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Photochemical behaviors of tetraphenyldiphosphine in the presence of alkynes

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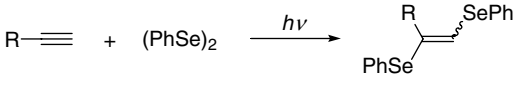
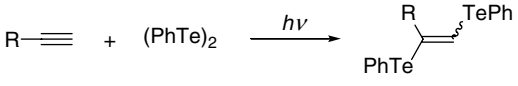
Abstract—Under an atmosphere of nitrogen, the photoinduced reaction of tetraphenyldiphosphine (**1**) with alkynes (**2**) generates vicinal bisphosphinated alkenes (**3**) as air-sensitive compounds, which can be isolated by treatment with elemental sulfur. A novel *E* to *Z* isomerization of **3** is revealed to take place upon continuous photoirradiation.

Radical addition of heteroatom compounds to carbon–carbon unsaturated bonds based on the photoinduced homolytic cleavage of heteroatom–heteroatom single bonds is one of the most useful and highly atom-economical methods for selective introduction of heteroatom functions into organic molecules.[1] Recently, we have disclosed novel photoinduced bisselenation[2] and bistelluration[3] of alkynes with organic diselenides and ditellurides, which provide a useful tool to vicinal bisseleno- and bistelluroalkenes, respectively (Eqs. 1 and 2).



(1)



(2)

However, similar transformations concerning group 15 heteroatom compounds have been largely unexplored.[4,5] In this letter, we wish to report detailed experiments, which have been done to develop the photoinduced bisphosphination of alkynes by using tetraphenyldiphosphine as the representative heteroatom compounds bearing a group 15 heteroatom–heteroatom linkage.[6]

Tetraphenyldiphosphine (Ph_2P–PPh_2, **1**)[5] is a commercially available white solid (mp 120–122 °C) and is stable in the solid state. However, in solvent, **1** is extremely air-sensitive, generating immediately several oxidation products, which can be assigned unambiguously by measurement of their ^{31}P NMR spectra.[7] The use of degassed solvent is effective for depressing the undesirable air-oxidation of diphosphine **1** (ca. 70% of **1** is survived by this treatment, see Chart 1[7,8]), and makes it possible to study the reactions of **1**.

Tetraphenyldiphosphine (**1**) exhibits its absorption maximum in 260 nm ($\varepsilon = 41.3$), and its absorption reaches to 330 nm.[9] Therefore, the irradiation with the light of the wavelength in these regions (e.g., near-UV light irradiation) induces the homolytic cleavage of the P–P single

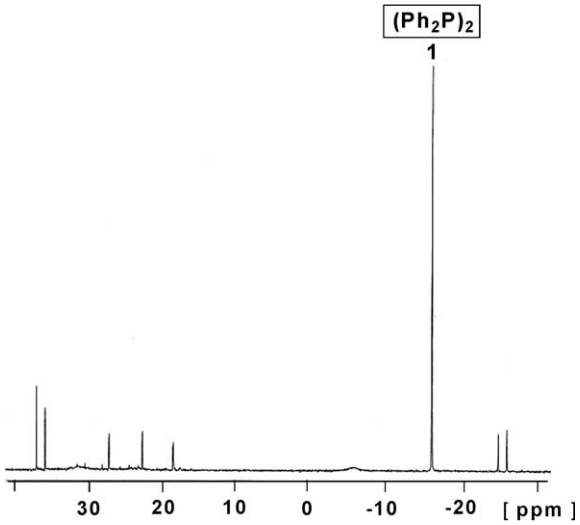


Chart 1. ^{31}P NMR spectrum of $(Ph_2P)_2$ in degassed $CDCl_3$.

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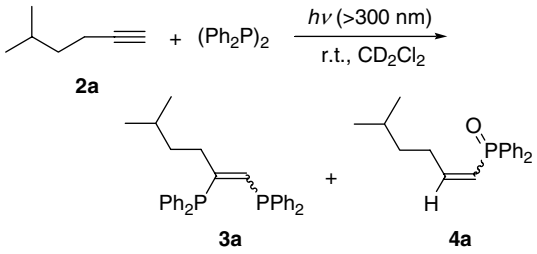
bond of **1** to generate the corresponding phosphorus-centered radical as a label species.[10,11] However, both the extremely high air-sensitivity of **1** and its lower solubility in organic solvents may contribute to the difficulty in realizing the radical addition of **1** to carbon–carbon unsaturated compounds.

To accomplish the desired radical addition of diphosphine **1** to terminal alkynes, the reaction was conducted in an NMR tube sealed carefully under nitrogen atmosphere by using degassed solvent. In an NMR tube ($\phi = 4$ mm, Pyrex) filled with nitrogen, were placed tetraphenyldiphosphine (0.132 mmol, stored in Schlenck tube under nitrogen), 5-methyl-1-hexyne (**2a**, 0.044 mmol), and CD_2Cl_2 (0.6 mL, degassed), and then the tube was sealed. Irradiation with a xenon lamp (500 W) was conducted at room temperature, and the reaction was monitored by ^1H and ^{31}P NMR using triphenylmethane as an internal standard for ^1H NMR.



(3)

	3a	4a
2 h	21% [*E*/*Z* = 81/19]	13% [*E*/*Z* = 38/62]
4 h	37% [*E*/*Z* = 73/27]	23% [*E*/*Z* = 39/61]
20 h	51% [*E*/*Z* = 29/71]	24% [*E*/*Z* = 37/63]
27 h	63% [*E*/*Z* = 24/76]	28% [*E*/*Z* = 43/57]
39 h	62% [*E*/*Z* = 18/82]	31% [*E*/*Z* = 55/45]

As can be seen from Eq. 3, the photoinduced reaction of diphosphine **1** with 5-methyl-1-hexyne (**2a**) provided the corresponding bisphosphination product (**3a**) as the major product, along with small amounts of hydrophosphinylation product (**4a**). The yield of **3a** increased with the reaction times. On the other hand, the hydrophosphinylation product (**4a**) was formed within 4 h, most probably by the reaction of **2a** with initially formed diphenylphosphine oxide ($Ph_2P(O)H$).[12]

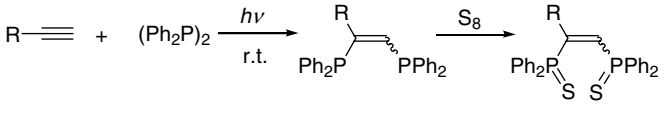
Noteworthy is that isomerization from (*E*)-**3a** to (*Z*)-**3a** was observed to take place gradually: After the irradiation for 39 h, (*Z*)-**3a** was obtained mainly (*E*/*Z* = 18/82). These results clearly indicate that the present photoinduced bisphosphination is promising as a useful tool to (*Z*)-isomers of *vic*-bis(diphenylphosphino)alkenes. The stereochemistry of **3a** can be easily determined by measurement of ^{31}P NMR: The coupling constant for (*E*)-**3a** ($J_{P-P} = 340$ Hz) is larger than that of (*Z*)-isomer ($J_{P-P} = 161$ Hz).

Similar conditions can be employed with 1-octyne (**2b**) and 5-chloro-1-pentyne (**2c**) (Table 1, entries 2–3). In these cases, the *Z* selectivity in the bisphosphination also increased with the prolonged photoirradiation. On the other hand, the bisphosphination of phenylacetylene proceeded very smoothly and provided only (*Z*)-isomer selectively (entry 4).[13]

Isolation of the bisphosphination product **3** was attempted by using preparative HPLC. However, the desired isolation of **3** failed, owing to the instability of **3** toward air. Thus, this letter deals with only spectral analyses of the bisphosphination products.[14] Since the direct isolation of the bisphosphination product **3** is very difficult, the isolation was examined by the treatment of the bisphosphination product **3** with elemental sulfur. Purification by preparative TLC provided **5** in good yields, as shown in Table 1[15].

A possible reaction pathway for the formation of bisphosphination product **3** is as follows (Scheme 1). Upon irradiation with near-UV light, tetraphenyldiphosphine

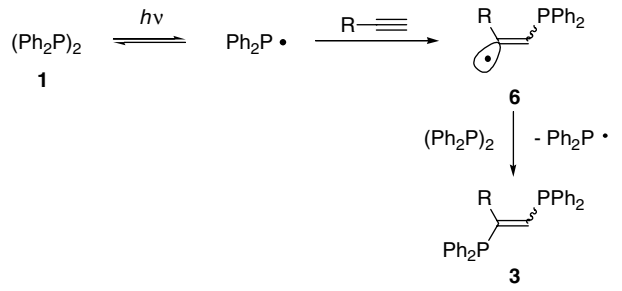
Table 1. Photoinduced bisphosphination of alkynes



2 **3** **5**

Entry	Alkyne	Solv.	Time (h)	Yield (%) [*E*/*Z*][a]	
				3	**5**
1	**2a**	CD_2Cl_2	39	62 [18/82]	54 [23/77]
2	^{n}Hex— **2b**	C_6D_6	26	68 [35/65]	53 [34/66]
3	Cl(CH$_2$)$_3$— **2c**	CD_2Cl_2	18	55 [42/58]	53 [53/47]
4	Ph— **2d**	CD_2Cl_2	1	45 [0/100]	46 [50/50]

[a] One unidentified product (R–CH_2=CH–P(O)Ph_2, **4**) was also obtained as byproduct: 31% [*E*/*Z* = 55/45] (**4a**, entry 1); 24% [*E*/*Z* = 50/50] (**4b**, entry 2); 18% [*E*/*Z* = 67/33] (**4c**, entry 3); 8% [*E*/*Z* = 25/75] (**4d**, entry 4).



Scheme 1. A possible pathway for bisphosphination.

1 undergoes homolytic dissociation to generate $Ph_2P^{\bullet}$, which attacks the terminal carbon of terminal alkynes to give the corresponding β-diphenylphosphino-substituted vinylic radical (**6**). The subsequent S_H2 reaction between the vinylic radical and the diphosphine **1** provides the bisphosphination product **3**.

On the other hand, the formation of **4** can be explained by the addition to terminal alkynes, of diphenylphosphine oxide, which is formed at the initial stage from $(Ph_2P)_2$ and water (contaminated). This was strongly supported by the fact that the reaction of $(Ph_2P)_2$ with D_2O led to the formation of Ph_2PD and $Ph_2P(O)D$ upon photoirradiation.[16] Furthermore, the formation of diphenylphosphine oxide was clearly accelerated in the presence of terminal alkynes, and this fact suggests that acetylenic proton can also be employed as a proton source for diphenylphosphine oxide.

In summary, we have disclosed the reactivity of tetraphenyldiphosphine upon photoirradiation conditions. Detailed mechanism of hydrophosphination and its synthetic utility are now under investigation.

Acknowledgment

We gratefully acknowledge Professor L.-B. Han (National Institute of Advanced Industrial Science and Technology (AIST)) for his useful suggestions.

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6. Our preliminary results of this photoinduced bisphosphination were presented at the 1st Pacific Symposium on Radical Chemistry (PSRC-1, November 15, 2004, Kanazawa, Japan).
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8. Integral condition: Relaxation delay is 1 [s], acquisition time is 0.2312 [s]. Ratio of integral value is $(Ph_2P)_2$:$Ph_2PP(O)$-Ph_2:$Ph_2P(O)P(O)Ph_2$:$Ph_2P(O)OP(O)Ph_2$:$Ph_2P(O)H$ = 70:8:5:7:10.
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11. In $CDCl_3$, diphosphine **1** was gradually decomposed to form chlorodiphenylphosphine (Ph_2PCl; ^{31}P NMR δ 82.38 ppm; Appel, R.; Milker, R. *Chem. Ber.* **1975**, *108*, 1783.) upon irradiation through Pyrex with a xenon lamp, whereas no conversion of **1** to Ph_2PCl was observed in CD_2Cl_2 and benzene. Thus, CD_2Cl_2 and benzene are suitable solvents for the reactions conducted under photo-irradiation conditions.
12. Semenzin, D.; Etemad-mogha, G.; Albouy, D.; Diallo, O.; Koenig, M. *J. Org. Chem.* **1997**, *62*, 2414.
13. The exclusive *Z* selectivity observed in the bisphosphination of phenylacetylene may arise from the interaction between the alkyne and diphosphine in the ground or excited state.
14. ^{31}P NMR (CD_2Cl_2), **3a**: For (*E*)-isomer, δ −30.1 ppm (d, $J = 418$ Hz), −14.35 ppm (d, $J = 426$ Hz); For (*Z*)-isomer, δ −25.20 ppm (d, $J = 161$ Hz), −6.02 ppm (d, $J = 157$ Hz). Compound **3b**: For (*E*)-isomer, δ −29.85 ppm (d, $J = 300$ Hz), −13.55 ppm (d, $J = 300$ Hz); For (*Z*)-isomer, δ −24.50 ppm (d, $J = 157$ Hz), −5.90 ppm (d, $J = 161$ Hz). Compound **3c**: For (*E*)-isomer, δ −30.3 ppm (d, $J = 444$ Hz), −14.35 ppm (d, $J = 422$ Hz); For (*Z*)-isomer, δ −24.80 ppm (d, $J = 161$ Hz), −6.75 ppm (d, $J = 157$ Hz). Compound **3d**: δ −24.55 ppm (d, $J = 144$ Hz), −3.51 ppm (d, $J = 144$ Hz).
15. Compound **5a**: [(*Z*)-isomer] ^1H NMR ($CDCl_3$) δ 0.70 (d, $J = 6.4$ Hz, 6H), 1.19–1.47 (m, 3H), 2.34–2.39 (m, 2H), 6.96 (dd, $J = 41.7$, 12.4 Hz, 1H), 7.24–7.76 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 22.18, 27.86, 37.82, 39.75, 128.22, 128.32, 131.27 (d, $J = 17.2$ Hz), 131.27 (d, $J = 4.7$ Hz), 131.34 (d, $J = 83.7$ Hz), 132.37 (d, $J = 16.3$ Hz), 132.37 (d, $J = 5.7$ Hz), 133.59 (d, $J = 87.3$ Hz), 134.88 (ddd, $J = 82.5$, 12.5, 11.5 Hz), 152.46 (d, $J = 65.2$ Hz); ^{31}P NMR ($CDCl_3$) δ 32.11 (d, $J = 17.4$ Hz), 42.28 (d, $J = 17.4$ Hz); IR (NaCl, neat) 2952, 1436, 1097, 705, 692, 642 cm^{-1}; HRMS calcd for $C_{31}H_{32}P_2S_2$: 530.1421, found: 530.1418; Anal. Calcd for $C_{31}H_{32}P_2S_2$: C, 70.16; H, 6.08%. Found: C, 69.96; H, 6.04%. [(*E*)-isomer] ^1H NMR ($CDCl_3$) δ 0.46 (d, $J = 5.0$ Hz, 6H), 0.99–1.07 (m, 2H), 1.19–1.22 (m, 1H), 2.69–2.73 (m, 2H), 7.34 (dd, $J = 27.0$, 20.2 Hz, 1H), 7.40–7.84 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 21.75, 28.37, 29.05, 37.56, 128.62 (d, $J = 9.5$ Hz), 128.70 (d, $J = 9.5$ Hz), 131.04 (d, $J = 7.6$ Hz), 131.34 (d, $J = 83.4$ Hz), 131.54, 131.87, 132.26 (d, $J = 9.5$ Hz), 133.73 (d, $J = 85.4$ Hz), 136.36 (dt, $J = 72.9$, 9.6 Hz), 156.71 (d, $J = 60.4$ Hz); ^{31}P NMR ($CDCl_3$) δ 28.60 (d, $J = 61.0$ Hz), 49.55 (d, $J = 61.0$ Hz); IR (NaCl, neat) 2954, 2358, 2341, 1436, 1099, 715, 692 cm^{-1}; **5b**: [(*Z*)-isomer] ^1H NMR ($CDCl_3$) δ 0.80 (t, $J = 7.3$ Hz, 3H), 1.21–1.23 (m, 6H), 1.54–1.60 (m, 2H), 2.34–2.41 (m, 2H), 6.94 (dd, $J = 41.7$, 12.7 Hz, 1H), 7.22–7.32 (m, 8H), 7.33–7.38 (m, 4H), 7.66–7.77 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.88, 22.37, 28.67, 30.57, 31.23, 39.65, 128.09 (d, $J = 12.5$ Hz), 128.32 (d, $J = 12.5$ Hz), 131.12 (d, $J = 16.3$ Hz), 131.12 (d, $J = 4.8$ Hz), 131.26 (d, $J = 83.5$ Hz), 132.28 (d, $J = 15.6$ Hz), 132.28 (d, $J = 5.7$ Hz), 133.59 (d, $J = 86.3$ Hz), 134.65 (ddd, $J = 81.5$, 9.6, 7.7 Hz), 152.20 (d, $J = 68.1$ Hz);^{31}P NMR ($CDCl_3$) δ 31.90 (d, $J = 17.4$ Hz), 42.28 (d, $J = 17.4$ Hz); IR (NaC1, neat) 2925, 1436, 1098, 693, 643 cm^{-1}; HRMS calcd for $C_{32}H_{34}P_2S_2$: 544.1577, found: 544.1573; Anal. Calcd for $C_{32}H_{34}P_2S_2$: C, 70.56; H, 6.29%. Found: C, 70.36; H, 6.27%. [(*E*)-isomer] ^1H NMR ($CDCl_3$) δ 0.71 (t, $J = 7.3$ Hz, 3H), 0.81–0.82 (m, 4H), 0.88–0.90 (m, 2H), 0.96–1.00 (m, 2H), 2.67–2.75 (m, 2H), 7.24 (dd, $J = 27.1$, 20.0 Hz, 1H), 7.39–7.50 (m, 10H), 7.51–7.53 (m, 2H), 7.75–7.81 (m, 8H); ^{13}C NMR ($CDC1_3$) δ 13.77, 13.87, 22.15, 29.20, 29.30, 30.85, 128.53 (d, $J = 14.4$ Hz), 128.64 (d, $J = 14.4$ Hz), 130.92, 130.96 (d, $J = 10.6$ Hz), 131.19 (d, $J = 83.4$ Hz), 132.12 (d, $J = 10.6$ Hz), 132.23, 133.66 (d, $J = 85.4$ Hz), 135.93 (ddd, $J = 72.9$, 19.2, 8.6 Hz), 156.38 (d, $J = 59.5$ Hz); ^{31}P NMR ($CDC1_3$) δ 28.66 (d, $J = 56.7$ Hz), 49.58 (d, $J = 61.0$ Hz); IR (NaCl, neat) 3054, 2926, 2854, 1435, 1100, 717, 692, 629, 614, 527 cm^{-1}. Compound **5c**: [(*Z*)-isomer] ^1H NMR ($CDCl_3$) δ 2.02–2.07 (m, 2H), 2.54–2.60 (m, 2H), 3.45 (t, $J = 6.5$ Hz, 2H), 7.00 (dd, $J = 41.1$, 12.8 Hz, 1H), 7.23–7.27 (m, 4H), 7.29–7.33 (m, 4H), 7.35–7.39 (m, 4H), 7.64–7.69 (m, 4H), 7.73–7.78 (m, 4H); ^{13}C NMR ($CDC1_3$) δ 33.67, 37.47 (t like, $J = 5.8$ Hz), 43.84, 128.4 (d, $J = 11.5$ Hz), 128.5 (d, $J = 11.5$ Hz), 130.91 (d, $J = 83.5$ Hz), 131.02 (d, $J = 15.4$ Hz), 131.02 (d, $J = 4.6$ Hz), 132.36 (d, $J = 15.4$ Hz), 132.37 (d, $J = 6.7$ Hz), 133.37 (d, $J = 87.5$ Hz), 136.10 (ddd, $J = 79.6$, 10.6, 6.7 Hz), 150.47 (d, $J = 69.2$ Hz); ^{31}P NMR ($CDC1_3$) δ 31.62 (d, $J = 17.4$ Hz), 42.13 (d, $J = 17.4$ Hz); IR (NaCl, neat) 3053, 1436, 1100, 910, 799, 692, 671, 613 cm^{-1}; HRMS calcd for $C_{29}H_{27}ClP_2S_2$: 536.0718, found: 536.0714. Anal. Calcd for $C_{29}H_{27}ClP_2S_2$: C, 64.86; H, 5.07%. Found: C, 63.99; H, 5.09%. [(*E*)-isomer] ^1H NMR ($CDC1_3$) δ 1.43–1.49 (m, 2H), 2.83–2.93 (m, 2H), 3.11 (t,$J = 6.7$ Hz, 2H), 7.33 (dd, $J = 25.4$, 6.4 Hz, 1H), 7.42–7.50 (m, 10H), 7.53–7.56 (m, 2H), 7.74–7.80 (m, 8H); ^{13}C NMR ($CDC1_3$) δ 28.16 (t, $J = 8.6$ Hz), 31.97, 44.37 (t, $J = 7.7$ Hz), 128.83 (d, $J = 12.5$ Hz), 128.86 (d, $J = 12.5$ Hz), 130.78 (d, $J = 83.4$ Hz), 130.98 (d, $J = 10.5$ Hz), 131.79, 132.12, 132.22 (d, $J = 7.7$ Hz), 133.44 (d, $J = 85.4$ Hz), 137.14 (dt, $J = 71.9$, 8.6 Hz), 154.88 (d, $J = 60.4$ Hz); ^{31}P NMR ($CDC1_3$) δ 28.42 (d, $J = 56.7$ Hz), 49.57 (d, $J = 56.7$ Hz); IR (NaCl, neat) 3053, 2330, 1437, 1099, 716, 691, 631, 613, 525, 496 cm^{-1}. Compound **5d**: [(*Z*)-isomer] ^1H NMR ($CDCl_3$) δ 7.10 (dd, $J = 26.1$, 12.4 Hz, 1H), 7.06–7.40 (m, 17H), 7.61–7.78 (m, 8H); ^{13}C NMR ($CDC1_3$) δ 127.96, 128.04, 128.19 (d, $J = 11.5$ Hz), 130.92 (d, $J = 7.7$ Hz), 131.11 (d, $J = 3.0$ Hz), 131.57 (d, $J = 15.3$ Hz), 131.57 (d, $J = 5.7$ Hz), 131.76 (d, $J = 85.4$ Hz), 131.95 (d, $J = 17.2$ Hz), 131.95 (d, $J = 3.8$ Hz), 132.69 (d, $J = 87.3$ Hz), 138.98 (ddd, $J = 74.8$, 11.5, 10.5 Hz), 141.89 (dd, $J = 16.3$, 10.5 Hz), 150.78 (d, $J = 69.0$ Hz); ^{31}P NMR ($CDCl_3$) δ 32.74 (d, $J = 13.0$ Hz), 38.38 (d, $J = 13.0$ Hz); IR (neat) 3053, 1436, 1097, 738, 717, 694, 644, 516 cm^{-1}; HRMS calcd for $C_{32}H_{26}P_2S_2$: 536.0951, found: 536.0955. Anal. Calcd for $C_{32}H_{26}P_2S_2$: C, 71.62; H, 4.88%. Found: C, 71.86; H, 5.12%.
16. (a) Yasui, S.; Shioji, K.; Yoshihara, M.; Maeshita, T.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2077; (b) Renard, P.-Y.; Vayron, P.; Leclerc, E.; Valleix, A.; Miskowski, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2389.