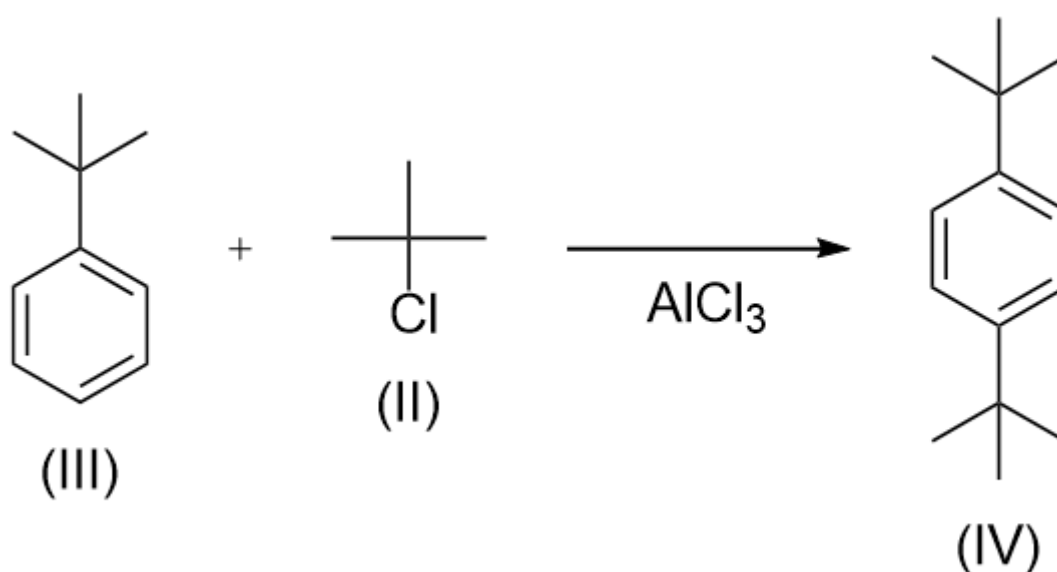
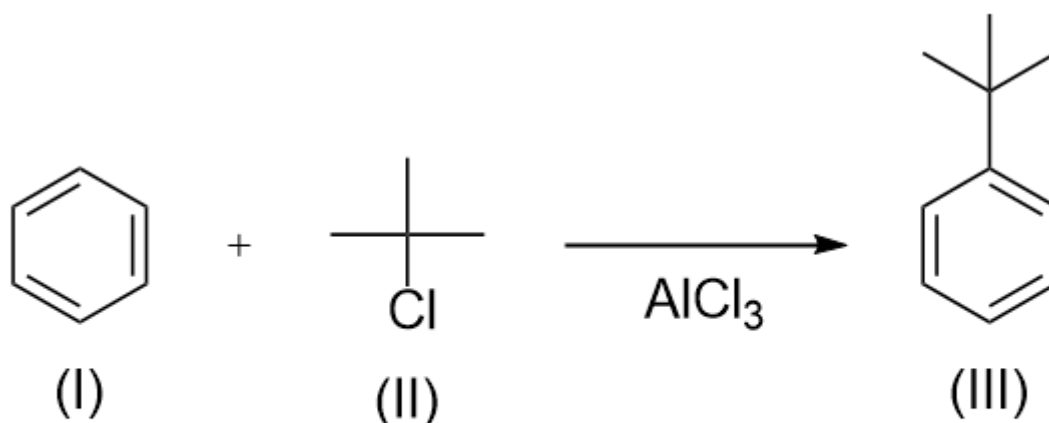


Friedel-Crafts alkylation of benzene**Abstract**

In this experiment, benzene (I) underwent Friedel-Crafts alkylation with tert-butyl chloride (II) in the presence of anhydrous aluminium chloride (AlCl_3) yielding a alkyl substituted benzene as the product. In the reaction benzene undergoes aromatic electrophilic substitution, where the tert-butyl cation generated from the tert-butyl chloride and AlCl_3 acts as an electrophile for the aromatic ring forming tert-butylbenzene (III), under reaction conditions further alkylation occurred, yielding 1,4-di-tert-butylbenzene (IV). The isolated product was then characterised using melting point determination returning a result of 78.8°C and its structure was confirmed to be 1,4-di-tert-butylbenzene (IV) using spectroscopic data. Percentage yield calculations showed that the final yield was 28.72% of the theoretical yield



Experimental

The experiment was performed as detailed in the CHEM202 laboratory manual (p25), without modification. The accurate masses used of the reagents are detailed below.

Substance	Formula	M _r	mass (g)	amount (mmol)
benzene	C ₆ H ₆	78.11	8.275	0.106
2-chloro-2-methylpropane (<i>t</i> -butyl chloride)	C ₄ H ₉ Cl	92.57	4.278	0.0462
aluminium chloride	AlCl ₃	133.34	0.5	0.00375

HCl gas generated during the reaction is neutralized using an inverted funnel gas trap in water. Aqueous waste generated during the washing of the diethyl ether was disposed of down the fumehood sink. Magnesium sulfate used to dry the organic extracts were also disposed of down the fumehood sink with the aid of cold water. Ether and unreacted benzene were distilled off using a rotary evaporator. Methanol waste from the recrystallization was disposed of in the non-halogen waste container.

Results and calculations

Microanalysis shows the following percentage composition by mass:

C: 88.35 %; H: 11.65 %

The empirical formula of the product can be calculated as follows:

$$\text{Mols of C: } \frac{88.35 \text{ g}}{12 \text{ g/mol}} = 7.3625 \text{ mol}$$

$$\text{Mols of H: } \frac{11.65 \text{ g}}{1 \text{ g/mol}} = 11.65 \text{ mol}$$

$$\text{Ratio of C: } \frac{7.3625 \text{ mol}}{7.3625 \text{ mol}} = 1$$

$$\text{Ratio of H: } \frac{11.65 \text{ mol}}{7.3625 \text{ mol}} = 1.58$$

For this formula, M_r = C₁H_{1.58} .

From the mass spectrum, m/z for M⁺ (product) = 190 g/mol

The product of the experiment is: (Formula : C₁₄H₂₂), and is therefore a (di)-substituted benzene derivative

Percentage yield calculation

The limiting reagent in this reaction was (*t-butyl chloride*).

$$\frac{8.275 \text{ g } t\text{-butyl chloride}}{95.57 \text{ g/mol}} = \frac{0.0894 \text{ mol}}{2} = 0.0447 \text{ mol}$$

$$\frac{4.278 \text{ g Benzene}}{78.11 \text{ g/mol}} = 0.0889 \text{ mol}$$

$$\therefore n(\text{product}) \text{ expected} = 0.0447 \text{ mol}$$

$$M(\text{product}) = 190 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{Theoretical yield} &= 0.0447 \text{ mol} \times 190 \text{ g mol}^{-1} \\ &= 8.493 \text{ g} \end{aligned}$$

$$\text{Actual yield} = 2.44 \text{ g}$$

$$\begin{aligned} \therefore \text{Percentage yield} &= \frac{2.44 \text{ g}}{8.493 \text{ g}} \times 100 \\ &= 28.72 \% \end{aligned}$$

Melting point data

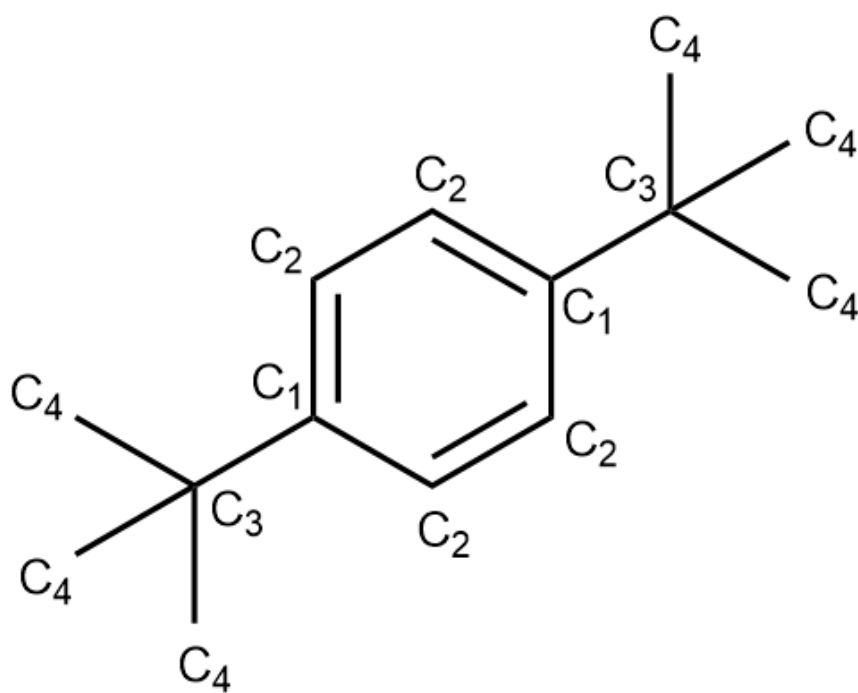
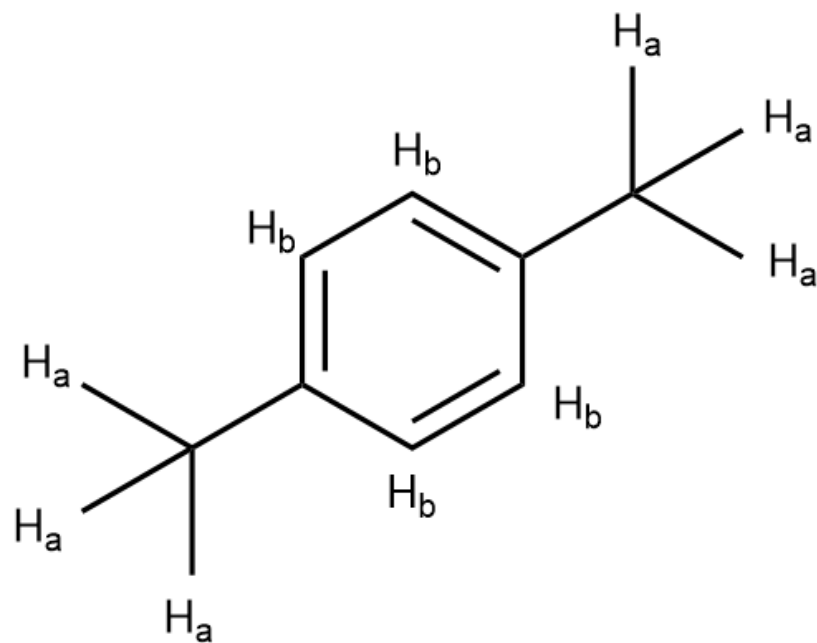
The melting point of the compound was recorded to be 78°C using a manual electric hot bench, this result fits exactly into the literature range of p-di-tert-butylbenzene of 76-78°C

IR spectrum of product(C₁₄H₂₂)

ν / cm^{-1}	intensity	appearance	assignment	inference
3081	w	sh	C-H stretch	Aromatic C-H
2957	s	sh	C-H stretch	Alkyl C-H
1600	w	sh	C=C stretch	Aromatic skeletal
1396	w	sh	C-H bending	Methyl C-H
1360	m	sh	C-H bending	Methyl C-H
829	s	sh	C-H deformations	1,4-disubstituted benzene derivative

The IR spectrum shows aromatic C-H stretches around 3081 cm⁻¹ consistent with an aromatic ring, additionally stretching at 2957 cm⁻¹ shows C-H stretching instead from an alkyl group. At 1600 cm⁻¹ we see C=C stretching characteristically seen in aromatic rings further suggesting ones presence. Looking at the fingerprint region of the IR spectrum peaks are visible at 1396 cm⁻¹ and 1360 cm⁻¹ showing C-H bending from a methyl group. We additionally see a peak 829 cm⁻¹ suggesting the aromatic ring is a 1,4-disubstituted derivative.

Structure of product



^1H NMR (500 MHz, CDCl_3)

δ/ppm	Integration	multiplicity	COSY shows coupling to	Assignment
7.33	4	s	~	H_b
1.32	18.4	s	~	H_a

¹³C NMR (125 MHz, CDCl₃)

δ/ppm	HETCOR shows coupling to	Assignment
148.2	~	C ₁
125.1	H _b	C ₂
34.5	~	C ₃
31.6	H _a	C ₄

Discussion (this should be no longer than 1.5 pages)

The structure of the product from this experiment was determined to be 1,4-di-tert-butylbenzene, this is supported by the elemental analysis, melting point determination, and spectroscopic data (IR, ¹H NMR, and ¹³C NMR). The Friedel–Crafts alkylation of benzene with tert-butyl chloride in the presence of AlCl₃ was expected to initially yield tert-butylbenzene, but an excess of tert-butyl chloride and the activating effect of the first alkyl substituent resulted in a second alkylation at the para-position, forming the 1,4-disubstituted product.

The composition of C: 88.35%, H:11.65% from the microanalysis led to an empirical formula of C₁₄H₂₂ which matches the formula of 1,4-di-tert-butylbenzene. The mass spectrum showed an ion peak at m/z =190 further supporting our determination.

The melting point of the isolated compound (78 °C) is in range of published values for 1,4-di-tert-butylbenzene (literature m.p. = 76-78°C), suggesting a high purity and correct identification. The percentage yield of 28.72% reflects losses due to inefficiencies during the work-up steps and incomplete conversion.

The IR spectrum provides further evidence for the proposed structure. Signals at 3081 cm⁻¹ and 1600 cm⁻¹ confirm the presence of aromatic C–H and C=C bonds. Strong alkyl C–H stretching at 2957 cm⁻¹, and methyl C–H bending at 1396 and 1360 cm⁻¹ are both consistent with tert-butyl groups. The intense absorption at 829 cm⁻¹ helps deducing the regioisomers of the product, indicating a 1,4-disubstituted aromatic (para-substitution), confirming the sole formation of this regioisomer.

¹H NMR spectra further supported the para-substituted structure. The singlet at 7.33 ppm (4H) corresponds to the aromatic protons (H_b) at the 2,3,5,6 positions as all are equivalent in a 1,4-disubstituted ring. The singlet at 1.32 ppm (18.4H) comes from the two chemically equivalent tert-butyl groups (H_a, 9H each) present on the ring. No signal is observed in the aromatic region indicative of mono-substitution (which would show additional peaks due to non-equivalent aryl hydrogens). ¹³C NMR shows resonances at 148.2, 125.1, 34.5, and 31.6 ppm, assignable to quaternary/aromatic carbons, aromatic CH, tert-butyl quaternary and methyl carbons, respectively, and confirmed by HETCOR assignments.

The melting point (78°C) and clean NMR/IR spectra, with no significant additional peaks, indicate a high degree of purity. The absence of additional signals in the ¹H NMR or IR spectrum further supports this.

This reaction undergoes Friedel–Crafts alkylation where AlCl₃ takes chloride from the tert-butyl chloride, generating a highly reactive tert-butyl carbocation. Benzene attacks this carbocation via electrophilic aromatic substitution initially giving tert-butylbenzene. The electron-donating effect of the first tert-butyl group strongly activates the aromatic ring toward further electrophilic

substitution, with the para position favored due to steric hindrance at ortho sites. Therefore with an excess of tert-butyl chloride, 1,4-di-tert-butylbenzene becomes the major product.

The high regioselectivity for para-disubstitution is directly from steric and electronic effects of the first tert-butyl group, which blocks ortho-substitution and directs incoming electrophiles to the para position. A reaction using a 1:1 equivalent of tert-butyl chloride and careful control of reaction time and conditions can favour tert-butylbenzene as the major product, but some di-substitution may still be present. To only obtain tert-butylbenzene, milder conditions and a substantial excess of benzene are preferred.

Friedel–Crafts alkylation is generally unsuitable for producing products with alkyl chains due to carbocation rearrangement. Alternative strategies such as Friedel–Crafts acylation (followed by reduction), are employed in these cases.

Reference

1,4-Di-tert-butylbenzene

(n.d.).https://www.sigmaaldrich.com/NZ/en/product/aldrich/113352?srsId=AfmBOooXsOGKr9GX46f2Jd4FJUflwMjst0iW_8JbtVcGJK_72Q2HbowS