

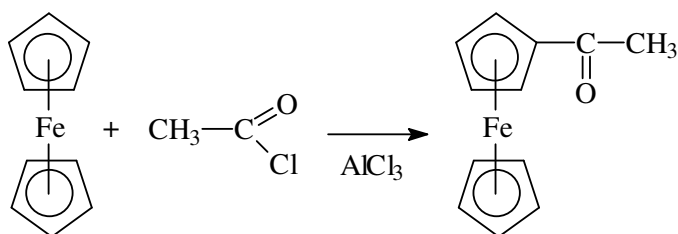
# PREPARATION OF ACETYLFERROCENE

In the year 2001 the chemists celebrate the 50<sup>th</sup> anniversary of the discovery of the first sandwich type organometallic compound – FERROCENE. Since 1951 a great number of the derivatives of this unique compound has been synthesised. Some of them are used as additives to polymers or fuel, some of them can be used as chiral catalysts, others are drugs again anaemia etc.

Chiral organometallic catalysts are many times used in stereoselective synthesis of the desired enantiomerically pure compounds – potential drugs, agrochemicals etc. Acetylferrocene is a suitable starting material for the preparation of enantiomerically pure (S)- or (R)-ferrocenylethylamine.

Acetylferrocene can be prepared by Friedel-Crafts acetylation of ferrocene.

## Reaction scheme:



Reagent	R codes	S codes	Notes
2.80 g (0.015 mol) ferrocene	11-22	16	ready for use
1.26 g (0.016 mol) acetylchloride	11-14-34	9-16-26-45	ready for use
2.20 g (0.0165 mol) anhydrous AlCl <sub>3</sub>	34	7/8-28-45	ready for use
200 cm <sup>3</sup> anhydrous CH <sub>2</sub> Cl <sub>2</sub>	36/37/38	26-36	ready for use
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> ca. 4 g	7-22-31	7/8-26-28-43	ready for use
Anhydrous Na <sub>2</sub> SO <sub>4</sub> ca. 10 g	36/37/38	22-26-36	ready for use
Silicagel for chromatography	36/37	26-36	ready for use
Hexane (eluent for chromatography)	11-48/20	9-16-24/25-29-51	ready for use
Ethyl acetate (eluent for chromatography)	11	16-23-29-33	ready for use
Acetone for washing	11	16-23-29-33	ready for use
Silufol for TLC			
Filter paper			
Crashed ice			

## ATTENTION!

- 1) *Synthesis of acetylferrocene is carried out in anhydrous condition – all parts of the apparatus must be thoroughly dry.*
- 2) *Students should be provided with the standards of ferrocene and acetylferrocene.*
- 3) *Some weighings must be proved and signed in the report by the referee.*

## Procedure:

100 cm<sup>3</sup> three-necked flask equipped with ground-glass stoppers, magnetic stirring bar and Liebig reflux condenser with adapter connected to balloon of argon (**Picture 1**) is purged by argon from the balloon (slightly open one stopper!). To this flask (with closed stopcock of the adapter) 2.80 g (0.015 mol) of ferrocene and 25 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> is quickly added (via powder funnel).

To the stirring solution of ferrocene, freshly distilled acetylchloride 1.26 g (1.1 cm<sup>3</sup>) (0.016 mol) is added from the syringe. Stirred reaction mixture is cooling in the ice bath for 15 min and then 2.20 g (0.0165 mol) of anhydrous AlCl<sub>3</sub> is added in small portions during 15 min. (from the special hooper). The cooling bath is then removed and the reaction mixture is stirred for additional 30 min. at room temperature. The colour of the reaction mixture should turn dark violet.

The formation of the product is checked twice by TLC (using silufol and ethylacetate/hexane 1:1) – firstly after removing the cooling bath (and compare with the standards) and secondly after the reaction is over.

The reaction mixture is then poured on 50 g of crashed ice in 50 cm<sup>3</sup> of water in the beaker. The flask is rinsed with small amount of CH<sub>2</sub>Cl<sub>2</sub> (using Pasteur pipette) and combined layers are transferred into separatory funnel. Organic layer is separated and the water layer is extracted with CH<sub>2</sub>Cl<sub>2</sub>. Combined organic layers are extracted twice with water and finally dried in Erlenmeyer flask (No 1) over ca. 5 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>.

To the combined water layers (dark blue) in the beaker Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is added in small portions till the colour is changed to yellow. The mixture is transferred into separatory funnel and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Organic layer is finally washed with water and dried in Erlenmeyer flask (No 2) over ca. 5 g of anhydrous Na<sub>2</sub>SO<sub>4</sub>.

The third TLC is prepared – comparing products in the flasks No1 and No 2. *All three chromatograms should be shown to the referee who should sign it in the Answer sheet.*

In the mean time chromatographic column is prepared – using 25.0 g of silicagel and hexane as the eluent (**Picture 2**).

Four (No 3, No 4, No 5 and No 6) empty 100 cm<sup>3</sup> round bottom flasks and three Petri dishes (No 7, No 8, No 9) are weighted.

To the flask No 3, equipped with magnetic stirring bar the solution from the Erlenmeyer flask No 2 is then filtered. Na<sub>2</sub>SO<sub>4</sub> on the filter is washed by CH<sub>2</sub>Cl<sub>2</sub>. The solvent is distilled off via Liebig condenser under continuous stirring (using magnetic stirrer and heater unit – **Picture 3**). After distillation is over, the stirring bar is removed, the flask with the dry solid residue is weighted and the amount of the products (to be separated by column chromatography), is calculated. (If the solid material is not dry enough, put the flask into fume-hood for a while – to evaporate last traces of the solvent.)

The solid material in the flask No 3 is dissolved in small amount of ethylacetate / hexane (1:1) mixture and the solution is transferred, using Pasteur pipette, onto chromatographic column. The same mixture is used as the eluent. Eluent from interlayers is collected into Erlenmeyer flasks. (The solutions from those flasks are collected in a prepared bottle.) Orange-yellow ferrocene solution is collected into previously weighted 100 cm<sup>3</sup> round bottom flask No 4 and reddish acetylferrocene solution is collected in the flask No 5.

The solvent from the flasks No 4 and No 5 is distilled off as described before. After distillation is over, the stirring bar is taken of, the flask with the dry residue is weighted and the amount of the product is calculated.

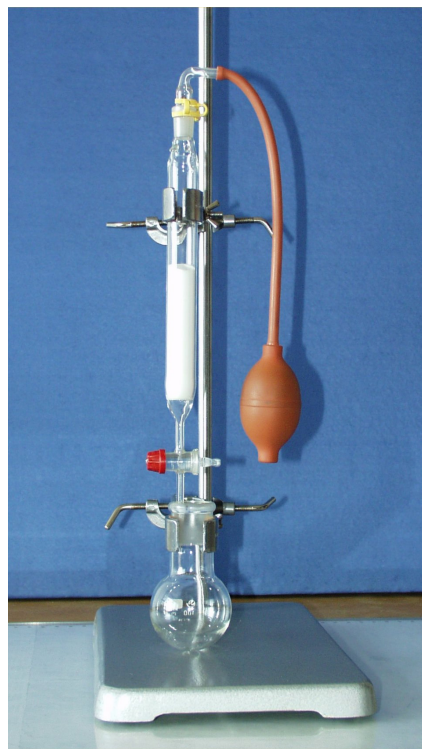
Finally the solution from the Erlenmeyer flask No 1 is filtered into previously weighted round bottom flask No 6 and the solvent is distilled off as described before. The flask with the dry residue is weighted and the amount of the product No 1 is calculated.

The products from the flasks No 4, No 5 and No 6 are transferred by spatula on the previously weighed Petri dishes No 7, No 8 and No 9 and the amount of the product is checked once more.

***In the case of spare time, ferrocene and acetylferrocene can be crystallized from hexane / ethylacetate mixture.***



Picture 1.



Picture 2



Picture 3.

Photo: J. Marák, R. Šebesta,