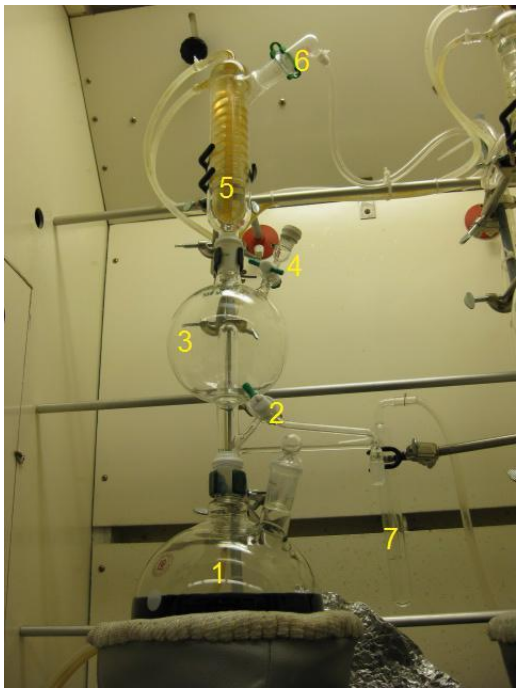
The Benzophenone/Ketyl Tetrahydrofuran(THF) Still

1. Introduction

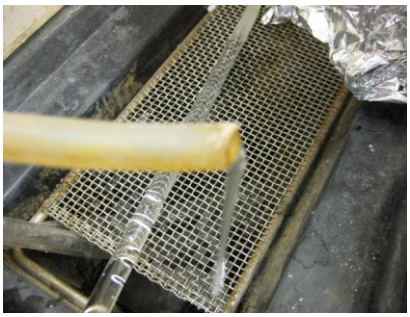
The benzophenone-sodium still is a widely used method to produce moisture, oxygen, and peroxide free organic solvents, especially for tetrahydrofuran (THF). The soluble benzophenone ketyls can be formed as radical anion by one-electron reduction of carbonyls with sodium. The ketyl molecule is intensively colored (deep blue) and reacts quickly with the water, oxygen, and peroxide dissolved in organic solvents. The deep blue coloration indicates dry and oxygen free conditions. (Schwartz, A. M. *Chem. Eng. News* **1978**, *24*, 88.)

2. Before getting started

Appropriate safety measures should be inplaces during all steps of solvent distillation. The largest danger with this distillation is fire due to spillage. THF is quite flamable and THF vapor is about two and a half times the density of air. Be aware of the risks inherent to the reaction you will perform and appropriate countermeasures. Do you know where the nearest chemical shower is located? Sodium metal is reactive to water and it is recommended to have a 500 mL beaker of isopropyl alcohol to remove small pieces of sodium generated during chopping. At least one carbon dioxide or dry-chemical fire extinguisher should be readily available when working with sodium. Perform all work inside an operating fume hood.



The distillation setup pictured to the left is fairly common. The boiling flask **1** is a 3000 mL, two necked variety with the secondary neck stoppered during normal operation. Use this neck to add additional THF. The stopcock **2** is used to collect THF or return the condensate to the boiling flask. Note the T marked on the stopcock. This T indicates the bored openings. The distillate trap **3** collects THF when the stopcock is closed. The second stopcock **4** is used to withdraw THF using a syringe. This is the preferred method of withdrawing THF since there is little opportunity to introduce water vapor or oxygen into the apparatus. To withdraw THF insert a sufficiently long needle nto the septum above the stopcock. Open the stopcock and thread the needle through the bore, then withdraw the necessary amount of THF that has collected in the distillate trap. When finished be sure to close the stopcock. The condenser **5** should receive a steady supply of water but not too much. Take note of the argon inlet **6** and bubbler **7**. When in doubt ask for assistance.

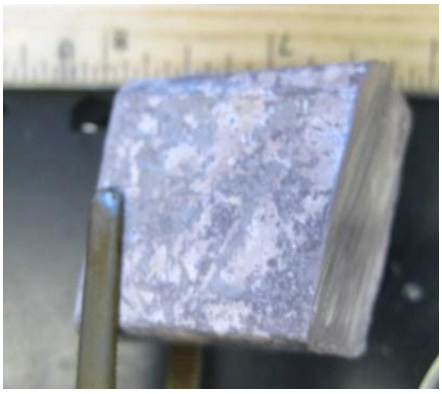


It doesn't take much water.

Check out the good deep blue. If it's not this color don't trust it.

Variac, heating mantle, and lab jack.

3. Setting solvent stills



Approximately 25 grams of sodium metal

All glassware you use in this reaction should be oven-dried and your work area should also be free of water. Tetrahydrofuran (THF) should be pre-dried overnight over potassium hydroxide (KOH) or molecular sieves (3 or 4 Å). Extract a block of sodium metal from the container and rinse with a minimum amount of hexanes to remove the oil or kerosene. Slice the sodium into pieces small enough to fit in the neck of the flask; smaller pieces allow more surface area but don't go nuts. Add sodium pieces equivalent to approximately 5 grams to the boiling flask, seal the flask and clean up any shavings you missed. Add about 30 g of benzophenone and 2 liters of THF to the boiling flask and restopper. Double-check the flow of water and argon then turn on and slowly ramp up the Variac until the THF starts to simmer. The heating mantle and Variac pictured work well at about 40V. Reflux the mixture under argon until the deep blue color of benzophenone ketyl forms ($Na[Ph_2O]$). If, after refluxing for several hours, the deep blue color does not develop, try to scratch the sodium with a glass rod until it shows partly blue color and continue to reflux it for several hours. The solution should be kept under argon atmosphere at all times. Do not distill it without sodium because THF will form peroxides which are an explosive hazard. The loss of the blue color in 2 or 3 days indicates the decomposition of the ketyl. It can be regenerated by addition of more benzophenone. The deep blue color of the ketyl does not necessarily indicate super dry condition (less than 10 ppm).

4. Use of THF

The distilled THF may be removed using a dry syringe via the septum cap. Under these conditions, the solution appears to be stable for 1-2 days. When you have all the THF you need (1) Turn off the Variac, (2) Allow the flask to cool to room temperature, (3) turn off the cooling water.

5. Cleaning

A cleaning step is necessary when the deep blue color of the ketyl is not regenerated after addition of benzophenone. If there is lots of THF in the flask, distill and collect the THF. After the solvent has cooled to room temperature, move the distillation flask in a fume hood. Carefully quench the brownish residual solvent with a small amount of isopropanol (2-propanol) under argon atmosphere over several hours

and allow the mixture to stand overnight. Then quench the residual solvent with a small amount of absolute methanol under argon over several hours until the sodium metal is destroyed and allowed to stand overnight again. Add small amount absolute methanol again, and then check the temperature of the flask. If the temperature is higher than room temperature, add more absolute methanol and place the flask in a fume hood overnight. If there is no discernable increase in temperature carefully add excess water under argon atmosphere, wait an hour, then properly dispose of the contents.