CHEMISTRY

Academician M. I. Kabachnik, Chung Jun-Noi, and E. N. Tsvetkov

1960

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician M. I. Kabachnik, Chung Jun-Noi, and E. N. Tsvetkov

A METHOD FOR THE SYNTHESIS OF TERTIARY VINYLPHOSPHINES AND THEIR OXIDES

Vinylphosphines have been almost completely unstudied. The intensive process of synthesis and investigation of vinyl derivatives of various elements, which developed with particular vigor after Normant' s discovery (1) of a method for obtaining vinyl organomagnesium compounds, has affected phosphorus only to an insignificant extent. In 1957, trivinyl- (2,3) and divinylphenylphosphines (2) were obtained in low yields. Somewhat later, the synthesis of vinyldichlorophosphine via divinylmercury (3,4) and tetravinyllead (5) was published. From vinyldichlorophosphine the first representative of the class of tertiary monovinylphosphines—dimethylvinylphosphine (3)—was obtained. The oxides of tertiary vinylphosphines have not been described in the literature up to the present time.

We have developed a method for the synthesis of tertiary monovinylphosphines and their oxides. As starting compounds we used esters of secondary phosphinous acids (6,7), which, on interaction with organomagnesium compounds in ether or tetrahydrofuran (in the case of vinylmagnesium bromide), exchange alkoxy groups for the corresponding alkyl or vinyl radicals with formation of tertiary phosphines:

$$\mathrm{RR'POR'' + R'''MgX \rightarrow RR'PR''' + R''OMgX.}$$

For the same purposes, the readily accessible dibutyl ester of vinylphosphinous acid (7) may also be used; however, replacement of two alkoxy groups by alkyl radicals does not always proceed with satisfactory yield:

$$\mathrm{CH_2{=}CHP(OC_4H_9)_2 + 2RMgX \rightarrow CH_2{=}CHPR_2 + 2C_4H_9OMgX.}$$

We also carried out the synthesis of divinylphenylphosphine from phenyldichlorophosphine and vinylmagnesium bromide. This compound, previously obtained (2) by essentially the same route in a yield of ∼ 6%, was described as a viscous yellow liquid with b.p. 55° at 0.5 mm (the refractive index and specific gravity were not given). Under low-temperature conditions we succeeded in obtaining divinylphenylphosphine in 59% yield. This substance is a colorless mobile liquid, relatively stable on storage in a nitrogen atmosphere. Monovinylphosphines are also comparatively stable compounds, which do not polymerize on storage or during distillation in a nitrogen atmosphere.

The yields, constants, and analytical data of the synthesized tertiary vinylphosphines are given in Table 1.

By oxidation of the vinylphosphines, oxides of tertiary vinylphosphines were obtained. Active manganese dioxide was chosen as the oxidizing agent, one that does not affect the double bond. This reagent had previously (8) been successfully used for the oxidation of unsaturated alcohols of the allylic type to unsaturated aldehydes and ketones; it was also applied for the conversion of triphenylphosphine into the corresponding oxide (9).

Oxidation of tertiary vinylphosphines with active manganese dioxide was carried out in petroleum ether, usually with heating to 40°,

Table 1

Compound	Yield, %	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	C, %, found	C, %, calc.	H, %, found	H, %, calc.	P, %, found	P, %, calc.
$CH_2{=}CHP(C_3H_7)_2$	68	69° (23)	1.4680	0.8144	49.22	48.92	66.86 66.7	66.6	11.91 11.9	11.9	21.12 21.2	21.5
$CH_2{=}CHP(C_4H_9)_2$	51	49° (2)	1.4710	0.8210	58.62	58.15	69.86 69.8	69.7	12.31 12.2	12.3	18.01 18.1	18.0
$CH_2{=}CHP(C_4H_9)_2$	82*	65.5° (3.5)	1.4700									
$CH_2{=}CHP(C_5H_{11})_2$	80	74° (1.5)	1.4708	0.8232	67.79	67.39	72.07 72.2	72.0	12.61 12.8	12.6	15.41 15.4	15.5
$CH_2{=}CHP(CH_3)(C_6H_5)$	59	90.5° (13)	1.5732	0.9741	50.83		72.07 71.2	72.0	7.5 7.6	7.4	20.42 20.4	20.6
$(CH_2{=}CH)_2P{-}C_6H_5$	69	55.5° (1.5)**	1.5832	0.9818	55.21		74.27 74.2	74.1	6.9 6.8	6.8	19.01 19.9	19.1

* Obtained from the butyl ester of dibutylphosphinous acid.
** Literature data; b.p. 55° (0.5 mm) (^{2}).

at the initial stage the reaction sometimes proceeded exothermically. The oxidation process proceeds without any side reactions; in many cases the yields of phosphine oxides are close to quantitative. The oxides of tertiary vinylphosphines are colorless hygroscopic crystals, readily soluble in water, and do not polymerize during distillation. The yields, constants, and analytical data for the compounds obtained are given in Table 2.

Table 2

Compound	Yield, %	B.p., °C (mm)	M.p., °C	C, %, found	C, %, calc.	H, %, found	H, %, calc.	P, %, found	P, %, calc.
$CH_2=CHP(O)(C_3H_7)_2$	97	89–89.5° (2)	36–37	59.960.0	60.0	10.810.7	10.7	19.719.6	19.3
$CH_2=CHP(O)(C_4H_9)_2$	62	103.5–104° (1.5)	37.5–38	64.164.0	63.8	11.511.3	11.2	16.216.3	16.5
$CH_2=CHP(O)(C_5H_{11})_2$	95	123–123.5° (1.5)	37.5–38	66.566.5	66.6	11.611.8	11.6	14.214.2	14.3
$CH_2=CHP(O)(CH_3)(C_6H_5)$	98	127–127.5° (2)	78–79	64.965.2	65.1	6.66.6	6.7	18.819.0	18.6
$(CH_2=CH)_2P(O)C_6H_5$	92	130–130.5° (2)	50–51	67.667.5	67.4	6.36.3	6.2	17.017.2	17.4

Experimental Part

All operations for the synthesis of tertiary phosphines are carried out in an atmosphere of purified nitrogen.

Dialkylvinylphosphines. 0.1 mole of the butyl ester of the corresponding dialkylphosphinous acid (6) is added to a solution of vinylmagnesium bromide (1), prepared from 0.13 g-atom of magnesium and 0.13 mole of vinyl bromide in 100 ml of tetrahydrofuran; the mixture is stirred for 10 h at 40°. The tetrahydrofuran is removed in vacuo, and 150 ml of benzene and 40 ml of water are added to the residue. The organic layer is separated, the aqueous layer is extracted with benzene (3 × 50 ml), and the combined extract is filtered through a layer of anhydrous sodium sulfate, evaporated in vacuo, and distilled. Dibutylvinylphosphine was also obtained by an analogous procedure from 0.04 mole of the butyl ester of dibutylvinylphosphinous acid (7) and butylmagnesium bromide in ether (0.12 g-atom of magnesium, 0.12 mole of butyl bromide, 50 ml of ether). Methylphenylvinylphosphine is synthesized analogously by the reaction of 0.054 mole of the butyl ester of phenylvinylphosphinous acid (7) with methylmagnesium iodide in ether (0.08 g-atom of magnesium, 0.08 mole of methyl iodide, 100 ml of ether).

Divinylphenylphosphine. 0.1 mole of phenyldichlorophosphine (10) in 20 ml of tetrahydrofuran is added to a solution of vinylmagnesium bromide (1) in tetrahydrofuran (0.22 g-atom of magnesium, 0.22 mole of vinyl bromide, 150 ml of tetrahydrofuran) at a temperature of $-40°$ ($\pm 5°$) and with vigorous stirring; the mixture is left to stand overnight and is then worked up as described above.

Oxides of tertiary vinylphosphines. A solution of 0.1 mole of the corresponding vinylphosphine in 100 ml of dry petroleum ether is stirred with 0.6 mole of active manganese dioxide (8) for 5-6 hr at 40°. The precipitate is filtered off and thoroughly washed with 200 ml of dry acetone; the solvents are removed in vacuo, and the residue is distilled.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
11 VIII 1960

CITED LITERATURE

[1] H. Normant, Bull. Soc. Chim., **1957**, 728; S. T. Ioffe, *Usp. Khim.*, **27**, 1010 (1958).
[2] L. Maier, D. Seyferth, F. G. A. Stone, E. G. Rochow, *Zs. Naturforsch.*, **12b**, 263 (1957); *J. Am. Chem. Soc.*, **79**, 5884 (1957).
[3] H. D. Kaesz, F. G. A. Stone, *J. Org. Chem.*, **24**, 635 (1959).
[4] B. Bartocha, F. E. Brinkman et al., *Proc. Chem. Soc.*, **1958**, 116.
[5] L. Maier, *Tetrahedron Letters*, **6**, 1 (1959).
[6] M. I. Kabachnik, E. N. Tsvetkov, *DAN*, **135**, No. 2 (1960).
[7] M. I. Kabachnik, E. N. Tsvetkov, *Zh. Obshch. Khim.*, **131**, 1334 (1960).
[8] J. Attenburrow, A. F. Cameron et al., *J. Chem. Soc.*, **1952**, 1094.
[9] M. Z. Bákarat, M. F. Abdel-Wahab, M. M. El-Sadr, *J. Chem. Soc.*, **1956**, 4685.
[10] E. L. Gefter, *ZhOKh*, **28**, 1338 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.