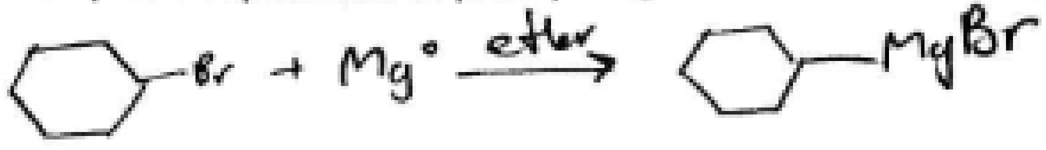
3. Example: Preparation of phenylmagnesium bromide



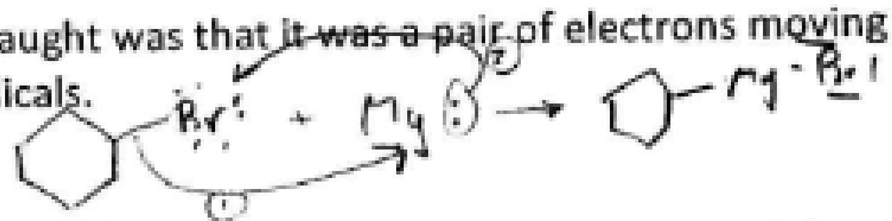
a. In this reaction, we oxidize Mg from standard state (Mg^0) to Mg^{2+}

b. Grignard reagents form coordination complexes that are solvated by ether – this adds to the stability of the Grignard reagent.

ether solvated protects the reaction

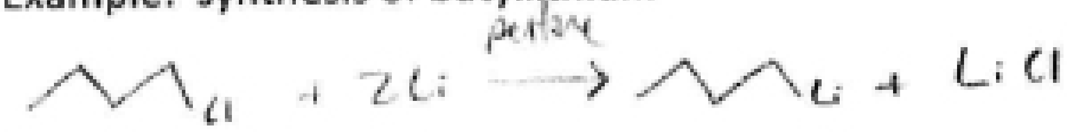
4. There's some argument as to the mechanism by which this reaction occurs, but there is a consensus that radicals are involved at some point.

a. The way I was taught was that ~~it was a pair~~ of electrons moving around, not radicals.



C. Organolithium compounds are prepared by treating an alkyl, aryl, or alkenyl halide with two equivalents of lithium metal

1. Example: synthesis of butyllithium



2. Organolithium compounds are very reactive as nucleophiles in carbonyl addition reactions – even at low temperatures

a. They also react very rapidly with atmospheric oxygen and moisture and have to be used under an inert atmosphere of N_2 or Ar almost 100% yield

D. The carbon-metal bond is described as being polar covalent where the C has partial ⊖ charge & the metal will have partial ⊕ charge.

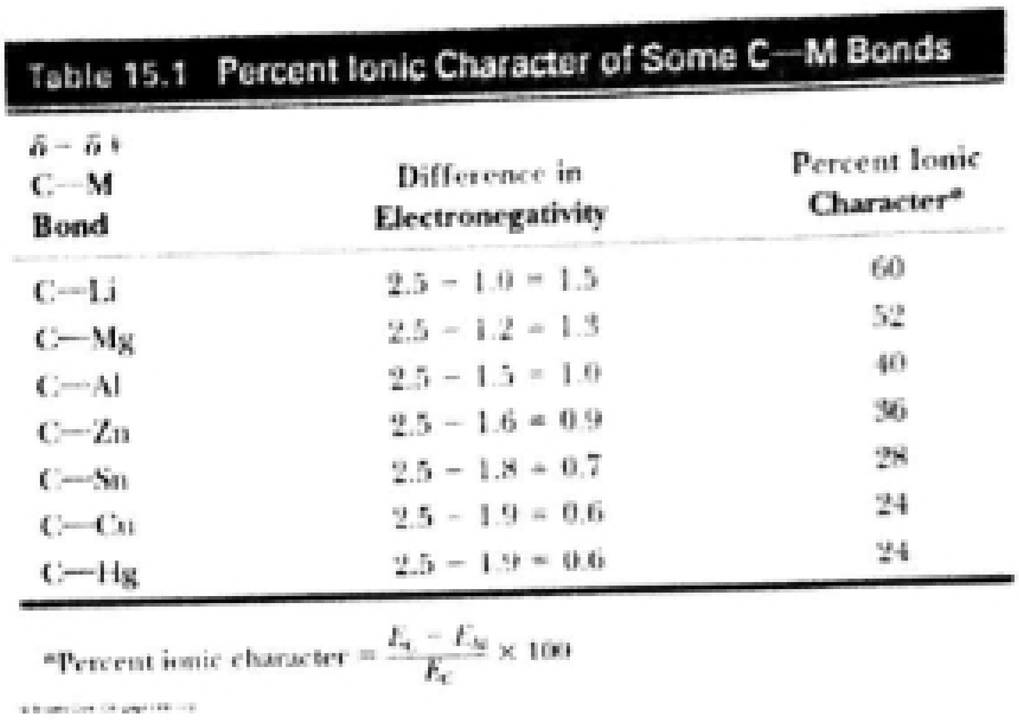
unshared pair of e^- ⊖

1. In this aspect, Grignard and organolithium compounds behave as **carbanions** (ions in which carbon has an unshared pair of electrons and bears a negative charge)

2. Organomagnesium + organolithium compounds

Electronegativity

Ionic = 1.7 - ↑
olar covalent = .5 - 1.7
n-polar
covalent 0 - .4



δ− δ+ C—M Bond	Difference in Electronegativity	Percent Ionic Character*
C—Li	2.5 − 1.0 = 1.5	60
C—Mg	2.5 − 1.2 = 1.3	52
C—Al	2.5 − 1.5 = 1.0	40
C—Zn	2.5 − 1.6 = 0.9	36
C—Sn	2.5 − 1.8 = 0.7	28
C—Cu	2.5 − 1.9 = 0.6	24
C—Hg	2.5 − 1.9 = 0.6	24

*Percent ionic character = $\frac{E_C - E_M}{E_C} \times 100$

Table 15.1 Percent Ionic Character of Some C—M Bonds

A. As the difference in electronegativity grows between carbon + metal so does % ionic character of the C-M bond

%↑ = C becomes carbanion or great nucleophile

3. Because the carbon takes on the appearance of a carbanion, that means that these compounds will react with the elctrophilic carbon atom of carbonyl groups – this means that we can form new carbon-carbon bonds! → aldehydes, ketones, carboxylic [illegible] acid chlorides

* we can form C-C bonds

E. Both Grignard and organolithium compounds are very strong bases and react readily with any acid stronger than the alkane that they were originally derived from.

pKa water ≈ 15.7

pKa = -35
Keq = 10^{35}

1. Example: reaction of ethylmagnesium bromide with water

$CH_3CH_2-MgBr + H-OH \longrightarrow CH_3CH_2-H + Mg^{2+} + OH^- + Br^-$

pKa = 15.7 pKa = 51

equilibrium → products (based on pKas)

F. The following are several classes of proton donors that can react readily with Grignard and organolithium compounds

memorize

					thiol	carboxylic
R_2NH	RC≡CH	ROH	HOH	ArOH	RSH	RCOOH
38-40	25	16-18	15.7	9-10	8-9	4-5
Not as reactive						very reactive

1. That means these organometallic compounds cannot be prepared from any organohalogen that has one of these functional groups.

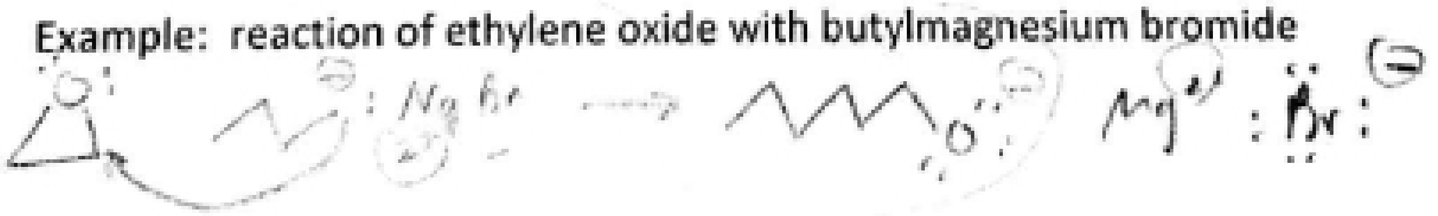
Example Problem #1. Write an equation for the acid-base reaction between ethylmagnesium iodide and an alcohol (R-OH). Use curved arrows to show the flow of electrons in this reaction. In addition, show by using appropriate pK_a values that this reaction is an example of a stronger acid and stronger base reacting to give a weaker acid and weaker base.

G. We can also react an organometallic compound with an epoxide (oxirane).

a. remember that an epoxide has incredible ring strain so they will undergo a ring opening attack

b.

c. Example: reaction of ethylene oxide with butylmagnesium bromide



Example Problem #2. Show how to prepare the following compound from an organohalogen compound and an oxirane.