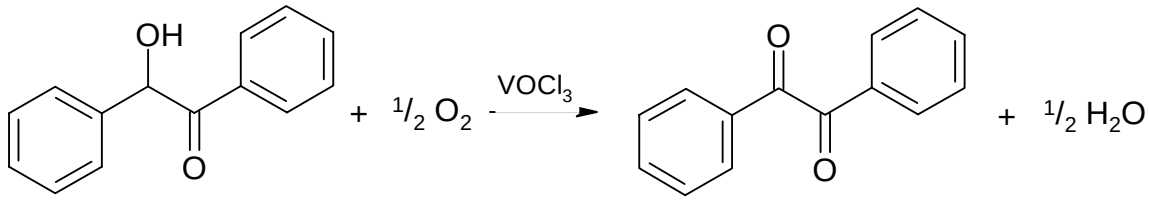
4002 Synthesis of benzil from benzoin



$C_{14}H_{12}O_2$ (212.3) + $^1/_2\ O_2$ —$VOCl_3$→ 173.3 + $C_{14}H_{10}O_2$ (210.2) + $^1/_2\ H_2O$

Classification

Reaction types and substance classes
oxidation
alcohol, ketone, transition metal catalyst

Work methods
introduction of gas, stirring with magnetic stir bar, shaking out, extracting, filtering, recrystallizing, evaporating with rotary evaporator

Instruction (batch scale 10 mmol)

Equipment
25 mL two-neck flask, magnetic stirrer, magnetic stir bar, adapter with ground-glass joint, ground-in stopcock and hose coupling, gas-filled balloon, separating funnel, rotary evaporator

Substances

benzoin (mp 132-134 °C)	2.12 g (10.0 mmol)
vanadium(V)-oxychloride	0.017 g (0.10 mmol)
acetone (dry) (bp 56 °C)	10 mL
acetic acid ethyl ester (bp 77 °C)	34 mL
diethyl ether (bp 35 °C)	15 mL
sodium hydrogen carbonate	about 3 g (for 30 mL saturated aqueous solution)
sodium chloride	about 6 g (for 16 mL saturated aqueous solution)
magnesium sulfate for drying	
oxygen	

Reaction
10 mL dry acetone are filled in a 25 mL two-neck flask with magnetic stir bar. 0.017 g (0.10 mmol) vanadium(V) oxychloride and 2.12 g (10.0 mmol) benzoin are added. One of the flask openings is equipped with an adapter with ground-glass joint, ground-in stopcock and hose coupling connected with an oxygen-filled balloon. The flask is briefly rinsed with

oxygen, then the second flask opening is closed. The stoppers on the flask must be secured against over-pressure. The reaction mixture is stirred under oxygen atmosphere for 3 hours at room temperature. The initially cloudy green solution becomes clear after one hour. If necessary, the gas balloon is refilled.

Work up

10 mL acetic acid ethyl ester are added to the reaction solution and the mixture is shaken out two times in a the separating funnel with 15 mL saturated sodium hydrogen carbonate solution each. The combined aqueous phases are shaken out three times with 8 mL acetic acid ethyl ester each. The combined organic phases are washed two times with 8 mL saturated sodium chloride solution each and dried over magnesium sulfate. After filtering off the drying agent the solvent is evaporated at a rotary evaporator. A crystalline residue remains as crude product.
Crude yield: 1.6 g

The crude product is recrystallized from about 15 mL diethyl ether and stored in the refrigerator for crystallization.
Yield: 1.13 g (5.37 mmol, 54%), yellow needles; mp 95-96°C

Comments

The product yield can be slightly increased if the mixture is stirred for further 2 hours at room temperature and the gas balloon is refilled with oxygen, if necessary. The reaction solution can also be stirred over night at room temperature.

Benzoic acid is formed as side product, which is transferred to the aqueous phase during the shaking out.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	aqueous waste, containing heavy metal
evaporated solvent mixture	organic solvents, halogen free
mother liquor from recrystallization	organic solvents, halogen free
magnesium sulfate	solid waste, free from mercury

Time

4-5 hours, without time for crystallization

Break

After stirring and before recrystallization

Degree of difficulty

Easy

Instruction (batch scale 100 mmol)

Equipment

250 mL two-neck flask, magnetic stirrer, magnetic stir bar, adapter with ground-glass joint, ground-in stopcock and hose coupling, gas-filled balloon, separating funnel, rotary evaporator

Substances

benzoin (mp 132-134 °C)	21.2 g (100 mmol)
vanadium(V) oxychloride	0.174 g (1.00 mmol)
acetone (dry) (bp 56 °C)	100 mL
acetic acid ethyl ester (bp 77 °C)	250 mL
diethyl ether (bp 35 °C)	about 5 mL
sodium hydrogen carbonate	about 30 g (for 300 mL saturated aqueous solution)
sodium chloride	about 60 g (für 160 mL saturated aqueous solution)
magnesium sulfate for drying	
oxygen	

Reaction

100 mL dry acetone are filled in a 250 mL two-neck flask with magnetic stir bar. 0.174 g (1.00 mmol) vanadium(V) oxychloride and 21.2 g (100 mmol) benzoin are added. One of the flask openings is equipped with an adapter with ground-glass joint, ground-in stopcock and hose coupling connected with an oxygen-filled balloon. The flask is briefly rinsed with oxygen, then the second flask opening is closed. The stoppers on the flask must be secured against over-pressure. The reaction mixture is stirred under oxygen atmosphere for 5 hours at room temperature. The initially cloudy green solution becomes clear after thee hours. If necessary, the gas balloon is refilled.

Work up

50 mL acetic acid ethyl ester are added to the reaction solution and the mixture is shaken out three times in a the separating funnel with 100 mL saturated sodium hydrogen carbonate solution each. The combined aqueous phases are shaken out three times with 50 mL acetic acid ethyl ester each. The combined organic phases are washed two times with 80 mL saturated sodium chloride solution each and dried over magnesium sulfate. After filtering off the drying agent the solvent is evaporated at a rotary evaporator. A crystalline residue remains as crude product.
Crude yield: 15.5 g

The crude product is recrystallized from about 50 mL acetic acid ethyl ester/diethyl ether (9:1) and stored in the refrigerator for crystallization.
Yield: 12.3 g (585 mmol, 59%), yellow needles; mp 93-94°C

Comments

The product yield can be slightly increased if the mixture is stirred for further 2 hours at room temperature and the gas balloon is refilled with oxygen, if necessary. The reaction solution can also be stirred over night at room temperature.

Benzoic acid is formed as side product, which during shaking out is transferred to the aqueous phase.

Waste management

Waste disposal

Waste	Disposal
aqueous phase	aqueous waste, containing heavy metal
evaporated solvent mixture	organic solvents, halogen free
mother liquor from recrystallization	organic solvents, halogen free
magnesium sulfate	solid waste, free from mercury

Time

7-8 hours, without time for crystallization

Break

After stirring and before recrystallization

Degree of difficulty

Easy

Analytics

Reaction monitoring with TLC

Sample preparation:

Using a Pasteur pipette, two drops from the reaction solution are taken and diluted with 1 mL dichloromethane.

TLC-conditions:

adsorbant:	TLC-aluminium foil (silica gel 60)
eluent:	petroleum ether (60/80)/diethyl ether/methanol = 14 : 6 : 2
visualizing agent:	The TLC-aluminium foil is dipped in 2N H_2SO_4 and then dried with a hot air dryer.
R_f (benzil)	0.49 (UV-active)

Reaction monitoring with GC

Sample preparation:

Using a Pasteur pipette, two drops of the reaction solution are taken and diluted with 10 mL dichloromethane. 0.2 µL from this solution are injected.

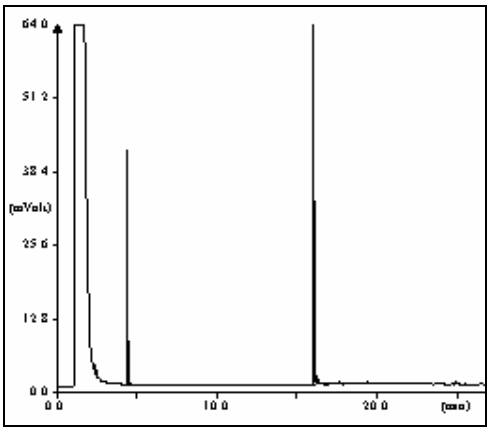
From the solid product 10 mg are dissolved in 10 mL dichloromethane. 0.2 µl from this soluion are injected.

GC-conditions:

column:	DB-1, 28 m, internal diameter 0.32 mm, film 0.25 µm
inlet:	on-column-injection
carriergas:	hydrogen (40 cm/s)
oven:	90 °C (5 min), 10 °C/min at 240 °C (30 min)
detector:	FID, 270 °C

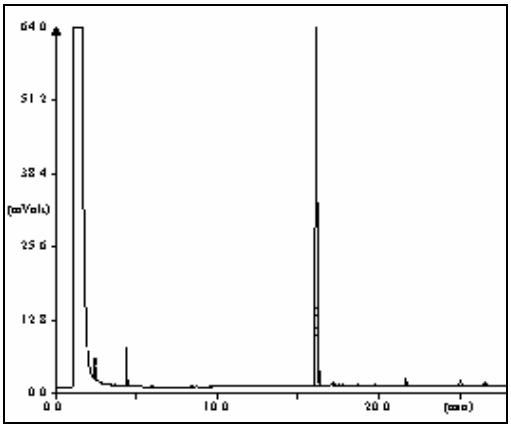
Percent concentration was calculated from peak areas.

GC of the reaction solution(Reaction time: 5 hours)



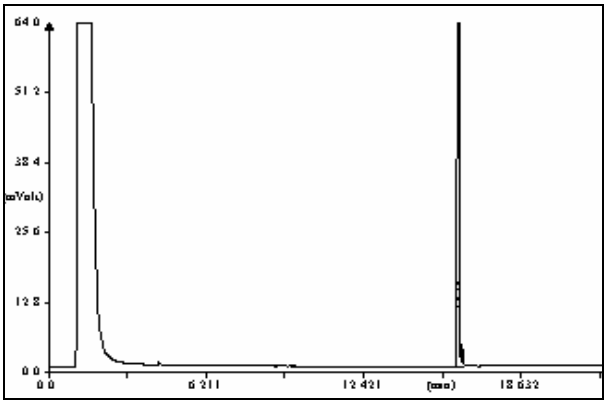
Retention time (min)	Substance	Peak area %
16.05	product (benzil)	87.8
4.40	benzoic acid	12.1

GC of the crude product



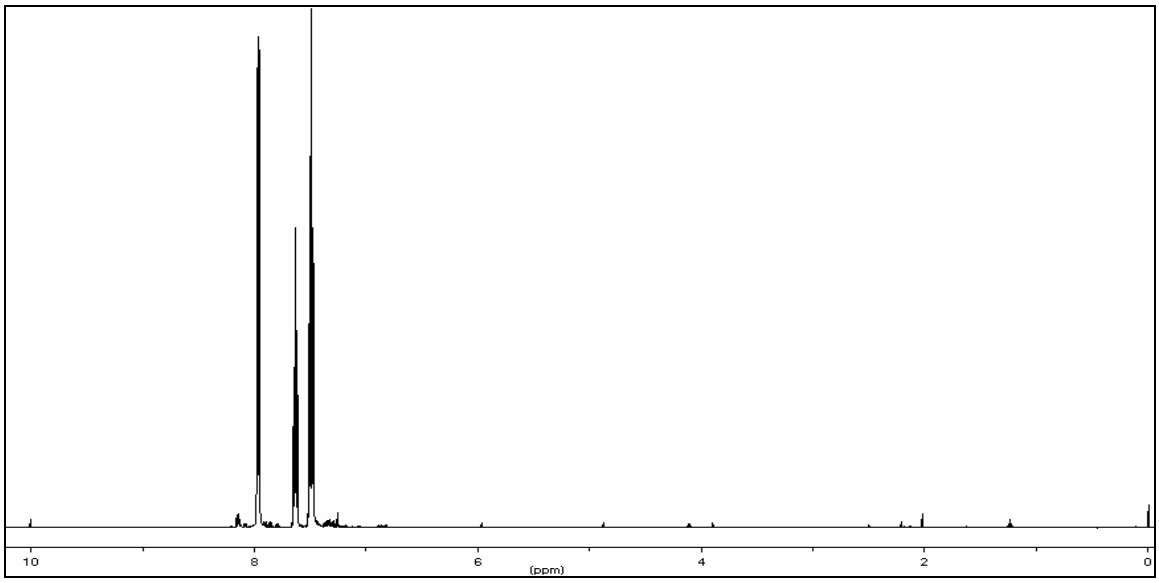
Retention time (min)	Substance	Peak area %
16.15	product (benzil)	92.7
4.40	benzoic acid	2.2

GC of the pure product

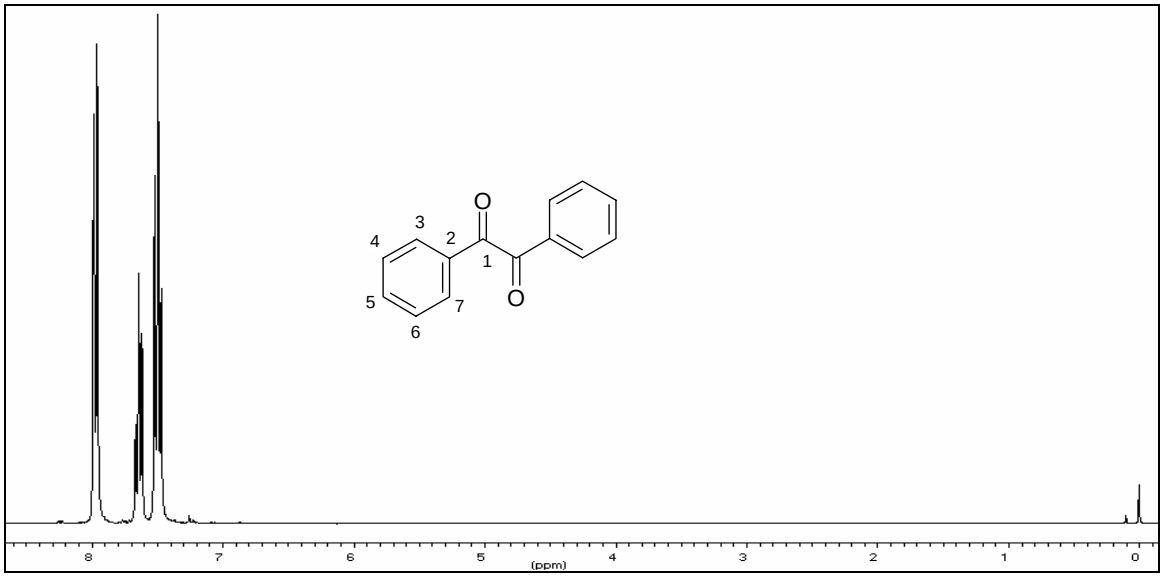


Retention time (min)	Substance	Peak area %
16.17	product (benzil)	98.8

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

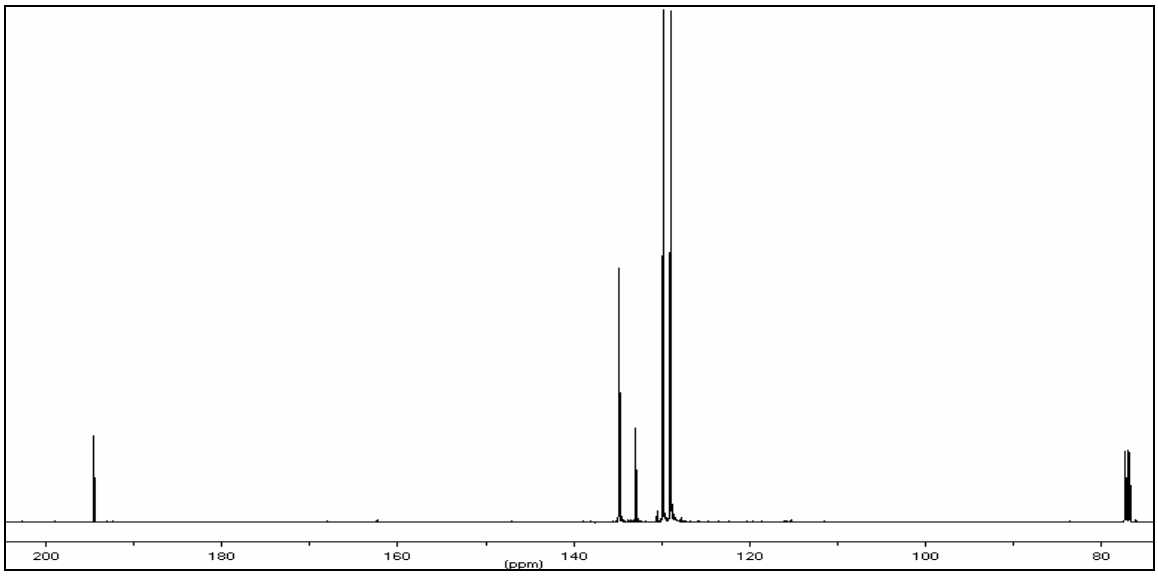


^{1}H NMR spectrum of the pure product (300 MHz, $CDCl_3$)

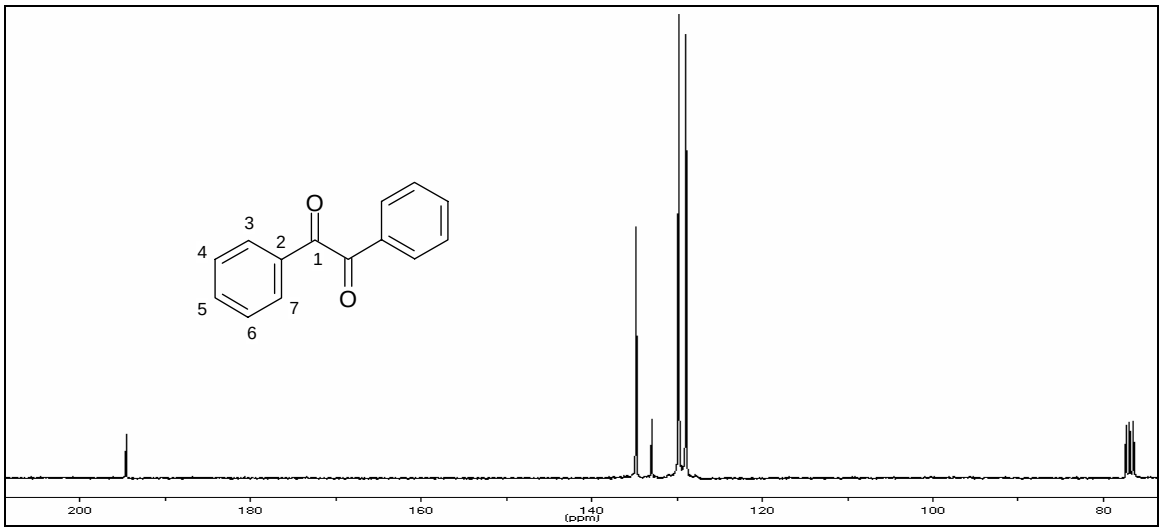


δ (ppm)	Multiplicity	Number of H	Assignment
7.50	m (d)	4	3-H, 7-H
7.64	m (dd)	2	5-H
7.95	m (dd)	4	4-H, 6-H

^{13}C NMR spectrum of the crude product (125.5 MHz, $CDCl_3$)

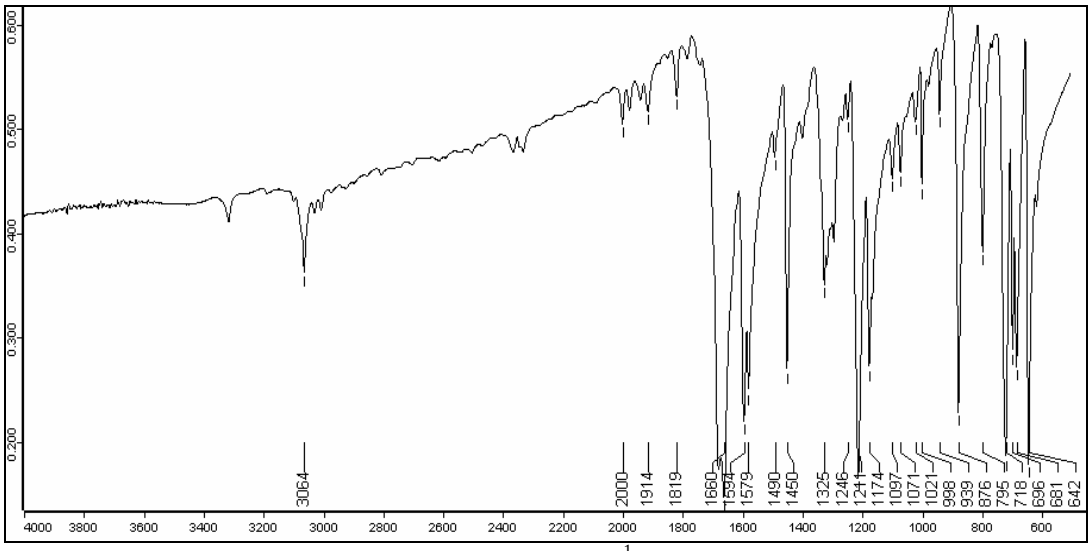


^{13}C NMR spectrum of the pure product (75.5 MHz, $CDCl_3$)



δ (ppm)	Assignment
194.5	C-1
154.8	C-2
133.0	CH arene
129.8	CH arene
129.0	CH arene
76.5-77.5	solvent

IR spectrum of the pure product (KBr)



(cm^{-1})	**Assignment**
3064	C-H-valence, arene
1660	C=O-valence, ketone
1594	C=C-valence, arene
1579	C=C-valence, arene