A Convenient Synthesis of Primary 2-Hydroxyorganophosphines from Red Phosphorus and Oxiranes

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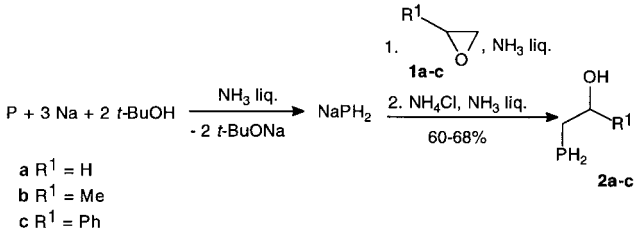
Abstract: A number of 2-hydroxyorganophosphines $HOCH(R^1)CH(R^2)PH_2$ **2** have been obtained in good yields by reaction of oxiranes with sodium monophosphide, generated in situ from red phosphorus, sodium and *tert*-butyl alcohol in liquid ammonia.

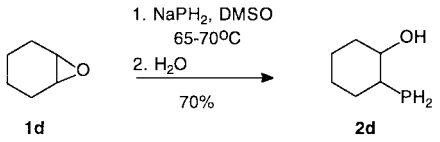
Key words: phosphines, oxiranes, ring opening, phosphorus, sodium, liquid ammonia

Primary 2-hydroxyorganophosphines, being amphiphilic compounds with polar hydrophilic functions and hydrophobic branched counterparts, can be prospective ligands for design of metallocomplex catalysts combining properties of phase transfer and micellar catalysts. They were synthesized earlier from hazardous phosphines and oxiranes in the system sodium/liquid ammonia.[1] It is also known that reaction of white[2] or red[3] phosphorus with oxiranes in the presence of bases (alkali metal hydroxides or alkoxides, amines) and proton donors (water, alcohols) gives phosphorus-containing polyols.

The present communication deals with an efficient method for preparing primary 2-hydroxyorganophosphines **2** by the direct interaction of oxiranes **1** with red phosphorus in the system sodium/*tert*-butyl alcohol/liquid ammonia. In this system, with the stoichiometry shown in the Scheme, sodium monophosphide is generated[4] to furnish, upon treatment with oxirane followed by a proton donor addition, phosphines **2** in 60–70% yields (Table).



Unlike the oxiranes **1a–c**, which react smoothly with sodium monophosphide in liquid ammonia, 7-oxabicyclo[4.1.0]heptane (**1d**) turned out to be less reactive, and the reaction with it occurred only in dimethyl sulfoxide (Table).



Orientation of ring opening in the case of monosubstituted oxiranes **1b,c** is in agreement with Krassusky's rule:[5] phosphide-anion attacks the less substituted carbon atom to result in secondary alcohols.

^1H spectra were recorded on a Bruker AC 300 (300 MHz) (for **1a,b,d**) or Varian EM-390 (90 MHz) (for **1c**) spectrometers using TMS as internal standard. ^{31}P spectra were taken on a Bruker AC 300 instrument (121.5 MHz). Mass spectra were recorded on a Jeol AX-505 at 70 eV. All operations were carried out under N_2.

2-Hydroxyorganophosphines 2a–c; General Procedure

To anhyd liquid ammonia (1.5 L), a slurry of red phosphorus (6.2 g, 0.2 mol) in anhyd THF (20 mL) was introduced, followed by addition of sodium (16.6 g, 0.72 mol), freshly cut into pieces of 0.2–0.4 g, over 10 min. A mixture of *t*-BuOH (38.5 g, 0.52 mol) and Et_2O (40 mL) or THF was then added dropwise over 1 h with very efficient stirring. The mixture was stirred until the blue colour had disappeared and a yellowish suspension formed. To the suspension, an oxirane **1a–c** (0.32 mol) was added in 5–7 min and the mixture was stirred for 40 min. Then NH_4Cl (20.0 g) was introduced and the mixture was stirred for an additional 30 min. The ammonia was evaporated at ~40°C. To the residue, 200 mL of a solvent (CH_2Cl_2, $CHCl_3$ and Et_2O were used for **2a**, **2b** and **2c**, respectively) and H_2O (500 mL) were successively added. After vigorous stirring, the layers were separated, followed by extraction with the solvent (3 × 150 mL). The combined organic extracts were dried ($MgSO_4$), the solvent and excess oxirane **1** were removed in a water pump vacuum, and the remaining liquid was distilled in vacuo through a 25–30 cm Vigreux column (Table). Phosphine **2c** decomposes so rapidly upon exposure to air, that combustion or even explosion can occur, styrene being identified among the decomposition products. Care must be taken also during evaporation of the solvent and distillation of the product, addition of a little amount of Et_3N was used to prevent explosion.

2-Hydroxycyclohexylphosphine (2d)

A suspension of $NaPH_2$ was prepared in a similar way as described above. Then ammonia was evaporated at ~40°C, DMSO (100 mL) introduced and **1d** (0.32 mol) added in 5–7 min. The mixture was stirred at 65–70°C for 1 h, cooled to r.t., diluted with H_2O (500 mL), after which extractions with Et_2O (3 × 150 mL) were carried out. The combined ethereal extracts were washed with H_2O (3 × 100

Table Hydroxyorganophosphines **2** Prepared

Product	R^1	R^2	Yield[a] (%)	bp (°C/Torr)	^1H, ^{31}P NMR ($CDCl_3$)[b] δ, *J* (Hz)	MS (EI), *m/z* (%)[c]
2a	H	H	68	50–53/20[d]	3.69 (m, 2 H, C*H*$_2$OH), 2.47 (dm, 2 H, $^1J_{H,P}$ = 196, H_2P), 1.74 (m, 2 H, CH_2P), *–154.8*	78 (M^+, 4), 60 ($M^+ - H_2O$, 100), 58 (46), 45 ($HOCH_2CH_2^+$, 35), 31 ($HOCH_2^+$, 27), 27 (12), 19 (3), 18 (2)
2b	Me	H	67	62–65/20[e]	3.87 (sept, 1 H, $^3J_{CH,P}$ = 6.1, ^3J (CH,CH_2) = 6.1, ^3J (CH,CH_3) = 6.1, C*H*OH), 2.67 (dm, 2 H, $^1J_{H,P}$ = 196, H_2P), 2.92 (br s, 1 H, OH), 1.73 (m, 2 H, CH_2P), 1.26 (d, *J* = 6.1, 3 H, CH_3), *–155.0*	92 (M^+, 1.8), 91 ($M^+ - H$, 1.3), 74 ($M^+ - H_2O$, 100), 57 (12), 48 ($CH_3PH_2^+$, 42), 45 (CH_3CHOH^+, 86), 41 (24), 31 (14), 28 (13), 27 (11), 19 (4), 18 (2)
2c	Ph	H	60	125–130/20	7.3 (m, 5 H, C_6H_5), 4.6 (m, 1 H, C*H*OH), 1.9 (m, 2H, CH_2P), *–154.7* ($^1J_{H,P}$ = 197)	–
2d[f]	$(CH_2)_4$		70	95–100/20	3.28 (m, 1 H, C*H*OH), 3.02 (br s, 1 H, OH), 2.81, 2.71 (AB part of doublet ABX system, 1 H each, $^1J_{H,P}$ = 197, $^2J_{A,B}$ = 12.1, $^3J_{A,X}$ = 5.2, $^3J_{B,X}$ = 6.4, PH_2), 2.1–1.2 (m, 9 H overall, CHP, CH_2), *–127.3*	132 (M^+, 2), 114 ($M^+ - H_2O$, 64), 98 ($M^+ - PH_3$, 7), 81 (*cyclo*-$C_6H_9^+$, 100), 67 (18), 55 (19), 41 (23), 28 (12), 27 (8), 18 (2)

[a] Yield based on phosphorus used.
[b] ^{31}P NMR values are given in italics.
[c] HRMS for **2a**: C_2H_7OP, *m/z* Calcd.: 78.0235, Found: 78.0180; **2b**: C_3H_9OP, Calcd.: 92.0391, Found: 92.0462; **2d**: $C_6H_{13}OP$, Calcd.: 132.0704, Found: 132.0665.
[d] Lit[1a] bp 139-140°C/760 Torr.
[e] Lit[1a] bp 37-39°C/2 Torr.
[f] Purity ~ 90% (GC, ^1H NMR).

mL), dried ($MgSO_4$), the solvent and excess **1d** were removed in a water pump vacuum, and the remaining liquid was distilled in vacuo through a 25–30 cm Vigreux column (Table).

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References

(1) (a) Knunyants, I.L.; Sterlin, R.N. *Dokl. Akad. Nauk. USSR.* **1947**, *66*, 47; *Chem. Abstr.* **1948**, *42*, 519.
(b) Perveev, F.Ya.; Rikhter, K. *Zh. Obshch. Khim.* **1960**, *30*, 784; *Chem. Abstr.* **1961**, *55*, 1580.
(2) (a) Boros, E.J.; Lanham, W.M.; Chisung, W. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 221.
(b) Ivanov, B.E.; Fridland, N.S.; Abul'khanov, A.G.; Krokhina, S.S.; Ilyasov, A.V. *Izv. Akad. Nauk. USSR, Ser. Khim.* **1987**, 1399; *Chem. Abstr.* **1988**, *109*, 23033.
(c) Fridland, N.S.; Ivanov, B.E.; Krokhina, S.S.; Abul'khanov, A.G. *Izv. Akad. Nauk. USSR, Ser. Khim.* **1988**, 710; *Chem. Abstr.* **1988**, *109*, 211554.
(3) Gusarova, N.K.; Trofimov, B.A.; Khilko, M.Ya.; Malysheva, S.F.; Rakhmatulina, T.N.; Nedolya, N.A. *Zh. Obshch. Khim.* **1990**, *60*, 1925; *Chem. Abstr.* **1991**, *114*, 42941.
(4) Trofimov, B.A.; Gusarova, N. ; Brandsma, L. *MGCN, Main Group Chemistry News* **1996**, *4*, 18; *Chem. Abstr.* **1996**, *125*, 142810.
(5) (a) Krassusky, K. *J. Prakt. Chem.* **1907**, *75*, 238.
(b) Krassusky, K. *Compt. Rend.* **1908**, *146*, 236.
(c) Parker, R.E.; Isaaks, N.S. *Chem. Rev.* **1959**, *59*, 737.

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