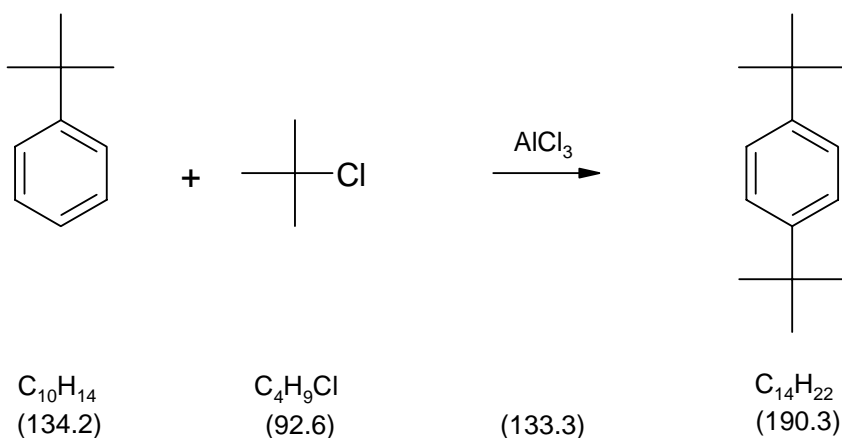


1011 Synthesis of 1,4-di-*tert*-butylbenzene from *tert*-butylbenzene and *tert*-butyl chloride



Classification

Reaktionstypen und Stoffklassen

electrophilic substitution of aromatics, Friedel-Crafts alkylation
 aromatic, alkylaromatic, chloralkane, acid catalysator

Work methods

working with moisture exclusion, working with wash bottles, draining of gases, stirring with magnetic stir bar, extracting, shaking out, filtering, evaporating with rotary evaporator, use of an ice cooling bath, recrystallizing, heating with oil bath

Instruction (batch scale 10 mmol)

Equipment

protective gas supply, 100 mL three-neck flask, internal thermometer, drying tube with gas draining, adapter with ground glass joint, ground-in stopcock and hose coupling, 2 wash bottles, heatable magnetic stirrer, magnetic stir bar, 250 mL separating funnel, rotary evaporator, 50 mL round bottom flask, reflux condenser, desiccator, ice/sodium chloride cooling bath, oil bath

Substances

<i>tert</i> -butylbenzene (bp 64 °C/27 hPa)	1.34 g (1.54 mL, 10.0 mmol)
<i>tert</i> -butyl chloride (bp 51 °C)	1.85 g (2.10 mL, 20.0 mmol)
aluminium chloride (water free)	100 mg (0.75 mmol)
<i>tert</i> -butyl methyl ether (bp 55 °C)	30 mL
methanol (bp 65 °C) for recrystallizing	about 8 mL
aqueous sodium hydroxide solution (10%)	about 50 mL
potassium carbonate for drying	
ice	

Reaction

The reaction apparatus consists of a well-dried 100 mL three-neck flask with magnetic stir bar, internal thermometer and a drying tube connected with a hose for gas draining. The third flask opening is equipped with an adapter with ground glass joint, ground-in stopcock and hose coupling to the nitrogen piping. The hose for gas draining is connected with an empty safety wash bottle and this one is connected with a second wash bottle containing about 50 mL of a 10% sodium hydroxide solution.

The reaction flask is rinsed with nitrogen, before 1.34 g (1.54 mL, 10.0 mmol) *tert*-butylbenzene and 1.85 g (2.10 mL, 20.0 mmol) *tert*-butyl chlorid are filled into the flask. The mixture is cooled down in an ice/sodium chloride bath to 0°C. The internal thermometer is removed for a short time and 200 mg water free aluminium chloride are added under strong stirring through the flask opening over a powder funnel. A solid light-yellow reaction mixture is formed. The cooling bath is removed and the reaction mixture is immediately worked up.

Work up

To the reaction mixture are added 20 g finely crunched ice, 10 mL water and 20 mL *tert*-butyl methyl ether. The mixture is transferred into a separating funnel and strongly shaken. The organic phase is separated and the aqueous phase is shaken once more with 10 mL *tert*-butyl methyl ether. The combined organic phases are washed in the separating funnel with 20 mL water and then are dried over potassium carbonate. The drying substance is filtered off and the solvent is evaporated. A colourless crystalline residue remains as crude product.

Crude yield: 2.24 g

The crude product is recrystallized from about 8 mL methanol. For crystallization of the product the solution is kept at room temperature; a cooling in the ice bath would lead to more crystallized side products. The product is sucked off over a Buechner funnel and dried in the desiccator over phosphorus pentoxide.

Yield: 1.39 g (7.30 mmol, 73%); mp 76-77 °C, colourless needles; GC purity: 99% (see analytics)

Comments

The 1,4-di-*tert*-butylbenzene is the result of the kinetic product control. It crystallizes under the reaction conditions and thereby avoiding a further alkylation and isomerisation. The 1,3,5-tri-*tert*-butylbenzene is the thermodynamical most stable product, which can be formed from the educts.

Waste management**Recycling**

The evaporated *tert*-butyl methyl ether is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous phases from shaking out	solvent water mixtures, containing halogen
mother liquor	organic solvents, containing halogen
potassium carbonate	solid waste, free from mercury

Time

2-3 hours

Break

Before recrystallizing

Degree of difficulty

Easy

Instruction (batch scale 100 mmol)**Equipment**

protective gas supply, 250 mL three-neck flask, internal thermometer, drying tube with gas draining, adapter with ground glass joint, ground-in stopcock and hose coupling, 2 wash bottles, heatable magnetic stirrer, magnetic stir bar, 500 mL separating funnel, rotary evaporator, 250 mL round bottom flask, reflux condenser, desiccator, ice/sodium chloride cooling bath, oil bath

Substances

<i>tert</i> -butylbenzene (bp 64 °C/27 hPa)	13.4 g (15.4 mL, 100 mmol)
<i>tert</i> -butyl chloride (bp 51 °C)	18.5 g (21.0 mL, 200 mmol)
aluminium chloride (water free)	1.0 g (7.5 mmol)
<i>tert</i> -butyl methyl ether (bp 55 °C)	80 mL
methanol (bp 65 °C) for recrystallizing	about 60 mL
aqueous sodium hydroxide solution (10%)	about 150 mL
potassium carbonate for drying	
ice	

Reaction

The reaction apparatus consists of a well-dried 250 mL three-neck flask with magnetic stir bar, internal thermometer and a drying tube connected with a hose for gas draining. The third flask opening is equipped with an adapter with ground glass joint, ground-in stopcock and hose coupling to the nitrogen piping. The hose for gas draining is connected with an empty safety wash bottle and this one is connected with a second wash bottle containing about 150 mL of a 10% sodium hydroxide solution.

The reaction flask is rinsed with nitrogen, before 13.4 g (15.4 mL, 100 mmol) *tert*-butylbenzene and 18.5 g (21.0 mL, 200 mmol) *tert*-butyl chloride are filled into the flask. The mixture is cooled down in an ice/sodium chloride bath to 0°C. 1.0 g water free aluminium chloride are added in four portions with two-minute time intervals under strong stirring. For each addition the internal thermometer is removed for a short time and the aluminium chloride is added over a powder funnel. A solid light-yellow reaction mixture is formed. The cooling bath is removed and the reaction mixture is immediately worked up.

Work up

To the reaction mixture are added 50 g finely crunched ice, 20 mL water and 40 mL *tert*-butyl methyl ether. The mixture is transferred into a separating funnel and strongly shaken. The organic phase is separated and the aqueous phase is shaken once more with 40 mL *tert*-butyl methyl ether. The combined organic phases are washed in the separating funnel with 20 mL water and then are dried over potassium carbonate. The drying substance is filtered off and the solvent is evaporated. A colourless crystalline residue remains as crude product.

Crude yield: 21.3 g

The crude product is recrystallized from about 60 mL methanol. For crystallization of the product the solution is kept at room temperature; a cooling in the ice bath would lead to more crystallized side products. The product is sucked off over a Buechner funnel and dried in the desiccator over phosphorus pentoxide.

Yield: 14.4 g (75.6 mmol, 77 %); mp 76-77 °C, colourless needles; GC purity: 98% (see analytics)

Comments

The 1,4-di-*tert*-butylbenzene is the result of the kinetic product control. It crystallizes under the reaction conditions and thereby avoiding a further alkylation and isomerisation. The 1,3,5-tri-*tert*-butylbenzene is the thermodynamical most stable product, which can be formed from the educts.

Waste management**Recycling**

The evaporated *tert*-butylmethylether is collected and redistilled.

Waste disposal**Waste disposal**

Waste	Disposal
aqueous phases from shaking out	solvent water mixtures, containing halogen
mother liquor	organic solvents, containing halogen
potassium carbonate	solid waste, free from mercury

Time

4-5 hours

Break

Before recrystallizing

Degree of difficulty

Easy

Analytics

GC

Sample Preparation:

A sample of the substance is diluted in 1 mL dichloromethane.

GC-conditions:

column: ZB-1, 7 HM-G001-115CB, length 30 m, internal diameter 0.32 mm, film 0.25 μm

inlet: injector temperature 210 $^{\circ}\text{C}$, split injection, injected volume 1 μL

carrier gas: H_2 , pre-column pressure 50 kPa

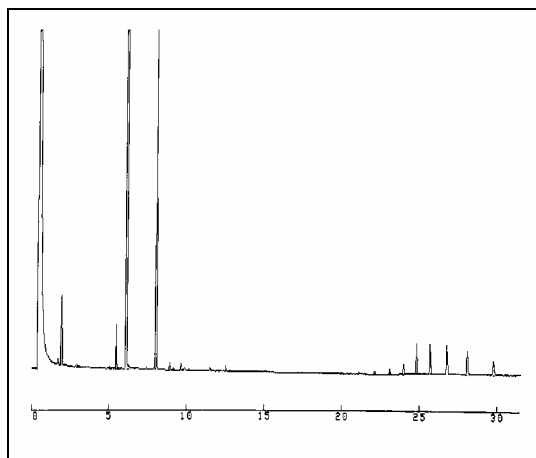
oven: 70 $^{\circ}\text{C}$ (2 min), heating rate 10 $^{\circ}\text{C}/\text{min}$, isotherme 300 $^{\circ}\text{C}$ (10 min)

detector: FID, 310 $^{\circ}\text{C}$

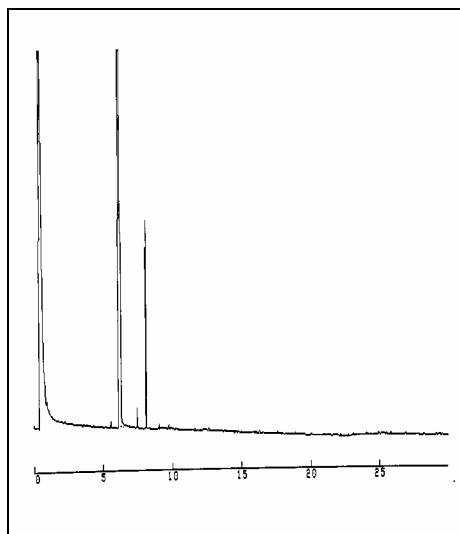
integrator: Shimadzu

Percent concentration was calculated from the peak areas.

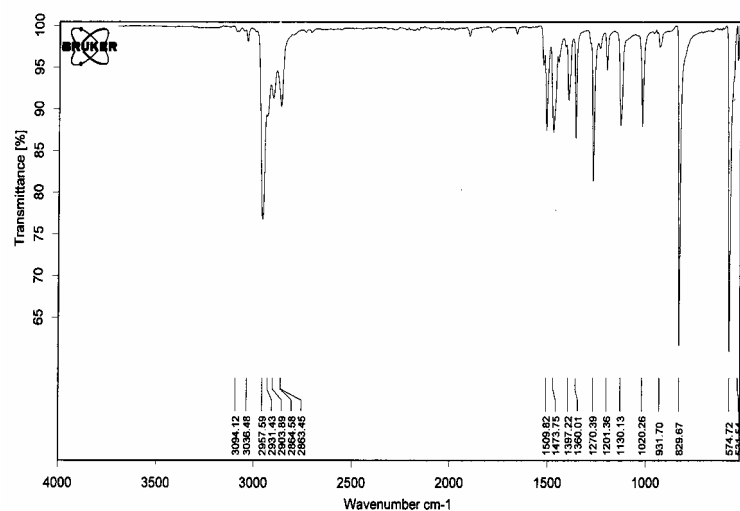
GC of the crude product



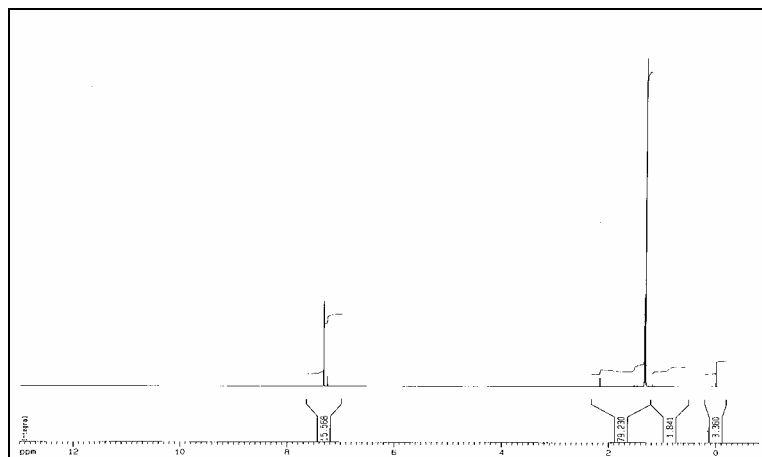
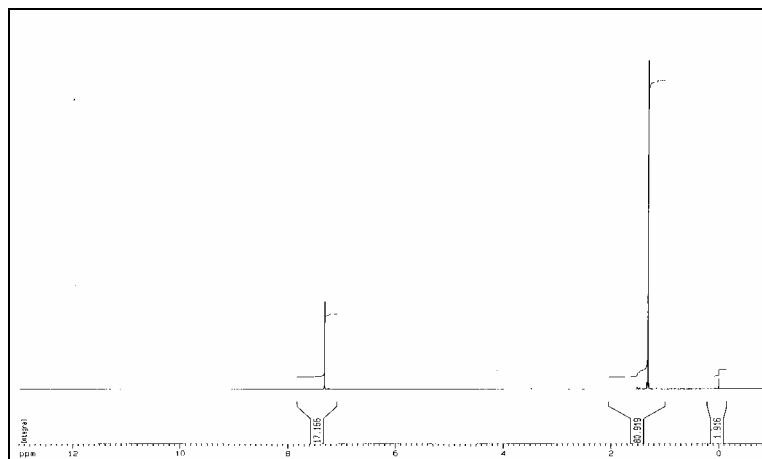
Retention time (min)	Substance	Peak area %
5.47	<i>tert</i> -butylbenzene	1
6.23	product (1,4-di- <i>tert</i> -butylbenzene)	79.2
8.03	side product (1,3,5-tri- <i>tert</i> -butylbenzene)	14.8
higher than 20	impurities	

GC of the recrystallized product

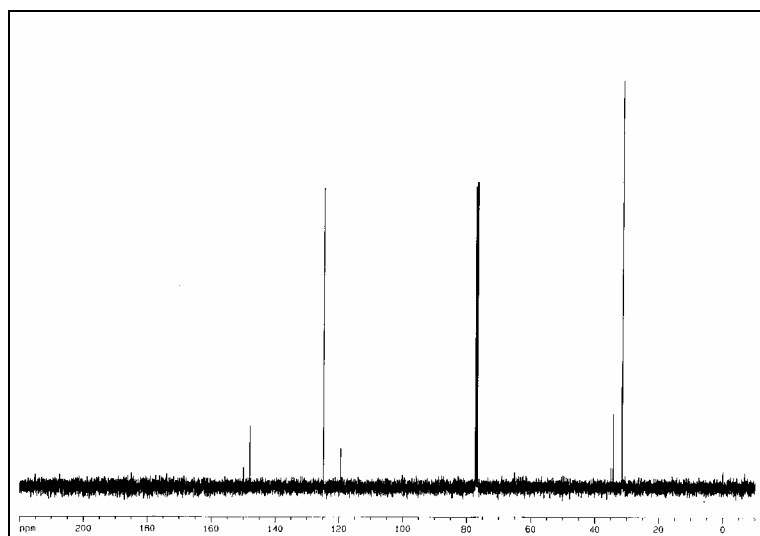
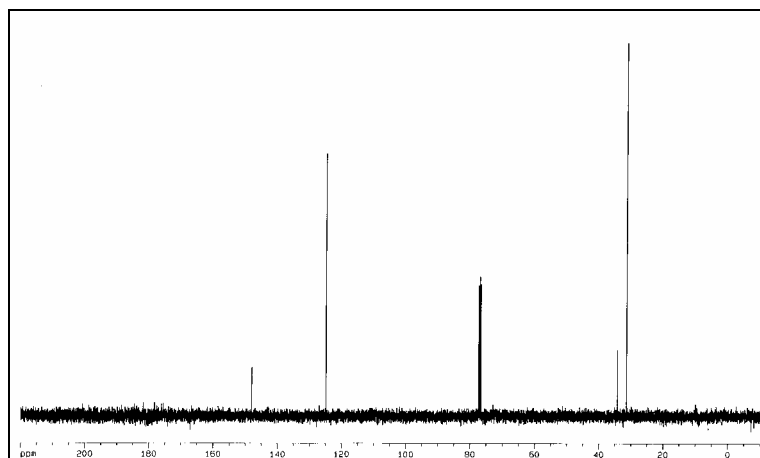
Retention time (min)	Substance	Peak area %
6.29	product (1,4-di- <i>tert</i> -butylbenzene)	98.9
8.12	side product (1,3,5-tri- <i>tert</i> -butylbenzene)	1.1
higher than 20	impurities	

IR spectrum of the recrystallized product (ATR)

(cm^{-1})	Assignment
3095, 3035	C-H-valence, arene
2960-2900	C-H-valence, alkane
1510	C=C-valence, arene
1395, 1360	C(CH ₃) deformation

^1H NMR spectrum of the crude product (400 MHz, CDCl_3) **^1H NMR spectrum of the recrystallized product (400 MHz, CDCl_3)**

δ (ppm)	Multiplicity	Number of H	Assignment
1.31	s	18	CH_3
7.31	s	4	arene-H

^{13}C NMR spectrum of the crude product (100 MHz, CDCl_3) **^{13}C NMR spectrum of the recrystallized product (100 MHz, CDCl_3)**

δ (ppm)	Assignment
31.41	CH_3
34.24	$\text{C}(\text{CH}_3)_3$
124.88	C-2
148.00	C-1
76.5-77.5	solvent

