

## Thermal and Photocontrol of the Equilibrium between a 2-Phosphinoazobenzene and an Inner Phosphonium Salt

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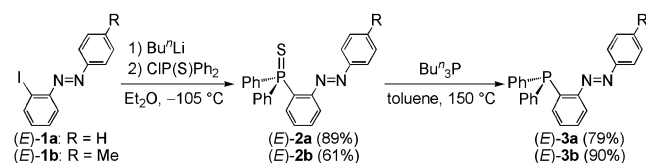
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Tertiary phosphines usually serve as soft bases and play an important role in catalytic reactions as ligands for transition metals. Quaternary phosphonium salts are involved as intermediates in many reactions, such as the Arbuzov reaction,<sup>1</sup> the Mitsunobu reaction,<sup>2</sup> and reactions with the Appel reagent.<sup>3</sup> Many phosphonium salts have been synthesized by a nucleophilic attack of tertiary phosphines on electrophiles, such as alkyl halides and activated double bonds.<sup>4</sup> If the reversible conversion between a phosphine and a phosphonium salt is possible by external stimuli, such as light and heat, the spectral properties and reactivity of each phosphorus compound can be controlled without addition of an external reagent. We previously reported the synthesis of 2-silylazobenzene derivatives and the control of both the coordination number of silicon and the reactivity of the compound by photoisomerization of the azo group.<sup>5</sup> In these cases, an azo group and a silicon atom operate as a nucleophile and an electrophile, respectively. A phosphine bearing a double bond, such as an azo group, in the vicinity of the phosphorus atom is expected to produce a phosphonium salt generated from an azo group as an electrophile and a phosphine as a nucleophile and to be controlled by photoisomerization.<sup>6</sup> We report here the synthesis of 2-phosphinoazobenzenes and their equilibrium with an inner phosphonium salt, as well as the photocontrol of the character as a phosphonium salt.

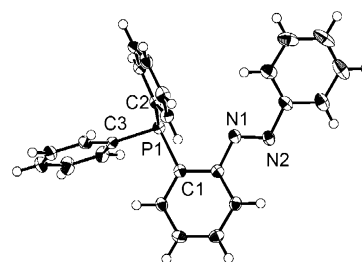
Successive treatment of 2-iodoazobenzenes<sup>7</sup> (*E*)-**1a** and (*E*)-**1b** with butyllithium (1 equiv) and diphenylthiophosphinoyl chloride (1 equiv) in Et<sub>2</sub>O at -105 °C gave phosphine sulfides (*E*)-**2a** (89%) and (*E*)-**2b** (61%), respectively (Scheme 1). Desulfurization of (*E*)-

## Scheme 1

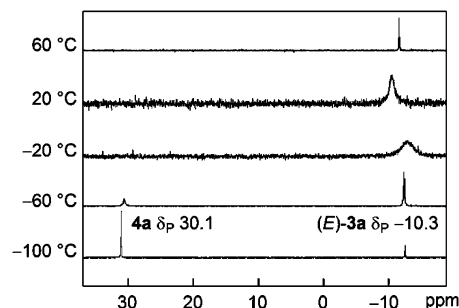


**2a** and (*E*)-**2b** with tributylphosphine (1 equiv) in toluene at 100 °C in a sealed tube and successive recrystallization from toluene/hexane gave red crystals of 2-(diphenylphosphino)azobenzenes (*E*)-**3a** (79%) and (*E*)-**3b** (90%), respectively. X-ray crystallographic analysis of triarylphosphine (*E*)-**3a** revealed that the bond angles (100.30–102.44°) around the phosphorus atom of (*E*)-**3a** were slightly smaller than those in triphenylphosphine (103°) (Figure 1).<sup>8,9</sup> The N=N bond length (1.263(2) Å) is almost as long as that in unsubstituted azobenzene (1.247 Å).<sup>10</sup> These results show no interaction between the phosphorus atom and the azo group in the crystalline state.

In the <sup>31</sup>P NMR spectra of (*E*)-**3a** in toluene-*d*<sub>8</sub>, only one singlet ( $\delta_P$  -9.2) was observed above 60 °C, while the signal was broadened between 20 and -60 °C and split into two singlets ( $\delta_P$



**Figure 1.** ORTEP drawing of (*E*)-**3a** with thermal ellipsoid plot (50% probability). Selected bond lengths (Å) and bond angles (deg) for (*E*)-**3a**: P1–C1, 1.844(2); P1–C2, 1.838(2); P1–C3, 1.842(2); N1–N2, 1.263(2); C1–P1–C2, 102.44(7); C1–P1–C3, 100.30(7); C2–P1–C3, 101.43(8).



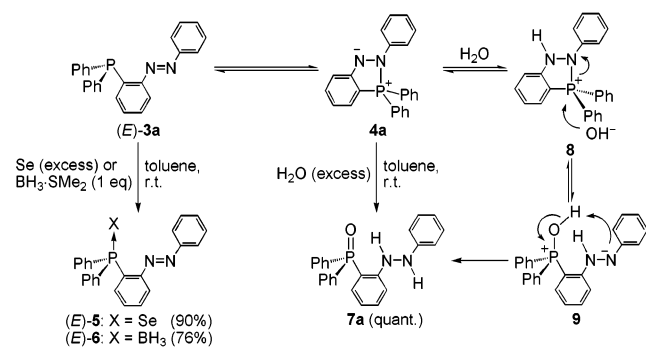
**Figure 2.** VT <sup>31</sup>P NMR spectra of (*E*)-**3a** and **4a** in toluene-*d*<sub>8</sub> solution.

-10.3 and 30.1) at -100 °C (Figure 2). The signal at high field ( $\delta_P$  -10.3), whose chemical shift is close to that of diphenyl[2-(phenylimino)phenyl]phosphine<sup>11</sup> ( $\delta_P$  -13.0), is assigned to the triarylphosphine (*E*)-**3a**. The signal at low field ( $\delta_P$  30.1) is reasonably assigned to the inner phosphonium salt **4a**, considering that the chemical shift of **4a** was calculated to be  $\delta_P$  27.2 by a gauge-including atomic orbital calculation at the B3LYP/6-31G-(d,p)//B3LYP/6-31G(d,p) level.<sup>12,13</sup> The phosphonium salt **4a** is considered to be formed by intramolecular nucleophilic attack of the phosphorus atom on the azo group in (*E*)-**3a**, and (*E*)-**3a** and **4a** are in equilibrium in solution. A van't Hoff plot for equilibrium constants calculated from the ratio of **4a** to (*E*)-**3a** at each temperature gave a good linear relationship, proving an equilibrium system between the two species (*E*)-**3a** and **4a**.<sup>14</sup> van't Hoff plots can be used to derive enthalpy and entropy changes for the [**4a**]/[(*E*)-**3a**] equilibrium. The enthalpy change in toluene ( $\Delta H^\circ$  = -17.3  $\pm$  0.3 kJ/mol) and in THF ( $\Delta H^\circ$  = -16.2  $\pm$  0.3 kJ/mol) are almost the same, while the entropy change in toluene ( $\Delta S^\circ$  = -88  $\pm$  2 J/mol·K) is much more negative than that in THF ( $\Delta S^\circ$  = -76  $\pm$  1 J/mol·K). The ratio of **4a** to (*E*)-**3a** in toluene (equilibrium constant:  $K_{eq}$  = 4.00 at -100 °C) is lower than that in THF ( $K_{eq}$  = 8.52 at -100 °C) because zwitterion **4a**, which has a large dipole moment, orders the nonpolar solvent, toluene, much more than the polar solvent, THF.<sup>15</sup>

Thermochromism was observed in solution, reflecting the thermal change of the equilibrium ratio. The toluene solution showed a red color at 100 °C based on the azobenzene unit of (*E*)-**3a** and black color at −78 °C, which was ascribed to the charge transfer excitation of the zwitterion **4a**. In the UV–vis spectra of (*E*)-**3a**, the absorption maximum at 320 nm is assigned to the  $\pi \rightarrow \pi^*$  transition of an azo group. The lower the temperature, the weaker the absorption at  $\lambda_{\text{max}}$  320 nm and the stronger the absorptions at  $\lambda_{\text{max}}$  350 and 380 nm. The results of the UV–vis spectra are consistent with the thermochromism.

Reaction of the mixture of (*E*)-**3a** and **4a** with an excess amount of elemental selenium gave phosphine selenide (*E*)-**5** in good yield (90%), and reaction with borane–dimethyl sulfide (1 equiv) gave the corresponding phosphine borane (*E*)-**6** (76%) (Scheme 2).

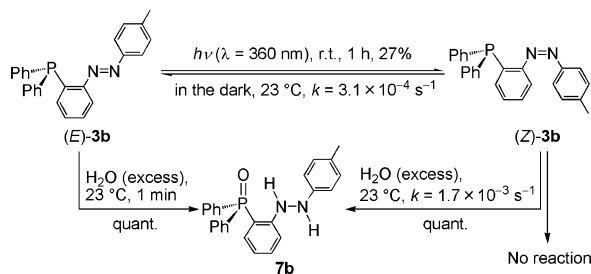
Scheme 2



Phosphine (*E*)-**3a** shows the usual reactivity of a triarylphosphine, although (*E*)-**3a** is in equilibrium with phosphonium salt **4a**. Conversely, the reaction with water gave phosphine oxide **7a** quantitatively. In the formation of **7a**, the phosphine moiety of (*E*)-**3a** was oxidized to a phosphine oxide, and the azo group of (*E*)-**3a** was reduced to a hydrazine. These conversions show a similarity between the present reaction and the Mitsunobu reaction, suggesting that inner phosphonium salt **4a** behaves as an intermediate in the Mitsunobu reaction.<sup>2,16</sup> Therefore, the reaction mechanism for hydrolysis is described as follows. The negatively charged nitrogen in phosphonium salt **4a** that is in equilibrium with (*E*)-**3a** is reversibly protonated, and subsequent substitution at phosphorus of **8** with hydroxide ion gives amido anion **9**, which undergoes internal proton transfer from the hydroxyphosphonium group to give hydrazine **7a**.

Although photoisomerization of (*E*)-**3a** did not proceed at all, that of (*E*)-**3b** bearing a methyl group at the 4'-position of azobenzene to produce (*Z*)-**3b** (27%) was achieved by irradiation ( $\lambda = 360$  nm) in benzene-*d*<sub>6</sub> for 1 h (Scheme 3). In the <sup>31</sup>P NMR spectra of (*Z*)-**3b** in toluene-*d*<sub>8</sub>, one singlet ( $\delta_{\text{P}} -16.0$ ) of (*Z*)-**3b** was not broadened between 20 and −100 °C, in contrast to (*E*)-**3b**.<sup>14</sup> This result suggests that there is no equilibrium between the phosphine and an inner phosphonium salt in (*Z*)-**3b** because the geometry of (*Z*)-**3b** prohibits a nucleophilic attack of the phosphine

Scheme 3



on the azo group. (*Z*)-**3b** was thermally isomerized to (*E*)-**3b** with a rate constant of  $3.1 \times 10^{-4} \text{ s}^{-1}$  at 296 K in benzene-*d*<sub>6</sub>. Addition of water to the mixture of (*E*)-**3b** and (*Z*)-**3b** in benzene-*d*<sub>6</sub> resulted in quantitative conversion of (*E*)-**3b** to hydrazine **7b** via phosphonium salt **4b** and no reaction of (*Z*)-**3b** after 1 min. (*Z*)-**3b** decayed with a rate constant of  $1.7 \times 10^{-3} \text{ s}^{-1}$  to give hydrazine **7b** at 296 K. Considering the reaction rate, the conversion of (*Z*)-**3b** proceeded via isomerization to (*E*)-**3b**. Photoisomerization of **3b** causes switching of the unique reactivity of phosphonium salt.

In summary, we have synthesized azobenzenes (*E*)-**3a** and (*E*)-**3b** bearing a diphenylphosphino group at the 2-position, which are in equilibrium with inner phosphonium salts **4a** and **4b**. The equilibrium constant changed depending on the temperature and the solvent, and thermochromism was observed in solution. (*E*)-**3a** shows the usual reactivity of a triarylphosphine, while **4a** was hydrolyzed to give hydrazinophenylphosphine oxide **7a** by a mechanism similar to the Mitsunobu reaction. Photoisomerization of (*E*)-**3b** to (*Z*)-**3b** changed the reactivity toward water. Such phosphines in equilibrium with inner phosphonium salts are expected to be useful for controlling organic reactions by taking advantage of the photoisomerization of the azobenzene moiety.

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**Supporting Information Available:** Synthetic procedure and spectral data of (*E*)-**2a**, (*E*)-**2b**, (*E*)-**3a**, (*E*)-**3b**, (*E*)-**5**, (*E*)-**6**, **7a**, and **7b**, complete ref 12, and X-ray crystallographic file in CIF format for (*E*)-**3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.
- Mitsunobu, O. *Synthesis* **1981**, 1.
- Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801.
- Beck, P. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley Interscience: New York, 1972; Vol. 2, Chapter 4, p 189.
- (a) Kano, N.; Komatsu, F.; Kawashima, T. *J. Am. Chem. Soc.* **2001**, *123*, 10778. (b) Kano, N.; Yamamura, M.; Komatsu, F.; Kawashima, T. *J. Organomet. Chem.* **2003**, *686*, 192. (c) Kano, N.; Yamamura, M.; Kawashima, T. *J. Am. Chem. Soc.* **2004**, *126*, 6250.
- (a) For an azobenzene bearing a tributylphosphonio group in the 2-position, see: Stringer, M. B.; Candeloro, V.; Bowie, J. H.; Prager, R. H.; Engelhardt, L. M.; White, A. H. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2529. (b) For tungsten complexes of azobenzenes bearing phosphino groups in the 2-position, see: Tran Huy, N. H.; Ricard, L.; Mathey, F. *New J. Chem.* **1998**, *22*, 75.
- Badger, G. M.; Drewier, R. J.; Lewis, G. E. *Aust. J. Chem.* **1964**, *17*, 1036.
- Crystal data for (*E*)-**3a**: C<sub>24</sub>H<sub>19</sub>N<sub>2</sub>P, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 11.043(4) Å, *b* = 10.218(4) Å, *c* = 10.504(6) Å,  $\beta$  = 92.803(2)°, *V* = 1901(2) Å<sup>3</sup>, *Z* = 4, MW = 366.38, *D*<sub>c</sub> = 1.280 g·cm<sup>−3</sup>, *T* = 120 K, *R*1 (*I* > 2σ(*I*)) = 0.0363, *wR*2 (all data) = 0.0889, GOF(*F*<sup>2</sup>) = 1.062.
- Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
- Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect. C* **1983**, *39*, 1121.
- Doherty, S.; Knight, J. G.; Scanlan, T. H.; Elsegood, M. R. J.; Clegg, W. *J. Organomet. Chem.* **2002**, *650*, 231.
- A calculation was performed using the Gaussian 03 program. See: Frisch, M. J. et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.
- For triphenyl(1,2-diphenylhydrazino)phosphonium perchlorate, see: Humphrey, R. E.; Hueske, E. E. *J. Org. Chem.* **1971**, *36*, 3994.
- See Supporting Information.
- Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: New York, 2003; pp 93–145.
- (a) Ahn, C.; Correia, R.; DeShong, P. *J. Org. Chem.* **2002**, *67*, 1751. (b) Harvey, P. J.; von Itzstein, M.; Jenkins, I. D. *Tetrahedron* **1997**, *53*, 3933.

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