Practice:

(1) Write the reaction of amide + ammonium and predict the direction.

NH4 +	NH	- 2 =	<u> </u>	2 NH <sub>3</sub>				
pKa= 9				pKa= 33				
(2) Given methanol $CH_3OH pKa = 16$ and water $pKa = 16$ . Why can NaOH not completely deprotonate methanol?								
Н₃С—ОН	+	но		H <sub>3</sub> C—O	+	H <sub>2</sub> O	Keq=1 so there is 50/50 on	
pKa= 16						pKa= 16	each side. A mess!	

(3) Hydride is a strong base, H:<sup>-</sup>. What is the CA of hydride? That acid has a pKa of 38.  $H_2 \implies H_2 + H_{CB}^+$   $H_{CB}^+$   $H_{CB}^+$ 

NMR Practice: The following spectra are based on simple alkyl bromides.

<sup>1</sup>H NMR spectra in this order: CH<sub>3</sub>CH<sub>2</sub>-EN (CH<sub>3</sub>)<sub>2</sub>CH-EN CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-EN Butyl-EN Sec-Butyl-EN Isobutyl-EN Which butyl is missing? What would the <sup>1</sup>H NMR of the missing group look like? Tert-Butyl-EN one peak <sup>13</sup>C NMR: Ethyl-EN Isopropyl-EN (2 types of C) Propyl-EN (3 types of C) Butyl-EN (4 types of C) sec-Butyl-EN (4 types of C) Hard to distinguish these two. *tert*-Butyl-EN (2 types of C) Isobutyl-EN (3 types of C)

NMR Practice: What is the degree of unsaturation of benzene  $C_6H_6$ ? 4= 3 double bonds and ring

What is the degree of unsaturation of acetone  $CH_3C=OCH_3$ ? 1= 1 double bond

What is the degree of unsaturation of allyl bromide  $CH_2=CHCH_2Br$ ? 1=1 double bond

Ch 14 Practice



2. Why is there no cis/trans for 1,3-butadiene? What about 1,3-hexadiene? s-cis/ s-trans rotation around a sigma bond



s-trans

3. Is 2,3-hexadiene conjugated? Explain. Cis/trans here? NO.



Two pi bonds but no overlap $-90^{\circ}$  relationship No cis/trans because the bonds are in different planes.

1. What would be the HBr addition products of 1,3-hexadiene?





no chiral C's

5. Cyclopentadiene when reacted with HBr by 1,2 or 1,4 only has one isomer. Explain. Only one allyl cation formed by electrophilic addition:



6. The 1,4 addition product is more stable, how can the 1,2 product be formed? The 1,4 being thermodynamic means that given enough time and energy, it will prevail The 1,2 being the kinetic product means it comes from the easier transition state. Keep the reaction cold and don't allow the system to reach equilibrium and you can force the reaction towards the product formed from the lowest energy transition state.

7.	Which is favored by high T, 1,2 or 1,	4? Which is favored by low T, 1,2 or 1,4?
Hig	h T == thermodynamic 1,4	most stable alkene
Lov	w T == kinetic = $1,2$	lowest transition state $2^0$ allylic C+

## Diels Alder Practice break here

