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Selective C−P(O) Bond Cleavage of Organophosphine Oxides by Sodium

Jian-Qiu Zhang, Eiichi Ikawa, Hiroyoshi Fujino, Yuki Naganawa, Yumiko Nakajima, and Li-Biao Han*

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ABSTRACT: Sodium exhibits better efficacy and selectivity than Li and K for converting $Ph_3P(O)$ to $Ph_2P(OM)$. The destiny of PhNa co-generated is disclosed. A series of alkyl halides R^4X and aryl halides ArX all react with $Ph_2P(ONa)$ to produce the corresponding phosphine oxides in good to excellent yields.

$R^1R^2R^3P(O) \xrightarrow{Na} R^1R^2P(ONa) \xrightarrow{R^4X} R^1R^2R^4P(O)$

Triorganylphosphine oxides $R_3P(O)$ are useful chemicals as extractants[1,2] and flame retardants.[3] They also have applications in organic synthesis.[4,5] However, methods for their preparation are immature.[6]

A large amount of $Ph_3P(O)$ is produced, as byproduct, from the chemical industry through the Witting reactions, etc.[7−9] Because $Ph_3P(O)$ is rather chemically stable,[10] its utilities are limited.[11] Recently, we briefly disclosed that $Ph_3P(O)$ could be readily converted to $Ph_2P(ONa)$ by using sodium (sodium finely dispersed in paraffin oil with μm-scale sizes, hereafter abbreviated as SD).[12] Herein, we report the details of the reaction. As shown in Scheme 1, in addition to $Ph_3P(O)$, the

Scheme 1. Easy Preparation of Phosphine Oxides via the Ready Cleavage of C−P and O−P Bonds by SD

$R^1R^2P(O)Ph$ (**1A**) or $R^1R^2P(O)(OR^3)$ (**1B**) $\xrightarrow{SD}$ $R^1R^2P(ONa)$ $\xrightarrow{R^4X}$ $R^1R^2P(O)R^4$ (**1A-1**)

$R^1P(O)(OR^3)_2$ (**1C**) $\xrightarrow{SD}$ $R^1PNa(ONa)$ $\xrightarrow{R^4X}$ $R^1P(O)R^4R^4$ (**1C-1**)

method can be applied to other phosphine oxides **1A**, phosphinates **1B**, and phosphonates **1C**, to produce the corresponding phosphine oxides in high yields.

It has been briefly disclosed that lithium also reacted with $Ph_3P(O)$ to give $Ph_2P(OLi)$.[12] Therefore, we decided to clarify the difference in reactivity of Li, Na, and K. Under an argon atmosphere, 2.5 equiv of an alkali metal cut into small pieces was added to $Ph_3P(O)$ dissolved in THF at room temperature (Scheme 2). All the three alkali metals could react quickly with $Ph_3P(O)$ as the initially colorless solution instantly changed to brown. The mixture was stirred at room temperature overnight, and then quenched using *n*-butyl bromide and analyzed by GC-MS and ^{31}P NMR spectroscopies (see Supporting Information for details). As reported before, the reaction of $Ph_3P(O)$ with Na after quenching with *n*-BuBr produced *n*-butyldiphenyl phosphine oxide $Ph_2P(O)n$-Bu **2**, 5-butyldibenzophosphole 5-oxide **3**, and 5-butyldibenzophosphole **4**, via the reactions of the corresponding sodium salts of **2′(Na)**, **3′(Na)**, and **4′(Na)**, in 69%, 26%, and 5% yields, respectively.[12] Under similar conditions, the reaction of $Ph_3P(O)$ with Li produced **2**, **5**, **4**, and **6** in 24%, 34%, 19%, and 18% yields, respectively. The dibenzophosphole oxide **3** observed with sodium could not be detected. Instead, two new phosphorus compounds **5**[24] and **6** via **5′(Li)** and **6′(Li)**, respectively, that were not observed for sodium, were generated. The new intermediate **5′(Li)** should arise via the reaction of **2′(Li)** with PhLi, and **6′(Li)** was from the reduction of **2′(Li)** by lithium. On the other hand, K gave five compounds **2**, **3**, **4**, **7**, and **8**. Both **7** and **8** were new compounds that were not observed with Li and Na, showing that K was more reactive than Na and Li, and even two P−Ph bonds of $Ph_3P(O)$ could be cleft by K! A reaction as shown in Scheme 2**C-2** was assumed to take place for the formation of **7** (*vide infra*).[13] Therefore, it is concluded that, as to the selective C−P bond cleavage of $Ph_3P(O)$ to generate $Ph_2P(OM)$, *Na is better than Li and K.*[14]

As shown in Scheme 2A, 1 equiv of PhNa was co-generated from the reaction of $Ph_3P(O)$ with SD. Although it is known that, unlike PhLi generated using lithium (Scheme 2B) which is stable in THF, PhNa decomposes quickly.[13] However, details about the decomposition of PhNa were not clear.[13c] To clarify this decomposition, PhNa was generated separately from PhCl and SD in THF, and then was quenched with *n*-$C_8H_{17}Br$ and $PhMe_2SiCl$, respectively (Scheme 3a). Although the reactions with *n*-$C_8H_{17}Br$ were omittable,[15] a silylvinyl ether **9** was detected, indicating the formation of vinylate **9′** from the reaction! However, the exact yield of **9′** was hard to determine due to the easy decomposition of **9** in water. Fortunately, this intermediate could be trapped by the in situ generated $Ph_2P(O)H$ (Scheme 3b). Thus, 80% yield of **10**, formed by the addition of $Ph_2P(O)H$ to acetaldehyde,[16] was obtained which indicated

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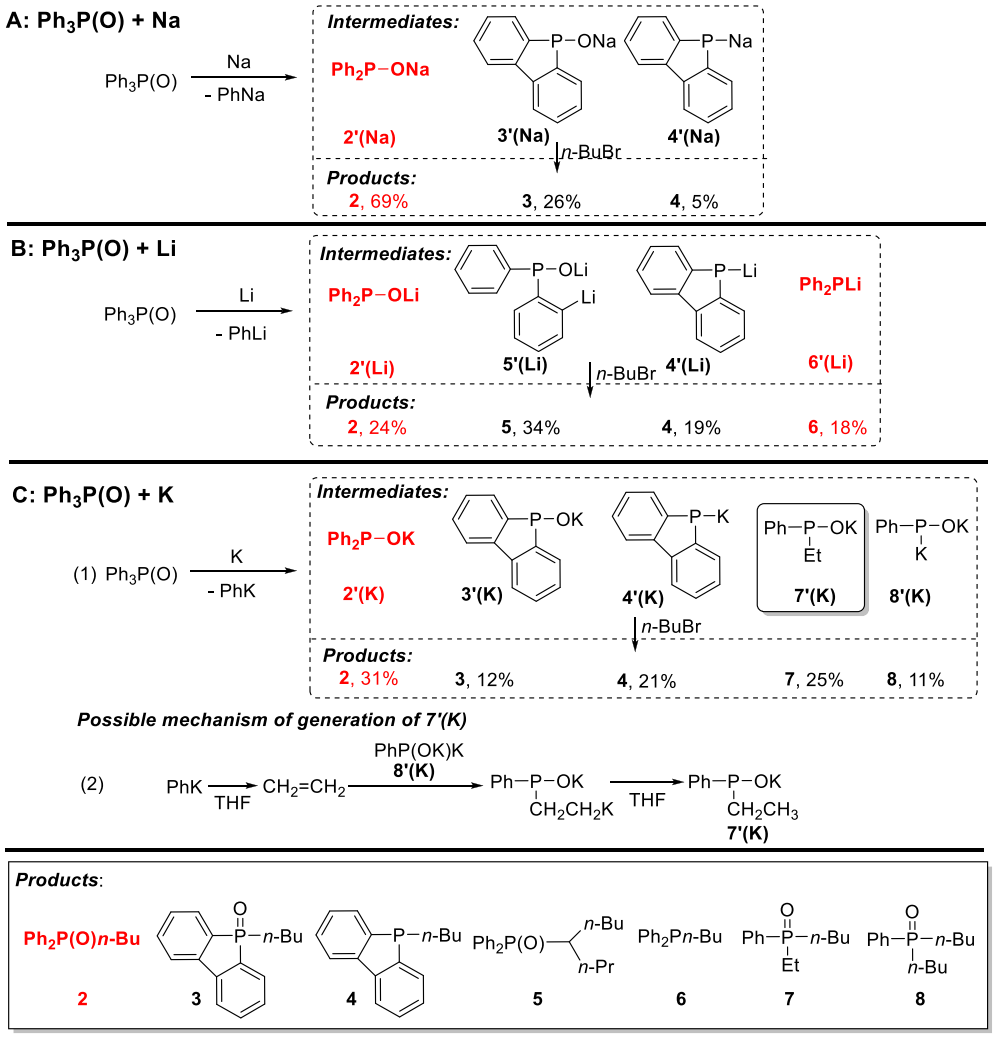
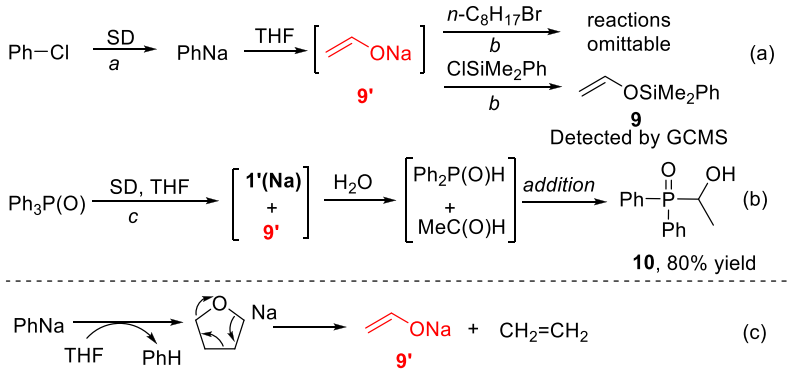
Scheme 2. Reactions of $Ph_3P(O)$ with Alkali Metals[a]



[a]Reaction conditions: under Ar, $Ph_3P(O)$ (1.0 mmol), alkali metal (2.5 mmol), THF (5.0 mL), 25 °C, overnight. Then *n*-BuBr (2.0 mmol), 25 °C, 0.5 h. Yields refer to ^{31}P NMR yields based on $Ph_3P(O)$ used.

Scheme 3. Decomposition of PhNa by THF[a]



[a]Conditions: (a) PhCl (1.0 mmol), SD (2.0 mmol), THF (5.0 mL), 25 °C, 1 h. (b) Electrophiles (1.2 mmol), 25 °C, 0.5 h. (c) $Ph_3P(O)$ (1.0 mmol), SD (2.5 mmol), THF (5 mL), 25 °C, 10 min.

that **9′** was the sodium alkoxide predominantly generated from the reaction of PhNa with THF (Scheme 3c).[13]

Therefore, **9′** was the main co-product in the solution of $Ph_2P(ONa)$ generated from $Ph_3P(O)$ and SD. The fortunate thing is that, unlike PhLi (Scheme 3b), the presence of **9′** affects little the following reactions of $Ph_2P(ONa)$ with an electrophile[17] such as RX because of its relatively low reactivity and the relatively high reactivity of $Ph_2P(ONa)$; i.e., in most cases, $Ph_2P(ONa)$ generated from $Ph_3P(O)$ and SD can be used as it in the presence of **9′**.[12]

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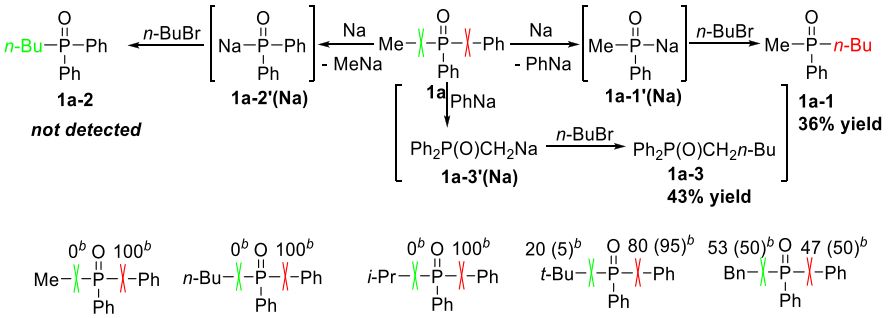
Scheme 4. Selectivity of the C−P Bond Cleavage[a]



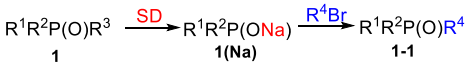
[a]Conditions: $Ph_2P(O)R$ (0.3 mmol), THF (2.0 mL), SD (0.3 mmol), 25 °C, 1 h. Then an excess amount of *n*-BuBr, 25 °C, 0.5 h. Yields were determined by GC. [b]The ratio of P−R bond and P−Ph bond cleavage was determined by GC. The data in parentheses were for reactions conducted in 1,4-dioxane.

As shown in Scheme 4, the C−P bond cleavages of unsymmetrical diphenylalkylphosphine oxides were studied. All these phosphine oxides reacted similarly to $Ph_3P(O)$ to generate the corresponding $R_2P(ONa)$. As exemplified by the reaction of $Ph_2P(O)Me$ **1a**, to the phosphine oxide in THF was added 1 equiv of SD at room temperature to generate an orange solution. The mixture was stirred for 1 h and then quenched with an excess amount of *n*-BuBr. Compound **1a-1** was obtained in 36% GC yield, and compound **1a-2** could not be detected at all. As expected, compound **1a-3** via the reactions of PhNa and **1a** was also obtained in 43% yield. By conducting similar reactions, the selectivity on the C−P bond cleavage of diphenyl(alkyl)-phosphine oxides $Ph_2P(O)R$ (P−Ph vs P−R) was determined. Thus, while cleavage on the P−Ph bond took place exclusively with Me, *n*-Bu, and *i*-Pr groups, interestingly, for $Ph_2P(O)t$-Bu, the selectivity of P−Ph vs P−*t*-Bu is 80/20, and for $Ph_2P(O)Bn$, the selectivity even became to 47/53, showing that it is equally easy to break the P−Bn bond and the P−Ph bond.

In order to make the present SD-mediated C−P bond cleavage a general method for the synthesis of organophosphine oxides, we first have to fix the abstraction problem of the α-protons at R of $Ph_2P(O)R$ by PhNa as exemplified by $Ph_2P(O)Me$ (Scheme 4). Since the generation of the side product **1a-3′(Na)** by PhNa (Scheme 4) is a competition reaction with the generation of the aimed product **1a-1′(Na)** by Na, we realized that, by using an excess amount of Na, this side reaction could be suppressed (see Supplementary Table 1).

As shown in Table 1, the reactions of representative phosphine oxides and related were investigated. Highly selective Ph−P bond cleavage of $Ph_2P(O)R$ took place efficiently, where R can be methyl (run 1), primary (runs 2 and 3), secondary (runs 4 and 5), and tertiary (run 6) alkyl groups, to produce the corresponding PhRP(ONa) that was trapped by an alkyl bromide to give the corresponding new phosphine oxides in good to excellent yields. However, $Ph_2P(O)CH_2Ph$ gave complicated results under similar conditions (run 7) due to the bad selectivity of the C−P bond cleavages (Scheme 4) and the easier deprotonation of the benzyl proton of $Ph_2P(O)$-CH_2Ph by a base. After carrying out an extensive study on the optimization of the reaction conditions, we found that, by conducting the reaction in 1,4-dioxane at 100 °C, $Ph_2P(O)n$-Bu **1g-1**, assumed from the P−Bn bond cleavage, was obtained in 53% yield.[18] Dibutylphenylphosphine oxide could be also used as the substrate, and the Ph−P bond was selectively cleft (run 8). However, trioctylphosphine oxide did not react even at a higher temperature (run 9).

Table 1. Conversion of Phosphine Oxides to Other Organophosphorus by SD[a]



run	1	1(Na)	1-1/yield
1	$Ph_2P(O)Me$	PhMeP(ONa)	PhMeP(O)*n*-Bu **1a-1**, 89%
2	$Ph_2P(O)n$-Bu	Ph*n*-BuP(ONa)	PhP(O)*n*-Bu_2 **1b-1**, 92%
3[b]	$Ph_2P(O)n$-Oct	Ph*n*-OctP(ONa)	PhP(O)*n*-Oct_2 **1c-1**, 96%
4	$Ph_2P(O)i$-Pr	Ph*i*-PrP(ONa)	Ph*i*-PrP(O)*n*-Bu **1d-1**, 92%
5	$Ph_2P(O)s$-Bu	Phs-BuP(ONa)	Phs-BuP(O)*n*-Bu **1e-1**, 99%
6	$Ph_2P(O)t$-Bu	Pht-BuP(ONa)	Pht-BuP(O)*n*-Bu **1f-1**, 90%
7	$Ph_2P(O)Bn$	$Ph_2P(ONa)$	$Ph_2P(O)n$-Bu **1g-1**, 53%
8	*n*-$Bu_2P(O)Ph$	*n*-$Bu_2P(ONa)$	*n*-$Bu_2P(O)n$-Bu **1h-1**, 87%
9	*n*-$Oct_3P(O)$	*n*-$Oct_2P(ONa)$	*n*-$Oct_2P(O)n$-Bu **1i-1**, none
10	$Ph_2P(O)Ot$-Bu	$Ph_2P(ONa)$	$Ph_2P(O)n$-Bu **1g-1**, 93%
11	$Ph_2P(O)OPh$	$Ph_2P(ONa)$	$Ph_2P(O)n$-Bu **1g-1**, 85%
12[c]	$PhP(O)(OPh)_2$	PhPNa(ONa)	PhP(O)*n*-Bu_2 **1b-1**, 69%
13[c,d]	$PhP(O)(OMe)_2$	PhPNa(ONa)	PhP(O)*n*-Bu_2 **1b-1**, 31%
14[e]	$P(O)(OPh)_3$	$PNa_2(ONa)$	P(O)*n*-Bu_3 **1h-1**, trace

[a]Reaction conditions: **1** (0.3 mmol), SD (1.0 mmol), 1,4-dioxane (2.0 mL), 60 °C, 24 h. Then *n*-BuBr (0.4 mmol), 25 °C, 0.5 h. Isolated yield. [b]*n*-OctBr (0.4 mmol) was used. [c]SD (1.8 mmol), *n*-BuBr (0.8 mmol). [d]Yield was determined by ^{31}P NMR based on **1m** used. [e]SD (2.4 mmol), *n*-BuBr (1.0 mmol).

In addition to tertiary phosphine oxides, the reactions of phosphinic (runs 10 and 11), phosphonic (runs 12 and 13), and phosphoric (run 14) esters were also examined. Only the products from the cleavage of the P−O bonds were obtained. Thus, diphenylphosphinates like $Ph_2P(O)Ot$-Bu and $Ph_2P(O)$-OPh generated Ph_2PONa in high yields (runs 10 and 11). Surprisingly, with $PhP(O)(OPh)_2$, the two P−O bonds could be readily broken and the product $PhP(O)n$-Bu_2 assumed via the reaction of PhP(Na)ONa and *n*-BuBr was obtained in good yield (run 12). However, under similar conditions, PhP(O)-

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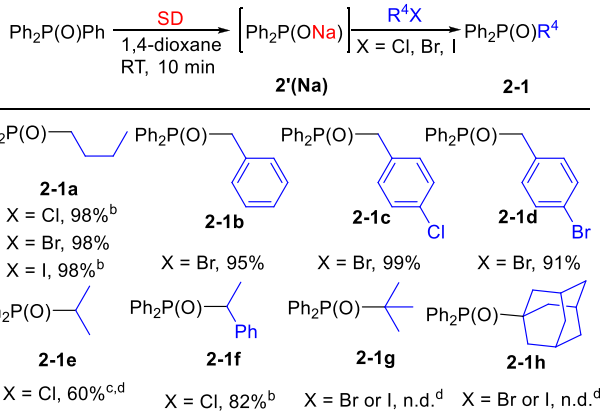
$(OMe)_2$ gave a complex mixture and only 31% PhP(O)*n*-Bu_2 was obtained (run 13). Although $(PhO)_3P(O)$ also reacted with SD rapidly, the result was complicated and only a trace amount of *n*-$Bu_3P(O)$ could be detected (run 14).

As outlined in Table 2, *n*-BuCl and *n*-BuI could also be used as electrophiles for trapping $Ph_2P(ONa)$ to generate the corresponding product in high yields, though heating is necessary for *n*-BuCl. Electrophiles were readily extended to other primary alkyl bromides with functional groups such as Cl and Br (**2-1b–d**) as well as secondary alkyl chlorides (**2-1e** and **2-1f**). Unfortunately, the reaction of $Ph_2P(ONa)$ with tertiary alkyl halides such as *t*-butyl and admantyl halides gave complex mixtures and no desired products could be obtained (**2-1g** and **2-1h**).

Table 2. Scope of Alkyl Halides[a]



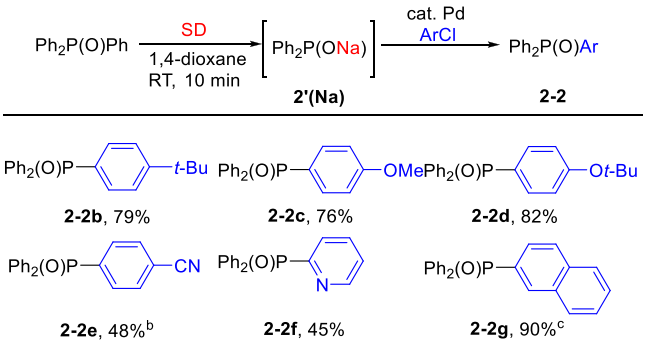
[a]Reaction conditions: $Ph_3P(O)$ (0.2 mmol), SD (0.5 mmol), 1,4-dioxane (1.0 mL), 25 °C, 10 min. Then R^4X (0.3 mmol), 25 °C, 0.5 h. Isolated yield. [b]60 °C, overnight. [c]15-Crown-5 ether (0.2 mmol) was added at step 2. [d]100 °C, overnight.

$Ph_2P(ONa)$ can also be used in the cross-coupling reactions with aryl halides ArX to produce diphenyl(aryl)phosphine oxides. Transition-metal-catalyzed couplings of $Ph_2P(O)H$ with the aryl bromides or aryl iodides were well-studied;[19] however, reactions with the less reactive aryl chlorides, especially the electron-rich aryl chlorides, were limited.[20] By using palladium as the catalyst, we could successfully couple Ph_2PONa with *p*-tolyl chloride to produce the coupling product in high yields (see Supplementary Table 2).[21] This Pd-catalyzed coupling reaction can be applied to a variety of other aryl chlorides (Table 3). For example, the electron-rich aryl chlorides including those with *tert*-butyl, methoxyl, and *tert*-butoxyl groups on the benzene ring were suitable substrates, affording the corresponding coupling products in high yields (**2-2b** to **2-d**). 2-Pyridyl chloride was also tolerated in this catalyzed reaction and formed the products in moderate yield (**2-2f**). The catalyst loading could be reduced to 2 mol % without reducing the reaction's efficacy, as 2-chloronaphthalene was readily phosphorylated to **2-2g** in 90% yield.

Although the detailed reaction path is not clear, we propose a single electron transfer (SET) mechanism for the cleavage of the P–R bond (Scheme 5) that might account for the results obtained above.[22,23]

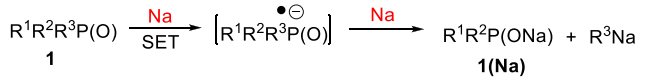
In summary, Na shows the best efficiency and selectivity for cleaving the C–Ph bond of $Ph_3P(O)$. A variety of phosphine oxides reacted with SD, via selective P–C or P–O bond cleavages, and efficiently produced P-ONa intermediates that can react with a variety of organic halides to afford the corresponding new phosphine oxides in good yields.

Table 3. Palladium-Catalyzed Cross-Coupling Reactions of Ph_2PONa and Aryl Halides[a]



[a]Reaction conditions: $Ph_3P(O)$ (0.2 mmol), SD (0.5 mmol), 1,4-dioxane (1.0 mL), 25 °C, 10 min. Then $Pd(Ph_3P)_2Cl_2$ (5 mol %) and ArX (0.2 mmol) were sequentially added, 100 °C, 24 h. Isolated yield. [b]$Pd(OAc)_2$/dppf (5 mol %) was used. [c]$Ph_3P(O)$ (1.0 mmol), SD (2.5 mmol), 1,4-dioxane (5.0 mL), 25 °C, 10 min. And then $Pd(Ph_3P)_2Cl_2$ (2 mol %), 2-chloronaphthalene (1.0 mmol), 120 °C, 30 h.

Scheme 5. Mechanism of P–R bond Cleavage



EXPERIMENTAL SECTION

General Information. The reactions were carried out in oven-dried Schlenk tubes under an argon atmosphere. The sodium we used was dispersed in paraffin oil with an average particle size smaller than 10 μm and a concentration of ~10.0 mol/L. MS (ESI) data were obtained on a SHIMADZU GC-MS 2010 plus. The High-resolution ESI mass spectra were obtained on a Bruker micrOTOF II. Column chromatography was performed using Silica Gel 60 N (TCI, spherical, neutral). HPLC (recycle GPC) isolation was performed using a JAPAN ANALYTICAL INDUSTRY LC-908, equipped with two preparative columns (20 mm × 600 mm; JAIGEL-1H and JAIGEL-2H). $CHCl_3$ (flow rate: 4.0 mL/min) was used as eluent. ^1H, ^{13}C, and ^{31}P NMR were recorded on a JEOL JNM-ECS400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR spectroscopy). Chemical shifts for ^1H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Chemical shifts for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm). The melting points were obtained on an SRS OptiMelt.

Typical Experimental Procedure for the Synthesis of Phosphine Oxide 1a-1 from 1a by SD. Under an argon atmosphere, to a stirring solution of diphenyl(methyl)phosphine oxide **1a** (0.3 mmol, 1 equiv, 64.8 mg) in 1,4-dioxane (2.0 mL) was added SD (1.0 mmol, 3.3 equiv, 0.1 mL) via a syringe. The mixture was then stirred at 60 °C for 24 h. After removal of the excessive Na by filtration, *n*-BuBr (0.4 mmol, 1.33 equiv, 43 μL) was added, and further stirring the mixture was continued for 0.5 h. After that, the resulting mixture was filtered and concentrated under vacuum. Next, the obtained residue was directly eluted with hexane via a silica gel column and then eluted with MeOH to give the crude product, which was then diluted in $CHCl_3$ and purified by GPC to afford pure product **1a-1** (52.3 mg, 0.267 mmol, 89% yield).

Experimental Procedure for 2 mmol Scale Synthesis of Phosphine Oxide 1b-1 from 1b by SD. Under an argon atmosphere, to a stirring solution of diphenyl(butyl)phosphine oxide **1b** (2.0 mmol, 1 equiv, 516.2 mg) in 1,4-dioxane (10.0 mL) was added

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SD (8.0 mmol, 4 equiv, 0.8 mL) via a syringe. The mixture was then stirred at 60 °C for 48 h. After removal of the excessive Na by filtration, *n*-BuBr (3.0 mmol, 1.5 equiv, 161 μL) was added, and further stirring the mixture for 2 h. After that, the resulting mixture was filtered and concentrated under vacuum. Next, the residue was then purified by flash column chromatography on silica gel with hexane/ethyl acetate (1:1) to give the desired product **1b-1** (409.6 mg, 1.72 mmol, 86% yield).

Typical Experimental Procedure for Pd-Catalyzed Coupling Reaction of $Ph_2P(ONa)$ with *p*-MeC_6H_4Cl Generating Diphenyl-(*p*-tolyl)phosphine Oxide 2-2a. Under an argon atmosphere, to a stirring solution of triphenylphosphine oxide (0.2 mmol, 1 equiv, 55.6 mg) in 1,4-dioxane (1.0 mL) was added SD (0.5 mmol, 2.5 equiv, 50.0 μL) via a syringe. The mixture was then stirred at 25 °C for 10 min. After removal of the excessive Na by filtration, $Pd(Ph_3P)Cl_2$ (5 mol %, 7.0 mg) and *p*-MeC_6H_4Cl (0.2 mmol, 1.0 equiv, 24.0 μL) were sequentially added, and further stirring the mixture at 100 °C for 24 h. After that, the resulting mixture was filtered and concentrated under vacuum. Next, the obtained residue was directly eluted with hexane via a silica gel column and then eluted with MeOH to give the crude product, which was then diluted in $CHCl_3$ and purified by GPC to afford pure product **2-2a** (49.7 mg, 0.17 mmol, 85% yield).

Comparison Experimental Procedure for the Treatments of $Ph_3P(O)$ with Alkali Metals (Na, Li, K, Mg). Under an argon atmosphere, to a solution of $Ph_3P(O)$ (1.0 mmol, 278.0 mg) in THF (5 mL) was added alkali (Li, Na, K) or alkaline-earth (Mg) metal (2.5 mmol) cut into tiny pieces. After stirring the mixture at room temperature for 24 h, excessive *n*-BuBr was added, and then the resulting mixture was analyzed by ^{31}P NMR, GC, and GC-MS.

Synthesis of Compound 5 by Literature Method.[24] Under an argon atmosphere, *s*-BuLi (2.0 mmol, 1.04 mol/L solution in hexane, 2.0 mL) was added in dropwise to the stirred solution of $Ph_2P(O)n$-Bu (1.0 mmol, 258.0 mg) in THF (4.0 mL) at −78 °C. After stirring for 30 min, the reaction mixture was warmed to 0 °C, *n*-BuBr (2.0 mmol, 215 μL) was added, and stirring the mixture for another 30 min. After that, the mixture was quenched with saturated NH_4Cl aqueous solution (5 mL) at 0 °C and extracted with CH_2Cl_2 (5 mL × 3); then the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was diluted in $CHCl_3$ and purified by GPC to afford pure product **5** (238 mg, 0.76 mmol, 76% yield).

Synthesis of Compound 10. Under an argon atmosphere, to a stirring solution of $Ph_3P(O)$ (1.0 mmol, 1 equiv) in THF (5.0 mL) was added SD (3.0 mmol, 3 equiv, 0.3 mL) via a syringe. After stirring the mixture at room temperature for 0.5 h, saturated NH_4Cl aqueous solution (5.0 mL) was added and then extracted with EtOAc (5 mL × 3); the combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was eluted with hexane via a silica gel column and then eluted with MeOH to give the crude product, which was then diluted in $CHCl_3$ and purified by GPC to afford pure product **10** (196 mg, 0.80 mmol, 80% yield).

^1H and ^{13}C NMR and ^{31}P NMR Spectral Data of the Products. *Butyl(methyl)(phenyl)phosphine Oxide (**1a-1**).* White solid: 52.3 mg, 89% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 2H), 7.49−7.42 (m, 3H), 2.01−1.80 (m, 2H), 1.67 (d, 3H, *J* = 12.4 Hz), 1.59−1.48 (m, 1H), 1.46−1.39 (m, 1H), 1.38−1.29 (m, 2H), 0.83 (t, 3H, *J* = 7.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 133.6 (d, $J_{p\text{-}c}$ = 95.3 Hz), 131.7 (d, $J_{p\text{-}c}$ = 2.1 Hz), 130.1 (d, $J_{p\text{-}c}$ = 9.0 Hz), 128.7 (d, $J_{p\text{-}c}$ = 11.3 Hz), 31.5 (d, $J_{p\text{-}c}$ = 70.1 Hz), 24.0 (d, $J_{p\text{-}c}$ = 15.1 Hz), 23.72 (d, $J_{p\text{-}c}$ = 4.0 Hz), 16.0 (d, $J_{p\text{-}c}$ = 69.4 Hz), 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.0. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{11}H_{17}OP$ 196, Found 196. This compound is known.[25a]

*Dibutyl(phenyl)phosphine Oxide (**1b-1**).* White solid: 65.7 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59−7.64 (m, 2H), 7.49−7.43 (m, 3H), 2.00−1.77 (m, 4H), 1.64−1.53 (m, 2H), 1.44−1.28 (m, 6H), 0.84 (t, 6H, *J* = 7.2 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.6 (d, $J_{p\text{-}c}$ = 91.4 Hz), 131.5 (d, $J_{p\text{-}c}$ = 2.4 Hz), 130.5 (d, $J_{p\text{-}c}$ = 8.6 Hz), 128.7 (d, $J_{p\text{-}c}$ = 11.1 Hz), 29.7 (d, $J_{p\text{-}c}$ = 68.1 Hz), 24.2 (d, $J_{p\text{-}c}$ = 14.4 Hz), 23.6 (d, $J_{p\text{-}c}$ = 4.2 Hz), 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.6. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{14}H_{23}OP$ 238, Found 238. This compound is known.[25b]

*Dioctyl(phenyl)phosphine Oxide (**1c-1**).* White solid: 100.8 mg, 96% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.62 (m, 2H), 7.49−7.41 (m, 3H), 1.97−1.76 (m, 5H), 1.63−1.50 (m, 2H), 1.44−1.17 (m, 21H), 0.83−0.79 (m, 6H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.5 (d, $J_{p\text{-}c}$ = 91.9 Hz), 131.5 (d, $J_{p\text{-}c}$ = 1.8 Hz), 130.5 (d, $J_{p\text{-}c}$ = 8.7 Hz), 128.6 (d, $J_{p\text{-}c}$ = 11.2 Hz), 31.8, 31.1, 30.9, 29.9 (d, $J_{p\text{-}c}$ = 67.9 Hz), 29.1, 22.6, 21.5 (d, $J_{p\text{-}c}$ = 3.8 Hz), 14.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.0. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{22}H_{39}OP$ 350, found 350. This compound is known.[25c,d]

*Butyl(isopropyl)(phenyl)phosphine Oxide (**1d-1**).* Colorless oil: 61.8 mg, 92% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.61 (m, 2H), 7.48−7.40 (m, 3H), 2.05−1.95 (m, 2H), 1.83−1.80 (m, 1H), 1.61−1.54 (m, 1H), 1.37−1.25 (m, 3H), 1.16 (dd, 3H, J_1 = 15.6 Hz, J_2 = 6.8 Hz), 0.88 (dd, 3H, J_1 = 16.0 Hz, J_2 = 7.2 Hz), 0.81 (t, 3H, *J* = 7.2 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 131.9, 131.4 (d, $J_{p\text{-}c}$ = 2.3 Hz), 131.0 (d, $J_{p\text{-}c}$ = 8.2 Hz), 128.5 (d, $J_{p\text{-}c}$ = 10.7 Hz), 28.6 (d, $J_{p\text{-}c}$ = 68.9 Hz), 26.4 (d, $J_{p\text{-}c}$ = 66.1 Hz), 24.2 (d, $J_{p\text{-}c}$ = 13.7 Hz), 23.5 (d, $J_{p\text{-}c}$ = 4.2 Hz), 15.8 (d, $J_{p\text{-}c}$ = 1.1 Hz), 15.2 (d, $J_{p\text{-}c}$ = 2.4 Hz), 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.4. HRMS (ESI-TOF): *m*/*z*: ($[M + Na]^+$) Calcd for $C_{13}H_{21}OPNa$ 247.1228, Found 247.1224.

*sec-Butyl(butyl)(phenyl)phosphine Oxide (**1e-1**).* White solid: 70.6 mg, 99% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63−7.59 (m, 2H), 7.44−7.39 (m, 3H), 2.04−1.89 (m, 1H), 1.82−1.72 (m, 2H), 1.55−1.54 (brs, 1H), 1.37−1.18 (m, 4H), 1.13 (dd, 2H, J_1 = 16.0 Hz, J_2 = 7.2 Hz), 0.98−0.70 (m, 8H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 131.3, 131.0 (d, $J_{p\text{-}c}$ = 5.3 Hz), 130.9 (d, $J_{p\text{-}c}$ = 5.6 Hz), 128.5 (dd, J_1 = 10.5 Hz, J_2 = 2.5 Hz), 35.5 (dd, J_1 = 68.2 Hz, J_2 = 10.1 Hz), 26.6 (d, $J_{p\text{-}c}$ = 65.6 Hz), 24.2 (d, $J_{p\text{-}c}$ = 13.8 Hz), 23.4, 22.3 (d, $J_{p\text{-}c}$ = 52.0 Hz), 13.6, 8.4 (dd, J_1 = 12.8 Hz, J_2 = 4.4 Hz), 11.8 (d, $J_{p\text{-}c}$ = 52.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.0. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{14}H_{23}OP$ 238, found 238. This compound is known.[25e]

*tert-Butyl(butyl)(phenyl)phosphine Oxide (**1f-1**).* White solid: 64.3 mg, 90% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.60 (m, 2H), 7.48−7.40 (m, 3H), 2.00−1.90 (m, 2H), 1.67−1.54 (m, 1H), 1.42−1.21 (m, 3H), 1.07 (d, 9H, *J* = 14.0 Hz), 0.82 (t, 3H, *J* = 7.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 131.9 (d, $J_{p\text{-}c}$ = 7.7 Hz), 131.4 (d, $J_{p\text{-}c}$ = 2.5 Hz), 130.9 (d, $J_{p\text{-}c}$ = 9.3 Hz), 130.2 (d, $J_{p\text{-}c}$ = 85.6 Hz), 128.7 (d, $J_{p\text{-}c}$ = 11.4 Hz), 128.3 (d, $J_{p\text{-}c}$ = 10.4 Hz), 32.7 (d, $J_{p\text{-}c}$ = 68.1 Hz), 24.6brs, 24. (d, $J_{p\text{-}c}$ = 13.9 Hz), 23.6 (d, $J_{p\text{-}c}$ = 4.2 Hz), 22.7 (d, $J_{p\text{-}c}$ = 64.4 Hz), 13.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 50.3. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{14}H_{23}OP$ 238, found 238. This compound is known.[25a]

*Diphenyl(butyl)phosphine Oxide (**1g-1**).* White solid: 41.0 mg, 53% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74−7.69 (m, 4H), 7.48−7.42 (m, 6H), 2.27−2.20 (m, 2H), 1.63−1.53 (m, 2H), 1.44−1.35 (m, 2H), 0.86 (t, 3H, *J* = 7.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 133.3 (d, $J_{p\text{-}c}$ = 96.9 Hz), 131.7 (d, $J_{p\text{-}c}$ = 2.1 Hz), 130.9 (d, $J_{p\text{-}c}$ = 9.2 Hz), 128.7 (d, $J_{p\text{-}c}$ = 11.4 Hz), 29.6 (d, $J_{p\text{-}c}$ = 71.8 Hz), 24.2 (d, $J_{p\text{-}c}$ = 15.1 Hz), 23.6 (d, $J_{p\text{-}c}$ = 3.7 Hz), 13.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.1. MS (ESI) *m*/*z*: ($[M]^+$) Calcd for $C_{16}H_{19}OP$ 258, Found 258. This compound is known.[25f]

*Diphenyl(1-phenylpentyl)phosphine Oxide (**1g-3**).* White solid: 44.9 mg, 43% yield. mp 205−208 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92−7.87 (m, 2H), 7.56−7.49 (m, 3H), 7.42−7.38 (m, 2H), 7.32−7.28 (m, 1H), 7.22−7.13 (m, 7H), 3.41−3.35 (m, 1H), 2.18−2.06 (m, 1H), 1.92−1.82 (m, 1H), 1.25−1.09 (m, 4H), 0.73 (t, 3H, *J* = 7.2 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 136.1 (d, $J_{p\text{-}c}$ = 5.2 Hz), 132.8 (d, $J_{p\text{-}c}$ = 27.0 Hz), 131.4 (d, $J_{p\text{-}c}$ = 8.3 Hz), 131.2 (d, $J_{p\text{-}c}$ = 1.9 Hz), 131.1 (d, $J_{p\text{-}c}$ = 8.7 Hz), 129.9 (d, $J_{p\text{-}c}$ = 5.8 Hz), 128.7 (d, $J_{p\text{-}c}$ = 10.9 Hz), 128.0 (d, $J_{p\text{-}c}$ = 11.4 Hz), 126.9 (d, $J_{p\text{-}c}$ = 2.2 Hz), 47.0 (d, $J_{p\text{-}c}$ = 67.0 Hz), 30.0 (d, $J_{p\text{-}c}$ = 12.9 Hz), 28.8, 22.2, 13.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.5. HRMS (ESI-TOF): *m*/*z*: ($[M + Na]^+$) Calcd for $C_{23}H_{25}OPNa$ 371.1541, Found 371.1538.

*Tributylphosphine Oxide (**1h-1**).* White solid: 56.9 mg, 87% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 1.62−1.55 (m, 6H), 1.53−1.41 (m, 6H), 1.39−1.27 (m, 6H), 0.86−0.81 (m, 9H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 27.7 (d, $J_{p\text{-}c}$ = 64.7 Hz), 24.3 (d, $J_{p\text{-}c}$ = 14.1 Hz), 23.8 (d, $J_{p\text{-}c}$ = 3.3 Hz), 13.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 49.1. MS (ESI)

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m/z: ([M]$^+$) Calcd for $C_{12}H_{27}OP$ 218, found 218. This compound is known.[25a]

*Octan-4-yldiphenylphosphine Oxide (**5**)*. Preparation by literature method.[24] White solid: 238 mg, 76% yield). mp 151−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81−7.76 (m, 4H), 7.48−7.42 (m, 6H), 2.25−2.16 (m, 1H), 1.73−1.59 (m, 2H), 1.56−1.39 (m, 4H), 1.25−1.13 (m, 4H), 0.80−0.75 (m, 6H); ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 133.2 (dd, J_1 = 93.6 Hz, J_2 = 2.9 Hz), 131.4 (d, $J_{p\text{-}c}$ = 2.4 Hz), 131.0 (dd, J_1 = 8.5 Hz, J_2 = 1.1 Hz), 128.6 (d, $J_{p\text{-}c}$ = 11.1 Hz), 37.1 (d, $J_{p\text{-}c}$ = 70.3 Hz), 30.3 (d, $J_{p\text{-}c}$ = 9.2 Hz), 29.9, 27.3, 22.8, 21.3 (d, $J_{p\text{-}c}$ = 9.4 Hz), 14.3, 13.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.3. HRMS (ESI-TOF): *m/z*: ([M + Na]$^+$) Calcd for $C_{20}H_{27}OPNa$ 337.1697, Found 337.1698.

*(1-Hydroxyethyl)diphenylphosphine Oxide (**10**)*. White solid: 196.7 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88−7.83 (m, 2H), 7.78−7.73 (m, 2H), 7.50−7.38 (m, 6H), 4.88 (brs, 1H), 4.57−4.52 (m, 1H), 1.39 (dd, 3H, J_1 = 15.6 Hz, J_2 = 7.2 Hz). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 132.5 (d, $J_{p\text{-}c}$ = 8.0 Hz), 132.1 (d, $J_{p\text{-}c}$ = 8.9 Hz), 132.0 (d, $J_{p\text{-}c}$ = 3.6 Hz), 131.6 (d, $J_{p\text{-}c}$ = 8.9 Hz), 130.7 (d, $J_{p\text{-}c}$ = 8.2 Hz), 129.8, 128.6 (d, $J_{p\text{-}c}$ = 10.6 Hz), 128.5 (d, $J_{p\text{-}c}$ = 10.7 Hz), 66.7 (d, $J_{p\text{-}c}$ = 84.0 Hz), 17.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.6. This compound is known.[25a]

*Benzyldiphenylphosphine Oxide (**2-1b**)*. White solid: 55.5 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 4H), 7.50−7.39 (m, 6H), 7.16−7.08 (m, 5H), 3.64 (d, 2H, J = 13.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.4 (d, $J_{p\text{-}c}$ = 98.5 Hz), 131.9 (d, $J_{p\text{-}c}$ = 2.3 Hz), 131.3 (d, $J_{p\text{-}c}$ = 9.2 Hz), 130.2 (d, $J_{p\text{-}c}$ = 5.4 Hz), 128.6, 128.5, 128.45 (d, $J_{p\text{-}c}$ = 1.9 Hz), 126.8 (d, $J_{p\text{-}c}$ = 1.7 Hz), 38.2 (d, $J_{p\text{-}c}$ = 66.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.0. This compound is known.[26a]

*(4-Chlorobenzyl)diphenylphosphine Oxide (**2-1c**)*. White solid: 64.6 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 4H), 7.53−7.48 (m, 2H), 7.45−7.41 (m, 4H), 7.14 (d, 2H, J = 8.4 Hz), 7.04−7.01 (m, 2H), 3.59 (d, 2H, J = 13.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.9 (d, $J_{p\text{-}c}$ = 3.2 Hz), 132.1 (d, $J_{p\text{-}c}$ = 98.8 Hz), 132.0 (d, $J_{p\text{-}c}$ = 2.3 Hz), 131.5 (d, $J_{p\text{-}c}$ = 5.2 Hz), 131.2 (d, $J_{p\text{-}c}$ = 9.3 Hz), 129.8 (d, $J_{p\text{-}c}$ = 8.2 Hz), 128.7, 128.6, 37.6 (d, $J_{p\text{-}c}$ = 65.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[26b]

*(4-Bromobenzyl)diphenylphosphine Oxide (**2-1d**)*. White solid: 67.3 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.65 (m, 4H), 7.53−7.49 (m, 2H), 7.46−7.41 (m, 4H), 7.29 (d, 2H, J = 8.4 Hz), 6.98−6.96 (m, 2H). 3.58 (d, 2H, J = 13.6 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.1 (d, $J_{p\text{-}c}$ = 100.7 Hz), 132.0 (d, $J_{p\text{-}c}$ = 2.3 Hz), 131.8 (d, $J_{p\text{-}c}$ = 5.3 Hz), 131.6 (d, $J_{p\text{-}c}$ = 2.0 Hz), 131.2 (d, $J_{p\text{-}c}$ = 9.0 Hz), 130.3 (d, $J_{p\text{-}c}$ = 8.0 Hz), 128.7, 128.6, 37.6 (d, $J_{p\text{-}c}$ = 65.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known.[26c]

*Isopropyldiphenylphosphine Oxide (**2-1e**)*. White solid: 29.3 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80−7.75 (m, 4H), 7.50−7.43 (m, 6H), 2.56−2.47 (m, 1H), 1.17 (dd, 6H, J_1 = 16.4 Hz, J_2 = 7.2 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 132.4 (d, $J_{p\text{-}c}$ = 94.1 Hz), 131.6 (d, $J_{p\text{-}c}$ = 2.0 Hz), 131.1 (d, $J_{p\text{-}c}$ = 8.5 Hz), 128.6 (d, $J_{p\text{-}c}$ = 11.0 Hz), 27.2 (d, $J_{p\text{-}c}$ = 72.4 Hz), 15.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.6. This compound is known.[26d]

*Diphenyl(1-phenylethyl)phosphine Oxide (**2-1f**)*. White solid: 50.2 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91−7.86 (m, 2H), 7.54−7.46 (m, 3H), 7.44−7.41 (m, 2H), 7.35−7.31 (m, 1H), 7.26−7.12 (m, 7H), 3.63−3.55 (m, 1H), 1.57 (dd, 3H, J_1 = 16.0 Hz, J_2 = 7.2 Hz). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 138.0 (d, $J_{p\text{-}c}$ = 5.3 Hz), 132.5 (d, J = 13.7 Hz), 131.8 (d, $J_{p\text{-}c}$ = 2.1 Hz), 131.6 (d, $J_{p\text{-}c}$ = 9.9 Hz), 131.5 (d, $J_{p\text{-}c}$ = 8.4 Hz), 131.4 (d, $J_{p\text{-}c}$ = 2.5 Hz), 131.2 (d, $J_{p\text{-}c}$ = 8.8 Hz), 129.3 (d, $J_{p\text{-}c}$ = 5.5 Hz), 128.7 (d, $J_{p\text{-}c}$ = 11.1 Hz), 128.3 (d, $J_{p\text{-}c}$ = 1.3 Hz), 128.1 (d, $J_{p\text{-}c}$ = 11.4 Hz),127.0 (d, $J_{p\text{-}c}$ = 1.8 Hz), 41.0 (d, $J_{p\text{-}c}$ = 66.8 Hz), 15.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.1. This compound is known.[26a]

*Diphenyl(p-tolyl)phosphine Oxide (**2-2a**)*. White solid: 49.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 4H), 7.55−7.48 (m, 4H), 7.44−7.39 (m, 4H), 7.25−7.22 (m, 2H), 2.37 (s, 3H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 142.6 (d, $J_{p\text{-}c}$ = 2.6 Hz), 132.8 (d, $J_{p\text{-}c}$ = 103.7 Hz), 132.2 (d, $J_{p\text{-}c}$ = 9.7 Hz), 132.1 (d, $J_{p\text{-}c}$ = 9.7 Hz), 132.0 (d, $J_{p\text{-}c}$ = 2.4 Hz), 129.6, 129.4 (d, $J_{p\text{-}c}$ = 12.5 Hz), 128.5 (d, $J_{p\text{-}c}$ = 11.9 Hz), 21.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.1. This compound is known.[27a]

*(4-(tert-Butyl)phenyl)diphenylphosphine Oxide (**2-2b**)*. White solid: 52.8 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.64 (m, 4H), 7.60−7.52 (m, 4H), 7.48−7.42 (m, 6H), 1.31 (s, 9H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 155.5 (d, $J_{p\text{-}c}$ = 2.8 Hz), 132.9 (d, $J_{p\text{-}c}$ = 103.6 Hz), 132.2 (d, $J_{p\text{-}c}$ = 10.0 Hz), 132.1 (d, $J_{p\text{-}c}$ = 10.8 Hz), 131.9 (d, $J_{p\text{-}c}$ = 2.1 Hz), 129.2 (d, $J_{p\text{-}c}$ = 105.9 Hz), 128.5 (d, $J_{p\text{-}c}$ = 12.0 Hz), 125.6 (d, $J_{p\text{-}c}$ = 12.1 Hz), 35.1, 31.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known.[27b]

*(4-Methoxyphenyl)diphenylphosphine Oxide (**2-2c**)*. White solid: 46.8 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.60 (m, 4H), 7.58−7.52 (m, 2H), 7.51−7.46 (m, 2H), 7.43−7.38 (m, 4H), 6.94−6.91 (m, 2H), 3.79 (s, 3H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 162.6 (d, $J_{p\text{-}c}$ = 2.6 Hz), 134.0 (d, $J_{p\text{-}c}$ = 11.3 Hz), 133.0 (d, $J_{p\text{-}c}$ = 103.9 Hz), 132.1 (d, $J_{p\text{-}c}$ = 9.7 Hz), 131.9 (d, $J_{p\text{-}c}$ = 2.1 Hz), 128.5 (d, $J_{p\text{-}c}$ = 12.2 Hz), 123.6 (d, $J_{p\text{-}c}$ = 109.8 Hz), 114.2 (d, $J_{p\text{-}c}$ = 13.1 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[27a]

*(4-(tert-Butoxy)phenyl)diphenylphosphine Oxide (**2-2d**)*. White solid: 57.4 mg, 82% yield. mp 135−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.63 (m, 4H), 7.55−7.50 (m, 4H), 7.46−7.42 (m, 4H), 7.05−7.02 (m, 2H), 1.38 (s, 9H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 159.3 (d, $J_{p\text{-}c}$ = 2.6 Hz), 133.4 (d, $J_{p\text{-}c}$ = 10.8 Hz), 132.3 (d, $J_{p\text{-}c}$ = 20.4 Hz), 132.2 (d, $J_{p\text{-}c}$ = 9.7 Hz), 131.9 (d, $J_{p\text{-}c}$ = 2.3 Hz), 128.5 (d, $J_{p\text{-}c}$ = 12.1 Hz), 125.9 (d, $J_{p\text{-}c}$ = 108.0 Hz), 122.9 (d, $J_{p\text{-}c}$ = 13.0 Hz), 79.6, 29.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.8. HRMS (ESI-TOF): *m/z*: ([M + Na]$^+$) Calcd for $C_{22}H_{23}NaO_2P$ 373.1333, Found 373.1335.

*4-(Diphenylphosphoryl)benzonitrile (**2-2e**)*. White solid: 29.1 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80−7.71 (m, 4H), 7.65−7.54 (m, 6H), 7.49−7.45 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 138.6 (d, $J_{p\text{-}c}$ = 98.5 Hz), 132.7 (d, $J_{p\text{-}c}$ = 10.9 Hz), 132.6 (d, $J_{p\text{-}c}$ = 3.1 Hz), 132.1 (d, $J_{p\text{-}c}$ = 10.5 Hz), 131.3 (d, $J_{p\text{-}c}$ = 104.9 Hz), 128.9 (d, $J_{p\text{-}c}$ = 12.3 Hz), 128.6 (d, $J_{p\text{-}c}$ = 12.1 Hz), 117.9, 115.7 (d, $J_{p\text{-}c}$ = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.3. This compound is known.[27c]

*Diphenyl(pyridin-2-yl)phosphine Oxide (**2-2f**)*. White solid: 25.2 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, 1H, J = 4.8 Hz), 8.29 (t, 1H, J = 4.8 Hz), 7.90−7.80 (m, 5H), 7.52−7.47 (m, 2H), 7.45−7.41 (m, 4H), 7.38−7.35 (m, 1H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 156.5 (d, $J_{p\text{-}c}$ = 131.2 Hz), 150.2 (d, $J_{p\text{-}c}$ = 19.1 Hz), 136.3 (d, $J_{p\text{-}c}$ = 9.1 Hz), 132.3 (d, $J_{p\text{-}c}$ = 103.7 Hz), 132.0 (d, $J_{p\text{-}c}$ = 2.4 Hz), 131.2 (d, $J_{p\text{-}c}$ = 9.4 Hz), 128.6 (d, $J_{p\text{-}c}$ = 9.3 Hz), 128.4 (d, $J_{p\text{-}c}$ = 12.2 Hz), 125.3 (d, $J_{p\text{-}c}$ = 2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.4. This compound is known.[27d]

*Naphthalen-2-yldiphenylphosphine Oxide (**2-2g**)*. White solid: 59.0 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 1H, J = 14.0 Hz), 7.89−7.83 (m, 3H), 7.72−7.68 (m, 4H), 7.65−7.60 (m, 1H), 7.56−7.49 (m, 4H), 7.46−7.42 (m, 4H). ^{13}C {1H} NMR (100 MHz, $CDCl_3$): δ 134.8 (d, $J_{p\text{-}c}$ = 1.6 Hz), 134.1 (d, $J_{p\text{-}c}$ = 9.3 Hz), 132.6 (d, $J_{p\text{-}c}$ = 103.8 Hz), 132.5 (d, $J_{p\text{-}c}$ = 13.0 Hz), 132.2 (d, $J_{p\text{-}c}$ = 9.8 Hz), 132.1 (d, $J_{p\text{-}c}$ = 2.2 Hz), 129.7 (d, $J_{p\text{-}c}$ = 103.7 Hz), 129.1, 128.7 (d, $J_{p\text{-}c}$ = 12.0 Hz),128.5, 128.4, 127.9, 127.1, 126.9 (d, $J_{p\text{-}c}$ = 10.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.9. This compound is known.[27a]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01642.

GC-MS spectra of results of comparation experiments associated with Na, Li, K; the verification experiments for compound **9**; and copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra for products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Li-Biao Han − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;*

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Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan; orcid.org/0000-0001-5566-9017; Email: libiao-han@aist.go.jp

Authors

Jian-Qiu Zhang − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan; Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan;* orcid.org/0000-0002-5220-3200

Eiichi Ikawa − *Katayama Chemical Industries Co., Ltd., Amagasaki, Hyogo 660-0892, Japan*

Hiroyoshi Fujino − *Katayama Chemical Industries Co., Ltd., Amagasaki, Hyogo 660-0892, Japan*

Yuki Naganawa − *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan;* orcid.org/0000-0002-3041-7638

Yumiko Nakajima − *Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan;* orcid.org/0000-0001-6813-8733

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c01642

Notes

The authors declare no competing financial interest.

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(18) It should be noted that the product PhBnP(O)*n*-Bu **1g-2** *via P−Ph bond's cleavage* was not detected under the current conditions (1,4-dioxane, 100 °C). And $Ph_2P(O)CH(Ph)$*n*-Bu **1g-3** *via benzylic C−H bond's cleavage* by BnNa was also isolated in 43% yield.

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