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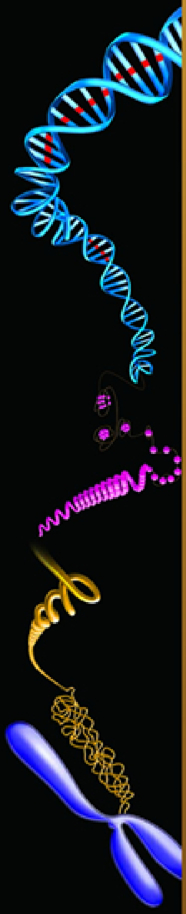

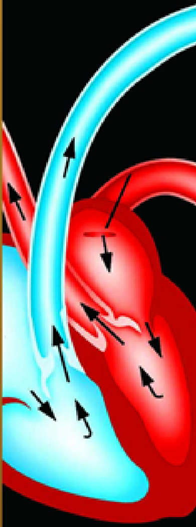

GAMSAT*

Organic Chemistry & Biology

Comprehensive Preparation for
GAMSAT Section 3: Biological Sciences

Book 3 from the 3-book GS GAMSAT Set

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THE BIOLOGICAL SCIENCES

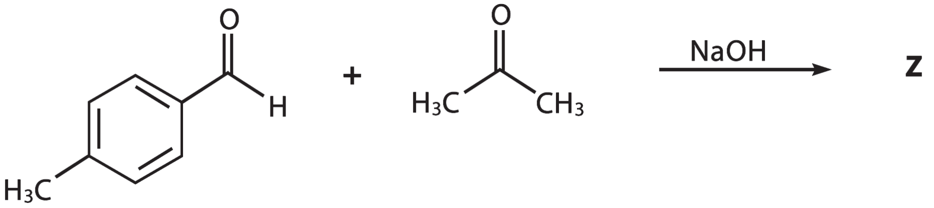
ORGANIC CHEMISTRY

BIOLOGY

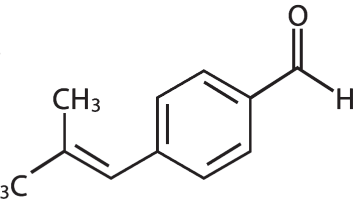
3. Which of the structures provided would be consistent with the condensation product and the intermediate (aldol), respectively?

A I & IV
B II & III
C II & V
D III & II

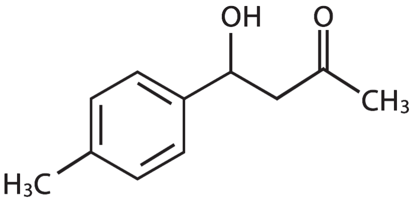
4. For the following reaction, choose the condensation product **Z**:



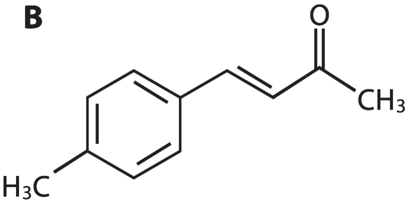
A



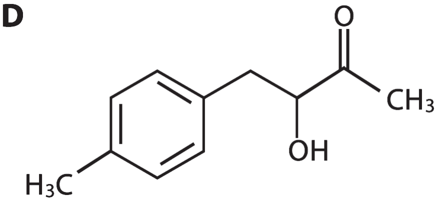
C



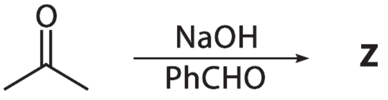
B



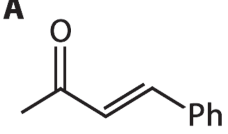
D



5. For the following reaction, the ketone reacts with PhCHO. Identify the condensation product **Z**:



A



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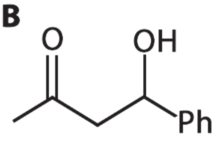

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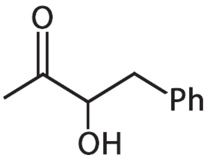
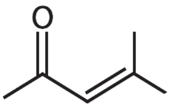


D



Unit 5, Question 8

The tarpon is among the world's most prized game fish. Adult tarpon are four to eight feet long and weigh 60 to 280 pounds. A graph (Figure 1) has been designed to provide a means to estimate the weight of a tarpon without killing and weighing the fish, using measurements of fork length and dorsal girth.

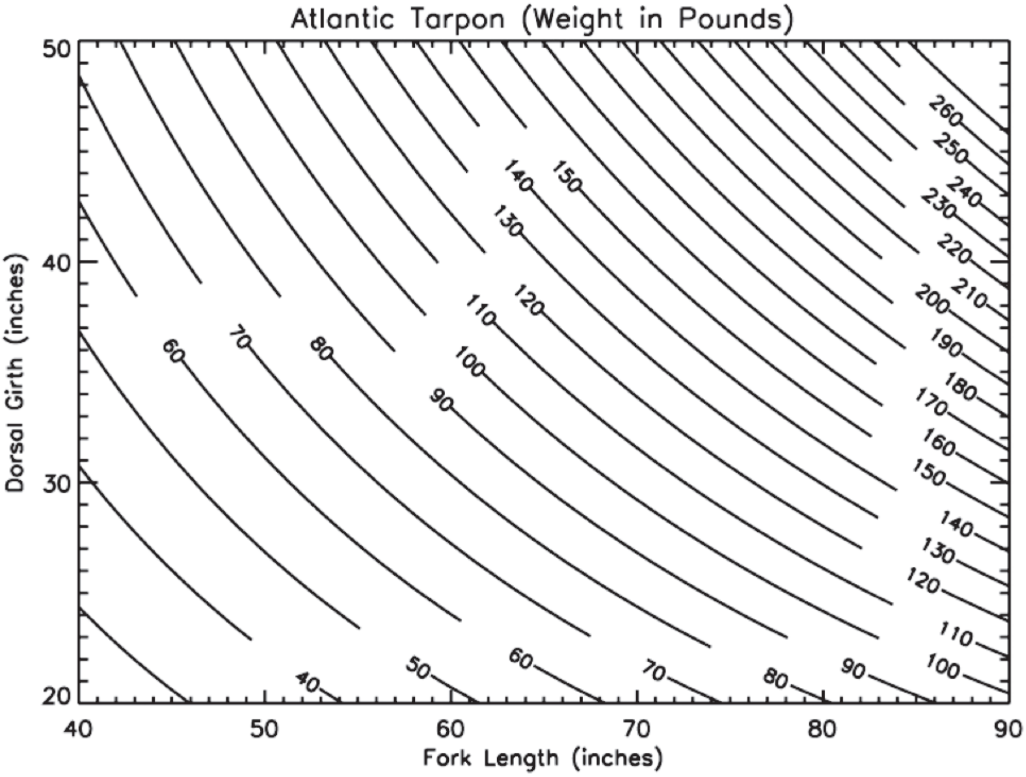


Figure 1: Estimating the weight of tarpon.
Jerald S Ault, PhD; University of Miami

Note that, drawing a straight line from a fork length of 61 inches and then from a dorsal girth of 30 inches intersects the curvilinear line consistent with a weight of approximately 80 pounds.

8. According to Figure 1, which of the following is the best estimate of the dorsal girth in inches of a 210-pound tarpon with a fork length of 83 inches?

A Less than 39
B 39
C 40
D Over 40

Unit 7, Questions 10-15

Coagulation (i.e. *clotting*) is the process by which blood changes from a liquid to a cross-linked fibrin gel referred to as a ‘blood clot’. This process may stop blood loss from a damaged vessel (*haemostasis*). For normal coagulation to occur, the necessary clotting factors must be present in the blood. There are a number of diseases that arise from disorders of coagulation which can range from bleeding (haemorrhage, bruising) to obstructive clotting (thrombosis).

The coagulation cascade (Figure 1) has two initial pathways which lead to fibrin formation. These are the contact activation (intrinsic) pathway, and the tissue factor (extrinsic) pathway, which both lead to the final ‘common pathway’ of factor X, thrombin and fibrin. The pathways are a series of reactions in which an inactive protein enzyme precursor, and sometimes its co-factor, are altered to become active components that then catalyse the next reaction in the cascade. Coagulation factors are generally indicated by Roman numerals, with a lowercase ‘a’ appended to indicate an active form.

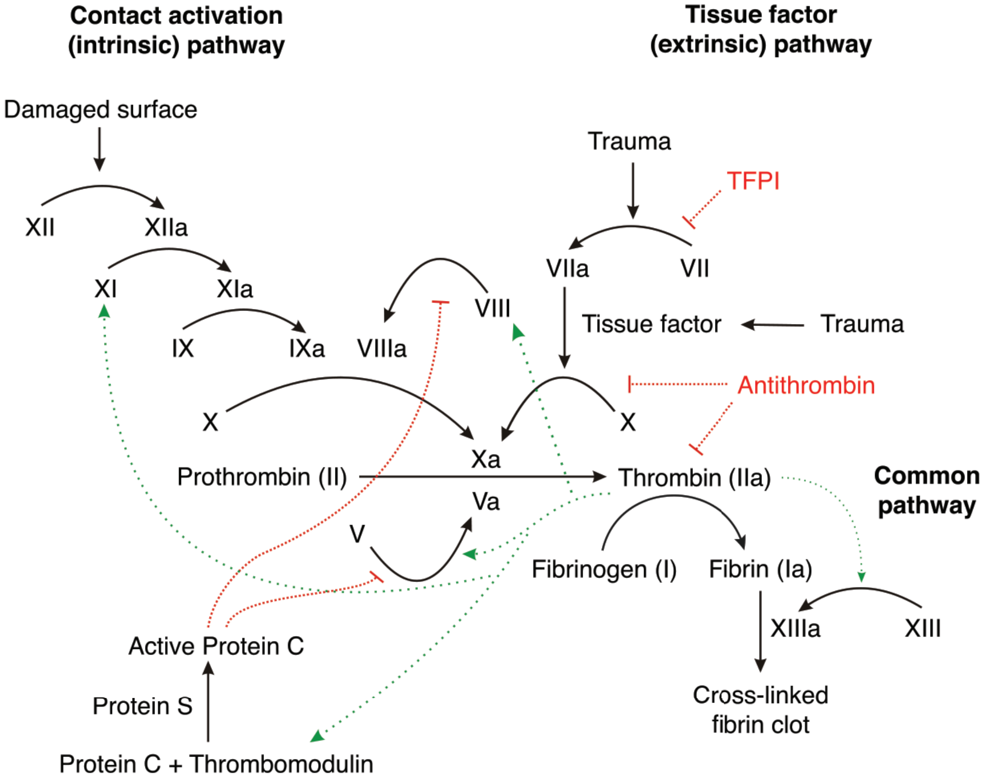
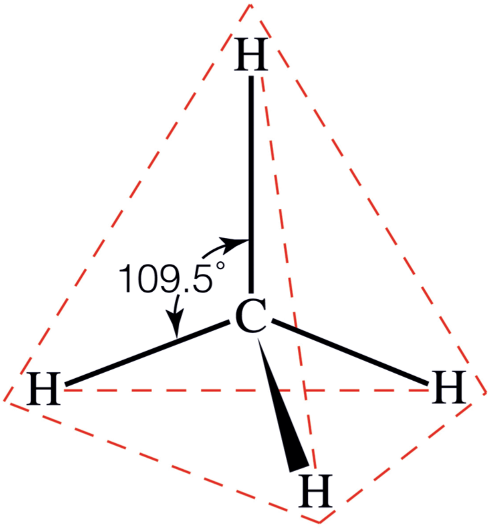
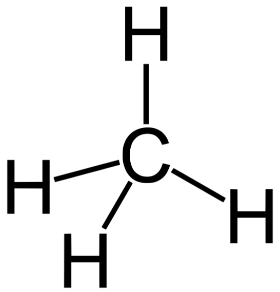
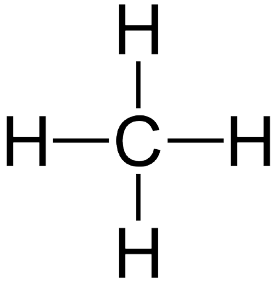


Figure 1: Coagulation cascade. Red dotted lines ending in “T” indicate negative (inhibitory) feedback; green dotted lines ending with an arrow head indicate positive (stimulatory) feedback; curvilinear black arrows indicate ‘conversion to’; a factor (or factors) written above and/or below an arrow indicate(s) a catalytic function. For example, factor XIIa catalyses the reaction that converts factor XI to factor XIa. Wikimedia; Joe D, 2007.



Note: in organic chemistry, a dark triangle means that the bond is coming towards you (i.e. it is coming OUT of the page), a straight line means that the bond is in the same plane as the page, and a dashed triangle means that the bond is going away from you. However, as we will see, there are many shorthand ways to draw molecules that ignore these rules for the sake of expediency. Here are just a couple of such shorthand representations of methane:





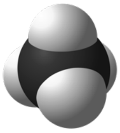
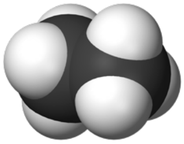
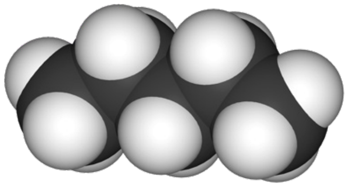
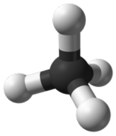
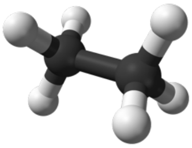
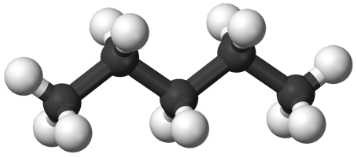
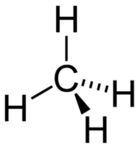
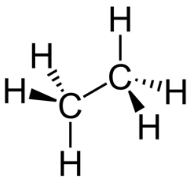
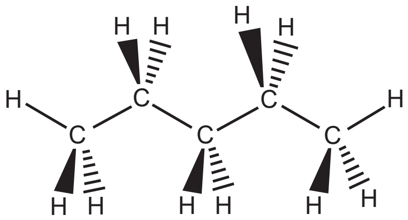
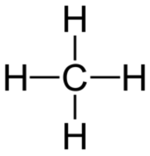
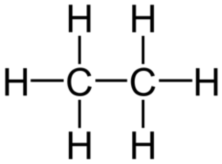
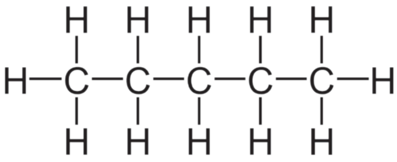
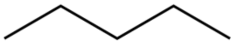
Organic chemistry requires a lot of imagination. Most students will be able to look at the hundreds of illustrations in this book without any difficulty. Some students prefer something more tangible: for example, either purchasing a molecular model set/kit, or making one with the help of YouTube, plasticine and/or Styrofoam. Here is tetrahedral methane using a molecular model set (notice that it is quite similar to the ball-and-stick model of the molecule, see Table IV.B.1.1 *au verso*):

In considering real molecules, how representative are models, skeletal structures and other illustrations? Well, they are really cartoons. How much does Bugs Bunny represent rabbits? I suppose there are some basic features in common, but...

The illustrations of molecules are all simplified representations that, of course, share important characteristics with the real thing. Ideally, you will develop the flexibility to seamlessly go from one way to represent a molecule to another, while reflexively accounting for the key atoms and bonds. By developing your observational skills, as opposed to trying to commit details to memory, you will have a much easier time when faced with typical GAMSAT exam questions.

Table IV.B.1.1: Various ways to represent the structures of carbon-based molecules.

STRUCTURES OF COMMON HYDROCARBONS
Hydrogen + Carbon = Hydrocarbons

	Methane, CH_4	Ethane, C_2H_6	Pentane, C_5H_{12}
Space-filling model Most accurately represents real molecules - compared to other models - but least used since it is not easy to draw and not all atoms or bonds are visible; C: grey, H: white.			
Ball-and-stick model Atoms, bonds and shapes are clearer (in each case, C is in the center of a tetrahedron); not any easier to draw!			
Skeletal structure AKA structural formula, line diagram, etc.; this form preserves the 3D shape with solid (*towards you*) and dashed (*away from you*) triangles.			
Skeletal structure During the real exam, you would usually use this form (+/- the H's) and/or the shorthand form below. 3D shape is not preserved.			
Shorthand Imagination and discipline: Every corner of a geometric figure is a carbon as well as the end of a line*. H's are assumed using the rule: 4 bonds to each C.	N/A		
Miscellaneous	N/A	CH_3CH_3, CH_3-CH_3 H_3C-CH_3	$CH_3CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_3CH_3$

*That is, as long as no other atom is present at the end of a line, then it can be assumed that carbon is present, and as many H's are bonded to that carbon so that neutral C has 4 bonds.

1.2 Hybrid Orbitals

In organic molecules, the orbitals of the atoms are combined to form **hybrid orbitals**, consisting of a mixture of the s and p orbitals. In a carbon atom, if the one s and three p orbitals are mixed, the result is four hybrid sp^3 orbitals. Three hybridized sp^2 orbitals result from the mixing of one s and two p orbitals, and two hybridized sp orbitals result from the mixing of one s and one p. The geometry of the hybridized orbitals is shown in Figure IV.B.1.1.

Take-home message regarding geometry and hybrids: When carbon is bonded 4 times, all 4 bonds are sp^3 and C is in the center of a tetrahedron; when neutral carbon is bonded to 3 atoms, the 3 hybrids are sp^2 and C is in the center of a flat triangle (= *trigonal planar*); when neutral carbon is bonded to 2 atoms, the 2 hybrids are sp and C is in the center of a straight line.

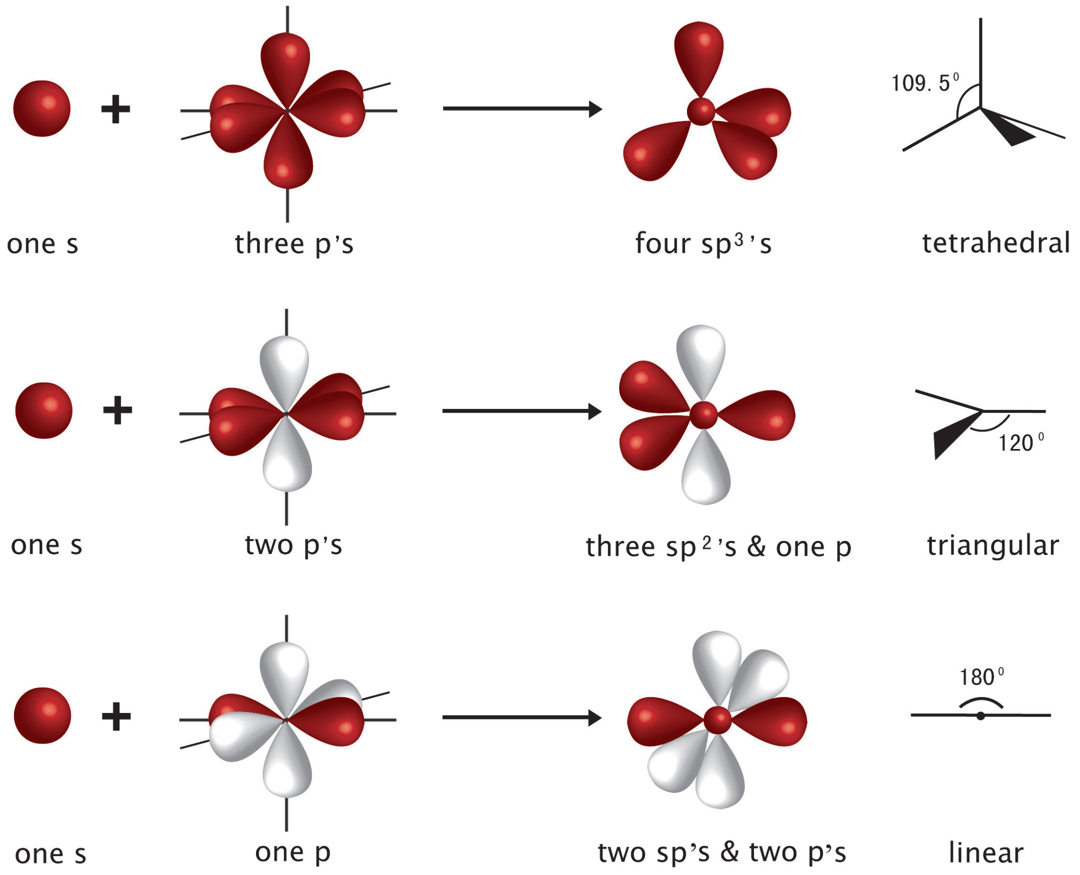
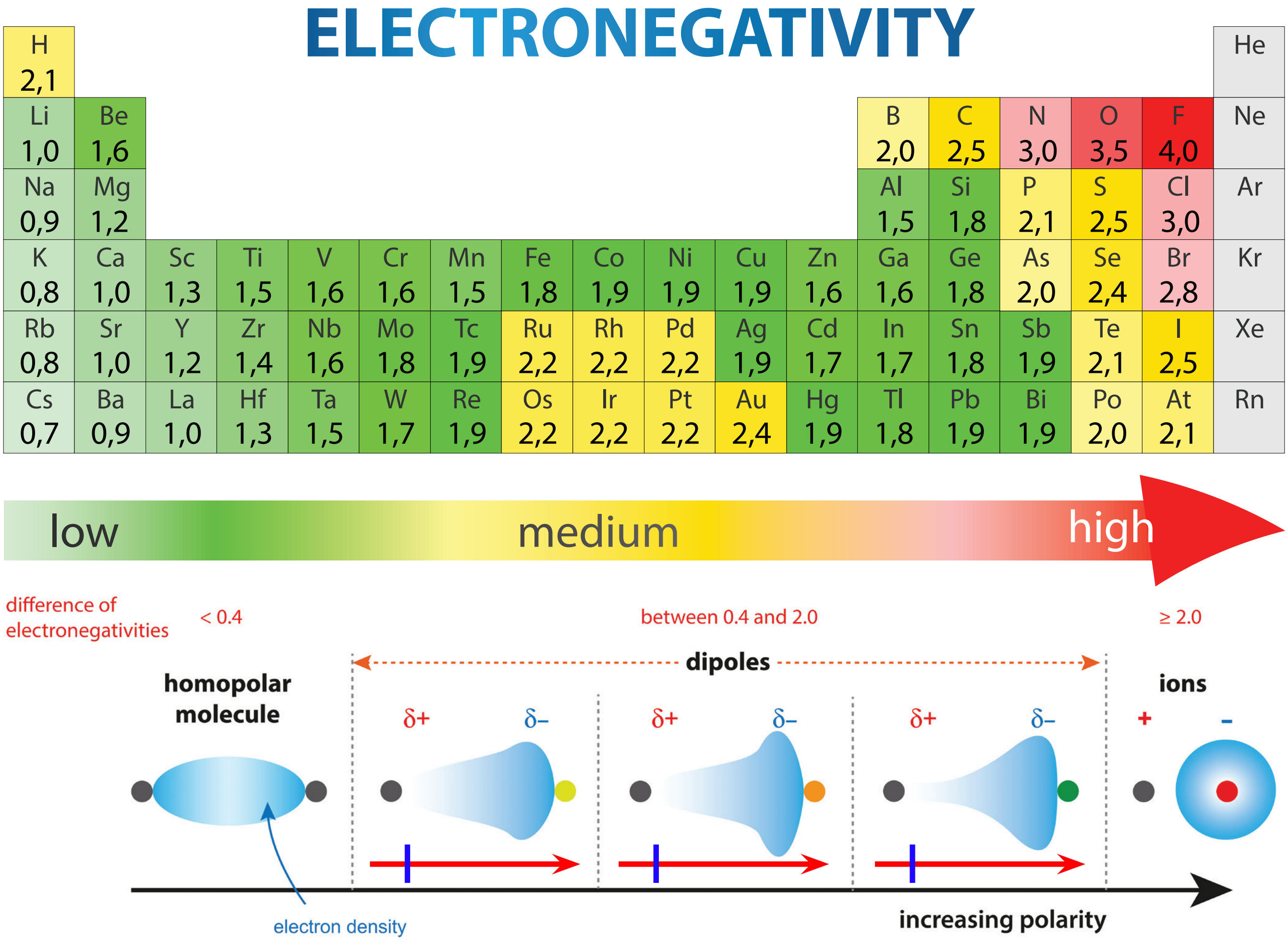


Figure IV.B.1.1: Hybrid orbital geometry

NOTE: For details regarding atomic structure and orbitals, see General Chemistry (CHM) sections 2.1, 2.2. For more details regarding hybridized bonds and bond angles (especially for carbon, nitrogen, oxygen and sulfur), see CHM 3.5. Notice in the first line of the image there are three p orbitals occupying the x, y and z axes (GM 3.6) thus p_x, p_y and p_z.

The most electronegative elements (in order, with electronegativities in brackets) are fluorine (4.0), oxygen (3.5), nitrogen (3.0), and chlorine (3.0). These elements will often be paired with hydrogen (2.1) and carbon (2.5), resulting in bonds with partial ionic character. The **dipole moment** is a measure of the charge separation and thus, the electronegativities of the elements that make up the bond; the larger the dipole moment, the larger the charge separation.



ELECTRONEGATIVITY

H 2,1																	He
Li 1,0	Be 1,6											B 2,0	C 2,5	N 3,0	O 3,5	F 4,0	Ne
Na 0,9	Mg 1,2											Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0	Ar
K 0,8	Ca 1,0	Sc 1,3	Ti 1,5	V 1,6	Cr 1,6	Mn 1,5	Fe 1,8	Co 1,9	Ni 1,9	Cu 1,9	Zn 1,6	Ga 1,6	Ge 1,8	As 2,0	Se 2,4	Br 2,8	Kr
Rb 0,8	Sr 1,0	Y 1,2	Zr 1,4	Nb 1,6	Mo 1,8	Tc 1,9	Ru 2,2	Rh 2,2	Pd 2,2	Ag 1,9	Cd 1,7	In 1,7	Sn 1,8	Sb 1,9	Te 2,1	I 2,5	Xe
Cs 0,7	Ba 0,9	La 1,0	Hf 1,3	Ta 1,5	W 1,7	Re 1,9	Os 2,2	Ir 2,2	Pt 2,2	Au 2,4	Hg 1,9	Tl 1,8	Pb 1,9	Bi 1,9	Po 2,0	At 2,1	Rn

Figure IV.B.1.4: Periodic table showing Pauling's values for electronegativity (CHM 3.1.1) and their impact on bonding. Homopolar - little to no polarity - produces a nonpolar covalent bond whereby the electron density/distribution is symmetric meaning the bond is equally shared (e.g. C-C bond: 2.5 – 2.5 = 0). As described in General Chemistry (CHM 3.1.1, 3.2), a difference in electronegativity between 0.4 and 2.0 creates a separation of charge or dipole. These bonds can be described as polar covalent, or covalent with ionic character, thus the electron distribution is unequal (= asymmetric, not symmetric; e.g. C-O bond: 3.5 – 2.5 = 1.0). When the difference is greater than 2.0, complete electron transfer occurs which results in ionic bonding (e.g. table salt, Na-Cl: 3.0 – 0.9 = 2.1).

For example, when substituents are added to a cyclic compound (i.e. *see* ORG 12.3.1, Fig. IV.B.12.1 Part II) the most stable position is equatorial (equivalent to the anti conformation, ORG 2.1) which minimizes ESR. This conformation is most pronounced when the substituent is bulky (i.e. isopropyl, t-butyl, phenyl, etc.). In other words, a large substituent takes up more space thus ESR has a more prominent effect.

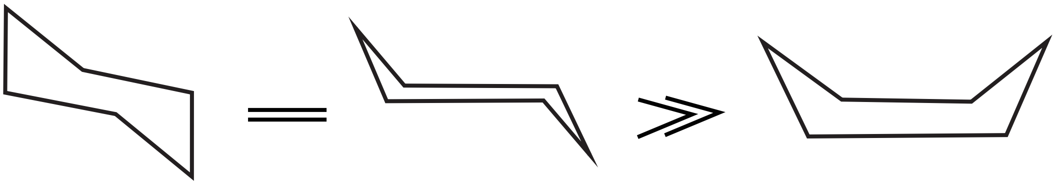


Figure IV.B.3.1: The chair and boat conformations of cyclohexane. Some students like to remember that you sit in a chair because a chair is stable. However, a boat can be tippy and so it's less stable.

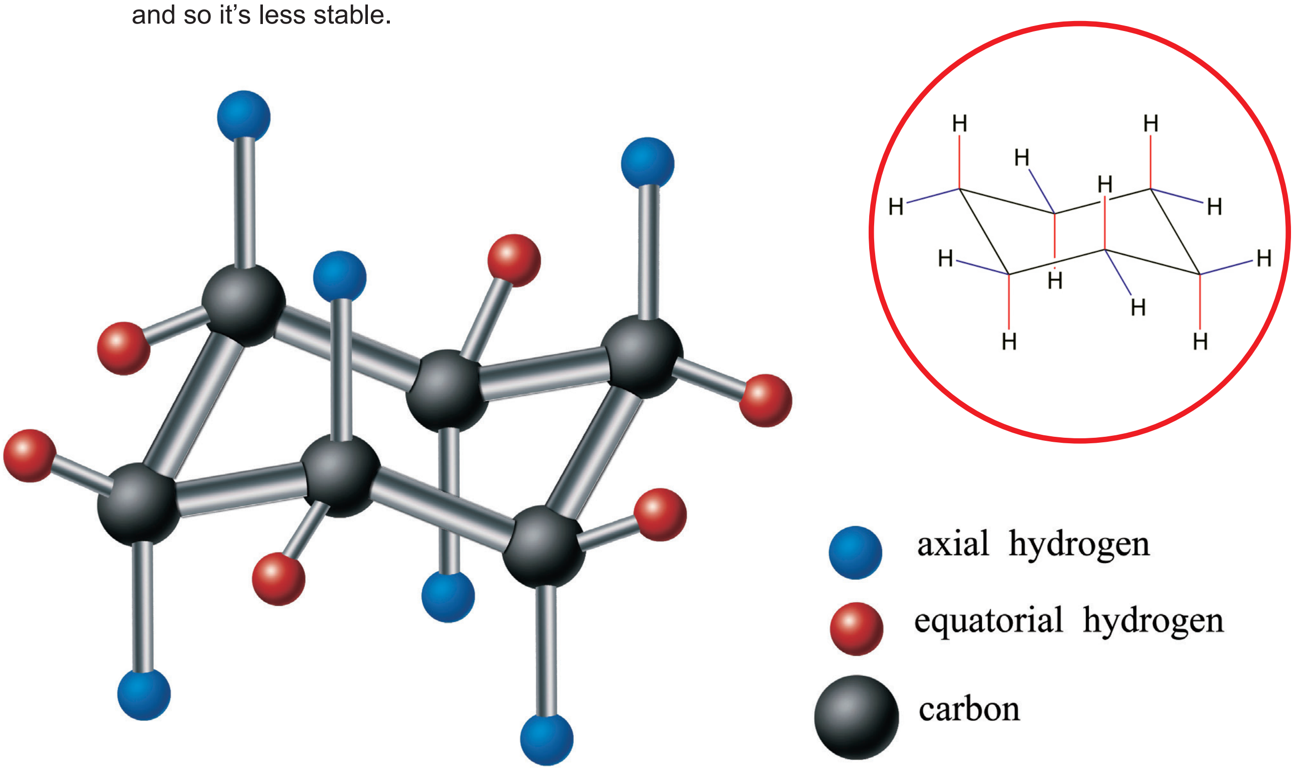


Figure IV.B.3.2: The chair conformation of cyclohexane. The hydrogens which are generally in the same plane as the ring are equatorial. The hydrogens which are generally perpendicular to the ring are axial. The hydrogen atoms are maximally separated and staggered to minimize electron shell repulsion. Note that the inset (in the circle) shows another way to present a chair conformer: the red bond indicates axial and the blue indicates equatorial. Note that cyclohexane can be presented in all the different ways seen on this page, as well as ORG 3.1.

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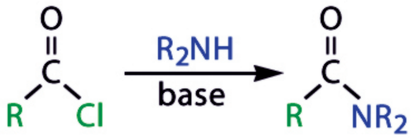
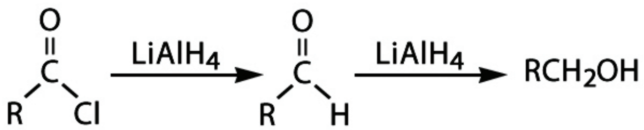
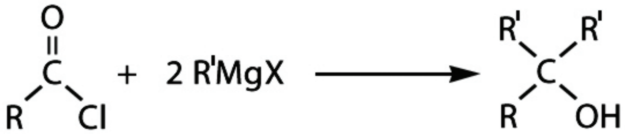


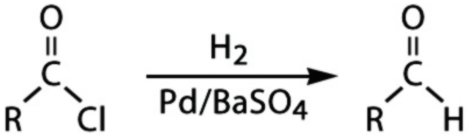
5. **Conversion into alcohols:** Acid chlorides are reduced by $LiAlH_4$ to yield primary alcohols. The reaction is a substitution reaction of -H for -Cl, which is then further reduced to yield the final product alcohol.



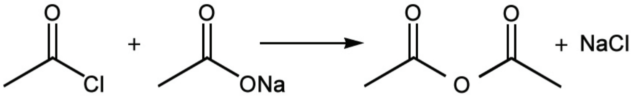
Acid chlorides react with Grignard reagents to yield tertiary alcohols. Two equivalents of the Grignard reagent attack the acid chloride yielding the final product, the tertiary alcohol.



Acid chlorides also react with H_2 in the presence of Lindlar's catalyst (Pd/$BaSO_4$, quinoline) to yield an aldehyde intermediate which can then be further reduced to yield an alcohol.

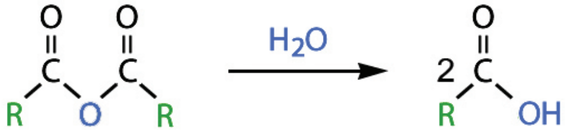


6. **Synthesis of acid anhydrides:** Acid anhydrides can be synthesized by a nucleophilic acyl substitution reaction of an acid chloride with a carboxylate anion.

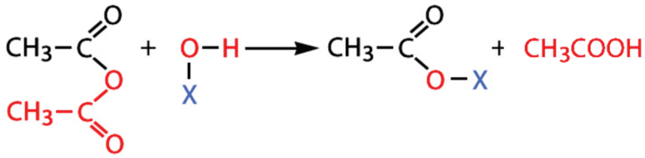


- Reactions of acid anhydrides: The chemistry of acid anhydrides is similar to that of acid chlorides. Since they are more stable due to resonance, acid anhydrides react more slowly.

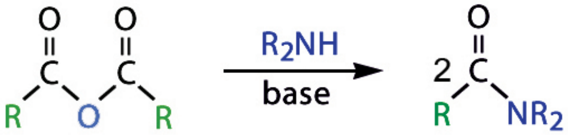
1. **Conversion into acids:** Acid anhydrides react with water to yield carboxylic acids. The nucleophile in this reaction is water and the leaving group is a carboxylic acid.



2. **Conversion into esters:** Acid anhydrides react with alcohols to form esters and acids as in the following example with ethanoic anhydride.



3. **Conversion into amides:** Ammonia (or an amine, ORG 11.1) attacks the acid anhydride, yielding an amide and the leaving group carboxylic acid, which is reacted with another molecule of ammonia to give the ammonium salt of the carboxylate anion.



1.1 Plasma Membrane: Structure and Functions

The plasma membrane is a semipermeable barrier that defines the outer perimeter of the cell. It is composed of lipids (fats) and protein. The membrane is dynamic, selective, active, and fluid. It contains phospholipids which are amphipathic molecules. They are amphipathic because their tail end contains fatty acids which are insoluble in water (*hydrophobic)*, the opposite end contains a charged phosphate head which is soluble in water (*hydrophilic*). The plasma membrane contains two layers or "leaflets" of phospholipids thus it is called a bilipid layer. Unlike eukaryotic membranes, prokaryotic membranes do not contain steroids such as cholesterol.

The Fluid Mosaic Model tells us that the hydrophilic heads project to the outside and the hydrophobic tails project towards the inside of the membrane. Further, these phospholipids are fluid - thus they move freely from place to place in the membrane. Fluidity of the membrane increases with increased temperature and with decreased saturation of fatty acyl tails. Fluidity of the membrane decreases with decreased temperature, increased saturation of fatty acyl tails and increase in the membrane's cholesterol content. The structures of these and other biological molecules were discussed in Organic Chemistry Chapter 12.

Glycolipids are limited to the extracellular aspect of the membrane or outer leaflet. The carbohydrate portion of glycolipids extends from the outer leaflet into the extracellular space and forms part of the glycocalyx. "Glycocalyx" is the sugar coat on the outer surface of the outer leaflet of plasma membrane. It consists of oligosaccharide linked to

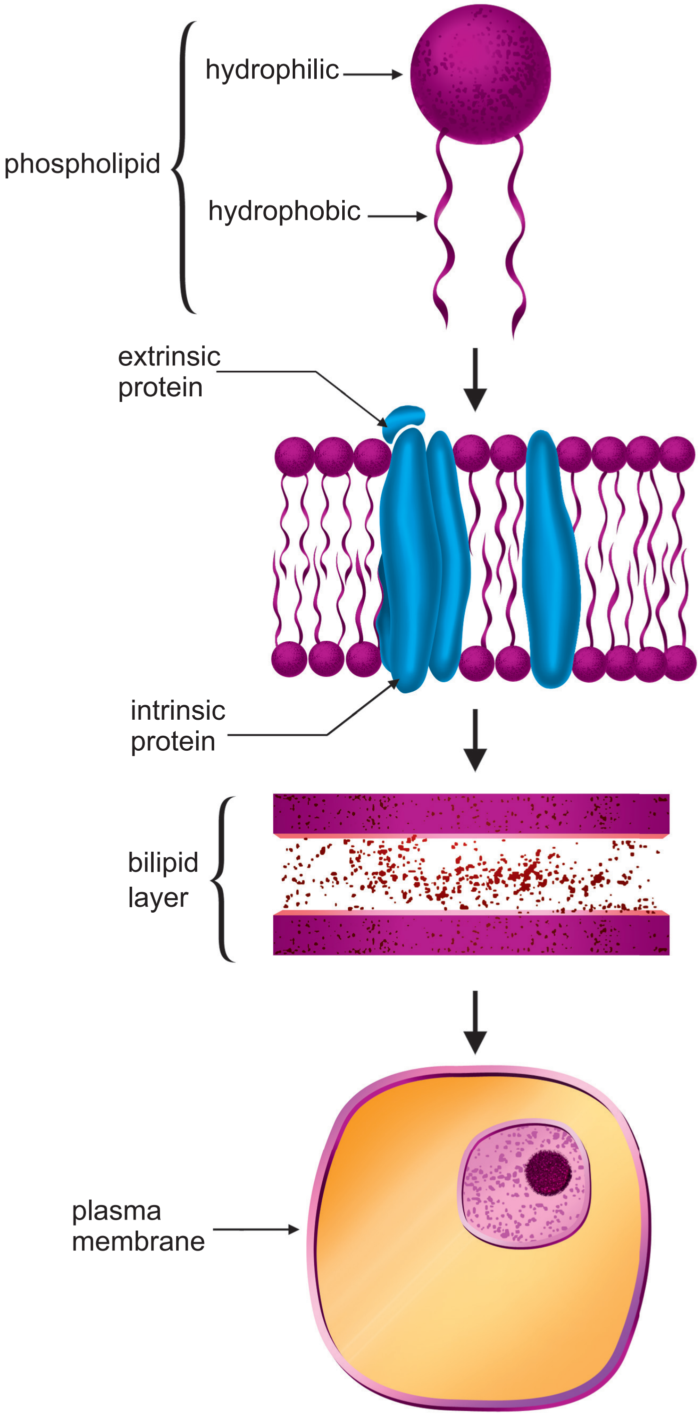


Figure IV.A.1.1: Structure of the plasma membrane. Note that: hydro = water, phobic = fearing, philic = loving

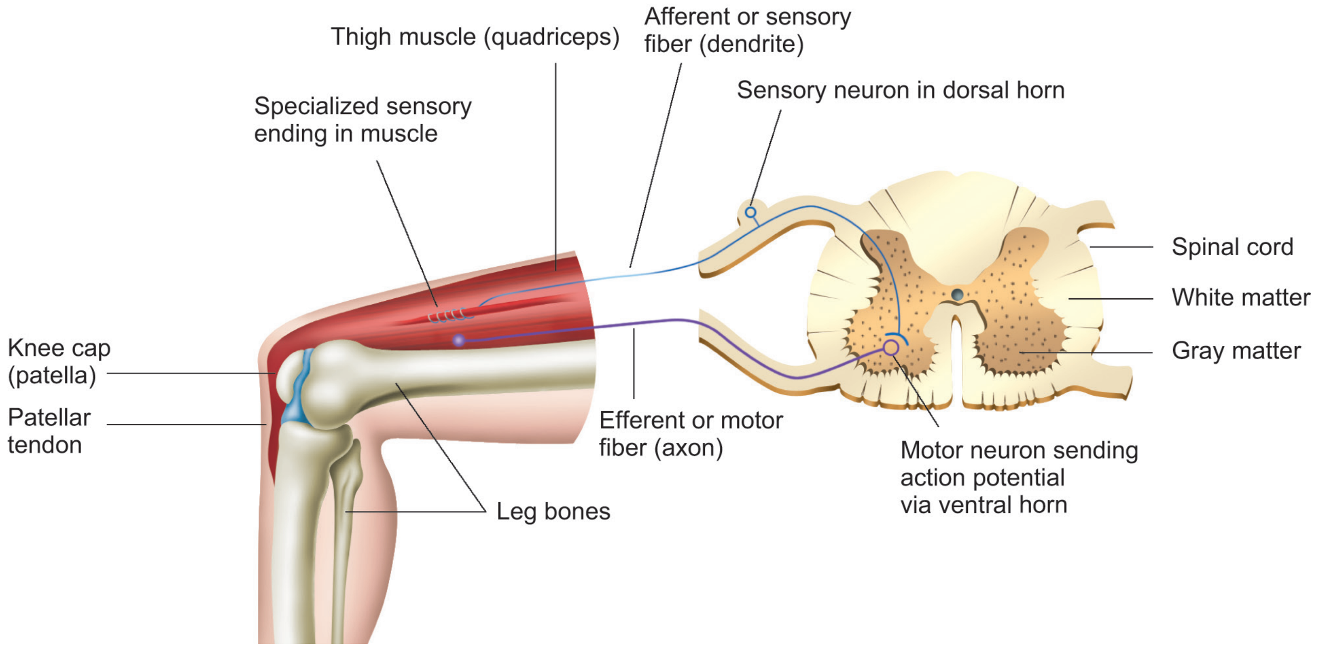


Figure IV.A.6.1: Schematic representation of the basis of the knee jerk reflex.

6.1.4 Autonomic Nervous System

While the Somatic Nervous System controls voluntary activities (i.e. innervates skeletal muscle), the Autonomic Nervous System (ANS) controls involuntary activities. The ANS consists of two components which often antagonize each other: the sympathetic and parasympathetic nervous systems.

The **Sympathetic Nervous System** originates in neurons located in the lateral horns of the gray matter of the spinal cord. Nerve fibers pass by way of anterior (ventral) nerve roots first into the spinal nerves and then immediately into the sympathetic chain. From here fiber pathways are transmitted to all portions of the body, especially to the different visceral organs and to the blood vessels.

The sympathetic nervous system uses norepinephrine as its primary neurotransmitter. This division of the nervous system is crucial in the “fight, fright or flight” responses (i.e. pupillary dilation, increase in breathing, blood pressure and heart rate, increase of blood flow to skeletal muscle, decrease of visceral function, etc.).

Parasympathetic Nervous System: The parasympathetic fibers pass mainly through the *vagus nerves*, though a few fibers pass through several of the other cranial nerves

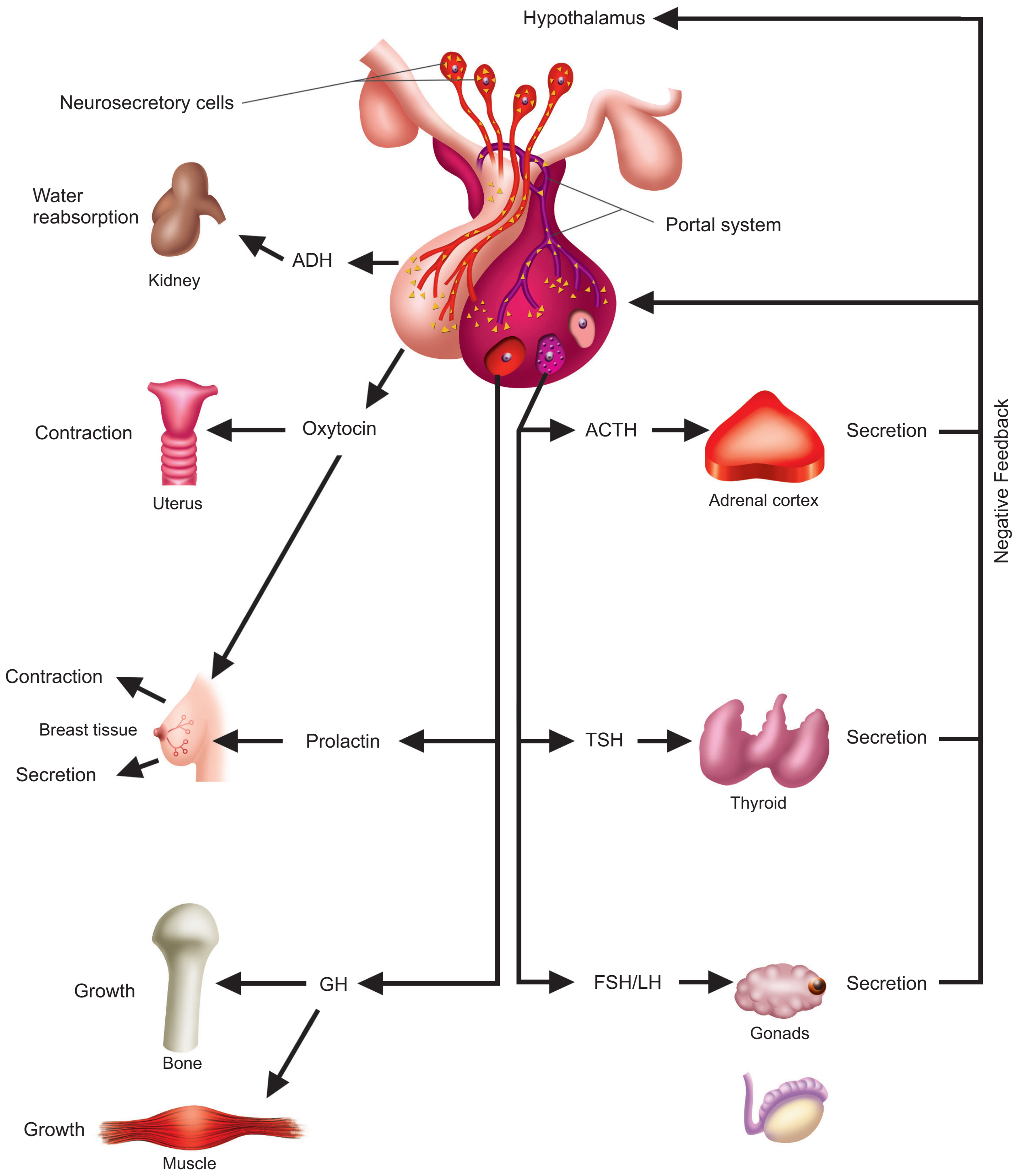


Figure IV.A.6.6: Pituitary hormones and their target organs.

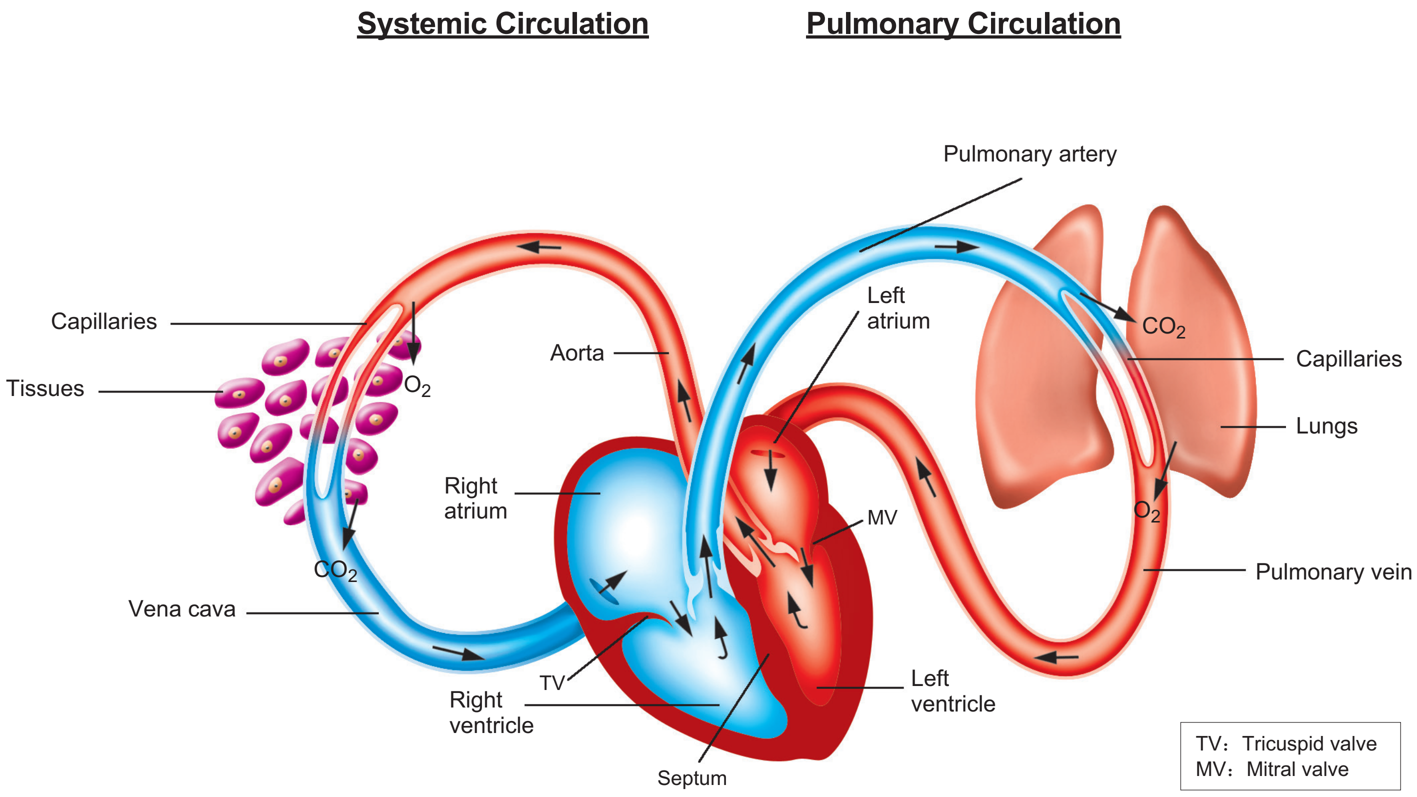


Figure IV.A.7.1: Schematic representation of the circulatory system.

Systemic circulation: transports blood from the left ventricle into the aorta then to all parts of the body and then returns to the right atrium from the superior and inferior venae cavae. *Pulmonary circulation:* transports blood from the right ventricle into pulmonary arteries to the lungs for exchange of oxygen and carbon dioxide and returns blood to the left atrium from pulmonary veins.

7.4 Blood Pressure

Blood pressure is the force exerted by the blood against the inner walls of blood vessels (esp. arteries). Maximum arterial pressure is measured when the ventricle contracts and blood is pumped into the arterial system (= *systolic pressure*). Minimal arterial pressure is measured when the ventricle is relaxed and blood is returned to the heart via veins (= *diastolic pressure*). Pulse pressure is the difference between the systolic pressure and the diastolic pressure. Blood pressure is usually measured in the brachial artery in the arm. A pressure of 120/80 signifies a systolic pressure of 120 mmHg and a diastolic pressure of 80 mmHg. The *pulse pressure* is the difference (i.e. 40 mmHg).