

Introductory Remarks:

At all times while you are in the laboratory you should wear safety spectacles or own spectacles if they have been approved. Eating of any kind of food or drinking is strictly prohibited in the laboratory.

Participants are expected to work safely, to behave socially and to keep equipment and working place clean. Violation of these rules may result in penalty points. Do not hesitate to ask laboratory assistant if you have any questions concerning safety issues.

For the experiment you will get two documents:

- description of experiment
- report sheet.

Please read carefully the text of the entire experimental task before you begin your experimental work. Check where instruments are located. You have 15 minutes to prepare yourself for the experimental tasks.

Work starts at 9:00 h and may only begin when the start signal is given. The work ends at 16:00 h and there will be a pre-warning 15 minutes before the end of your time. You must stop your work immediately after the stop command is given.

Write your name and personal identification code (posted at your working place) in the appropriate box of the protocol sheets.

Use the list of the R/S safety codes to protect yourself.

All results must be written in an appropriate places on the answer sheets. Data written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need additional paper or a replacement answer sheet, request it from the laboratory assistant.

When you have finished the examination, you must put all papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.

Do not leave the laboratory until you have permission to do so.

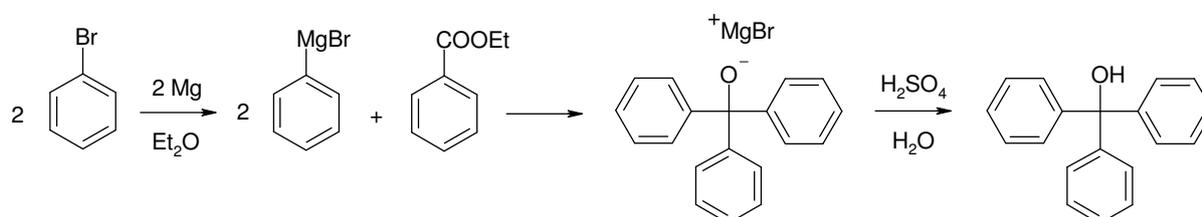
The number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. The inability to perform calculations correctly will result in penalty points, even if your experimental technique is flawless.

An official English-language version is available only on request.

SYNTHESIS OF TRIPHENYLMETHANOL

The goal of this experiment is the preparation of triphenylmethanol. The procedure starts by transformation of bromobenzene to phenylmagnesium bromide. Subsequent Grignard reaction with ethyl benzoate affords the corresponding triphenylmethoxide, which is acidified by diluted sulfuric acid to yield the target triphenylmethanol. Extraction of the crude reaction mixture with diethyl ether and evaporation of solvents on rotary vacuum evaporator leads to the crude product contaminated with biphenyl. Product is isolated by column chromatography followed by distilling off part of the solvent and final suction filtration.

Reaction Scheme



List of equipment

a) Personal equipment (located at the working place)

Item	Quant.	Item	Quant.
Erlenmeyer flask, 1000 ml, NJ 29	1	Erlenmeyer flask, 250 ml, NJ 29	1
Round bottom flask, 250 ml, NJ 14	2	Round bottom flask, 100 ml, NJ 14	1
Round bottom flask, 50 ml, NJ 14	2	Erlenmeyer flask, 50 ml, NJ 14	1
Erlenmeyer flask, 25 ml, NJ 14	1	Erlenmeyer flask, 5 ml, NJ 14	1
Reflux condenser, NJ 14	1	Drying tube, NJ 14	1
Microcondenser, NJ 14	1	Filtration adapter, NJ 14	1
Separatory funnel, 50 ml	1	Graduated cylinder, 10 ml	1
Chromatographic column	1	Glass tube, 20 ml	20
Petri dish	1	TLC chamber	1
Plastic syringe 20 ml	1	Plastic syringe 10 ml	2
Plastic syringe 2 ml	1	Plastic syringe 1 ml	1
Syringe needle	5 + 2	Rubber tubing	2
Thermometer, NJ 14, 0 – 250 °C	1	Magnetic stirbar	1
Magnetic stirrer	1	Tube stand	1
Rubber septum	4 + 2	Glass capillaries for TLC	20
TLC plates	3 + 3	Glass bottle, 5 ml	7
Spatula	1	Glass funnel	1
Pasteur pipettes + bulb	5 + 1	Tweezers	1
Support stands, clamps			

b) Common equipment

Item	Item
Rotary vacuum evaporator	Vacuum line
Laboratory oven	Laboratory balances
Ultraviolet lamp for TLC	

List of chemicals

Reagent	Amount	R codes	S codes	Location
Bromobenzene, anh. density 1.491 g/ml	1.57 g	10-38-51/53	61	Glass bottle 5 ml, bench
Ethyl benzoate, anh. density 1.045 g/ml	0.75 g			Glass bottle 5 ml, bench
Magnesium, activated	0.24 g			R. b. flask 50 ml, bench
Sulfuric acid, diluted	10 ml	35	26-30-45	Glass bottle 5 ml, bench
Diethyl ether, anh.	10 ml	12-19-22-66-67	9-16-29-33	Erlen. flask 25 ml, bench
Diethyl ether for ext.	20 ml	12-19-22-66-67	9-16-29-33	Erlen. flask 50 ml, bench
Dichloromethane - hexane 2:1	750 ml	40 11-38-48/20-62-65-67	23-24/25-36/37 9-16-29-33-36/37-62	Erlen. flask 1000 ml, bench
Silica, Ø 63-200 nm	30 ml		22-24/25	Erlen. flask 250 ml, bench

Relative atomic masses:

H: 1.01

C: 12.01

O: 16.00

Br: 79.90

Procedure

Step 1

Assembling of the reaction apparatus (see Fig. on page 7) should be as quick as possible to avoid contamination of the apparatus by excessive moisture. Place the stoppered flask with magnesium and stirbar on the stand with magnetic stirrer. Fit it with reflux condenser and septum. Attach the rubber tubing to a water source, reflux condenser and a sink. Carefully turn on the cooling water. Pierce the septa on the apparatus and on the flask with anhydrous diethyl ether with short needles to vent out excessive air and add to the reaction flask 5 ml of dry diethyl ether by a 10 ml syringe and long needle (for work with syringes, see Fig. on page 7). Remove the venting needle from the flask with diethyl ether and connect to it the used syringe with needle to avoid its contamination with moisture. Add similarly bromobenzene from the 5 ml flask by a 2 ml syringe to the reaction mixture, remove the septum from the condenser and quickly attach the drying tube. Leave the mixture for about 5 min and then begin gently stirring. If the reaction does not start in the course of 10 min, what is accompanied by vigorous reflux, ask laboratory assistant for help. Stir the mixture until the reflux ceases (about 10 min), then gently heat the reaction mixture on the water bath (stop stirring, remove the stirrer, fill the aluminum dish with hot water, put it below the reaction flask, return the stirrer and resume stirring), start heating with stirrer (on about 100 °C on the stirrer). After 15 min stop stirring and heating, remove stirrer, wait for about 5 min, fill the aluminum dish with cold water, reassemble and stir the mixture while cooling for about 5 min.

Step 2

Remove the cooling bath, substitute quickly the drying tube with rubber septum and vent the reaction apparatus, as well as the flask with anhydrous diethyl ether with short needles. Add to the reaction mixture while stirred 5 ml of anhydrous diethyl ether by the 10 ml syringe with long needle, followed by careful dropwise addition of ethyl benzoate to the mixture by a 1 ml syringe with long needle. Quickly remove the septum from the reaction apparatus and reattach the drying tube. Stir the reaction mixture for 15 min and then similarly as in step 1 heat it by the water bath to gentle reflux for another 15 min. Remove heating and cool the reaction mixture by a cold water bath. Reassemble the stirrer, remove drying tube and decompose the reaction mixture while stirring by careful dropwise addition of diluted sulfuric acid. Stir the reaction mixture for 10 min.

Step 3

Remove the stirbar from the mixture by a magnetic teflon-covered rod. Pour the reaction mixture into separatory funnel and separate the lower aqueous layer. Weigh empty 100 ml flask and pour ether layer to it. Return the aqueous layer back the separatory funnel and extract it twice with 10 ml on diethyl ether. Combine the ether layers in the 100 ml flask. Remove the ether on the rotary vacuum evaporator (10 min, 40 °C). Record the weight of the flask with product. Put small amount of the crude reaction product (using a tip of the spatula, about 2 mg) into the 5 ml bottle and dissolve it in about 0.5 ml of dichloromethane-hexane mixture (one load of Pasteur pipette). Apply the solution on the start (this has to be above the surface of the mobile phase in the developing chamber!) of the TLC plate and develop the chromatogram (see Fig. on page 7). Leave the plate dry for about 5 min, observe the spots on the plate under UV light and mark them with a pencil. The first spot with higher R_f belongs to the side product, biphenyl, the last spot with lowest R_f corresponds to the product.

Step 4

Pour into closed chromatography column about 20 ml of mobile phase for column chromatography (dichloromethane/hexane 2:1). Add about 50 ml of the mobile phase to silica gel in the flask, mix carefully, then close the flask and shake intensively. Immediately pour the mixture into the column, open the stopcock and leave silica to settle. Wash the silica off the walls of the column carefully with the mobile phase (use 10 ml syringe with long needle). If necessary, refill the column with fresh mobile phase carefully. When the height of the silica in the column remains constant, close the stopcock adjusting the mobile phase level about 5 cm above the top of the silica column. Carefully push paper ring into the column and leave it to cover the top of the column. Open the stopcock, allow the mobile phase level to reach the top of the column and close again. Dissolve your crude product in 5 ml of mobile phase and transfer the solution on the top of the column. Open the stopcock and leave the solution to adsorb on the silica. Wash the flask and the syringe with 2 ml of the mobile phase, apply on the top of the column and leave to adsorb again. Wash the syringe twice with 10 ml of the mobile phase. Apply with the washed syringe 2 ml of mobile phase on the top of the column, leave to adsorb and repeat once more with another 2 ml of mobile phase. Fill carefully the column to the top with the mobile phase (do not raise the silica on the top of the column) and start chromatography immediately. Each tube should be filled by the eluent in about 30 s, about 4 cm to the top. If needed, refill the mobile phase on the column

periodically. After the chromatography is finished (20 tubes), test each fourth tube content by TLC (use wider plate, the distance between the injections should be between 0.5 - 1 cm. Record which tubes contain the spot corresponding the desired product. Test five tubes preceding the first tube containing only the spot of the product similarly.

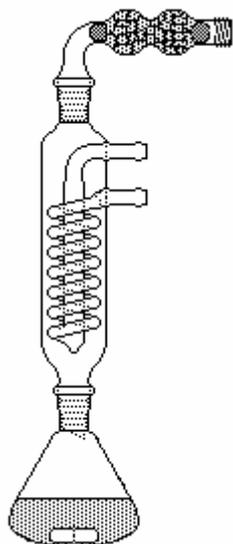
Step 5

Collect all fractions containing the purified product into the 250 ml flask. Distil off the solvent carefully using the microcondenser and another 250 ml flask as a receiver using the magnetic stirrer, stirbar and hot water bath (see Fig. on page 7, attach the third rubber tubing to the outlet of the condenser and place the other end of the tubing into the sink to minimize the contamination of the laboratory with distilled off dichloromethane vapours). As soon as the temperature on the thermometer reaches 54 °C, stop distillation (in any case, at least 2 ml of liquid should remain in the distillation flask, do not distill to dryness!). Cool the distillation flask with ice bath for 15 min and isolate the crude product by suction filtration (see Fig. on page 7). Record the weight. Leave the product to dry on a Petri dish for 15 min in the hood and re-record its weight. Put the product into the marked bottle. Dissolve about 2 mg of the product in about 0.5 ml of the mobile phase and repeat TLC analysis. Mark all spots.

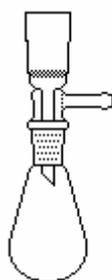
Step 6

Calculate the yields of the crude and purified product, attach to the protocol all TLC analyses.

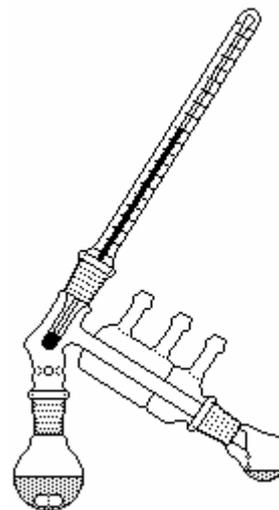
Apparatuses:



Grignard reaction

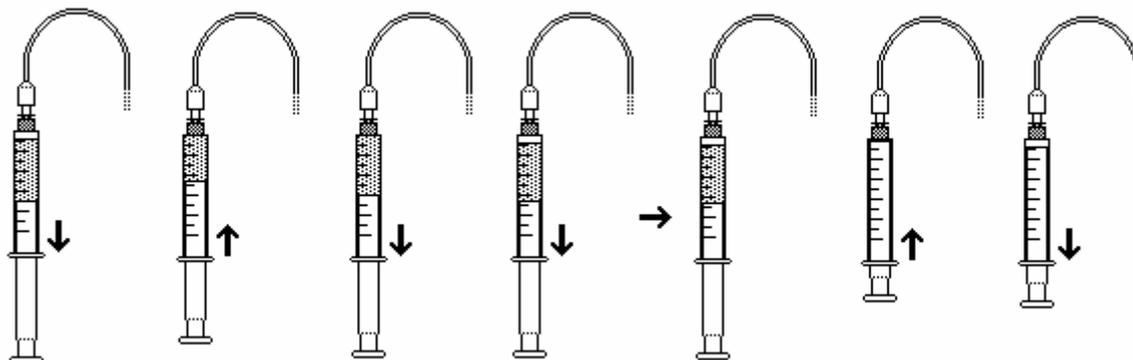


Filtration



Distillation

Work with syringes:



take a liquid

remove bubble

take exact amount of liquid

add some air or inert before removal

transfer the liquid

add liquid to the flask

take some air or inert before removal

TLC chromatography:

