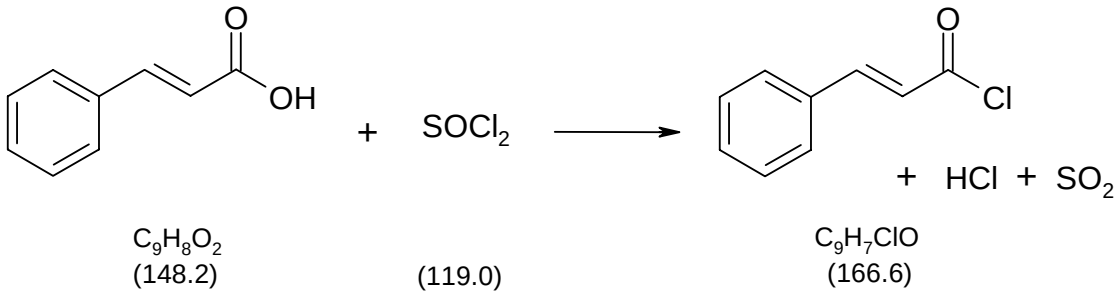
2013 Reaction of cinnamic acid with thionyl chloride to cinnamoyl chloride



Classification

Reaction types and substance classes
reaction of the carbonyl group in carboxylic acids
carboxylic acid, carboxylic acid chloride

Work methods
Working with moisture exclusion, stirring with magnetic stir bar, draining of gases, working with wash bottles, distilling under reduced pressure, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment
100 mL three-neck flask, reflux condenser, bubble counter, 2 wash bottles, distillation apparatus, heatable magnetic stirrer, magnetic stir bar, hot-air dryer, vacuum pump, oil bath

Substances

trans-cinnamic acid (mp 135-136 °C)	14.8 g (100 mmol)
thionyl chloride (freshly distilled) (bp 76 °C)	17.8 g (10.9 mL, 150 mmol)
aqueous solution of sodium hydroxide (20%)	100 mL

Reaction
The reaction apparatus consists of a 100 mL three-neck flask with magnetic stir bar and reflux condenser. For draining of the evolving gases HCl and SO_2 the reflux condenser is connected consecutively to a bubble counter filled with paraffin oil, an empty safety wash bottle and a wash bottle filled with 100 mL of an aqueous solution of sodium hydroxide (20%).

The reaction flask is charged with 17.8 g (10.9 mL, 150 mmol) freshly distilled thionyl chloride. Whilst stirring, 14.8 g (100 mmol) *trans*-cinnamic acid is added in several portions by means of a powder funnel. The last added portions are firstly insoluble, accordingly stirring with the magnetic stirrer is temporarily not possible. The remaining flask openings are closed with stoppers and the reaction mixture is initially slowly heated whilst stirring (as far

as possible) in an oil bath (strong formation of gas!) up to 50 °C bath temperature, afterwards stirring is continued for 2 additional hours at 80 °C bath temperature.

Work up

After the cooling down of the reaction mixture, the reflux condenser is replaced by a distillation bridge and the excess of thionylchloride is removed by distillation under reduced pressure (about 20 hPa). A trap between apparatus and vacuum pump, which is cooled with liquid nitrogen is used to condensate the thionyl chloride. A yellowish solid remains as residue.
Crude yield: 13.5 g (81.0 mmol, 81%); mp 30-33 °C

The crude acid chloride is for most uses pure enough, so that one can do without distillation.

For further purification a fractional distillation at 1 hPa is required. A trap between apparatus and vacuum pump, which is cooled with liquid nitrogen serves to condensate the last amounts of thionyl chloride. To avoid a crystallization of the product in the condenser of the distillation bridge, it is only air-cooled and, if necessary, the condenser is briefly heated with a hot-air dryer. The product is a colourless, strong refractive liquid, which crystallizes whilst cooling as a colourless solid product.

Yield: 12.2 g (73.2 mmol, 73%); bp 75-80 °C (0.1 hPa), mp 30-33 °C
Distillation residue: about 1 g of a brown solid

Comments

In experiment Number 2017 this product is used as educt.

One should calculate the volume of the NaOH-solution in the wash bottle so that the building gases HCl and SO_2 are completely absorbed.

Waste management

Waste disposal

Waste	Disposal
excess of thionyl chloride	dissolve in diluted aqueous NaOH-solution, then: aqueous waste, alkaline
solution from the wash bottle	aqueous waste, alkaline
distillation residue	dissolve in a small amount of acetone, then: organic solvents, containing halogen

Time

Without distillation about 4 hours, distillation 1 hour

Break

Before distillation of the thionyl chloride

Degree of difficulty

Medium

Instruction (batch scale 10 mmol)

Equipment

50 mL two-neck flask, reflux condenser, bubble counter, 2 wash bottles, distillation apparatus, heatable magnetic stirrer, magnetic stir bar, hot-air dryer, vacuum pump, oil bath

Substances

trans-cinnamic acid (mp 135-136 °C)	1.48 g (10.0 mmol)
thionyl chloride (freshly distilled) bp 76 °C)	1.8 g (1.1 mL, 15 mmol)
aqueous solution of sodium hydroxide (20%)	20 mL

Reaction

The reaction apparatus consists of a 50 mL two-neck flask with magnetic stir bar and reflux condenser. For draining the evolving gases HCl und $SO_{2,}$ the reflux condenser is connected consecutively to a bubble counter filled with paraffin oil, an empty safety wash bottle and a wash bottle filled with 20 mL of an aqueous solution of sodium hydroxide (20%).

The reaction flask is charged with 1.8 g (1.1 mL, 15 mmol) freshly distilled thionyl chloride. Whilst stirring 1.48 g (10.0 mmol) *trans*-cinnamic acid are added by means of a powder funnel in several portions. The remainig flask openings are closed with stoppers and the reaction mixture is initially slowly heated in an oil bath (strong formation of gas!) up to 50 °C bath temperature, afterwards stirring is continued for two additional hours at 80 °C bath temperature.

Work up

After cooling down of the reaction mixture the reflux condenser is replaced by a distillation bridge and the excess of thionyl chloride is removed by distillation under reduced pressure (about 20 hPa). A trap between apparatus and vacuum pump, which is cooled with liquid nitrogen is used to condensate the thionyl chloride. A yellowish solid remains as residue.
Crude yield 1.40 g (8.40 mmol, 84%); mp 30-33 °C

The crude acid chloride is pure enough for most uses, so that one can do without distillation. According to the used apparatus the distillation at the small batch scale is loss making.

If a further purification of the crude product is required, it is distilled at 1 hPa.. A trap between apparatus and vacuum pump, which is cooled with liquid nitrogen, serves to condensate the last amounts of thionyl chloride. To avoid a crystallization of the product in the condenser of the distillation bridge, it is only air-cooled and, if necessary, the condenser is briefly heated with a hot-air dryer. The product is a colourless, strong refractive liquid, which crystallizes whilst cooling as a colourless solid.

Yield: 950 mg (5.70 mmol, 57%); Sdp 75-80 °C (0.1 hPa), mp 30-33 °C
Distillation residue: small amount of a brown solid

Comments

In experiment Number 2017 this product is used as educt.

One should calculate the volume of the NaOH-solution in the wash bottle so that the building gases HCl and SO_2 are completely absorbed.

Waste management

Waste disposal

Waste	Disposal
excess of thionyl chloride	dissolve in diluted aqueous NaOH-solution, then: aqueous waste, alkaline
solution from wash bottle	aqueous waste, alkaline
distillation residue	dillute in a small amount of acetone, then: organic solvents, containing halogen

Time
Without distillation about 3.5 hours, distillation 30 minutes

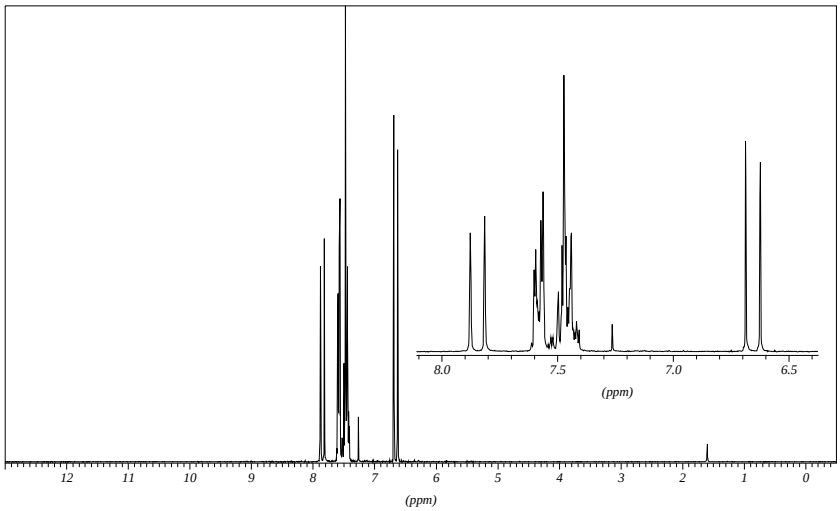
Break
Before distillation of the thionyl chloride

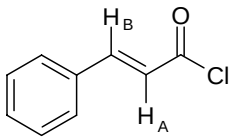
Degree of difficulty
Medium

Analytics

Reaction control
The end of gas formation is a rough indicator for the end of reaction.

^{1}H NMR spectrum of the pure product (250 MHz, $CDCl_3$)

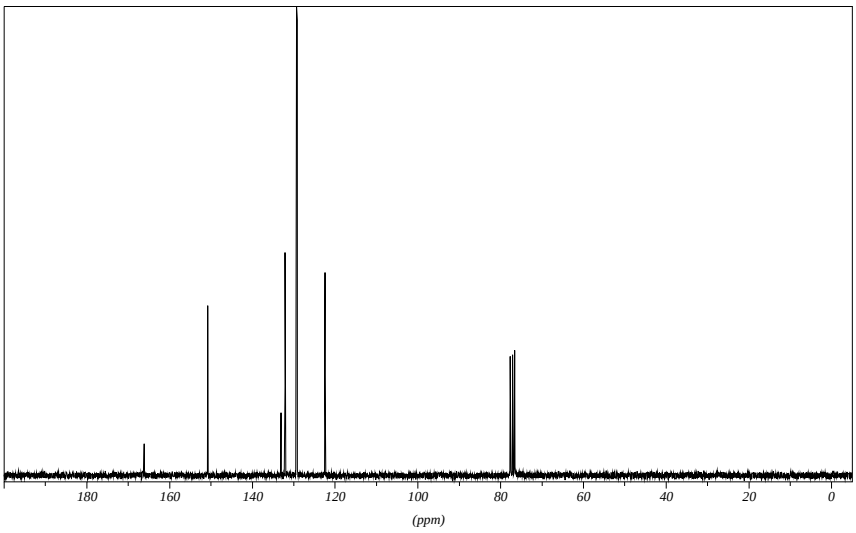




δ (ppm)	Multiplicity	Connection constant (Hz)	Number of H	Assignment
6.64	D	J_{AB} = 15.5	1	H_A
7.39 – 7.61	M		5	CH arene
7.85	D	J_{AB} = 15.5	1	H_B

The ^{1}H NMR-Spectrum of the undistilled acid chloride is identical with that of the pure product.

^{13}C NMR spectrum of the pure product (250 MHz, $CDCl_3$)



δ (ppm)	Assignment
122.38	– CH = **C**H – COCl
129.13	**C**H aromatic
129.28	**C**H aromatic
132.07	**C**H aromatic
133.06	$\mathbf{C}_{quart}$ aromatic
150.75	– **C**H = CH – COCl
166.16	– **C**OCl
76.5-77.5	solvent