Organic LETTERS

Letter

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Synthesis of π-Extended Dibenzophospholes by Intramolecular Radical Cyclization and Their Properties

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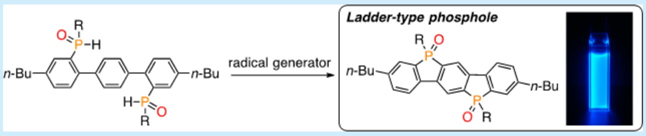
Supporting Information

ABSTRACT: Intramolecular radical cyclization of phosphine oxides ($R^1R^2P(O)H$) induced by radical generators affords the corresponding dibenzophosphole oxides in excellent yields. By applying this method, linearly π-extended ladder-type dibenzophosphole oxides were successfully synthesized.



The phosphorus-containing π-conjugated five-membered ring, phosphole, has attracted attention because of its relatively small HOMO−LUMO energy gap and because its properties can be tuned through diverse functionalization of the phosphorus atom.[1] Recently, π-extended phospholes have been applied in organic electronic devices such as light-emitting diodes[2] and organic photovoltaic devices,[3] and the potential utility of this class of compounds has led to the development of unique synthetic methods.[4] For simple dibenzophospholes, several synthetic methods have been reported including intramolecular Friedel−Crafts type cyclization of 2-biphenylphenylphosphinic acid or aryldichlorophosphines,[5] the reaction of tetraphenylphosphonium bromide with lithium diethylamide,[6] and the anionic intramolecular cyclization of triphenylphosphine oxide with 2 equiv of phenyllithium.[7] However, reports on the synthesis of π-extended dibenzophospholes are limited; available methods include palladium-catalyzed intramolecular dehydrogenative cyclization of hydrophosphine oxides[8] and a 4-fold free-radical phosphonylation reaction of a tetrabromo-*p*-terphenylene or biphenylthiophene.[9] These methods avoid the use of highly reactive polylithiated species, which can lead to the formation of oligomeric side products during the construction of further π-extended phosphole skeletons.[9] In a similarly directed approach, we have developed an efficient method that avoids the requirement for a rare metal catalyst. In this paper, we report on intramolecular radical cyclization of secondary phosphine oxides that can effectively yield π-extended dibenzophosphole oxides.

We hypothesized that hydrogen abstraction from the P−H bond would efficiently form a P-centered radical intermediate because of the small bond dissociation energy of such bonds (322 kJ/mol).[10] Subsequent addition of the radical species to unsaturated bonds in a Pudovik-type reaction[11] followed by hydrogen elimination would then give cyclized dibenzophosphole oxides (Scheme 1).

This intramolecular cyclization strategy was considered to be a promising method with which to construct π-extended dibenzoheteroles; indeed, we have previously demonstrated such an approach for silicon analogues.[12]

It was found that treatment of 2-biphenylarylphosphine oxides **1** with radical generators affords the desired dibenzophosphole oxides **2** (Table 1). The reaction of [4,4′-di-*tert*-butyl-(1,1′-biphenyl)-2-yl](phenyl)phosphine oxide (**1a**) with a typical radical generator such as 2,2′-azobis(isobutyronitrile) (AIBN) or benzoyl peroxide (BPO) under heating in benzene gave the corresponding cyclized product **2a** in moderate yields (41−48%) (entries 1−2). Performing the reaction under milder conditions by using triethylborane with oxygen as a radical generator gave the product in higher yield

Scheme 1. Strategy To Construct a Dibenzophosphole Framework by Intramolecular Radical Cyclization

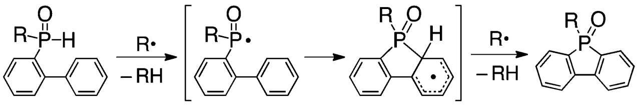
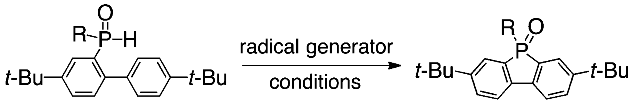


Table 1. Reaction Conditions for the Intramolecular Radical Cyclization



1a (R = Ph)
1b (R = *p*-anisyl)
1c (R = *t*-Bu)

2a (R = Ph)
2b (R = *p*-anisyl)
2c (R = *t*-Bu)

		conditions			
entry	R	radical generator (equiv)	solvent	temp (°C)	conv[a] (%)
1	Ph	AIBN (1.1)	benzene	90	48
2	Ph	BPO (1.1)	benzene	90	41
3	Ph	Et_3B (1.0)/O_2[b]	MeOH	rt	73
4	Ph	Et_3B (2.1)/O_2[b]	MeOH	rt	87
5	*p*-anisyl	Et_3B (2.1)/O_2[b]	MeOH	rt	96
6	*t*-Bu	Et_3B (12)/O_2[b]	MeOH	rt	85

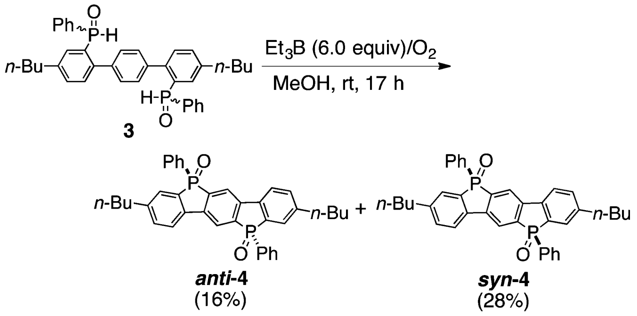
[a] The conversion was determined by ^1H NMR spectroscopy. [b] Air was added by a syringe to an argon-filled vessel.

Received: May 1, 2014

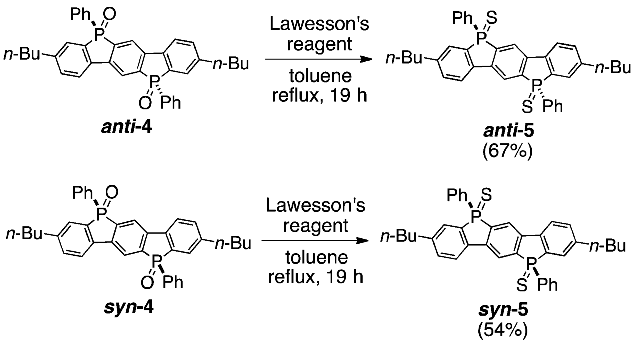
(73%) at room temperature (entry 3). After optimization of the reaction conditions, we found that the use of 2.1 equiv of triethylborane in the presence of oxygen gave the best result (87%) (entry 4). These reaction conditions were applicable to other substrates bearing a *p*-anisyl group **1b** (entry 5) or a *tert*-butyl group **1c** (entry 6) on the phosphorus atom, and they gave the desired products **2b** and **2c** in good yields (96% and 85%, respectively). For the bulky substrate **1c**, an excess of triethylborane was required for high conversion, which may be because of the kinetically stabilized P−H bond in **1c** and the short lifetime of the ethyl radical generated in the triethylborane/O_2 system.

This intramolecular cyclization was also applicable to the construction of π-extended ladder-type dibenzophospholes. By adding a small excess of triethylborane to bis(phenylphosphinyl)-*p*-terphenyl **3** in the presence of oxygen, doubly cyclized phosphole oxides ***anti*-4** and ***syn*-4** were obtained as a diastereomeric mixture (Scheme 2). These diastereomers were successfully separated by silica gel column chromatography to give ***anti*-4** and ***syn*-4** in 16% and 28% isolated yields, respectively. In an attempt to confirm the *anti*/*syn* conformation of the products **4**, single crystals of the products were not suitable for single-crystal X-ray crystallographic analysis. The conformation was, however, determined from X-ray crystallographic analysis of the corresponding phosphole sulfide **5**, which were obtained from **4** with retention of configuration by using Lawesson's reagent (Scheme 3).[13] As expected, phosphole sulfides ***anti*-5** and ***syn*-5**, prepared from phosphole oxides ***anti*-4** and ***syn*-4**, respectively, afforded single crystals that were suitable for X-ray analysis. The X-ray structures of ***anti*-5** and ***syn*-5** revealed that both compounds have almost flat, ladder-type *p*-terphenyl units (Figure 1).

Scheme 2. Double Intramolecular Radical Cyclization



Scheme 3. Conversion of Phosphole Oxides to Phosphole Sulfides with Lawesson's Reagent



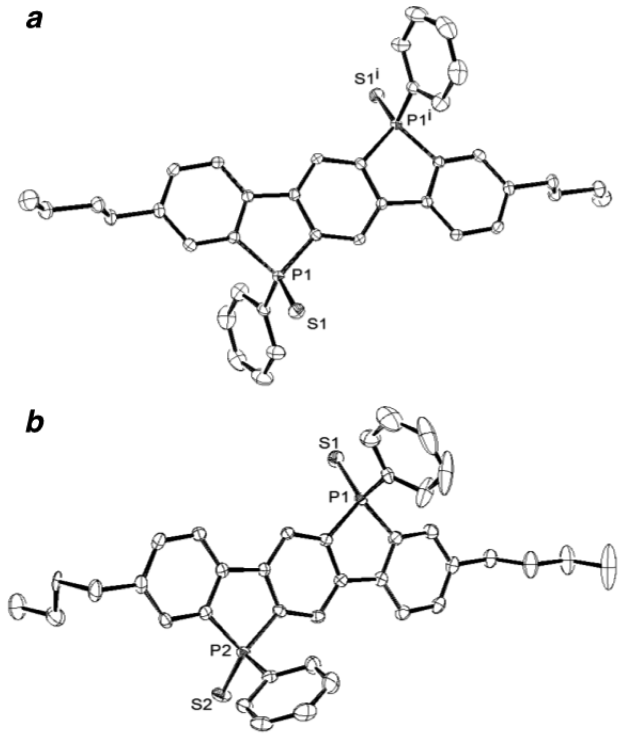


Figure 1. ORTEP drawings of dibenzophosphole sulfides ***anti*-5** (a) and ***syn*-5** (b) (50% probability).

The photophysical properties of the ladder-type dibenzophosphole oxides **4** and sulfides **5** were evaluated by UV−vis absorption and fluorescence spectroscopy, and the obtained data are summarized in Table 2, together with those of simple dibenzophosphole oxide **2a**. Dibenzophosphole oxide **2a** showed an absorption maximum at λ_{abs} = 340 nm (log ε = 3.19) that was derived from the HOMO−LUMO transition (Figure S1). In the ladder-type phosphole oxide ***anti*-4**, the absorption maximum was significantly red-shifted to 391 nm (log ε = 3.68) because of the π-expansion through the σ^*−π^* conjugation of the main π-framework to the σ^* orbital of the exocyclic P−C bonds. This result is consistent with a previous report for the ladder-type dibenzophosphole oxide.[9] The diastereomer ***syn*-4** showed a similar absorption profile to that of ***anti*-4**. Fluorescence spectra showed that the emission wavelengths of the ladder-type derivatives **4** are also red-shifted (λ_{em} = 426, 438 nm for both ***anti*-4** and ***syn*-4**) compared with that of **2a** (λ_{em} = 382 nm). The ladder-type dibenzophosphole oxides **4** showed high fluorescence quantum yields of 0.89 and

Table 2. Photophysical Data for Ladder-Type Phosphole Oxide and Sulfide Derivatives

			fluorescence			
	absorption[a]		solution[a]		solid	
compd	λ_{abs} [nm]	log ε	λ_{em} [nm]	Φ_F[b]	λ_{em} [nm]	Φ_F[b]
2a	340	3.19	382	0.67	–	–
***anti*-4**	391	3.68	426, 438	0.89	454	0.46
***syn*-4**	391	3.61	426, 438	0.79	476	0.63
***anti*-5**	385	3.73	430	0.004	437, 471, 501	0.12
***syn*-5**	386	3.72	431	0.004	476, 500	0.04

[a] In CH_2Cl_2. [b] Absolute quantum yield determined by an integrating sphere system.

0.79 for ***anti***- and ***syn*-4**, respectively, which result from their rigid main π-framework. Interestingly, a slight difference in the fluorescence spectra was found between ***anti*-4** and ***syn*-4** in the solid state. The emission maximum of the latter in the solid state (λ_{em} = 476 nm) was slightly red-shifted compared with that of the former (λ_{em} = 454 nm) (Figure S2), and the fluorescence quantum yield of ***syn*-4** (Φ_F = 0.63) was larger than that of ***anti*-4** (Φ_F = 0.46). These results suggest that intermolecular interactions in the solid state are different in the *anti* and *syn* forms of **4** because of their conformational difference.

We also found that phosphole oxides and sulfides have drastically different photophysical properties. Dibenzophosphole sulfides **5** showed absorption maxima at 385 nm (log ε = 3.73) and 386 nm (log ε = 3.72) for ***anti***- and ***syn*-5**, respectively (Figure 2). DFT calculations suggested that the HOMO of the sulfide **5** is mainly localized on the lone pairs of the exocyclic sulfur atoms, whereas the LUMO is composed of the π*-orbital of the main π-skeleton (Figure S3). TD-DFT calculations revealed that these absorption maxima mainly correspond to HOMO−4 → LUMO with a relatively large oscillator strength (f = 0.0994), because HOMO → LUMO and other transitions involving the orbitals of the lone pairs were calculated to be forbidden transitions (f < 0.00339) (Table S1). These electronic properties lead to blue-shifted absorption maxima of phosphole sulfides compared with those of phosphole oxides. The fluorescence quantum efficiencies of the sulfides **5** in the solution state were much lower (Φ_F = 0.004 for both ***anti*-5** and ***syn*-5**) than those of oxides **4**. This may result from nonradiative decay of the (n,π*) excited state and an internal heavy atom effect of the sulfur atoms. On the other hand, fluorescence quantum efficiencies of these sulfides in the solid state increased to 0.12 and 0.04 for ***anti*-5** and ***syn*-5**, respectively. Crystal packing of these conformers indicated that rotation of the phenyl rings on the phosphorus atoms is restricted because of interactions between neighboring molecules in the solid state (Figure S4), with the result that thermal decay of the excited state would be partially suppressed. Such a phenomenon is now commonly referred to as aggregation-induced emission, and this interesting property of phosphole derivatives is expected to have applications in fluorescence sensors.[1b,2b,14]

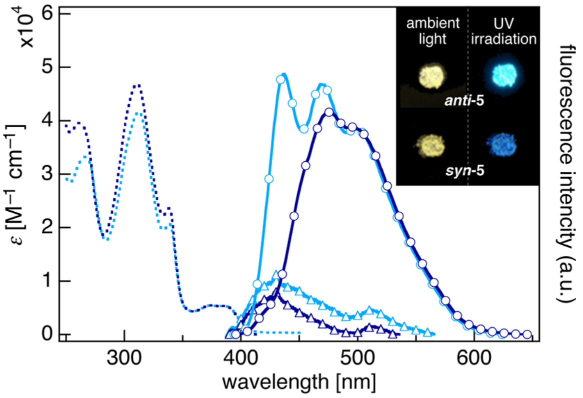


Figure 2. Absorption (dashed lines) and emission (solid lines) spectra of ladder-type phosphole sulfides ***anti*-5** (light blue) and ***syn*-5** (blue) in CH_2Cl_2 (triangle) and in the solid state (circle).

In conclusion, we have developed an intramolecular radical cyclization of 2-biphenylarylphosphine oxides **1** that can be used to produce dibenzophosphole oxides **2**. This intramolecular radical cyclization can be applied to double cyclization, which affords ladder-type π-extended dibenzophosphole oxides **4**. The *anti*/*syn* conformations of the products were determined by X-ray crystallographic analysis of the corresponding dibenzophosphole sulfides **5**. We also investigated the photophysical properties of the isolated *anti*/*syn* forms of dibenzophosphole oxides and sulfides and found that the conformational difference between the diastereomers affects the absorption and emission properties especially in the solid state. This new synthetic approach involving intramolecular radical cyclization will facilitate the creation of novel phosphorus-containing π-conjugated molecules and will contribute to further developments in the field of materials science.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental procedure, NMR spectra, CIF for ***anti*-5** and ***syn*-5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This paper is dedicated to Professor Renji Okazaki (professor emeritus at The University of Tokyo) on the occasion of his 77th birthday. This work was supported by the Global COE Program for Chemistry Innovation. Partial financial support from MEXT (Kakenhi, 20685005, 21108507) is gratefully acknowledged. We also thank Tosoh Finechem Co., Ltd. for the generous gifts of alkyllithium reagents. We would also like to thank Prof. Mao Minoura (Rikkyo University) for his valuable advice in the crystallographic analysis.

■ REFERENCES

(1) (a) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681−4727. (b) Ren, Y.; Baumgartner, T. *Dalton Trans.* **2012**, *41*, 7792−7800. (c) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578−1604.

(2) (a) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254−9255. (b) Su, H.-C.; Fadhel, O.; Yang, C.-J.; Cho, T.-Y.; Fave, C.; Hissler, M.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 983−995. (c) Joly, D.; Tondelier, D.; Deborde, V.; Geffroy, B.; Hissler, M.; Réau, R. *New J. Chem.* **2010**, *34*, 1603−1611. (d) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. *J. Mater. Chem.* **2009**, *19*, 3364−3366.

(3) (a) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. *Chem.—Asian. J.* **2010**, *5*, 1294−1297. (b) Matano, Y.; Saito, A.; Suzuki, Y.; Miyajima, T.; Akiyama, S.; Otsubo, S.; Nakamoto, E.; Aramaki, S.; Imahori, H. *Chem.—Asian J.* **2012**, *7*, 2305−2312. (c) Matano, Y.; Ohkubo, H.;

Miyata, T.; Watanabe, Y.; Hayashi, Y.; Umeyama, T.; Imahori, H. *Eur. J. Inorg. Chem.* **2014**, 1620−1624.

(4) (a) Fukazawa, A.; Hara, M.; Okamoto, T.; Son, E.-C.; Xu, C.; Tamao, K.; Yamaguchi, S. *Org. Lett.* **2008**, *10*, 913−916. (b) Fukazawa, A.; Yamaguchi, S. *Chem.—Asian J.* **2009**, *4*, 1386−1400. (c) Matano, Y.; Ohkubo, H.; Honsho, Y.; Saito, A.; Seki, S.; Imahori, H. *Org. Lett.* **2013**, *15*, 932−935. (d) Matano, Y.; Saito, A.; Fukushima, T.; Tokudome, Y.; Suzuki, F.; Sakamaki, D.; Kaji, H.; Ito, A.; Tanaka, K.; Imahori, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 8016−8020.

(5) (a) Campbell, I. G. M.; Way, J. K. *J. Chem. Soc.* **1961**, 2133−2141. (b) Durán, E.; Velasco, D.; López-Calahorra, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 591−594. (c) Diaz, A. A.; Young, J. D.; Khan, M. A.; Wehmschulte, R. J. *Inorg. Chem.* **2006**, *45*, 5568−5575.

(6) Ezzell, B. R.; Freedman, L. D. *J. Org. Chem.* **1969**, *34*, 1777−1780.

(7) Ogawa, S.; Tajiri, Y.; Furukawa, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3182−3184.

(8) Kuninobu, Y.; Yoshida, T.; Takai, K. *J. Org. Chem.* **2011**, *76*, 7370−7376.

(9) Hanifi, D.; Pun, A.; Liu, Y. *Chem.—Asian J.* **2012**, *7*, 2615−2620.

(10) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998; p 152.

(11) (a) Pudovik, A. N.; Konovalova, I. V. *Zh. Obshch. Khim.* **1959**, *29*, 3342−3346. (b) Pudovik, A. N.; Konovalova, I. V. *Synthesis* **1979**, 81−96. (c) Rey, P.; Taillades, J.; Rossi, J. C.; Gros, G. *Tetrahedron Lett.* **2003**, *44*, 6169−6171. (d) Kagayama, T.; Nakano, A.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2006**, *8*, 407−409.

(12) (a) Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 14192−14193. (b) Furukawa, S.; Kobayashi, J.; Kawashima, T. *Dalton Trans.* **2010**, *39*, 9329−9336.

(13) Mikołajczyk, M.; Łuczak, J.; Kiełbasiński, P.; Colonna, S. *Tetrahedron: Asymmetry* **2009**, *20*, 1948−1951.

(14) (a) Fukazawa, A.; Ichihashi, Y.; Yamaguchi, S. *New J. Chem.* **2010**, *34*, 1537−1540. (b) Shiraishi, K.; Kashiwabara, T.; Sanji, T.; Tanaka, M. *New J. Chem.* **2009**, *33*, 1680−1684. (c) Sanji, T.; Shiraishi, K.; Tanaka, M. *ACS Appl. Mater. Interfaces* **2009**, *1*, 270−273. (d) Shiraishi, K.; Sanji, T.; Tanaka, M. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1379−1382.