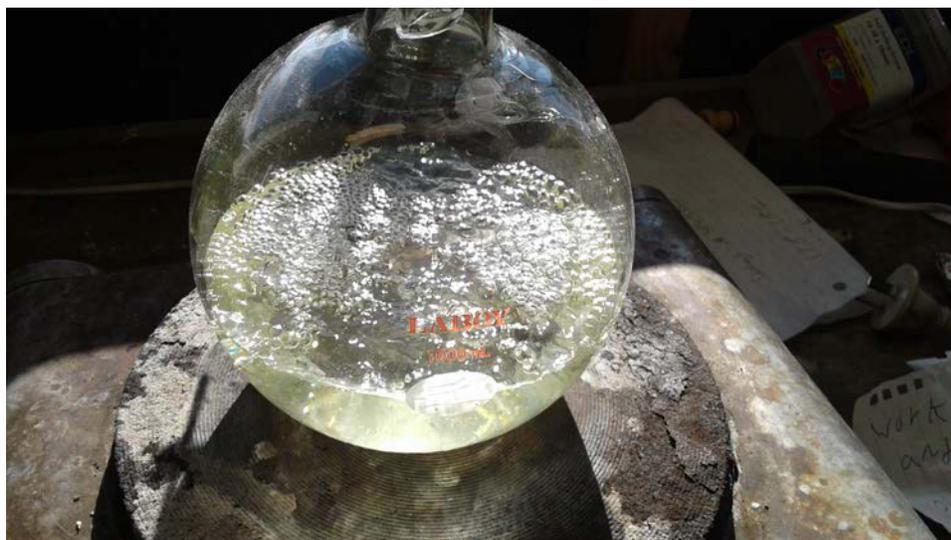


Benzylamine via the delepine reaction

To a 1 L flat bottom boiling flask was added 289ml of anhydrous denatured ethanol, 12ml of water and 30g of crushed hexamine tablets. 27ml of benzyl chloride was then added and a Liebig condenser with a crude stopper was attached to the flask. The mixture was refluxed for 2 hours on high heat.



Above: reaction mixture refluxing

All undissolved hexamine was dissolved after a few minutes of reflux, but after this, there was very little visible change in the reaction mixture. Once the reflux was complete, I turned off the heat and allowed the mixture to cool to room temperature, whereupon lots of fine white crystals precipitated. These crystals were presumed to consist of the benzylhexaminium salt intermediate.



Above: reaction mixture with the precipitated benzylhexaminium salt

A hydrogen chloride gas generator was set up and loaded with 47g of sodium chloride and 96g of sodium bisulfate (25% excess of hydrogen chloride). The reaction mixture was then saturated with hydrogen chloride at a fairly rapid rate with good stirring. Since the flask I was using was not big enough to hold all the bisulfate and chloride, I opted to only add a portion of the mix at a time to the flask. Once the first portion was consumed the flask was washed, dried then loaded with another portion of the mix and the process repeated until HCl generation was complete.



Above: hydrogen chloride generation system

The previous precipitated benzylhexaminium salt seemed to be replaced with a much heavier precipitate of (presumably) ammonium chloride. Once hydrogen chloride gassing was complete, I left the mixture to stand for 20 minutes, then filtered the mixture to remove ammonium chloride, washing it on the filter with 15 ml of anhydrous denatured ethanol. I then heated the filtrate to boiling and some more ammonium chloride separated. After cooling, I filtered this off too. The slightly yellow filtrate was poured into a 1 L flat-bottom boiling flask and carefully distilled to near dryness (when a slightly syrupy liquid is obtained, the heat should be turned off).



Above: halfway through distillation

Upon cooling, lots of crystals separated. I transferred the crystals/remaining liquid to a 250ml beaker and carefully boiled off all the remaining volatile liquid. Eventually the mixture became significantly higher boiling. It was at this point that I noticed a very strong marzipan smell and some oily droplets floating on the top of the liquid. I guess this is benzaldehyde produced via the Sommelet side reaction. Anyway, I allowed the flask to cool, then filtered off the crude benzylamine hydrochloride crystals, washing them on the filter with 10ml of anhydrous denatured ethanol to remove benzaldehyde.



Above: crude benzylamine hydrochloride

The crude benzylamine hydrochloride was added to a 125ml beaker containing 11g of sodium hydroxide dissolved in 42ml of water. After a bit of stirring, an intense rotten fish smell reminiscent of methylamine was noticed. Unfortunately no separate layer on benzylamine formed. I tried adding in some sodium chloride and stirring, but alas, the benzylamine did not separate. At this point I decided to give up since there wasn't enough benzylamine present for it to be worth performing a distillation to isolate the product.

Discussion

Although I didn't manage to isolate freebase benzylamine, I still managed to get the hydrochloride salt. This experiment doesn't feel like a failure to me. I certainly learnt a lot along the way. I'm confident that with a bit of tweaking and a slightly different workup near the end, the Delepine reaction could be quite a worthwhile route to benzylamine.

My brief encounter with benzaldehyde has got me thinking, perhaps the Sommelet reaction might be a great source of this compound. It certainly seems a lot more appealing than any other route I have seen to benzaldehyde starting from toluene.

Anyway, I would like to say thank you to everyone on this incredible forum who has helped me get this far.