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The Reaction of Red Phosphorus with 1-Bromonaphthalene in the KOH–DMSO System: Synthesis of Tri(1-Naphthyl)phosphane

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ABSTRACT: *Red phosphorus reacts with 1-bromonaphthalene in the KOH–DMSO system upon heating (47–70°C, 3 h) to give tri(1-naphthyl)phosphane in 10% yield. Microwave activation (600 W, 6 min) of the reaction affords the above-mentioned phosphane in 25% yield.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:198–203, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20671

INTRODUCTION

One-pot phosphorylation of available electrophiles with red phosphorus in superbase systems like KOH–DMSO or under phase-transfer conditions represents one of the most convenient and promising approaches to the C—P bond formation and synthesis of important organophosphorus compounds, in particular, phosphanes, phosphane oxides, and phosphinic acids [1]. For example, alkyl, arylalkyl, allyl halides [1c] as well as aryl- and hetarylalkenes, and acetylenes have been employed in this reaction. At the same time, the attempts to carry out the reaction of elemental phosphorus with halobenzenes in the above superbasic systems have failed. Meanwhile, it was reported on the reaction of red phosphorus with halobenzenes in alkali metal–liquid ammonia system, the reaction being considered to proceeding via the $S_{RN}1$ mechanism [2]. In the literature, there are no explicit data on straightforward phosphination of 1-bromonaphthalene by red phosphorus to furnish tri(1-naphthyl)phosphane. The latter, being a sterically hindered tertiary phosphane, was found be an excellent ligand for metal complex catalysts inducing many types of transformations. This ligand was employed for the preparation of complexes [3], showing high catalytic activity in the cross-coupling reactions [4], synthesis of diaryl ketones [5] and alcohols [6], hydrogenation [7], cyclization [8], and reduction reaction [9] as well as the complexes having intense long-lived luminescence and photoluminescence [10].

However, the known syntheses of tri(1-naphthyl) phosphane are multistep and laborious and require aggressive and poisonous phosphorus halogenides

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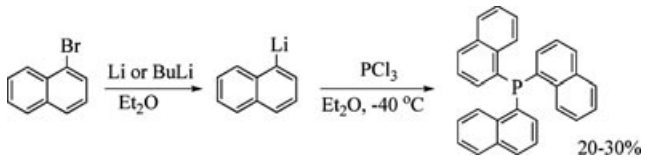


SCHEME 1 Synthesis of tri(1-naphthyl)phosphane.

and flammable unstable organometallic reactants [11]. For example, tri(1-naphthyl)phosphane has been prepared from 1-bromonaphthalene, metal Li (or *n*-BuLi), and phosphorus trichloride in absolute ethyl ether in 20–30% yield (Scheme 1).

Therefore, the development of a simple straightforward approach to the synthesis of tri(1-naphthyl)phosphane represents a challenging goal.

RESULTS AND DISCUSSION

Herein, we report a simple and straightforward synthesis of tri(1-naphthyl)phosphane (**2**) by the direct phosphination of 1-bromonaphthalene (**1**) with red phosphorus. The reaction proceeds in the KOH–DMSO system in the presence of small quantity of H_2O (as a cocatalyst) at 47–70°C for 3 h under argon blanket to give phosphane **2** in 10% yield (Scheme 2). Apart from the target phosphane, naphthalene (**3**) (27%) and phosphonic acid **4** (4%) were detected in the reaction mixture.

In addition, two isomers of binaphthalene (**5**, M^+ 253) and 1-[(methylsulfinyl)methyl]naphthalene (**6**, M^+ 204) (total yield of compounds **5** and **6** is ~1%) were identified in the reaction mixture (MS).

In the presence of hydroquinone, the reaction was almost stopped: Only acid **4** and naphthalene **3** were formed in 6% and 3% yields, respectively. In the absence of KOH, red phosphorus did not practically react with 1-bromonaphthalene.

It is a common knowledge that microwave irradiation can be very effective to initiate $S_{RN}1$ reactions [12]. The microwave activation (600 W, 6 min) of the system red phosphorus, 1-bromonaphthalene, KOH, DMSO, and H_2O increased efficacy, chemoselectivity, and rate (by 30 times) of the reaction to afford phosphane **2** in 25% yield, the naphthalene being formed in 26% yield.

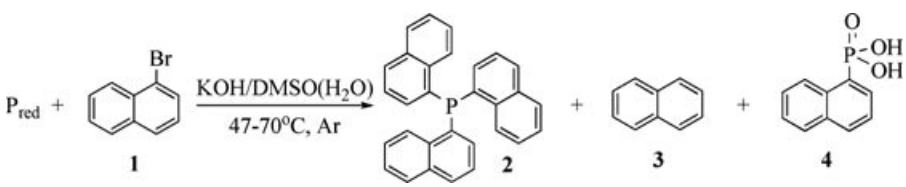
Interestingly, the ultrasound irradiation (1.5 h, 120–125°C) of the reaction delivered mainly naphthalene (58%), whereas compounds **2** and **4** were detected only in trace amounts.

A plausible mechanism of phosphination of electrophile **1** can be rationalized as follows (Scheme 3): The reaction is triggered by the generation of polyphosphide (**A**) and polyphosphinite (**B**) anions (step 1) from red phosphorus under the action of a superbase [1c]. Then, the anions **A** and **B** interact with electrophile **1**. Eventually, phosphane **2** might be formed from phosphide anions (step 2), whereas acid **4** may be produced from polyphosphinite anions (step 3).

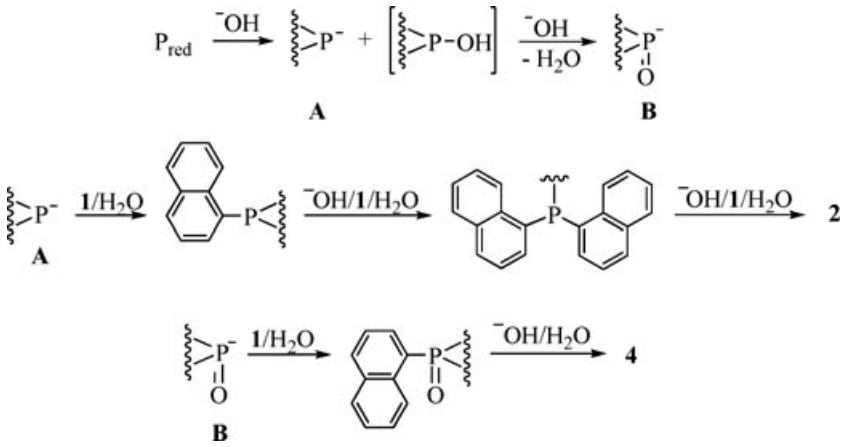
However, mechanism shown in Scheme 3 does not match entirely with the data on hydroquinone inhibition of the phosphination. Also, it does not allow the formation of naphthalene and its derivatives **5** and **6** to be explained. It can be assumed that the mechanism of the formation of compounds **3,5,6** involves the generation of radical anion **C** via the electron transfer from the phosphide anion to bromide **1** (the initiation step) [12,13]. The radical anion **C** is unstable (decay rate $k_1 = 2 \times 10^8$ s^{-1} in DMSO [14]), and its fragmentation affords 1-naphthyl radical **D** and bromine anion [15]. The known interaction of radical **D** with DMSO through the abstraction of a hydrogen atom from DMSO gives naphthalene **3** and radical DMSO [16]. The latter is coupled with radical **D** to form compound **5**. The formation of binaphthalenes **6** results from radical **D** recombination (Scheme 4).

Indeed, a signal of naphthalene radical **D** [17] (g = 2.0034, ΔH = 10 G) was registered by the ESR technique.

The single-electron transfer mechanism of the reaction studied may also be responsible for the formation of phosphane **2** from phosphorus red and



SCHEME 2 Reaction of red phosphorus with 1-bromonaphthalene.



SCHEME 3 Plausible mechanism of phosphination of 1-bromonaphthalene.

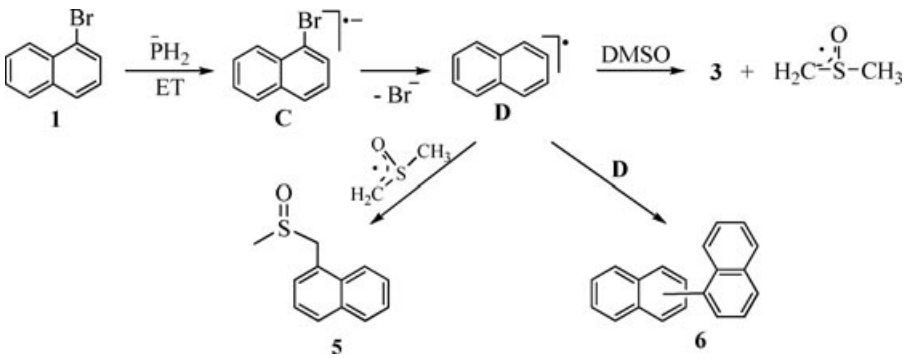
1-bromonaphthalene. According to [12,13,18], radical **D** can react with phosphide anions to yield new radical anion **E**.

The electron transfer from radical anion **E** to bromide **1** renders the 1-naphthylphosphane (**9**) and the radical anion **C**, which continues the chain propagation cycle (Scheme 5). It is known [19] that 1-bromonaphthalene possesses a higher electron affinity than the substitution product (in this case, phosphane **9**) that facilitates the removal of extra electron from its radical anion. Furthermore, compound **9** in the presence of a strong base gives phosphide anion **F**. The latter reacts with radical **D** followed by the electron transfer to bromide **1** to furnish the disubstitution product, bi(1-naphthyl)phosphane **10**, which finally affords (via the same reaction sequence) the trisubstitution product, tri(1-naphthyl)phosphane **2**.

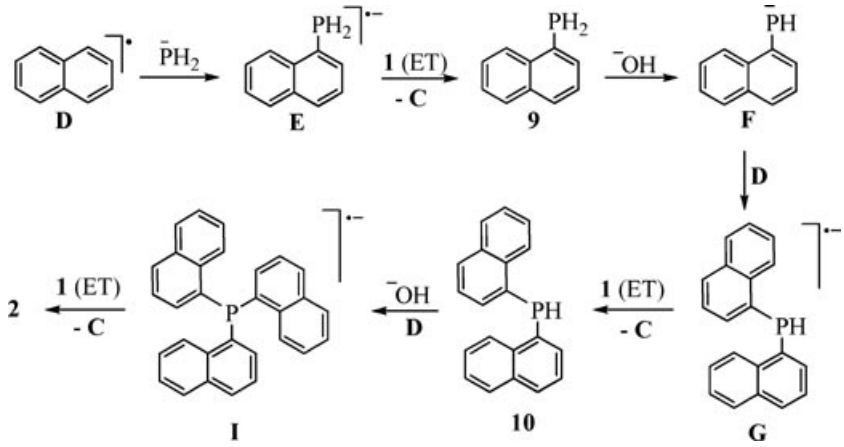
This mechanism is in agreement with the data obtained for the reaction of halonaphthalenes with C- [12,20], N- [21], O- [21,22], P- [12,13,18], S- [14b,15,21,23], and As-centered nucleophiles [20d,24].

The most striking feature of the reaction observed is its chemo- and regioselectivity, namely the formation of tri(1-naphthyl)phosphane only without retaining the phosphanes **9** and **10** in the reaction mixture. This is more surprising that the every next coupling (second and third) of the naphthyl radical meets the all-growing steric hindrance. This phenomenon may result from high stationary concentration of the naphthyl radicals and easy dissociation of 1-naphthylphosphane **9** and bi(1-naphthyl)phosphane **10** to the corresponding anions due to the electron-withdrawing effect of the napththyl radicals.

In conclusion, the straightforward reaction of red phosphorus with 1-bromonaphthalene in the superbase system KOH–DMSO (including the microwave-assisted version) has been accomplished for the first time. A simple one-pot synthesis of tri(1-naphthyl)phosphane, an excellent ligand of growing popularity for metal complex catalysts inducing many types of transformations, has been developed on the basis of this reaction.



SCHEME 4 Ways of byproducts formation.



SCHEME 5 Synthesis of phosphane **2** by radical nucleophilic substitution reaction.

EXPERIMENTAL

All manipulations were carried out in argon atmosphere. IR spectra were measured with a Bruker IFS 25 instrument in KBr (cm^{-1}). The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker DPX 400 spectrometer (400.13, 100.61, and 161.98 MHz, respectively) in $CDCl_3$ or DMSO-d_6 solutions and referenced to internal HMDS (^{1}H), $CHCl_3$ (^{13}C), and external 85% H_3PO_4 (^{31}P) standards. The EI mass spectra were obtained on a Shimadzu GCMS-QP5050 mass spectrometer. Melting points were obtained with a Stanford Research Systems' Optimelt automatic melting-point device without correction. ESR spectra were recorded on an ELEXSYS spectrometer

E-580 (Bruker) instrument was used in a stationary mode. Microwave irradiation was performed in multimode modified microwave oven, Samsung M181DNR, (maximum power level 850 W) equipped with a reflux condenser. We used open vessel microwave technology (atmospheric pressure). The reaction of red phosphorus with styrene was performed in a round-bottom flask (Pyrex). A 500-mL one-necked flask was placed into the multimode reactor (impulse magnetron OM75P(31), power 1.25 MW/2.45 GHz), and was equipped with a reflux condenser, which was brought out via a special hole. The brand red phosphorus of the USSR was employed.

*Preparation of Tri(1-naphthyl)phosphane (**2**)*

Method a. A mixture of red phosphorus (3.1 g, 0.1 mol), 1-bromonaphthalene **1** (10.87 g, 0.05 mol), KOH (10 g, 0.18 mol), H_2O (4 mL), and DMSO (40 mL) was stirred at 47–50°C for 2.5 h. Then temperature was raised up to 70°C, and the mixture was stirred additionally for 30 min. The suspension was diluted with water (50 mL) and extracted with toluene (3 × 70 mL). The combined organic extracts were washed with brine (3 × 20 mL) and evaporated under reduced pressure. A liquid residue was heated under 2 Torr (90°C oil bath), and 1.1 g (yield 27%) of naphthalene (**3**) was sublimated. The latter was identified by ^{1}H, ^{13}C NMR, and mass-spectrometry (*m/z* 128). After removal of **3**, the prepared crude product was allowed to stand for 24 h at 0–5°C, and precipitated crystals were filtered off, washed with ether, and dried under vacuum to give 0.25 g of phosphane **2**. The filtrate was fractionated in vacuum (2 Torr, 125°C oil bath) to recover 4.9 g (55% conversion) of unreacted **1** (*m/z* 206 (M^+)). Undistillable waxy product (0.3 g) was dissolved in 10 mL benzene and reprecipitated into hexane (30 mL). The precipitate was filtered off, washed with hexane, and dried under vacuum to give 0.15 g of phosphane **2**. Thus, total yield of phosphane **2** was 0.4 g (10%) (calculated with conversion **1**).

The aqueous layer was acidified with a 35% aq. HCl up to pH 4–5 (to neutralize 1-NpP(O)$(OK)_2$) and extracted with chloroform (3 × 20 mL). The combined chloroform extracts were washed with brine (3 × 15 mL) and dried over $CaCl_2$. The solvent was removed, and the residue was washed with hexane (5 × 5 mL). Hexane was removed, and the residue was dried in vacuum to give 0.2 g (3%) 1-naphthylphosphonic acid **4**.

Method b. Under microwave irradiation, a mixture of red phosphorus (3.1 g, 0.1 mol), 1- bromonaphthalene **1** (10.87 g, 0.05 mol), KOH (10 g, 0.18 mol), H_2O (4 mL), and DMSO (35 mL) was irradiated (600 W) for 6 min. The reaction mixture was treated by the above-mentioned protocol (method a)

to give 0.85 g (25%) of phosphane **2** and naphthalene (1.72 g, yield 26%). Conversion of initial bromide **1** was 47%.

*Tri(1-naphthyl)phosphane (**2**).* Crystalline powder. mp 280–282°C (benzene). (lit. [11]) IR (KBr) (cm^{-1}): 760, 795 δ = CH,C=C, 1320, 1380, 1500, 1550, 1585, 1610 υC=C, 3040, 3070 υ = CH. ^{1}H NMR (DMSO-d_6, 400.13 MHz) δ: 6.81 (dd, 3H, 3-H, ^3J 5.7, ^4J 5.7), 7.33 (dd, 3H, 2-H, ^3J 7.5, ^3J 7.5), 7.49 and 7.53 (m, 6H, 6,7-H), 7.95 and 7.98 (d, 6H, 4,5-H, ^3J 8.2), 8.36 (ddd, 3H, 8-H, ^3J 8.0, ^4J 4.5, ^4J 0.5); ^{13}C NMR (DMSO-d_6, 100.62 MHz) δ: 125.97, 126.26, 126.77, 127.76, 128.97, 129.97, 131.96 (d, ^3J 10.7), 132.89, 133. 31 (d, ^3J 5.0), 135.00 (d, ^3J 23.63); ^{31}P NMR (DMSO-d_6, 161.98 MHz) δ: –33.9. Anal. Calcd for $C_{30}H_{21}P$: C, 81.31; H, 9.95; P, 8.74. Found: C, 81.47; H, 10.03; P, 8.81.

*1-Naphthylphosphonic acid [1-NpPO(OH)$_2$](**4**).* Light-yellowish powder. mp 204–206°C (benzene) (lit. [26]). IR (KBr) (cm^{-1}): 470 δ_{as}CPO, 550 δPO_2 670 δ = CC, 750, 780 γ = CH, δ = CH,C=C, 830 δ_{as}CH, 920, 940 γOH, 985 $\upsilon_s PO_2$,PO_3, 1110, 1150, 1170, 1200 br υP=O, $\upsilon_{as}PO_2$, PO_3, 1320, 1350, 1420 δCH,CH_2, 1450, 1500, 1550, 1585, 1610 υC=C, 1700, 2260, 2520 υOH, 2850, 2900, 3040 υ = CH. ^{1}H NMR ($CDCl_3$) δ: 6.35 (m, 2H, OH), 7.30 (m, 1H, 6-H), 7.41–7.35 (m, 1H, 3-H), 7.50 (m, 1H, 7-H), 7.78 (d, 1H, 5-H), 7.89 (d, 1H, 4-H), 8.16 (dd, 1H, 2-H, J15, 5.8 Hz), 8.50 (d, 1H, 8-H, J 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 124.51 (d, J14.7 Hz), 126.03 (s), 126.62 (d, J3.7 Hz), 127.20 (d, J31.7 Hz), 128.59 (d, J8.8 Hz), 132.66 (d, J10.3 Hz), 132.68 (d, J130.5 Hz), 133.10 (s), 133.13 (d, J22.8 Hz), 133.50 (d, J9.0 Hz). ^{31}P NMR ($CDCl_3$) δ: 35.5. Anal. Calcd for $C_{10}H_9O_3P$: C, 57.70; H, 4.36; P, 14.88. Found: C, 59.07; H, 4.95; P, 14.61.

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