

PRODUCTION OF 1-PHENYL-2-NITROPROPENE

Set up the 22-liter RB in the heating mantle. Add 10-20 PTFE(Teflon) boiling stones to the vessel. Through the wide center neck, add 5000ml of toluene, 2500ml of benzaldehyde, and 1875ml of nitroethane, in that order, with stirring. Have the fitting reducer, Dean-Stark trap, and a West condenser greased up and assembled nearby. We will need to assemble the pieces quickly once the n-butylamine is added. Using a wooden dowling rod as a stirrer, quickly add 550ml of n-butylamine with stirring. The reaction mixture will turn from clear to a milky consistency as a Schiff's base and a molecule of water are formed(the water turns the solution milky). Assemble the fitting reducer, the Dean-Stark trap, and the West condenser on top of each other and plug the two side necks. Attach a fitting to the top of the condenser and run an exhaust line into your fume cabinet. Start the water running through the condenser. Wrap some aluminum foil around the top half of the reaction vessel and the Dean-Stark trap to avoid excessive cooling.

Turn on both heating elements and set the temperature controls at 20%. At this setting it will take a long time to heat up the solution. After one has some experience with this reaction, one can start out with the heating mantle at a higher setting(70% for 20min on my rig). One must be aware that we are using only a small West condenser for cooling and that it takes very little extra heat to blow material out the top. On my equipment, the proper setting is 18%--20% is too hot. Be very careful with the heat. The idea here is to boil the solution just hard enough to reach the bottom of the condenser where the water-toluene azeotrope can condense out into the Dean-Stark trap and be removed from the reaction solution. This occurs at 85°C.

Once the reaction reaches the condenser, the water will begin to accumulate rapidly. For a 25 mole reaction, 25 moles of water will be created and must be removed for the reaction to reach completion. This writer's Dean-Stark trap holds 25ml of water, resulting in a total of 18 full water-traps to complete a 25-mole reaction. Use a piece of paper and make a mark every time the trap is emptied. The water will come over rapidly at first, taking only a few minutes to fill the trap, and then slows down as water molecules get harder to find. The reaction should take about five hours to complete, but one should not use time as a definitive indicator. One will do much better at judging the quality and state of one's reaction by observing the color of the reaction mixture. As the water is removed, the solution will begin to turn a light orange color and deepen as the reaction nears completion. The use of too much catalyst, n-butylamine, will cause the reaction to polymerize to some degree, resulting in a dark brown solution color, poor quality nitropropene crystals, and a greatly reduced yield. Unfortunately, this reaction is very sensitive to the quantity and quality of the catalyst. Too little catalyst will reduce the yield significantly and too much will burn(polymerize) it. This writer advises that one do test batches of 1 and 5 moles in order to home in on the exact amount of n-butylamine required. If the reaction is allowed to continue once all the water is removed, it will begin to polymerize, so one should carefully watch the color of the reaction solution and keep careful track of the amount of water removed. Even if all of the theoretical amount of water has not been removed, if the solution color starts turning dark, pull it. Turn off the heat, allow the boiling to subside into the vessel, remove the condenser and Dean-Stark trap, then carefully lift the vessel out of the heating mantle and place it on a plastic bucket inside the fume cabinet. Leave it to cool down to room temperature overnight.

We will now strip the toluene solvent from the solution by performing a vacuum distillation. One needs a high-volume adjustable vacuum source in order to perform this distillation. Do not use a vacuum pump to strip solvents-it's hard on the pump and poses a high fire hazard. Always use an aspirator when vacuum-distilling solvents. Your typical university aspirator that runs off 40psi of water pressure is not adequate to pull a decent vacuum in a large volume, let alone an adjustable vacuum. We will be working with a system volume of about 27 liters. Attach two West condensers in series and support them carefully with tri-grips or wooden blocks with grooves cut into the tops. Attach a 5000ml round-bottom flask that has been marked at the 5000ml level. We will use this mark to determine when we have finished. Once completely

assembled, turn on the heating mantle and set the controls at 30%. Once again, the reader's system/equipment will be slightly different from mine and he must make some minor adjustments. The idea here is to distill off the toluene at a temperature high enough to allow the condenser to liquefy the toluene so it doesn't get sucked into the vacuum system where it can cause damage. About 26-27"Hg or thereabouts will produce a distillation temperature range of about 40-60°C, which is hot enough to be condensed out by water at 10°C. One should not attempt to distill off the toluene at a normal atmosphere because the added heat quickly polymerizes the product as the toluene is removed. One must also make sure one has removed ALL of the toluene; even a small amount will prevent the crystals from forming or will produce poor quality crystals that polymerize rapidly in the open air. Since we started with 5000ml of toluene, we need to strip off at least that much. Use a mark on the receiver.

Once the toluene has been stripped off, turn off the heat, disassemble the equipment, and then pour the hot, orange liquid remaining in the vessel into two 5-liter plastic buckets, filling each of them to about 1/3 full and then covering. Quickly rinse and wash the big reaction vessel with methanol before the residue adheres to the walls. Let the liquid nitropropene cool for a few hours, then cover and place at the bottom of the freezer overnight. In the morning, the crystals will be formed and we must remove any unreacted material and contaminants. To accomplish this, pour about one liter of methanol which has been frozen for a week or two into one of the buckets holding the solid mass of crystal and break up the mass with a big screwdriver. The yellow nitropropene crystals are only slightly soluble in cold methanol, but the undesirable reaction remnants are very soluble, so we will dissolve the gunk while leaving the crystals intact. Once converted into a slurry, filter through a Buchner. Do the same to the other bucket. Empty the bright yellow crystals into a large cake tray and let them dry. Once dry, place into a 5gal bucket, cover, and place in the deep freeze. Left in the open air, the nitropropene crystals will polymerize in about one month. Stored in the freezer, these crystals will keep nicely for at least two years.

The yield on this reaction is not 100%, as stated in other literature. The theoretical yield is 79%, but the best this writer has achieved is 74%, with 70% being the average. Since one mole of 1-phenyl-2-nitropropene weighs 168g, one should end up with 25 moles x .7, or 17.5 moles of nitropropene crystals which weigh about 2940g. This writer advises that the chemist make and store all of his yellow nitropropene crystals before proceeding to the next step.

The chemist may wish to experiment with other strong bases in order to find an alternative to n-butylamine, which is rare enough to be a choke point.