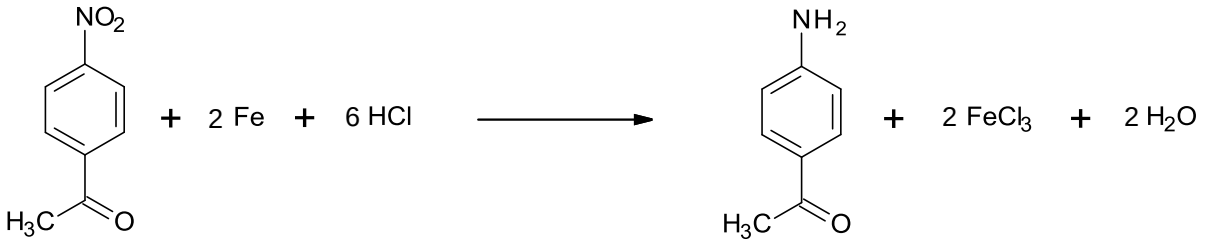
Reduction of 4-Nitroacetophenone

1. Introductory Remarks

The reduction of aromatic nitro compounds to the corresponding aryl amines is an useful chemical transformation since many aryl amines find a multitude of industrial applications, being important intermediates in the production of many pharmaceuticals, photographic materials, agrochemicals, polymers, dyes and rubber materials.
The Bechamp reduction, which is the oldest industrially practiced method, involves the use of finely divided iron metal and water in the presence of an acid.

Follow all safety procedures.
Dispose of the waste material in the labelled containers.

2. Reaction Scheme



[165,15] [55,85] [36,46] [135,17] [162,21] [18,02]

3. Reagents

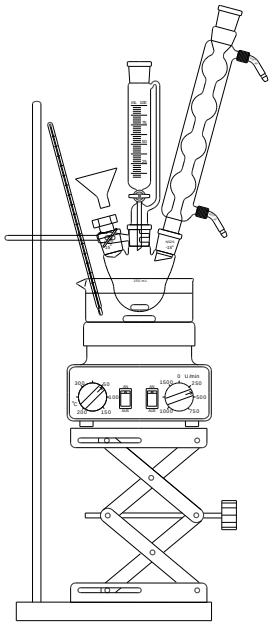
Reagents	Amount		Informations	Safety Information
4-Nitroacetophenone	3,30	g		See MSDS
Iron powder	4,19	g		
Ethanol	70,00	mL		
Hydrochloric acid conc.	15,00	mL		
Ethyl acetate	150	mL		
NaOH solution c=2 mol/L				
Sodium sulfate anhyd.			Drying agent	
n-Hexane			for TLC	
1,2-Propylene glycol			Heating bath	

4. Equipment

4.1. Preparation		***4.2. Isolation***	
Item		**Item**	
3-necked round bottom flask, 250 mL	1	**Extraction**	
Reflux condenser	1	Separatory funnel, 500 mL	1
Dropping funnel	1	Support ring for separatory funnel	1
Glass stopper 29/32	1	Watch glass	1
		Beaker, 250 mL	1
Powder funnel	1	Duran flask, 1000 mL	1
Filtration funnel	1	Büchner funnel	1
		Rubber cone	1
Stirring hot plate	1	Suction flask	1
Stirring bar for preparation	1	Water-jet vacuum pump	
Stirring bar for heating bath	1	pH-paper	
Thermometer, immersion	1		
Crystallizing dish	1	**Distillation**	
Measuring cylinder	1	Round bottom flask, 250 mL	2
		Claisen adapter	1
Laboratory lift	2	Liebig condenser	1
		Receiver adapter with side tube	1
Clamps	4	Cork ring	1
Clamp holders	4	Thermometer with ground glass joint	1
		Glass stopper, 14/23	1
Support stand with rod	2	Gas washing bottle	1
Rubber tubes			

4.3. Purification		***4.4. Characterization***	
Item		**Item**	
Recrystallisation		**Thin layer chromatography**	
Glassware of 4.1 and 4.2		Chromatography jar	1
		Silica plate $Si0_2$-F245	
Desiccator	1	Microcapillary tubes	
		UV lamp	
		Vials	2

5. Procedure

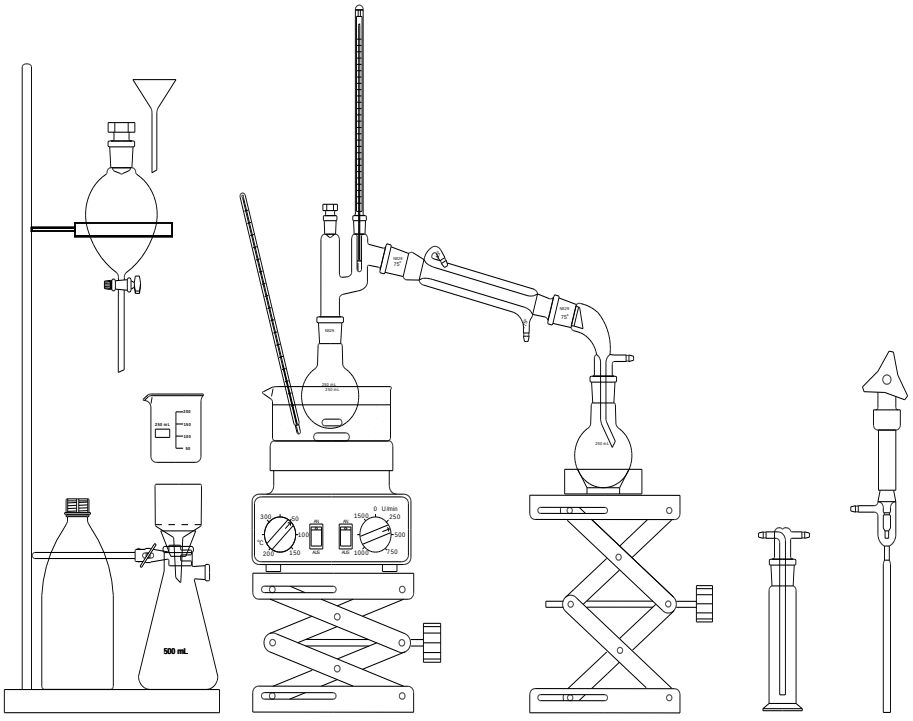


5.1. Preparation

The crystallizing dish is filled with ca. 600 mL of 1,2-propylene glycol (heating bath).
70 mL of ethanol are placed in a 250 mL–three-necked round bottom flask equipped with a reflux condenser, a dropping funnel, a glass stopper and a magnetic stirring bar. 3.30 g (20.0 mmol) of 4-Nitroacetophenone and 4.19 g (75.0 mmol) of iron powder are added. The mixture is heated to 60°C and 15 mL of concentrated hydrochloric acid are added dropwise within 30 min. Subsequently, the reaction mixture is refluxed for 1 hour until the iron powder is mostly dissolved.

5.2. Isolation

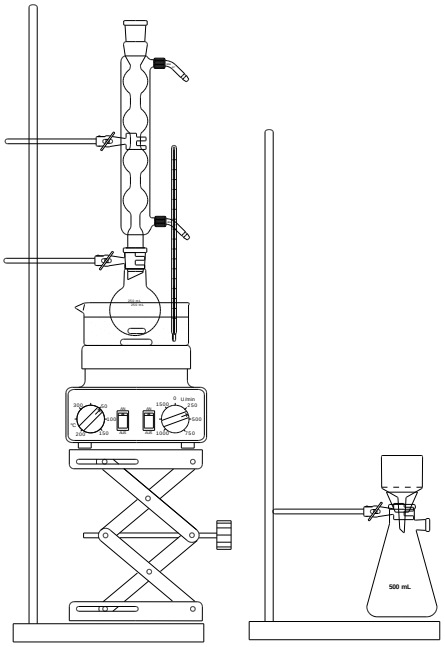
The reaction mixture is cooled down and poured into a 1000 mL Duran flask containing 200 mL of water and a magnetic stirring bar. Stirring is commenced and the solution is neutralized with diluted sodium hydroxide solution (c = 2 mol/L) (formation of iron hydroxide sludge!!). The pH is measured by means of a pH-paper. Subsequently, 150 mL of ethyl acetate are added. Extraction of the organic compounds is achieved by stirring the mixture for 15 min. The stirring process is stopped. Wait until the two phases have separated. Decant most of the upper organic layer into the beaker. The residual extraction liquids are poured into a 500 ml separating funnel. Wait until the two layers have separated. Gently swing the separating funnel in upright position so that the solid iron hydroxide settles out. (Do not shake vigorously, since an emulsion can be formed). Separate the two layers. The combined organic layers are dried over anhydrous sodium sulfate. Subsequently, the drying agent is sucked off.



The organic layer is transferred into a 250 mL round bottom flask which had been weighed. The organic solvent is distilled off under vacuum. Based on the reaction scheme calculate the percent yield of the crude product.

The iron hydroxide contaminated glass-ware can be cleaned with diluted hydrochloric acid.

5.3. Purification



For recrystallisation the as-prepared raw material is boiled in 150 mL of water. The hot solution is filtered under suction through a Büchner funnel. The pure product crystallizes on cooling, is filtered off and dried in a desiccator. Based on the reaction scheme calculate the percent yield of the product.

5.4. Characterization

The purity of the product is determined by means of TLC (Thin Layer Chromatography). Tiny amounts of the organic starting material (4-nitroacetophenone) and the product (4-aminoacetophenone) are dissolved in about 2 mL of ethyl acetate placed in a vial. The diluted solutions are spotted by means of a capillary tube on the stationary phase (silica plate SiO_2-F_{254}). The mobile phase consists of hexane/ethyl acetate (20:80 v/v). After the development of the plate, the spots are visualized by the aid of an UV lamp. The spots are circled with a pencil. Show the plate to the juror. Calculate the corresponding retention factors R_f.