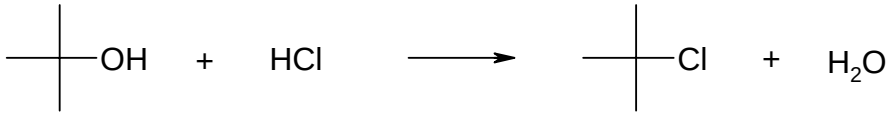
4026 Synthesis of 2-chloro-2-methylpropane (tert-butyl chloride) from tert-butanol



$C_4H_{10}O$ (74.1) | (36.5) | C_4H_9Cl (92.6)

Classification

Reaction types and substance classes
nucleophilic substitution
chloroalkane, alcohol

Work methods
stirring with magnetic stir bar, column distillation, filtering, use of an ice cooling bath, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment
10 mL two-neck flask, reflux condenser, bubble counter, heatable magnetic stirrer, magnetic stir bar, ice bath, separating funnel, distillation apparatus, 10 cm Vigreux column

Substances

tert-butanol (bp 82-83 °C)	741 mg (0.950 mL, 10.0 mmol)
hydrochloric acid (conc., 36%)	3.04 g (2.56 mL, 30.0 mmol)
sodium chloride	
sodium sulfate for drying	

Reaction
3.0 g (2.6 mL, 30 mmol) conc. hydrochloric acid are filled in a 10 mL two-neck flask equipped with a magnetic stir bar and a reflux condenser with bubble counter (filled with paraffin oil). The mixture is cooled in an ice bath. Under further cooling and strong stirring 741 mg (0.950 mL, 10.0 mmol) *tert*-butanol are added. The reaction mixture is stirred over night at room temperature.

Work up
Sodium chloride is added to the reaction mixture until the aqueous phase is saturated. The phases are separated with a separating funnel, the organic phase is dried with sodium sulfate.

After the drying agent has been filtered off, the crude product is distilled over a 10 cm Vigreux column at normal pressure, leading to only one product fraction.
Yield: 639 mg (6.90 mmol, 69%); bp 50–52 °C, colourless liquid; n_D^{20} = 1.384

Comments
A small amount of unreacted *tert*-butanol can be detected in the crude product. After the distillation only few side products (< 5%) are detectable. A small amount of isobutene is formed during the reaction.

Waste management

Waste disposal

Waste	Disposal
aqueous phases	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time
4 hours

Break
Before distillation

Degree of difficulty
Easy

Instruction (batch scale 100 mmol)

Equipment
100 mL three-neck flask, reflux condenser, bubble counter, heatable magnetic stirrer, magnetic stir bar, ice bath, separating funnel, distillation apparatus, 10 cm Vigreux column

Substances

tert-butanol (bp 82-82 °C)	7.41 g (9.50 mL, 100 mmol)
hydrochloric acid (conc., 36%).	30.4 g (25.6 mL, 300 mmol)
sodium chloride	
sodium sulfate for drying	

Reaction
30.4 g (25.6 mL, 300 mmol) conc. hydrochloric acid are filled in a 100 mL three-neck flask equipped with a magnetic stir bar and a reflux condenser with bubble counter (filled with paraffin oil). The mixture is cooled in an ice bath. Under further cooling and strong stirring 7.41 g (9.50 mL, 100 mmol) *tert*-butanol are added. The reaction mixture is stirred over night at room temperature.

Work up
Sodium chloride is added to the reaction mixture until the aqueous phase is saturated. The phases are separated with a separating funnel, the organic phase is dried with sodium sulfate. After the drying agent has been filtered off, the crude product is distilled over a 10 cm Vigreux column at normal pressure, leading to only one product fraction.
Yield: 7.60 g (82.1 mmol, 82%); bp 50–52 °C, colourless liquid; n_D^{20} = 1.3858

Comments
A small amount of unreacted *tert*-butanol can be detected in the crude product. After the distillation only few side products (< 5%) are detectable. A small amount of isobutene is formed during the reaction.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time
4 hours

Break
Before distillation

Degree of difficulty
Easy

Instruction (batch scale 1 mol)

Equipment
500 mL three-neck flask, reflux condenser, bubble counter, heatable magnetic stirrer, magnetic stir bar, ice bath, separating funnel, distillation apparatus, 10 cm Vigreux column

Substances

tert-butanol (bp 82-82 °C)	74.1 g (95.0 mL, 1.00 mol)
hydrochloric acid (conc., 36%)	304 g (256 mL, 3.00 mol)
sodium chloride	
sodium sulfate for drying	

Reaction
304 g (256 mL, 3.00 mol) concentrated hydrochloric acid are filled in a 500 mL three-neck flask equipped with a magnetic stir bar and a reflux condenser with bubble counter (filled with paraffin oil). The mixture is cooled in an ice bath. Under further cooling and strong

stirring 74.1 g (95.0 mL, 1.00 mol) *tert*-butanol are added. The reaction mixture is stirred over night at room temperature.

Work up
Sodium chloride is added to the reaction mixture until the aqueous phase is saturated. The phases are separated with a separating funnel, the organic phase is dried with sodium sulfate. After the drying agent has been filtered off, the crude product is distilled over a 10 cm Vigreux column at normal pressure, leading to only one product fraction.
Yield: 78.1 g (843 mmol, 84%); bp 50–52 °C, colourless liquid; n_D^{20} = 1.384

Comments
A small amount of unreacted *tert*-butanol can be detected in the crude product. After the distillation only few side products (< 5%) are detectable. A small amount of isobutene is formed during the reaction.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
distillation residue	organic solvents, containing halogen
sodium sulfate	solid waste, free from mercury

Time
5 hours

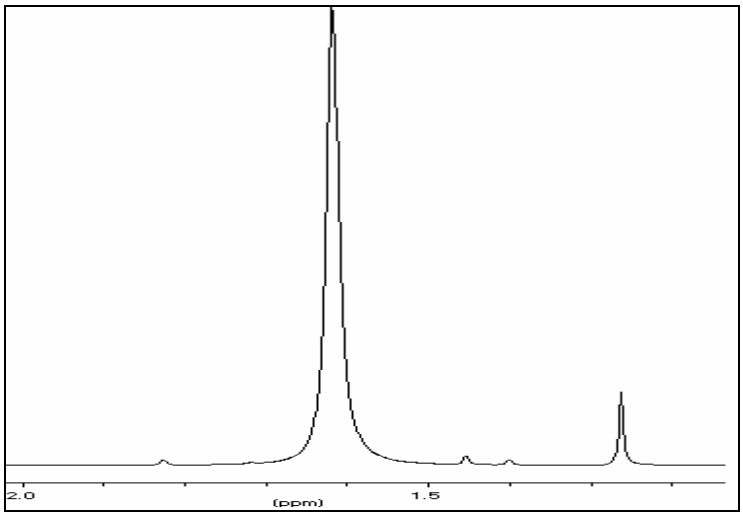
Break
Before distillation

Degree of difficulty
Easy

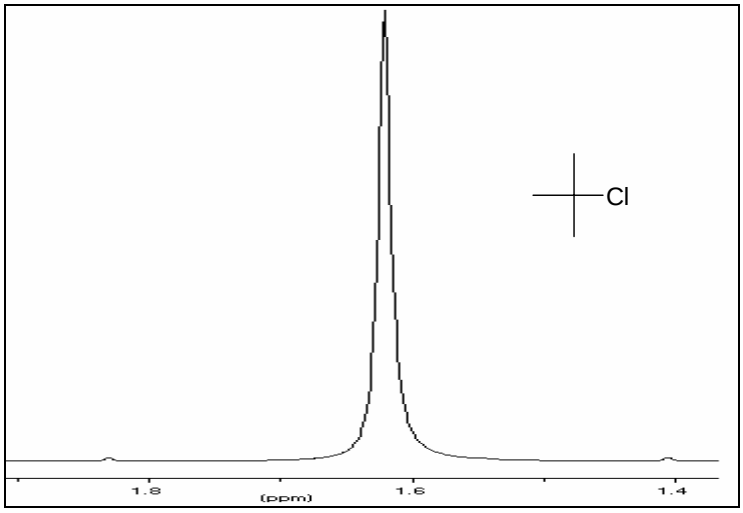
Analytics

Reaction monitoring with IR spectroscopy
1 g of the organic phase is taken from the reaction mixture and distilled over a short-path still. The distillate is used undiluted for the IR spectroscopy. The lacking of the OH-band at about 3400 cm^{-1} indicates, that the reaction is complete.

^{1}H NMR spectrum of the crude product (300 MHz, $CDCl_3$)



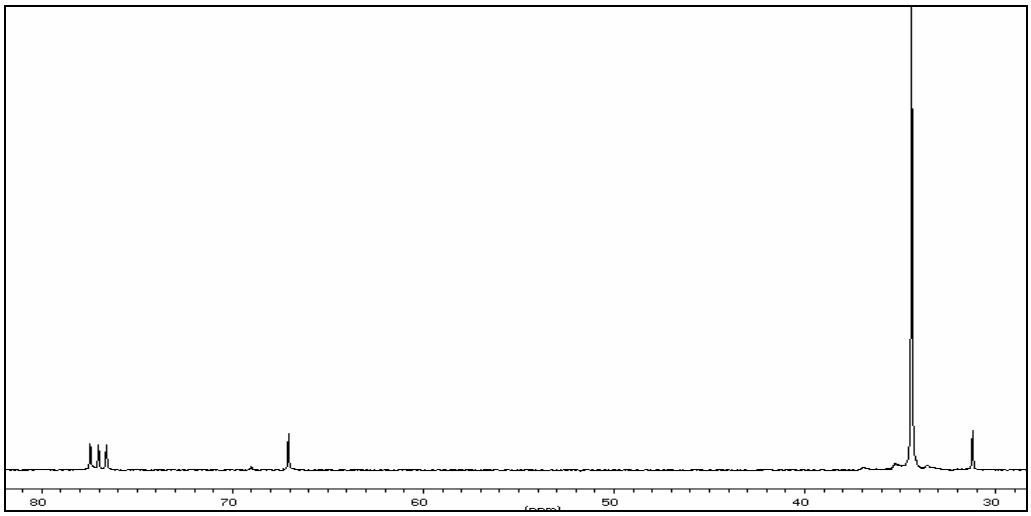
^{1}H NMR spectrum of the pure product (300 MHz, $CDCl_3$)



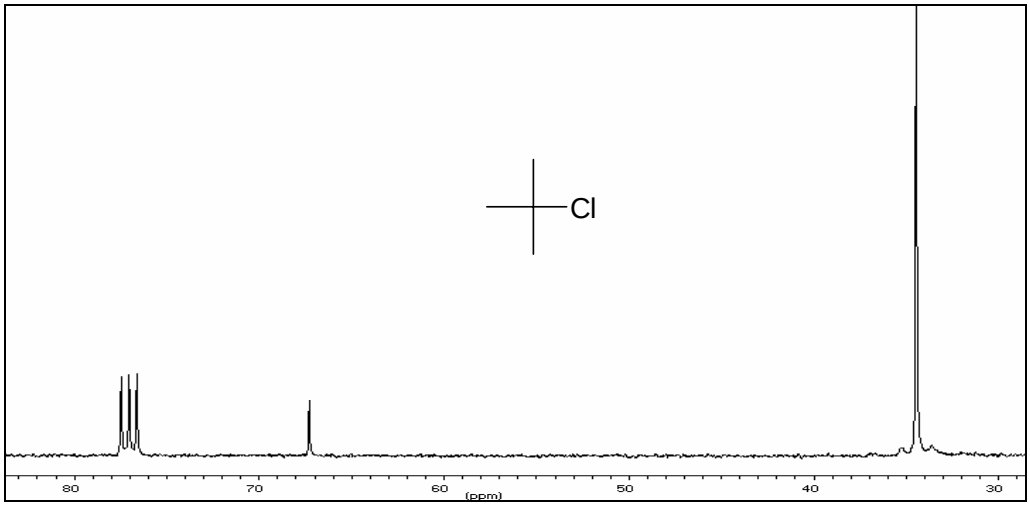
δ (ppm)	Multiplicity	Number of H	Assignment
1,62	s	9	CH_3

The ^{1}H NMR spectrum of the crude product shows at 1.27 ppm the signal for the methylgroups of *tert*-butanol.

^{13}C NMR spectrum of the crude product (75.5 MHz, $CDCl_3$)



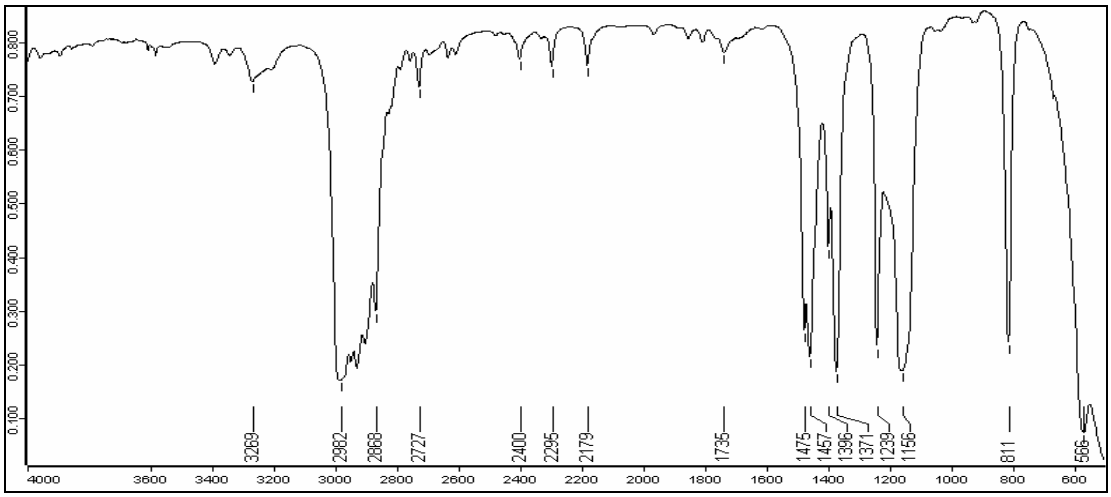
^{13}C NMR spectrum of the pure product (75.5 MHz, $CDCl_3$)



δ (ppm)	Assignment
67.25	**C**-CH_3
34.43	CH_3
76.5-77.5	solvent

The ^{13}C NMR-spectrum of the crude product shows at 31.3 ppm the signal for the methylgroups of *tert*-butanol.

IR spectrum of the pure product (film)



cm^{-1}

(cm^{-1})	**Assignment**
2982, 2868	C-H-valence, alkane
1457	C-H-deformation
811	C-Cl-valence