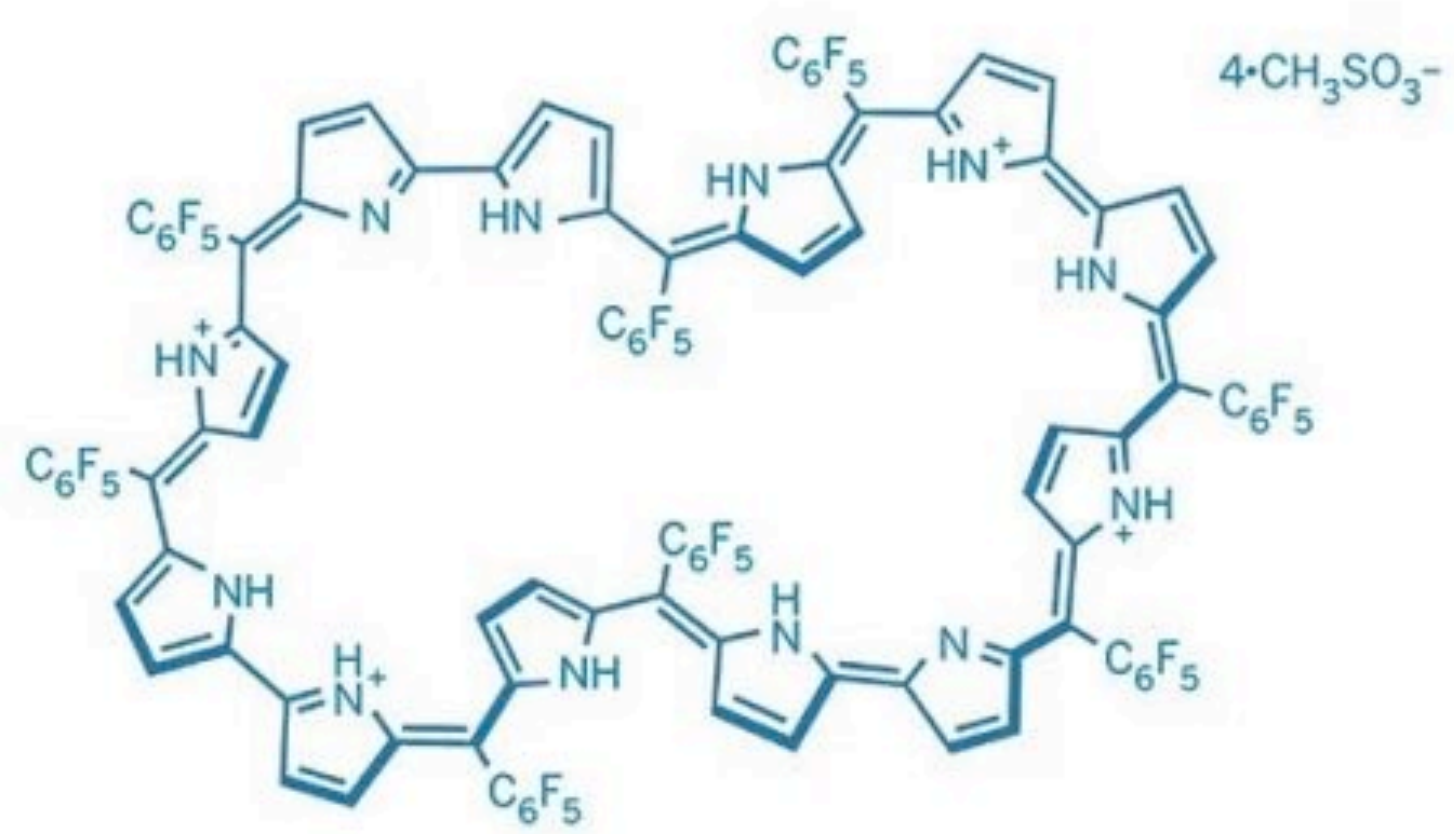


Key features in an infrared spectrum of a mixture of ionized polycyclic aromatic hydrocarbons match those of spectra of star-forming regions, such as this one from the Orion Nebula.

CEN, 5/4/15, p. 26 Science and Technology Concentrates

Largest Aromatic Molecule Known

50 π electrons



But Wait ….

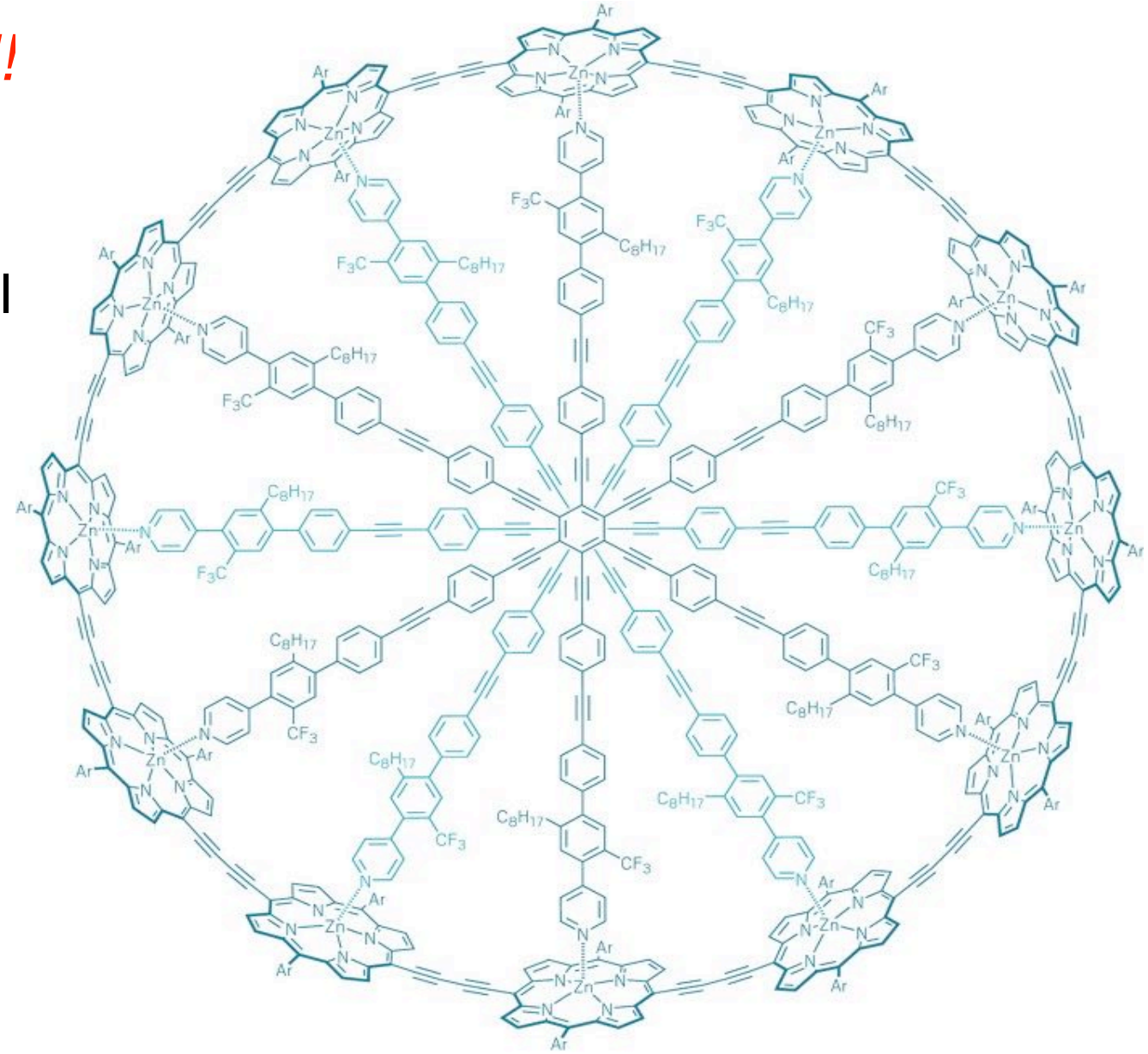
There's More!!

CEN, 2/3/20, p. 6

Science Concentrates

Porphyrin Wheel Sets Aromatic Record

162 π electrons



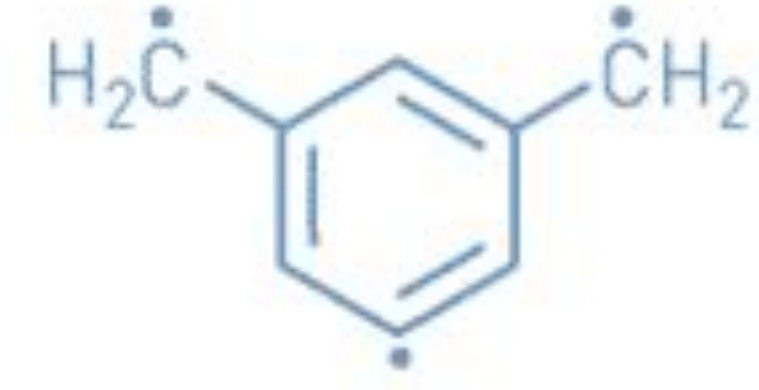
CEN, 3/7/16, p. 28, Smallest possible aromatic ring

(http://cen.acs.org/articles/94/i10/littlest-aromate.html)

	Bond length	Ring area	Claim to fame
 H_3^+	87.5 pm	3,315 pm^2	Smallest, lightest σ aromatic species, observed in gas phase
N_3^+	132.9	7,648	Smallest π aromatic ring, experimentally unknown
C_3^{2+}	136.4	8,057	Smallest double aromatic carbon ring, experimentally unknown
 $C_3H_3^+$	136.8	8,106	Breslow's classic compound, smallest isolated π aromatic molecule
$C_3R_3^+$	138	8,250	Smallest π aromatic compounds for which X-ray structures are available
 B_3^-	156.4	10,586	Lightest double aromatic species, observed in gas phase
$[B_3(CO)_3]^+$	156.5	10,605	Frenking and Zhou's π aromatic B_3^+ ring, observed in gas phase
$Na_4[B_3(NR_2)_3]_2$	162	11,401	Braunschweig's π aromatic B_3^{2-} ring, characterized by X-ray analysis
Be_3^{2-}	207.8	18,698	Lightest π aromatic ring, experimentally unknown
 Li_3^+	300	39,085	σ aromatic cation, possibly made in the gas phase

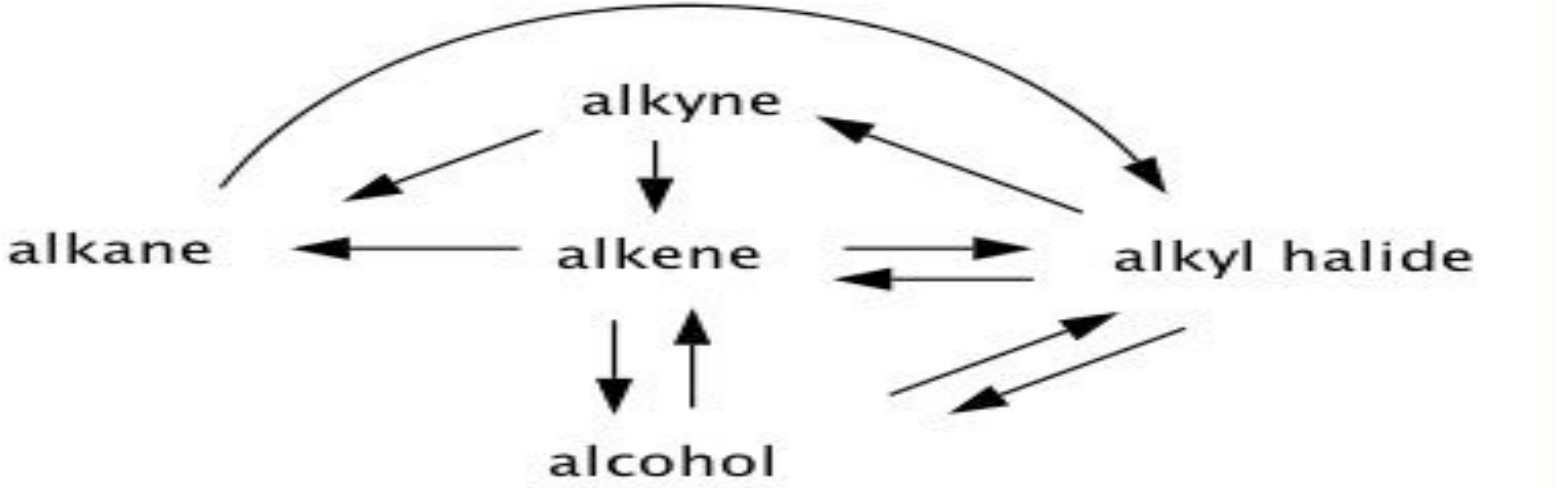
Triradical breaks the rules

The first example of an organic triradical with three un-paired electrons in an "open-shell" doublet ground state has been reported by the research groups of chemists Paul G. Wenthold of Purdue University and Anna I. Krylov of the University of Southern California [Angew. Chem. Int. Ed., 43, 742 (2004)].



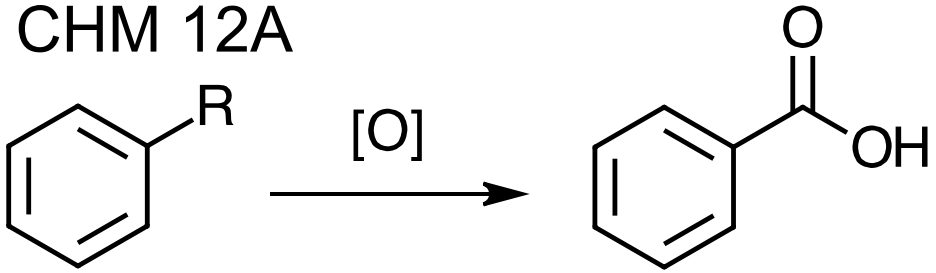
this state is unprecedented in a hydrocarbon and is contrary to the Aufbau principle and Hund's rules, which govern electron occupancy of molecular orbitals.

How do arene side chain reaction and EAS fit into CHM 12 Functional Group Conversions?



Arene side chain reactions are CHM 12A reactions, *except for*

Ar-R -- [O] --> Ar-COOH



When you see aromatic compound, you

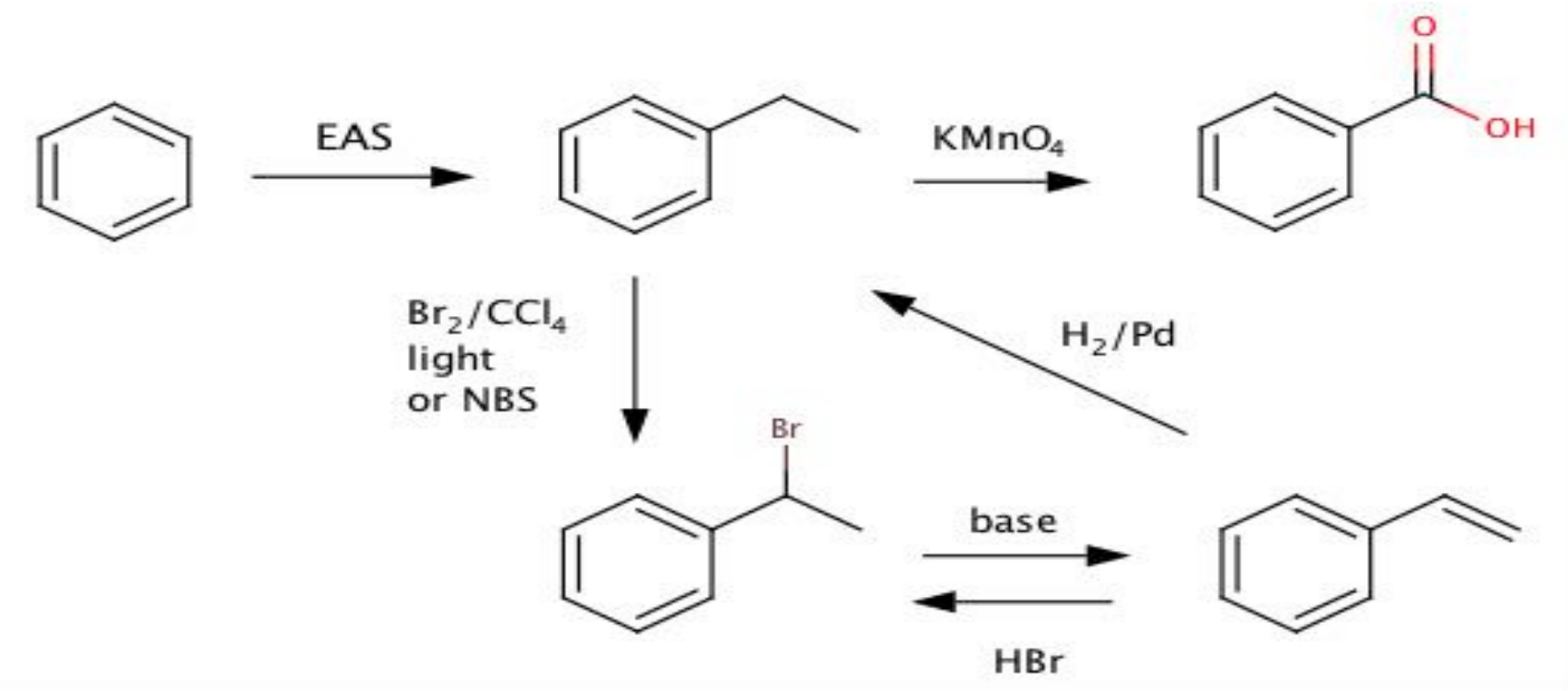
a) Panic
b) Freeze
c) Think EAS

Arenes Undergo Reactions in the:

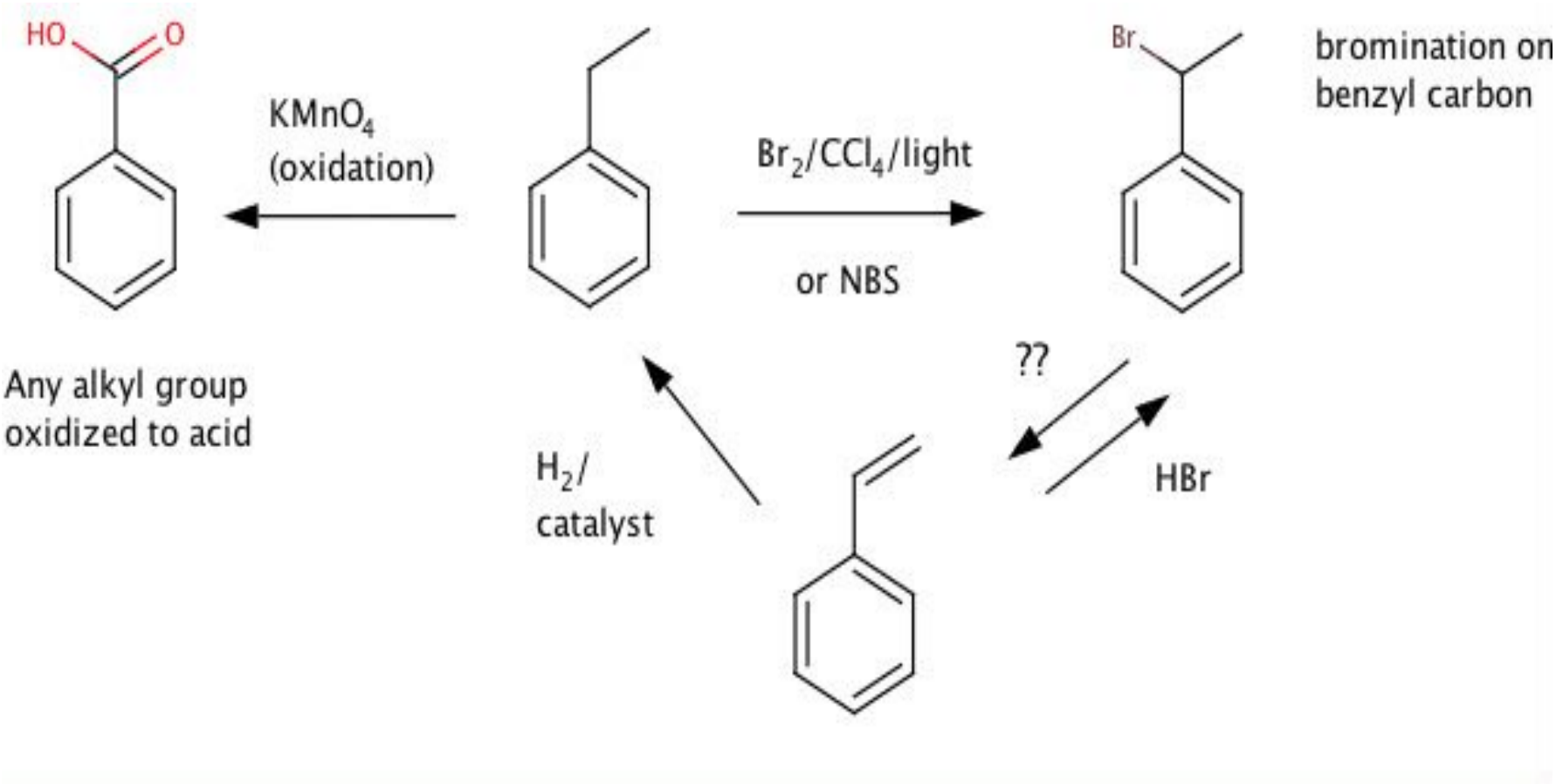
Ring: Electrophilic Aromatic Substitution (EAS)

Side Chain:

- Halogenation: alkane ---> R-X at benzylic C (like allylic C)
- Oxidation: alkane chain (any # of C's) ---> -COOH
- Hydrogenation: alkene ---> alkane (seen before)
- Elimination: R-X ---> alkene (seen before)



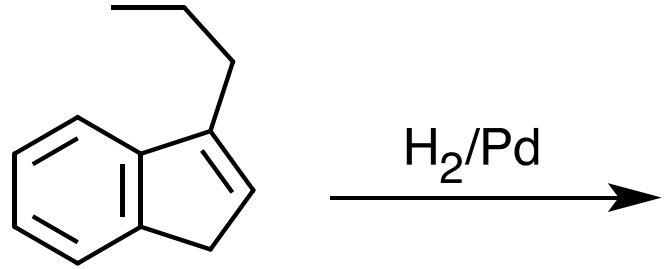
Groups Bonded to Benzene (Arene Side Chains) Undergo Reactions We Have Seen Before

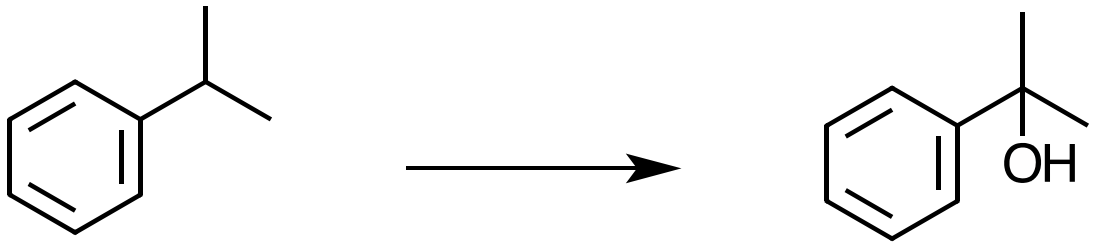


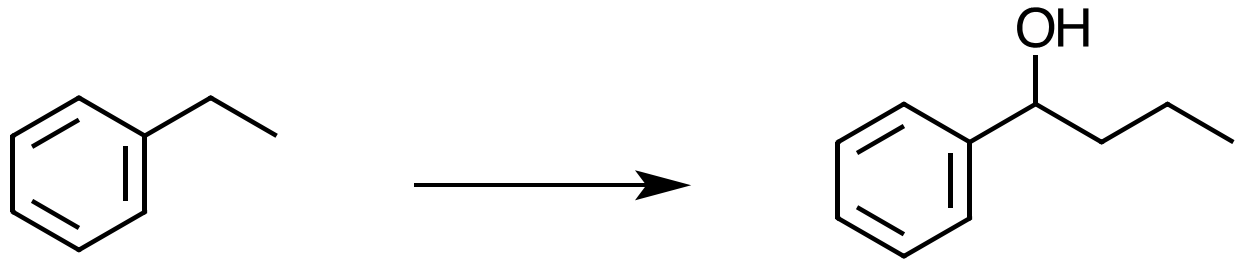
?? Conditions: a. H_2SO_4 b. $NaOCH_3$ c. $KHSO_4$

Problem solving steps: 1. Identify functional group(s)
2. Relate reaction conditions to reaction type

Draw the structure or Identify reaction conditions or propose a synthesis:

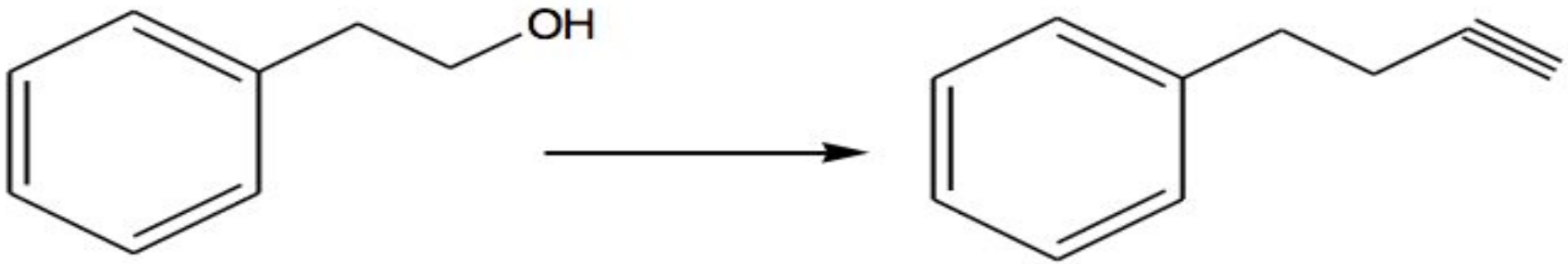






Problem solving steps: 1. Identify functional group(s)
2. Relate reaction conditions to reaction type

1. Suggest reagents suitable for carrying out the following conversions. More than one synthetic operation may be necessary.



Problem solving steps: 1. Identify functional group(s)
2. Relate reaction conditions to reaction type

The following reaction has been described in the chemical literature and gives a single organic product in good yield. Identify the product.