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# 1,8-Bis(diphenylmethylium)naphthalenediyl Dication as an Organic Oxidant: Synthesis of Benzidines via Self-Coupling of *N,N*-Dialkylanilines

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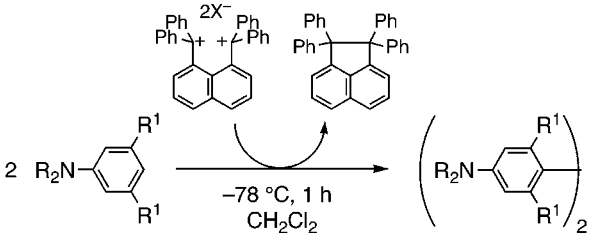
## ABSTRACT



**1,8-Bis(diphenylmethylium)naphthalenediyl dications promoted oxidative coupling of various *N,N*-dialkylanilines to afford the corresponding para-coupled bisanilines, benzidines, in good to excellent yield. The dications were readily prepared from a cyclic ether precursor, derived from 1,8-dibromonaphthalene, via deoxygenation with a silylating reagent in 1,1,1,3,3,3-hexafluoro-2-propanol under anhydrous conditions.**

Triarylmethyliums, readily prepared from the corresponding alcohols[1] or halides,[2] constitute a class of versatile carbocations with functions such as hydride and alkoxy abstraction,[3] Lewis acid catalysis,[4] and others.[5] Recently, dicationic systems in which two triarylmethylium ions are linked by a carbon skeleton such as 2,2′-biphenylene,[6] [1,1′-binaphthalene]-2,2′-diyl,[7] and 1,8-naphthalenediyl[8] groups have been prepared and exhibited unique electrochemical properties. These dications undergo electrochemical reduction, leading to the corresponding neutral compounds via C−C bond formation between the two carbocation centers. Among these, the two cationic centers are closest in the dications with a 1,8-naphthalenediyl tether, which resulted in an especially high oxidation potential compared with those of other dications and triarylmethyliums (monocations) examined using cyclic voltammogram analysis. Despite their potential as an oxidant, there have been no reports on their application in organic synthesis. In this communication, we report a convenient synthetic method for 1,8-bis(diarylmethylium)naphthalenediyl dications **4** and their function as a new organic oxidant in the coupling reaction of aniline derivatives.

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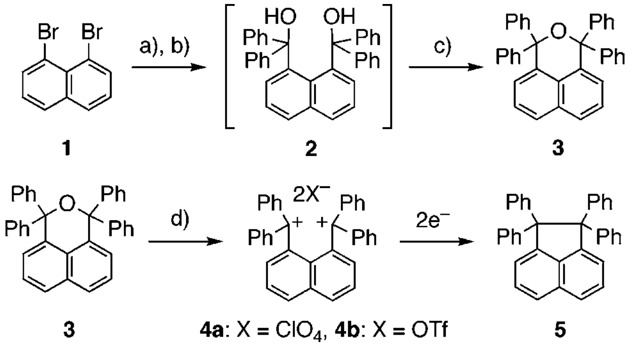
The bistriarylmethyliums mentioned above were previously prepared by treatment of the corresponding diols with aqueous $HBF_4$ or $HClO_4$ in $Ac_2O$ or $(CF_3CO)_2O$.[8] These methods have a drawback in purification of the product dications due to the low volatility of water, acid anhydrides, and in situ-generated carboxylic acids. Therefore, the development of a more convenient and practical method for the dications is still required to isolate them in pure forms so they can be used as reagents in synthetic organic reactions. Our synthetic plan relied on the following two features: (1) dications **4** would be generated from cyclic ether **3** via deoxygenation, and (2) this process would proceed readily in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solvent (Scheme 1).[9,10] Treatment of **3** with a strong silylating reagent was expected to allow removal of the oxygen as a disiloxane ($R_3SiOSiR_3$), leading to the desired dication 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.

**Scheme 1.** Synthesis of 1,8-Bis(diphenylmethylium)naphthalene Dications **4**[a]

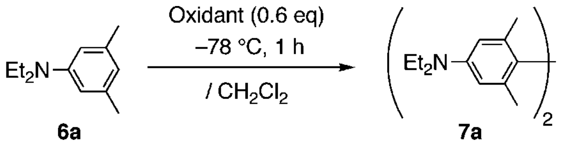


[a] Reagents and conditions: (a) *n*-BuLi (2.2 equiv), $Et_2O$, rt, 2 h. (b) $Ph_2CO$ (2.4 equiv), reflux, 4 h. (c) $CF_3CO_2H$ (0.1 equiv), $CH_2Cl_2$, rt, 10 h. (d) TMSX (3.0 equiv) in toluene, $(CF_3)_2CHOH$ (HFIP), rt, 2 days.

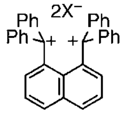
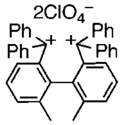
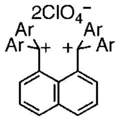
Benzophenone was added to the dilithium species, prepared by treating the known 1,8-dibromonaphthalene **1** with *n*-BuLi, to afford the crude diol **2**.[11] On successive treatment of its $CH_2Cl_2$ solution with a catalytic amount of $CF_3CO_2H$ and then MeOH, ether **3** (the precursor of dications **4a**,**b**) was obtained as white crystals in 80% yield from **1** by filtration. Neither workup nor purification was needed to isolate **3**. Moreover, this procedure for cyclic ether **3** was applied to the preparation of dications **4c** and **8** (Table 1).

Cyclic ether **3** was treated with $TMSClO_4$, prepared in situ from $AgClO_4$ and TMSCl in toluene,[12] in order to deoxygenate it. HFIP successfully promoted deoxygenation of **3** as expected, to afford the desired dication **4a** in 94% yield as dark red crystals, whereas dication **4a** was not obtained at all in dichloromethane, toluene, or benzene. Dication **4b** was also prepared from **3** on treatment with TMSOTf instead of $TMSClO_4$ under similar conditions, although the dication proved to be unstable for use as a reagent.

**Table 1.** Coupling of Aniline **6a** with Organic Oxidants



**6a** **7a**

| oxidant | % yield | oxidant | % yield |
|---|---|---|---|
|  **4a**<br>**4b** | 98<br>93 |  **8** | complex mixture |
|  **4c**<br>Ar : 4-MeOC$_6$H$_4$ | 57 | $Ph_3C^+BF_4^-$ (1.2 eq) | 0 |
| | | DDQ | 0 |
| | | $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (1.2 eq) | <50 |

Recently, *N*,*N*′-perarylated derivatives of benzidine have 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.[13] Oxidative coupling of aniline derivatives provides an efficient access to benzidine derivatives. Although several methods for the coupling reaction have been reported, most of them are low-yielding processes.[14] Among these methods, $TiCl_4$-mediated oxidative coupling seemed to be the most practical to afford the benzidines, despite the requirement of a large excess of starting anilines.[13,14a] These facts prompted us to try dication **4** as an oxidant in the coupling reaction of anilines.

*N*,*N*-Diethylaniline **6a** was smoothly transformed to the desired para-coupled bisaniline, *N*,*N*,*N*′,*N*′-tetraalkylbenzidine **7a** in 98% yield on treatment with a small excess of **4a**, which was quantitatively recovered as acenaphthene **5** (Table 1).[15,16] The C−C bond formation between the two carbocation centers of **4a** leading to **5** indicates that **4a** acted as an oxidant in the coupling reaction of **6a** (Scheme 1).

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(10) For recent reports on the cationic reactions conducted in HFIP, see: Ichikawa, J.; Jyono, H.; Kudo, T.; Fujiwara, M.; Yokota, M. *Synthesis*, in press, and references therein.

(11) Letsinger, L. R.; Gilpin, A. J.; Vulio, J. W. *J. Org. Chem.* **1962**, *27*, 673.

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(14) (a) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2000**, *65*, 3548 and references therein. (b) López-Cortés, J. G.; Penieres-Carrillo, G.; Ortega-Alfaro, M. C.; Gutiérrez-Pérez, R.; Toscano, R. A.; Alvarez-Toledano, C. *Can. J. Chem.* **2000**, *78*, 1299.

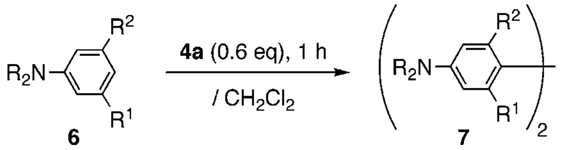
(15) Although acenaphthene **5** regenerated dication **4a** on treatment with $HClO_4$ in HFIP, dication catalysis has not been successful so far and is now under investigation. See also: Wang, H.; Gabbaï, F. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 184.

(16) Electron-rich benzenes other than anilines such as anisole and 1,4-dimethoxy- and 1,3,5-trimethoxybenzenes gave no dimeric products on treatment with dication **4a**.

Dication **4c**, bearing methoxy groups on the four benzene rings, was less effective in this reaction, giving **7a** in a lower yield. Dication **8**, bearing a 2,2′-biphenylene backbone, gave a complex mixture, and $Ph_3C^+BF_4^-$ afforded no coupling products. These facts suggest that two methylium cations in close proximity are essential. Treatment of **6a** with DDQ or a triarylaminium radical cation, $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$, both of which are widely used in organic chemistry as a one-electron oxidant, gave no bisaniline or many side products other than **7a**, respectively. These results (Table 1) clearly show that dication **4a** is the oxidant of choice for the self-coupling reaction of aniline derivatives.[14]

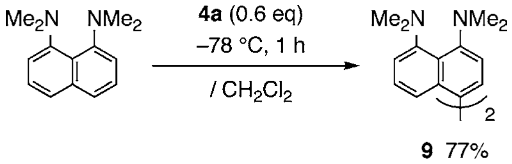
To expand the scope of the present oxidative coupling, several other dialkylanilines were treated with **4a**, and the results are summarized in Table 2. The desired dimers **7** were obtained in high to excellent yield from 3,5-disubstituted and 3-halogenated *N*,*N*-dialkylanilines. The self-coupling proceeded smoothly even when the amine nitrogen was protected by an allyl or benzyl group, while the reactions of aniline or a monoalkylated aniline led to complex mixtures. *N*,*N*,*N*′,*N*′-Tetramethyl-1,8-diaminonaphthalene, Proton Sponge, also underwent reaction to give the product of coupling at the 4-position **9** in 77% yield (Scheme 2). All of the coupling reactions regioselectively occurred to afford the para-coupled dimer of dialkylanilines without formation of ortho- and meta-coupled products.

**Table 2.** Synthesis of Benzidines **7** from Anilines **6**



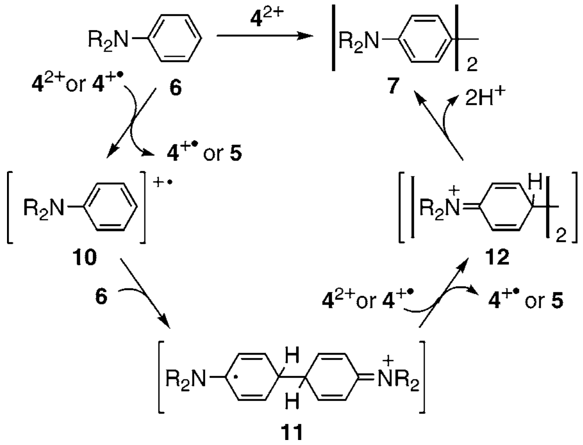
| entry | R | R¹ | R² | temp. | % yield |
|---|---|---|---|---|---|
| 1 | Me | Me | Me | −78 °C | 95 |
| 2 | Et | Me | Me | −78 °C | 98 |
| 3 | Et | Cl | Cl | rt | 78 |
| 4 | Et | Br | H | rt | 86 |
| 5 | Allyl | Me | Me | rt | 81 |
| 6 | Bn | Me | Me | −78 °C | 77 |

**Scheme 2.** Coupling of Proton Sponge with **4A**



A plausible mechanism for the oxidative coupling is shown in Scheme 3. Dication **4** promotes oxidation of dialkylanilines **6** to generate cation radicals **10**, which in turn react with **6** leading to the coupled intermediates **11**. The produced **11** is further oxidized by **4** or $4^{+\bullet}$ to give diiminium ions **12**, which provide dimers **7** after deprotonation during the workup procedure. Dication **4** is transformed to acenaphthene **5**[15] via two-electron reduction, effected by two molar amounts of dialkylanilines **6**.

**Scheme 3.** Plausible Reaction Mechanism for the Oxidative Coupling of **6**



In conclusion, the oxidative coupling reaction of aniline derivatives has been successfully achieved by the use of 1,8-bis(diphenylmethylium)naphthalenediyl dication **4a**, which was easily prepared from the corresponding cyclic ether **3** by deoxygenation using a silylating reagent in HFIP.

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**Supporting Information Available:** Spectroscopic data, X-ray crystallographic data (CIF), and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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