XIV. Grand Prix Chimique

Preparative task

Synthesis of ammonium tetraphenylborate via Grignard reaction

Debrecen, Hungary 2019

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Abbreviations in the text:

- deionized water = DIW
- mol/dm^3 = mol/L = M = molar
- cm^3 = mL
- relative atomic mass = A_r
- diethyl ether = ether = Et_2O
- chloroform - methanol 2:1 = CM 2:1
- thin layer chromatography = TLC
- retardation factor = R_f

Lab Safety

- In the laboratory, safety equipment (lab coat, gloves, safety glasses) must be worn all times. Safety glasses can be found at each workstation. Gloves are available in multiple sizes at the teacher's desk.
- Please thoroughly study the hazards and safety precautions of the provided chemicals.
- Before using an equipment, always check for damage. Do not use damaged equipment or cracked glassware, but report it to a jury member immediately.
- Eating and drinking in the lab (including chewing gum) is prohibited.
- The safety rules must be obeyed.

General Notes:

- Read the task carefully before you start working.
- 30 minutes before the end of the lab session a warning will be issued. Plan your work accordingly.
- If you need to leave the lab, ask a jury member or lab assistant. Do not leave the lab without permission.
- Please write all your answers, calculations and notes in pen. The back of your exam sheet can be used if you run out of space but your final answers must be written in the dedicated area.
- English version of the exam sheet is considered to be standard.
- It is advised to inspect whether the equipment you work with is clean and dry, especially if performed measurement/reaction is sensitive.
- Some equipment and chemical are shared among multiple contestants. Do not take them for yourself and always put them back to their original place after use. Plan ahead to avoid jams.
- Deionized water can be refilled from plastic barrels. Crushed ice can be obtained from Styrofoam boxes placed in the lab.
- Cleaning the glassware:
    - wash with tap water and dish soap
    - rinse with deionized water
    - rinse with acetone
    - if the glassware is heat resistant dry it with hairdryer, if not wait until the acetone evaporates
- The following waste requires special treatment:
    - distilled diethyl ether should be collected in glass bottles labelled 'Ether Waste'
    - waste resulting from quenching the Grignard reaction should be collected in glass bottles labelled 'Quench Waste'
    - waste filtrate should be collected in glass bottles labelled 'Aqueous Waste'
    - leftover eluent should be collected in glass bottles labelled 'Eluent Waste'
- Always use the fume hood when measuring ether and during solvent extraction. When transporting reaction mixtures, the flasks should be stoppered to avoid evaporation of ether and volatile side products.
- Two different types of diethyl ether are available. Please use the anhydrous ether only for performing the Grignard reaction. After the reaction is quenched, use puriss. ether for rinsing and extraction.
- When assembling reflux or distillation apparatus, ground glass joints can be sealed with Teflon tape if necessary, to prevent the escape of ether vapor.
- The glassware assembly diagrams are just recommendations and are not necessarily accurate in every detail. It may not include all aspect of the correct assembly.

Please obey the rules of fair play. We wish you good luck for the competition.

Available equipment for each contestant			
Equipment	**Quantity**	**Equipment**	**Quantity**
Allihn condenser	1	Pencil for TLC	1
Beaker, 150 mL	1	Permanent marker	1
Beaker, 250 mL	2	Petri dish	2
Beaker, 400 mL	2	Plastic box (to lift magnetic stirrer)	1
Bosshead	2	Plastic stopper NS29/32	2
Büchner funnel, porcelain, 120 mL	1	Powder funnel, plastic, ⌀80mm	1
Claisen adapter	1	Pressure equalizing addition funnel	1
Clamp	2	Round-bottom flask, 1 neck, 250 mL	1
Cork ring for round-bottom flasks	3	Round-bottom flask, 1 neck, 500 mL	1
Crystallizing dish	2	Round-bottom flask, 2 neck, 250 mL	1
Distillation bridge	1	Rubber conical gasket	1
Drying tube	1	Rubber tube, for condenser available at the teacher's desk	2
Glass funnel, ⌀80mm	1		
Glass stopper NS14/23	2	Separating funnel, 250 mL	1
Glass stopper NS19/26	1	Spatula (plastic)	1
Glass stopper NS29/32	3	Stirring rod	1
Graduated cylinder, 50 mL	1	Thermometer, -30-100 °C	1
Keck clip	2	Thermometer adapter	1
Lab stand, 50 cm	1	TLC plate (silica gel 60 F254)	1
Lab stand, 30 cm	1	Tweezers	1
Magnetic stir bar	1	Vacuum filtering flask, 250 mL	1
Magnetic stirrer	1	Wash bottle (for DIW)	1

Shared equipment	
Equipment	**Location**
Capillary tubes, for TLC	On teacher's desk
Cotton wool, for packing drying tubes	On teacher's desk
Electric kettle *(3 pcs.)*	Shared between 4 contestants
Filter papers, 2 µm, ⌀70mm	On teacher's desk
Hairdryer	In fume hood
Infrared lamp, for drying *(3 pcs.)*	Under 'INFRA' sign
Lab scale, for measuring $CaCl_2.6H_2O$ and ice	On the same bench as infrared lamps
Magnetic stir bar retriever	On teacher's desk
pH indicator paper (pH 8-10)	On teacher's desk
Precision balance	On the same bench as infrared lamps
Ring stand with retort ring *(3 pcs.)*	In fume hood
Ruler, for TLC	Next to TLC separating chambers
Scissors	Next to TLC separating chambers
Teflon tape, for sealing ground glass joints	On teacher's desk
TLC plate (silica gel 60 F254)	On teacher's desk
TLC separating chamber *(5 pcs.)*	Under 'TLC' sign
UV lamp, for TLC	Under 'UV' sign
Transfer pipettes (LDPE)	On teacher's desk
Wash bottle (with acetone) *(4 pcs.)*	Shared between 3 contestants
Water aspirator with vacuum tubing for vacuum filtration	Shared between 2 contestants
Weighing boat (PS)	Next to lab scales

Required chemicals				
Chemical	**Location**	**GHS Hazard and Precautionary Statements**		
		Pictograms	Hazards	Precautions
Acetone	In wash bottles, shared between 4 contestants		H225, H319, H336 EUH066	P210, P233, P261, P305+351+338, P370+378, P280
Ammonia *(exact concentration on burette)*	In fume hood		H315, H318, H412	P280, P305+351+ 338+310
Ammonium chloride	Next to lab scales		H302, H319	P301+312+330, P305+351+338
Ammonium tetraphenylborate *(reference standard in acetone)*	At each workstation in small vials		H225, H319, H336 EUH066	P210, P233, P261, P303+361+353, P370+378, P280
Bromobenzene 335 g/dm^3 in dry diethyl ether	In fume hood		H224, H302, H336, H315, H411 EUH019, EUH066	P210, P261, P273, P403+235
Calcium chloride anhydrous *(for drying tube)*	Next to lab scales		H319	P280, P305+351+338
Calcium chloride hexahydrate *(for ice bath)*	Next to lab scales		H319	P280, P305+351+338
Chloroform - Methanol 2:1 *(eluent for TLC)*	Next to TLC developing chambers		H225, H301, H311, H315, H319, H331, H336, H351, H361d, H370	P210, P260, P264, P302+352+312, P304+340+312, P305+351+338, P370+378, P280
Diethyl ether, anhydrous *(only for Grignard reaction)*	In fume hood		H224, H302, H336	P210, P261
Diethyl ether, puriss. *(for extraction)*	In fume hood		H224, H302, H336	P210, P261
Iodine *(initiator)*	Next to lab scales		H312+332+315, H319, H335, H372, H400	P261, P273, P280, P302+352, P305+351+338, P314
Magnesium turnings	Next to lab scales		H228, H252, H261	P210, P223, P235, P280, P410
Sodium carbonate 1 mol/dm^3	Next to lab scales		H319	P305+351+338, P337+313
Sodium chloride *(ice cold saturated solution)*	In Styrofoam box with ice	-	-	-
Sodium tetrafluoroborate	Next to lab scales		H314	P260, P280, P301+330+331, P305+351+338

Task 1

Synthesis of ammonium tetraphenylborate via Grignard reaction

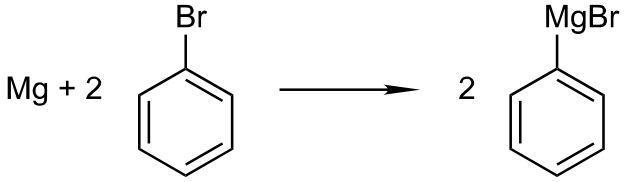
Introduction:

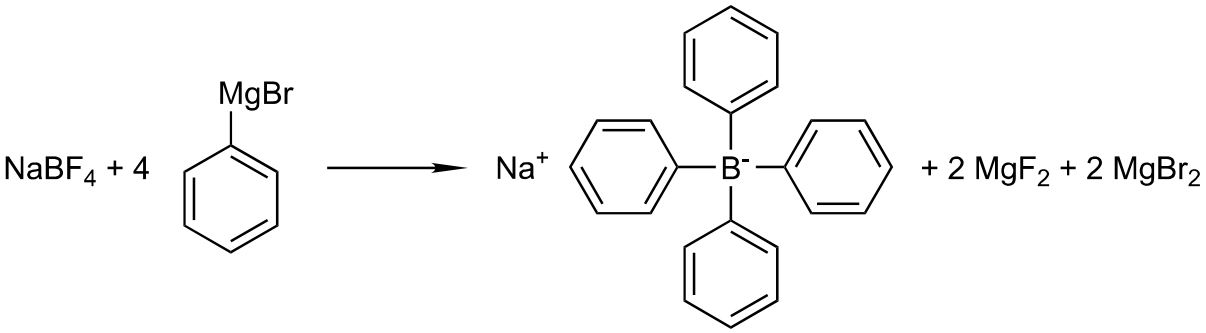
Tetraarylborate anions consists of a negatively charged boron center with four aryl substituents and is stabilized by the negative charge distribution between the aromatic rings. Polyfluorinated derivatives, which has remarkable stability, are weakly coordinating anions and are extensively used in the field of coordination chemistry and are common counterions of catalysts. Owing to their nonpolar substituents tetraarylborates confer lipophilicity to their salts. They are also used in analytical chemistry exploiting their formation of water-insoluble salts with K^+, Rb^+, Cs^+, NH_4^+ and organic ammonium cations. For example, $NaBPh_4$ is used for the titration of potassium ions.

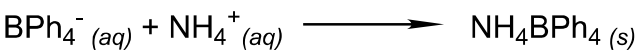
Basic principle and procedure:

Synthesis of the tetraphenylborate anion itself is a nucleophilic substitution reaction, where the boron source can be either boron trifluoride diethyl etherate or a tetrafluoroborate salt. In our case $NaBF_4$ is chosen because it is easier to handle. Phenylmagnesium bromide, a Grignard reagent is used as the nucleophile and is made from bromobenzene and magnesium, then in situ reacts with the $NaBF_4$ to produce the sodium salt of our product in an exothermic reaction. Magnesium fluoride and bromide precipitates out from the reaction mixture.
$NaBPh_4$ has good solubility in water, polar organic solvents and ether. After extraction and workup, the tetraphenylborate anion is precipitated out as its insoluble ammonium salt from water. However, it can be recrystallized from acetone and ethanol due to its good solubility in these solvents.
Grignard reactions are very sensitive, especially for moisture, and a lot of side products are formed if the conditions are not ideally controlled.

Reaction equation:







I. Synthesis

1. Assemble a reflux apparatus by placing an Allihn condenser and an addition funnel on the top of a dry, clean 250 mL two-neck round-bottom flask fitted with a Claisen adapter.
   Put a drying tube packed with anhydrous $CaCl_2$ on the top of the condenser.
   Use a thermometer with an adapter to be able to check the temperature of the solution in the round-bottom flask.
   Place a magnetic stirrer and a lab jack under the flask, making sure that a heating or cooling bath can be applied if necessary.
   Connect the condenser to the tap and set a constant flow of water through the condenser. *(Figure 1)*
2. Weigh 2.06 g of sodium tetrafluoroborate, then transfer it to the round-bottom flask. Add 1.82 g magnesium turnings, 40 mL of anhydrous diethyl ether and a single iodine crystal. Stir the reaction mixture for 15 minutes or until most of the sodium tetrafluoroborate dissolves.

$m_{sodium\ tetrafluoroborate}$ = _____ g	$m_{magnesium}$ = _____ g

3. Measure 35 mL of ethereal bromobenzene solution, pour it into the addition funnel and stopper it.
4. Add ca. 5-10 mL of solution in one go from the addition funnel to the flask.
5. The initiation of the reaction is indicated by the complete disappearance of the color of iodine, and the reaction mixture becomes turbid and grey or slightly yellowish in color (this takes maximum 20 minutes). Apply heating bath or add a little more bromobenzene solution to help initiate the reaction if necessary.
6. After the reaction has started, begin dripping in the bromobenzene solution at a pace that maintains the exothermic reaction (which is indicated by the boiling of ether), but avoid a vigorous reaction. This takes about 1 to 1 and a half hours. The reaction rate can be controlled by applying heating (in the case when the reaction slows down) or cooling (when the reaction becomes too vigorous) baths when necessary.
7. After the addition is complete, stir the reaction mixture for 30 minutes while it cools to room temperature and the boiling ceases.
8. Then add around 3 mL of acetone into the mixture through the addition funnel and stir for another 10 minutes.
9. Under the fume hood, pour the room-temperature solution slowly, under constant stirring into a 400 mL beaker containing 75 mL of ice cold saturated NaCl solution.
10. Separate the phases using a separatory funnel, then extract the aqueous phase 3 times with 20 mL puriss. ether each.
11. Collect the organic phases into a 500 mL round-bottom flask, then add 100 mL 1M sodium carbonate to it.
12. Return to your workstation and set up a distillation apparatus.
13. Place a calcium chloride - ice bath under the receiver flask, prepared by thoroughly mixing 150 g crushed ice with 150 g $CaCl_2.6H_2O$. Be careful, as this ice bath can reach temperatures as low as -29 °C.
14. Distill the ether under vigorous stirring using a hot (50-70 °C) water bath. Stop heating when no more ether comes over.
    Boiling point of diethyl ether: 34-35 °C
15. Filter the residue fraction using vacuum. Pour the filtrate into a 250 mL beaker.

16. Prepare 20mL ca. 1.5 M NH_4Cl/NH_3 buffer solution with a pH value of 9.00 by measuring the calculated amount of solid ammonium chloride and aqueous ammonia, then diluting it with deionized water. Ignore volume changes during calculation. Check the pH of the resulting solution.
    Calculations for buffer solution preparation (before preparing the buffer, show your calculation to a jury member):

$pK_a(NH_4^+) = 9.25$ Required chemicals: $m_{ammonium\ chloride}$ = _____ g $V_{ammonia}$ = _____ cm^3

17. Add the prepared buffer solution to the filtrate.
18. Vacuum filter the precipitate, then recrystallize it from acetone.
    For recrystallization, place the filtered material into a 400 mL beaker and dissolve it in the minimum possible amount of acetone, then add deionized water until the final percentage of acetone by volume is less than 10%.
19. Filter the precipitated product on a Büchner funnel, then wash it with deionized water.
20. Transfer the precipitate onto a Petri dish and dry it under an infrared lamp.

II. <u>Characterization</u>

- Weigh the final product and calculate the yield based on sodium tetrafluoroborate.

$m_{ammonium\ tetraphenylborate}$ = _____ g η = _____ %

- Dissolve a small amount of your product in a few drops of acetone and apply it on a TLC plate along with the reference standard. Develop the plate using a mixture of chloroform - methanol 2:1 as an eluent, then dry the plate with a hairdryer. The product and the aromatic side products (if present) can be visualized under UV light at 254 nm. Carefully evaluate the TLC plate with a pencil and calculate the R_f values of the product and the standard.

R_f (product)= _____ R_f (standard)= _____

- The final product and the finished TLC plate must be handed in with this task sheet.

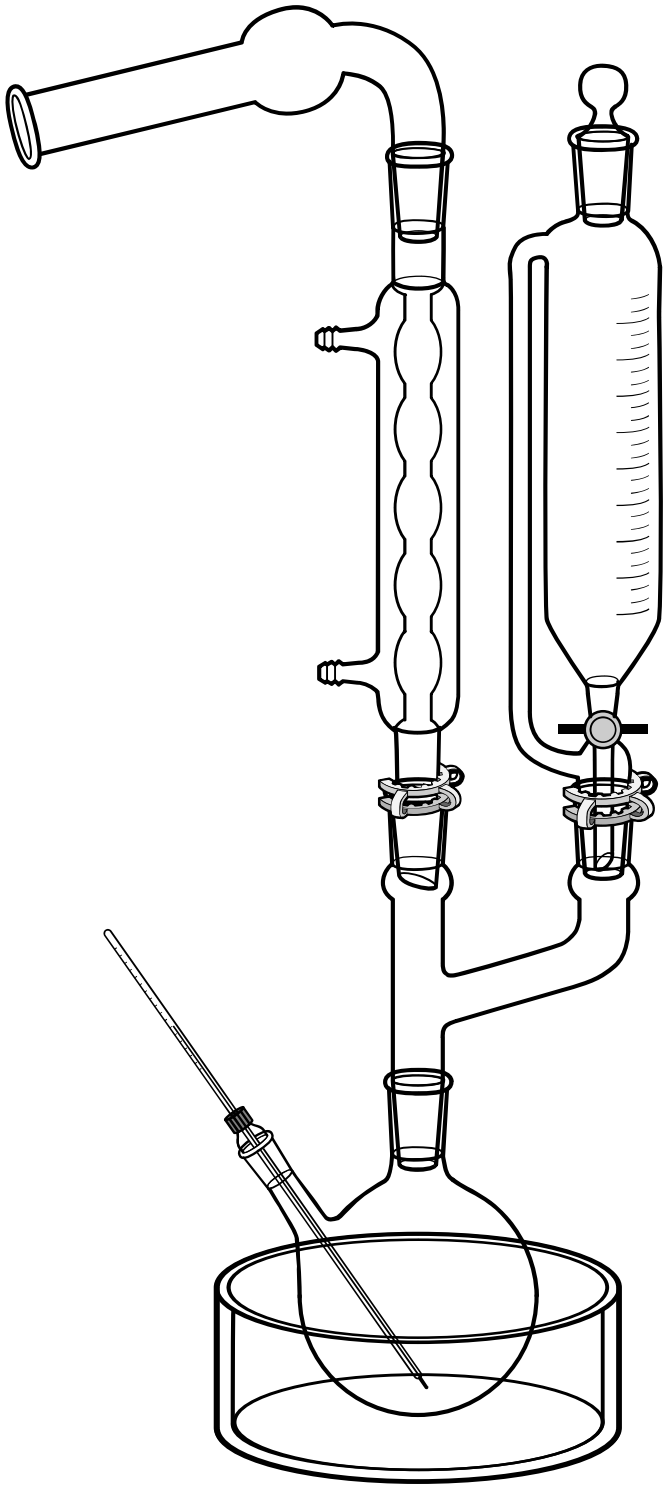


Figure 1