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Base-Mediated Cyclization Reaction of 2-Alkynylphenylphosphine Oxides: Synthesis and Photophysical Properties of Benzo[*b*]phosphole Oxides

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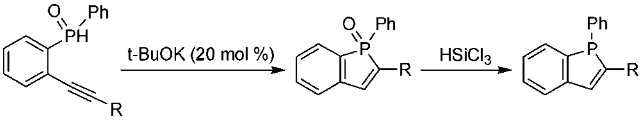
ABSTRACT



The base-mediated intramolecular cyclization reaction of 2-alkynylphenylphosphine oxides affords benzo[*b*]phosphole oxides, which show intense blue-green fluorescence. Benzo[*b*]phospholes are also prepared by the reduction of benzo[*b*]phosphole oxides.

Among the variety of π-conjugated systems with potential applications as electronic materials, such as organic thin film transistors and organic electroluminescent (EL) devices, main group element-containing π-conjugated molecules have attracted considerable interest recently.[1] This is because the orbital interaction of the main group element moiety plays an intriguing role in the π-conjugated framework, and the resultant π-systems reduce the HOMO−LUMO gaps compared with the parent π-system. In this context, phosphacyclopentadienes (phospholes) form interesting building blocks for the construction of conjugated systems, where an interaction between the butadiene π^* orbital and the low-lying σ^*(P-R) orbital takes place in the ring.[2] In addition, phosphorus-containing π-systems retain a versatile reactivity of a central phosphorus atom, and this makes it possible to tune the electronic and optical properties of the materials using simple chemical modifications, such as oxidation. Several reports have addressed the synthesis of phospholes,[3,4] dibenzophospholes,[5,6] dithienophospholes,[7] and their derivatives.[8]

Indoles are basic skeletons in organic chemistry and are found in natural products and biologically active substances.[9,10] On the other hand, synthesis and properties of benzo[*b*]phosphole, phosphorus analogues of indoles, have not been explored to date.[11,12] Here, we report the synthesis and photophysical properties of benzo[*b*]phosphole oxides and benzo[*b*]phospholes.[13–15]

Because the metal- and base-mediated cyclization reaction of alkynylamines, which proceeds through intramolecular addition of the N−H bond to the triple bond, is one of the

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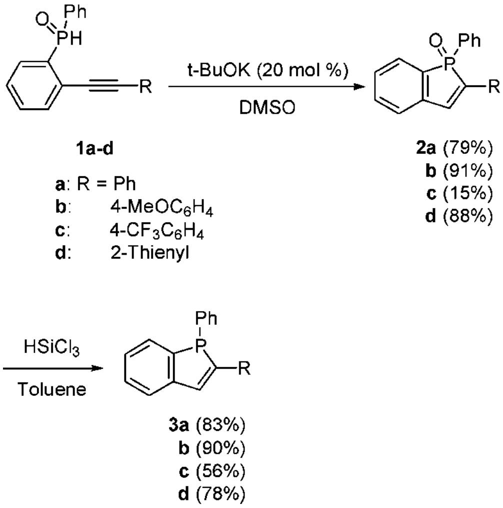
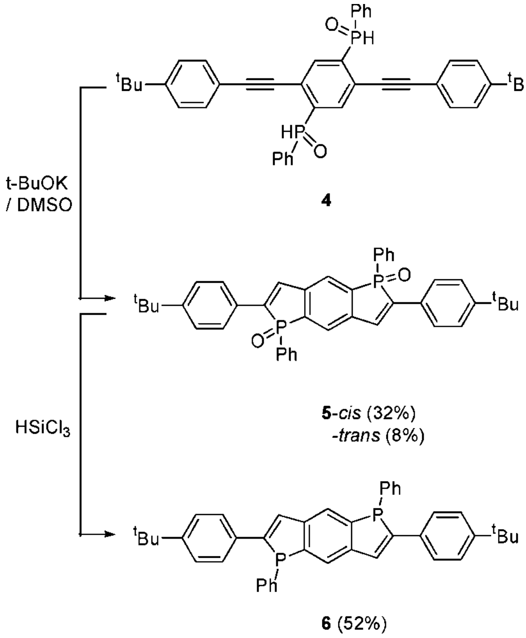
most powerful tools for synthesizing indoles,[16] our synthetic strategy for the benzophosphole oxides was the base-mediated intramolecular cyclization reaction of 2-alkynylphenylphosphine oxides **1**.[17,18] Scheme 1 shows the synthesis of benzo*b*phosphole oxides **2**a-d. For example, the reaction of **1a** (R = Ph) in the presence of potassium *t*-butoxide (20 mol %) as a base in DMSO at 70 °C for 24 h led to a phosphole oxide **2a** in 79% yield.[19,20] The reaction of **1b** (R = 4-MeOC$_6$H$_4$) and **1d** (R = 2-thienyl) gave **2b** and **2d**, respectively, in good yields, but the reaction of **1c** (R = 4-CF$_3$C$_6$H$_4$) gave **2c** only in 15% yield. Subsequently, reduction of the benzophosphole oxides was examined. The reaction of **2a-d**with trichlorosilane in toluene at 110 °C afforded benzo[*b*]phospholes **3a-d** in 56−90% yields. The structures of **2a**−**d** and **3a**−**d** were fully characterized using ^{1}H, ^{13}C, and ^{31}P NMR, MS, and elemental analysis.

Scheme 1



Scheme 2



The base-mediated intramolecular addition reaction of H−P(O) compounds to alkynes was employed for π-extended starting materials with two alkyne parts, as shown in Scheme 2. For example, the reaction of **4**, which has two H−P(O) groups at the central benzene ring, gave **5** as a mixture of *cis* and *trans* isomers with respect to the directions of the P═O bonds.[21] The isomers were easily separated from

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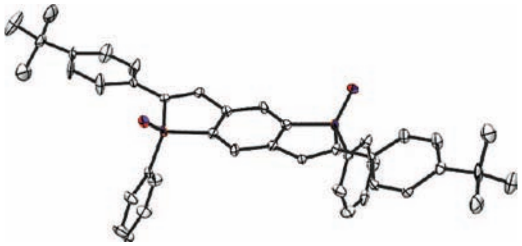

Figure 1. ORTEP drawing of **5**-*cis* (major isomer).

Scheme 3

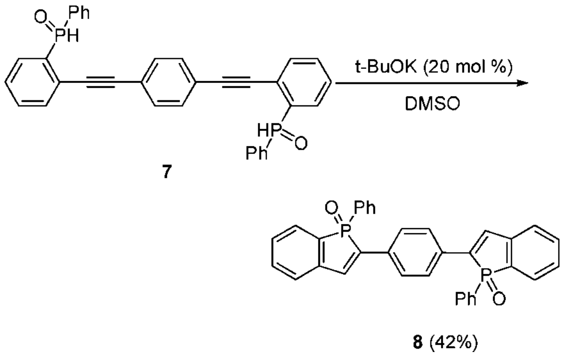

Table 1. Photophysical Properties of Benzo[*b*]phosphole Oxide Derivatives and Related Compounds[a]

	absorption		fluorescence	
compd	$\lambda_{max}{}^{b}$/nm	ε /cm^{-1} M^{-1}	λ_{FLmax}/nm^{c}	$\Phi_{FL}{}^{d,e}$
2a	347	8800	417	0.30
2b	362	12600	443	0.41
2c	342	8400	414	0.65
2d	368	12000	444	0.23
3a	321	13800	n.d.[f]	–
3b	340	16600	412	0.09
3c	329	13600	n.d.[f]	–
3d	350	15600	417	0.07
5[g]	433	23800	495	0.44
6[h]	396	28500	438, 463	0.61
8[h]	387	32700	431, 456	0.29

[a] In THF. [b] Longest wavelength absorption maximum is shown. [c] Excited at the wavelength of the absorption maximum. [d] Fluorescence quantum yield. [e] Determined with quinine sulfate as a standard. [f] Not detectable. [g] Major isomer (*cis*). [h] Mixture of *trans* and *cis* isomers.

each other using silica gel chromatography, the isomers of **5** being obtained in 32% and 8% yields. The structure of the major isomer was identified to be a *cis* structure from single-crystal X-ray analysis (Figure 1). **5**-*cis* showed a nearly coplanar structure with the dihedral angles between the benzene ring and the two phosphole oxide rings of 7.2−7.2 ° along with moderate C−C/C═C bond length alternations (Δd = 0.04−0.13 Å). The reduction of **5** with trichlorosilane gave a diphospholenobenzene-type compound **6** in good yield as a mixture of *cis* and *trans* isomers. The ratio of the two isomers was found to be 1/0.9, estimated from the integration ratio of the NMR spectra.[22] However, the separation of these isomers from each other using chromatography failed at this stage. The reaction of **7**, having two H−P(O) groups at the terminal phenyl rings, also led to **8** in 42% yield (Scheme 3).[23]

The photophysical properties of benzophosphole oxides **2a-d**, benzophospholes **3a-c**, and the related compounds are of interest. The photophysical data in solution are summarized in Table 1 and the fluorescence spectra of **2a-d**, **5**, and **8** are shown in Figure 2. In the absorption spectra, the benzophosphole oxides **2a-d** display an absorption band at 350−370 nm, where the position of the absorption depends on the substituent on the benzophosphole ring. When substituted with a 4-methoxyphenyl (**2b**) or 2-thienyl group (**2d**) on the phosphole oxide ring, the absorption maximum is red-shifted relative to that of **2a** (R = Ph). Introduction of a 4-trifluoromethylphenyl group causes a blue shift of the

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(20) The reaction conditions were not optimized completely, and based on the intermolecular addition of H-P(O). to alkenes.[16d] We found the reaction time depends on the substrate. For example, the reaction of **2d** proceeded with *ca*. 50% conversion for 7 h, but the reaction of **4** completes in 2 h.

(21) After the reaction, the isomer ratio was 1/0.32, estimated from the integration ratio of the ^{31}P NMR spectra.

(22) The ratio of *cis*/*trans* isomers was not changed ranging in temperature from 0 to 50 °C by measurement with the ^{31}P NMR. See Supporting Information.

(23) The isomer ratio could not be estimated because of the overlap of the NMR chemical shifts. An attempt to separate these isomers from each other using chromatography also failed.

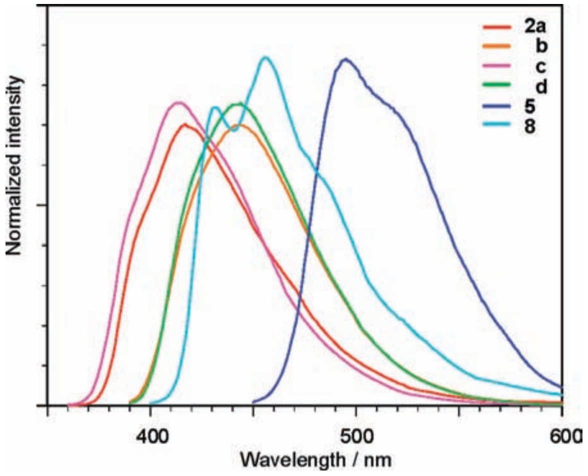

Figure 2. Fluorescence spectra of **2a-d**, **5**-*cis*, and **8** in THF.

absorption maximum. In the fluorescence spectra, **2a-d** display an emission at 420−440 nm with a quantum yield of 23−65%. The emission maxima are also shifted to longer wavelengths with increasing electron-donating ability of the group on the ring. On the other hand, the benzophospholes **3a**−**c** exhibit absorption maxima at 320−350 nm, which are blue-shifted relative to those of the benzophosphole oxides. In the fluorescence spectra, **3b** and **3d** exhibit only weak emissions at around 415 nm with quantum yields of 9 and 7%, respectively, and **3a** and **3c** show practically no emission.

Compound **5** with two benzophosphole oxides has a red-shifted absorption maximum at 433 nm and also a red-shifted emission maximum at 495 nm, where the photophysical properties of the *cis*/*trans* isomers are essentially identical to each other. This indicates that the π-conjugated system is successfully extended. For **8**, the absorption (387 nm) and emission maxima (431 and 456 nm) are slightly red-shifted compared with those of the parent compound **2a**. The quantum yields of **5** and **8** are relatively high. The benzophosphole derivative **6** exhibits an absorption maximum at 396 nm and emission maximum at around 450 nm, which are blue-shifted relative to those of the benzophosphole oxides **5**. These examples demonstrate that the $P = O$ moieties in **5** and **8** cause the significant red-shift of 20−30 nm for the absorption and emission maxima as compared with the silicon analogues,[13e] due to the low-lying LUMO of the phosphole oxide ring.

In summary, we have demonstrated the synthesis of benzo[*b*]phosphole oxides by means of the base-mediated reaction of 2-alkynylphenylphosphine oxides. These benzophosphole oxides display blue-green emission with good quantum yield. In addition, benzo[*b*]phospholes are easily synthesized by reduction of the phosphorus atom of the phosphole ring. The base-mediated cyclization reaction of 2-alkynylphenylphosphine oxides offers a simple procedure for obtaining phosphorus-containing extended π-systems. Benzo[*b*]phosphole oxides should be more seriously scrutinized as new candidates for π-conjugated systems with potential applications as optoelectronic materials. Further study is in progress.

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Supporting Information Available: Experimental procedures, spectral data of all new compounds and details of the X-ray analysis of 5-*cis*. This material is available free of charge via the Internet at http://pubs.acs.org.

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