Supporting Information

Ruthenium-Catalyzed Formation of Aryl(diphenyl)phosphine Oxides by Reactions of Propargylic Alcohols with Diphenylphosphine Oxide

Gen Onodera,[†] Hideyuki Matsumoto,[†] Marilyn Daisy Milton,[†] Yoshiaki Nishibayashi^{*,‡} and Sakae Uemura[†]

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan, and Institute of Engineering Innovation, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

ynishiba@sogo.t.u-tokyo.ac.jp

List of the Contents of the Supporting Information

1. Ruthenium-Catalyzed Intramolecular Cyclization Reaction of Propargylic Alcohols with Diphenylphosphine Oxide	Page S2
2. Reaction of 1-(2-Phenylphenyl)-2-propyn-1-ol (6) with Diphenylphosphine Oxide	Page S4
3. Reduction of Phosphine Oxide (4a)	Page S4
4. Bromination of 4a with NBS	Page S5
5. Preparation of 11 with NaOEt	Page S5
6. X-ray Crystallographic Studies of 4a ·(H₂O) _{0.5}	Page S6
7. ¹ H NMR Charts of 4f , 7 , 9 , 10 and 11	Page S8

[†] Kyoto University

[‡] The University of Tokyo

General Method. ^1H NMR (400, 300, and 270 MHz) and ^{31}P NMR (161.7 MHz) spectra were recorded using CDCl_3 as solvent. Elemental analyses were performed at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

Ruthenium-Catalyzed Intramolecular Cyclization Reaction of Propargylic Alcohols with Diphenylphosphine Oxide. A typical experimental procedure for the reaction of 1,1-diphenyl-1-pentene-4-yn-3-ol (**3a**) with diphenylphosphine oxide (**2**) catalyzed by $[\text{Cp}^*\text{RuCl}(\text{SMe})]_2$ (**1a**) is described below. In a 20 mL flask were placed **1a** (9.8 mg, 0.015 mmol) and NH_4BF_4 (3.5 mg, 0.033 mmol) under N_2 . Anhydrous $\text{ClCH}_2\text{CH}_2\text{Cl}$ (5 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **3a** (69.8 mg, 0.30 mmol) and **2** (90.0 mg, 0.45 mmol), the reaction flask was kept at 80 °C for 48 h. The solvent was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (50% AcOEt/Hexane) to yield 114.3 mg (0.27 mmol, 92%) of 1-methyl-4-phenyl-2-diphenylphosphinylnaphthalene (**4a**) as white crystals (mp 112.1-112.9 °C). ^1H NMR δ 2.89 (s, 3H), 7.01-7.89 (m, 20H). ^{31}P NMR δ 29.3 (s). Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{O}_{1.5}\text{P}$: C, 81.48; H, 5.66. Found: C, 81.53; H 5.73.

The reactions of propargylic alcohol (**3a**) with diphenylphosphine oxide (**2**) catalyzed by diruthenium complex were investigated under various reaction conditions. Typical results are shown in Table S1. The reaction of **3a** with 1.5 equiv. of **2** in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (5 mL) at 80 °C for 48 h proceeded to give **4a** in the highest yield of 92% (run 7).

Table S1. Reactions of Propargylic Alcohol (**3a**) with Diphenylphosphine Oxide (**2**) Catalyzed by Diruthenium Complexes (**1a**).^a

Reaction scheme: Propargylic alcohol **3a** (1-phenyl-2-phenyl-3-propyn-1-ol) reacts with diphenylphosphine oxide **2** (5 equiv) in the presence of 5 mol% **1a** and 10 mol% NH_4BF_4 in a solvent to yield product **4a** (7-methyl-1-methyl-4-(4-methylphenyl)-2-diphenylphosphinylnaphthalene).

run	solvent	temperature (°C)	time (h)	yield (%) ^b
1	THF	60	24	25
2	toluene	60	24	43
3	$\text{ClCH}_2\text{CH}_2\text{Cl}$	60	24	71
4	$\text{ClCH}_2\text{CH}_2\text{Cl}$	80	24	77
5	$\text{ClCH}_2\text{CH}_2\text{Cl}$	80	48	82
6	$\text{ClCH}_2\text{CH}_2\text{Cl}$	80	72	83
7 ^c	$\text{ClCH}_2\text{CH}_2\text{Cl}$	80	48	92

^a All the reactions of propargylic alcohol (**3a**) (0.30 mmol) with diphenylphosphine oxide (**2**) (1.50 mmol) were carried out in the presence of **1a** (0.015 mmol) and NH_4BF_4 (0.03 mmol) in solvent (5 mL). ^b Isolated yield. ^c 0.45 mmol of **2** was used.

Spectroscopic data and isolated yield of other products are as follows.

7-Fluoro-1-methyl-4-(4-fluorophenyl)-2-diphenylphosphinylnaphthalene (4b). Yield 94%. White crystals, mp 182.0-182.8 °C. ^1H NMR δ 2.94 (s, 3H), 7.12-8.20 (m, 18H). ^{31}P NMR δ 29.8 (s). Anal. Calcd for $\text{C}_{29}\text{H}_{21}\text{F}_2\text{OP}$: C, 76.64; H, 4.66. Found: C, 76.71; H 4.62.

7-Chloro-1-methyl-4-(4-chlorophenyl)-2-diphenylphosphinylnaphthalene (4c). Yield 89%. White crystals, mp 197.5-198.1 °C. ^1H NMR δ 2.88 (s, 3H), 7.04-8.18 (m, 18H). ^{31}P NMR δ 29.2 (s). Anal. Calcd for $\text{C}_{29}\text{H}_{21}\text{Cl}_2\text{OP}$: C, 71.47; H, 4.34. Found: C, 71.20; H 4.13.

7-Methyl-1-methyl-4-(4-methylphenyl)-2-diphenylphosphinylnaphthalene (4d). Yield 85%. White crystals, mp 160.3-160.8 °C. ^1H NMR δ 2.36 (s, 3H), 2.52 (s, 3H), 2.91 (s, 3H), 7.00-7.96 (m, 18H). ^{31}P NMR δ 30.0 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{27}\text{OP}$: C, 83.39; H, 6.09. Found: C, 83.41; H 6.18.

7-Methoxy-1-methyl-4-(4-methoxyphenyl)-2-diphenylphosphinylnaphthalene (4e).

Yield 88%. White crystals, mp 146.7-147.1 °C. ^1H NMR δ 2.88 (s, 3H), 3.84 (s, 3H), 3.95 (s, 3H), 6.91-7.87 (m, 18H). ^{31}P NMR δ 30.1 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{27}\text{O}_3\text{P}$: C, 77.81; H, 5.69. Found: C, 77.79; H 5.63.

3-Methyl-2-diphenylphosphinylfluoranthene (4f). Yield 22%. Yellow crystals, mp 218.1-218.7 °C. ^1H NMR δ 2.95 (s, 3H), 7.24-8.07 (m, 18H). ^{31}P NMR δ 30.4 (s). HRMS: Calcd for $\text{C}_{29}\text{H}_{21}\text{OP}$ [M] 416.1330, found 416.1329.

Reaction of 1-(2-Phenylphenyl)-2-propyn-1-ol (6) with Diphenylphosphine Oxide. In a 20 mL flask were placed **1a** (19.1 mg, 0.03 mmol) and NH_4BF_4 (6.3 mg, 0.06 mmol) under N_2 . Anhydrous $\text{ClCH}_2\text{CH}_2\text{Cl}$ (10 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **6** (125.0 mg, 0.60 mmol) and **2** (606.6 mg, 3.00 mmol), the reaction flask was kept at 60 °C for 24 h. The solvent was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (50% AcOEt/Hexane) to yield 207.3 mg (0.53 mmol, 89%) of 3-(2-phenylphenyl)-3-diphenylphosphinyl-1-propyne (**7**) as white crystals (mp 134.6-135.5 °C). ^1H NMR δ 2.27 (dd, 1H, J = 2.8 and 5.6 Hz), 4.85 (dd, 1H, J = 2.8 and 13.8 Hz), 7.07-7.92 (m, 19H). ^{31}P NMR δ 33.4 (s). HRMS: Calcd for $\text{C}_{27}\text{H}_{21}\text{OP}$ [M] 392.1333, found 392.1330.

Reduction of Phosphine Oxide (4a). In a 20 mL flask was placed **4a** (167.2 mg, 0.40 mmol) under N_2 . Anhydrous benzene (6 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of $\text{Ti}(\text{O}^i\text{Pr})_4$ (35.2 mg, 0.12 mmol) and $(\text{EtO})_3\text{SiH}$ (200 μL , 1.2 mmol), the reaction flask was stirred for 30 min under reflux. After cooling to room temperature, the solvent was concentrated in vacuo. The residue was purified by silica gel column chromatography (5% AcOEt/Hexane) to yield 145.5 mg (0.36 mmol, 90%) of 1-methyl-4-phenyl-2-diphenylphosphinonaphthalene (**9**) as white crystals (mp 100.5-110.1 °C). ^1H NMR δ 2.95 (s, 3H), 6.95 (d, 1H, J = 3.6 Hz), 7.28-7.58 (m, 17H), 7.90 (d, 1H, J = 8.4 Hz), 8.16

(d, 1H, $J = 8.4$ Hz). ^{31}P NMR δ -15.3 (s). HRMS: Calcd for $\text{C}_{29}\text{H}_{23}\text{P}$ [M] 402.1533, found 402.1537.

Bromination of 4a with NBS. In a 20 mL flask was placed **4a** (118.9 mg, 0.28 mmol) under N_2 . Anhydrous CCl_4 (4 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of NBS (*N*-bromosuccinimide) (55.2 mg, 0.31 mmol) and dibenzoyl peroxide (3.2 mg, 0.013 mmol), the reaction flask was stirred for 3 h under reflux. After cooling to room temperature, the solvent was concentrated in vacuo. The residue was purified by silica gel column chromatography (50% AcOEt/Hexane) to yield 120.8 mg (0.24 mmol, 86%) of 1-bromomethyl-4-phenyl-2-diphenylphosphinylnaphthalene (**10**) as white crystals (mp 102.3-102.8 °C). ^1H NMR δ 5.74 (s, 2H), 6.85-8.02 (m, 20H). ^{31}P NMR δ 30.3 (s). HRMS: Calcd for $\text{C}_{29}\text{H}_{23}\text{OBrP}$ [MH^+] 497.0669, found 497.0670.

Preparation of 11 with NaOEt. In a 20 mL flask was placed **10** (46.5 mg, 0.093 mmol) under N_2 . Anhydrous EtOH (2 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of 2 mol/L NaOEt in EtOH (0.08 mL, 0.16 mmol), the reaction flask was stirred for 3 h under reflux. After cooling to room temperature, the reaction mixture was treated with 1 *N* HCl aq (2 mL) and then extracted with diethyl ether (20 mL $\times$ 3). The ether layer was washed with a saturated aqueous NaHCO_3 (20 mL $\times$ 1) and dried over anhydrous MgSO_4 . For isolation, the extract was concentrated in vacuo. The residue was purified by silica gel column chromatography (50% AcOEt/Hexane) to yield 33.7 mg (0.073 mmol, 78%) of 1-ethoxymethyl-4-phenyl-2-diphenylphosphinylnaphthalene (**11**) as white crystals (mp 125.2-125.8 °C). ^1H NMR δ 0.96 (t, 3H, $J = 7.1$ Hz), 3.19 (q, 2H, $J = 7.1$ Hz), 5.27 (s, 2H), 7.13-8.38 (m, 20H). ^{31}P NMR δ 29.4 (s). HRMS: Calcd for $\text{C}_{31}\text{H}_{27}\text{O}_2\text{P}$ [M] 462.1749, found 462.1755.

X-ray Crystallographic Studies of 4a·(H₂O)_{0.5}. Colorless crystals of 4a·(H₂O)_{0.5} suitable for X-ray analysis were obtained by recrystallization from CH₂Cl₂/*n*-hexane. A single crystal was sealed in a Pyrex glass capillary under N₂ atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation. Details of crystal and data collection parameters are summarized in Table S2. The positions of nonhydrogen atoms were determined by direct methods (SIR92) and subsequent Fourier syntheses (DIRDIF99). An ORTEP drawing of 4a·(H₂O)_{0.5} is shown in Figure S1.

Table S2. Crystallographic Data for 4a·(H₂O)_{0.5}.

formula	C ₂₉ H ₂₄ O _{1.50} P
formula weigh	427.48
cryst size (mm ³)	0.70 × 0.60 × 0.40
cryst system	monoclinic
space group	C2/c (#15)
cryst color	white
<i>a</i> (Å)	22.652(8)
<i>b</i> (Å)	10.982(4)
<i>c</i> (Å)	18.713(4)
β (°)	95.607(11)
<i>V</i> (Å ³)	4632.8(26)
<i>Z</i>	8
<i>d</i> _{calc} (g cm ⁻³)	1.226
<i>F</i> (000)	1800.00
μ _{calc} (cm ⁻¹)	1.393
no. of unique data	5288
no. of data used	3122
no. of params refined	381
<i>R</i> ^a (all reflections)	0.0595
<i>R</i> _w ^b (all reflections)	0.0581

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$$

Figure S1. Crystal structure of **4a**·(H₂O)_{0.5}.