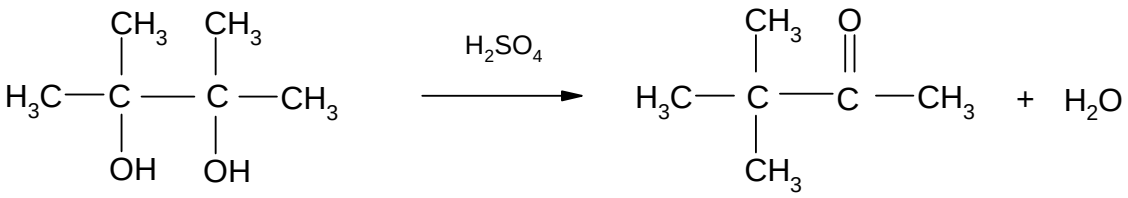
3028 Pinacol pinacolone rearrangement



$C_6H_{14}O_2$ (118.2) — (98.1) — $C_6H_{12}O$ (100.2)

Literature
C. J. Collins, *Quart. Rev.* **1960**, *14*, 357

Classification

Reaction types and substance classes
rearrangement, pinacol rearrangement, Wagner-Meerwein rearrangement,
alcohol, ketone

Work methods
simultaneous distillation extraction (SDE), column distillation, stirring with magnetic stir bar, heating with oil bath

Instruction (batch scale 100 mmol)

Equipment
100 mL round bottom flask, 50 mL round bottom flask, simultaneous distillation extraction (SDE) apparatus, two heatable magnetic stirrers, two magnetic stir bars, Vigreux column, distillation apparatus, two oil baths

Substances

pinacol (mp 38-42 °C)	11.8 g (100 mmol)
sulfuric acid (24%)	50 mL
tert-butyl methyl ether (bp 55 °C)	40 mL

Reaction
11.8 g (100 mmol) pinacol are heated with 50 mL 24% of sulfuric acid and 40 mL *tert*-butyl methyl ether for 45 minutes in a SDE-apparatus.

Work up
In a distillation apparatus combined with a Vigreux column the solvent is distilled off from the organic phase under normal pressure. Then the resulting residue is carefully fractional

distilled in the same apparatus also under normal pressure. The fraction with boiling point 105 °C is the product.
Yield: 7.3 g (72.9 mmol, 73%); bp 105 °C, colourless liquid

Comments
It is important not to use sulfuric acid, which is more diluted than 24%, otherwise some of the elimination product, 2,3-dimethyl-but-3-en-2-ol (or the rearranged isomer), can be formed. This side product has a higher boiling point (115-117 °C) and remains in the residue, when the distillation is performed carefully (see analytics).

Waste management

Recycling
Distilled *tert*-butyl methyl ether from the reaction mixture is collected and redistilled.

Sulfuric acid from the reaction mixture can be reused about five times for this reaction.

Waste disposal

Waste	Disposal
acidic aqueous phase	neutralize with diluted NaOH solution, then: solvent water mixtures, halogen free
residue of distillation	organic solvents, halogen free

Time
2-3 hours

Break
Before distillation

Degree of difficulty
Easy

Instruction (batch scale 10 mmol)

Equipment
50 mL round bottom flask, 25 mL round bottom flask, simultaneous distillation extraction (SDE) apparatus, two heatable magnetic stirrers, two magnetic stir bars, Vigreux column, small distillation apparatus, two oil baths

Substances

pinacol (mp 38-42 °C)	1.18 g (10.0 mmol)
sulfuric acid (24%)	12 mL
tert-butyl methyl ether (bp 55 °C)	30 mL

Reaction
1.18 g (10 mmol) pinacol are heated with 12 mL 24% of sulfuric acid and 30 mL *tert*-butyl methyl ether for 45 minutes in a SDE-apparatus

Work up

In a distillation apparatus combined with a Vigreux column the solvent is distilled off from the organic phase under normal pressure. Then the resulting residue is carefully fractional distilled in a small distillation apparatus also under normal pressure. The fraction with boiling point 105 °C is the product.

Yield: 621 mg (6.19 mmol, 62%); bp 105 °C, colourless liquid

Comments

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acidic aqueous phase	neutralize with diluted NaOH solution, then: solvent water mixtures, halogen free
residue of distillation	organic solvents, halogen free

Time

2-3 hours

Break

Before distillation

Degree of difficulty

Easy

Analytics

GC

Sample preparation:

Two drops of the organic phase of the reaction mixture are diluted with 2 mL *tert*-butyl methyl ether. 2 µL of this solution are injected.

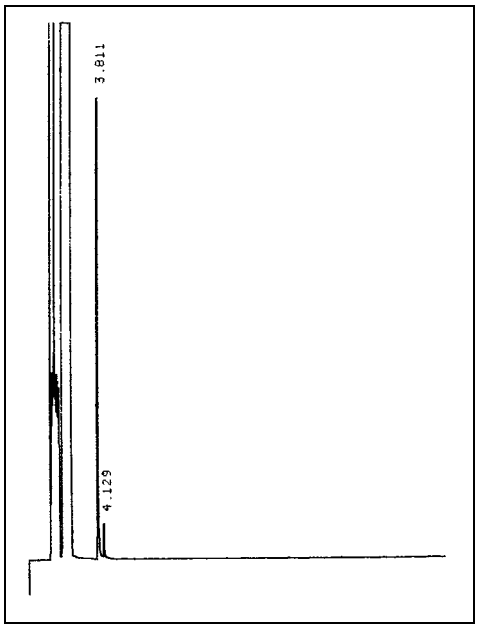
One drop of the distilled product is dissolved in 2 mL *tert*-butyl methyl ether. 2 µL of this solution are injected.

GC-conditions:

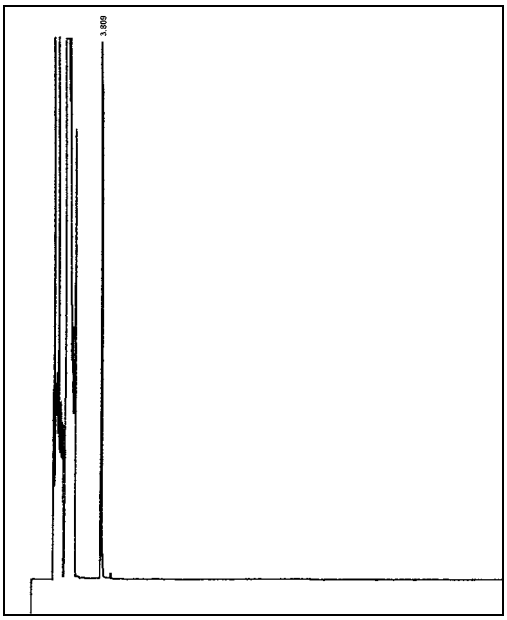
column:	Macherey and Nagel, SE-54, 326-MN-30705-9, 25 m, ID 0.32 mm, DF 0.25 µm
inlet:	Gerstel KAS, injector 250 °C; split injection 1:20, injected volume 2 µL
carrier gas:	nitrogen, pre-column pressure 62 kPa, flow rate 1.04 mL/min
oven:	50 °C isotherm
detector:	FID, 275 °C

Percent concentration was calculated from peak areas.

GC of the crude product

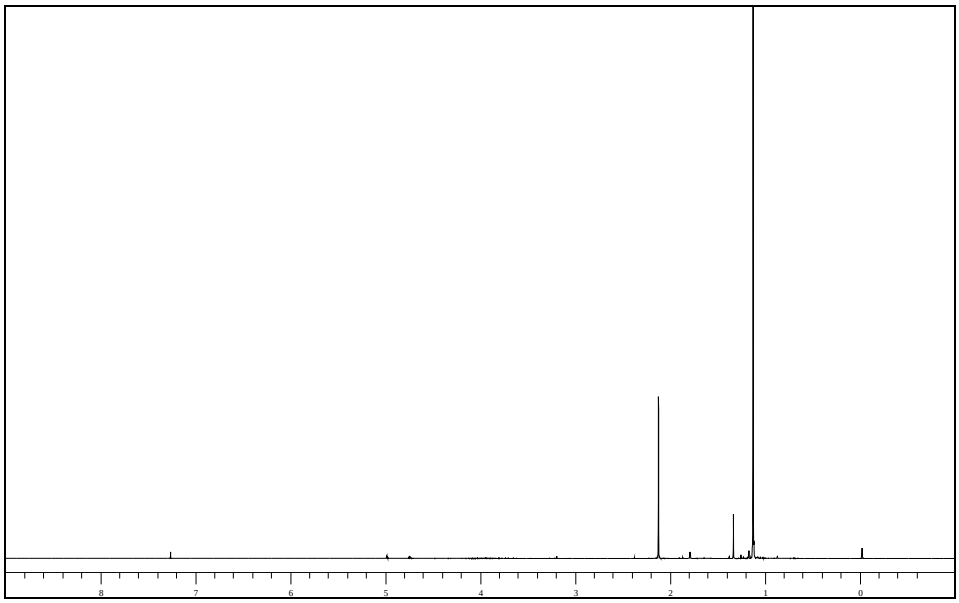


GC of the pure product



Retention time (min)	Substance	Peak area %	
		Crude product	Pure product
3.8	product (pinacolone) determined by GC/MS, m/e: 100, 85, 57	92.5	100
4.1	side product (2,3-dimethyl-but-3-en-2-ol) determined by GC/MS, m/e: 100, 85, 67, 59, 57, 53	7.5	

^{1}H NMR spectrum of the crude product (250 MHz, $CDCl_3$)



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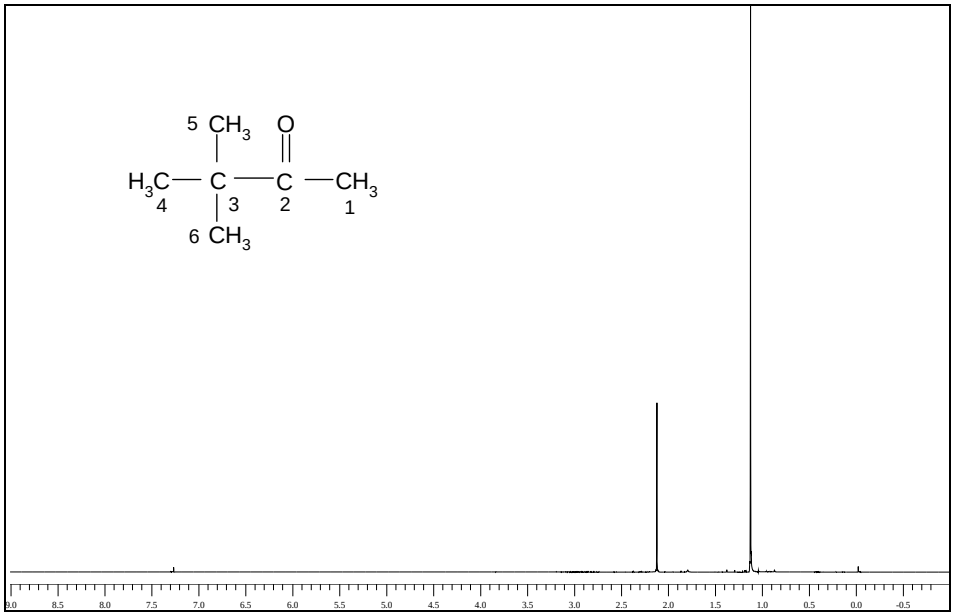
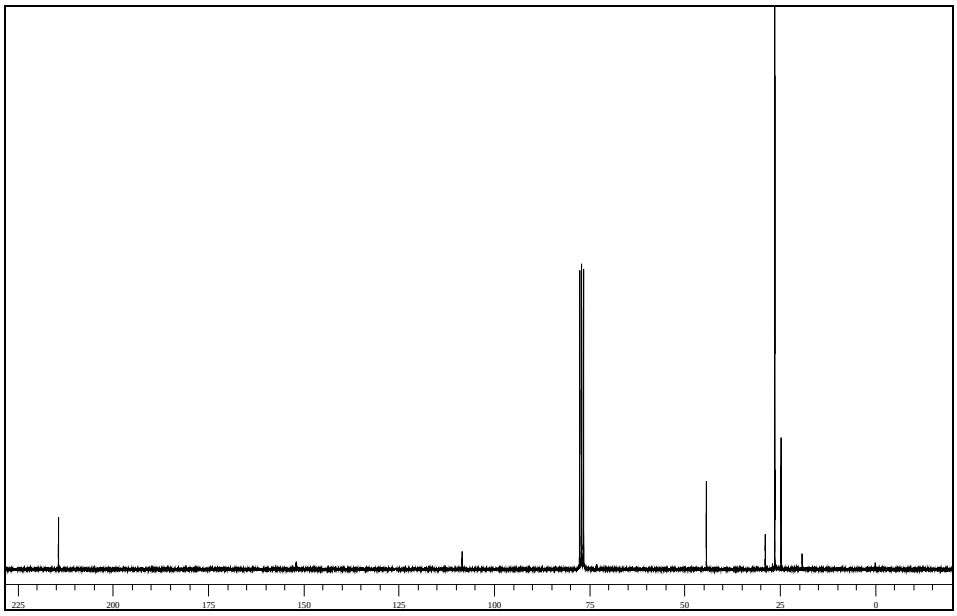
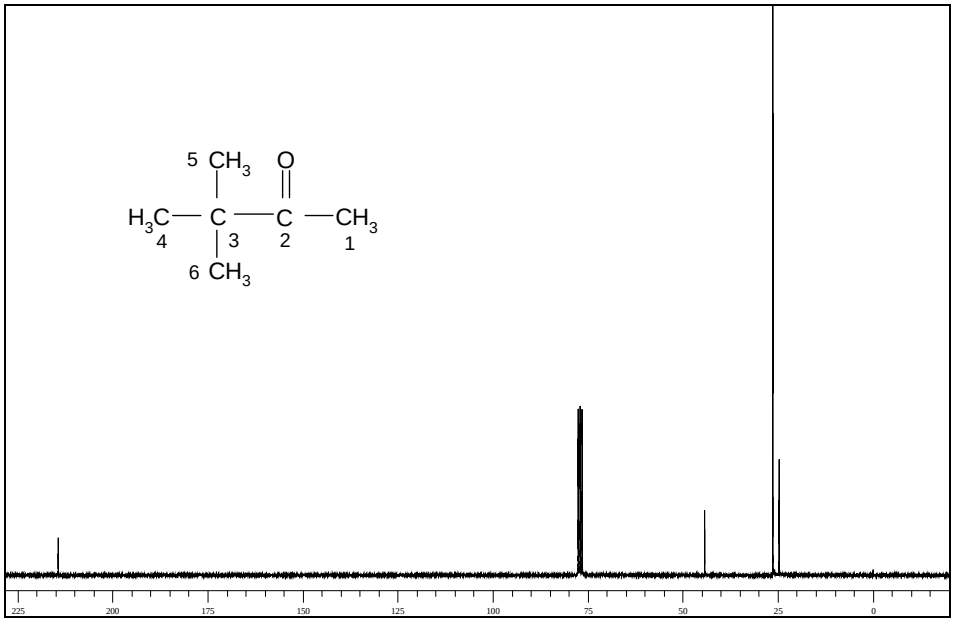


δ (ppm)	Multiplicity	Number of H	Assignment
1.12	s	9	4-H, 5-H, 6-H
2.12	s	3	1-H

^{13}C NMR spectrum of the crude product (62.5 MHz, $CDCl_3$)

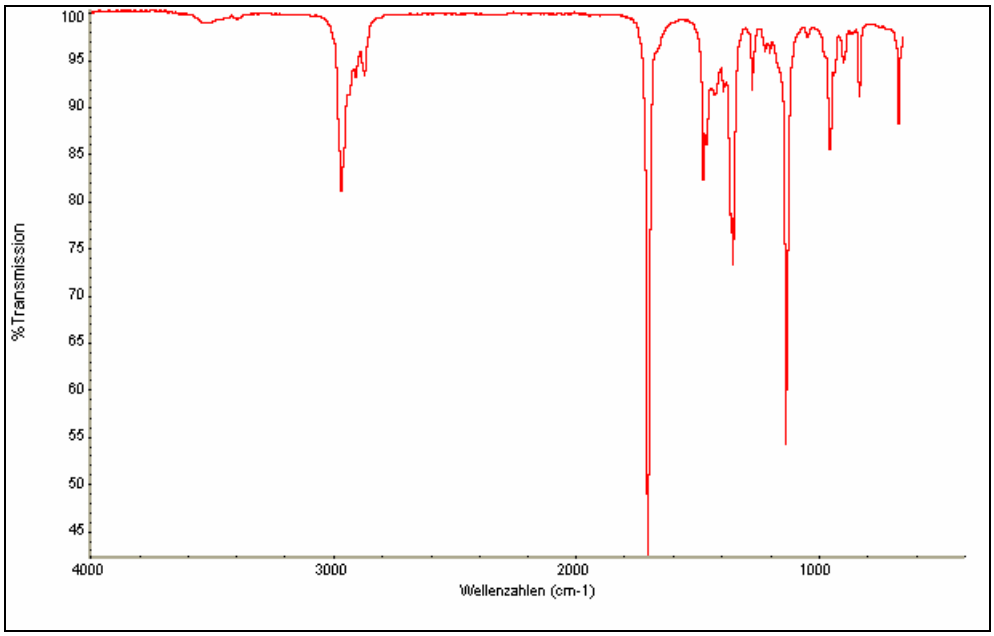


^{13}C NMR spectrum of the pure product (62.5 MHz, $CDCl_3$)

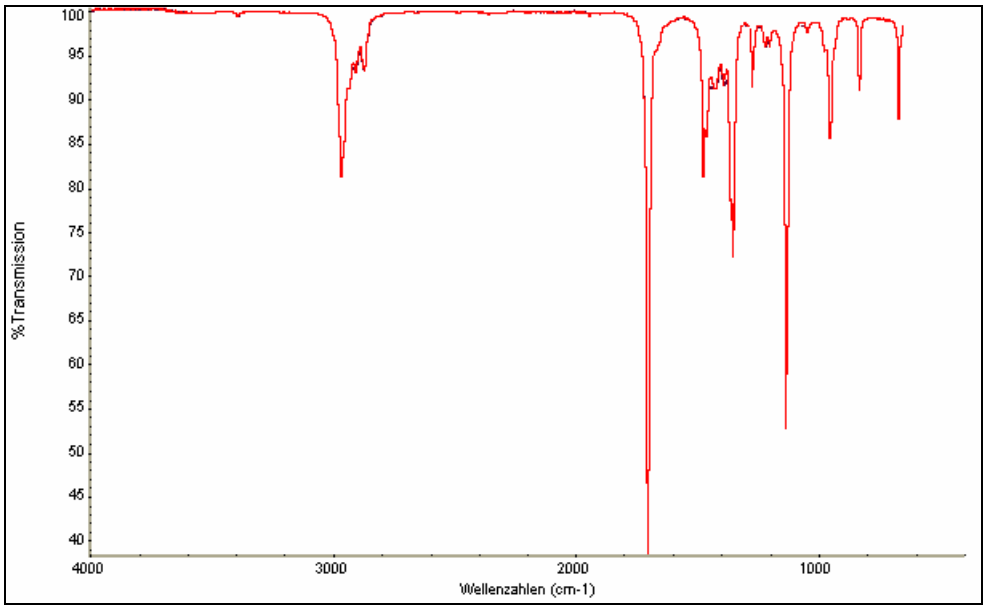


δ (ppm)	Assignment
24.6	C-1
26.3	C-6, C-4, C-5
44.3	C-3
214.3	C=O
76.5-77.5	solvent

IR spectrum of the crude product (ATR)



IR spectrum of the pure product (ATR)



(cm^{-1})	**Assignment**
2969, 2874	C-H-valence, alkane
1705	C=O-valence, ketone
1355, 1365	characteristic bands for *tert*-butyl groups