A “Green” Route to Perylene Dyes: Direct Coupling Reactions of 1,8-Naphthalimide and Related Compounds under Mild Conditions Using a “New” Base Complex Reagent, *t*-BuOK/DBN

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The direct coupling reactions of 1,8-naphthalimide compounds efficiently occurred at 130 or 170 °C without the intervention of the leuco form dyes in the presence of base complex reagent, *t*-BuOK/1,5-diazabicyclo[4.3.0]non-5-ene (DBN), to give the corresponding perylene dyes in good yields with >95% purities. A possible mechanistic speculation for these oxidative coupling reactions is briefly discussed.

Introduction

Base-promoted condensation reactions of organic compounds are of synthetic importance as a general class of organic reactions, in which the activation of acidic CH, OH, or NH by base reagents is generally involved as an essential rate-determing process.[1] In the case of low acidic CH, therefore, base-promoted reactions of relevant compounds require severe reaction conditions, e.g., the use of a large excess of base reagents and high reaction temperatures. A typical example is the production of perylene dyes that has been carried out, not only in commercial scale but also in laboratory scale, by the coupling reactions of 1,8-naphthalimide compounds in molten alkaline salts at very high temperatures (>200 °C).[2−4] This alkaline-fusion method is simple but has some crucial problems as follows: (1) Molten alkaline salts very often cause extensive corrosion of the reaction vessel. (2) Isolation of the final products requires multistep procedures such as dissolution of the excess alkaline salts with a plentiful amount of water, isolation of the leuco form dyes, and their air oxidation to the final perylene products. (3) The applicability of the alkaline-fusion reaction is rather limited because attempted reactions often fail in production of the desired products or result in only poor yields and/or low purities of the perylene dyes. (4) Environmental pollution may occur by formation of alkaline mists during the reactions as well as upon dissolution of the alkaline salts and also by massive alkaline waste. Moreover, such severe reaction conditions might limit applications of the coupling reactions to attempted synthesis of “modern” functional dyes having extended π-conjugations,[5] even though outstanding chemical and optical functionalities are expected.[2,4,6] As an extension of our research project on the development of simple synthetic methods for the production of pure functional compounds,[7] we attempted to find new base reagents with which the aryl-coupling reactions can be successfully achieved under mild conditions to produce perylene dyes in high purities without tedious procedures. In this paper, we wish to report that the *t*-BuOK/1,5-diazabicyclo[4.3.0]non-5-ene (DBN) reagent efficiently promotes the direct coupling reactions of 1,8-naphthalimide (**1a**) and related compounds (**1b**−**p**) to the corresponding perylene dyes (**2a**-**p**) at 130 or 170 °C without the intervention of the leuco form dyes (Chart 1).

Results and Discussion

Direct Coupling Reaction of Naphthalimide 1a to Perylene Dye 2a. As already mentioned, the coupling reaction of 1,8-naphthalimide (**1a**) in the presence of alkaline salts occurs only at high temperatures (>200 °C), presumably because of low basicity of the inorganic bases. It can therefore be easily predicted that highly basic reagents might promote the coupling reaction at lower temperatures, while the reagents are required to be stable at those reaction temperatures. From this viewpoint, we initially used various combinations of MOH (M = Li, Na, and K) and organic bases for the coupling reaction of **1a** because base combinations may often generate stronger base reagents, like BuLi/*t*-BuOK[8] and $BuLi/Me_2N(CH_2)_2OLi$,[1,9] than the component bases. In fact, it was found that heating of a 1:3:5 mixture of **1a**, KOH, and DBN at 170 °C under N_2 gave directly perylene-3,4,9,10-tetracarboxylic bisimide (**2a**) in a 13%

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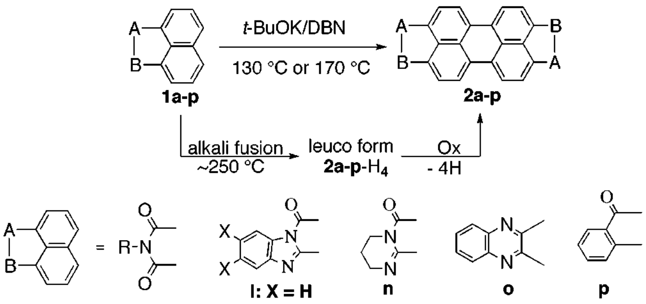
Chart 1



a: R = H
b: R = CH_3
c: R = $n$$C_8H_{17}$
d: R = cyclohexyl
e: R = phenyl
f: R = *p*-methoxyphenyl
g: R = *p*-chlorophenyl
h: R = benzyl
i: R = methoxypropyl
j: R = hydroxyethyl
k: R = dimethylaminoethyl

yield. This finding is of synthetic significance, since the alkaline-fusion reaction of **1a** does not directly give **2a** but its leuco form as the initial product. Among the organic bases investigated, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is an effective substitute for DBN. The coupling reaction of **1a** did not occur at all with the combinations of KOH and such amines as triethylamine, *N*-ethylpiperidine, DABCO, and *N*,*N*-dimethylaniline or with the combinations of MOH (M = Li and Na) and DBN or DBU.

This finding encouraged us to search more suitable base combinations with which the direct coupling reaction of **1a** to **2a** can efficiently occur at <200 °C. After many attempts, it was found that *t*-BuOK/DBN combinations can efficiently promote the direct coupling reaction even at 130 °C, while the coupling reaction did not occur at all with *t*-BuOM (M = Li and Na)/DBN pairs or with KX (X = F, SCN, and AcO)/DBN combinations. Consequently, we focused our efforts to establish optimum conditions for the direct coupling reaction of **1a** to **2a** using the *t*-BuOK/DBN reagent.

Upon the heating of a 1:3:4 mixture of **1a**, *t*-BuOK, and DBN at 130 °C under N_2 for 4 h in the absence of solvent, >95% pure **2a** was obtained in a 24% yield. On the other hand, the coupling reaction of **1a** using a larger amount of *t*-BuOK (9 equiv) in the presence of DBN was found to give **2a** in >90% yield under similar reaction conditions, while **1a** was mostly recovered in the absence of DBN. The use of both *t*-BuOK and DBN in amounts of 3 equiv or more seems to be requisite for the efficient formation of **2a**, since attempted reactions using an equimolar mixture of **1a**, *t*-BuOK, and DBN under various reaction conditions gave only poor results. A further notable observation of synthetic significance is that this reaction was remarkably affected by solvents. Diglyme was found to be the most favorable solvent among those examined in the present investigation. Quinoline can be used as an equally effective solvent, and toluene is also an effective, but less favorable, solvent. The reactions of a 1:3:4 mixture of **1a**, *t*-BuOK, and DBN using each of these solvents gave **2a** in 73% to >90% yields, much higher than the yield (24%) in the absence of solvent. On the other hand, such solvents as 1-methylpyrrolidone, DMF, tetramethylurea, and decaline exerted unfavorable effects on the coupling reaction of **1a**; yields (7–17%) are very poor, and purities (21–89%) of the isolated **2a** are not high. Moreover, no reaction of **1a** occurred at all in the presence of DMSO, ethylene glycol, hexanol, and water, which are all acidic enough to quench *t*-BuOK. This finding indicates that *t*-BuOK paired with DBN should play an essential role in the coupling reaction.

Thus, we established optimum reaction conditions for the efficient coupling reaction of **1a**. A typical run is as follows. After a mixture of *t*-BuOK (9 mmol), DBN (12 mmol), and 3 mL of diglyme had been heated at 130 °C for 1 h, **1a** (3 mmol) was added to this mixture while keeping the temperature at 130 °C, and then the mixture was vigorously stirred for 3 h at 130 °C. After the reaction mixture had been cooled to room temperature, a solid was collected by filtration and then treated with water to give pure **2a** in quantitative yield (0.58 g from 0.59 g of **1a**). This product shows an absorption maximum at 595 nm ($\epsilon = 8.1 \times 10^4$), which is almost identical with that (595 nm, $\epsilon = 7.8 \times 10^4$) of an authentic sample obtained by a known method.[3]

The reaction of **1a** was investigated in more detail as follows. (1) The coupling reaction of **1a** efficiently occurred under Ar or N_2, while the reaction under O_2 resulted in poor yield of **2a** (<20%). (2) When all the reactants were admixed and heated at 130 °C, **2a** was again formed but in a slightly lower yield (85%) compared with the run in which the *t*-BuOK/DBN pair had been preheated prior to the reaction of **1a**. (3) The leuco form of **2a** was not significantly detected during the course of the reaction, while the leuco form dye prepared according to a known method[2] was recovered for the most part even after heating at 130 °C under Ar in the presence of *t*-BuOK, DBN, and diglyme for 4 h. (4) The coupling reaction of 4,5-dideuterio-1,8-naphthalimide (**1a**-d_2) was extremely inefficient, showing a large net isotope effect in the formation of **2a**; (yield of **2a** from **1a**)/(yield of **2a** from **1a**-d_2) was >90 under identical reaction conditions. (5) No reduction of DBN to the saturated compound or to the half-reduced dimers of **1a** was observed. These reduced compounds would be possible reduction products accompanied by the apparent oxidative coupling reactions. (6) No reaction of **1a** occurred at all in the presence of 18-crown-6 used in place of diglyme; this crown ether is known to bind K^+.[10]

Direct Coupling Reactions of Various Arenes. As shown in Table 1, the *t*-BuOK/DBN reagent was successfully applied to the coupling reactions of the other related arenes (**1b**–**p**) under modified reaction conditions (II–V). The corresponding products (**2b**–**k**) were isolated in moderate to excellent yields and were fully characterized by direct comparison with authentic samples. In all cases except for **1j**, the reactions were carried out at 170 °C, since yields of the products were lower at lower reaction temperatures but were not significantly improved at 180–200 °C. The amounts of *t*-BuOK and DBN used under the reaction conditions II–V were 2 or 3 times more than those used under the optimum conditions for the reaction of **1a**. Otherwise, yields of the products were significantly or largely lower than those listed in Table 1. Thus, the coupling reactions of N-substituted naphthalimides proceeded quantitatively in the cases of 1-methyl- and 1-cyclohexyl-1,8-naphthalimides (**1b** and **1d**) under the conditions II and III, respectively, and in

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[10] Pearson, D. E.; Buehler, C. A. *Chem. Rev.* **1974**, *74*, 45.

Table 1. Coupling Reactions of Various Arenes

reactants	products	conditions[a]	yield/%
1a	**2a**	I	>95
1b	**2b**	II	>95
1c	**2c**	III	36
		IV	45
		V	43
1d	**2d**	III	>95
1e	**2e**	IV	47
1f	**2f**	IV	67
1g	**2g**	V	48
1h	**2h**	V	52
1i	**2i**	IV	57
1j	**2j**	I	26
		IV	28
		V	25
1k	**2k**	IV	12
		V	15
1l	**2l**	V	90
1m	**2m**	IV	28
1n	**2n**	IV	55
1o	**2o**	IV	78
1p	**2p**	II	>95

[a] For the reactions of **1a**−**p** (3 mmol) at 130 °C (**1a** and **1j**) and at 170 °C (the other arenes) using the reactants and solvent in the following ratios: *t*-BuOK (mmol)/DBN (mmol)/solvent (mL) = (I) 9:12:3 (diglyme as solvent); (II) 18:24:0 (no solvent); (III) 18:24:3 (diglyme as solvent); (IV) 27:27:3 (diglyme as solvent); and (V) 27:27:5 (quinoline as solvent).

moderate yields in the other cases under the condition IV or V where the major difference is the solvent used (diglyme or quinoline). These results appear to be of synthetic interest compared with the classical alkaline-fusion method which is effective only for the coupling reaction of short-chain *N*-alkyl-1,8-naphthalimides.[4] Moreover, the other functional arenes (**1l**−**p**) also underwent the coupling reactions at 170 °C to give the products (**2l**−**p**) in moderate to excellent yields. An interesting example is the coupling reaction of **1o** since the yield (78%) of **2o** is remarkably higher than that (0.7%) in the alkaline-fusion reaction of **1o** using a 32-fold excess of KOH at 235−245 °C.[11] Moreover, it should be noted that large-scale syntheses can be easily achieved for all the coupling products described above. For instance, a 30-fold scale reaction of **1a** gave 6 g of **2a** (99% yield) along with >90% recovery of DBN and diglyme.

Mechanistic Investigation. The present investigation clearly demonstrates that the *t*-BuOK/DBN pair does work as an excellent base reagent for the aryl coupling reactions. However, a crucial question should emerge as to why the present reactions did not yield the leuco form compounds as the initial products unlike the conventional alkaline-fusion reactions. To obtain a reasonable understanding of the mechanistic pathways, we investigated the coupling reaction of **1a** in more detail using the reagents which had been thoroughly dried. After the heating of a mixture of **1a**, *t*-BuOK, and DBN in diglyme at 130 °C under dry Ar, the reaction mixture was carefully filtered in an Ar-filled drybox, and then the collected solid (**D**) was thoroughly washed with deaerated dry diglyme under Ar. This solid (**D**) is not **2a** or its leuco form **F**[2] (vide infra) but an extremely deliquescent and air-sensitive compound. When **D** was treated with water under air, **2a** was formed in quantitative yield, as described in the previous section. Moreover, even careful treatment of **D** with thoroughly deaerated water under Ar did not give **F** but **2a** in 5% yield, probably due to the oxidation by a small amount of air contaminated in Ar and/or water. On the other hand, we confirmed that the oxidation of the leuco dye to **2a** requires extensive bubbling of air into a suspension of the leuco dye in water.[3,4] Since atomic absorption analysis of the filtrate obtained after water treatment of **D** showed the presence of K, **D** can be considered to be a potassium-containing precursor that is readily air-oxidized to **2a** in the presence of water.

Unfortunately, all attempts failed to determine the exact structure of **D** because this compound is extremely deliquescent and essentially insoluble in water as well as in conventional organic solvents. Mass spectra (EI, DI, and FAB) of **D** and **F** exhibited similar complex fragmentation patterns but no signal assignable as the expected parent peak. Since **D** and **F** are substantially soluble in such highly acidic media as concentrated sulfuric acid and CF_3CO_2H, we attempted to take their ^1H NMR spectra in D_2SO_4 and CF_3CO_2D. Unfortunately, only the signals assignable to **1a** were detected, indicating that the two compounds are commonly decomposed into **1a** without the formation of **2a** in the strong acids. On the other hand, **2a** was confirmed to be stable in the acids. A structure difference between **D** and **F** is indicated by their FTIR spectra, which were carefully taken under dry Ar for KBr disks that had been prepared under dry Ar. As shown in Figure 1, the spectral features of the two compounds in the region of 400−1600 cm^{-1} are very similar to each other but significantly different from that for **2a**. It is therefore suggested that **D** has a skeletal arrangement similar to that of **F** but is different from the highly symmetric structure of **2a**. On the other hand, substantial differences between **D** and **F** can be seen in the N−H and C═O absorption regions. Both **F** and **2a** show similar N−H absorption behavior characteristics of imides, i.e., a weak broad band at 3300−3600 cm^{-1} for free N−H and a strong one at ~3180 cm^{-1} for bonded N−H. In the case of **D**, however, a broad strong band appears at ~3400 cm^{-1} but little absorption due to bonded N−H can be seen at 3100−3200 cm^{-1}. While the C═O absorption of **F** occurs at 1660 and 1635 cm^{-1}, **D** shows a sharp band at 1635 cm^{-1} with a weak shoulder at ~1690 cm^{-1}. These spectral features strongly suggest that **D** has no discrete CO−NH−CO linkage unlike **F** and **2a**.

To explain the IR spectra as well as the chemical and physical nature of **D**, we assume that **D** is a potassium salt of the enolate form of the leuco dye as shown in Scheme 1. This structure can reasonably explain the IR spectral behavior, i.e., the lack of bonded N−H absorption and the appearance of a single C═O band at significantly lower frequency compared with that of **2a** (1690 cm^{-1}). The broad absorption at ~3400 cm^{-1} might arise from adsorbed water and, at least in part, from free N−H and/or enol O−H formed by partial hydrolysis of **D** with adsorbed water. The shoulder at 1690 cm^{-1} would be due to partial formation of **2a** by oxidation of **D** which might occur during the preparation of KBr disks.

On the basis of the above arguments, a working hypothesis is shown in Scheme 1 for possible explanation of the mechanistic pathways. We assume that an active species **A** would be generated from the *t*-BuOK/DBN pair preferably upon preheating the pair. This species should be capable of undergoing the proton abstraction from the 4-position of **1a** at 130−170 °C to generate arylide anion

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[11] Bradley, W.; Pexton, F. W. *J. Chem. Soc.* **1954**, 4436.

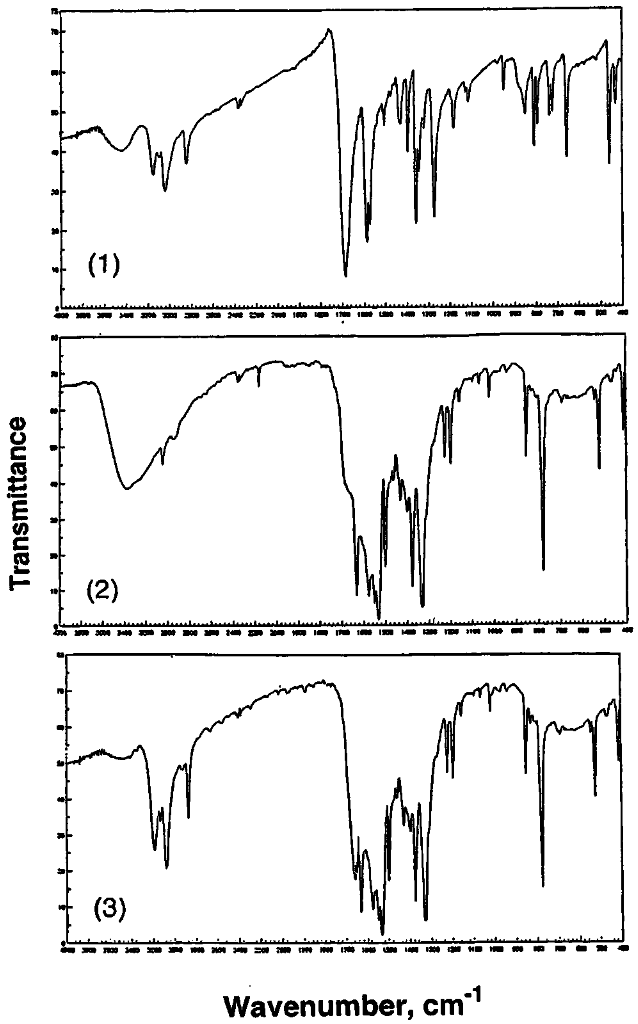
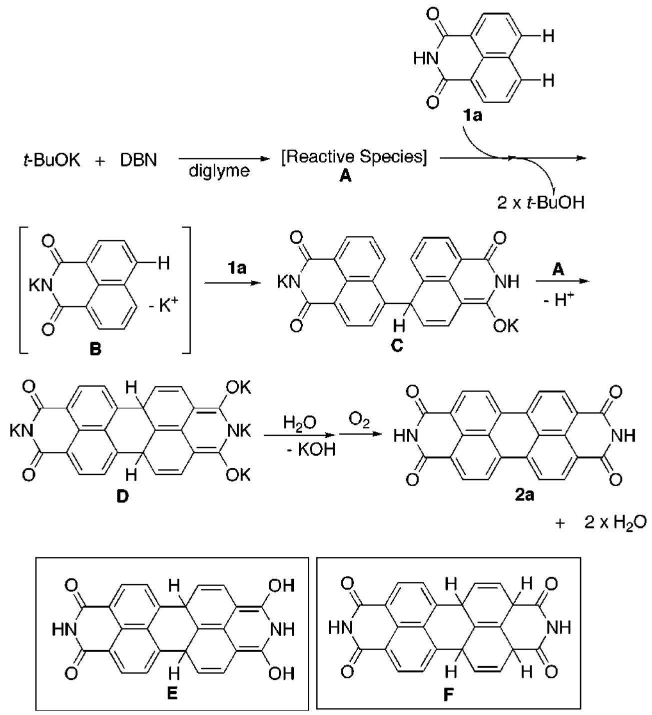


Figure 1. IR spectra of (1) **2a**, (2) intermediate **D**, and (3) leuco form dye **F**.

B. The nucleophilic addition of arylide anion **B** to **1a** generates adduct **C** which then undergoes the base-promoted cyclization to give the deliquescent initial product, **D**. Presumably, K^+ should play essential roles in the formation of **A** and also in the following reaction pathways since either *t*-BuOLi or *t*-BuONa is ineffective. Compared with hard cations Li^+ and Na^+, strong binding of soft cation K^+ with DBN would occur to generate the key base reagent **A** and, moreover, the arylide anion paired with K^+ would be highly nucleophilic to undergo the initial addition to **1a**. With regard to the final product formation, it is not well understood why **D** did not give enol **E** or leuco-form **F** but underwent the exclusive air oxidation to **2a**. However, it should be noted that possible reactions of **D** in water proceed in the solid state. We assume that the air oxidation of **D** to **2a** would efficiently occur even in the solid state[12] while both the hydrolysis of **D** to enol **E** and its isomerization to **F** would be very slow in the solid state. This seems to be the reason the leuco dye was not isolated in the present reactions.

In summary, the *t*-BuOK/DBN pair has proven to be a potential reagent that can efficiently promote the coupling reactions of the arenes under mild reaction conditions. Another interesting observation of mechanistic interest is the lack of leuco dye formation in the present reactions, providing a possible insight into the mechanisms of the alkaline-fusion reactions that are still unknown in detail. Finally it should be noted that the *t*-BuOK/DBN reagent is potentially applicable to other types of base-promoted reactions of compounds containing very low acidic CH. Efforts for further synthetic applications are underway.

Scheme 1



Experimental Section

General Methods. Potassium *t*-butoxide (*t*-BuOK), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), diglyme, 1,8-naphthalimide (**1a**), and 7*H*-benz[*de*]anthracen-7-one (**1p**) (Wako Pure Chamicals Industries, Ltd.) were used as received. The naphthalene compounds (**1b-n**) were prepared by usual condensation reactions of 1,8-naphthalic anhydride with the corresponding primary amines, *o*-phenylenediamine, 4,5-dimethyl-1,2-diaminobenzene, and 1,3-propanediamine, and acenaphtho-[1,2-*b*]quinoxaline (**1o**) was obtained from acenaphthenequinone and *o*-phenylenediamine (Chart 2). Preparation of **1a**-d_2 was performed according to the procedures shown in Chart 2 as follows: 4,5-Dibromoacenaphthene prepared by the bromination of acenaphthene with NBS in DMF[14] was lithiated with BuLi in THF at −78 °C and then quenched by D_2O to give 4,5-dideuterioacenaphthene in 24% yield. The dichromate oxidation of this compound followed by the condensation with NH_3 gave the analytical pure imide **1a**-d_2 in 24% over all yield. Unless stated otherwise, all the other reagents and chemicals were obtained commercially and used without further purification.

General Procedure for the Oxidative Coupling of Arenes by the *t*-BuOK/DBN System. As a typical run, the coupling reaction of **1a** is shown as follows. A 30-mL three-necked round-bottom flask was charged with *t*-BuOK (1.01 g, 9 mmol), DBN (1.49 g, 12 mmol), and diglyme (3 mL), and a

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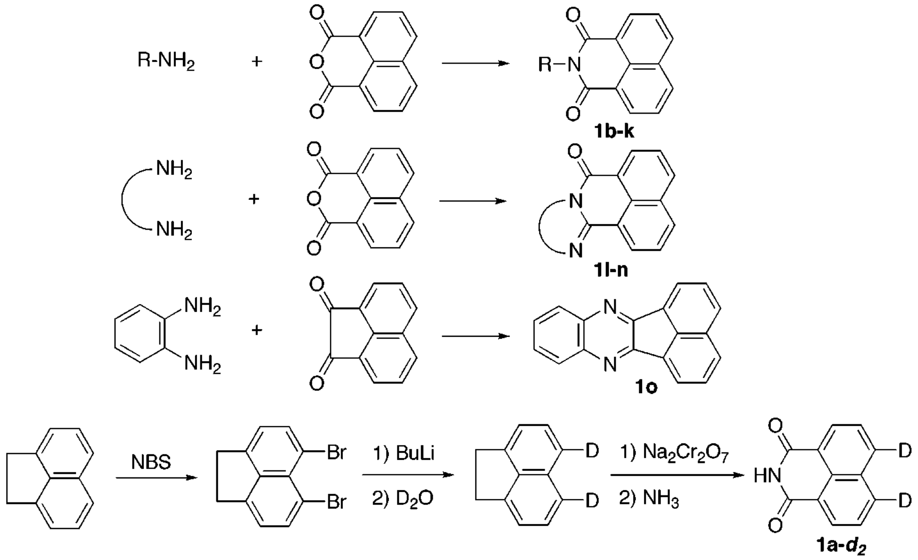
[12] It was recently reported that an enol dihydroaromatic intermediate involved in the KOH-catalyzed bisimide−lactam ring construction of N,N′-substituted naphthalene-1,8:4,5-tetracarboxylic bisimides is relatively stable in oxygen-free solution but instantly oxidized upon exposure to air.[13]

[13] Langhals, H.; von Unold, P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2234.

[14] Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

Chart 2



Teflon-coated stirring bar was added. The mixture was stirred vigorously at 130 °C for 1 h under N_2, and then, **1a** (0.59 g, 3 mmol) was added and stirred at the same temperature for 3 h. The mixture was cooled to room temperature and filtered. The collected solid was washed with diglyme (10 mL × 3). Distillation of the combined filtrate under reduced pressure gave 32 mL of a mixture of diglyme and DBN. The solid was washed with water (10 mL × 3), acetone (10 mL × 3), and dichloromethane (10 mL × 3) and then dried at 120 °C for 6 h under reduced pressure to give >95% pure **2a** (0.58 g, 99%). This reaction using 30-fold amounts of **1a** (17.75 g, 90 mmol), *t*-BuOK (30.3 g, 270 mmol), DBN (44.71 g, 360 mmol), and diglyme (90 mL) was undertaken under identical reaction conditions to give 17.39 g of pure **2a** (99% yield) after the isolation procedures described above.

Isotope Effect for the Oxidative Coupling of the 1a-*d*$_2$ by *t*-BuOK/DBN System. The reaction of **1a**-*d*$_2$ (0.6 g, 3 mmol) using *t*-BuOK (1.01 g, 9 mmol), DBN (1.49 g, 12 mmol), and diglyme (3 mL) was undertaken under conditions identical to those for **1a** described above. The mixture was cooled to room temperature and filtered. The collected solid was washed with water (10 mL × 3), acetone (10 mL × 3), and dichloromethane (10 mL × 3) and then dried at 120 °C for 6 h under reduced pressure to give 0.006 g of pure **2a** (yield, 1%). Acid treatment of the combined organic filtrate followed by filtration of the solid gave 0.57 g of **1a**-*d*$_2$ (95% recovery).

Isolation and Water-Treatment of Compound D. All the operations were performed in an Ar-filled drybox. The reaction of **1a** (0.59 g, 3 mmol) was undertaken under conditions identical to those described above, and then the mixture cooled to room temperature was filtered and washed with dry diglyme (5 mL). GC analysis of the filtrate indicated the presence of *t*-BuOH (5.7 mmol). The collected solid was further washed with dry diglyme (10 mL × 3) and dry acetone (10 mL × 3) and then dried at room temperature for 5 h under reduced pressure to give 0.81 g of light brown deliquescent solid **D**; IR (KBr) 2600−3680, 1640, 1580, 1535, 1330, 780, 530 cm^{-1}. To a dried 30-mL three-necked round-bottom flask connected with a dropping funnel was added the obtained solid **D** (0.81 g), and then water (3 mL) was added dropwise to the flask. The mixture was filtered and the collected solid was then washed with water (10 mL × 2), acetone (10 mL × 2), and dichloromethane (10 mL × 2) and then dried at 120 °C for 6 h under reduced pressure to give pure **2a** (0.57 g, 98%). Atomic absorption analysis of the filtrate indicated the presence of K$^+$ (6 mmol).

Acknowledgment. We are indebted to the Analysis Center of Dainippon Ink & Chemicals Co. for analytical support of this work.

Supporting Information Available: ^{1}H NMR, IR, and MS spectral data of **2a**−**p**. This material is available free of charge via the Internet at http://pubs.acs.org.

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