

Chapter 14

Organometallic Compounds

Chapter 14 suggested problems: 13, 17, 18, 19, 20, 21, 22

web sites: [Organic Synthesis and Carbon-Carbon Bond Forming Reactions](#), [Multi-step Organic Synthesis](#)

I. General

A. Organometallic compounds: carbon is bonded to a metal, such as Li, Na, K, Zn, Hg, Pb, Tl, etc.

1. Carbon-metal compounds of virtually every sort have been synthesized
2. The properties vary depending on a number of factors, including the various metal atoms involved

B. Organometallic nomenclature

1. Organometallic compounds are named as substituted metal compounds
2. The metal is the base name
3. Alkyl groups are named as prefixes
 - a. Propyllithium
 - b. Dipropylmagnesium
4. If the metal also is bonded to an atom other than carbon, that atom is treated as an anion w.r.t. nomenclature unless it is also a metal atom
 - a. Butylmagnesium bromide
 - b. Phenylmagnesium iodide
 - c. Lithium diethyl copper (Et_2CuLi)

C. Carbon-metal bonds in organometallic compounds

1. When carbon bonds with other nonmetals, the bond is often polar and carbon

bears a partial positive charge

2. When carbon bonds to metals, the bond is generally polar but since carbon is the more electronegative of the two bonding atoms it bears a partial negative charge
3. Carbanions: an anion that contains a negatively charged carbon atom
4. Organometallic compounds are not true carbanions but have carbanion character
5. The greater the difference in EN between carbon and the metal to which it bonds, the greater the partial negative charge on the carbon atom and the greater the carbanionic character of the compound
6. Side bar: are the carbon-metal bonds ionic or covalent? (**percent ionic character graphic**)

Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

7. Why lithium and magnesium?
 - a. "The metals in these two groups are the most electropositive of the elements. The polarity of the bond is such as to place high electron density on the carbon." (C&S B:249)
 - b. They seem to be the best at balancing stability with reactivity

D. Preparation of Group 1 organometallic compounds

1. $RX + 2M \rightarrow RM + M^+X^-$
2. R can be 1°, 2°, 3°, cycloalkyl, alkenyl, or aryl
3. The carbon can be either sp³ or sp² hybridized, although sp² hybridized carbons react more slowly
4. The halogen can be any of the four, with reactivity I > Br > Cl > F (mostly unreactive)
5. The synthesis of Group 1 organometallic compounds must take place in anhydrous solvents, typically alkanes such as pentane
 - a. Group 1 metals are extremely reactive with water and alcohols
 - b. Organolithium compounds are powerful Brønsted bases and react with even weak Brønsted acids (see below)
6. Mechanism: reaction takes place at the metal surface
 - a. $RX + Li \cdot \rightarrow Li^+ + RX \cdot^-$ (formation of radical anion)



E. Preparation of organomagnesium compounds: Grignard reagents

1. $\text{RX} + \text{Mg} \rightarrow \text{RMgX}$
2. R can be 1°, 2°, 3°, cycloalkyl, alkenyl, or aryl
3. The carbon can be either sp^3 or sp^2 hybridized, although sp^2 hybridized carbons react more slowly (this is implied by the need for "more vigorous conditions" such as THF)

	BP (°C)	dielectric constant	dipole moment (D)
pentane	36	1.84	0
diethyl ether	35	4.335	1.15
THF	66	7.58	1.75
water	100	84.2	2.2

4. The halogen can be any of the four, with reactivity $\text{I} > \text{Br} > \text{Cl} > \text{F}$ (mostly unreactive)
5. The synthesis of Group 1 organometallic compounds must take place in anhydrous solvents, typically diethyl ether or TFH
6. Mechanism: similar to that of lithium except that each Mg atom can participate in two x 1-step electron transfers
 - a. $\text{RX} + \text{Mg}^{\cdot-} \rightarrow \text{Mg}^{\cdot+} + \text{RX}^{\cdot-}$ (formation of radical anion)
 - b. $\text{RX}^{\cdot-} \rightarrow \text{R}^{\cdot} + \text{X}^-$ (fragmentation of radical anion)
 - c. $\text{R}^{\cdot} + \text{Mg}^{\cdot+} \rightarrow \text{R-Mg-X}$

F. Organolithium and organomagnesium compounds as Brønsted bases

1. The stronger the acid, the weaker its conjugate base; the weaker the acid, the stronger its conjugate base

2.

compound	formula	K_a	pK_a	conjugate base
2-methylpropane	$(CH_3)_3C-H$	10^{-71}	71	$(CH_3)_3C^-$
ethane	CH_3CH_2-H	10^{-62}	62	$CH_3CH_2^-$
methane	CH_3-H	10^{-60}	60	CH_3^-
ethylene	$CH_2=CH-H$	10^{-45}	45	$CH_2=CH^-$
benzene	C_6H_5-H	10^{-43}	43	$C_6H_5^-$
ammonia	H_2N-H	10^{-36}	36	H_2N^-
acetylene	$H-C\equiv C-H$	10^{-26}	26	$H-C\equiv C^-$
ethanol	CH_3CH_2O-H	10^{-16}	16	$CH_3CH_2O^-$
water	$H-OH$	1.8×10^{-16}	15.7	^-OH

- Think of the implication of these numbers as equilibria constants, given that $pK_a + pK_b = pK_w$
- Any weak Brønsted acid (containing O-H, S-H, N-H) will react with a carbanion to form the hydrocarbon through proton transfer
- Can take advantage of this to reduce any alkyl halide to the corresponding hydrocarbon by first converting it to an organomagnesium compound and then adding water or alcohol

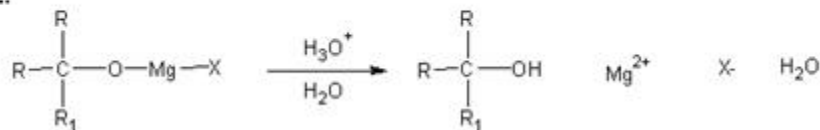
II. Synthesis of alcohols: Grignard and organolithium reagents are most commonly used in the reduction of carbonyl compounds to form alcohols

A. Using Grignard reagents: see Table 14.3, p. 555

Step 1.



Step 2.



- Grignards react with formaldehyde to give primary alcohols
- Grignards react with all other aldehydes to give secondary alcohols

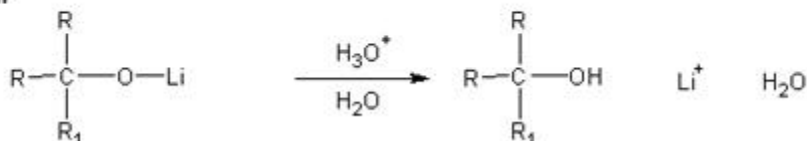
3. Grignards react with ketones give tertiary alcohols

B. Using organolithium reagents: somewhat more reactive than Grignard reagents

Step 1.



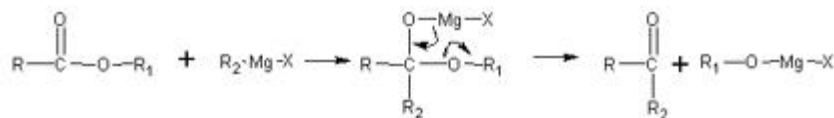
Step 2.



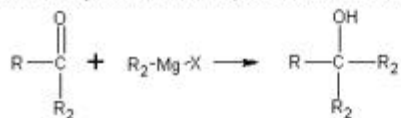
C. Preparation of tertiary alcohols from esters and Grignard reagents

1. By using an ester as the carbonyl compound can form a tertiary alcohol by adding two alkyl groups to the carbonyl carbon

Step 1. in diethyl ether

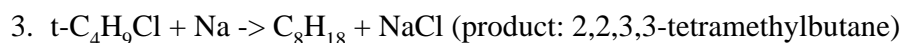
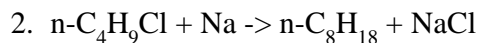
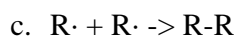
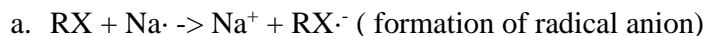
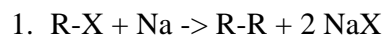


Step 2. in diethyl ether, then aqueous acid is added



III. Other syntheses using organometallic compounds

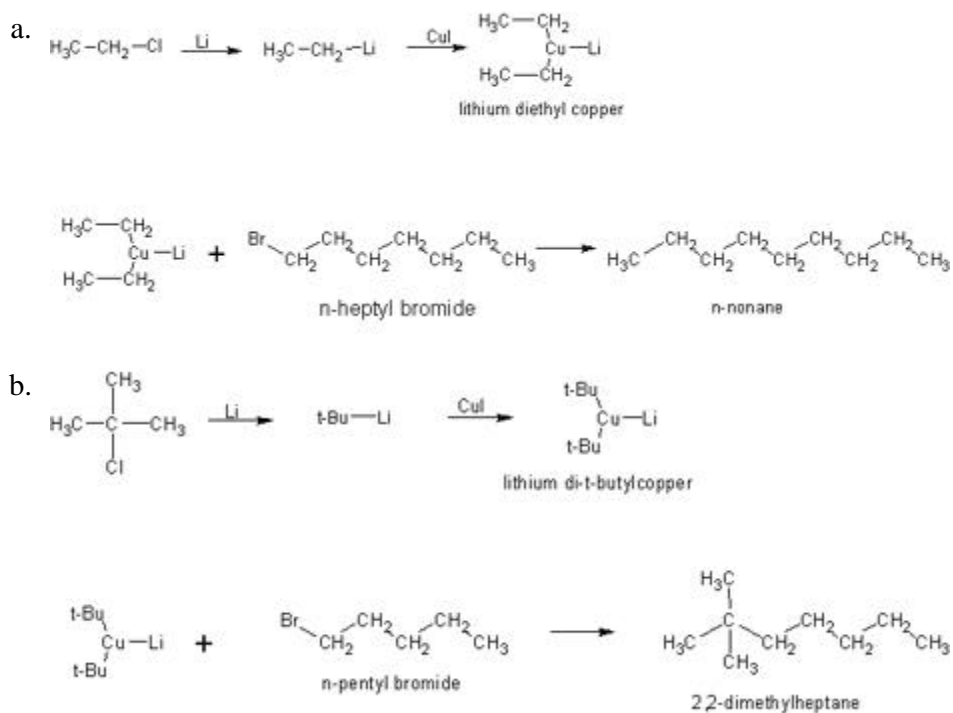
A. Wurtz Reaction (Wurtz coupling): organosodium compounds can be formed as described in (I.D) above, but the resulting compounds are so reactive that combine as they are being formed and result in a symmetric alkane as the product



B. Alkane synthesis using organocopper compounds: a variety of organocopper compounds have been prepared, but the most useful are the lithium dialkylcuprate compounds (R_2CuLi)

1. General reaction: $R_2CuLi + R'-X \rightarrow R-R' + RCu + LiX$
2. Dialkylcuprate compounds also add to a,b-unsaturated aldehydes and ketones (discussed later)
3. Preparation of lithium dialkylcuprates and lithium diarylcuprates
 - a. $2 RLi + CuX \rightarrow R_2CuLi + LiX$
 - b. Mixed in ether at low temperatures
4. Reactivities
 - a. Primary alkyl halides (especially iodides) are best (if not the only); 2° & 3° alkyl halides may have problems with elimination
 - b. Note: according to March (p. 401) primary alkyl, allylic, benzylic, aryl, vinylic, and allenic
 - c. Primary organocuprates are best; 2° & 3° often decompose before reacting with the alkyl halide

5. Examples



C. An organozinc reagent for cyclopropane synthesis

1. Carbenes and carbenoids

- a. Carbenes: highly reactive molecules with lifetimes far quicker than 1 second
 - b. Highly unstable but have been studied at low temperature
 - i. Neutral divalent carbon atom
 - ii. Only six valence electrons, four involved in bonding and two that may be paired or not
 - iii. Only forms two single bonds, no multiple bonds
 - c. Parent species CH_2 is called methylene or carbene
 - d. Most common carbenes are methylene and dichloromethylene (dichlorocarbene)
 - e. Dihalocarbenes are formed by the reaction of a strong base (potassium t-butoxide) with trihalomethane compounds
 - i. The trihalomethane loses its hydrogen atom without its electron pair
 - ii. A halogen atom leaves with an electron pair
 - f. Carbenoids: if a compound appears to form a carbene during the course of a reaction but there is no evidence that free carbene is formed or when there is doubt
2. Iodomethylzinc iodide (ICH_2ZnI) reacts with alkenes to form cyclopropane and its derivatives seemingly via a carbene intermediate
 3. Simmons-Smith reaction: $\text{RCH=CHR}' + \text{ICH}_2\text{ZnI} \rightarrow \text{cyclopropyl derivative} + \text{ZnI}_2$
 4. Stereospecific: cis substituents remain cis, and trans remain trans
 5. Example: the reaction of iodomethylzinc iodide with 2-pentene

D. Transition metal organometallic compounds

1. Many transition metal complexes obey the "18 electron rule:" the sum of bonding and nonbonding electrons around a central transition metal atom should equal 18
2. $2s + 10 d + 6 p = 18 e^-$
3. Examples
 - a. Nickel carbonyl $\text{Ni}(\text{CO})_4$

b. Ferrocene

IV. Retrosynthetic analysis: the process of working backwards from the desired product to available reactants (start complex and work to simple)

A. Steps (on paper)

1. Examine the target molecule
2. Can it be made in one step?
3. What functional groups are in the molecule and how can they be prepared?
4. What is the carbon backbone like? Will carbons, rings, etc. need to be added?
5. Work backwards

B. Examples

[Chemistry 2320 Index Page]

Last Modified Monday, July 15, 2002 22:03:24
