Magpie
lab constructor
★★★★★

Posts: 5939
Registered: 1-11-2003
Location: USA
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Mood: Chemistry: the subtle science.

posted on 3-9-2015 at 18:31

A lab report

Introduction
Based on my successful preparation of PCl5 from white P (see Prepublication) I decided to try the same technique in making PCl3.

Solvent Selection
As PCl3 is a liquid I planned to separate the PCl3 from the solvent by distillation. The boiling point of PCl3 is 76°C so I wanted a solvent that had a significantly higher or lower boiling point. My original selection was pentachloroethane (bp 162°C) as it is a chlorocarbon and therefore I assumed it would be as good a solvent as CHCl3 (1g/40 ml) or CCl4. But I could not find a source although it could be made from trichloroethylene, which is available on eBay. I probably could also use heptachloropropane but I also would have to make this (from perchloroethylene).

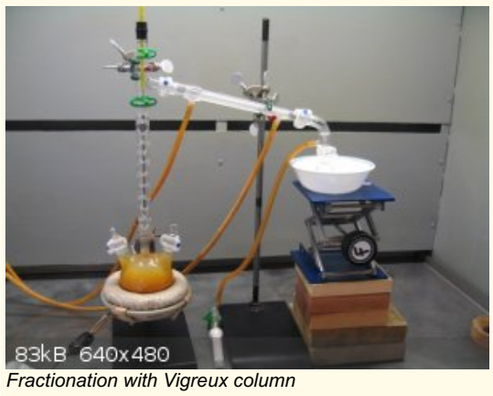
My next thought was to use dichloromethane (bp 40°C). But I suspected that the chlorination would produce significant CHCl3 (bp 61°C) and CCl4 (bp 77°) as by-products. These would be difficult or next to impossible to separate from PCl3 by distillation.

Then I remembered that I had 500 ml of chlorobenzene (bp 131°C) on hand from a trade with a forum member. Benzene is a good solvent for white P (1g/35 ml) being, in fact, the best I have seen in the literature excepting CS2. I therefore assumed that chlorobenzene would also be a good solvent. Availability and fire hazard preclude me from using CS2 although it is by far the best solvent for P.

Chlorination
A 3-neck 500ml RBF with reflux condenser was loaded with 250ml of dried, redistilled chlorobenzene and 5.2g of white P. The pot was heated with a mantle and magnetically stirred. The P slowly and steadily dissolved until complete dissolution was achieved. Dried Cl2 was then slowly injected into the hot chlorobenzene. The mantle was then turned off as the heat of reaction kept the pot very hot although not boiling.

Because I had not pre-purged the gas train, condenser, and RBF headspace with an inert gas, considerable P2O5 smoke initially formed. This deposited on the dome of the RBF. It was white with an orange cast, due to slight tar formation I assume. This was dangerous as it tended to plug the CaCl2 guard tube and I changed out the tube's cotton plug twice during the initial part of the chlorination when the smoke was being generated.

Fractional Distillation
The RBF was set up for fractional distillation using a 20cm Vigreux column. With the ΔT in bps of 55°C I assumed this would easily give a good separation. It did not, and the still head temperature went up over 110°C. So I changed to a 20cm Hempel column packed with a ss scrub pad. This also did not provide a separation no matter how carefully I adjusted the mantle heat. After collecting about 15ml of condensate I quit for the night.



Fractionation with Vigreux column

Fractionation with Hempel column

Today I set up the 25mL RBF pot containing the distillate for a second fractional distillation, again using the Hemple column. I placed an aluminum foil tent on the pot and heated the column up very slowly. When the temperature reached 75°C distillate started coming over. It continued to come over at 74°-75° steadily

(0.5d/s) until there was insufficient heat to bring any more distillate over. So I did manage to capture 6.4g of PCl3. About 12 ml of liquid remained in the pot, ie, chlorobenzene.

2nd fractionation

PCl3 distillate

Yield
The yield was 6.4g for a 27.8% yield.

Discussion
The difficulty encountered during the fractionation really has me puzzled. With a 55° degree separation in boiling points this fractionation should have been easy. I can't believe it was just poor technique.

Clearly I made a mistake in not first purging the system with an inert gas (I have argon). But this cannot account for the low yield entirely. I'm wondering if the bulk of the phosphorus is still in the 500ml RBF pot.

Comments, questions, and suggestions are welcomed.

The single most important condition for a successful synthesis is good mixing - Nicodem

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posted on 5-9-2015 at 17:19

Yesterday and today I have done some labwork to try to find the missing P from my PCl3 synthesis posted above.

Missing P: (1-0.278)5.2g = 3.75g

Firstly, I weighed the 500 mL RBF before and after cleaning. Assuming the weight differential was P2O5 this accounts for 0.39g of P. This is nearly twice my estimate of 0.2g. Perhaps more O2 was sucked in through the CaCl2 guard tube as the existing O2 was consumed. Incidentally, the RBF cleaned up easily using only soap and water.

Secondly, I redistilled the residual 200 ml of chlorobenzene left in the 500 ml pot. I only recovered about 6mL of distillate. To this I added about 10ml of fresh chlorobenzene then redistilled this in a 25ml RBF. I only retrieved a few ml of doubtful quality PCl3 and chose not to add it to my yield. I did add water to it in a small beaker. At first I saw nothing then noticed about 3 large drops of PCl3 on the bottom of the beaker. I also noticed that the beaker was getting very hot. Eventually the drops disappeared. The assumed reaction is:

PCl3 + 3H20 ---> H3PO3 + 3HCl

Based on this small scale experiment I have to conclude that this is not a good way to make PCl3. DJF90 has informed me that the German chemistry forum Lambda-Syn has a high yielding method using PCl5 and red phosphorus.

Edit:
Other hiding places are possible for the missing P:
(1) unreacted P dissolved in the chlorobenzene, and
(2) dissolved PCl5.

I may do some more investigations.

[Edited on 6-9-2015 by Magpie]

[Edited on 6-9-2015 by Magpie]

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PROFILE FIND

macckone
International Hazard

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Location: Over a mile high
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Mood: Electrical

posted on 6-9-2015 at 06:08

Chlorobenzene seems a poor choice as it will get chlorinated just like the dichloromethane. There could be polymeric side products with insufficient chlorine.

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posted on 6-9-2015 at 07:44

> **Quote: Originally posted by macckone**
>
> Chlorobenzene seems a poor choice as it will get chlorinated just like the dichloromethane. There could be polymeric side products with insufficient chlorine.

Isn't a Lewis acid required for chlorination of the benzene ring? However, chlorination of CHCl3 isn't supposed to happen either without radical formation by UV light but it does to a certain extent. I suppose heat can substitute for the UV.

I wouldn't be surprised to find some dichlorobiphenyl. A small amount of biphenyl is formed when making benzene from benzoic acid.

[Edited on 6-9-2015 by Magpie]

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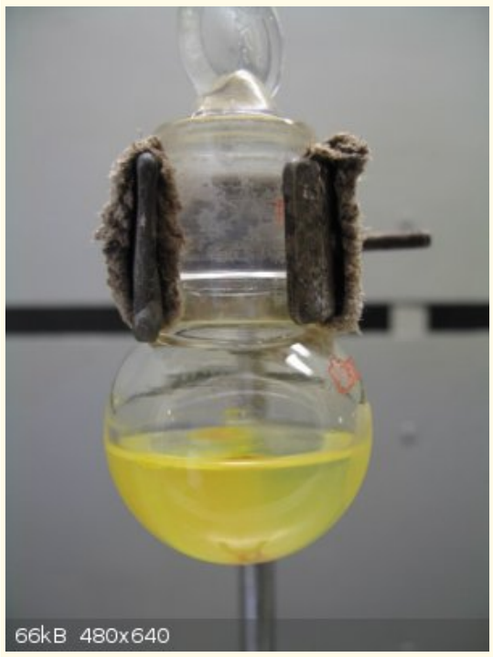
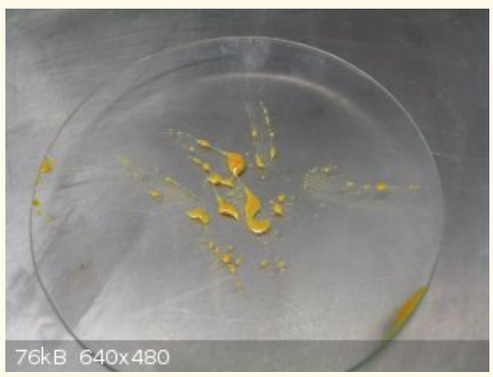
posted on 7-9-2015 at 13:39

I am now convinced that most all of the missing P is still dissolved in the chlorobenzene. In my effort to not form PCl5 I simply did not chlorinate long enough.

The below picture shows an abandoned distillation to recover the chlorobenzene. You can see the P2O5 smoke in the pot as the hot P reacts with the oxygen in the air.

The composition of the yellow colored residue is still unknown. It is not soluble in the chlorobenzene and settles out as a gummy yellow residue. At first I though it was P4S10, but where would the sulfur come from (thiophene?). I carefully cleaned and redistilled the chlorobenzene before use. Also, I have never smelled a sulfur smell. When I heated some strongly with a match it did not catch fire but melted slightly and turned partially black. It is soluble in water and turns the water pH acid.





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Mood: Chemistry: the

posted on 9-9-2015 at 14:24

I gave some thought to continuing the chlorination but decided to just cut my losses. There are reactions taking place that I don't understand. Also, I'm getting tired of running the hood fan, cleaning glassware, and generating used nitrile gloves. Working with dissolved phosphorus and a halogenated solvent requires extra caution and maintenance of good hygiene.

The product continues to form the yellow residue. Today I filtered most of it out then set up for distillation to recover the chlorobenzene and try to burn off the P to P2O5 using a controlled burn, ie, get it hot and expose

subtle science.	it to the air. This did occur during the distillation. As the P vapor came in contact with air at the entrance to the condenser it would form smoke. This in turn would cause a partial vacuum and suck in more air, repeating on and on. I would have taken a picture but my camera quit as the battery needs recharging. The distillation is done. The distillate is tainted a fluorescein yellow and there is an orange deposit in the pot. [Edited on 9-9-2015 by Magpie] [Edited on 9-9-2015 by Magpie] The single most important condition for a successful synthesis is good mixing - Nicodem PROFILE FIND
macckone International Hazard Posts: 2124 Registered: 1-3-2013 Location: Over a mile high Member Is Offline **Mood:** Electrical	posted on 10-9-2015 at 09:47 Chlorination of chlorobenzene happens more readily than benzene. In an ideal world you would need a catalyst or UV light or heat. But we don't live in an ideal world. And even a regular light bulb emits some UV and glass is not totally opaque to UV. Plus you have some activated chlorine floating around from your primary reaction. PROFILE FIND
Magpie lab constructor Posts: 5939 Registered: 1-11-2003 Location: USA Member Is Offline **Mood:** Chemistry: the subtle science.	posted on 10-9-2015 at 10:26 Also, I no doubt created some FeCl3 due to the SS316 welding rod immersed in Cl2. But there is much more going on in this product mix. The pot residue from yesterday's distillation contained most of the remaining P, ~ a gram, mixed with a lot of orange gunk. I burnt most of it off. I will treat the rest of the waste with 1M CuSO4 using a 1 week soak. I still think this method could be successful if the right solvent could be found. Chlorobenzene is **not** the right solvent, however. The single most important condition for a successful synthesis is good mixing - Nicodem PROFILE FIND
PHILOU Zrealone International Hazard Posts: 2880 Registered: 20-5-2002 Location: Brussel Member Is Offline **Mood:** Bis-diazo-dinitro-hydroquinonic	posted on 10-9-2015 at 11:58 @Magpie, Based on the "tiny amount" of reactants, your Hemple column with glass beads must hold quite some PCl3 (by capilarity you may have several grams in there)...this may account for the apparent low yield. PH Z (PHILOU Zrealone) "Physic is all what never works; Chemistry is all what stinks and explodes!"-"Life that deadly disease, sexually transmitted."(W.Allen) PROFILE FIND
Magpie lab constructor Posts: 5939 Registered: 1-11-2003 Location: USA Member Is Offline **Mood:** Chemistry: the subtle science.	posted on 10-9-2015 at 12:22 I didn't use glass beads but ss scrub pad. But, yes, there was some of the yellow residue on the pad coils. The 1M CuSO4 reacts fast with the small particles of waste, turning them black immediately. I will let it set a few days then treat this with 5% NaOCl to destroy the phosphides. The only waste left will then be ~ 150ml of chlorobenzene*. I see my choices here as 1) incineration, 2) evaporation, or 3) absorb in kitty litter. I have tried some incineration on a small scale: very nasty with sooty smoke likely containing nasties like HCl and dioxin. I think this choice is out. *It is interesting to note that there was a fair amount of solid waste (orange gunk) in the chlorobenzene distillate. The chlorobenzene is therefore also getting treated with 1M CuSO4. The single most important condition for a successful synthesis is good mixing - Nicodem PROFILE FIND