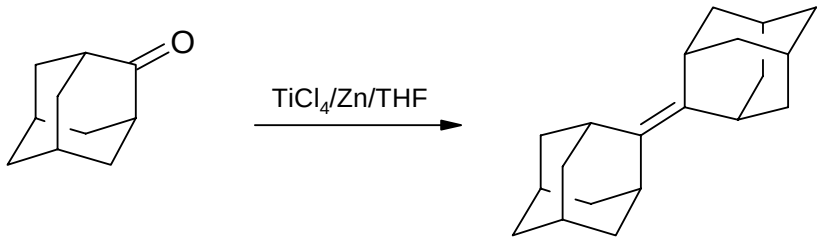
3012 Synthesis of adamantylidene adamantane from adamantanone



$C_{10}H_{14}O$	$TiCl_4$	Zn	$C_{20}H_{28}$
(150.2)	(189.7)	(65.4)	(268.4)

Literature

D. Lenoir, *Synthesis*, **1989**, 883-896

Classification

Reaction types and classes of compounds

McMurry reaction, reductive coupling, alkene synthesis
ketone, alkene

Work Methods

working with protective gas, adding dropwise with a piston-operated pipette, adding dropwise with an addition funnel, stirring with magnetic stir bar, heating under reflux, extracting, shaking out, filtering, evaporating with rotary evaporator, recrystallizing, use of ice cooling bath, heating with oil bath

Instruction (batch scale of 100 mmol)

Equipment

1000 mL three neck round bottom flask, heatable magnetic stirrer, magnetic stir bar, thermometer for inside of the flask, Buechner funnel, suction flask, bubble counter, piston operated pipette, protective gas piping, addition funnel with pressure balance, separating funnel, rotary evaporator, ice bath, oil bath

Substances

2-adamantanone (mp 250-255 °C)	15.0 g (100 mmol)
titanium(IV) chloride, $TiCl_4$ (bp 136 °C)	20.3 g (11.8 mL, 100 mmol)
zinc dust	14.3 g (218 mmol)
tetrahydrofuran (bp 66 °C) (abs. dry)	430 mL
potassium carbonate	about 21 g
cyclohexane (bp 81 °C)	250 mL
ethanol	
sodium sulfate for drying	about 5 g

Reaction

The reaction must be performed under inert atmosphere (argon or nitrogen). The addition of $TiCl_4$ is delicate and should bee performed in the presence of an experienced adviser.

The reaction is performed in a 1000 mL three neck round bottom flask connected to a reflux condenser and equipped with a magnetic stir bar and a connection to vacuum and a protective gas piping. The flask is heated under vacuum, the nitrogen is flown to it. After cooling 280 mL of dry tetrahydrofuran is added into the flask, which is cooled by an ice bath until the inner temperature reaches about 0 °C. Under inert atmosphere and stirring 11.8 mL (20.3 g, 100 mmol) $TiCl_4$ is added with a pipette at a temperature between 0 and 5 °C (that means about 1 drop of $TiCl_4$ is added within 5 seconds). To this yellow mixture is added 14.3 g (218 mmol) of zinc dust under stirring in small portions. A black precipitate is observed during addition of zinc. After 5 minutes of the last zinc addition the solution of 15.0 g (100 mmol) 2-adamantanone in 150 mL dry tetrahydrofuran is added dropwise from an addition funnel with stirring. Then the mixture is heated for 20 hours under reflux.

Work up

After cooling of the reaction mixture to room temperature 215 mL of a 10% aqueous solution of K_2CO_3 is added. The mixture is extracted 5 times with 50 mL cyclohexane each. The combined organic extractions are washed twice with 50 mL of water each, then the solution is dried over sodium sulfate. After filtration from sodium sulfate the solution is evaporated, yielding 12.3 g of crude product.

The crude product is purified by recrystallization from ethanol with a small amount of cyclohexane.
Yield: 11.4 g (42.5 mmol, 85%); white solid material, mp 189-190°C

Comments

Performing the reaction on 1 mmol scale 2-hydroxyadamantane is observed as main product.
Substitution of THF by *tert*-butyl methyl ether does not give any reaction products.

Waste management

Waste	Disposal
evaporated solvent mixture	organic solvents, halogen free
aqueous phase after extraction	solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury

Time

About 3 hours, without the time for refluxing

Break

After the addition of the K_2CO_3 solution and after the extraction

Degree of difficulty

Difficult

Instruction (batch scale 10 mmol)

Equipment

100 mL three neck round bottom flask, heatable magnetic stirrer, magnetic stir bar, thermometer for inside of the flask, Buechner funnel, suction flask, bubble counter, piston-operated pipette (micropipette), protecting gas piping, addition funnel with pressure balance, separating funnel, rotary evaporator, ice bath, oil bath

Substances

2-adamantanone (mp 250-255 °C)	1.5 g (10.0 mmol)
titan(IV) chloride, $TiCl_4$ (bp 136 °C)	2.03 g (1.18 mL, 10.0 mmol)
zinc dust	1.43 g (21.8 mmol
tetrahydrofuran (bp 66 °C) (dry)	40 mL
potassium carbonate	about 2 g
cyclohexane (bp 81 °C)	about 50 mL
ethanol	
sodium sulfate for drying	about 1 g

Reaction

The reaction must be performed under inert atmosphere (argon or nitrogen). The addition of $TiCl_4$ is delicate and should bee performed in the presence of an experienced adviser.

The reaction is performed in a 100 mL three neck round bottom flask connected to a reflux condenser and equipped with a magnetic stir bar and a connection to vacuum and a protective gas piping. The flask is heated under vacuum, the nitrogen is flown to it. After cooling 30 mL of dry tetrahydrofuran is added into the flask, which is cooled by an ice bath untill the inner temperature reaches about 0 °C. Under inert atmosphere and stirring 1.18 mL (2.03 g, 10.0 mmol) of $TiCl_4$ is added with a pipette at a temperature between 0 and 5 °C (that means about 1 drop of $TiCl_4$ is added within 5 seconds). To this yellow mixture is added 1.43 g (21.8 mmol) of zinc dust under stirring in small portions. A black precipitate is observed during addition of zinc. After 5 minutes of the last zinc addition the solution of 1.50 g (10.0 mmol) 2-adamantanone in 20 mL dry tetrahydrofuran is added dropwise from an addition funnel with stirring. Then the mixture is heated for 20 hours under reflux.

Work up

After cooling of the reaction mixture to room temperature 22 mL of a 10% aqueous solution of K_2CO_3 is added. The mixture is extracted 5 times with 10 mL cyclohexane each. The combined organic extractions are washed twice with 5 mL of water each, then the solution is dried over sodium sulfate. After filtration from sodium sulfate the solution is evaporated, yielding 12.3 g of crude product.

The crude product is purified by recrystallization from ethanol with a small amount of cyclohexane.
Yield: 1.10 g (4.10 mmol, 82%); white solid, mp 189-190 C

Comments
Performing the reaction on 1 mmol scale only 2-hydroxyadamantane is formed.
Substitution of tetrahydrofuran by *tert*-butyl methyl ether is not possible.

Waste management

Waste	Disposal
evaporated solvent mixture	organic solvents, halogen free
aqueous phase after extraction	solvent water mixtures, containing halogen
sodium sulfate	solid waste, free from mercury

Time
About 3 hours without the time for refluxing

Break
After the addition of the K_2CO_3 solution and after the extraction

Degree of difficulty
Difficult

Analytics

GC

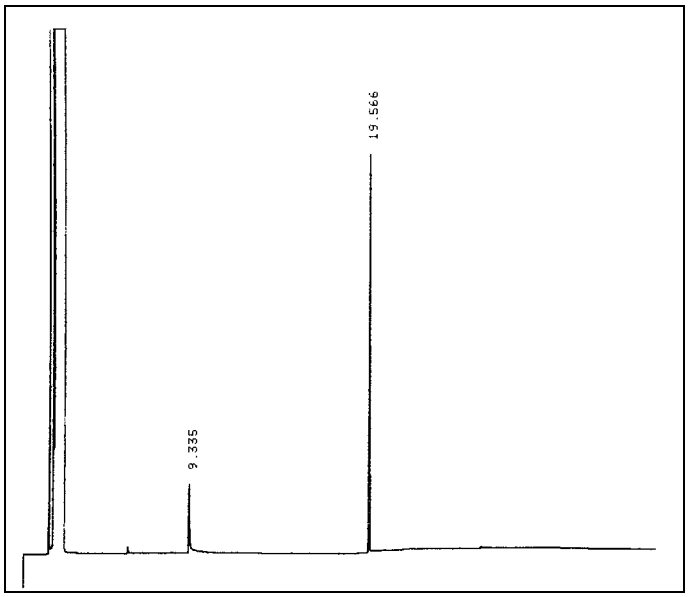
Sample preparation:
A sample of the product is diluted in 1 mL *tert*-butyl methyl ether, 1 µL is injected.

GC conditions:

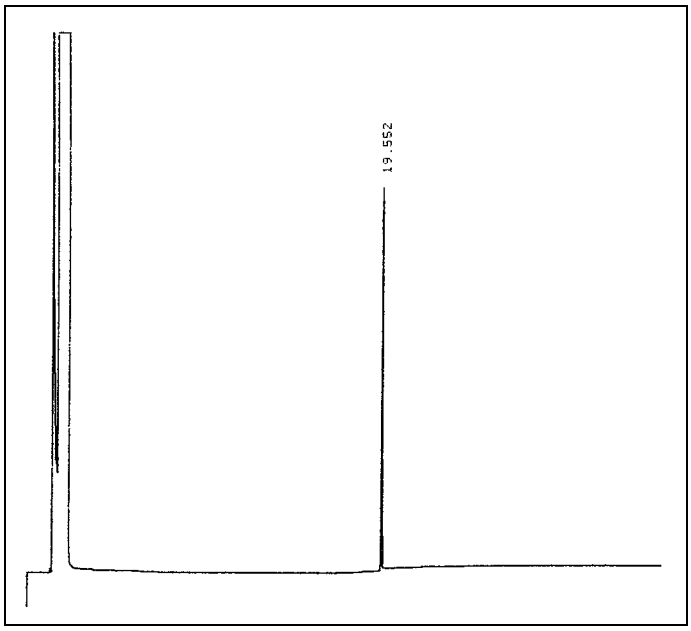
column:	Macherey und Nagel, SE-54, 326-MN-30705-9, 25 m, ID 0.32 mm, DF 0.25 µm
inlet:	Gerstel KAS, injector 250 °C;
	split injection: 1:20, injected volume 1 µL
carrier gas:	nitrogen, pre-column pressure 62 kPa, flow rate 1.04 mL/min
oven:	100 °C (1 min), 10 °C/min (250 °C) (30 min)
detector:	FID, 275 °C

Percent concentration was calculated from peak areas.

GC of the crude product

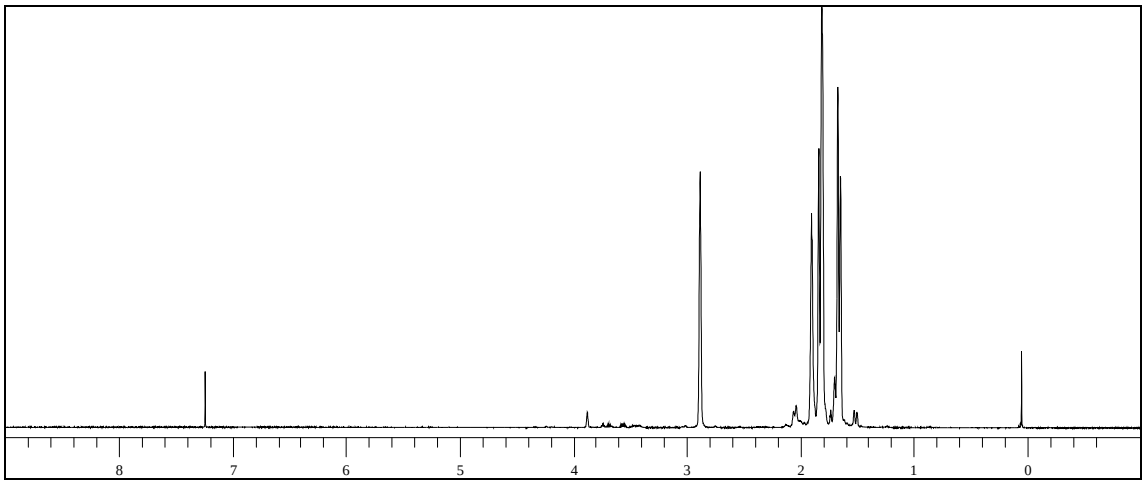


GC of the pure product

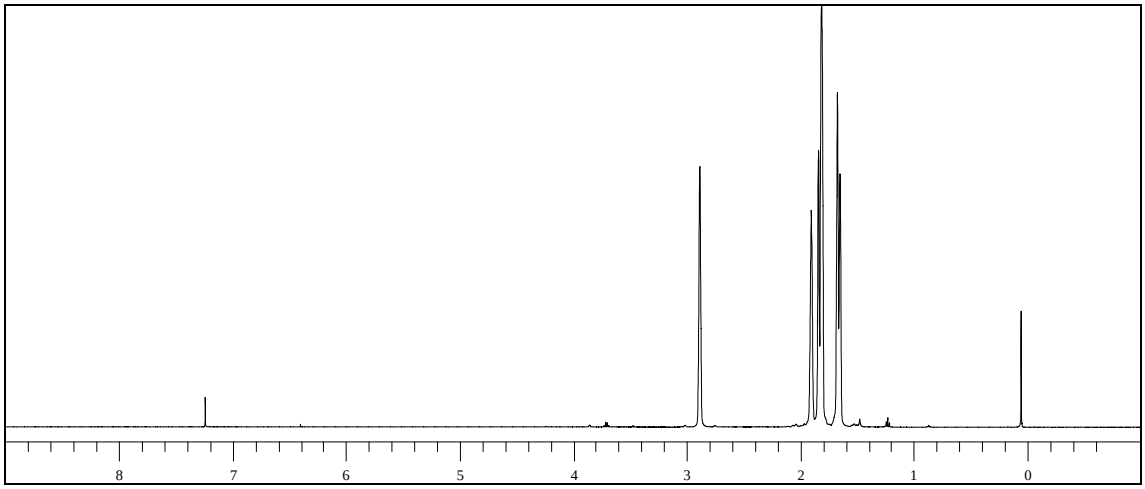


Retention time (min)	Substance	Peak area %	
		Crude product	Pure product
19.5	product (adamantylidene adamantane)	83.2	100
9.3	side product (2-hydroxyadamantane, determined by GC/MS)	16.9	

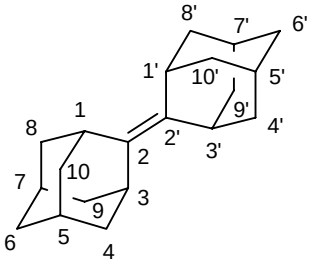
^{1}H NMR spectrum of the crude product (500 MHz, $CDCl_3$)



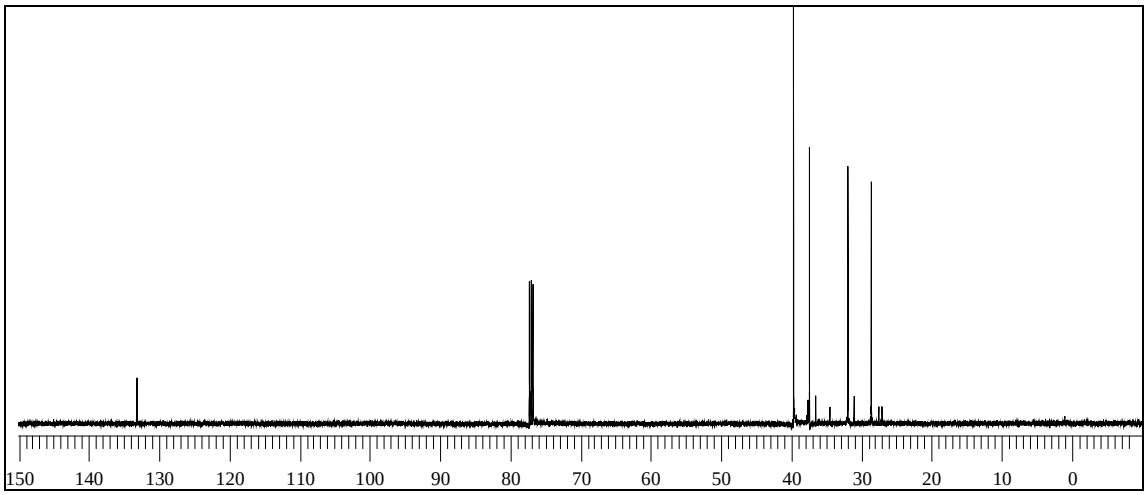
^{1}H NMR spectrum of the pure product (500 MHz, $CDCl_3$)



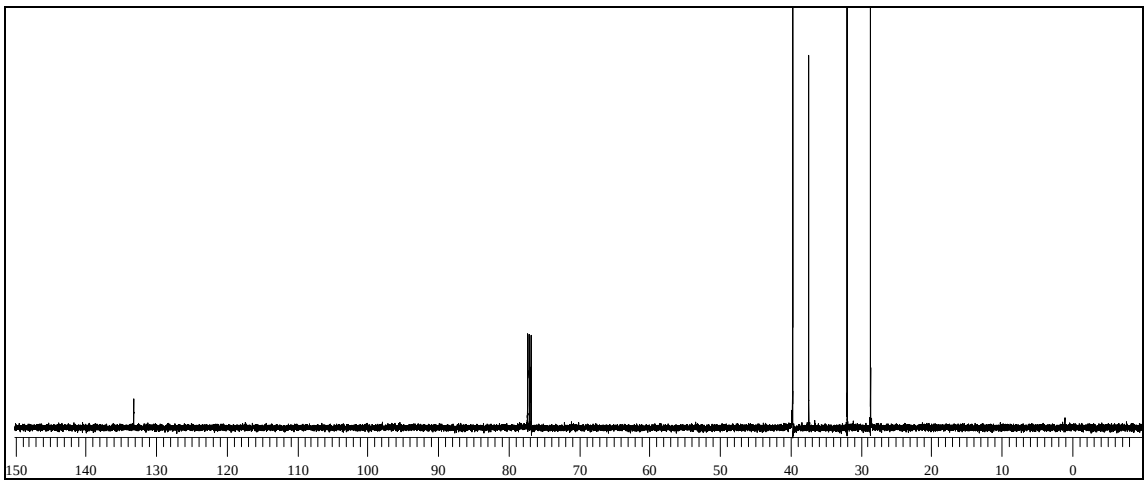
δ (ppm)	Multiplicity	Number of H	Assignment
1.63 - 1.69	m	8	CH_2
1.79 - 1.86	m	12	CH_2
1.90	m	4	5-H, 5'-H, 7-H, 7'-H
2.88	m	4	1-H, 1'-H, 3-H, 3'-H



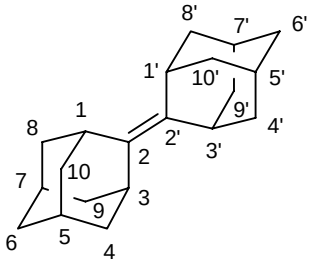
^{13}C NMR spectrum of the crude product (125 MHz, $CDCl_3$)



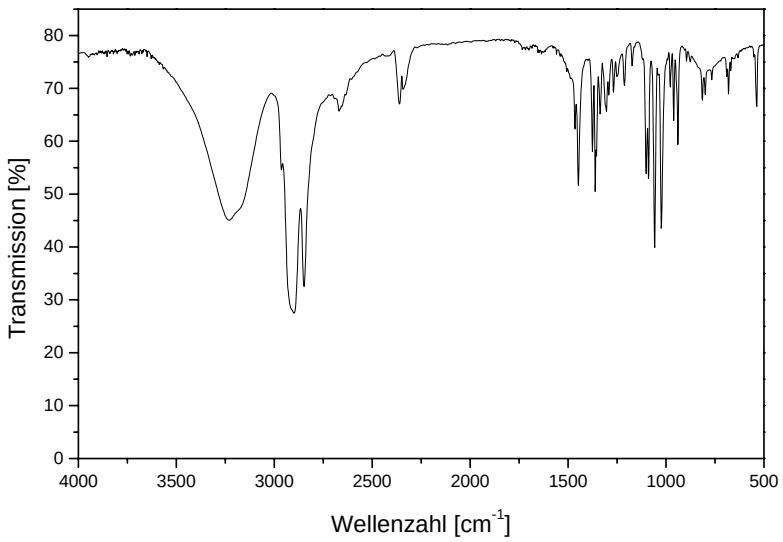
^{13}C NMR spectrum of the pure product (125 MHz, $CDCl_3$)



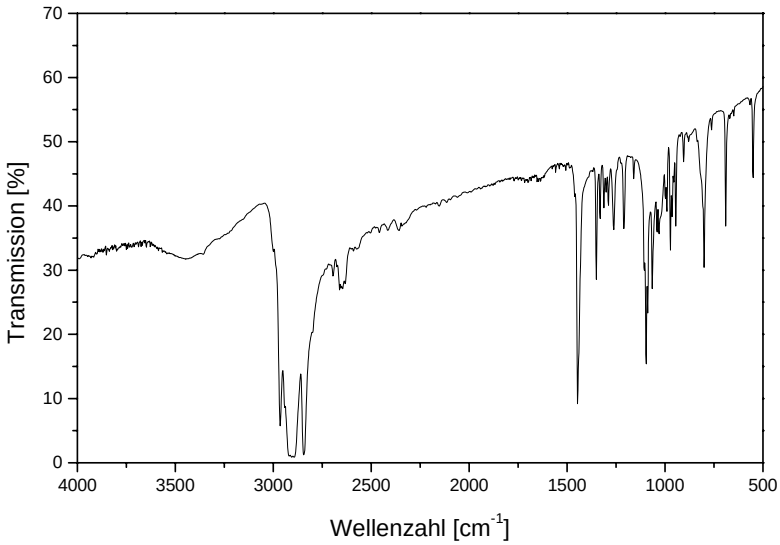
δ (ppm)	Assignment
28.6	C-5, C-5', C-7, C-7'
31.9	C-1, C-1', C-3, C-3'
37.3	C-6, C-6'
39.6	C-4, C-4', C-8, C-8', C-9 ,C-9', C-10, C-10'
133.1	C-2, C-2'



IR spectrum of the crude product (KBr)



IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
2966, 2916, 2848	C-H-valence, alkane