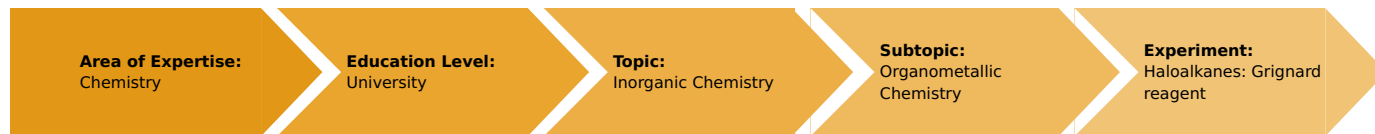


Haloalkanes: Grignard reagent (Item No.: P3101000)

Curricular Relevance



Difficulty



Difficult

Preparation Time



10 Minutes

Execution Time



20 Minutes

Recommended Group Size



2 Students

Additional Requirements:

- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

n-propyl bromide, magnesium, Haloalkanes, Grignard reagent, organometallic compounds

Overview

Short description

Principle

Haloalkanes react with magnesium to the so-called Grignard reagents in accordance with the general formula RMgX . With $\text{X} =$ bromide or iodide, the reaction works best. Chlorides are usually more inert and require higher temperatures and longer reaction times for the conversion. The compounds that were discovered by Victor Grignard probably exist as dimeric structures.

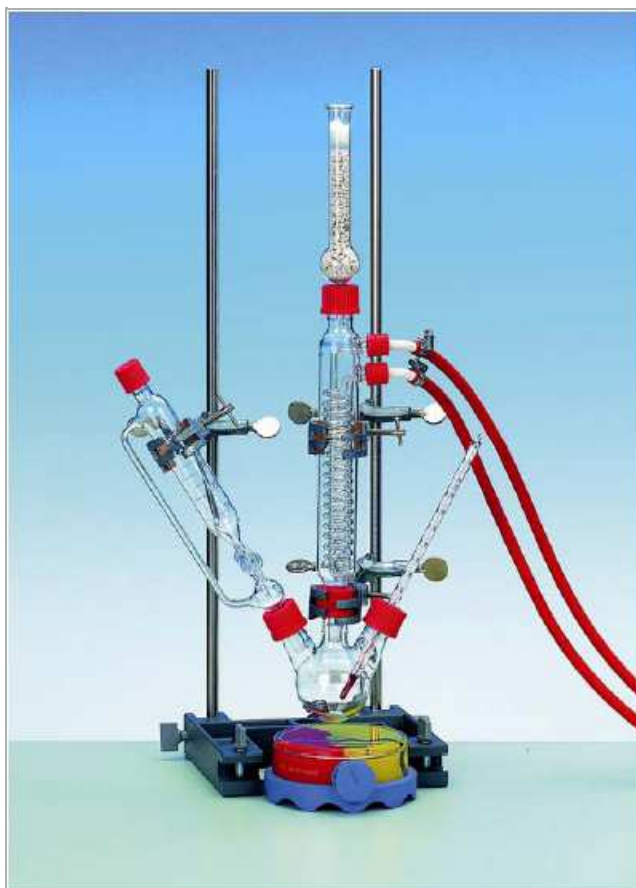
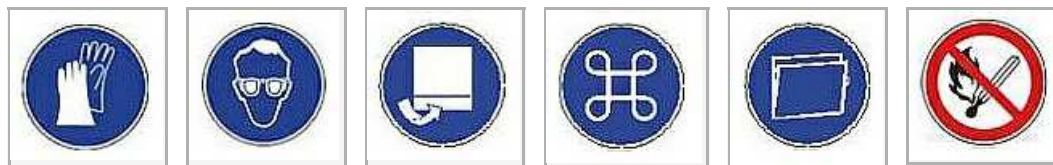


Fig. 1: Experimental setup.

Safety instructions



Tetrahydrofuran is a highly flammable liquid that can be mixed with water. In combination with air, its vapours may form explosive mixtures. Tetrahydrofuran irritates the skin, eyes, and respiratory tract. Cases of systemic poisoning are not known. n-propyl bromide irritates the skin and eyes. Danger of poisoning if inhaled.

Water-free potassium hydroxide has a strong irritating effect on the skin, eyes, and mucous membranes. Dusts and mists irritate the respiratory organs. Chemical burns lead to the destruction of the tissue and intense pain.

First aid: Wash the affected skin areas with water and soap. Let splashes to the eyes evaporate with the lid gap wide open (blow carefully into the eyes). Then, rinse the eyes with water.

If inhaled: Fresh air.

Disposal: Solutions must be diluted with water, neutralised (pH 6-8), and flushed away.

Halogen-containing compounds and solutions must be collected separately from other organic substances in their own collecting vessel that is marked accordingly.

Iodine

H315: Causes skin irritation.
H319: Causes serious eye irritation.
H400: Very toxic to aquatic life.
P273: Avoid release to the environment.

Potassium hydroxide

H290: May be corrosive to metals.
H302: Harmful if swallowed.
H314: Causes severe skin burns and eye damage.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Magnesium, grignard

H228: Flammable solid.
H252: Self-heating in large quantities; may catch fire.
H261: In contact with water releases flammable gas.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

N-propylbromide

H225: Highly flammable liquid and vapour.
H319: Causes serious eye irritation.
H360: May damage fertility or the unborn child.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

Quartz glass wool

H332: Harmful if inhaled.
H335: May cause respiratory irritation.
P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

Tetrahydrofuran

H225: Highly flammable liquid and vapour.
H302: Harmful if swallowed.
H351: Suspected of causing cancer.
EUH019: May form explosive peroxides.
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233: Keep container tightly closed.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Propane

H220: Extremely flammable gas
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P381: Eliminate all ignition sources if safe to do so.

Mg(OH)Br

H315: Causes skin irritation.
H411: Toxic to aquatic life with long-lasting effects.
P273: Avoid release to the environment.

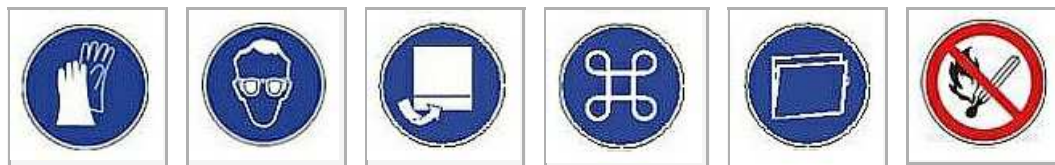
Equipment

Position No.	Material	Order No.	Quantity
1	Support base DEMO	02007-55	1
2	Support rod, stainless steel, l = 600 mm, d = 10 mm	02037-00	2
3	Retort stand, h = 750 mm	37694-00	1
4	Right angle boss-head clamp	37697-00	6
5	Universal clamp	37715-00	6
6	Round flask, 100 ml, 3-n., 3 x GL25	35677-15	1
7	Round bottom flask, 100ml, GL 25/12	35841-15	1
8	Separating funnel, 50ml, GL18	35853-15	1
9	Funnel for gas generator, 50 ml, GL18	35854-15	1
10	Condenser, Dimroth type GL25/12	35815-15	1
11	Gasket for GL25, 8mm hole, 10 pcs	41242-03	1
12	Calcium chloride tube, str. 150 mm	36941-00	2
13	Stopcock, 3-way, t-shaped, glass	36731-00	1
14	Gasometer 1000 ml	40461-00	1
15	Plastic bag w. hose 10 u.	40469-00	1
16	Pinchcock, width 15 mm	43631-15	1
17	Graduated cylinder 100 ml	36629-00	1
18	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
19	Magnetic stirring bar 15 mm, cylindrical	46299-01	1
20	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
21	Magnetic stirring bar, 50 mm, cylindrical	46299-03	1
22	Separator for magnetic bars	35680-03	1
23	Lab thermometer, -10..+100 °C	38056-00	1
24	Weather monitor, 6 lines LCD	87997-10	1
25	Rubber tubing, i.d. 6 mm	39282-00	3
26	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	2
27	Filtration stand for 2 funnels	33401-88	1
28	Funnel, glass, top dia. 80 mm	34459-00	1
29	Circular filter, d 150 mm, 100 pcs	32977-06	1
30	Powder funnel, upper dia. 65mm	34472-00	1
31	Spoon, special steel	33398-00	1
32	Microspoon, steel	33393-00	1
33	Wash bottle, plastic, 500 ml	33931-00	1
34	Rubber stopper, d = 22/17 mm, 1 hole	39255-01	1
35	Quartz glass wool 10 g	31773-03	1
36	Calcium chloride, granul. 250 g	48021-25	1
37	N-propyl bromide 250 ml	31756-25	1
38	Tetrahydrofuran 1000 ml	31883-70	1
39	Potassium hydroxide pellets, 500 g	30103-50	1
40	Magnesium, turnings, grignard 50 g	30134-05	1
41	Iodine resublimed 25 g	30093-04	1
42	Water, distilled 5 l	31246-81	1

Tasks

Investigate the reaction of n-propyl bromide with magnesium turnings in tetrahydrofuran.

Setup and procedure



Safety information

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First aid: Wash the affected skin areas with water and soap. Let splashes to the eyes evaporate with the lid gap wide open (blow carefully into the eyes). Then, rinse the eyes with water.

If inhaled: Fresh air.

Disposal: Solutions must be diluted with water, neutralised (pH 6-8), and flushed away.

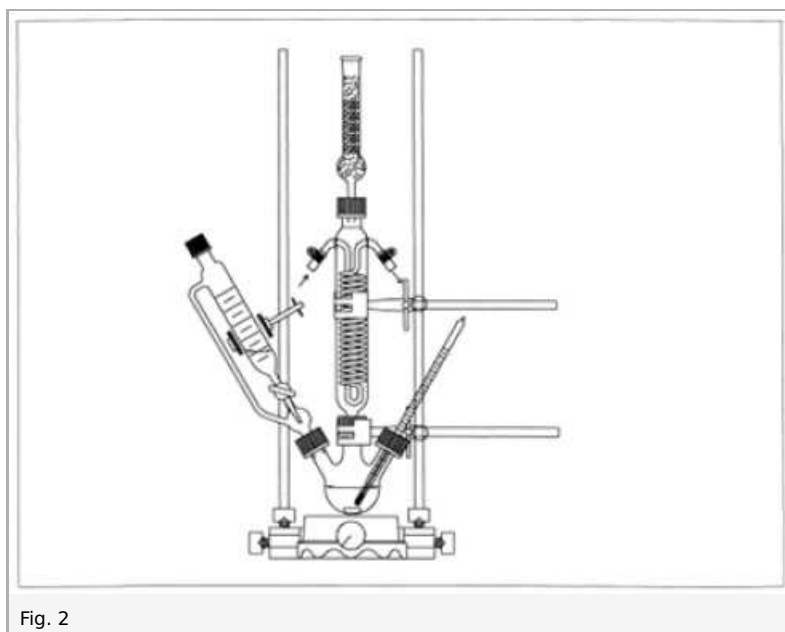
Halogen-containing compounds and solutions must be collected separately from other organic substances in their own collecting vessel that is marked accordingly.

Procedure

In order to dry the tetrahydrofuran, fill it into a bottle and add some potassium hydroxide flakes so that the bottom is covered approximately 1 to 2 cm high. Seal the bottle and shake it. During shaking, open the seal from time to time in order to avoid any excessive pressure inside the bottle. The potassium hydroxide flakes can remain in the bottle. (You can also fill the potassium hydroxide flakes into the original bottle. It is in this way that you will always have dried tetrahydrofuran.)

Fill the calcium chloride tubes with water-free calcium chloride that is secured with quartz glass wool.

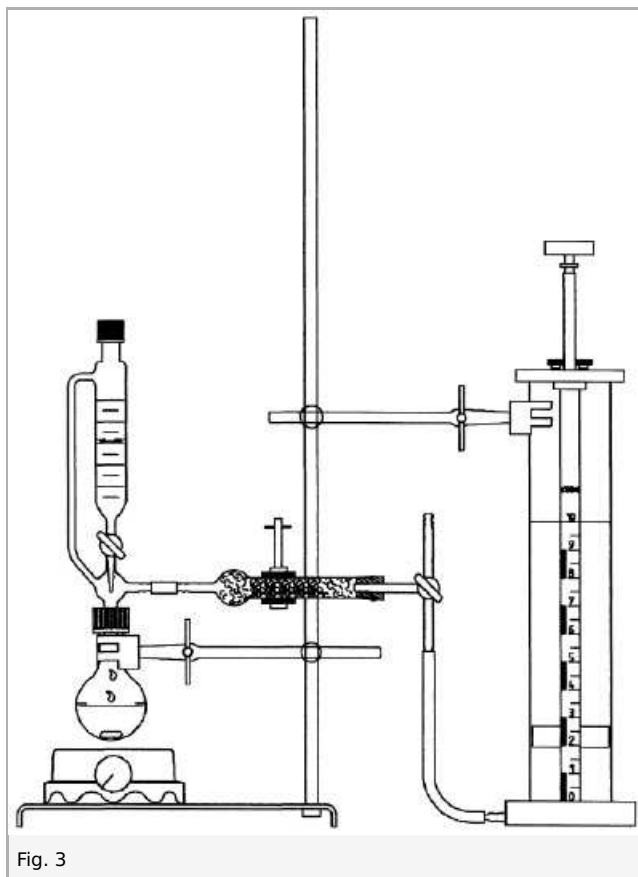
Fill 50 ml of dry tetrahydrofuran into the three-neck flask with a dropping funnel and Dimroth condenser and add approximately 3.6 g of magnesium turnings.



Turn on the cooling water and drip 1.23 g of n-propyl bromide from the dropping funnel carefully into the three-neck flask while stirring. If the reaction does not start after the first drop (the tetrahydrofuran starts to boil), interrupt the dropping process and add a flake of crystalline iodine to the reaction mixture. Continue to drip in the remaining n-propyl bromide after the reaction has started. Let everything cool down and filter the solution quickly into a 100 ml round bottom flask in order to remove the

remaining magnesium turnings. Connect this round bottom flask immediately to the funnel of the gas generator through which water must be dripped carefully to the Grignard solution while stirring. The gas is collected in the gasometer after it has pushed the air out of the apparatus.

If the molar mass of the gas is to be determined, we recommend adjusting a volume at the gasometer prior to the experiment and in accordance with the operating instructions. Under standard conditions, the volume should correspond precisely to one litre. Push this standardised volume of the unknown gas into the plastic bag (shorten the hose of the bag to 10 cm beforehand). Seal the supply hose with a pinchcock and weigh the filled plastic bag. The difference of this mass with regard to the mass of the empty bag (do not forget the mass of the pinchcock) yields the mass of the gas per litre while the buoyancy of the air must also be taken into consideration. The conversion into the molar volume of an ideal mass leads to the molar mass of the gas as a good approximation.



Theory and evaluation

Result

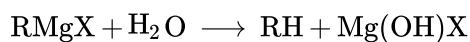
When n-propyl bromide is dripped into a mixture of tetrahydrofuran and magnesium turnings the solvent heats until it boils. In order to determine the molar mass of the gas, the weighing results lead to a mass difference of 0.711 g, for example. Since one litre of air weighs 1.293 g under normal conditions, the mass of the gas is 2.004 g. The conversion into the molar mass results in 44.9 g/mol.

Interpretation

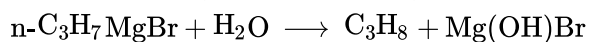
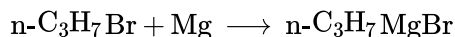
Haloalkanes react with magnesium to the so-called Grignard reagents in accordance with the general formula RMgX . With $\text{X} =$ bromide or iodide, the reaction works best.

Chlorides are usually more inert and require higher temperatures and longer reaction times for the conversion.

The compounds that were discovered by Victor Grignard probably exist as dimeric structures. For reasons of simplicity, however, the formula RMgX is maintained. The carbon-magnesium bond in the Grignard reagents is strongly polarised, with the carbon atom having a negative partial charge. This is the reason for the high level of reactivity with regard to positively polarised centres in other molecules (nucleophilicity). Combined with water, an alkane is formed in an irreversible step.



The reaction sequence of the experiment would be:



Data

Liter mass air: 1.293 g/l

Molar gas volume: 22.414 l/mol

Molar mass propane: 44.10 g/mol