**Electronic supplementary materials** *Mendeleev Commun.*, 2019, **29**, 328–330

# Single-stage synthesis of alkyl-*H*-phosphinic acids from elemental phosphorus and alkyl bromides

**Nina K. Gusarova, Anastasiya O. Sutyrina, Vladimir A. Kuimov,**
**Svetlana F. Malysheva, Natalia A. Belogorlova, Pavel A. Volkov**
**and Boris A. Trofimov**

## Table of Contents

## General remarks

The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13, 100.61 and 161.98 MHz, respectively) and referenced to $H_3PO_4$ ($^{31}$P NMR) as external standards. Chemical shifts (δ) are expressed in ppm downfield from HMDS as internal standards. The C, H microanalyses were performed on a Flash EA 1112 SHNS-O/MAS analyzer, while the P contents were determined by combustion method. Red phosphorus “KSAN Sia”, white phosphorus (China), $KOH{\cdot}0.5H_2O$, alkyl bromides were used as purchased. All experiments were carried out under Ar atmosphere.

CAUTION: *White phosphorus is highly toxic and burns spontaneously when exposed to air. It should be handled with extreme care. All the reactions and handling of white phosphorus should be carried out under an inert atmosphere in a well ventilated hood.*

## Experimental: Selected example

To a mixture of red phosphorus (3.10 g, 100 mg-atom), toluene (50 ml) and $BnEt_3NCl$ (0.4 g), a solution of $KOH{\cdot}0.5H_2O$ (20.00 g, 307 mmol) in water (13 ml) was added dropwise within 10 min at 40 °C (argon). The resulted mixture was heated to 60-62 °C, and the solution of *n*-hexyl bromide **1a** (4.95 g, 30 mmol) in toluene (10 ml) was added dropwise for 40 min. Then a mixture was stirred at 60-62 °C for 5 h, cooled to room temperature and diluted with water (80 ml). The aqueous and organic (toluene) layers were separated. The aqueous layer was extracted with chloroform (3 × 30 ml) to give extract **A**. Chloroform extract **A** and toluene layer were combined, the solvents and unreacted *n*-hexyl bromide **1a** were removed in vacuum, where **1a** (0.4 g) was recovered (conversion 92%). The residue contained 1.15 g of a mixture of *n*-$Hex_2P(O)H$ ($\delta_P$ 32 ppm) and *n*-$Hex_3P{=}O$ ($\delta_P$ 45 ppm) in the ratio 2:1 (the $^{31}P$ NMR data).

The remaining aqueous layer was acidified with 15% aqueous HCl to pH 4–5, extracted with chloroform (3 × 30 ml) to deliver extract **B**, which was dried with $CaCl_2$, chloroform was distilled off, and the residue was dried in a vacuum (40 °C, 1 Torr) to give *n*-hexylphosphinic acids **2a**.

Conversion of alkyl bromides was determined by $^1H$ NMR using $CH_2Cl_2$ as internal standard.

*n-Hexyl-H-phosphinic acid* **2a**: isolated yield 1.85 g (38%, $P_n$) or 2.12 g (37%, $P_4$); light yellow oil. $^1H$ NMR ($CDCl_3$) $\delta$: 0.85 (t, 3H, Me, $^3J$ 6.8 Hz), 1.29-1.38 (m, 6H, $(CH_2)_3$), 1.57 (m, 2H, $CH_2Bu$), 1.72 (m, 2 H, $CH_2P$), 7.00 (d, 1 H, PH, $^1J_{HP}$ 545 Hz), 11.7 (s, 1 H, OH). $^{31}P$ NMR ($CDCl_3$) $\delta$: 38.8 (d, $^1J_{PH}$ 545 Hz); lit.[S1] $\delta_P$ 39.07 ($^1J_{PH}$ 540 Hz). Found (%): C, 48.29; H, 9.8; P, 20.82. Calc. for $C_6H_{15}O_2P$ (%): C, 47.99; H, 10.07; P, 20.63.

*Isobutyl-H-phosphinic acid* **2b**: isolated yield 0.30 g (7%), purity 90%, light yellow oil. $^1H$ NMR ($CDCl_3$) $\delta$: 1.00 (d, 6H, Me, $^3J_{HH}$ 6.6 Hz), 1.81 (m, 1H, CH), 2.10 (m, 2H, $PCH_2$), 7.22 (d, 1H, PH, $^1J_{PH}$ 552 Hz), 11.28 (s, 1H, OH); lit.[S2] ($D_2O$); $^{31}P$ NMR ($CDCl_3$) $\delta$: 32.7 (d, $^1J_{PH}$ 553 Hz).

*n-Butyl-H-phosphinic acid* **2c**: isolated yield 0.66 g (12%, $P_n$) or 0.92 g (19%, $P_4$), light yellow oil. $^1H$ NMR ($CDCl_3$) $\delta$: 0.90 (t, 3H, Me, $^3J_{HH}$ 7.2 Hz,), 1.39 (m, 2H, $CH_2Me$), 1.55 (m, 2H, $CH_2Et$), 1.71 (m, 2H, $CH_2P$), 7.04 (d, 1H, PH, $^1J_{PH}$ 545 Hz), 12.08 (s, 1H, OH). $^{31}P$ NMR ($CDCl_3$) $\delta$: 33.4 ($^1J_{PH}$ 549 Hz); lit.[S3] $\delta_P$: 37.9 ($^1J_{PH}$ 539 Hz). Found (%): C, 39.69; H, 8.95; P, 24.88. Calc. for $C_4H_{11}O_2P$ (%): C, 39.57; H, 8.80; P, 24.67.

*3-Methylbutyl-H-phosphinic acid* **2d**: isolated yield of crude acid 0.50 g (11%), purity 90%, light yellow oil. $^{31}P$ NMR ($CDCl_3$) $\delta$: 33.5 (d, $^1J_{PH}$ 549 Hz).

*n-Pentyl-H-phosphinic acid* ***2e***: isolated yield 1.51 g (25%, $P_n$) or 1.80 g (32%, $P_4$), light yellow oil. $^1H$ NMR ($CDCl_3$) $\delta$: 0.89 (t, 3H, Me, $^3J$ 7.0 Hz), 1.33 (m, 4H, $(CH_2)_2$), 1.58 (m, 2H, $CH_2Pr$), 2.06 (m, 2H, $CH_2P$), 7.19 (d, 1H, PH, $^1J_{PH}$ 553 Hz), 11.08 (s, 1H, OH). $^{31}P$ NMR ($CDCl_3$) $\delta$: 34.2 (d, $^1J_{PH}$ 551 Hz); lit.[2] ($D_2O$) $\delta_P$: 35.8 ($^1J_{PH}$ 546 Hz). Found (%): C, 44.3; H, 9.5; P, 22.46. Calc. for $C_5H_{13}O_2P$ (%): C, 44.12; H, 9.63; P, 22.75.

*n-Octyl-H-phosphinic acid* ***2f***: isolated yield 1.60 g (15%, $P_n$) or 1.44 g (19%, $P_4$), light yellow oil. $^1H$ NMR ($CDCl_3$) $\delta$: 0.90 (t, 3H, Me, $^3J$ 6.8 Hz), 1.29 (m, 6H, $(CH_2)_3$), 1.36 (m, 2H, $CH_2Bu$), 1.60 (m, 2H, $CH_2Am$), 1.62 (m, 2H, $CH_2Hex$), 2.09 (m, 2H, $CH_2P$), 7.09 (d, 1H, PH, $^1J_{HP}$ 558 Hz). $^{31}P$ NMR ($CDCl_3$) $\delta$: 37.52 (d, $^1J_{PH}$ 558 Hz); lit.[3] $\delta$: 37.6; lit.[1] $\delta$: 39.45 ($^1J_{PH}$ 540 Hz). Found (%): C, 53.93; H, 10.50; P, 17.61. Calc. for $C_8H_{19}O_2P$ (%): C, 53.82; H, 10.69; P, 17.32.

The corresponding phosphine oxides **3** and **4** were formed in ~36% (entry 5), 15% (entry 12), 35% (entry 11) and 22% (entry 13) total yields.

$^1$H and $^{31}$P NMR data for compounds **3a**,**c**,**e**,**f** and **4a**,**c**,**e**,**f** are in accordance with the known data.[S4] For example:
*tri(n-hexyl)phosphine oxide* **3a**, $\delta_P$ = 44.1 ppm (lit.[S4a] $\delta_P$ = 40 ppm); *di(n-hexyl)phosphine oxide* **4a**, $\delta_P$ = 32.4 ppm (lit.[S4b] $\delta_P$ = 32.85 ppm); *tri(n-butyl)phosphine oxide,* **3c**, $\delta_P$ = 41.8 ppm (lit.[S4c] $\delta_P$ = 42.0 ppm); *di(n-butyl)phosphine oxide,* **4c**, $\delta_P$ = 36.09 ppm (lit.[S4b] $\delta_P$ = 34.91 ppm); *tri(n-pentyl)phosphine oxide* **3e**, $\delta_P$ = 51.2 ppm; *di(n-pentyl)phosphine oxide* **4e**, $\delta_P$ = 35.60 ppm (lit.[S4b] $\delta_P$ = 35.64 ppm); *tri(n-octyl)phosphine oxide* **3f**, $\delta_P$ = 48.91 ppm (lit.[S4d] $\delta_P$ = 49.50 ppm); *di(n-octyl)phosphine oxide* **4f**, $\delta_P$ = 35.0 ppm (lit.[S4d] $\delta_P$ = 35.2 ppm).

## References

[S1] P. Troupa, G. Katsiouleri and S. Vassiliou, *Synlett*, 2015, **26**, 2714.

[S2] I. Devedjiev and G. Borisov, *Phosphorus Sulfur Silicon Relat. Elem.*, 1990, **53**, 37.

[S3] S. I. Verkhoturova, S. N. Arbuzova, T. I. Kazantseva, N. K. Gusarova, and B. A. Trofimov, *Russ. J. Gen. Chem.,* 2017, **87**, 1876 (*Zh. Obshch. Khim*., 2017, **87**, 1390).

[S4] (*a*) *Organic Phosphorus Compounds*, eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1972, vol. 3; (*b*) W. Zhang, G. Ye and J. Chen, *J. Mater. Chem. A*, 2013, **1**, 12706; (*c*) N. K. Gusarova, S. F. Malysheva, T. N. Rakhmatulina, V. I. Dmitriev, S. I. Shaikhutdinova, L. M. Sinegovskaya and B. A. Trofimov, *Zh. Obshch. Khim.*, 1990, **60**, 828 (*Chem. Abstr.* 1990, **113**, 172181c); (*d*) F. D. Wang, R. Tang and W. E. Buhro, *Nano Lett.*, 2008, **8**, 3521.