



Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

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To cite this article: Chun-Hong Zhong & Wenhua Huang (2021) Synthesis of tertiary phosphine oxides by alkaline hydrolysis of quaternary phosphonium zwitterions using excess *t*-BuOK and stoichiometric water, Synthetic Communications, 51:10, 1537-1546, DOI: 10.1080/00397911.2020.1868006

To link to this article: https://doi.org/10.1080/00397911.2020.1868006



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Published online: 04 Jan 2021.

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Synthesis of tertiary phosphine oxides by alkaline hydrolysis of quaternary phosphonium zwitterions using excess *t*-BuOK and stoichiometric water

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ABSTRACT

Hydrolysis of quaternary arylphosphonium zwitterions bearing COO⁻ and those in situ generated from the corresponding salts bearing Ac or OH at the aryl ring by using excess *t*-BuOK and stoichiometric water affords tertiary arylphosphine oxides in moderate to excellent yield, in contrast to hydrolysis of these zwittertion or salts in aqueous NaOH that mainly provides phosphine oxides with the loss of the aryl group. Under the *t*-BuOK/water conditions, hydrolysis of carbonyl stabilized ylides $Ph_3P = CHCOR$ (R = Ph, Me, and OEt), which partially exist as phosphonium enolates, prefers to produce $Ph_2P(O)CH_2COR$. Further reduction of $Ph_2P(O)CH_2COMe$ by $PhSiH_3$ allows the preparation of Ph_2PCH_2COMe in 43% yield.

GRAPHICAL ABSTRACT



ARTICLE HISTORY

Received 1 June 2020

KEYWORDS

Alkaline hydrolysis; phosphorus ylide; quaternary phosphonium salt; quaternary phosphonium zwitterion; tertiary phosphine oxide

Introduction

Tertiary phosphine oxides have been widely used as carbanion sources in the Horner-Wittig reaction,^[1] as precursors to synthesize tertiary phosphines^[2–6] including chiral tertiary phosphines,^[7] as organocatalysts in asymmetric synthesis,^[8] and as ligands to form complexes with transition metals.^[9–12] They have also been applied in the synthesis of photoelectronic materials.^[13] Considering the phosphorus starting materials, tertiary phosphine oxides can be synthesized from (1) secondary phosphine oxides by

C Supplemental data for this article can be accessed on the publisher's website

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$$\mathbb{R}^{4} \xrightarrow{P^{+}_{\mathbf{R}^{2}}}_{\mathbb{R}^{3}} \xrightarrow{-\operatorname{OH}} \mathbb{R}^{1} \xrightarrow{P^{+}_{\mathbf{R}^{2}}}_{\mathbb{R}^{4}} \mathbb{R}^{2} \xrightarrow{\operatorname{OH}}_{\mathbb{R}^{4}} \mathbb{R}^{2} \xrightarrow{\operatorname{OH}}_{\mathbb{OH}^{4}} \mathbb{R}^{2} \xrightarrow{\mathbb{OH}^{4}_{\mathbf{R}^{2}}}_{\mathbb{OH}^{4}_{\mathbf{H}^{2}}} \mathbb{R}^{1} \xrightarrow{\mathbb{P}^{+}_{\mathbf{R}^{2}}}_{\mathbb{Q}^{4}_{\mathbf{R}^{4}}} \mathbb{R}^{2} \xrightarrow{\mathbb{P}^{+}_{\mathbf{R}^{4}}}_{\mathbb{R}^{4}_{\mathbf{R}^{3}}} \xrightarrow{\mathbb{P}^{+}_{\mathbf{R}^{4}}}_{\mathbb{R}^{4}_{\mathbf{R}^{3}}} \mathbb{R}^{1} \xrightarrow{\mathbb{P}^{+}_{\mathbf{R}^{2}}}_{\mathbb{R}^{4}_{\mathbf{R}^{3}}}$$

Scheme 1. Mechanism of alkaline hydrolysis of quaternary phosphonium salts.

arylation^[14–18] with aryl halides or pseudohalides, and phosphinylation of alkynes^[19,20] or arynes,^[21] (2) phosphinic chloride by nucleophilic substitution with Grignard reagent,^[22,23], (3) tertiary phosphine by oxidation,^[24–26] and (4) quaternary phosphonium salts by alkaline hydrolysis in aqueous NaOH.^[27–30] The last route is based on a long-established mechanism^[31]: nucleophilic attack by ⁻OH at phosphorus to form a hydroxyphosphorane followed by deprotonation by ⁻OH to form an oxyanionic phosphorane which undergoes fragmentation to produce a phosphine oxide and concurrently expel a carbanion which after protonation gives an alkane or arene (Scheme 1). The easiness of R⁴ group to leave depends on the stability of carbanion ⁻R⁴, and is generally in the order: benzyl > phenyl > methyl.^[32] Therefore, if R⁴ is the easiest group to leave, the synthesis of phosphine oxides bearing R⁴ by this route will be challenging.

Recently we have developed a metal-free method for the synthesis of aryltriphenylphosphonium bromides from Ph_3P and aryl bromides bearing a wide range of functional groups.^[33] Phosphonium salt **1a** (Scheme 2a) can also be prepared from p-BrC₆H₄Ac and Ph₃P by this method. After hydrolysis of **1a** in aqueous NaOH, it was hoped that a two-step, transition metal-free route would be found to synthesize phosphine oxide **2a**. Unfortunately, attempts at hydrolysis of **1a** in 3 M NaOH (aq) at room temperature afforded no **2a** but four degradation products: **3** (47%), PhCOMe (20%), Ph₃PO (22%), and Ph₂HPO (21%) (Scheme 2a). According to the mechanism shown in Scheme **1**, PhCOMe and Ph₃PO form from intermediates **I** and **II** followed by leaving a 4-acetylphenyl anion, which is the more stable than a phenyl anion (path *a*, Sch. 2b). Product **3** is probably from ligand coupling^[34] of intermediate **II** involving a phenyl migration and the leave of Ph₂PO⁻ which upon protonation affords Ph₂HPO (path *b*, Scheme 2b). In paths both *a* and *b*, the electron-withdrawing acetyl group plays a key role, leading to the failure to produce **2a**.

We reasoned that if **1a** is at first deprotonated by a strong, excess base such as t-BuO⁻ to ensure the formation of phosphonium enolate zwitterion **IV** and then a stoichiometric water is added to in situ generate ⁻OH, the following hydrolysis of **IV** would form intermediate **V** and after deprotonation by t-BuO⁻ intermediate **VI** (Scheme 3). There would be two decomposition pathways for **VI**: (1) the loss of a phenyl anion to form enolate **VII**, which upon protonation produces **2a** (path *a*), and (2) the loss of dianion **VIII** to form Ph₃PO (path *b*). However, dianion **VIII** is expected to be highly unstable, so path *b* would be inhibited, leading to the formation of **2a** as the major product. Herein we report the utilization of this strategy to synthesize tertiary phosphine oxides from either stable quaternary phosphonium zwitterions or those zwitterions generated in situ from the corresponding phosphonium salts.



Scheme 2. (a) Alkaline hydrolysis of (4-acetylphenyl)triphenylphosphonium bromide 1a. (b) Mechanism for alkaline hydrolysis of 1a.



Scheme 3. Hydrolysis of (4-acetylphenyl)triphenylphosphonium bromide 1a in the presence of t-BuOK

Results and discussion

When phosphonium salt 1a was treated with 3.2 equiv of *t*-BuOK in THF and then water (1.0 equiv) in THF, phosphine oxide 2a was isolated in 53% yield (Table 1),



Table 1. Synthesis of tertiary phosphine oxides by alkaline hydrolysis.^a

^aReaction conditions: phosphonium salt 1 (0.5 mmol), THF (3.4 mL), *t*-BuOK (1.6 mmol), rt, 10 min, then water (0.5 mmol) in THF (3 mL), rt, 3 h. For comparison, the yields obtained by hydrolysis using 3 M NaOH are listed in the parentheses. nd = not detected. ${}^{b}Ph_{3}PO$ and PhCOOH were obtained in 83% and 89% yields, respectively. ${}^{c}Ph_{3}P = CHCOPh$ was isolated in 73% yield. ^dPh₃PO was isolated in 58% yield. ^ePh₃PO was isolated in 98% yield.

indicating the success of our strategy. This strategy is also applicable to aryltriphenylphosphonium salts bearing a p- or m-COO⁻ group at the aryl ring as phosphine oxides 2b and 2c were in 65% and 61% yields, respectively. The hydrolysis of 1b and 1c in 3 M NaOH gave 2b and 2c in much lower yields probably due to the protonation of COO⁻ to COOH, leading to the loss of the aryl bearing COOH during the hydrolysis. This suggests that it is necessary to use a strong base like t-BuO⁻ to prevent COO⁻ from the formation of COOH. For phosphonium salt 1d, however, phosphine oxide 2d was isolated in only 7% yield; its hydrolysis in 3 M NaOH did not produce 2d but Ph₃PO (83%) and PhCOOH (89%). At this stage, we do not know the exact reason why both reaction conditions did not work for this specific substrate. Fortunately, phosphonium salt le bearing an o-OH provided phosphine oxide 2e in 76% yield, whereas its hydrolysis in 3 M NaOH gave 2e in only 6% yield. Although the hydrolysis of phosphonium salt 1f in 3 M NaOH gave 2f in 75% yield, using t-BuOK/H₂O improved the vield of 2f to 95%. Phosphonium salt 1g bearing a methyl substituent at phosphorus could also afford the corresponding phosphine oxide 2g in a reasonable yield, still higher than that obtained by 3 M NaOH. These results indicate that although the phenolic OH itself is an electron-donating in the context of conjugation, its deprotonation by a strong base like t-BuO⁻ to ensure the formation of stronger electron-donating O⁻ could further improve the yield of phosphine oxide bearing this phenolic OH. When phosphonium salt 1h was hydrolyzed in 3 M NaOH, phosphine oxide 2h was not detected and instead the stabilized ylide, i.e., $Ph_3P = CHCOPh$, was isolated in 73%



Scheme 4. Alkaline hydrolysis of carbonyl-stabilized phosphonium ylides.

yield, indicating that this ylide is relatively stable to 3 M NaOH. It has been reported^[35] that $Ph_3P = CHCOPh$ can be prepared from **1h** by treating with 2 M NaOH (aq). By using *t*-BuOK/H₂O, however, **2h** could be obtained in 85% yield probably via the formation of $Ph_3P = CHCOPh$ which was further hydrolyzed to give **2h** under stronger basic condition. Alkaline hydrolysis of some acidic phosphonium salts has been suggested^[36] to proceed through the corresponding phosphonium ylides, especially those stabilized ylides. For the hydrolysis of benzylphosphonium salt **1i**, neither using 3 M NaOH nor using *t*-BuOK/H₂O led to the formation of phosphine oxide **2i**; instead, Ph_3PO was isolated in 98% and 58% yield, respectively, possibly due to the instability of the formed semi-stabilized ylide.^[37]

Phosphonium salts 1a-g can be readily prepared by our recently developed method^[33] in the absence or presence of a catalytic amount of NiBr₂. This method coupled with their hydrolysis by using *t*-BuOK/water provides a two-step sequence to tertiary arylphosphine oxides bearing acidic groups such as OH, COOH, and Ac at the aryl ring. This two-step sequence compares quite favorably to the known synthetic methods requiring the use of either stoichiometric ZnCl₂ and a ligand for 2a,^[38] or a Pd catalyst for 2b and 2c,^[39] or a three-step sequence for 2e-g.^[40,41] For the synthesis of 2h, our hydrolysis method also compares very well with the reported method by the Arbuzov reaction at 160 °C starting from Ph₂POMe and BrCH₂COPh.^[42]

With the success in the hydrolysis of phosphonium salt 1h through the ylide $Ph_3P = CHCOPh$, we next investigated the direct hydrolysis of two stabilized phosphorus ylides 4 and 5. After treated with *t*-BuOK/H₂O, phosphorus ylide 4 provided phosphine oxide 2j in 65% yield (Scheme 4A). It is noteworthy that COOEt could survive the reaction condition and the transesterification product was not observed. Phosphorus ylide 5 also underwent smoothly hydrolysis to give phosphine oxide 2k in 80% yield on a 1 mmol scale; the preparation on a larger scale (10 mmol) gave 2k in a higher yield (95%), indicating that our hydrolysis strategy is practical (Scheme 4B). Attempts to reflux the ylide 5 in 3 M NaOH led to the formation of phosphine oxide 2k in only 8% yield, and Ph₃PO in 57% yield (see supporting information). This is

possibly because the ylide **5** might be in an equilibrium with phosphonium hydroxide **IX** (Scheme 4C) in aqueous NaOH. The decomposition of **IX** according to the general mechanism (Scheme 1) is favorable for the loss of the carbonylmethyl group instead of a phenyl group and the formation of Ph₃PO. Under *t*-BuOK/H₂O conditions, the ylide **5** mainly exists as phosphonium enolate zwitterion **X**, which prefers to lose a phenyl anion rather than enolate dianion during hydrolysis, leading to the formation of phosphine oxide **2k**. As the ylides **4** and **5** are commercially available, their hydrolysis under *t*-BuOK/H₂O provides a facile access to phosphine oxides **2j** and **2k**, which are usually prepared by the Arbuzov reaction at 160 °C^[42] and lithiation of Ph₂P(O)Me using BuLi followed by treating with EtOCOMe^[43], respectively. Moreover, **2k** could be reduced to phosphine **6** in 43% yield by using Beller's method^[6] (Scheme 4B). The synthesis of **6** from acetone and Ph₂PCl has been reported^[44] but suffers from the use of LDA and low temperature (-78 °C).

Conclusions

In summary, we have developed a method for hydrolysis of quaternary phosphonium zwitterions including carbonyl-stabilized phosphorus ylides by using excess *t*-BuOK and stoichiometric water to generate or keep a negatively charged substituent on phosphorus, making it difficult to leave during the hydrolysis. This method should extend the utility of alkaline hydrolysis of quaternary phosphonium salts by providing ready access to phosphine oxides bearing functional groups such as OH, COOH, COOEt, COPh and Ac.

Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. HRMS spectra were recorded on a Varian 7.0 T FTMS. The 1 M solution of *t*-BuOK in THF and THF (SuperDry) were purchased from a local company. The preparation of phosphonium salts **1b**, **1d**, and **1f** has been reported in our previous paper.^[33] The same procedure was used for the preparation of phosphonium salt **1a**. Phosphonium salts **1c**, **1e**, and **1g** were prepared by the same procedure except that a catalytic amount of NiBr₂ was added. Phosphonium salts **1h** and **1i** as well as ylides **4** and **5** were purchased from a local company.

Typical procedure for the synthesis of 1-(4-(diphenylphosphoryl)phenyl)ethanone 2a using t-BuOK/water

To a round-bottom flask (25 mL) containing phosphonium salt **1a** (231 mg, 0.5 mmol) and THF (3.4 mL), a solution of *t*-BuOK in THF (1 M, 1.6 mL) was added. The resulting mixture was stirred at rt for 10 min, then a solution of water (9 mg, 0.5 mmol) in THF (3 mL) was added. After stirred further for 3 h, the reaction mixture was treated with 1 M HCl (15 mL), and then extracted with CH_2Cl_2 (10 mL \times 3). The combined extract was evaporated under reduced pressure, and the residue was isolated by preparative TLC ($CH_2Cl_2/^i$ PrOH, 30/1, v/v) to give phosphine oxide **2a** as a yellow solid in 53%

(84 mg) yield. ¹H-NMR (400 MHz, DMSO-*d*₆) δ 2.62 (s, 3 H), 7.54–7.70 (m, 10 H), 7.75–7.82 (m, 2 H), 8.09 (d, J=7.4 Hz, 2 H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ 27.4, 128.7 (d, J_{C-P} = 11.8 Hz), 129.4 (d, J_{C-P} = 11.9 Hz), 132.0 (d, J_{C-P} = 10.0 Hz), 132.4 (d, J_{C-P} = 10.0 Hz), 132.6 (d, J_{C-P} = 103.3 Hz), 132.8 (d, J_{C-P} = 2.7 Hz), 138.1 (d, J_{C-P} = 99.5 Hz), 139.7 (d, J_{C-P} = 2.8 Hz), 198.2; ³¹P-NMR (162 MHz, DMSO-*d*₆) δ 25.09. These NMR data are consistent with those reported.^{[45} In addition, the hydrolysis of phosphonium salt **1a** in 3 M NaOH provided no phosphine oxide **2a** but *p*-AcC₆H₄Ph **3** (46 mg, 47%), PhCOMe (60 mg, 20%), Ph₃PO (30 mg, 22%), and Ph₂HPO (21 mg, 21%), which are identified by comparing with authentic samples. NMR data for **3**: ¹H-NMR (400 MHz, DMSO-*d*₆) δ 2.62 (s, 3 H), 7.41 – 7.47 (m, 1 H), 7.49 – 7.54 (m, 2 H), 7.75 (d, J=7.2 Hz, 2 H), 7.83 (d, J=8.5 Hz, 2 H), 8.05 (d, J=8.5 Hz, 2 H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ 27.2, 127.3, 127.5, 128.8, 129.4, 129.6, 136.1, 139.4, 145.0, 197.9. These NMR data are also consistent with those reported.^[46]

Full experimental detail, and NMR spectra (1H and 13C). This material can be found via the "Supplementary Content" section of this article's webpage.

Funding

We thank the National Natural Science Foundation of China for their financial support of our program [Grant No. 21272170].

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