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# Naphthalene-1,8-diylbis(diphenylmethylium) as an Organic Two-Electron Oxidant: Benzidine Synthesis via Oxidative Self-Coupling of *N*,*N*-Dialkylanilines

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*Received March 28, 2006*

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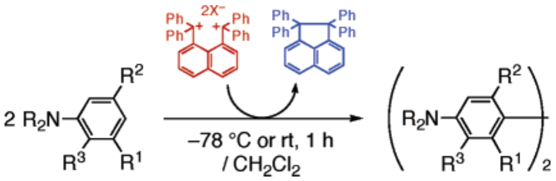

Naphthalene-1,8-diylbis(diphenylmethylium) exhibits a unique electron-transfer reduction behavior due to the close proximity of the two triarylmethyl cations, which form a C−C bond while accepting two electrons, leading to 1,1,2,2-tetraphenylacenaphthene. The preparation of the dication was readily accomplished under anhydrous conditions starting from a cyclic bis(triarylmethyl) ether, derived from 1,8-dibromonaphthalene. The process proceeded via deoxygenation accompanying the formation of a disiloxane on treatment with a silylating agent (Me$_3$SiClO$_4$ or Me$_3$SiOTf) in 1,1,1,3,3,3-hexafluoropropan-2-ol. The dication was successfully employed for oxidative coupling of *N*,*N*-dialkylanilines at the para-position to afford the corresponding benzidines in good to excellent yield.

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## Introduction

Carbocations generally exist as short-lived intermediates, which are immediately converted to more stable compounds via reactions such as rearrangement, elimination, and addition. While the detailed studies of carbocations with NMR, IR, and X-ray crystal structure analysis have been accomplished by Olah and others,[1] their applications as synthetic reagents are still limited. Among them, triarylmethyliums, which are rather stable carbocations and are readily prepared from the corresponding alcohols or halides,[2] constitute a class of versatile carbocations with functions[3] such as hydride and alkoxy abstraction[4] and Lewis acid catalysis.[5]

Recently, dicationic systems in which two triarylmethylium ions were linked by a carbon skeleton, such as 1,1′-biphenyl-2,2′-diyl,[6] 1,1′-binaphthalene-2,2′-diyl,[7] and naphthalene-1,8-diyl[8,9] groups, have been prepared and exhibited unique electrochemical properties. These dications were reduced with two electrons leading to the corresponding stable neutral compounds 1,1,1,2,2,2-hexaarylethane derivatives, as exempli-

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(2) (a) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201. (b) Fukui, K.; Ohkubo, K.; Yamabe, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 312.

(3) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons Ltd.: Chichester, UK, 1995; Vol. 8, pp 5348−5357.

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10.1021/jo060662s CCC: $33.50

**SCHEME 1. Dication as an Organic Two-Electron Oxidant**

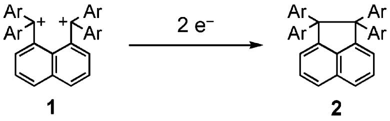
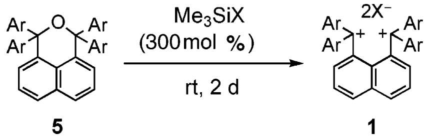


**TABLE 1. Preparation of Naphthylene-1,8-diylbis(diarylmethylium) Salts 1a−c**



| entry | Ar | X | solvent | **1**/% |
|---|---|---|---|---|
| 1 | $C_6H_5$ | $ClO_4$ | $CH_2Cl_2$ | no reaction |
| 2 | $C_6H_5$ | $ClO_4$ | toluene | no reaction |
| 3 | $C_6H_5$ | $ClO_4$ | benzene | no reaction |
| 4 | $C_6H_5$ | $ClO_4$ | HFIP | 93 (**1a**) |
| 5 | $C_6H_5$ | OTf | HFIP | 99 (**1b**) |
| 6 | $C_6H_4$-4-OMe | $ClO_4$ | HFIP | 76 (**1c**) |

fied in Scheme 1. Such C−C bond formation between two carbocation centers was not observed in the one-electron reduction of triphenylmethylium (trityl cation), which afforded a dimer with a quinoid structure.[10]

Bis(triarylmethylium) **1** (Ar = Ph) with a naphthalene-1,8-diyl tether was first introduced by Gabbaï as the $BF_4^-$ salt,[8b] and we accomplished an independent synthesis of the $ClO_4^-$ and $TfO^-$ salts.[9b] Dication **1** has two cationic centers in closest proximity, which brings about an especially high reduction peak potential compared with those of other bis(triarylmethylium)s and triarylmethyliums in cyclic voltammogram analysis.[8a,c] Moreover, steric congestion around the cationic centers in **1** prevents nucleophilic attack at the carbocation, which might allow oxidation of nucleophilic species. Despite these advantages as a reagent for electron-transfer oxidation, there had been no reports on its application in organic synthesis until our recent reports.[9]

*N*,*N*,*N*′,*N*′-Tetraarylated benzidines have recently received much interest because of their tunable electric conductivity, which finds diverse applications such as organic light-emitting diodes, organic field-effect transistors, organic solar cells, and organic photoconductors.[11a] Oxidative coupling of aniline derivatives provides efficient access to benzidines. Although several methods for the oxidative coupling with clay,[12a] a molten salt,[12b] a peroxide,[12c] $VCl_4$,[12d] or an electrochemical process[13] have been reported, most of them are low-yielding processes. Among these methods, $TiCl_4$-mediated oxidative coupling seemed the most practical to afford benzidines, despite the requirement of a large excess amount of starting anilines.[11]

These facts prompted us to use dication **1** in the electron-transfer oxidation of *N*,*N*-dialkylanilines, nucleophilic substrates. We have thus achieved the synthesis of benzidines via oxidative coupling of a variety of anilines. After our preliminary report,[9b] Xi's group reported practical methods for a similar coupling with $Ce(NH_4)_2(NO_3)_6$ (CAN)[14a] or $CuBr/H_2O_2$,[14b] although neither approach was applied to anilines functionalized on the benzene rings. On the other hand, reductive coupling of 4-haloanilines with a palladium catalyst (Ullmann-type coupling) readily occurred to produce benzidines in good yield under mild conditions, although its scope for benzidine synthesis is unclear.[15]

Herein we give a full account of a convenient method for the preparation of naphthalene-1,8-diylbis(diarylmethylium)s **1** and their application as a new organic oxidant to the coupling reaction of aniline derivatives leading to benzidine synthesis.

## Results and Discussion

**(a) Preparation of Dications 1.** Bis(triarylmethylium)s with a carbon tether were previously prepared on treatment of the corresponding diols with aqueous $HBF_4$ or $HClO_4$ in $Ac_2O$, $(EtCO)_2O$, or $(CF_3CO)_2O$.[6−8] These methods had a drawback in purification of the produced dications, due to the low volatility of water, acid anhydrides, and in situ-generated carboxylic acids. Therefore, the development of a convenient and practical method for the dications was still required to isolate them in a pure form so that they could be used as synthetic reagents. Our synthetic plan relied on the following two features: (1) dications **1** would be generated from cyclic ethers **5** via deoxygenation and (2) this process would proceed readily in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) solvent (Table 1). Treatment of **5** with a strong silylating agent was expected to allow removal of the oxygen as a disiloxane ($R_3SiOSiR_3$), leading to the desired dications under anhydrous conditions. HFIP would assist the generation of the dications and be easily removed afterward, due to its strong ionizing power, low nucleophilicity, and high volatility.[16]

Benzophenones were added to the dilithium species, prepared by treating 1,8-dibromonaphthalene **3** with *n*-BuLi, to afford the crude diols **4**.[17] On successive treatment of their $CH_2Cl_2$ solution with a catalytic amount of $CF_3CO_2H$ and then MeOH, cyclic ethers **5a** and **5b** (the precursors of dications **1a−c**) were obtained as white crystals in 80% and 48% yield from **3** by filtration, respectively (Scheme 2). Thus, neither extraction nor purification was needed to isolate **5**. The procedure for cyclic ethers **5** was also applied to the preparation of cyclic ether **8** (the precursor of dication **9**) starting from diester **6**.[18]

Cyclic ether **5a** was treated with $Me_3SiClO_4$, prepared in situ from $AgClO_4$ and $Me_3SiCl$ in toluene,[19] to deoxygenate it. Whereas **5a** was recovered unchanged in $CH_2Cl_2$, toluene, or benzene, only HFIP allowed deoxygenation of **5a** successfully as expected to afford the desired dication **1a** (X = $ClO_4$) in

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[11] (a) Gerstner, P.; Rohde, D.; Hartmann, H. *Synthesis* **2002**, 2487 and references therein. (b) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2000**, *65*, 3548.

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[13] (a) Vettorazzi, N.; Fernandez, H.; Silber, J. J.; Sereno, L. *Electrochim. Acta* **1990**, *35*, 1081. (b) Mizoguchi, T.; Adams, R. N. *J. Am. Chem. Soc.* **1962**, *12*, 178.

[14] (a) Xi, C.; Jiang, Y.; Yang, X. *Tetrahedron Lett.* **2005**, *46*, 3909. (b) Jiang, Y.; Xi, C.; Yang, X. *Synlett* **2005**, 1381.

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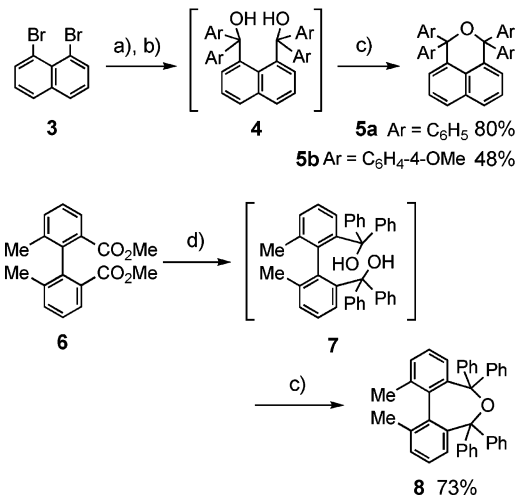
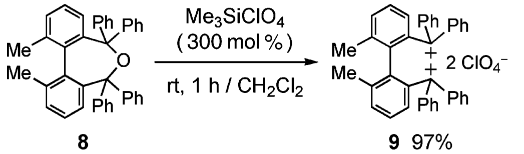
**SCHEME 2. Preparation of Cyclic Ethers 5 and 8 (Precursors of Dications 1 and 9)**[a]

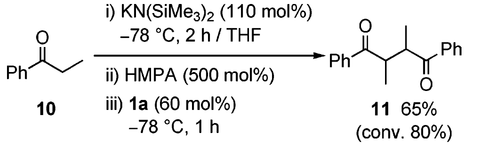


[a] Reagents and conditions: (a) *n*-BuLi (220 mol %), rt, 2 h/$Et_2O$. (b) $Ar_2CO$ (240 mol %), reflux, 4 h. (c) $CF_3CO_2H$ (10 mol %), rt, 10 h/$CH_2Cl_2$. (d) PhLi (500 mol %), −78 °C, 1 h/THF.

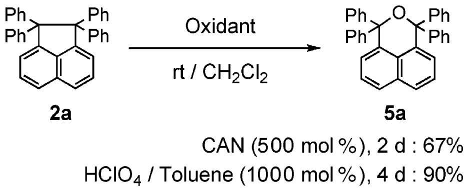
**SCHEME 3. Synthesis of 6,6′-Dimethyl-1,1′-biphenyl-2,2′-diylbis(diphenylmethylium) (9)**



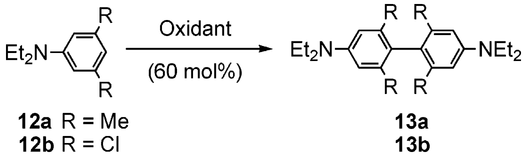
**SCHEME 4. Oxidative Coupling of Enolate**



**SCHEME 5. Reoxidation of Acenaphthene 2a to Cyclic Ether 5a (Precursor of Dications 1a and 1b)**



**SCHEME 6. Oxidative Coupling of Anilines 12**



93% yield as dark red crystals (Table 1, entry 4). Dication **1b** (X = OTf) was also prepared from **5a** in quantitative yield on treatment with $Me_3SiOTf$ instead of $Me_3SiClO_4$ under similar conditions (entry 5).[20] $Me_3SiBF_4$, $Me_3SiPF_6$, $Me_3SiSbF_6$, and $Me_3SiReO_4$ gave no dications with the corresponding countercation.

We also prepared dication **9** bearing a 1,1′-biphenyl-2,2′-diyl backbone for comparison. In contrast to dications **1a** and **1b**, **9** was much more easily generated at room temperature for only 1 h on treatment of **8** with $Me_3SiClO_4$ in $CH_2Cl_2$ without HFIP (Scheme 3).

**(b) Dications 1 as an Oxidizing Agent.** We first examined the oxidation behavior of dications **1** toward nucleophilic substrates in the reaction with metal enolates as an example of an anionic species. When the potassium enolate generated from propiophenone (**10**) was treated with 60 mol % of **1a** in the presence of hexamethylphosphoric triamide (HMPA) at −78 °C, the expected self-coupling product **11**, 2,3-dimethyl-1,4-diphenylbutane-1,4-dione, was obtained in 65% yield (80% yield based on the consumed **10**, *dl*/*meso* = 65/35).[21] The addition of the enolate to dication **1a** was suppressed in contrast to trityl cation, probably due to steric hindrance around the cations (Scheme 4). Thus, dication **1a** was found to act as an organic one-electron-transfer oxidant even for nucleophilic substrates.

During the reaction, **1a** was reduced to acenaphthene **2a** via C−C bond formation between the two carbocation centers. While **2a** regenerated **1a** by reoxidation with $HClO_4$ in HFIP, isolation of cyclic ether **5a**, a stable precursor of dications **1a** and **1b**, after an aqueous workup was more practical. On treatment with CAN or $HClO_4$, **2a** was transformed to **5a** in 67% or 90% yield, respectively (Scheme 5). Acenaphthene **2a** can now be recycled, which makes the dication oxidants practical.

**(c) Synthesis of Benzidines.** Oxidation of anilines with dications **1** was then investigated. On treatment of *N*,*N*-diethyl-3,5-dimethylaniline **12a** ($E^{ox} = 0.32$ V vs $Fc/Fc^+$) with a small excess amount (60 mol %) of **1a** or **1b**, the reaction proceeded smoothly even at −78 °C to give exclusively the desired para-coupled bisaniline, *N*,*N*,*N*′,*N*′-tetraethylbenzidine **13a**, in 98% or 93% yield, respectively (Scheme 6; Table 2, entries 1 and 2). Dications **1** were quantitatively recovered as acenaphthene **2a**, which indicates that **1a** and **1b** acted as a two-electron oxidant in the coupling reaction of **12a**.[22] Dication **1c** bearing methoxy groups on the four benzene rings was less effective in this reaction, giving **13a** in 57% yield (entry 3), presumably due to its lower oxidizing power.[23] Dication **9** with a biphenyl backbone gave a complex mixture, and $Ph_3C^+BF_4^-$ afforded no coupling products, partly due to the nucleophilic attack of **12a** on the cations (entries 4 and 5). These facts clearly suggest that two methylium ions in close proximity are essential for efficient oxidation.

Moreover, other oxidants such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), a triarylaminium radical cation [$(4\text{-}BrC_6H_4)_3N^{+\bullet}\ SbCl_6^-$], and $Ce(NH_4)_2(NO_3)_6$ (CAN), which are widely used in organic synthesis, were also examined in the coupling reaction. Treatment of **12a** with DDQ or $(4\text{-}BrC_6H_4)_3N^{+\bullet}\ SbCl_6^-$ gave no oxidation products or many side products other than **13a**, while **13a** was obtained in 83% yield with CAN at room temperature (entries 6−8). To investigate the difference in reactivity between the dication **1a** and other oxidants such as CAN, $FeCl_3$, $PhI(OAc)_2$, and $PhI(OCOCF_3)_2$, we examined the oxidative coupling of 3,5-dichloro-*N*,*N*-

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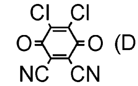
[20] The $TfO^-$ salt **1b** is more moisture sensitive than **1a** and has to be handled and stored with care.

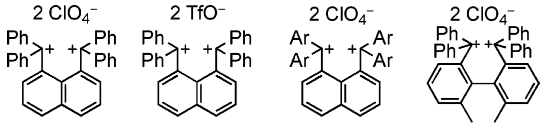
[21] Schmittel, M.; Burghart, A.; Malisch, W.; Reising, J.; Söllner, R. *J. Org. Chem.* **1998**, *63*, 396.

[22] Electron-rich benzenes other than anilines, such as anisole and di- and trimethoxybenzenes, gave no dimeric products on treatment with dication **1a**.

[23] The reduction peak potentials of dications **1** (Ar = Ph and $C_6H_4$-4-OMe) were reported to be 0.20 and −0.17 V vs $Fc/Fc^+$, determined from the cyclic voltammogram of **2a** and **1c**, respectively.[8a,c]

**TABLE 2. Oxidative Coupling of Aniline 12a**[a]

| entry | oxidant | yield of **13a** /% |
|---|---|---|
| 1 | **1a** | 98 |
| 2 | **1b** | 93 |
| 3 | **1c** | 57 |
| 4 | **9** | complex mixture |
| 5 | $Ph_3C^+BF_4^-$ (120 mol%) | 0 |
| 6 |  (DDQ) | 0 |
| 7 | $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (120 mol%) | <50 |
| 8[b] | $Ce(NH_4)_2(NO_3)_6$ (CAN) (120 mol%) | 83 |



**1a** **1b** **1c** **9**

Ar : 4-MeOC$_6$H$_4$

[a] −78 °C, 1 h/CH$_2$Cl$_2$. [b] rt, 2 h/MeCN−H$_2$O.

**TABLE 3. Oxidative Coupling of Aniline 12b**[a]

| entry | oxidant | time/h | yield of **13b**/% |
|---|---|---|---|
| 1 | **1a** | 1 | 78 |
| 2[b] | CAN (120 mol %) | 24 | 12 |
| 3 | $FeCl_3$ (120 mol %) | 24 | 24 |
| 4 | $PhI(OAc)_2$ | 24 | 0 |
| 5 | $PhI(OCOCF_3)_2$ | 24 | 7 |

[a] rt/CH$_2$Cl$_2$. [b] rt/MeCN−H$_2$O.

**SCHEME 7. Plausible Reaction Mechanism for the Oxidative Coupling of 12**

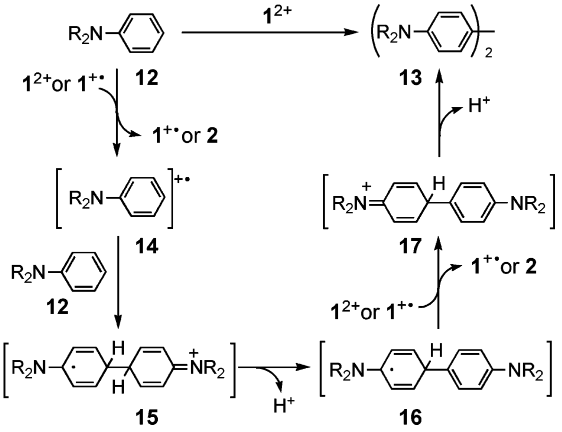
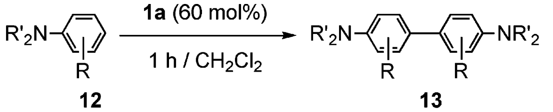
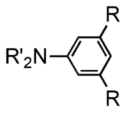
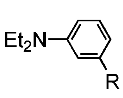
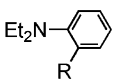


**TABLE 4. Synthesis of Benzidines 13 from Aniline 12**



| entry | 12 | R | R' | 12 | temp. | yield /% |
|---|---|---|---|---|---|---|
| 1 |  | Me | Me | **12c** | −78 °C | 95 |
| 2 | | Me | Et | **12a** | −78 °C | 98 |
| 3 | | Me | Allyl | **12d** | rt | 81 |
| 4 | | Me | Bn | **12e** | −78 °C | 77 |
| 5 | | Cl | Et | **12b** | rt | 78 |
| 6 |  | Me | — | **12f** | −78 °C | 55 |
| 7 | | OMe | — | **12g** | −78 °C | ca. 10 |
| 8 | | Cl | — | **12h** | rt | 74 |
| 9 | | Br | — | **12i** | rt | 86 |
| 10 | | CO$_2$Et | — | **12j** | −78 °C | 80 |
| 11 |  | H | — | **12k** | −78 °C | 49 |
| 12[a] | | H | — | **12k** | −78 °C | 66 |
| 13 | | Me | — | **12l** | −78 °C | 39 |
| 14 | | OMe | — | **12m** | −78 °C | 39 |

[a] 2,6-Di-*tert*-butylpyridine (240 mol %) was added. **1a** (120 mol %) was employed.

diethylaniline (**12b**) ($E^{ox} = 0.73$ V vs Fc/Fc$^+$), whose oxidation potential is higher than that of **12a**.[24] The reaction of **12b** with **1a** was complete at room temperature in 1 h to afford **13b** in 78% yield, whereas the other oxidants used here gave poor results (Scheme 6, Table 3). Dication **1a** proved far more efficient as an oxidant to produce benzidine **13b** from **12b**.

A plausible reaction mechanism for the oxidative coupling with **1** is shown in Scheme 7. Dication **1** oxidizes *N*,*N*-dialkylaniline **12** to generate cation radical **14**, which in turn reacts with **12**, leading to the coupled cation radical **15**. Deprotonation of **15** gives radical **16**, which is further oxidized to cation **17** with dication **1** or its one-electron reduced form. Dimer **13** is finally produced after deprotonation of **17** and exists in equilibrium with its ammonium salt. Overall, dication **1** is transformed to acenaphthene **2** via two-electron reduction, effected by two molar amounts of *N*,*N′*-dialkylaniline **12**.

To expand the scope of the present oxidative coupling, several other *N*,*N*-dialkylanilines were treated with **1a**. As summarized in Table 4, all of the coupling reactions occurred regioselectively to afford the para-coupled dimer of *N*,*N*-dialkylanilines without formation of ortho- and meta-coupled products. *N*,*N*-Dimethylaniline **12c** gave the corresponding benzidine **13c** in 95% yield without demethylation on the nitrogen atom, which has been reported to occur in its oxidation.[25] Furthermore, the self-coupling proceeded successfully even when the aniline nitrogen had removable protecting groups such as allyl or benzyl groups (entries 3 and 4). However, the reactions of *N*-unsubstituted and *N*-monoethylated anilines led to complex mixtures, and no reaction was observed with *N*-acylated anilines. Dimers **13** were obtained in high to excellent yield from 3,5-disubstituted and 3-halogenated *N*,*N*-dialkylanilines **12a**−**e**, **12h**, and **12i** (entries 1−5, 8, and 9). Aniline **12j** bearing an ethoxycarbonyl group at the 3-position was transformed to the corresponding benzidine without affecting the ester moiety (entry 10).

Because the oxidative coupling of *N*,*N*-diethylaniline **12k** resulted in 49% yield of **13k** with 36% recovery of **12k**, the addition of base was examined to scavenge the eliminated protons, which might protonate the starting aniline **12k** and retard its oxidation. While triethylamine and 2,6-lutidine were

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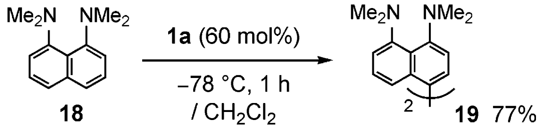
(24) It was reported that the CuBr/H$_2$O$_2$ system did not promote the coupling reaction of anilines bearing an electron-withdrawing group such as chlorine on the aromatic ring.[14b]

(25) Hunter, D. H.; Barton, D. H. R.; Motherwell, W. J. *Tetrahedron Lett.* **1984**, *25*, 603.

**SCHEME 8. Coupling of Proton Sponge with 1a**



oxidized with **1a**, 2,6-di-*tert*-butylpyridine promoted the coupling reaction of **12k** as expected. The addition of the base (240 mol %) and 120 mol % of dication **1a** improved the yield of **13k** to 66%. In addition, a diamine substrate, *N*,*N*,*N*′,*N*′-tetramethyl-1,8-diaminonaphthalene (**18**, Proton Sponge), was also subjected to the reaction to give the coupling product **19** at the 4-position in 77% yield (Scheme 8).

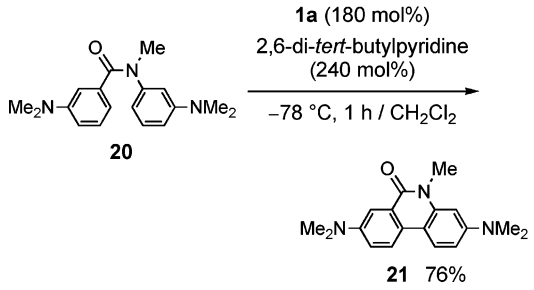
3,5-Disubstituted or 3-substituted anilines generally afforded better yields of benzidines, compared with the other anilines. This fact was explained by the overoxidation of the products. Two-electron oxidation of the produced dimers **13** gave rise to the formation of diiminium salts **15**, which led to a decrease in yield of **13**. Benzidines **13** having substituents at the 2,2′,6,6′-positions were less easily oxidized to give **15** than nonsubstituted and 3,3′-disubstituted benzidines, because steric inhibition of resonance decreased the stability of the intermediary radical cations **14** and diiminium salts **15** (Figure 1). This effect was confirmed with cyclic voltammetry measurements: whereas the oxidation potential of **14a** ($E^{ox} = 0.46$ V vs Fc/Fc$^+$) was higher than that of aniline **12a** ($E^{ox} = 0.32$ V vs Fc/Fc$^+$), that of **14c** ($E^{ox} = 0.36$ V vs Fc/Fc$^+$) was lower than that of aniline **12c** ($E^{ox} = 0.77$ V vs Fc/Fc$^+$).

As an application of the oxidative benzidine synthesis, we also tried to construct a phenanthridin-6(5*H*)-one skeleton, which is found in poly(ADP-ribose) polymerase-l (PARP 1) inhibitors.[26] When the intramolecular coupling of amide **20** was attempted with 120 mol % of **1a** under high dilution conditions (0.01 M in $CH_2Cl_2$), the desired phenanthridinone **21** was obtained in 46% yield. To drive the reaction to completion, the addition of 2,6-di-*tert*-butylpyridine (240 mol %) with 180 mol % of **1a** was examined (vide supra). Thus, the reaction proceeded cleanly to improve the yield of **21** to 76% (Scheme 9).

## Conclusion

Naphthalene-1,8-diylbis(diphenylmethylium) salts **1a** and **1b** were easily prepared from the corresponding cyclic ether **5a** via deoxygenation on treatment with a silylating agent in HFIP. The oxidative coupling of *N*,*N*-dialkylanilines has been successfully achieved by the use of **1a** or **1b** to provide facile access to a variety of benzidine derivatives including a phenanthridin-6(5*H*)-one. These results have clearly revealed that the salts of dication **1** (Ar = Ph) function as organic reagents for electron-transfer oxidation involving two electrons.

**SCHEME 9. Synthesis of Phenanthridin-6(5*H*)-one 21 with Dication 1a**[a]



[a] The reaction was carried out in 0.01 M.

## Experimental Section

**1,1,3,3-Tetraphenyl-1*H*,3*H*-benzo[*d*,*e*]isochromene (5a).**[17] To a solution of 1,8-dibromonaphthalene (2.0 g, 7.0 mmol) in $Et_2O$ (35 mL) was added *n*-BuLi (6.6 mL, 2.60 M in hexane, 17.2 mmol) at 0 °C under argon. The reaction mixture was stirred at room temperature for 2 h, and then benzophenone (3.1 g, 17.0 mmol) was added. After heating at reflux for 5 h, the reaction was quenched with saturated aqueous $NH_4Cl$. Organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was dissolved in $CH_2Cl_2$ (10 mL), and a catalytic amount of trifluoroacetic acid (0.05 mL, 0.7 mmol) was added at room temperature. The reaction mixture was stirred for 10 h, and then MeOH (20 mL) was added. After the solution was stirred at room temperature for 1 h, the resulting precipitate was collected by filtration, washed with MeOH, and dried under reduced pressure to give **5a** (2.7 g, 80%) as white crystals. Mp 244−245 °C ($CH_2Cl_2$−MeOH). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.95−7.15 (22H, m), 7.37 (2H, dd, $J = 8.0$, 7.2 Hz), 7.80 (2H, d, $J = 8.0$ Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 84.3, 124.9, 126.4, 126.5, 126.6, 126.7, 127.0, 129.5, 132.9, 136.1, 146.5. IR (KBr) 1578, 1546, 1452, 1359, 1087, 704, 623 cm$^{-1}$. FAB HRMS calcd for $C_{36}H_{27}O$ 475.2062 (M + 1), found 475.2067.

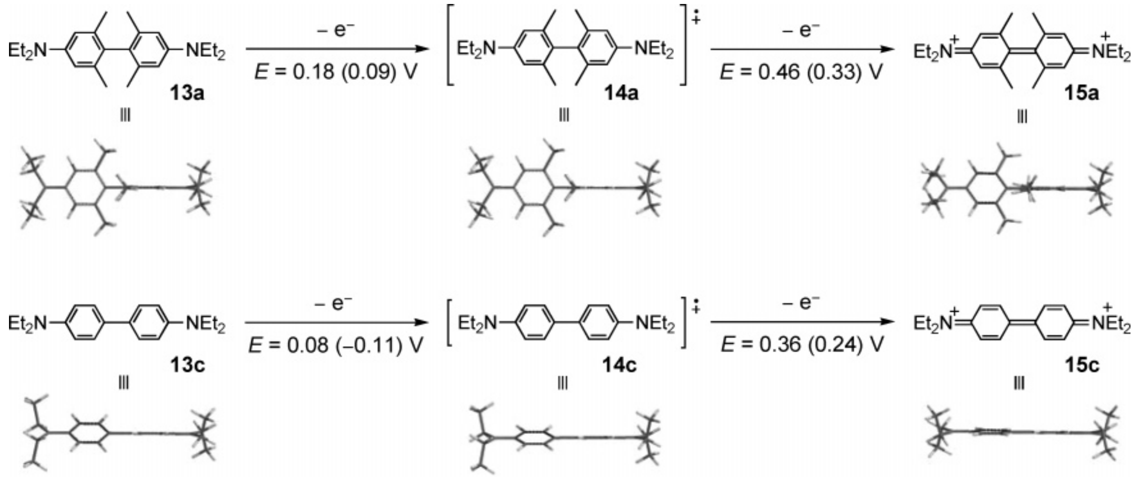


**FIGURE 1.** Cyclic voltammetry analysis [$E^{ox}$ ($E^{red}$) vs Fc/Fc$^+$] and conformation analysis (DFT calculations were perfoned with B3LYP/6-31G*) of **13a**,**c**−**15a**,**c**.

**Trimethylsilyl Perchlorate ($Me_3SiClO_4$ toluene solution).** To a solution of $AgClO_4$ (4.6 g, 22 mmol) in toluene (30 mL) was added trimethylsilyl chloride (2.8 mL, 22 mmol) under argon. After this mixture was stirred at room temperature for 0.5 h and then left standing for 0.5 h without stirring, the supernatant was used as a reagent ($Me_3SiClO_4$, 0.74 M in toluene) for the preparation of the dications.

**Naphthalene-1,8-diylbis(diphenylmethylium) Diperchlorate (1a).** To a stirred solution of **5a** (2.0 g, 4.2 mmol) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 30 mL) was added $Me_3SiClO_4$ (17.1 mL, 0.74 M in toluene, 12.6 mmol) at room temperature under argon, and the mixture was stirred at the same temperature for 2 d. The solvent was removed under reduced pressure, and the crude product was dissolved in $CH_2Cl_2$ (3.0 mL) and $Et_2O$ (10 mL). After the mixture was stirred at room temperature for 1 h, the resulting black precipitate was collected by filtration, washed with $Et_2O$ (10 mL) and then $CH_2Cl_2$ (3.0 mL) under argon, and dried under reduced pressure to give **1a** (2.6 g, 95%) as dark red crystals. Mp 170 °C dec ($Et_2O$−$CH_2Cl_2$−HFIP). $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 6.54 (2H, br s), 6.73 (2H, br s), 7.37 (2H, br s), 7.41−7.65 (10H, m), 7.75 (2H, br s), 7.98 (2H, br s), 8.05 (2H, dd, $J = 7.6, 7.6$ Hz), 8.23 (2H, br s), 8.95 (2H, dd, $J = 8.4, 1.6$ Hz). $^{13}$C NMR (100 MHz, $CD_3CN$) $\delta$ 127.7, 128.0, 129.7, 130.1, 131.9, 136.6, 137.5, 139.7, 144.8, 151.0, 207.6. IR (KBr) 1489, 1444, 1217, 1184, 1018, 742, 694 cm$^{-1}$. **Crystal data:** $C_{36}H_{26}Cl_2O_8$, $M = 657.47$, monoclinic, $a = 16.090(7)$ Å, $b = 10.544(4)$ Å, $c = 17.881(7)$ Å, $U = 2936(2)$ Å$^3$, $T = 120(2)$ K, space group $P2_1/a$, $Z = 4$, $\mu$(Mo K$\alpha$) $= 0.279$ mm$^{-1}$, 16 652 reflections measured, 5037 unique ($R_{int} = 0.0296$) which were used in all calculations. The final $wR(F^2)$ was 0.1467 (all data). The largest residual electron density hole was −0.773 e·Å$^{-3}$.

**Procedure for the Transformation of Acenaphthene 2a to Cyclic Ether 5a.** To a solution of **2a** (32.9 mg, 0.072 mmol) in $CH_2Cl_2$ (2.0 mL) was added $HClO_4$ (1.7 mL, 0.42 M in toluene, 0.72 mmol: see the Supporting Information) at room temperature under argon. After stirring for 4 d, the reaction was quenched with saturated aqueous $NaHCO_3$. Organic materials were extracted with EtOAc three times, and the combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by PTLC (toluene−hexane−$CHCl_3$ 1:3:2) to give **5a** (31.9 mg, 90%).

***N,N,N′,N′*-Tetraethyl-2,2′,6,6′-tetramethylbenzidine (13a).** To a solution of **12a** (27.5 mg, 0.16 mmol) in $CH_2Cl_2$ (2.0 mL) was added **1a** (61.8 mg, 0.10 mmol) at −78 °C. The reaction mixture was stirred at the same temperature for 1 h. After completion of the oxidative coupling (TLC monitoring), the reaction was quenched with saturated aqueous $NaHCO_3$. Organic materials were extracted with EtOAc three times and the combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by PTLC (toluene−hexane−$CHCl_3$ 1:3:2) to give **13a** (26.7 mg, 98%) as white crystals along with acenaphthene **2a** (42.8 mg, 99%). Mp 119−120 °C (EtOH). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.18 (12H, t, $J = 6.8$ Hz), 1.87 (12H, s), 3.34 (8H, q, $J = 6.8$ Hz), 6.45 (4H, s). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 12.9, 20.8, 44.2, 111.0, 128.3, 137.0, 146.4. IR (neat) 2964, 1601, 1473, 1373, 1286, 1198, 825 cm$^{-1}$. Anal. Calcd for $C_{24}H_{36}N_2$: C, 81.76; H, 10.29; N, 7.95. Found: C, 81.50; H, 10.31; N, 7.69.

**3-(Dimethylamino)-*N*-[3-(dimethylamino)phenyl]-*N*-methylbenzamide (20).** To a solution of 3-nitroaniline (1.80 g, 13 mmol) and triethylamine (2.5 mL, 18 mmol) in $CH_2Cl_2$ (5.0 mL) was added a solution of 3-nitrobenzoyl chloride (2.00 g, 11 mmol) in $CH_2Cl_2$ (5.0 mL) at 0 °C under argon. After stirring for 12 h, the reaction was quenched with water. Organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, EtOH (20 mL) was added to the residue. To the resulting suspension were added 10% Pd/C (2.18 g, 2.1 mmol) and aqueous HCl (2.5 mL, 10 M, 25 mmol). After the reaction mixture was stirred under $H_2$ for 2 d, aqueous $NaHCO_3$ was added. Organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue and iodomethane (4.5 mL, 72 mmol) were successively added to a suspension of NaH (3.08 g, 60% dispersion in mineral oil, 77 mmol) in THF (10 mL) at 0 °C under argon. After being stirred at 50 °C for 20 h, the reaction was quenched with water. Organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexanes−EtOAc 5:1) to give **20** (0.72 g, 22%) as pale yellow crystals. Mp 98−99 °C (EtOH). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.80 (6H, s), 2.80 (6H, s), 3.48 (3H, s), 6.35 (1H, dd, $J = 2.5, 2.5$ Hz), 6.43 (1H, dd, $J = 8.2, 1.2$ Hz), 6.48 (1H, dd, $J = 8.2, 2.5$ Hz), 6.60 (1H, dd, $J = 8.2, 2.5$ Hz), 6.67 (1H, d, $J = 8.2$ Hz), 6.74−6.75 (1H, m), 7.00 (1H, dd, $J = 8.2, 8.2$ Hz), 7.06 (1H, dd, $J = 8.2, 8.2$ Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 38.4, 40.5, 40.6, 110.4, 111.4, 113.1, 113.7, 114.6, 117.0, 128.1, 129.3, 136.7, 146.0, 149.8, 151.0, 171.2. IR (neat) 2883, 2802, 1637, 1595, 1570, 1496, 1433, 1344, 1284, 1227, 1107, 993, 839, 771 cm$^{-1}$. Anal. Calcd for $C_{18}H_{23}N_3O$: C, 72.70; H, 7.80; N, 14.13. Found: C, 72.55; H, 7.80; N, 13.97.

**3,8-Bis(dimethylamino)-5-methylphenanthridin-6(5*H*)-one (21).** To a solution of **20** (35.0 mg, 0.12 mmol) and 2,6-di-*tert*-butylpyridine (54.1 mg, 0.28 mmol) in $CH_2Cl_2$ (10 mL) was added **1a** (141 mg, 0.21 mmol) at −78 °C under argon. The reaction mixture was stirred at the same temperature for 1 h. After completion of the oxidative coupling (TLC monitoring), the reaction was quenched with saturated aqueous $NaHCO_3$. Organic materials were extracted with EtOAc three times, and the combined extracts were washed with brine and dried over $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexanes−EtOAc 1:1) to give **21** (26.5 mg, 76%) as a pale yellow solid. Mp 209−210 °C (EtOH). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.06 (12H, s), 3.79 (3H, s), 6.53 (1H, s), 6.72 (1H, d, $J = 7.4$ Hz), 7.18 (1H, dd, $J = 8.9, 2.4$ Hz), 7.72 (1H, s), 7.97−8.00 (2H, m). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 29.9, 40.6, 40.7, 97.5, 108.1, 109.6, 109.9, 118.7, 121.8, 122.9, 124.2, 124.5, 137.8, 148.8, 150.1, 162.5. IR (neat) 2999, 2891, 2800, 1635, 1604, 1498, 1435, 1363, 1321, 1234, 1105, 1063, 1005, 958, 904, 870, 804, 742, 667 cm$^{-1}$. FAB HRMS calcd for $C_{18}H_{22}N_3O$ 296.1763 (M + 1), found 296.1745.

**Acknowledgment.** We are grateful to Central Glass Co., Ltd., for a generous gift of HFIP. We thank Dr. N. Kanoh (the University of Tokyo) for the X-ray crystal structure analysis of compound **1a**. This work was supported by the Grant-in-Aid for the 21st century COE program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

**Supporting Information Available:** Experimental procedures and spectroscopic data of compounds **5b**, **1b**, **1c**, **8**, **9**, **11**, **12a**−**m**, **2a**, **13b**−**m**, and **19**; X-ray data of compound **1a**; copies of $^{13}$C spectra of compounds **2a**, **5a**, **5b**, **13c**, **13d**, **13f**, **13g**, **13j**, **13*l***, **13m**, and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060662S

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