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Preparation of benzene, compiled by CHROMIUM, special contributions by IPN, ORDENBLITZ, S.C. WACK, and ORGANIKUM

Introduction

This is an extract of the benzene thread:

<http://www.sciencemadness.org/talk/viewthread.php?tid=325> As I want make benzene myself I started to read it and made notes for my own use. I soon realized that there is not much additional work if I try to make it a bit more systematic so that it can be used by others as well. Benzene has many interesting and useful properties and is not always readily available. It is of great interest to make it from available chemicals. Various methods of making benzene were proposed by members. Dry distillation of sodium benzoate with hydroxides appeared most promising after some discussion. This idea was tested by several members. Decent amounts of benzene were obtained using self-made distillation setups.

Proposed methods of benzene production

1. By decarboxylation of benzoates or benzoic acid by heating per se or with hydroxides.
2. By Friedel-Crafts reaction: AlCl_3 will catalyze the conversion of toluene into benzene and methylbenzenes, which are easily separated (and equilibrium pushed in the right direction) by distillation.
3. By reacting 1,3,5- trichlorocyclohexane with a strong base.
4. By aldol condensation – involving adding a strong base to acetaldehyde.
5. By dry distillation of phthalic acid with hydroxides.
6. From acetone via trimethylbenzene, followed by Friedel-Crafts.
7. By condensation of acetylene using a nickel catalyst.

8. Aluminum foil placed in toluene, chlorine or hydrochloric acid gas passed through the mixture. This is a Friedel-Crafts variation with aluminum halide catalyst made in situ (chlorine would probably react excessively with toluene).
9. From Chloramine-B by heating per se or with phosphoric acid to about 225°C. There was also warning that Chloramine-B could decompose explosively at 185°C.
10. By condensation of methane with AlCl₃ catalyst and heating.
11. From benzene diazonium sulfate.
12. By heating p-xylene with AlCl₃ or other Friedel-Crafts catalysts, much as already proposed for toluene.
13. By organometallic methods: electrolysis of para-dichlorobenzene dissolved with LiCl in acetone or pyridine.
14. By disproportionation of toluene or xylene using the Radzivanovskii in-situ AlCl₃ catalyst (this is essentially method 8 with a more specific reference to documented techniques).
15. By distillation of phenol and zinc powder.
16. By passing vapours of phenol over red-hot zinc dust.
17. By the Kolbe reaction, in which an alkali metal carboxylate is electrolysed.
18. By the Hunsdiecker reaction, reacting silver benzoate with Br₂ in carbon tetrachloride, then reducing the brominated product with zinc in dilute acid (!!!).
19. By decarboxylation of various substances in DMSO environment at <100°C.

Most of these methods were not tested or further discussed. There was some discussion on converting toluene with AlCl₃ catalyst to benzene. It was proposed that this catalyst can be made in situ conducting chlorine through toluene which contains some Al foil. Other members claimed that this would just chlorinate toluene and gaseous HCl instead of chlorine should be used. Experiments with this method by members were not reported as handy ways to benzene were soon found, all of them based on the dry distillation of benzoates with an alkali, alkaline earth, or mixed hydroxide.

First success with dry distillation

The first successful attempt was by a user called IPN who conducted dry distillation of sodium benzoate mixed with sodium hydroxide. From 50 g sodium benzoate and 14 g sodium hydroxide 24 mL of crude distillate was obtained. This was orange liquid with sharp smell boiling at 82°C. There was at least one serious problem: the bottom of his 250 mL rb flask was badly dissolved, probably because of the NaOH.

Table 1: Ordenblitz's experiments with benzoate decarboxylation by dry distillation

sodium benzoate	base	benzene yield
25 g	7 g Ca(OH) ₂	6 mL
25 g	7 g KOH	6.8 mL
25 g	7 g NaOH	7 mL

The crude product was distilled again and 22.6 mL water clear liquid with a boiling point of 81°C and with a scent like that of benzene was obtained. It was observed that temperature control is of remarkable importance. If heated too strongly there appeared a lot of orange oil-like substance that discolored the crude product. Slow heating was claimed to be good for obtaining less contaminated product and better yield.

This experiment was repeated with other members. Ordenblitz used 7 g of NaOH and 25g sodium benzoate that were roughly crushed together in a mortar and pestle. The mix was placed in a 500 mL rb flask, equipped with a condenser. Heat was applied by heating mantle in a slow manner for 30 minutes before a slightly orange/yellow low viscosity condensate began to collect. The process continued for 35 more minutes until no more was collected. The product was then redistilled rather quickly, easily separating the orange solid from the desired material. The final result was roughly 8 mL of, by all appearances, a fairly pure product. No visible damage to the flask was noted even though the reactants were not milled to a fine state as was suggested.

Ordenblitz repeated this experiment with various hydroxides as shown in Table 1. He also tested his product with FTIR and it appeared very good.

Instructions found by S.C. Wack

Preparation of a Hydrocarbon by Distillation of a Salt of an Acid with Soda-Lime. Benzene, C₆H₆.

Literature.—Mitscherlich : *Ann. Chem.* (Liebig), 9, 39 ; Marignac: *Ibid*, 42, 217; Wohler: *Ibid*, 51, 146; Berthelot: *Ann. Chim. Phys.* [4], 9, 469; Hofmann ; *Ber. d. chem. Ges.*, 4, 163; Baeyer : *Ibid*, 12, 1311 ; V. Meyer : *Ibid*, 16, 1465.

Mix 20 grams of benzoic acid with 40 grams of soda lime by grinding together in a mortar. Put the mixture in a small flask, connect with a condenser, and distill over the free flame. Separate the benzene from the water, dry it with calcium chloride, and distill. If perfectly dry benzene is desired, distill it a second time over metallic sodium. Yield 8 to 9 grams. Benzene solidifies at a low temperature, and melts at 5.42°C: it boils at 80.36°C. This method of preparation is no longer practically used, but it was of very great importance in the early study of the aromatic hydrocarbons, and illustrates a method very general in its application.

From Norris' *Experimental Organic Chemistry*, Preparation of Benzene from Benzoic Acid:

In a 6-inch evaporating dish place 10 grams of sodium hydroxide and 25 cc. of water. Heat over a free flame and stir until the sodium hydroxide dissolves; then stir in gradually 12 grams of benzoic acid. Evaporate to dryness over a free flame, which is kept constantly in motion; this will take about 10 minutes. Grind the mixture of sodium benzoate and sodium hydroxide in a mortar, and transfer it to an 8-inch test-tube. Clamp the test-tube in an inclined position so that the mouth of the tube is slightly lower than the other end; this will prevent any water given off during the heating from running back into the tube and cracking it. Connect the tube with a condenser and receiver, and heat with a free flame kept constantly moving, until no more liquid distils over. Measure the volume of the benzene and calculate the number of grams and the percentage yield obtained. Separate the benzene from the water, dry it with calcium chloride, and distill, noting the temperature. Benzene melts at 5.5°C, boils at 79.6°C, and has the density 0.878 g/mL at 20°C. The yield should be about 6 grams.

NOTE—By converting the benzoic acid into sodium benzoate in the presence of an excess of sodium hydroxide, an intimate mixture of the two substances is obtained. In this condition the compounds enter into reaction more readily and at a lower temperature than does a mixture of the acid and soda-lime; such mixtures are commonly used in the preparation of hydrocarbons from acids.

The benzene prepared in this way contains a small amount of biphenyl, which may be isolated from the residue left after the distillation of the hydrocarbon. The residue on crystallization from alcohol yields crystals of biphenyl, which after two sublimations melt at 71°C.

Organikum develops suitable apparatus

Organikum repeated experiment that IPN and Ordenblitz did before. He used 100 g benzoate and 60 g NaOH in a 500 mL RB flask. It appeared that scaling up is difficult. "It was found that the lower part of the mixture has molten but the upper part formed a kind of cover not falling down to the bottom. Some agitation with a strong wire brought this down, some more benzene came over, but the amount is too small to be called a satisfying result. The first fluffy then sticky consistence of the benzoate/hydroxide mixture seems to cause problems."

The main problem was sticking of the fused mass to the glass threatening to destroy it. Another problem was that not all benzoate reacted. "The fused mass is a nice insulator and makes it hard if not impossible to get all to react after a certain amount has fused."

He made another experiment using a 1000 mL Erlenmeyer flask with 100 g sodium benzoate and 60g NaOH and 50 g table salt as filler. "Hydroxide and some salt were grinded together in the coffee mill and admixed with the benzoate by the ol' 'inflated plasticbag' (tm) method, whereby some ungrinded salt was added into the Erlenmeyer, put in a sandbath isolated with glasswool and heated up."

This experiment appeared to be successful. Clear distillate came over at about 85°C (the temperature of the vapors measured in Claisen adapter). This process ap-

Figure 1: Robust metal can distillation apparatus



peared destructive to glassware. Every experiment ended with flask cracking because "fused mass clings so badly to the glass that the different thermal expansion breaks it whilst cooling down."

Various ways were proposed to solve cracking glassware problem:

1. To use nickel or silver plating on the inner surface of the flask.
2. To place gold or silver foil into the flask so that reaction mixture can not contact glass surface.
3. To use common glass bottles as cheap disposable flasks.
4. To use metal vessels.

Steelwool as filler was proposed by Organikum to solve heat transfer problems. Use of metal rods or short tubes was also proposed.

Organikum started to use a metal can as a heating flask (Figure 1). The metal can was connected to the glass condenser by copper tubing. 1" thread of this tubing was screwed to the metal can and the other end was used as socket for a 29 mm ground glass joint. The connection was tightened with teflon tape.

This metal can setup was used for several runs and always gave at least 120 mL benzene from 300 g sodium benzoate (molar yield of 68%). NaOH and sodium benzoate were ground and well mixed, steel wool was used to improve thermal conductivity. Old solvent cans were used. One can lasted for about three to four runs and was then replaced. Organikum also tried to replace NaOH with $\text{Ca}(\text{OH})_2$: "A run with calcium hydroxide instead of grinded sodium hydroxide gave less product which was much more decolorized, that's a pity as $\text{Ca}(\text{OH})_2$ comes already as a fine powder and would make the grinding unnecessary. So I stay with my (new-old) coffeegrinder and NaOH.... "

He also noted that the crude distillate must be washed with water: "When the product of the sodium benzoate destructive distillation is NOT washed with water before distillation a clear distillate with a sharp pungent smell comes over at about 70°C. This is obviously an azeotrope of benzene with an unknown compound."

Afterwards Organikum improved his setup by making it all metal. The condenser of the new setup was essentially a copper tube cooled by tapwater falling onto its external surface.

Ordenblitz scales up

Ordenblitz worked similarly on an even larger scale. He constructed a distillation setup with metal can and water jacketed copper condenser, similar to that of Organikum but bigger and more elaborate (Figure 2).

In the can was put 4 or 5 shredded stainless steel scrubber pads, for a conduction aid and a specially wet granulated, densified and beaded mix of 2500 gm sodium benzoate + 1250 gm calcium hydroxide. I prefer to use $\text{Ca}(\text{OH})_2$ since I have to use less personal protection when mixing and granulating. Clean up is easier and of course the stuff is cheaper.

Very strong heating was needed. The first 3 hours on gas burner yielded only 250 mL of distillate. After another hour or two things started to slow down.

650 stinking milliliters for all that hard work and waiting, pathetic! I expected about 1500 mL. After opening the can I noticed that most of the center of the mass was un-reacted and the top looked all but untouched. I had the lower 1/3 of the can cherry red after the 3rd hour. My conclusion is that scaling this reaction up without a lot of fairly technical hardware, is probably just not worth the effort.

Taking a second look at the monster distillation can for benzene, I decided to scale the quantity back and shorten the time. I put 1100 g of my 2/1 sodium benzoate/calcium hydroxide mix (about 30% of the original load) into the can. This filled it roughly 1.3 inches. I wanted a thin layer this time. I then connected the condenser and fired up the burner. In 30 minutes the distillate stopped coming over and I had 210 mL of product (Figure 3). Not bad for 40 minutes of work. Next I decided to try sodalime to see if the lower melting point would hasten the reaction or increase the

Figure 2: Ordenblitz's large-scale distillation apparatus



yield. So to 1100 g of the mix I added 200 mL 40% NaOH solution, mixed thoroughly and added to my can. I turned on the flames and in less than 20 minutes it was all over. This time I had 200 mL of liquid goodies. So, faster yes but slightly poorer yield.

While the can is still hot I open it up and hit it with the hose and the thermal shock breaks the clinker into a thousand pieces and I simply dump out the chunks, load her up and off we go again. A day of this and quite a bit of benzene could be had.

I have run this now about 4 times and I think the can should last quite a while. The only thing I need to replace is the cap seals, which I cut out of high temp silicone.

It is interesting to note that the faster you push this reaction the redder the product gets. Compared to my first batch it looks a deep red. The only difference between the first run and the second was load in the can and how fast I heated it up. The final test will be when it's distilled and the tally taken. I assume that I made a bit more biphenyl by pressing it hard. I will sort out the final count and post. ...

All the batches are now finished and from 2500 gm / 1250 gm, sodium benzoate/calcium hydroxide and some time I have about 1.4 liters of benzene. Not too bad at all. I managed to save the unreacted material from my first run and add it to subsequent runs. As long as I keep the load in the can at about 1000 grams, I get very good yields.

I distilled the darker batches and the lighter yellow ones separately. While the distillate from the faster hotter runs is more toward the red/orange, it results in less solid matter (biphenyl etc) remaining after the finish distillation. So I say, hotter and faster is better.

I got a picture of the clinker that I broke out of the can. It is very light and porous looking a lot like lava rock or pumice. One other interesting thing is that it is very hard after coming out of the can but upon exposure to the air for a day it completely disintegrates into dust. So to make cleanup easy after a run, just let your vessel sit open for a while and dump out the powder.

About starting materials

There was not much discussion on starting materials as alkali benzoates are easily available. Benzoates are used as food additives, antiseptics and antioxidants. There were short references to oxidizing toluene with potassium permanganate to get potassium benzoate.

Figure 3: Crude product of Ordenblitz's second scaled-up benzene production run

