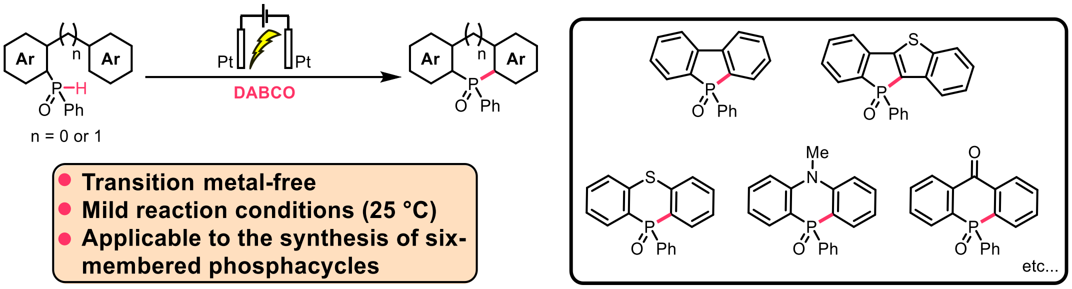
Electrosynthesis of Phosphacycles via Dehydrogenative C–P Bond Formation Using DABCO as a Mediator

Yuji Kurimoto, Jun Yamashita, Koichi Mitsudo,* Eisuke Sato, and Seiji Suga*

Supporting Information Placeholder



ABSTRACT: The first electrochemical synthesis of diarylphosphole oxides (DPOs) was achieved under mild conditions. The practical protocol employs commercially available and inexpensive DABCO as a hydrogen atom transfer (HAT) mediator, leading to various DPOs in moderate to good yields. This procedure can also be applied to the synthesis of six-membered phosphacycles such as phenophosphazine derivatives. Mechanistic studies suggested that the reaction proceeds via an electro-generated phosphinyl radical.

Phosphole oxide-containing π-conjugated molecules have been attracting attention because they have high electron acceptability and thermal and chemical stability, and have been used as basic skeletons for organic functional materials.[1] Among them, diarylphosphole oxide (DPO) is a key motif in the design of phosphole-containing organic functional materials.[2] DPOs are generally synthesized by bislithiation of 2,2′-dihalobiaryl derivatives followed by trapping with $PhPCl_2$ (Scheme 1A),[3] but this conventional synthetic procedure requires tedious and multistep sequences with complicated and unstable starting substrates and/or reagents. As a more straightforward access to DPOs, intramolecular cyclization of biarylphosphine oxides (BPOs) has recently received attention. BPOs are readily available and easy-to-handle starting substrates. Several efficient methods have been reported for synthesizing DPOs with this protocol (Scheme 1B, black arrows).[4] However, these methods require transition metal catalysts, strong acids or excess amounts of acid. Therefore, the development of a transition metal-free and environmentally benign synthetic methodology for synthesizing DPOs is highly desirable.

Meanwhile, electrochemistry offers a green and efficient alternative to conventional chemical approaches.[5] By employing only electric current as an inexpensive and sustainable reducing or oxidizing agent, the amount of waste is diminished and toxic reagents can be avoided. To the best of our knowledge, the synthesis of DPOs from BPOs via an electrochemical method has never been reported. On a related topic, electrochemical dehydrogenative C–H/P–H cross-coupling using secondary hydrophosphine oxide as a substrate has been reported.[6,7] In these methods, the target products were synthesized by direct electrolysis[6] or mediated electrolysis[7] using a transition metal mediator such as Cu,[7a] Rh,[7b] Ag,[7c] Mn,[7d,7e] or Ni.[7f] Mediated electrolysis is usually that more practical than direct electrolysis because it has a wider substrate scope and facilitates reactions under milder conditions. Furthermore, a mediated electrolysis using a nonmetallic mediator is useful as a more attractive methodology from the perspective of green chemistry. Thus, we aimed to develop a method for the synthesis of DPOs from BPOs by a mediated electrolysis (Scheme 1B, red arrow). We report here the first electrochemical synthesis of DPOs. This synthetic method can also be applied to the synthesis of six-membered phosphacycles such as phenophosphazine derivatives.

We started optimization studies with BPO (biphenylphenylphosphine oxide: **1a**) as a model substrate (Table 1). The electrolysis was first conducted under a constant current of 2.5 mA in an undivided cell equipped with a platinum (Pt) anode and a Pt cathode using Bu_4NBF_4 as a supporting electrolyte in a mixed solvent of CH_3CN/H_2O (99:1). By direct electrolysis at room temperature, the corresponding product **2a** was obtained in 8% yield, and the starting material **1a** was mainly recovered (entry 3). We next examined mediated electrolysis using tertiary amine as a mediator.[8] The reaction with DABCO gave **2a** in 71% yield (entry 1). A 1.0 mmol scale reaction could also be conducted to afford **2a** in moderate yield, indicating scalability of this protocol (entry 2). The use of quinuclidine and Et_3N instead of DABCO resulted in inferior efficiency (entries 4 and 5). When Bu_4NBF_4 was replaced by other supporting electrolytes, such as $LiBF_4$ and Bu_4NClO_4, was found to be inappropriate for this reaction (entries 6 and 7). Reducing or increasing the electric current resulted in poor results (entries 8 and 9). Increasing the amount of charge decreased the yield (entries 10 and

11). Changing the amount of DABCO and the amount of H_2O negatively affected the yield (entries 12–17). Moreover, without electric current, this electrochemical progression was mostly suppressed (entries 18 and 19). These results suggest that both the electric current and DABCO are essential for the progress of this reaction.

Scheme 1. Synthesis of Diarylphosphole Oxides (DPOs)

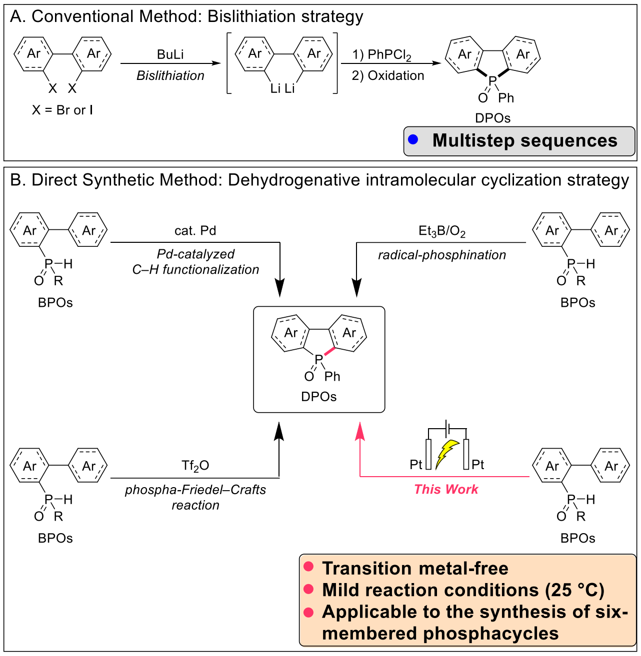
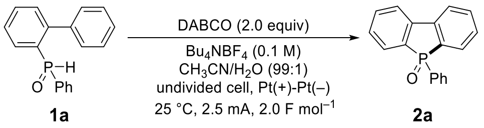


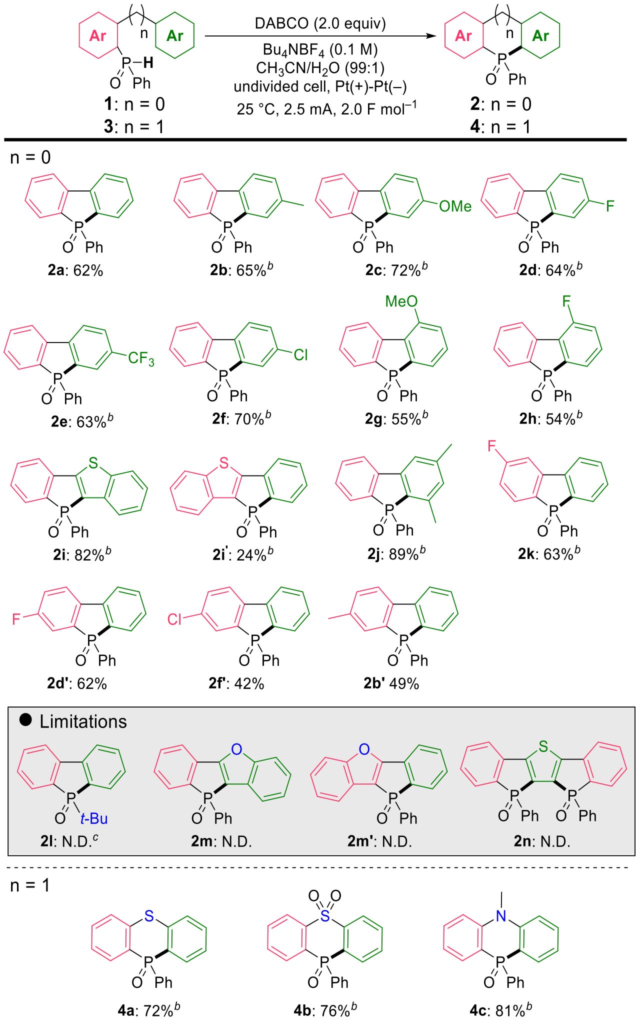
Table 1. Optimization for the Synthesis of DPO 2a[a]



entry	Deviation from standard conditions	yield (%)
1	none	71 (62)[b]
2	1.0 mmol scale	48
3	no DABCO	8
4	quinuclidine instead of DABCO	27
5	Et_3N instead of DABCO	16
6	$LiBF_4$ instead of Bu_4NBF_4	61
7	Bu_4NClO_4 instead of Bu_4NBF_4	49
8	2.0 mA instead of 2.5 mA	64
9	3.0 mA instead of 2.5 mA	54
10	2.5 F mol^{-1} instead of 2.0 F mol^{-1}	62
11	3.0 F mol^{-1} instead of 2.0 F mol^{-1}	59
12	DABCO (0.5 equiv)	29
13	DABCO (1.0 equiv)	43
14	DABCO (2.5 equiv)	58
15	Performed in CH_3CN/H_2O (99.5/0.5)	67
16	Performed in CH_3CN/H_2O (98/2)	66
17	Performed in CH_3CN	50
18	no electric current	11
19	no electric current, no DABCO	N.D.

[a] Reaction conditions: **1a** (0.4 mmol) and DABCO (0.8 mmol) in CH_3CN/H_2O (3.96/0.04 mL) with 0.1 M Bu_4NBF_4 as a supporting electrolyte were electrolyzed with 2.0 F mol^{-1} of charge under a constant current of 2.5 mA at 25 °C. Yield was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yield

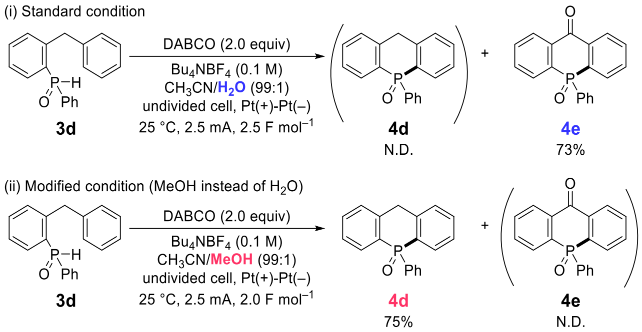
Scheme 2. Substrate Scope[a]



[a] Reaction conditions: **1** or **3** (0.4 mmol) and DABCO (0.8 mmol) in CH_3CN/H_2O (3.96/0.04 mL) with 0.1 M Bu_4NBF_4 as a supporting electrolyte were electrolyzed with 2.5 F mol^{-1} of charge under a constant current of 2.0 mA at 25 °C. Isolated yield. [b] Performed with 2.5 F mol^{-1} [c] N.D. = Not Detected.

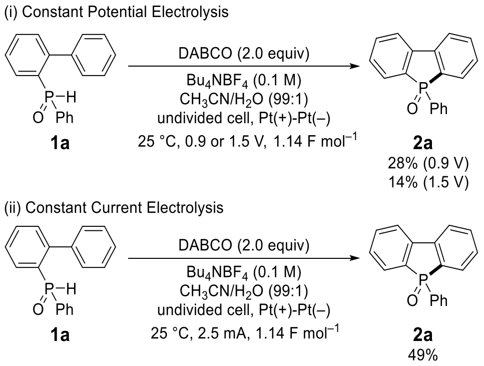
We next investigated the substrate scope for the synthesis of DPOs **2** via electrochemical cyclization (Scheme 2). BPOs bearing several substituents including Me, OMe, F, CF_3, and Cl on the benzene ring were applicable, and the corresponding products **2b–n** were obtained in moderate to high yields. Furthermore, this reaction can be applied to the synthesis of heteroring-fused DPOs **2i** and **2i′**. The reactions were slightly inhibited by a substituent at the ortho position, and the corresponding DPOs **2g** and **2h** were isolated in respective yields of 55% and 54%. Unfortunately, the reaction of substrates (**1l–n**) did not give the desired product (**2l–n**). This synthetic method can also be applied to the synthesis of six-membered phosphacycles (**4a**–**4c**). To the best of our knowledge, this is the first electrochemical synthesis of **4** from **3**.[9] In the case of substrate **3d**, the corresponding product **4d** was not observed under the standard conditions, and oxidized six-membered phosphacycle **4e** was selectively obtained (Scheme 3(i)). After further investigation, we were delighted to find that **4d** was selectively obtained when MeOH was used instead of H_2O (Scheme 3(ii)). These results suggest that the oxygen source for **4e** would be H_2O.[8]

Scheme 3. Switching Synthesis of Six-Membered Phosphacycles



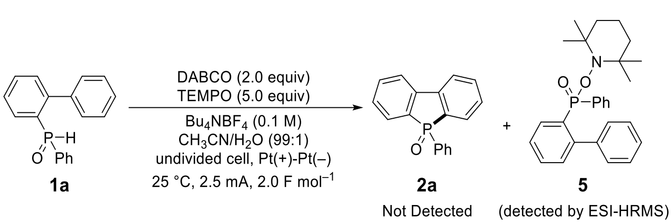
To get further insight into the reaction mechanism, cyclic voltammetry (CV) was performed.[10] CV of DABCO exhibits a quasi-reversible redox couple (E_{Ox1} = 0.32 V vs. Fc/Fc^+) and an irreversible wave (E_{Ox2} = 1.50 V), corresponding to the oxidation of DABCO to form $DABCO^{\bullet+}$ and of $DABCO^{\bullet+}$ to the DABCO biradical cation. Model substrate **1a** showed an irreversible oxidation wave around 1.83 V. A catalytic current was not observed in the mixture of **1a** and DABCO. We next examined constant potential electrolysis (Scheme 4(i)). The electrolysis was first conducted under a constant potential at 0.9 V vs. Ag/Ag^+ (22.8 h), and target product **2a** was obtained in 28% yield. Similarly, **2a** was obtained in 14% yield by the constant potential electrolysis at 1.5 V (3.6 h). From these results, $DABCO^{\bullet+}$ generated by electro-oxidation of DABCO should serve as a key reactive intermediate.

Scheme 4. Mechanistic Studies



Other control experiments were carried out to gain additional insights. When 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) was added to the system, target product **2a** was not obtained, and TEMPO–trapped product **5** was detected by ESI-HRMS (Scheme 5).[11, 12] This result strongly suggests that a phosphinyl radical was generated in situ by the reaction of **1a** with $DABCO^{\bullet+}$, and the reaction should proceed via a radical pathway.

Scheme 5. Radical Trapping Experiment



On the basis of CVs and the control experiments described above as well as related references,[6,8] a plausible mechanism for the electrochemical synthesis of DPO is suggested in Figure 1. First, DABCO is oxidized into $DABCO^{\bullet+}$ by anodic oxidation. Subsequently, $DABCO^{\bullet+}$ abstracts a hydrogen atom from the P–H bond of BPO to generate intermediate **A** and $DABCOH^+$. Finally, intramolecular cyclization of the intermediate **A** followed by hydrogen elimination would then give DPO.[13] Two reaction pathways can be considered in this hydrogen elimination step. One possibility is that DPO is produced by anodic oxidation of intermediate **B** (path A). The other possibility is that $DABCO^{\bullet+}$ generated by anodic oxidation acts as a HAT mediator and abstracts hydrogen atom from intermediate **B** (path B).[4c] Generated $DABCOH^+$ or H_2O would be reduced at the cathode. $DABCOH^+$ would be relatively unstable under the reaction conditions and the reduction of added H_2O would promote the electrochemical process efficiently.

The experimental results shown in Scheme 5 support the formation of this intermediate **A**. As mentioned above, no catalytic current was observed in the CV measurement of the mixture of **1a** and DABCO. This is probably due to the slow reaction rate between **1a** and $DABCO^{\bullet+}$. CV measurement also revealed the instability of $DABCO^{\bullet+}$, which could be why a stoichiometric amount of DABCO was required for the reaction.

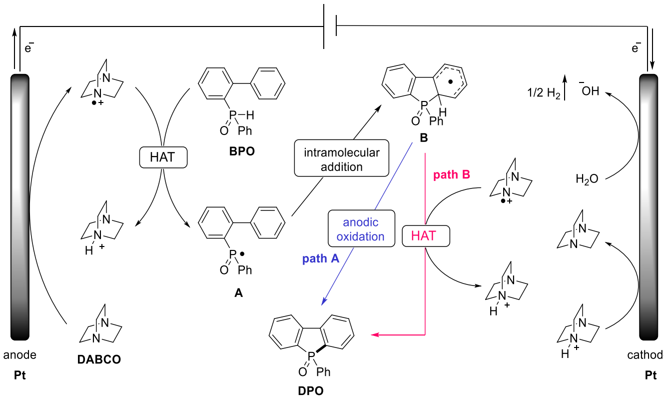


Figure 1. Plausible reaction mechanism of the electrochemical synthesis of DPO

In conclusion, we achieved the first electrochemical synthesis of DPOs from BPOs under mild conditions. The protocol does not use a transition metal mediator and instead uses readily available and inexpensive DABCO as an organic HAT mediator. A variety of BPOs could be obtained by the electrochemical method. This method can also be applied to the synthesis of six-membered phosphacycles. The control experiments suggest that a phosphinyl radical was generated in situ and the reaction would proceed via a radical pathway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/.XXXXXXX
Experimental details, spectral data for all new compound (PDF).

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Notes

The authors declare no competing financial interest.

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(10) For details, see Figure S3 in the Supporting Information (SI)

(11) For details, see Figure S2 in the Supporting Information (SI)

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