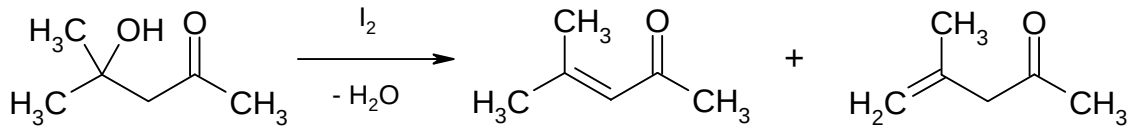
1024 Elimination of water from 4-hydroxy-4-methyl-2-pentanone



$C_6H_{12}O$ (116.2) | I_2 (253.8) | $C_6H_{10}O$ (98.2)

Classification

Reaction types and substance classes
elimination
alcohol, alkene, ketone, acid catalyst

Work methods
distilling, stirring with magnetic stir bar, filtering, heating with oil bath

Instruction (batch scale 50 mmol)

Equipment
10 mL round bottom flask, distillation apparatus, heatable magnetic stirrer, magnetic stir bar, 100 mL separating funnel, small glass frit, straight delivery tube (for sucking off a filtrate into a flask), oil bath

Substances

4-hydroxy-4-methyl-2-pentanone (bp 166 °C)	5.81 g (6.18 mL, 50.0 mmol)
iodine (mp 114°C)	60 mg (0.24 mmol)
sodium sulfate for drying	

Reaction
In a 10 mL round bottom flask with magnetic stir bar 60 mg (0.24 mmol) iodine are dissolved in 5.81 g (6.18 mL, 50.0 mmol) 4-hydroxy-4-methyl-2-pentanone. Initially the solution is heated in a distillation apparatus to 120 °C, then during reaction gradually to 150-160 °C, until no more distillate is condensing (about 45 minutes).
Distillate: 4.60 g; distillation residue: 1.28 g.

Work up
The distillate is transferred in a small separating funnel. The upper organic phase is filled in a small Erlenmeyer flask, dried with as little sodium sulfate as possible and then sucked off

from the sodium sulfate over a small glass frit with a straight delivery tube directly into a 10 mL round bottom flask which is used for the following distillation.
Crude yield: 3.20 g

The crude product is fractional distilled at normal pressure. Fractions with identical refractive index are combined.
Yield: 2.30 g (23.4 mmol, 47%); bp 125-130 °C, colourless liquid; the refractive index is very similar for all fractions: n_D^{20} = 1.4420 - 1.4450. More than 90% of the product is the conjugated ketone (mesityloxide) (see analytics).

Black tar remains as distillation residue.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury
distillation residue	dissolve in little acetone, then: organic solvents, containing halogen

Time
3-4 hours

Break
Before the second distillation

Degree of difficulty
Easy

Instruction (batch scale 250 mmol)

Equipment
50 mL round bottom flask, distillation apparatus, heatable magnetic stirrer, magnetic stir bar, 100 mL separating funnel, glass frit, straight delivery tube (for sucking off a filtrate into a flask), oil bath

Substances

4-hydroxy-4-methyl-2-pentanone (bp 166 °C)	29.1 g (30.9 mL, 250 mmol)
iodine (mp 114°C)	0.30 g (1.2 mmol)
sodium sulfate for drying	

Reaction
In a 50 mL round bottom flask with magnetic stir bar 0.30 g (1.2 mmol) iodine are dissolved in 29.1 g (30.9 mL, 250 mmol) 4-hydroxy-4-methyl-2-pentanone. Initially the solution is

heated in a distillation apparatus to 120 °C, then during reaction gradually to 150-160 °C, until no more distillate is condensing (about 90 minutes).
Distillate: 23.5 g; distillation residue: 5.31 g.

Work up
The distillate is transferred in a small separating funnel. The upper organic phase is filled in a small Erlenmeyer flask, dried with as little sodium sulfate as possible and then sucked off from the sodium sulfate over a small glass frit with a straight delivery tube directly into a 50 mL round bottom flask which is used for the following distillation.
Crude yield: 13.7 g

The crude product is fractional distilled at normal pressure. Fractions with identical refractive index are combined.
Yield: 12.7 g (130 mmol, 52%); bp 125-130 °C, colourless liquid; the refraktive index is very similar for all fractions: n_D^{20} = 1.4420 - 1.4450. More than 90% of the product is the conjugated ketone (mesityloxide) (see analytics).

Black tar remains as distillation residue.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury
distillation residue	dissolve in little acetone, then: organic solvents, containing halogen

Time
4-5 hours

Break
Before the second distillation

Degree of difficulty
Easy

Analytics

TLC

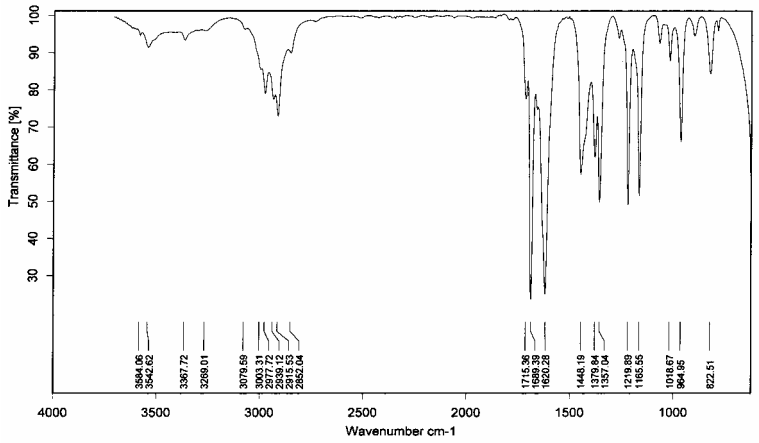
TLC-conditions:

adsorbant:	Macherey and Nagel Polygram SilG/UV foils, 0.2 mm
eluent:	diethyl ether/cyclohexane = 3 : 7
R_f (educt)	0.33
R_f (product mesityloxid)	0.55
R_f (distillation residue)	0.55 (product) and 0.92

GC

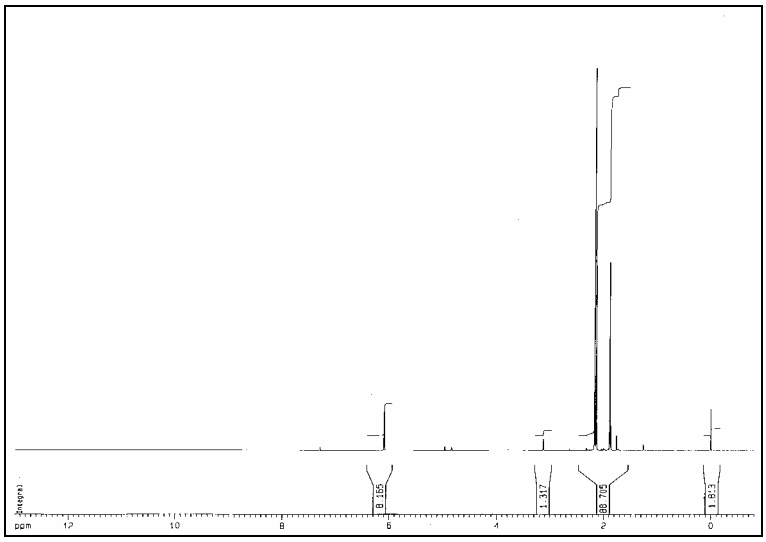
During examination of the product with GC rearrangements occured.

IR spectrum of the pure product (Film)

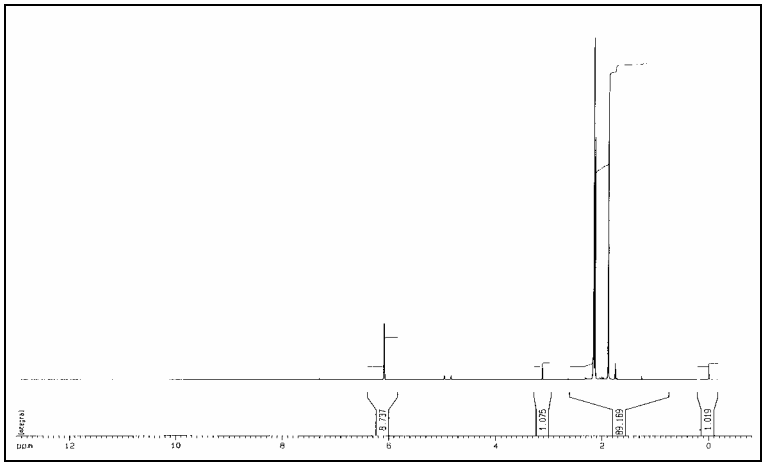


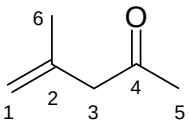
(cm^{-1})	Assignment
2977, 2937, 2914	C-H-valence, alkane
1690	C=O-valence conjugated to C=C
1625	C=C-valence conjugated to C=O

^{1}H NMR spectrum of the crude product (400 MHz, $CDCl_3$)

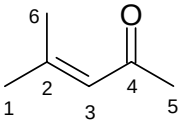


^{1}H NMR spectrum of the pure product (400 MHz, $CDCl_3$)





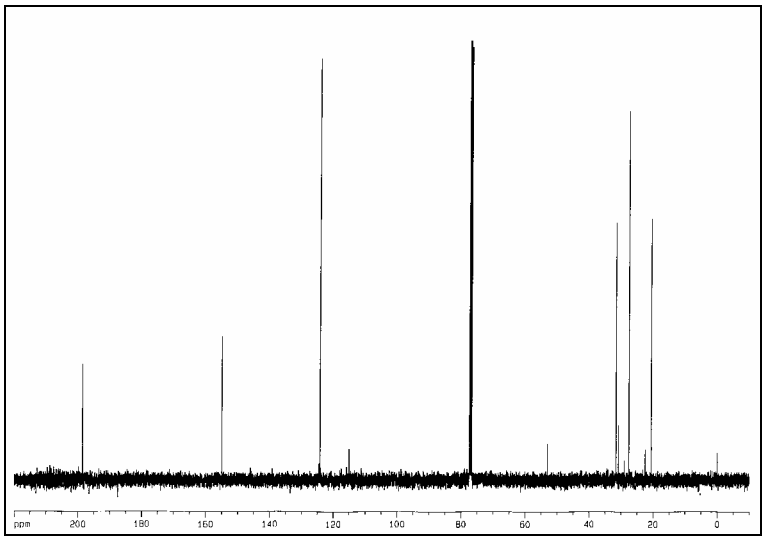
A



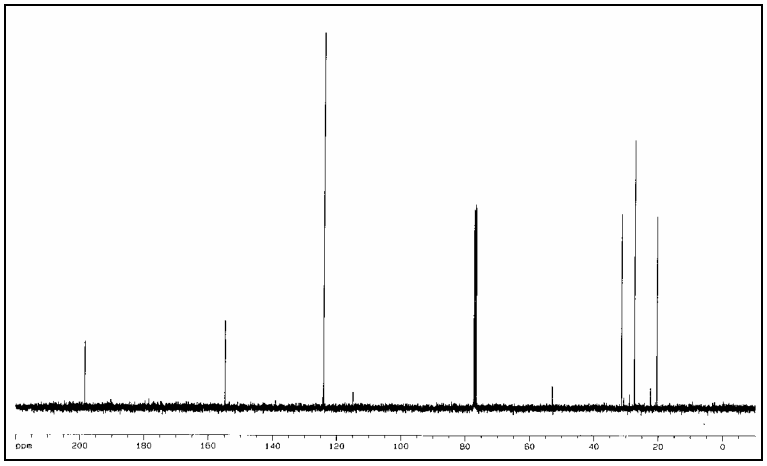
B

δ (ppm)	Multiplicity	Number of H	Assignment A	Assignment B
1.75	s	3	6-H	
1.88	s	3		1-H
2.00	s	3	5-H	
2.13	s	3		6-H
2.16	s	3		5-H
3.12	s	2	3-H	
4.83	s	1	1-H	3-H
4.96	s	1	1-H	
6.09	s	1		3-H

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



^{13}C NMR spectrum of the pure product (100 MHz, $CDCl_3$)



δ (ppm)	Assignment
20.47	C-6
27.55	C-1
31.58	C-5
124.11	C-3
154.85	C-2
198.47	C-4
76.5.77.5	solvent