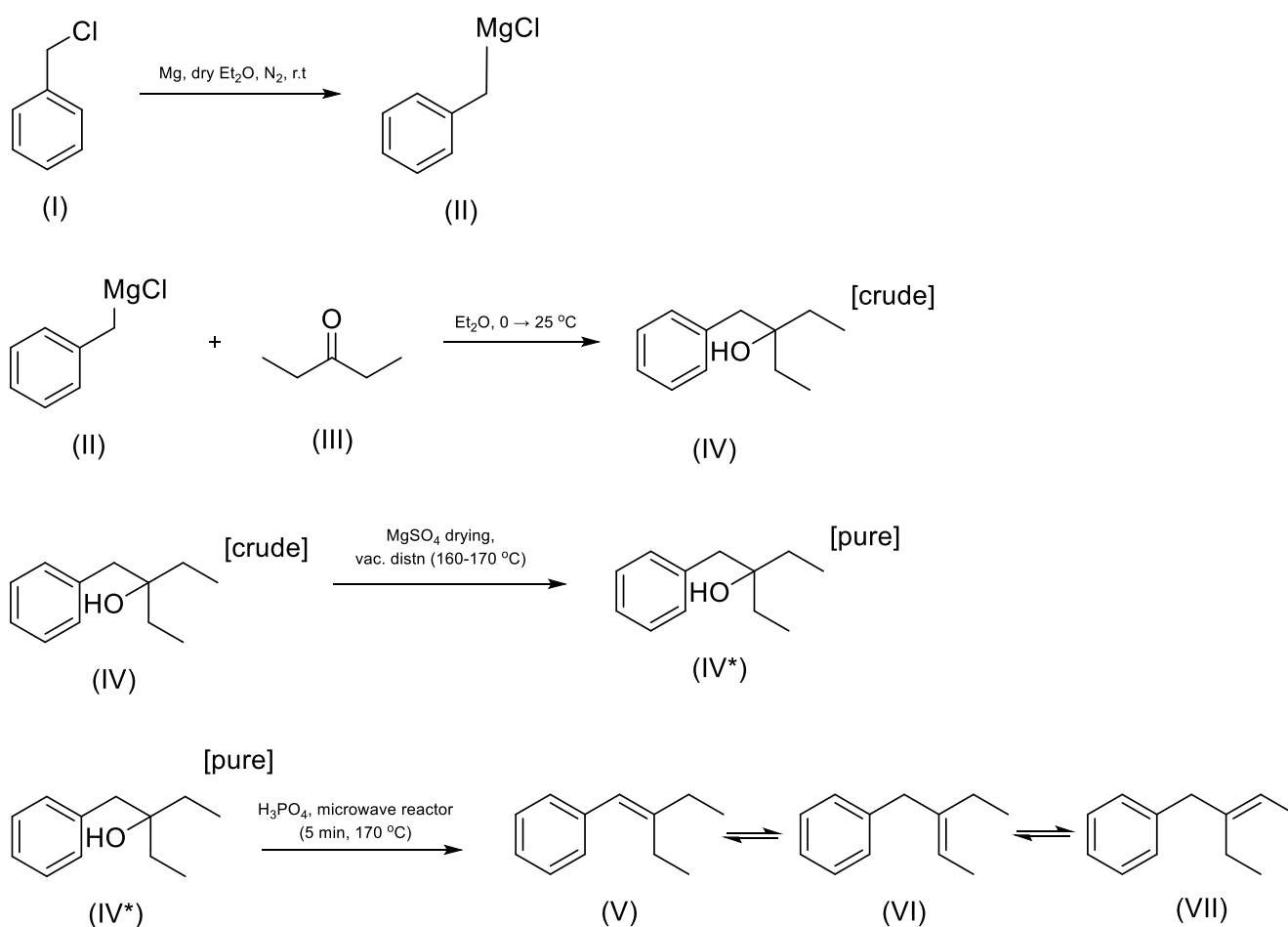


**CHEM202 LABORATORY REPORT****Name:** Harry Stanley**Experiment 5****Lab Day:** Thursday**Date:** 17/04/25**Synthesis of a substituted quinoline****Abstract**

A Grignard reagent was prepared by refluxing benzyl chloride(I) with magnesium turning in dry ethyl ether under anhydrous conditions. After initiation with iodine, benzylmagnesium chloride (II) was formed and reacted pentan-3-one (III) to give a tertiary alcohol 3-benzylpentan-3-ol (IV). The crude alcohol was purified by vacuum distillation (b.p. 110 °C, 40 mbdr) to yield 4.683 g of (IV) (39.7 % yield). IR spectroscopy showed complete disappearance of the carbonyl band ( $1712\text{ cm}^{-1}$ ) and the appearance of a broad O-H stretch showed at  $3425\text{ cm}^{-1}$ . Full  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterisation (including COSY, HECTOR, DEPT) allowed unambiguous assignment of all resonance, confirming the structure of (IV)

Dehydration of (IV) was completed by reacting our tertiary alcohol with orthophosphoric acid in a microwave reactor for 15 minutes to furnish a mixture of three alkenes in a combined yield of 50 % (0.7 g). Analysis of the  $^1\text{H}$  NMR spectrum (integrals of olefinic vs benzylic signals) have a product ratio of 1:1.10:1.03. NOESY experiment revealed key through-space cross-peaks that enabled assignment of E/Z geometry of the olefinic protons in each isomer. The observed chemical shift agreed with predicted values.



## Experimental

The experiment was performed as detailed in the CHEM202 laboratory manual (p33), without modification. The accurate masses used of the reagents are detailed below.

Substance	Formula	M <sub>r</sub>	mass (g)	amount (mmol)
Magnesium turnings	Mg	24.305	2.521	103.72
Benzyl chloride	PhCH <sub>2</sub> Cl	126.58	12.65	99.94
Pentan-3-one	C <sub>5</sub> H <sub>10</sub> O	86.1	5.70	66.20
Orthophosphoric acid	H <sub>3</sub> PO <sub>4</sub>	97.994	3.79	43.17
3-benzylpentan-ol	C <sub>12</sub> H <sub>18</sub> O	174.14	1.512	8.68

All reactions were carried out in a fume-hood to contain ether and acid vapours. After the Grignard reaction the mixture was quenched by slow addition of ice-cold saturated NH<sub>4</sub>Cl, the aqueous layer was separated and washed down the fume-hood sink with excess water. The organic layer was dried over anhydrous MgSO<sub>4</sub>, the drying agent was filtered off and washed into the sink with water; diethyl ether was removed on the rotary evaporator. The final extracts were dried, filtered and stripped of solvent by rotavap. Contaminated waste when in the contaminated waste bin.

## Results and calculations

### Reaction 1 percentage yield calculation:

The limiting reagent in this reaction was (Pentan-3-one)

$$\therefore n(\text{product}) \text{ expected} = 0.0662 \text{ mol}$$

$$M(\text{product}) = 178.14 \text{ g mol}^{-1}$$

$$\text{Theoretical yield} = N \times M$$

$$= 0.0662 \text{ mol} \times 178.14 \text{ g mol}^{-1}$$

$$= 11.792 \text{ g}$$

$$\text{Actual yield} = 4.683 \text{ g}$$

$$\therefore \text{Percentage yield} = \frac{4.683}{11.792} \times 100$$

$$= 39.7 \%$$

Reaction 2 percentage yield calculation:

The limiting reagent in this reaction was (3-benzylpentan-ol)

$$\therefore n(\text{product}) \text{ expected} = 0.00868 \text{ mol}$$

$$M(\text{product}) = 160.13 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{Theoretical yield} &= N \times M \\ &= 0.00868 \text{ mol} \times 160.13 \text{ g mol}^{-1} \\ &= 1.39 \text{ g} \end{aligned}$$

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

$$\begin{aligned} \therefore \text{Percentage yield} &= \frac{0.7}{1.39} \times 100 \\ &= 50.3 \% \end{aligned}$$

IR spectrum of ketone(C<sub>5</sub>H<sub>10</sub>O)

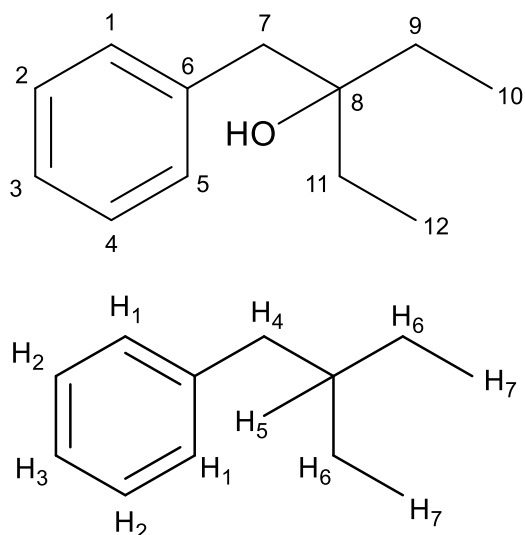
<b>v / cm<sup>-1</sup></b>	<b>intensity</b>	<b>appearance</b>	<b>assignment</b>	<b>inference</b>
2997	m	sh	C-H stretch	alkyl C-H
2940	m	sh	C-H stretch	alkyl C-H
1712	s	sh	C=O stretch	non-conjugated ketone
1376	m	sh	C-H bend	methyl C-H
1357	m	sh	C-H bend	methyl C-H

IR spectrum of intermediate product(C<sub>12</sub>H<sub>18</sub>O)

<b>v / cm<sup>-1</sup></b>	<b>intensity</b>	<b>appearance</b>	<b>assignment</b>	<b>inference</b>
3425	w	br	O-H stretch	alcohol
3028	w	sh	C-H stretch	aromatic C-H
2966	w	sh	C-H stretch	alkyl C-H
2938	w	slightly br	C-H stretch	alkyl C-H
1602	w	sh	C=C stretch	aromatic skeletal stretch
1495	w	sh	C=C stretch	aromatic skeletal stretch
1453	w	sh	C-H bend	sp <sup>3</sup> hybridised carbon
1380	w	slightly br	C-H bend	methyl C-H
756	w	sh	C-H deformation	monosubstituted benzene derivative
696	s	sh	C-H deformation	monosubstituted benzene derivative

*IR spectrum of final product(C<sub>12</sub>H<sub>16</sub>)*

<b>v / cm<sup>-1</sup></b>	<b>intensity</b>	<b>appearance</b>	<b>assignment</b>	<b>inference</b>
3061	w	sh	C-H stretch	alkene or benzene derivative
3026	w	sh	C-H stretch	alkene or benzene derivative
2963	w	sh	C-H stretch	alkyl C-H
2931	w	slightly br	C-H stretch	alkyl C-H
1648	w	sh	C=C stretch	C=C conjugated with aromatic ring
1601	w	sh	C=C stretch	Aromatic skeletal stretch
1493	w	sh	C=C stretch	aromatic skeletal stretch
1452	w	sh	C-H bend	sp <sup>3</sup> hybridised carbon
839	w	sh	C-H deformation	trisubstituted alkene
722	s	sh	C-H deformation	monosubstituted benzene derivative
695	s	sh	C-H deformation	monosubstituted benzene derivative

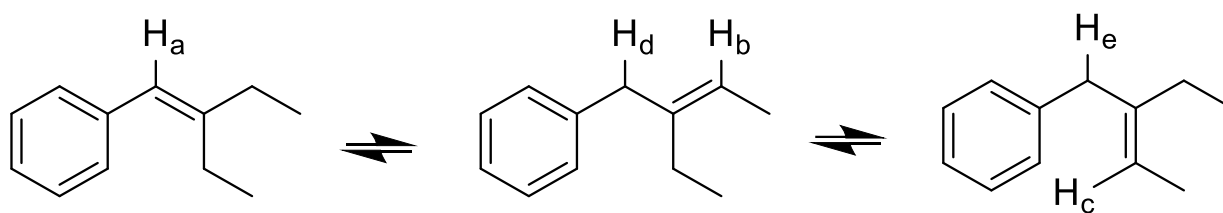


*<sup>13</sup>C NMR Intermediate product (125 MHz, CDCl<sub>3</sub>)*

d/ppm	HETCOR shows coupling to	Assignment
130.6		C-1, C-5
128.2	H <sub>1</sub>	C-2, C-4
126.4	H <sub>3</sub>	C-3
74.6	~	C-8
44.8	H <sub>4</sub>	C-7
30.5	H <sub>6</sub>	C-9, C-11
8.0	H <sub>7</sub>	C-10, C-12

*<sup>1</sup>H NMR Intermediate product (500 MHz, CDCl<sub>3</sub>)*

d/ppm	Integration	multiplicity	J/Hz	Assignment
7.28	2	m	~	H <sub>2</sub> , H <sub>3</sub>
7.23	3	m	~	H <sub>1</sub>
2.75	2	s	~	H <sub>4</sub>
1.46	4	q <sub>d</sub>	H <sub>7</sub>	H <sub>6</sub>
0.93	6	t	H <sub>6</sub>	H <sub>7</sub>



*<sup>1</sup>H NMR Final product (500 MHz, CDCl<sub>3</sub>)*

d/ppm	Integration	multiplicity	J/Hz	NOESY shows coupling to	Assignment
6.28	1.00	s	~	~	H <sub>a</sub>
5.45	1.10	q	6.7	~	H <sub>b</sub>
5.27	1.03	q	6.7	H <sub>d</sub>	H <sub>c</sub>
3.45	2.25	s	~	H <sub>c</sub>	H <sub>d</sub>
3.34	2.15	s	~	~	H <sub>e</sub>

The olefinic region (6.3-5.0 ppm) of the <sup>1</sup>H-NMR spectrum contained three well-separated signals that each integrated for a single proton. The most down-field resonance, a singlet at 6.28 ppm was assigned to H<sub>a</sub>, the vinylic proton of the conjugated product, because conjugation with the aromatic ring is expected to deshield the proton by 0.7 ppm relative to a simple internal alkene. Two further quartets, at 5.45 and 5.27 ppm (J = 6.7 Hz) were attributed to the vinylic protons of the two possible internal alkenes. The quartet at 5.45 ppm showed no through-space correlation to any benzylic signal in the NOESY spectrum and was therefore assigned to H<sub>c</sub>, the E-isomer. The quartet at 5.27 ppm displayed a clear through-space correlation to a benzylic proton at 3.45 ppm, placing the olefinic and benzylic protons on the same side of the double bond and confirming it as H<sub>b</sub> of the Z-isomer.

Only the two internal alkene retain the benzylic CH<sub>2</sub> group, and two singlets at 3.45 ppm (H<sub>d</sub>) and 3.34 ppm (H<sub>e</sub>) together integrated for 4.40 H. the NOESY cross-peak between the 3.45 ppm and 5.27 ppm quartet linked these signal to the Z-alkene, leaving the singlet at 3.45 ppm as the benzylic CH<sub>2</sub> of the E-isomer.

## Discussion