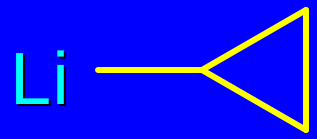
Chapter 14
Organometallic Compounds

14.1
Organometallic Nomenclature

Metal is the parent



Cyclopropyllithium

$H_2C{=}CHNa$

Vinylsodium

$CH_3CH_2MgCH_2CH_3$

Diethylmagnesium

CH_3MgI

Methylmagnesium iodide

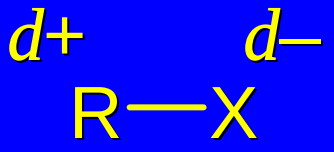
14.2
Carbon-Metal Bonds
in
Organometallic Compounds

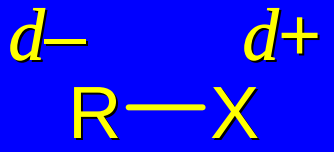
Table 14.1 (p 547)

F	4.0
O	3.5
N	3.0
C	2.5
H	2.1

H	2.1
Cu	1.9
Zn	1.6
Al	1.5
Mg	1.2
Li	1.0
Na	0.9
K	0.8

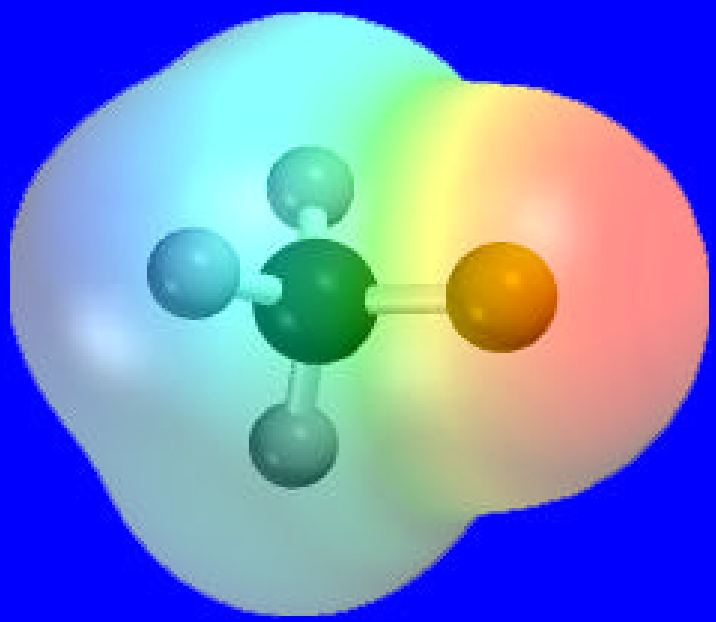
Polarity of Bonds



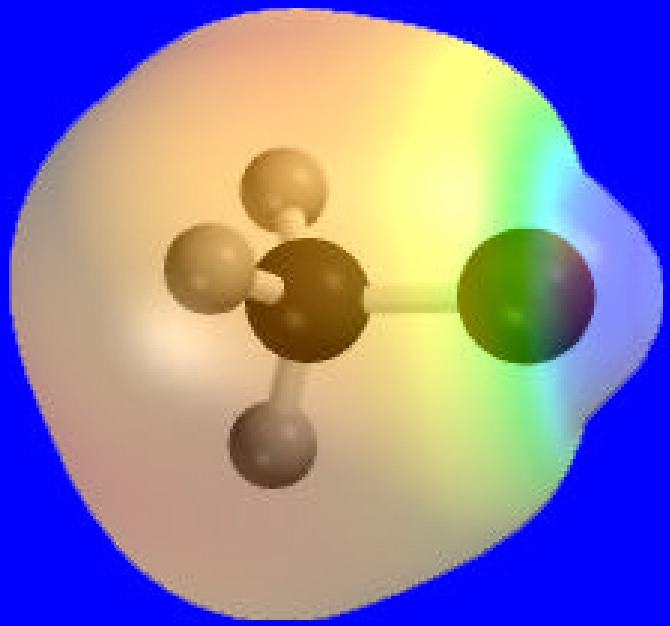


organometallics are a source of nucleophilic carbon

Polarity of Bonds



CH_3F



CH_3Li

14.3

Preparation of Organolithium Compounds

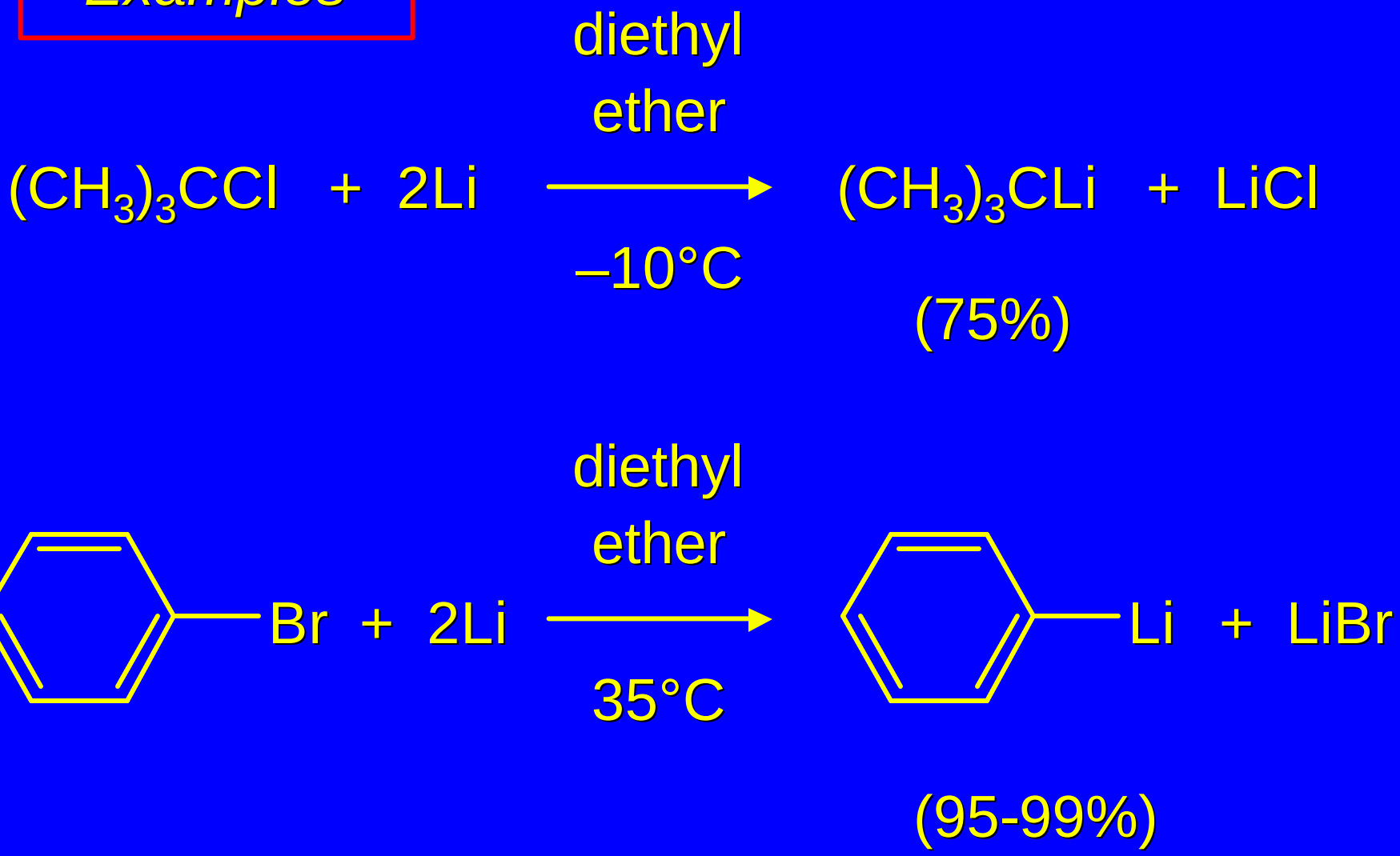
Organolithium Compounds

normally prepared by reaction of alkyl halides with lithium

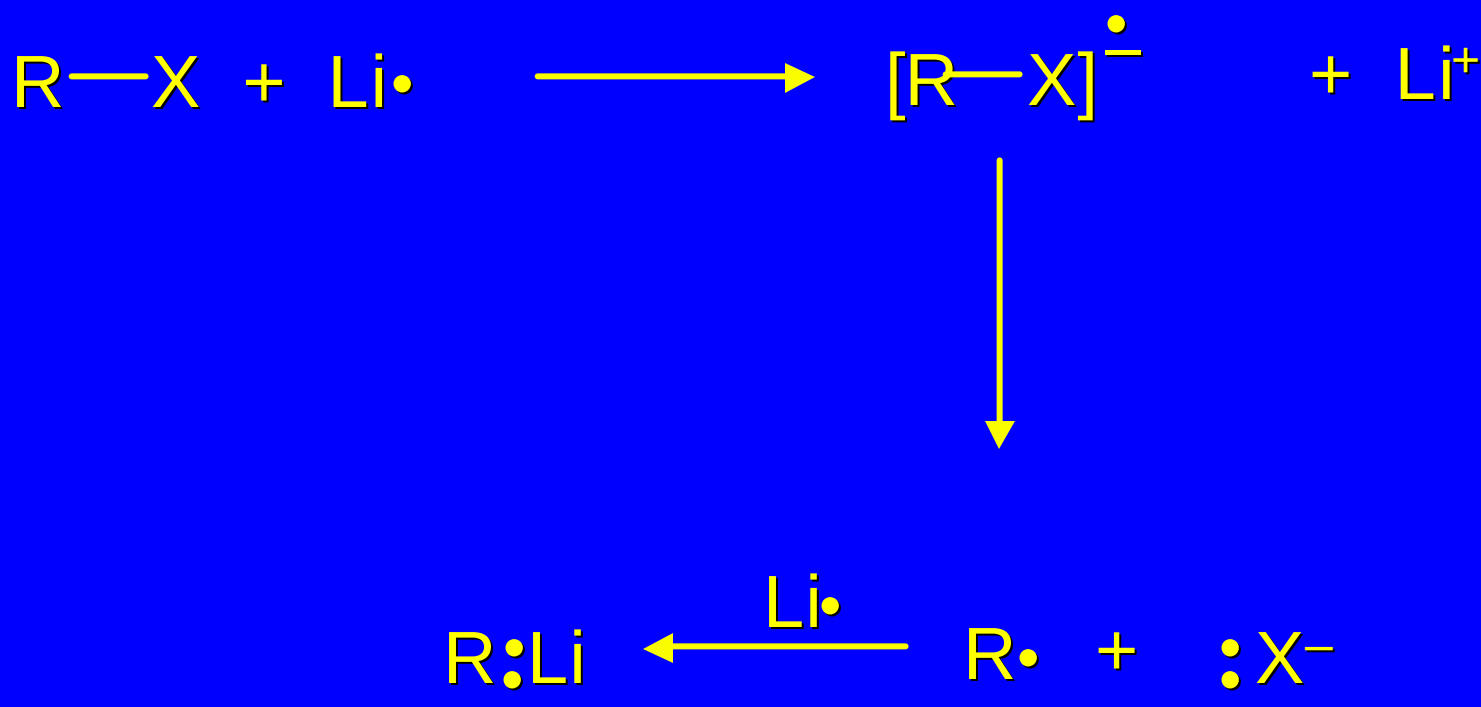
same for Ar—X

is an oxidation-reduction reaction: carbon is reduced

Examples


diethyl ether
$(CH_3)_3CCl + 2Li \longrightarrow (CH_3)_3CLi + LiCl$
–10°C
(75%)
diethyl ether
Br + 2Li
Li + LiBr
35°C
(95-99%)

Electron Bookkeeping



14.4
Preparation of Organomagnesium Compounds: Grignard Reagents

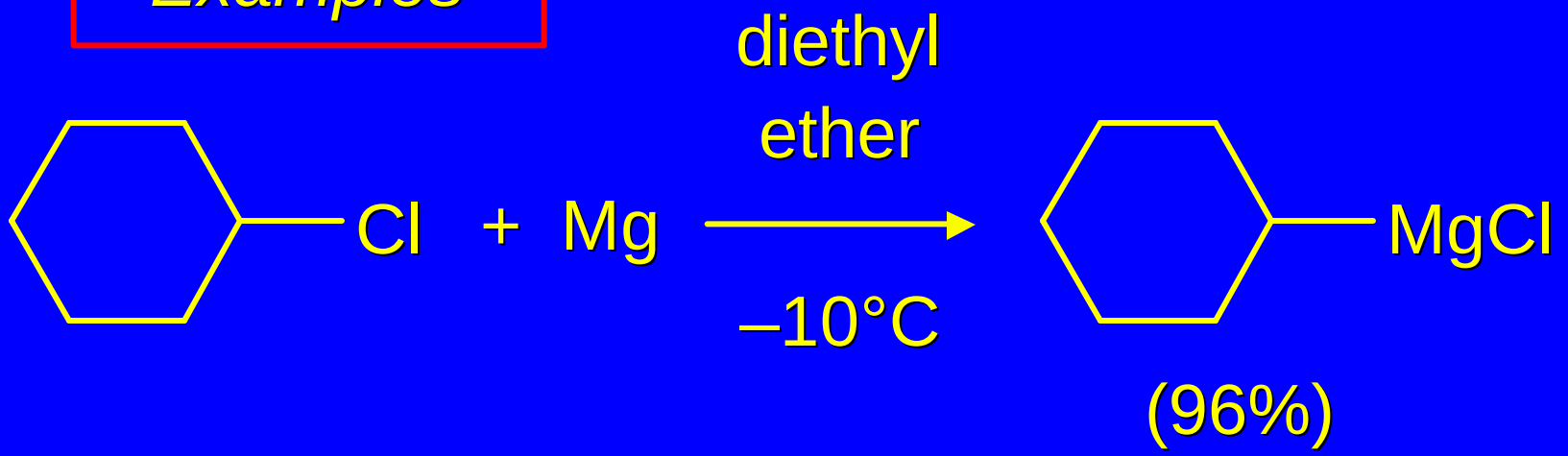
Grignard Reagents

prepared by reaction of alkyl halides with magnesium

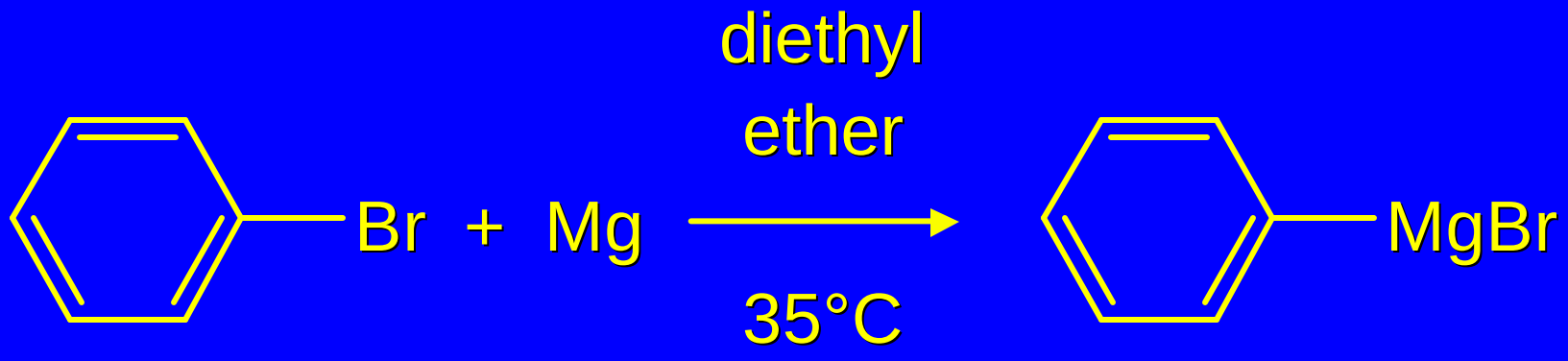
same for Ar—X

Diethyl ether is most often used solvent.
Tetrahydrofuran is also used.

Examples

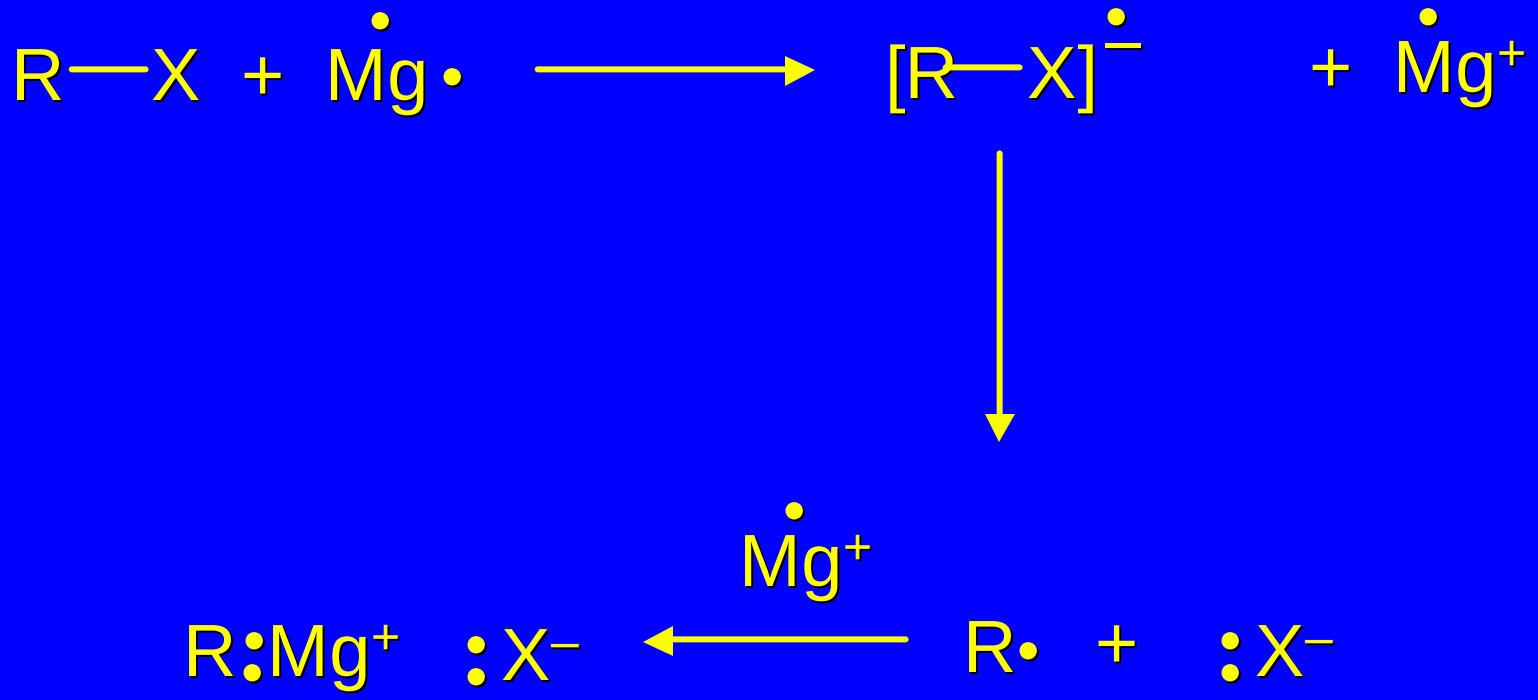


(96%)



(95%)

Electron Bookkeeping



Order of Reactivity

I > Br > Cl >> F

RX > ArX

Forbidden Groups

certain groups cannot be present in

the solvent

the halide from which the Grignard reagent is prepared

the substance with which the Grignard reagent reacts

Forbidden Groups

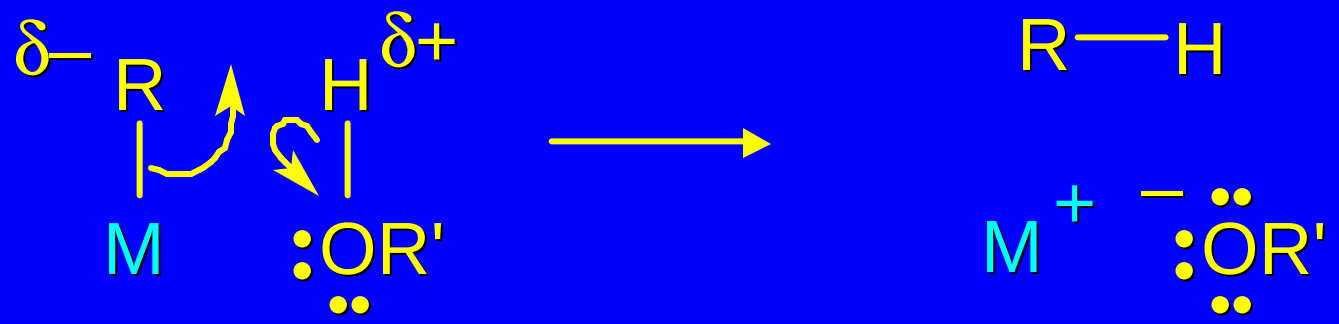
Anything with an OH, SH, or NH group

therefore cannot use H_2O, CH_3OH, CH_3CH_2OH, etc. as solvents

cannot prepare Grignard reagent from substances such as $HOCH_2CH_2Br$, etc.

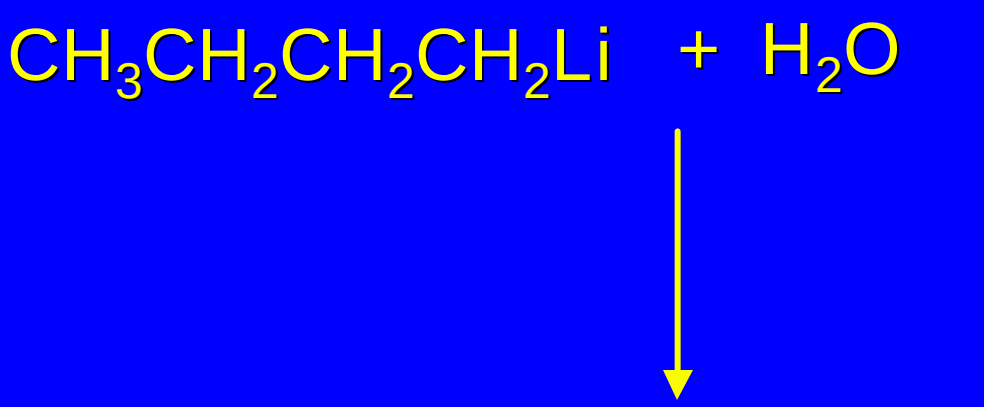
14.5
Organolithium and Organomagnesium Compounds as Brønsted Bases

Brønsted basicity



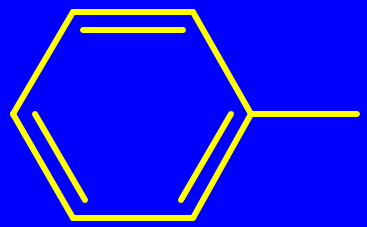
Grignard reagents (M = MgX) and organolithium reagents (M = Li) are strong bases.

Example



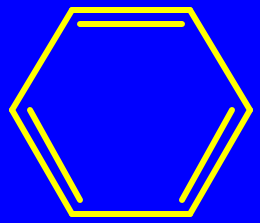
water is a stronger acid than butane

Example



MgBr + CH_3OH

methanol is a stronger acid than benzene



+ CH_3OMgBr

(100%)

Table 14.2
Approximate Acidities of Hydrocarbons

Hydrocarbon	p*K*a
$(CH_3)_3CH$	71
CH_3CH_3	62
CH_4	60
Ethylene	45
Benzene	43
Ammonia	36
Acetylene	26
Water	16

Hydrocarbons are very weak acids.

Their conjugate bases are very strong bases.

Grignard reagents and organolithium reagents are strong bases.

Acetylenic Grignard Reagents

are prepared by an acid-base reaction