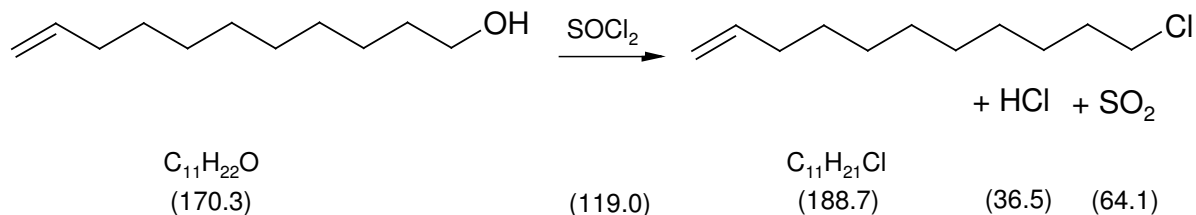


4027 Synthesis of 11-chloroundec-1-ene from 10-undecen-1-ol**Classification****Reaction types and substance classes**

nucleophilic substitution
chloroalkane, alcohol

Work methods

heating under reflux, stirring with magnetic stir bar, adding dropwise with an addition funnel, distilling under reduced pressure, draining of gases, working with wash bottles, use of an ice cooling bath, cooling with liquid nitrogen, heating with oil bath

Instruction (batch scale 10 mmol)**Equipment**

10 mL two-neck flask, reflux condenser, bubble counter, addition funnel with pressure balance, 2 wash bottles, heatable magnetic stirrer, magnetic stir bar, distillation head, vacuum pump, cooling bath with liquid nitrogen, ice bath, oil bath

Substances

10-undecen-1-ol (bp 132 °C, 20 hPa)	1.70 g (10.0 mmol)
thionyl chloride (freshly distilled) (bp 76 °C)	1.7 g (1.0 mL, 14 mmol)
sodium hydroxide solution (2 M) for wash bottle	

Reaction

1.70 g (10 mmol) 10-undecen-1-ol are filled in a 10 mL two-neck flask with magnetic stir bar, addition funnel with pressure balance and reflux condenser. The reflux condenser is for draining of developing gases (HCl, SO₂!) successively connected with a bubble counter (filled with paraffin oil), an empty safety wash bottle and another wash bottle, filled to 1/3 with 2 M sodium hydroxide solution. 1.7 g (1.0 mL, 14 mmol) thionyl chloride are added dropwise with an addition funnel under stirring within 10 minutes (gas development). Afterwards the reaction mixture is stirred and heated at an oil bath temperature of 110 °C until in the reaction mixture with thin layer or gas chromatography neither educt nor intermediate product can be detected (see analytics). Normally, the reaction is finished after 5 hours.

Work up

After cooling down of the reaction mixture the reflux condenser is replaced through a small distillation bridge and the excessive thionyl chloride is condensed under slightly heating at a pressure of about 20 hPa into a trap, which is cooled with liquid nitrogen. Then the remaining crude product is fractional distilled at about $5 \cdot 10^{-1}$ hPa. The receiving flasks are cooled in an ice bath.

Yield: 1.52 g (8.06 mmol, 81%); bp 52 °C ($2.4 \cdot 10^{-1}$ hPa), oil bath temperature 90 °C; colourless liquid; $n_D^{20} = 1.4511$

Comments

Diundecenyl sulfite is formed as intermediate, which reacts under the described reaction conditions – excess of thionyl chloride – almost quantitatively to the product.

Waste management**Waste disposal**

Waste	Disposal
thionyl chloride from the cold trap	dissolve in diluted sodium hydroxide solution, then: aqueous alkaline waste
distillation residue	dissolve in acetone, then: organic solvents, containing halogen
solution from the wash bottle	aqueous alkaline waste

Time

7.5 hours, inclusive 5 hours reflux

Break

After heating under reflux

Degree of difficulty

Medium

Instruction (batch scale 100 mmol)**Equipment**

50 mL two-neck flask, reflux condenser, bubble counter, addition funnel with pressure balance, 2 wash bottles, heatable magnetic stirrer, magnetic stir bar, distillation head, vacuum pump, cooling bath with liquid nitrogen, ice bath, oil bath

Substances

10-undecen-1-ol (bp 132 °C, 20 hPa)	17.0 g (100 mmol)
thionyl chloride (freshly distilled) (bp 76 °C)	16.7 g (10.3 mL, 140 mmol)
sodium hydroxide solution (2 M) for wash bottle	

Reaction

17.0 g (100 mmol) 10-undecen-1-ol are filled in a 50 mL two-neck flask with magnetic stir bar, addition funnel with pressure balance and reflux condenser. The reflux condenser is for draining of developing gases (HCl, SO₂!) successively connected with a bubble counter (filled with paraffin oil), an empty safety wash bottle and another wash bottle, filled to 1/3 with 2 M sodium hydroxide solution. 11.9 g (7.3 mL, 100 mmol) thionyl chloride are added dropwise with an addition funnel under stirring within 30 minutes (gas development). Afterwards the reaction mixture is stirred and heated at an oil bath temperature of 110 °C for a total of 6 hours, whilst after one hour again 4.8 g (3 mL, 40 mmol) thionyl chloride are added dropwise. The reaction is followed by thin layer or gas chromatography (see analytics) and shows after the specified reaction time a quantitative reaction of the educt and the intermediate product.

Work up

After cooling down of the reaction mixture the reflux condenser is replaced through a distillation bridge and the excessive thionyl chloride is condensated under slightly heating at a pressure of about 20 hPa into a trap, which is cooled with liquid nitrogen. Then the remaining crude product is fractional distilled at about $5 \cdot 10^{-1}$ hPa. The receiving flasks are cooled in an ice bath.

Yield: 16.8 g (89.2 mmol, 89%); bp 62 °C ($3.4 \cdot 10^{-1}$ hPa), oil bath temperature 90 °C; colourless liquid; $n_D^{20} = 1.4511$

Comments

Diundecenyl sulfite is formed as intermediate, which reacts under the described reaction conditions – excess of thionyl chloride – almost quantitatively to the product.

Waste management**Waste disposal**

Waste	Disposal
thionyl chloride from the cold trap	dissolve in diluted sodium hydroxide solution, then: aqueous alkaline waste
distillation residue	dissolve in acetone, then: organic solvents, containig halogen
solution from the wash bottle	aqueous alkaline waste

Time

9.5 hours, inclusive 6 hours reflux

Break

After heating under reflux

Degree of difficulty

Medium

Instruction (batch scale 1 mol)

Equipment

500 mL two-neck flask, reflux condenser, bubble counter, addition funnel with pressure balance, 2 wash bottles, heatable magnetic stirrer, magnetic stir bar, distillation head, vacuum pump, cooling bath with liquid nitrogen, ice bath, oil bath

Substances

10-undecen-1-ol (bp 132 °C, 20 hPa)	170 g (1.00 mol)
thionyl chloride (freshly distilled) (bp 76 °C)	128 g (77.9 mL, 1.07 mol)
sodium hydroxide solution (2 M) for wash bottle	

Reaction

170 g (1.00 mol) 10-undecen-1-ol are filled in a 500 mL two-neck flask with magnetic stir bar, addition funnel with pressure balance and reflux condenser. The reflux condenser is for draining of developing gases (HCl, SO₂!) successively connected with a bubble counter (filled with paraffin oil), an empty safety wash bottle and another wash bottle, filled to 1/3 with 2 M sodium hydroxide solution. 119 g (73 mL, 1.0 mol) thionyl chloride are added dropwise with an addition funnel under stirring within 2 hours, whilst the reaction mixture is heated at an oil bath temperature of 60 °C (gas development). After the addition of the 73 mL thionyl chloride, the oil bath temperature is increased to 110 °C and the reaction mixture is heated for further 2 hours, whilst after one hour further 7.7 g (5 mL, 65 mmol) thionyl chloride are added. The sodium hydroxide solution in the wash bottle is changed five times (strong and long-lasting gas development). The course of the reaction is followed by means of thin layer or gas chromatography and shows a quantitative reaction of the educt and the intermediate product after the above specified reaction time.

Work up

After cooling down of the reaction mixture the reflux condenser is replaced through a distillation bridge and the excessive thionyl chloride is condensed under slightly heating at a pressure of about 20 hPa into a trap, which is cooled with liquid nitrogen. Then the remaining crude product is fractional distilled at about $5 \cdot 10^{-1}$ hPa. The receiving flasks are cooled in an ice bath.

Yield: 180 g (0.956 mol, 96%); bp 55 °C ($3.1 \cdot 10^{-1}$ hPa), oil bath temperature 80 °C; colourless liquid; $n_D^{20} = 1.4511$

Comments

Diundecenyl sulfite is formed as intermediate, which reacts under the described reaction conditions – excess of thionyl chloride – almost quantitatively to the product.

Waste management**Waste disposal**

Waste	Disposal
thionyl chloride from the cold trap	dissolve in diluted sodium hydroxide solution, then: aqueous alkaline waste
distillation residue	dissolve in acetone, then: organic solvents, containing halogen
solution from the wash bottle	aqueous alkaline waste

Time

10 hours, inclusive 5 hours for distillation

Break

After heating under reflux

Degree of difficulty

Medium

Analytcs**Reaction monitoring**

The course of the reaction can be controlled with thin layer or gas chromatography

TLC

Sample preparation:

Using a Pasteur pipette, one drop is taken from the reaction mixture and diluted with 1 mL CH₂Cl₂.

TLC-conditions:

adsorbant: TLC-aluminium foil (silica gel 60)
 eluent: petroleum ether (60-80 °C) : acetic acid ethyl ester = 6 : 4
 visualizing: The TLC-aluminium foil is dipped in 2N H₂SO₄ and then dried with a hot air dryer.

R_f (10-undecene-1-ol) 0.40

R_f (11-chloroundec-1-en). 0.64

GC

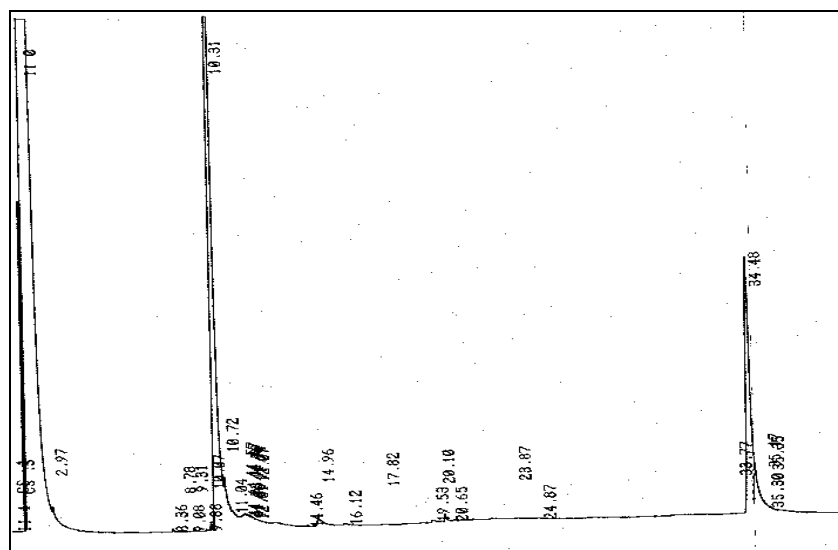
Sample preparation:

Using a Pasteur pipette, one drop is taken from the crude product or the pure product, respectively and is diluted with 10 mL dichloromethane. 0.2 µL from this solution are injected.

GC-conditions:

column: DB-WAX, 30 m, internal diameter 0.33 mm, film 0.25 µm
 inlet: on-column-injection
 carrier gas: hydrogen (40 cm/s)
 oven: 90 °C (5 min), 10 °C/min at 240 °C (30 min)
 detector: FID, 270 °C

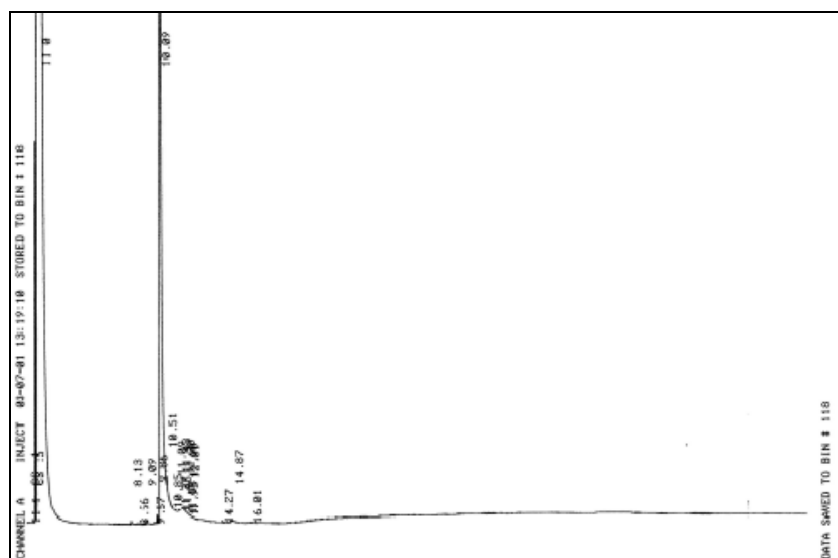
Percent concentration was calculated from peak areas.

GC of the reaction solution (reaction time: 3.5 hours)

Retention time (min)	Substance	Peak area %
10.31	product (11-chlorundec-1-en)	82.6
34.48	intermediate product (diundecenyl sulfite)	13.0

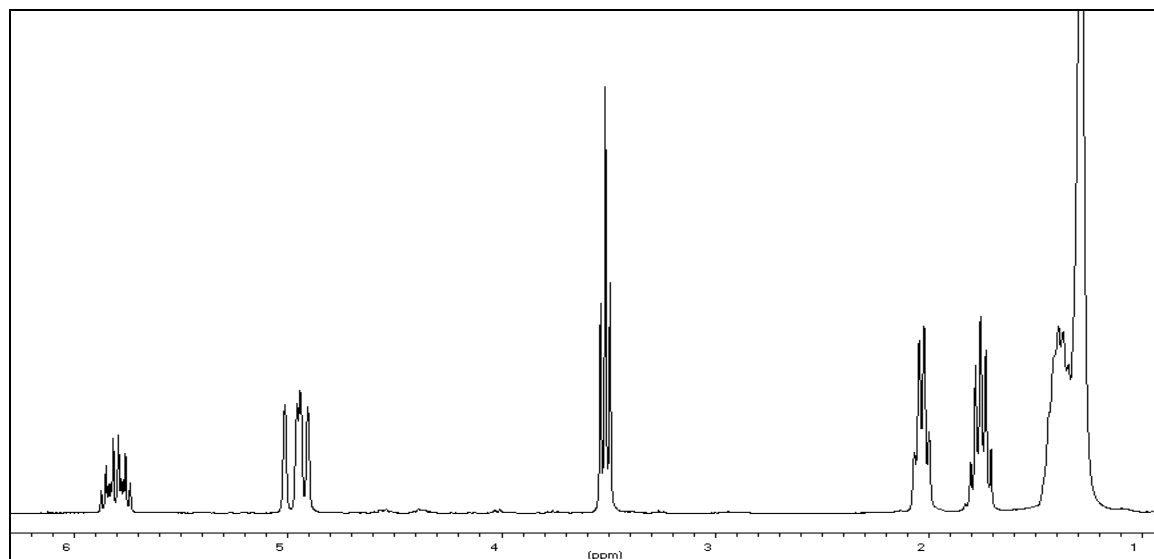
GC of the crude product

GC-conditions equivalent to those for reaction monitoring

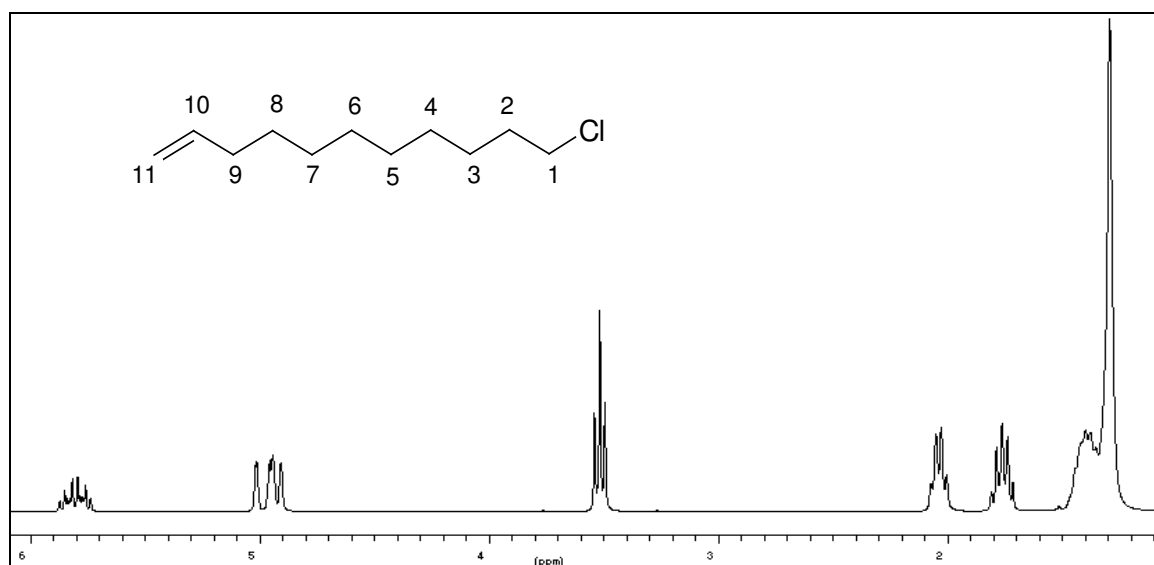


Retention time (min)	Substance	Peak area %
10.12	product (11-chlorundec-1-en)	95.4

^1H NMR spectrum of the crude product (reaction mixture before distillation)
(300 MHz, CDCl_3)

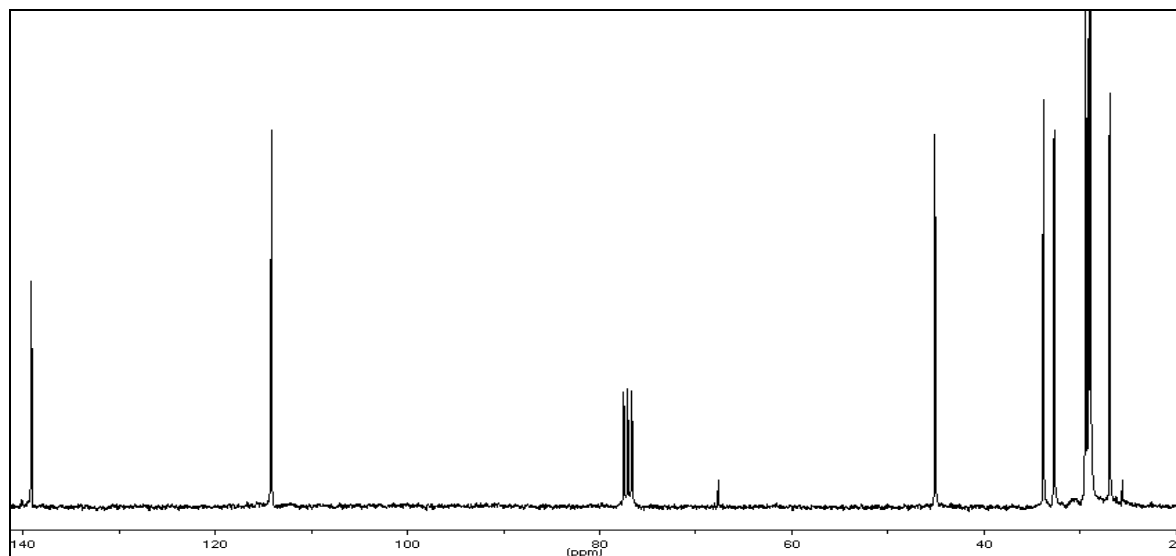


^1H NMR spectrum of the pure product (300 MHz, CDCl_3)

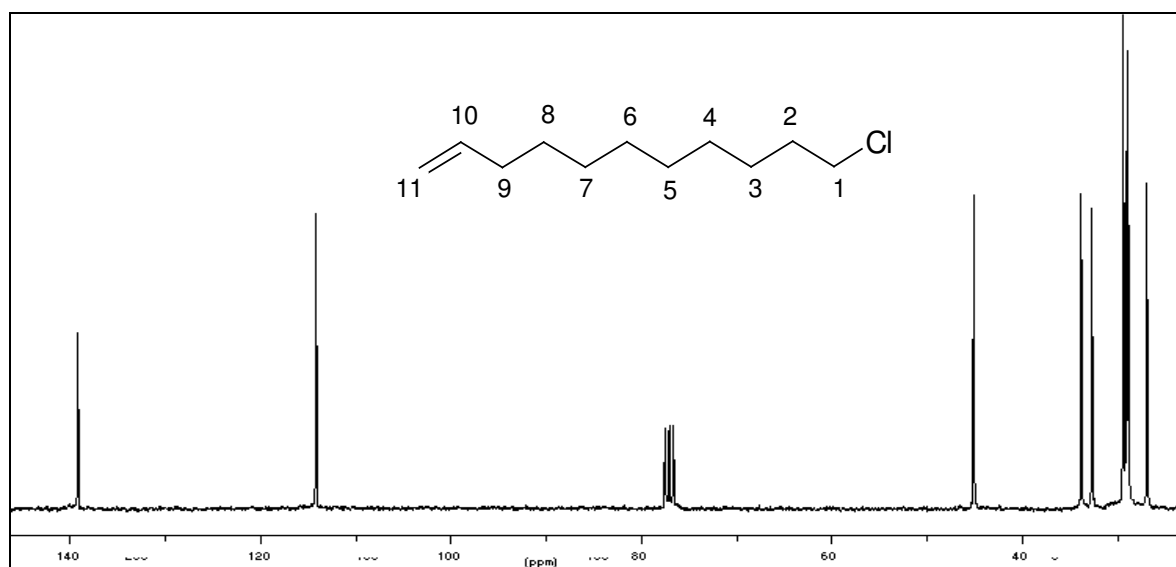


δ (ppm)	Multiplicity	Number of H	Assignment
1.1-1.5	m	12	CH_2
1.75	tt	2	2-H
2.02	dt	2	9-H
3.51	t	2	1-H
4.95	2 x dd	2	11-H
5.80	m	1	10-H

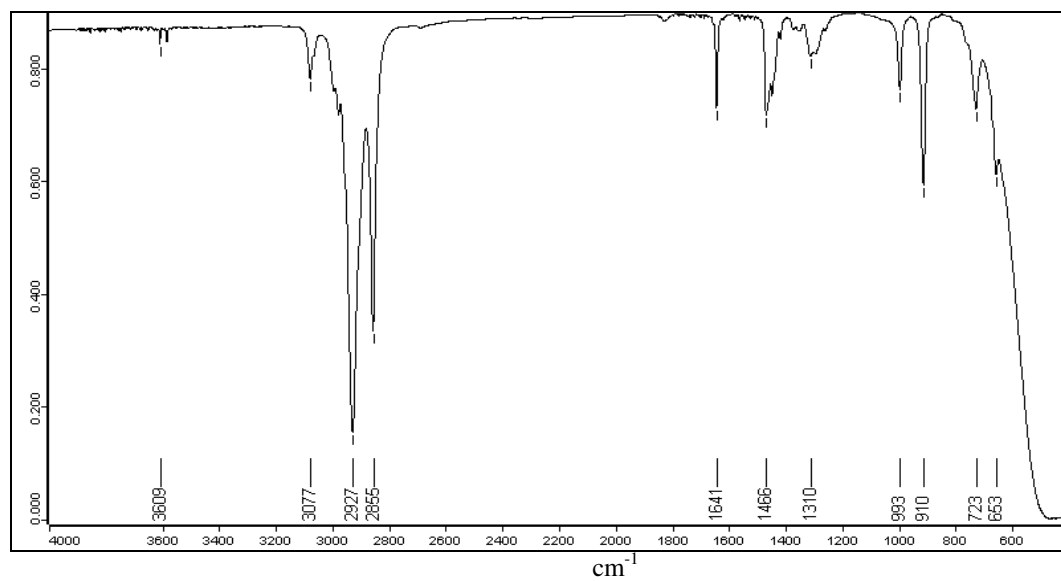
^{13}C NMR spectrum of the crude product (reaction mixture before distillation)
(75.5 MHz, CDCl_3)



^{13}C NMR spectrum of the pure product (75.5 MHz, CDCl_3)



δ (ppm)	Assignment
139.1	C-10
114.1	C-11
45.0	C-1
33.8	C-9
32.7	C-2
76.5-77.5	solvent

IR spectrum of the pure product (film)

(cm ⁻¹)	Assignment
3077	C-H-valence, alkene, H ₂ C=C
2927, 2855	C-H-valence, alkane
993, 910	C-H-deformation, alkene, H ₂ C=CHR
723	C-Cl, valence