

Toluene: bromination in the nucleus (Item No.: P3101300)

Curricular Relevance

Area of Expertise:
Chemistry**Education Level:**
University**Topic:**
Organic Chemistry**Subtopic:**
Organic Synthesis**Experiment:**
Toluene: bromination
in the nucleus**Difficulty**

Difficult

Preparation Time

10 Minutes

Execution Time

20 Minutes

Recommended Group Size

2 Students

Additional Requirements:

- household aluminium foil

Experiment Variations:**Keywords:**

bromine, toluene, Lewis acid, bromination, distillation

Overview

Short description

Principle

Bromine is polarised and, thereby, activated by zinc chloride as a Lewis acid. It can attach itself in an ionic manner to the toluene nucleus via several complex intermediate stages. Following a dehydrobromination, bromotoluene is formed, i.e. the product of bromination in the nucleus. In the absence of a catalyst and under the influence of light, however, side chain bromination takes place via radical intermediate stages. The reaction can be controlled in a targeted manner by varying the reaction conditions.

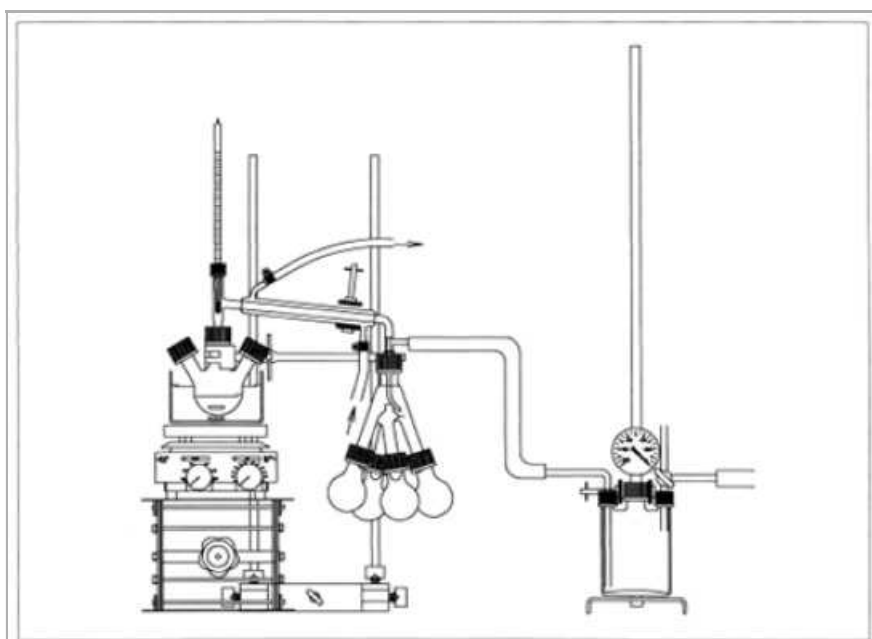


Fig. 1.

Safety instructions



Experiments involving bromine must be performed under an exhaust hood. Bromine vapours irritate the mucous membranes and cause inflammation. Liquid bromine burns the skin.

Bromine must be kept under lock and key. Wear protective gloves when transferring bromine into another vessel.

First aid: Rinse the affected skin areas immediately with plenty of water and ethyl alcohol (petroleum, benzine or similar are also possible).

If inhaled: Fresh air.

Concentrated acids are highly caustic. They burn the skin and destroy textile fabrics. For diluting, first add the water, then the acid (protective glasses, laboratory coat, gloves).

First aid: Rinse the affected skin areas and eyes with the lid gap wide open thoroughly with plenty of water.

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

Dichloromethane (methylene chloride) is a colourless, sparingly water-soluble liquid that decomposes in naked flames and hot surfaces ($\geq 120^{\circ}\text{C}$) while forming irritant, corrosive substances. Degreasing of the skin. Increases the carbon monoxide level in the blood if ingested in small concentrations.

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: Halogen-containing compounds and solutions must be collected separately from other organic substances in their own collecting vessel that is marked accordingly. Collect any solutions that contain heavy-metal ions in a collecting vessel for heavy-metal salt solutions.

Solid residues that contain heavy metals or their ions must also be collected in this vessel.

Silver-containing solutions and solids must be collected in their own collecting vessels (treatment of the silver to obtain silver nitrate).

Bromine

H314: Causes severe skin burns and eye damage.

H330: Fatal if inhaled.

H400: Very toxic to aquatic life.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P273: Avoid release to the environment.

Nitric acid, 65%

H272: May intensify fire; oxidizer.

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Silver nitrate

H272: May intensify fire; oxidizer.

H314: Causes severe skin burns and eye damage.

H410: Very toxic to aquatic life with long-lasting effects.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P221: Take any precaution to avoid mixing with combustibles.

P273: Avoid release to the environment.

Toluene

H225: Highly flammable liquid and vapour.

H304: May be fatal if swallowed and enters airways.

H361d: Suspected of damaging the unborn child.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

Dichloromethane

H315: Causes skin irritation.

H319: Causes serious eye irritation.

H335: May cause respiratory irritation.

P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Zinc chloride

H302: Harmful if swallowed.

H314: Causes severe skin burns and eye damage.

H410: Very toxic to aquatic life with long-lasting effects.

P273: Avoid release to the environment.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

o-bromotoluene

H304: May be fatal if swallowed and enters airways.

H315: Causes skin irritation.

H411: Toxic to aquatic life with long-lasting effects.

P273: Avoid release to the environment.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Hydrogen bromide

H314: Causes severe skin burns and eye damage.

H331: Toxic if inhaled.

H335: May cause respiratory irritation.

P260: Do not breathe dust/fumes/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

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	3
5	Universal clamp	37715-00	3
6	Lab jack, 200 x 200 mm	02074-01	1
7	Round flask, 100 ml, 3-n., 3 x GL25	35677-15	1
8	Closure caps, 10, GL25	41221-03	1
9	Liebig Condenser, with head, GL18/8	35795-15	1
10	Separating funnel, 50ml, GL18	35853-15	1
11	Round bottom flask, 50ml, GL25/12	35840-15	5
12	Adapter for 4 flasks, GL25	35869-15	1
13	Cristallizing dish, boro 3.3, 500ml	46244-00	1
14	Lab thermometer, w. stem, -10..+250C	38061-01	1
15	Magnetic stirrer with heater MR Hei-Standard	35751-93	1
16	Magnetic stirring bar 15 mm, cylindrical	46299-01	1
17	Magnetic stirring bar 30 mm, cylindrical	46299-02	1
18	Magnetic stirring bar, 50 mm, cylindrical	46299-03	1
19	Separator for magnetic bars	35680-03	1
20	Graduated cylinder 25 ml	36627-00	2
21	Beaker, low, BORO 3.3, 400 ml	46055-00	1
22	Secure bottle, 500 ml, 2 x GL 18/8, 1 x 25/12	34170-01	1
23	Spring manometer, 0...-1000 mbar	34170-02	1
24	Glass tube, right-angled, 10 pcs.	36701-52	1
25	Glass tubes, right-angled, 10	36701-57	1
26	Stopcock, 3-way, t-shaped, glass	36731-00	1
27	Water jet pump, plastic	02728-00	1
28	Funnel, glass, top dia. 55 mm	34457-00	1
29	Test tube, 160 x 16 mm, 100 pcs	37656-10	1
30	Test tube rack for 12 tubes, holes d= 22 mm, wood	37686-10	1
31	Pasteur pipettes, 250 pcs	36590-00	1
32	Rubber caps, 10 pcs	39275-03	1
33	Bromine filler w. rubber cap	45100-00	1
34	Rubber gloves, size 10	39324-00	1
35	Teclu burner, DIN, natural gas	32171-05	1
36	Safety gas tubing, DVGW, sold by metre	39281-10	1
37	Lighter f. natural/liquified gases	38874-00	1
38	Hose clip f. 12-20 diameter tube	40995-00	2
39	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	2
40	Spoon, special steel	33398-00	1
41	Glass rod, boro 3.3, l=300mm, d=7mm	40485-05	1
42	Wash bottle, plastic, 500 ml	33931-00	1
43	Rubber tubing, i.d. 6 mm	39282-00	3
44	Rubber tubing, vacuum, i.d. 6mm	39286-00	2
45	Silicone oil 500 ml	31849-50	1
46	Dichloromethane 250 ml	31255-25	1
47	Toluene 250 ml	30236-25	1
48	Bromine 100 ml	30046-10	1
49	Zinc chloride, dry, 250 g	31983-25	1
50	Silver nitrate, cryst. 15 g	30222-00	1
51	Nitric acid, 65% 1000 ml	30213-70	1
52	Copper foil, 0.1 mm, 100 g	30117-10	1
53	Water, distilled 5 l	31246-81	1

Tasks

1. Brominate toluene using bromine.
2. Change the reaction conditions to optimize your results.
3. Distillate the resulting mixture.

Setup and procedure

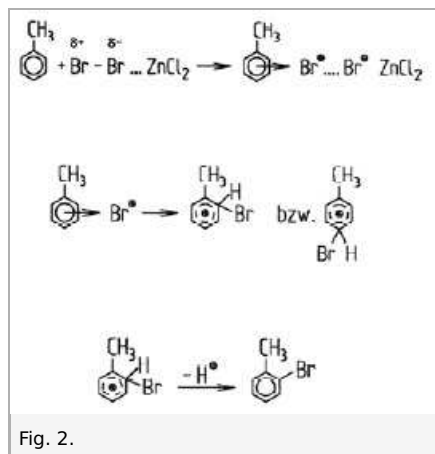


Procedure

In order to perform the reaction without light, cover the distillation flask, i.e. the part that is not immersed in the heating bath, and the dropping funnel with household aluminium foil. Fill the distillate flask to two thirds with dichloromethane. A piece of rubber tubing runs from the hose connector of the vacuum adapter to the rim of the beaker that is three quarters full with water.

Fill approximately 40 ml of toluene and a small quantity of waterfree zinc chloride (covering the tip of a spatula) into the three-neck flask. Fill the dropping funnel with a solution of 10 ml of bromine and 10 ml of toluene and seal the third neck of the flask with a GL 25 sealing cap. Let the bromine solution drip slowly into the content of the flask while stirring. After the start of the reaction, gas flows through the apparatus. This gas is washed by the dichloromethane in the adapter and absorbed by the water in the beaker.

When the reaction is complete, remove the dropping funnel from the three-neck flask and seal this neck also with a sealing cap. Replace the 50 ml round bottom flask with an adapter with four 40 ml round bottom flasks and distil the reaction mixture in the water jet pump vacuum. Put several drops of the distillate onto a thoroughly heated piece of copper foil and heat it over the non-luminous burner flame. Acidify part of the aqueous solution from the beaker in a test tube with diluted nitric acid and add an aqueous silver nitrate solution. As a reference, add some bromine to a toluene sample in a test tube and shake it.



Theory and evaluation

Result

After a short period, a reaction commences that becomes increasingly stronger over time. The gas that is formed dissolves in the water in the beaker while displaying streaks. Caused by the silver nitrate solution, a yellow substance precipitates from the acidified sample.

The bromine vapours that are dragged along during the gas development are dissolved in the dichloromethane. In the water jet pump vacuum (approximately 20 hPa), a liquid passes over at 60°C. A Beilstein test of this liquid leads to a positive result.

The toluol, to which bromine was added, also decolours over time. This reaction, however, is comparatively slow.

Interpretation

Bromine is polarised and, thereby, activated by zinc chloride as a Lewis acid. It can attach itself in an ionic manner to the toluene nucleus via several complex intermediate stages. Following a dehydrobromination, bromotoluene is formed, i.e. the product of bromination in the nucleus.

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Remember:

Cold, catalyst ~ nucleus

Boiling heat, sunlight ~ side chain