Recipe for Stills

Diethyl Ether

= “Tube”

At-a-glance

- 2 tubes of Na
- 4 g Benzophenone (measure it!)

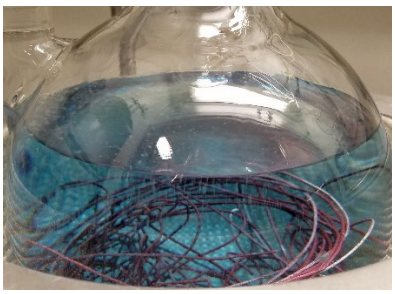
Procedure

1. Dry glassware in oven
2. While warm (not hot) fill with diethyl ether
3. Add 2 tubes of Na wire to flask
    a. Cut it into small pieces as you add the Na to the flask
4. Reflux <u>without</u> benzophenone for 24 hours
5. Add benzophenone
    a. The drums used to refill the still have large amounts of water in them and can sometimes take up to 3 days to dry. So, be patient after refilling the ether still. **Only consider destroying the still if it takes more than 1 week to dry after refilling**.

Appearance and Behavior

- Will be deep blue when hot
- May turn colorless (with blue pooled at bottom of flask) when cooled
- Rapidly returns to deep blue when heated
- Will last 3+ months

Early Color Progression



To ensure it lasts 3+ months

- Add ~0.5 g benzophenone when refilled
    - **Concept:** The more benzophenone in the still, the shorter its life. Thus, we always want to have the <u>minimum</u> amount of benzophenone necessary to maintain a blue/purple color. However, refilling with wet solvent kills some benzophenone and we need to replace it to achieve the desired color. Eventually, the still will no longer go “colorless” when refilling, and no more benzophenone needs to be added (until it stops turning blue again).
- Early in the still’s life it will start getting salty and turning green or even orange (perhaps as early as week 2!). At this point, add 5 mL tetraglyme and it should return to purple (or at least blue).

    - **Concept:** Diethyl ether is not very good at dissolving the **red dianion**. As the still gets saltier, the ionic strength of the solution grows and due to the "common ion effect" the amount of dianion that can be dissolved drops below detectable levels. Tetraglyme helps dissolve the salts and restores the color.
- Keep the amount of tetraglyme in the still to a minimum.
    - **Concept**: The more tetraglyme, the shorter the life of the still. I think a superbase is formed after a certain amount of tetraglyme is added. The superbase probably reacts with benzophenone and speeds up the death of the still.
- You MUST discard all ether from the still and start a fresh one, once it dies.
    - We used to reuse the ether since peroxide formation was minimal. However, our stills now regularly get *extremely dry* and *last for very long amounts of time*, making peroxides a bigger problem than they were in the past. It is not worth it, use fresh ether when making a fresh still!
- Add more sodium if it is running low
    - If the still looks "good" but the sodium is running low, feel free to add more
    - On caveat to this: If the still is starting to look "salty" or otherwise questionable, the need for more sodium is a great excuse for simply making a fresh still!

Recipe for Stills

THF

At-a-glance

- 2 tubes of Na
- 4 g Benzophenone (measure it!)

= “Tube”

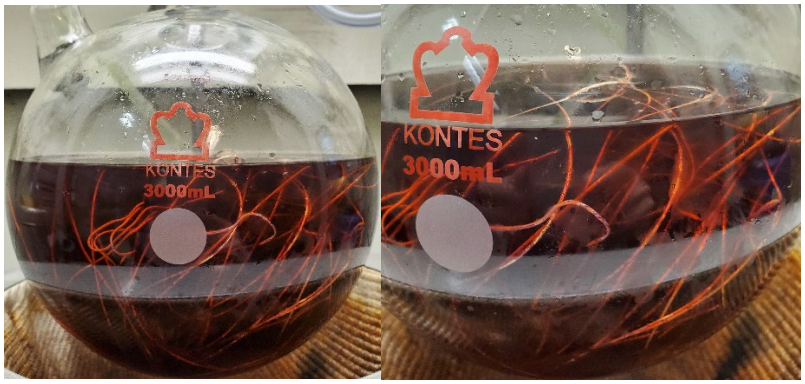
Procedure

1. Dry glassware in oven
2. While warm (not hot) fill with thf
    a. Use ONLY THF stabilized with 250 ppm BHT
3. Add 2 tubes of Na wire to flask
    a. Cut it into small pieces as you add the Na to the flask
4. Reflux <u>without</u> benzophenone for 24 hours
5. Add benzophenone

Appearance and Behavior

- Will be purple
- Will last 3+ months

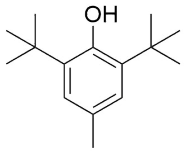
If done properly, the still will turn purple within 1 week. (deep blue within 24 hours)



If created, maintained, **<u>AND</u>** used properly without **any** errors, the still may turn red after ~1 month. In fact, after 3 months of sitting during COVID-19, the still was **purple** the first day it was turned on and became red 3 weeks later. **Red** is **perfection**, and it is possible to obtain!

To ensure it lasts 3+ months

- Add ~0.5 g benzophenone when refilled
    - **Concept:** The more benzophenone in the still, the shorter its life. Thus, we always want to have the <u>minimum</u> amount of benzophenone necessary to maintain a blue/purple color. However, refilling with wet solvent kills some benzophenone and we need to replace it to achieve the desired color. Eventually, the still will no longer go "colorless" when refilling, and **no more benzophenone needs to be added** (until it stops turning blue again).
- Avoid adding tetraglyme until the very end of the still's life. Even then, try to keep it to small amounts (add no more than 5 mL per week)
    - **Concept**: The more tetraglyme, the shorter the life of the still. THF already dissolves the basic species very well. As a result, the superbase forms pretty easily in THF. Tetraglyme in THF will probably *only buy you 1 or 2 weeks more before the still must be changed*.
- NEVER add non-stabilized THF to the still
    - **Concept**: Peroxides form to a significant amount in non-stabilized THF. These peroxides are **<u>not</u>** destroyed by sodium AND **<u>they distill</u>** with the THF. In otherwords, peroxide containing THF will still contain peroxides after collecting the distillate.
        - If you accidentally add non-stabilized THF to the still, prompt addition of 200 mg BHT can save the still for 2-3 weeks, but this is generally not worth anyone's time. Re-make the still!



BHT

- You MUST discard all THF from the still and start a fresh one, once it dies.
- Add more sodium if it is running low
    - If the still looks "good" but the sodium is running low, feel free to add more
    - On caveat to this: If the still is starting to look "salty" or otherwise questionable, the need for more sodium is a great excuse for simply making a fresh still!

Special Considerations in THF – The Psychological Impact of Red Dianions

Once the group began to regularly perfect the procedure for creating and maintaining the stills (early 2020), we saw a sudden resurgence of rapid still "deaths". We now have attributed this to confusion caused by semi-regular formation perfect stills filled with **red dianions**. The story is instructive.

First, it must be explained that the absorption coefficient of the **monoradical monoanion** is much higher than the absorption coefficient of the **diradical dianion**. Thus, as the equilibrium shifts from primarily **monoanion** to **dianion**, the color intensity drops. In a relatively dilute solution of **monoanion**, the solution appears nearly black and the internal contents of the still are not visible. This can be readily seen in the pictures provided of the "**purple** still" above. However, the same concentration of **dianion** (see the "**red** still" pictures above) results in a solution that is much easier to see through! If one does not look closely, it is easy to mistake the red color of **dianion** for the orange color of **decomposition**. However, if one looks at a picture of a truly **orange** "dead" still -provided at the very beginning of this document (of the same concentration, mind you!)- the mixture is much more opaque. But a stressed graduate student, worried about solvent dryness, may sometimes struggle to tell the difference between a "clear light-**red** solution" and an "opaque-**orange** mixture".

One easy check to see if the still is **red** or **dead** is to simply add more benzophenone. If the still contains only **dianion** and neutral benzophenone is added a disproportionation will occur, resulting in two equivalents of **monoanion** and a deep blue color. The reaction can be nearly instantaneous or require an

hour or two to occur, depending on the ionic strength of the still at the time. However, assuming the still is handled "perfectly," the formation of **monoanion** is not due to the presence of oxygen, and it does not take too long for the sodium metal to re-reduce the **monoanion** to the red **dianion**. Thus, the cycle of anxiety → benzophenone addition begins anew. In one occurrence, eventually so much benzophenone was added that the still "died" as discussed earlier.

Now, we have created a sign-up sheet. There, people can notify others of the date and how much benzophenone was added so we avoid repeatedly adding large amounts of indicator, hopefully avoiding self-imposed still-death.

Lessons learned: A perfect THF still will turn red after roughly 1 month and will stay so until oxygen or water are added to the system. Thus, if we are all excellent practitioners, we will see red stills frequently. It is a sad day when we mistake a **perfect** still for a **dead** one! Consequently, remember to check dryness with small amounts of benzophenone, and communicate this to others (note on the sheet) so that we don't do it excessively.

Further, if the above procedure is enacted "perfectly" then the still will remain **red** until its ultimate **death**. **As the still slowly encounters water and oxygen, benzophenone decomposition will grow ever present. It will become increasingly difficult to tell the difference between light-red and orange, *especially when they are mixed together*.** Thus, the more excellently we maintain the still, the more diligent and careful we will have to be to avoid confusion! What an interesting dilemma!

Recipe for Stills

 = “Tube”

Benzene

At-a-glance

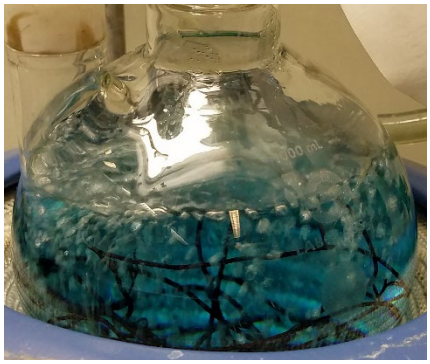
- 1 tube of Na
- 2 g Benzophenone (measure it!)
- 5 mL tetraglyme (measure it!)

Procedure

1. Dry glassware in oven
2. While warm (not hot) fill with benzene
3. Add 1 tube of Na wire to flask
    a. Cut it into small pieces as you add the Na to the flask
4. Reflux <u>without</u> benzophenone for 24 hours
5. Add benzophenone and tetraglyme

Appearance and Behavior

- Will be deep blue/purple when hot
- May turn colorless (with blue pooled at bottom of flask) when cooled
- Rapidly returns to deep blue when heated
- Will last 4+ months.




To ensure it lasts 4+ months

- Add ~0.5 g benzophenone when refilled
    - **Concept:** The more benzophenone in the still, the shorter its life. Thus, we always want to have the <u>minimum</u> amount of benzophenone necessary to maintain a blue/purple color. However, refilling with wet solvent kills some benzophenone and we need to replace it to achieve the desired color. Eventually, the still will no longer go “colorless” when refilling, and no more benzophenone needs to be added (until it stops turning blue again).
- Tetraglyme is always necessary, but keep to a minimum.
    - **Concept:** benzene is terrible at dissolving both the **blue monoanion** and **red dianion**. As the still gets saltier, the ionic strength of the solution grows and due to the “common ion

effect" the amount of **anions** that can be dissolved drops below detectable levels. Tetraglyme helps dissolve the salts and restore the color.

- When cold, the still will almost always revert to a salty orange color. It should return to blue upon heating. Don't freak out!
    - **Concept:** If, upon heating for 1-2 hours, the still has not returned to blue, either benzophenone or tetraglyme must be added. First, try 0.5 g benzophenone. If this does not fix it in 1-2 more hours, add 3 mL tetraglyme. If 0.5 g benzophenone AND 3 mL tetraglyme do not fix it, add 5 mL more tetraglyme. If the still is not better after 48 hours, you need to redo it.

Recipe for Stills

= “Tube”

Pentane

At-a-glance

- 1 tube of Na
- 3 g Benzophenone (measure it!)
- 25 mL tetraglyme (measure it!)
    - Yes, **25 mL**

Procedure

6. Dry glassware in oven
7. While warm (not hot) fill with pentane
8. Add 1 tube of Na wire to flask
    a. Cut it into small pieces as you add the Na to the flask
9. Add benzophenone and tetraglyme
    a. Tetraglyme without benzophenone can sometimes cause problems. Pentane is normally fairly dry to begin with, just add it all together.

Appearance and Behavior

- Will be deep blue/purple when hot
- May turn colorless (with blue pooled at bottom of flask) when cooled
- Rapidly returns to deep blue when heated
- Can last more than **1 year**.

Story-form notes on pentane

Pentane does not dissolve sodium salts efficiently. Essentially, tetraglyme is the solvent for the indicator and if there is not enough of it around, the indicator will not be sufficiently soluble. So, a fresh still needs many milliliters of tetraglyme at the start, but too much seems to cause “weird” behaviors and reduce the still lifetime. If you measure out the tetraglyme between 25-30 mL everything should be fine. As the still lives more than a year, tetraglyme is sometimes added (as well as benzophenone), which is okay. Just do not add more than 5 mL in a 1-week period. If 5 mL doesn’t work, something else must be done (either benzophenone must be added or still redone).

Regarding the color progression. I frequently see pentane **blue**, **purple** (**blue** + **red**), and “dark **green**” (**blue** and **orange**) Any of these colors are good and are normally a result of solubility changes (for unknown reasons). It seems that pentane stills are pronounced dead simply because they have huge **orange** flakes floating around inside them that make up the most pronounced colors in the still, making people uncomfortable.

Pentane is an easy still to make, feel free to make it once the indicator is no longer doing its job (which is making people feel confident and comfortable!).