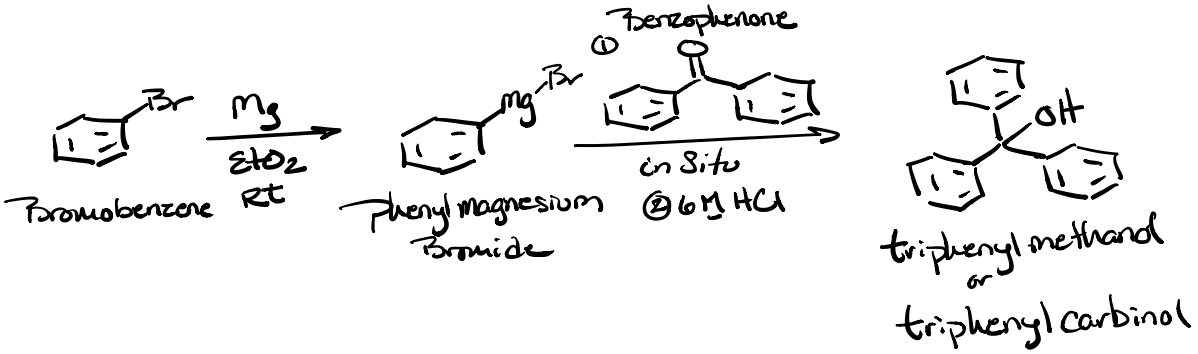
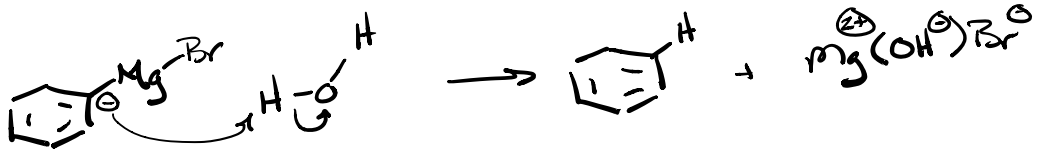
Experiment 33A

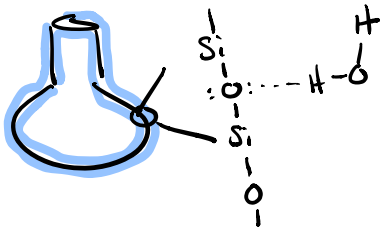


Purpose - To look at C-C making reaction and practice synthesis using organometallics.

Grignard reagents are strong base



⟹ All solvents & Glassware need to be dry for rxn to work.

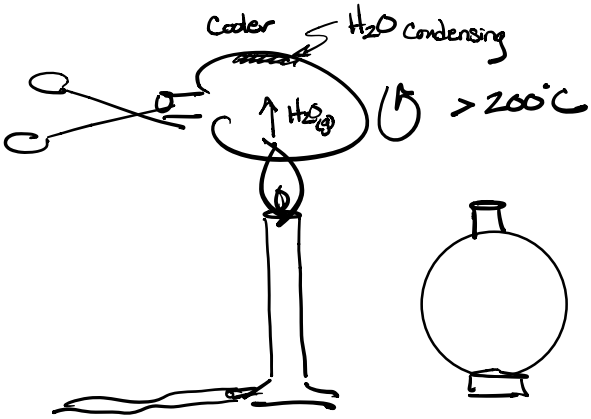


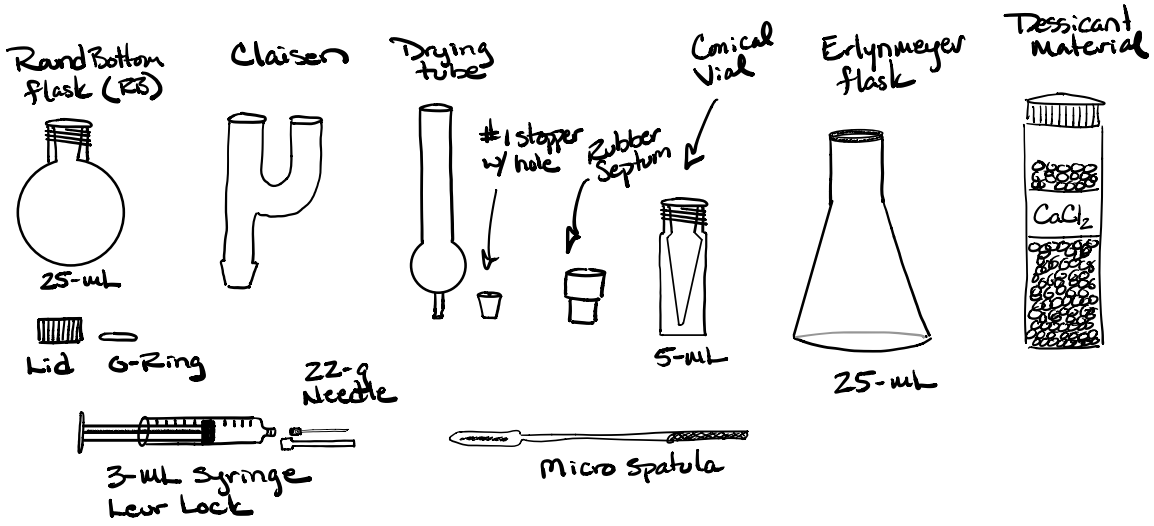
methods to try glassware

① oven bake 24hrs @ 110°-115°C

or

② flame dry over bunsen burner

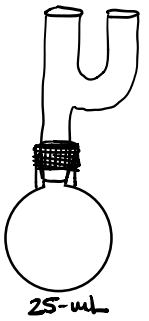


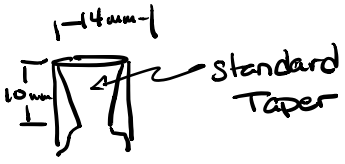


Small 14/10 microscale
14/20

25mL - 100mL 19/22

100mL - 2L 24/40





$ 14/20 or 14/10

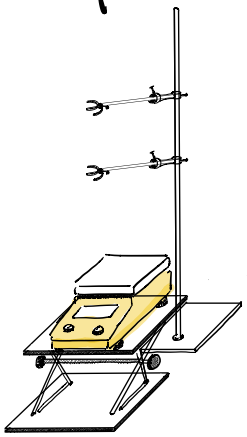
Diameter

Depth

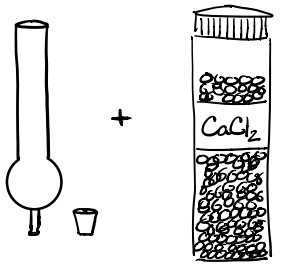
14/10

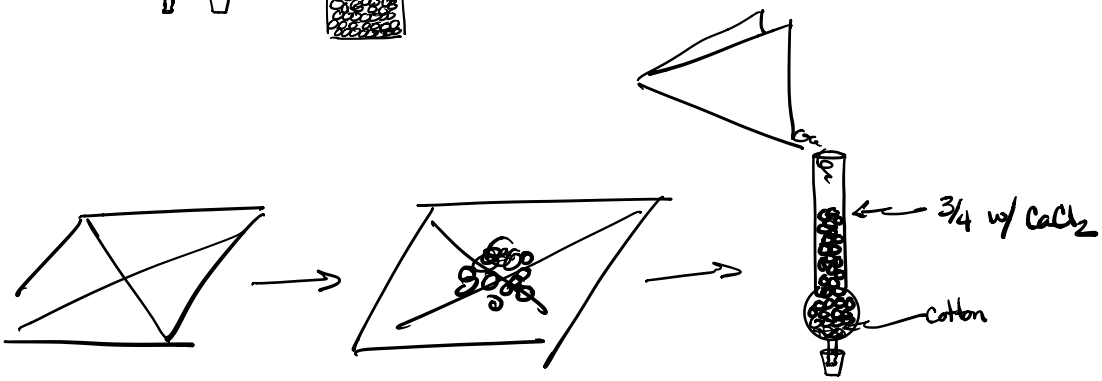
Procedure

① Set up Jackstand, Hotplate, Ringstand, Clamps

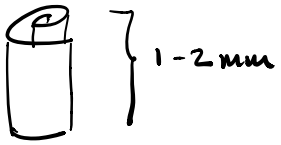


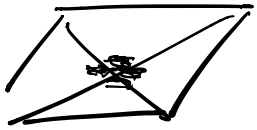
② Pull drying tube from oven & set up.





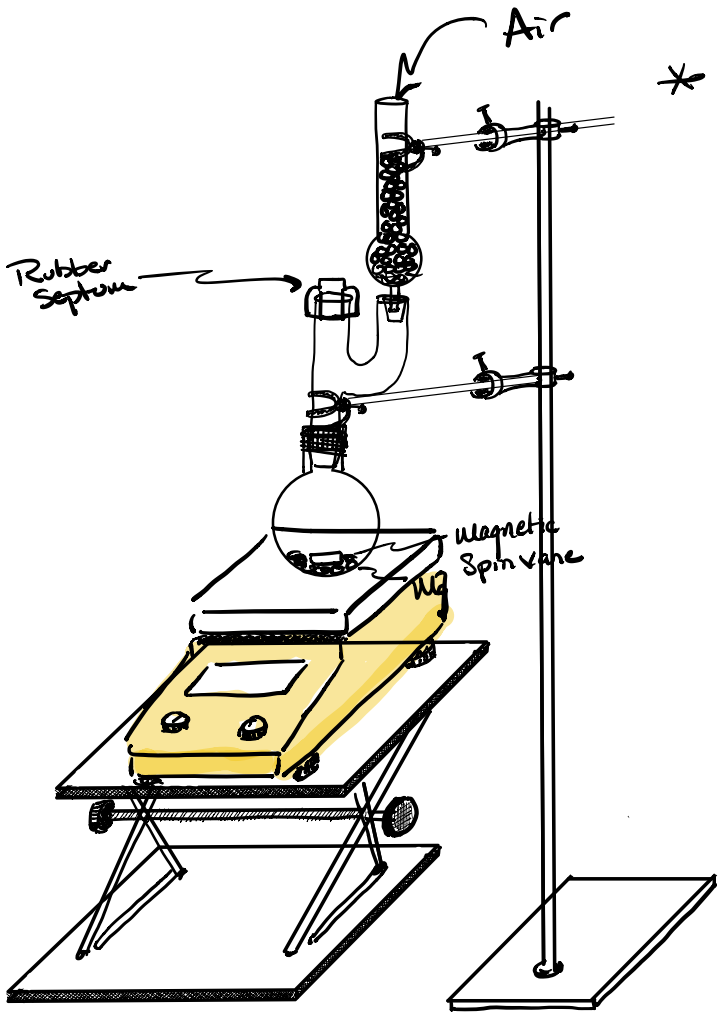
③ Weigh out ~0.15g Mg turnings





0.15g

④ Pull RB flask & Claisen & Set up w/ spin vane, Mg turning, drying tube, Rubber Septa



* Hook together while warm

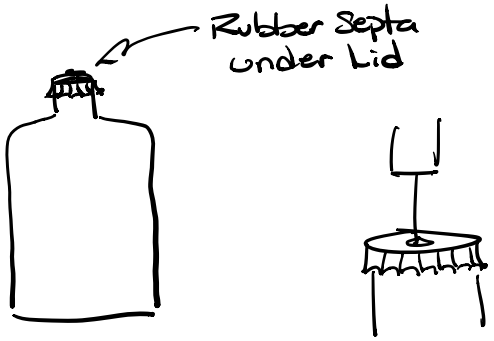
⑤ - Cool a 5-mL Conical vial

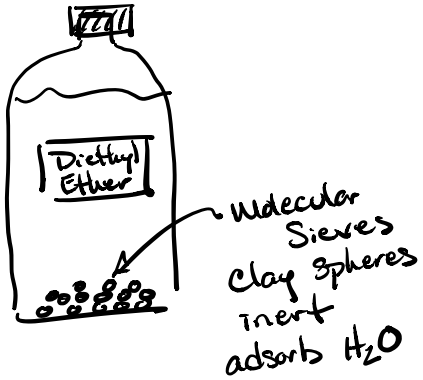
* - Tare vial

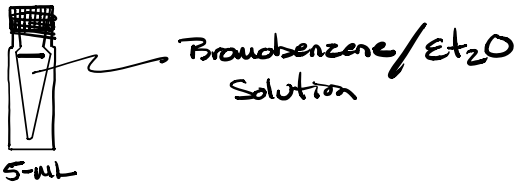
- Add ~0.70 mL bromobenzene 

* - Re-weigh the flask to get mass of bromobenzene

- Add ~ 4.0 mL Anhydrous Et_2O

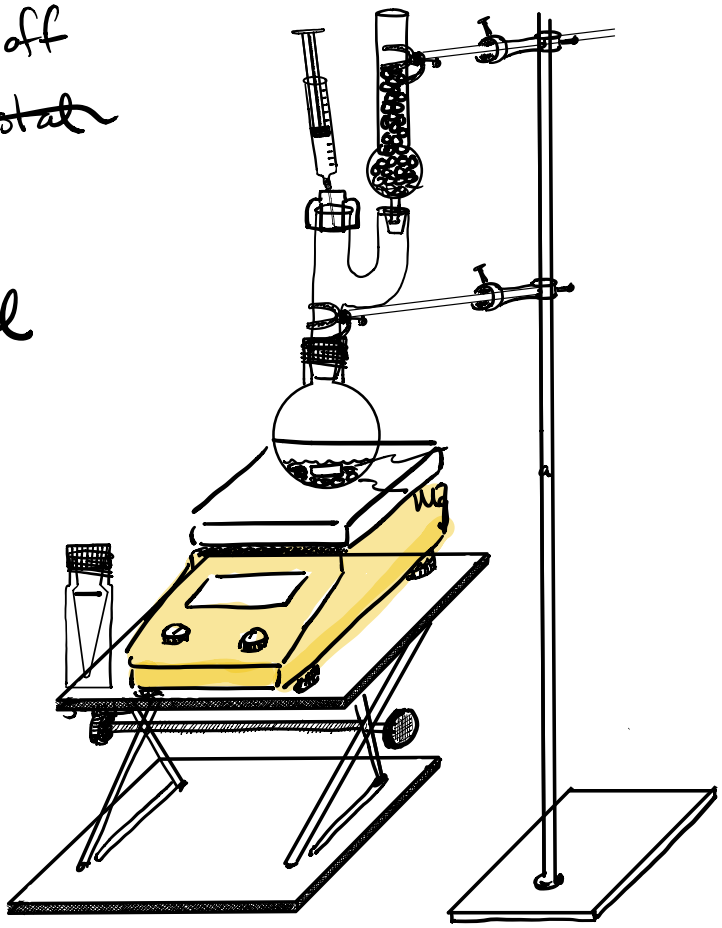






⑥ - Add ~ 1 mL bromobenzene solution to RB flask via syringe through the septa
- Call me to help start Rxn

ways to kick off
- ~~Add I_2 crystals~~
- Sonicator
- Physically grind metal



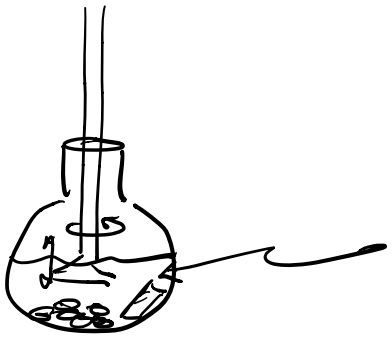
$R\text{-}Br \xrightarrow{\cdot Mg\cdot} R^{\ominus} \; {}^{(2+)}Mg^{\ominus}\text{-}Br$

$Mg^{2+}O^{2-}$

Mg^{0}

$Mg^{2+}O^{2-}$

↳ no valence e^-



Looking for transition from Clear & Colorless to turbid

(7) once Rxn is started you return flask and add bromobenzene/Et_2O solution over 15 min at a rate <u>below</u> boiling.

Rxn exothermic

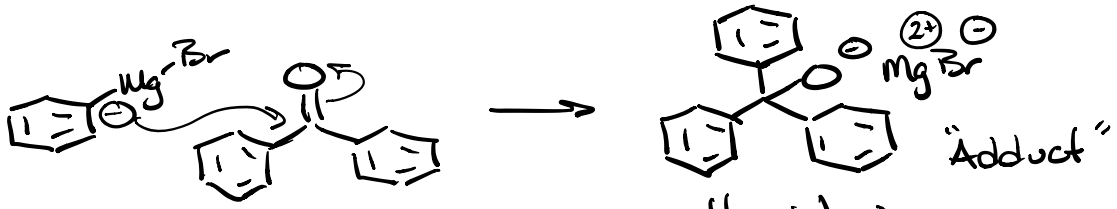
Bp Et_2O 32°C

(8) Rinse conical vial w/ 2 mL Et_2O & add to the reaction.

(9) Use the same 5-mL conical vial to make Benzophenone solution

- Tare vial
- Add ~ 1.09 g Benzophenone solid
- Weigh accurately
- Add ~ 2mL of Et_2O
- Stir/Mix to dissolve & Make homogeneous

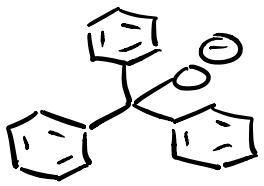
(10) - Add Benzophenone Solution to RB flask quickly — * But at a rate below boiling



alkoxide ion
Ionic
Not Soluble in Et_2O
precipitates as a solid

(11) Rinse conical vial w/ 1 mL of Et_2O & add to Rxn.

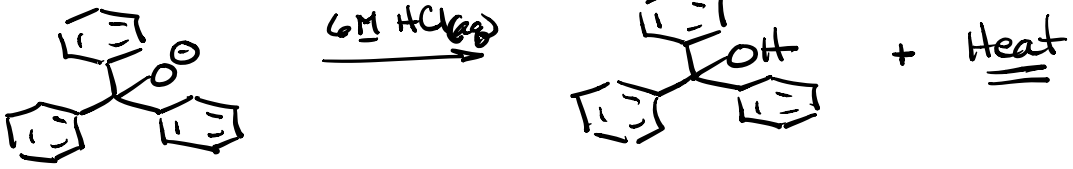
(12) When spin vane fails we open the flask & stir by hand w/ glass rod until the Rxn is a homogeneous grey color.



Strong Base
Like hydroxide

Workup

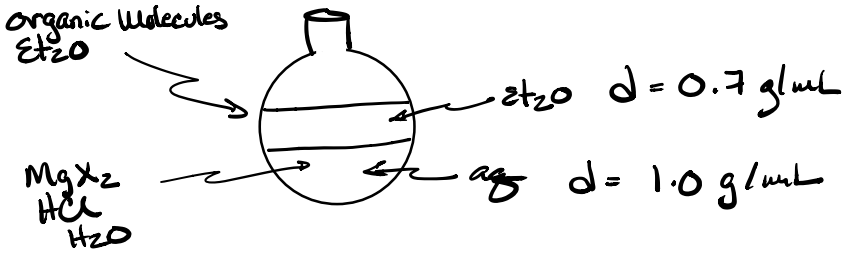
① Acidic workup



$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}\uparrow$$

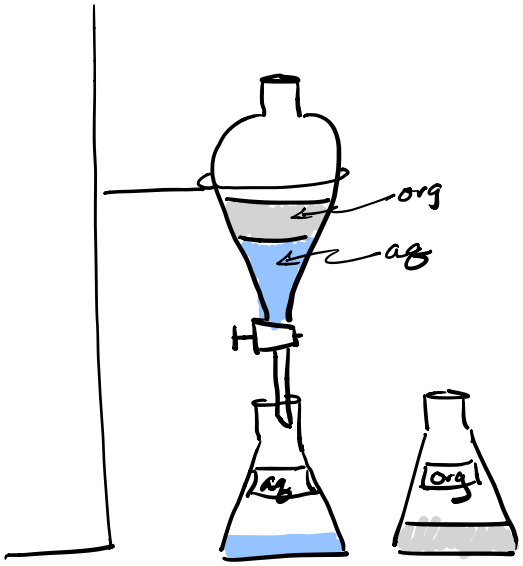
$Et_2O_{(l)} \rightarrow Et_2O_{(g)}$ } Heat
bp 32°
$Mg + 2HCl \rightarrow H_{2(g)}$ }

- Add 6mL 6M HCl dropwise
  ⇒ Do Not Cap
- Continue to stir until Rxn becomes biphasic & clear & colorless and no bubbles ($H_{2(g)}$)
- Add Et_2O or H_2O to make 2 clear layers (~2-5mL if needed)

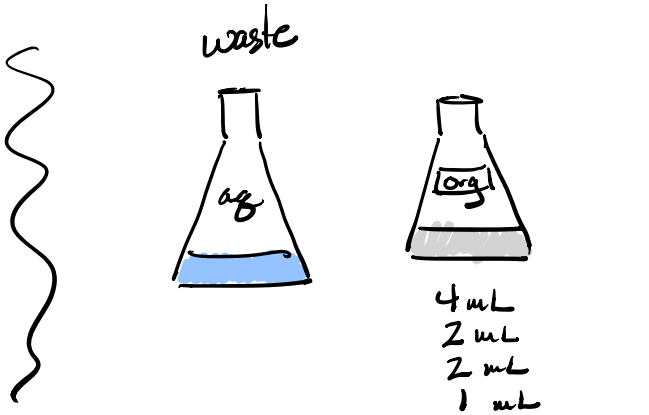


② Extraction

- move contents into Separatory funnel & extract organic layer



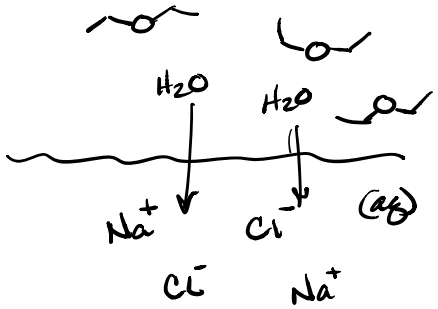
- Add aqueous layer back into Sep funnel & Re-extract w/ 5-mL clean Et_2O
- Combine organic fractions



4 mL
2 mL
2 mL
1 mL
+ 5 mL
~ 14 mL Et_2O

③ Pre-drying Step

- add organic layer back into Sep funnel & Extract with 5-mL saturated aqueous NaCl solution (Brine Solution)



Draws H_2O out of Et_2O by osmotic pressure

④ – Take Et_2O layer and add $MgSO_4$

$$MgSO_{4(s)} \text{ (powder)} + H_2O_{(l)} \longrightarrow \underbrace{MgSO_4 \cdot 7H_2O}_{\text{hydrate}}{}_{(s)}$$

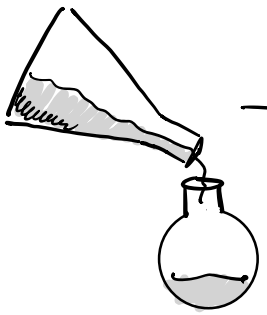
sticky solid

Snowglobe ⇒ indicates correct amount

Clumps = too little

⑤ – *Tare Round bottom flask

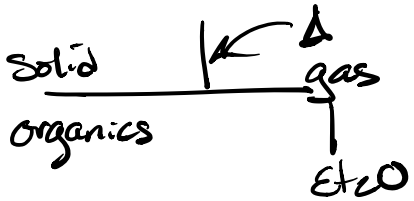
– Decant Et_2O into Round bottom



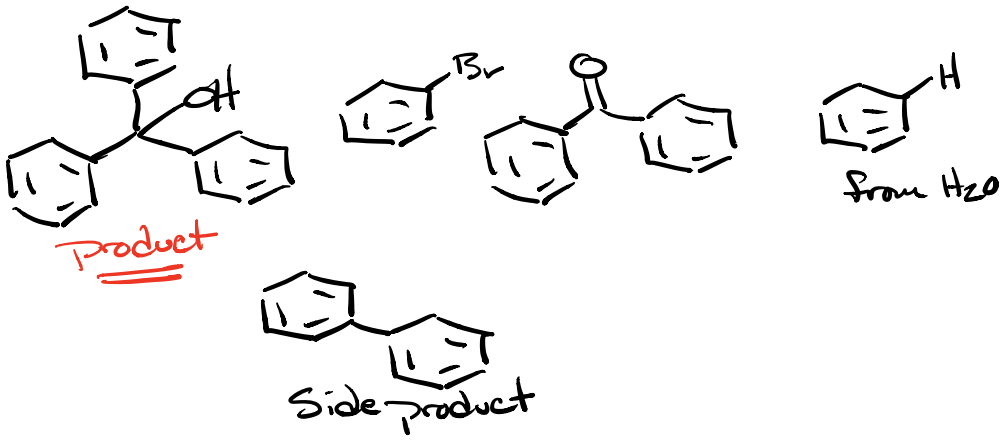
Decant

⑥ Rotovap

Crude product ⇐ *get mass



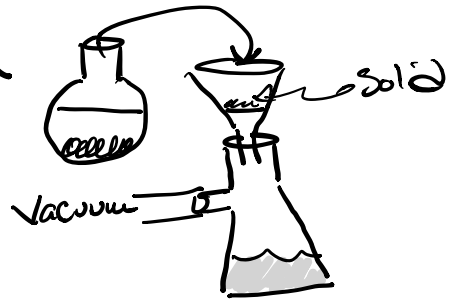
⑦ Crude



Trituration - The use of a solvent to remove unwanted contaminants from a solid.

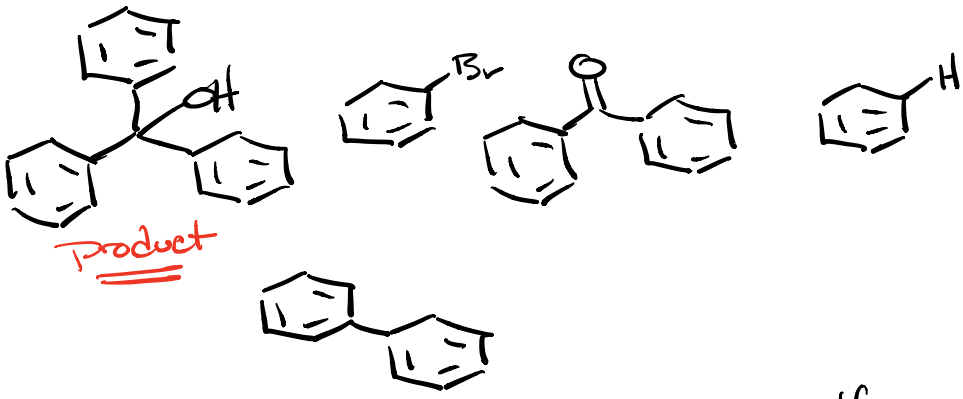
Petroleum ether ⇒ not an ether
a hydrocarbon mixture
C_5-C_7 isomers
Bp 32-35°C
⇒ non-polar

- Triturate w/ 3mL petroleum ether
- Filter on hirsh funnel
- Weigh the solid
- Recrystallice from 2-propanol

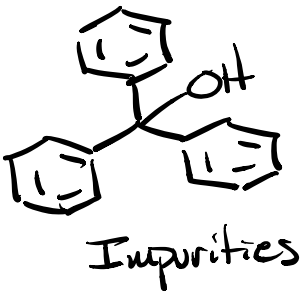


- Weigh Solid
- Take MP
- Take an FTIR
- Calc % Yield

} Characterization



Solid | petroleum ether → Non-Polar Liquid



Impurities

petroleum ether