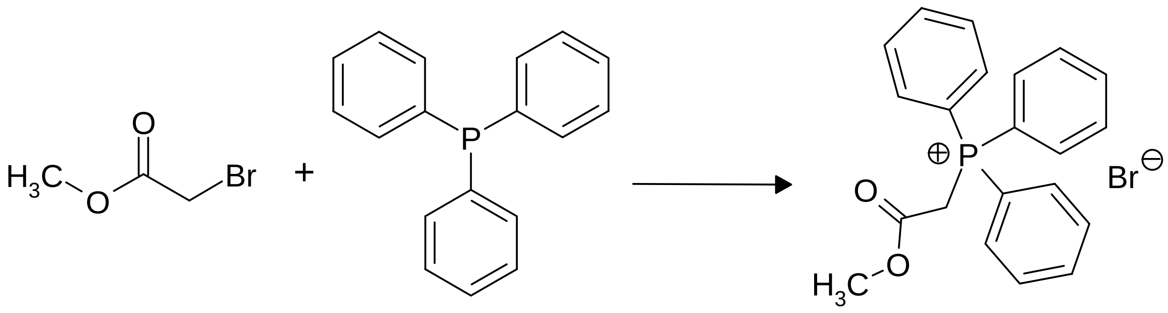
2029 Reaction of triphenylphosphane with bromoacetic acid methyl ester to (carbomethoxymethyl)triphenylphosphonium bromide



$C_3H_5BrO_2$ (153.0)

$C_{18}H_{15}P$ (262.3)

$C_{21}H_{20}BrO_2P$ (415.3)

Literature

G.P. Schiemenz, H. Engelhard, *Chem. Ber*. **1961**, 94, 578

Classification

Reaction types and substance classes

nucleophile substitution

phosphor organic compound, phosphonium salt, phosphane, halogenecarboxylic acid ester

Work methods

stirring with magnetic stir bar, adding dropwise with an addition funnel, extracting, filtering, evaporating with rotary evaporator

Instruction (batch scale 150 mmol)

Equipment

500 mL three-neck flask, reflux condenser, addition funnel with pressure balance, magnetic stirrer, magnetic stir bar, internal thermometer, 1 L round-bottom flask or two 500 mL round-bottom flasks, 500 mL wide-neck Erlenmeyer flask, suction flask, Buechner funnel (diameter 110 cm), rotary evaporator, desiccator

Substances

bromoacetic acid methyl ester (bp 144-146 °C)	23.0 g (13.9 mL, 150 mmol)
triphenylphosphane (mp 78-81 °C)	39.3 g (150 mmol)
toluene (bp 111 °C)	225 mL
water	2.7 mL (0.15 mmol)
methanol (bp 65 °C)	60 mL
n-heptane (bp 98 °C)	about 480 mL

Reaction

A solution of 39.3 g (150 mmol) triphenylphosphane in 150 mL toluene is placed in a 500 mL three-neck flask with reflux condenser, internal thermometer and magnetic stir bar**.** A solution of 23.0 g (13.9 mL, 150 mmol) bromoacetic acid methyl ester in 75 mL toluene is added whilst stirring (this takes 20-30 minutes), resulting in a translucent white clouding after the addition of about 10 mL, the inside temperature increases by 5-10 °C. Afterwards 2.7 mL (150 mmol) water is added and then 60 mL methanol whilst continuosly stirring, the reaction mixture becomes clear and colourless. It is kept 20 hours at room temperature.

Work up

The reaction mixture is filled in a 1 L round bottom flask (or separated in two 500 mL round-bottom flasks) and the solvent mixture is evaporated at the rotary evaporator under reduced pressure. The crude phosphonium salt remains as a colourless solid.
Crude yield: 62.3 g; mp 153-155 °C

Soluble impurities are removed from the crude product by repeated digesting with n-Heptane:
For this purpose, the crude product is stirred in a 500 mL Erlenmeyer flask with 120 mL n-heptane for about 10 minutes with a magnetic stirrer and then sucked off. The solvent is evaporated from the n-heptane solution at the rotary evaporator, a colourless solid remains as residue: triphenylphosphane with little triphenylphosphane oxide. This procedure is repeated with the remaining crude product unless hardly any residue remains from the n-heptane solution after the solvent has been evaporated.

Example for digesting four times:

Solution charge	**Amount of residue (mg) from the *n*-Heptan-solution**	**mp**	**Relation PPh_3 : $POPh_3$ (GC)**
1	253	77-79 °C	92 : 8
2	236	75-78 °C	87 : 13
3	110	74-77 °C	87 : 13
4	21.0	71-76 °C	75 : 25

The insoluble residue in the *n*-heptane is the phosphonium salt. It is dried in the desiccator under reduced pressure until it is constant in weight.
Yield: 60.2 g (145 mmol, 97%), mp 154-157 °C

Comments

In experiment Number 2030 the phosphonium salt is used as educt.

The low amount of triphenylphosphane oxide must have been formed during reaction, since the used triphenylphosphane contained no triphenylphosphane oxide (see also literature).

Waste management

Recycling

The evaporated *n*-heptane is collected and redistilled.

Waste disposal

Waste	Disposal
distilled solvent mixture (toluone, methanol, little water)	organic solvents, halogen free
solid residue from the *n*-heptane solutions	solid waste, free from mercury

Time

2 hours, then standing overnight, then additional 5 hours

Break

Anytime after addition of water and methanol

Degree of difficulty

Easy

Analytics

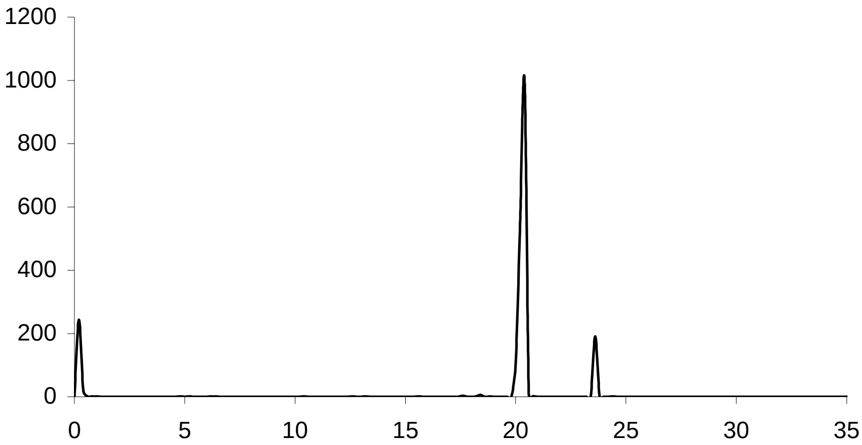
GC of the residue of a *n*-heptane solution (solution charge 1)

Sample preparation:
25 mg substance is dissolved in 0.5 mL dichloromethane

GC-conditions:

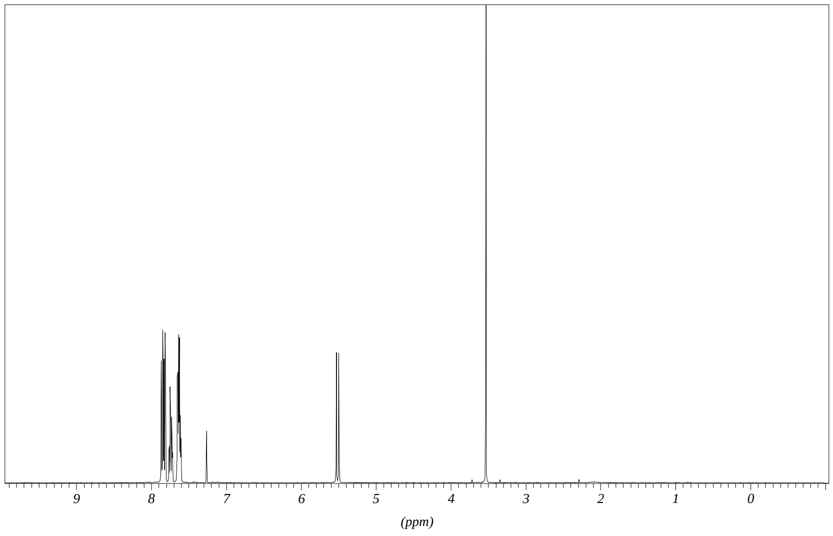
column:	Zebron ZB-1, length 15 m, internal diameter 0.25 mm, film = 0.25 µm (Phenomenex, Torrance, CA, USA)
inlet:	injector temperature 280 °C; splitinjection; injected volume 0.1 µL
carrier gas:	H_2, pre-column pressure 150 kPa
oven:	start temperature 30 °C (2 min), 8 °C/min at 250 °C (2 min)
detector:	FID, 300 °C, H_2 25.1 mL/min; synth air 393 mL/min
integration:	integrator 4290 (Thermo Separation Products)

Percent concentration was calculated from peak areas



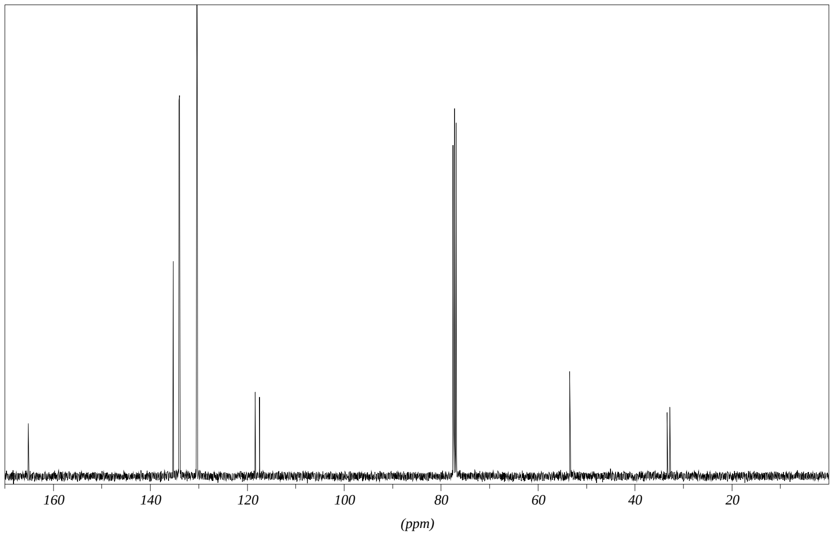
Retention time(min)	Substance	Peak area %
20.5	triphenylphosphane	91.6
23.5	triphenylphosphane oxide	8.4

^{1}H NMR spectrum of purified phosphonium salt (400 MHz, $CDCl_3$)



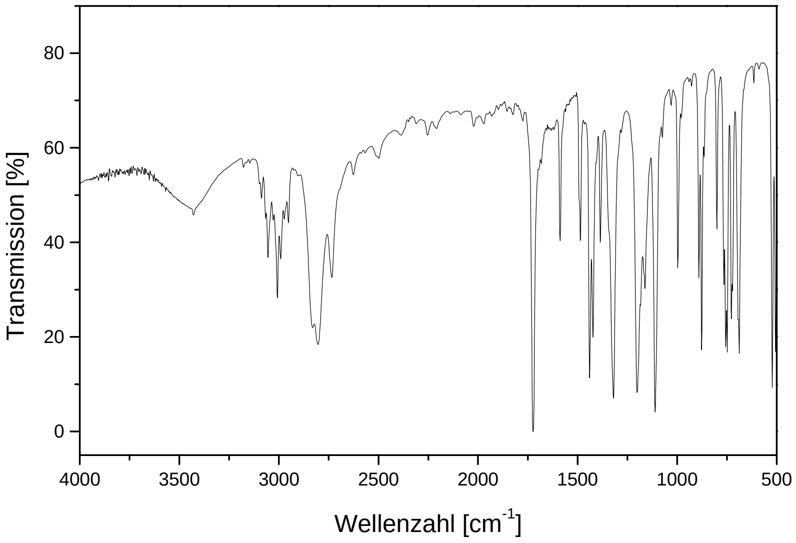
δ (ppm)	Multiplicity	Number of H	Assignment
3.53	S	3	O – C**H**$_3$
5.43 J(H,P) = 13.6 Hz	D	2	P – C**H$_2$**
7.6–7.9	M	15	C**H** arene
7.26			solvent

^{13}C NMR spectrum of purified phosphonium salt (400 MHz, $CDCl_3$)



δ (ppm)	Multiplicity	Assignment
31.87 J(C,P = 57.7 Hz)	D	**C**H$_2$
53.44	S	O **–** **C**H$_3$
117.88 J(C,P = 89.3 Hz)	D	P **–** **C** arene
130.33 J(C,P = 12.9 Hz)	D	**C**H arene
133.98 J(C,P = 10.7 Hz)	D	**C**H arene
135.23 J(C,P = 2.9 Hz)	D	**C**H arene
165.12 J(C,P = 3.6 Hz)	D	O – **C** = O
76.5–77.5		solvent

IR spectrum of purified phosphonium salt (KBr)



(cm^{-1})	**Assignment**
3050, 3005	C – H – valence, arene
2810, 2730	C – H – valence, alkane
1730	C = O – valence, ester
1590, 1490	C = C – valence, arene

IR-, ^{1}H NMR- and ^{13}C NMR-spectrum of the crude phosphonium salt are identical to those of the purified salt.