ORGANIC LETTERS

2011
Vol. 13, No. 7
1634–1637

Sequential Oxidative Transformation of Tetraarylethylenes to 9,10-Diarylphenanthrenes and Dibenzo[*g*,*p*]chrysenes using DDQ as an Oxidant

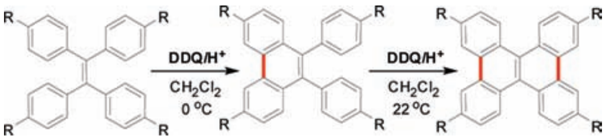
Tushar S. Navale, Khushabu Thakur, and Rajendra Rathore*

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201, United States

Raj.Rathore@marquette.edu

Received January 10, 2011

ABSTRACT



Tetraarylethylenes can be sequentially transformed into 9,10-diarylphenanthrenes and dibenzo[*g*,*p*]chrysenes using 1 and 2 equiv of DDQ, respectively, in CH_2Cl_2 containing methanesulfonic acid, in excellent yields. Efficient access to substituted dibenzochrysenes from tetraarylethylenes establishes the versatility of this procedure over the existing multistep syntheses of dibenzochrysenes. Moreover, the ready regeneration of DDQ from easily recovered reduced DDQ−H_2 continues to advance the use of DDQ/H^+ for the oxidative C−C bond forming reactions.

Efforts toward the design and synthesis of polycyclic aromatic hydrocarbons (PAHs) for use as functional materials in electronic and optoelectronic devices continue to grow with an unabated pace owing to their potential applications in the ever evolving areas of molecular electronics and nanotechnology.[1,2] Of these, dibenzochrysene, a twisted polycyclic aromatic hydrocarbon, and its derivatives have been explored by Swager and co-workers[3] and others[4] for the preparation of sensors, nonlinear optical and liquid-crystalline materials, etc. Unfortunately, however, the preparation of parent dibenzochrysene (DBC)[5] as well as its various substituted derivatives requires multistep syntheses.[3−5]

In principle, various dibenzochrysenes should be accessible via a pair of oxidative C−C bond formations in readily available symmetrical (via McMurry coupling)[6] as well as unsymmetrical[7] tetraarylethylenes (via a recently developed procedure from our laboratory) using oxidants similar to those employed for the Scholl reaction.[8] Unfortunately, such oxidative transformations of tetraarylethylenes (TAE) to dibenzochrysenes (DBC) are rarely employed[9] (Scheme 1).

In this context, it is noteworthy that Olah and co-workers[10] have shown that treatment of tetraarylpinacols with a superacid (CF_3SO_3H) affords 9,10-diarylphenanthrenes (DAP) via a dicationic intermediate TAE^{+2} (Scheme 1). Interestingly, it is also well-known[11] that the same dicationic intermediate (i.e., TAE^{+2}) can also be

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(1) Heath, J. R. *Annu. Rev. Mater. Res.* **2009**, *39*, 1–23 and references cited therein.

(2) Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267.

(3) (a) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087. (b) Rose, A.; Tovar, J. D.; Yamaguchi, S.; Nesterov, E. E.; Zhu, Z.; Swager, T. M. *Philos. Trans. R. Soc. London, Ser. A* **2007**, *365*, 1589 and references therein.

(4) (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9203. (b) Toal, S. J.; Trogler, W. C. *J. Mater. Chem.* **2006**, *16*, 2871. (c) Chaudhuri, R.; Hsu, M.-Y.; Li, C.-W.; Wang, C.-I.; Chen, C.-J.; Lai, C. K.; Chen, L.-Y.; Liu, S.-H.; Wu, C.-C.; Liu, R.-S. *Org. Lett.* **2008**, *10*, 3053.

(5) Buckles, R. E.; Serianz, A.; Naffziger, D. *Proc. Iowa Acad. Sci.* **1973**, *80*, 45.

(6) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

(7) Banerjee, M.; Emond, S. J.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2007**, *72*, 8054.

(8) (a) Scholl, R.; Mansfeld, J. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.

(9) Navale, T. S.; Zhai, L.; Lindeman, S. V.; Rathore, R. *Chem. Commun.* **2009**, 2857.

(10) Klumpp, D. A.; Baek, D. N.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1997**, *62*, 6666.

(11) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931.

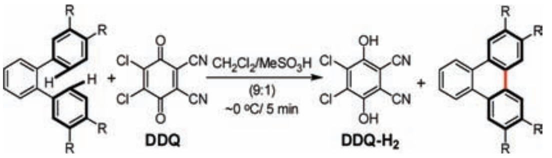
10.1021/ol200069c

Scheme 1. Sequential Oxidative Transformation of TAE to DAP and DBC

accessed from tetraarylethylenes via two successive 1-e$^-$ oxidations (i.e., Scheme 1).

Accordingly, our initial attempts to transform parent tetraphenylethylene to either 9,10-diphenylphenanthrene or dibenzochrysene using $FeCl_3$ (an extensively utilized oxidant for the oxidative C−C bond forming reactions)[8] gave a complex mixture of products.[12] We recently demonstrated[13] that the DDQ/H$^+$ system, which oxidizes a variety of aromatic electron donors with oxidation potentials as high as ~1.6 V vs SCE to their cation radicals, can be used as an effective oxidant for C−C bond forming reactions; e.g., see Scheme 2.

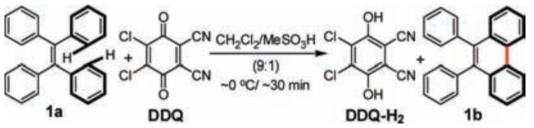
Scheme 2. Oxidative Transformation of a *o*-Terphenyl to the Corresponding Triphenylene Using DDQ as Oxidant



Herein, we now report that the same DDQ/H$^+$ system as in Scheme 2 can also be employed for the sequential transformations of a variety of symmetrical and unsymmetrical tetraarylethylenes to corresponding 9,10-diarylphenanthrenes (DAP) using 1 equiv of DDQ or to dibenzochrysenes (DBC) using 2 equiv of DDQ in excellent yields. The preliminary details of these findings including the involvement of the tetraarylethylene cation radicals as intermediates in a rapid conversion of TAE to DAP, as well as a relatively slow transformation of DAP to DBC, are discussed in the context of an electron transfer mechanism as follows.

Thus, a 0.1 M solution of tetraphenylethylene (**1a**) in a 9:1 mixture of dichloromethane and methanesulfonic acid (10 mL) was reacted with 1 equiv of DDQ at ~0 °C, under an argon atmosphere, to afford a blue-violet solution[14] which turned brown during the course of 30 min. The resulting brown mixture was quenched by an addition of saturated aqueous sodium bicarbonate solution (20 mL). The dichloromethane layer was separated and washed with a saturated brine solution (2 × 10 mL), dried over anhydrous magnesium sulfate, and evaporated to afford the corresponding 9,10-diphenylphenanthrene (**1b**) in quantitative yield (Scheme 3).

Scheme 3. Oxidative Transformation of **1a** to **1b** Using DDQ as Oxidant



It is important to note that the reduced hydroquinone (DDQ−H_2) in Scheme 3 readily dissolves into the aqueous sodium bicarbonate layer and can be recovered quantitatively by acidification (using aqueous hydrochloric acid, 10%) followed by extraction with diethyl ether. Furthermore, DDQ can be regenerated from DDQ−H_2 by a simple oxidation using either conc. nitric acid or N_2O_4.[15]

A series of TAE **1a**−**8a** (with oxidation potentials varying from ~1.1 to ~1.5 V vs SCE) were converted to the corresponding DAP **1b**−**8b** in good to excellent yields when subjected to the oxidative cyclodehydrogenation reaction according to the reaction conditions depicted in Scheme 3 (see Table 1). It is noteworthy that the reaction time for the conversion of TAEs to DAPs increased from ~30 min to 24 h with the increasing oxidation potentials of TAEs (see Table 1). The most electron-poor tetrabromo derivative **8a** (E_{ox} = 1.51 V), among the TAEs in Table 1, underwent only partial conversion (56%) to **8b** in 96 h.

The structures of various DAPs in Table 1 were established by ^{1}H/^{13}C NMR spectroscopy and further confirmed by X-ray crystallography (see Supporting Information).

The symmetrical tetraarylethylenes with both electron-donating (**2a**) and electron-withdrawing substituents (**8a**) also produced minor amounts of diarylmethylidene-fluorene **2c** and **8c**, respectively, together with the expected **2b** and **8b** as major products (Table 1).[16a] The unsymmetrical tetraarylethylenes **3a**, **5a**, **6a**, and **7a**,[16b] on the other hand, underwent regioselective conversion to the corresponding

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(12) An NMR analysis of the crude reaction mixture suggested that it contained traces of parent dibenzochrysene **1d** and 9,10-diphenylphenathrene (**1b**) together with a multitude of products arising from the electrophilic aromatic chlorination of **1a**, **1b**, and **1d**.

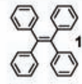
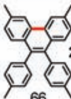
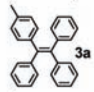
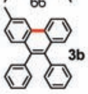
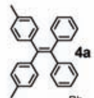
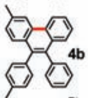
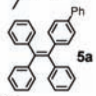
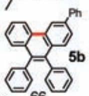
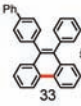
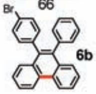
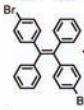
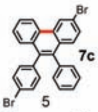
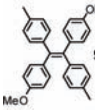
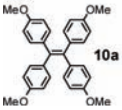
(13) (a) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474. (b) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748.

(14) The blue-violet color in reaction of **1a** with DDQ/H$^+$ arises due to the formation of $\mathbf{1a}^{+\bullet}$ and $\mathbf{1}^{+2}$, as confirmed by comparison of the UV−vis absorption spectrum of the reaction mixture with that of the authentic spectra[11] of $\mathbf{1a}^{+\bullet}$ and $\mathbf{1}^{+2}$.

(15) (a) Brook, A. G. *J. Chem. Soc.* **1952**, 5040. (b) Newman, M. S.; Khanna, V. K. *Org. Prep. Proc. Int* **1985**, *17*, 422.

(16) (a) Oxidative cyclizations of symmetrical TAEs to corresponding diarylphenanthrenes and diarylmethylidenefluorene have been previously observed; see: Ciminale, F.; Lopez, L.; Mele, G. *Tetrahedron* **1994**, *50*, 12685. (b) It is well known that the cation radicals and dications of of TAEs are twisted around the ethylenic C=C bond by ~30°−60° and undergo ready isomerization under oxidative conditions; see ref 11.

Table 1. Oxidative Transformation of TAEs to DAPs Using DDQ/H$^+$ Oxidant System in Dichloromethane at 0 °C

reactant	E_{ox1}/E_{ox2} (V vs SCE)	products		time (h)	% yield[a]
 **1a**	1.36/1.67	 **1b**		~0.5	99
 **2a**	1.11/1.39	 **2b** 66	:  **2c** 33	~0.5	97
 **3a**	1.29/1.57	 **3b**		~0.5	97
 **4a**	1.23/1.53	 **4b**		~0.5	97
 **5a**	1.31/1.57	 **5b** 66	:  **5c** 33	~0.5	99
 **6a**	1.40/1.69	 **6b**		10.0	99
 **7a**[b]	1.44/1.69	 **7b** 95	:  **7c** 5	24.0	98
 **8a**	1.51/1.71	 **8b** 97	:  **8c** <3	96.0	99[c]
 **9a**	0.89/1.02	-none-		24.0	0
 **10a**	0.79/0.91	-none-		24.0	0

[a] The yields refer to both b and c products in cases of entries **2**, **5**, **7**, and **8**. [b] *cis*-1,2-bis(4-bromophenyl)-1,2-diphenylethylene also gave an identical mixture of products (i.e. **7b** and **7c**). [c] Yield is based on conversion (56%) and recovered **8a** (44%). [d] See Figure 1.

9,10-diarylphenanthrenes where the oxidative C−C bond formation occurred between the relatively electron-rich aryl rings (see Table 1).

Interestingly, the most electron-rich 1,2-dianisyl-1,2-ditolylethylene[11] (**9a**, E_{ox1} = 0.89 V) and tetraanisylethylene[11] (**10a**, E_{ox1} = 0.79 V) produced intensely colored solutions when treated with DDQ and methanesulfonic acid according to the Scheme 3. The quenching of the resulting reaction mixtures, after 24 h, using aqueous sodium bicarbonate, afforded a quantitative recovery of the starting TAEs **9a** and **10a**. Photospectrometric analyses in Figure 1 of the highly colored reaction mixtures of **9a** and **10a**, prior to aqueous workup, produced characteristic absorption spectra which were readily assigned to the corresponding dications of the TAEs (i.e., **9a**$^{+2}$ and **10a**$^{+2}$) by comparison with the reported spectra of **9a**$^{+2}$ and **10a**$^{+2}$.[11]

As such, the singular lack of formation of DAPs from tetraarylethylenes **9a** and **10a** is not surprising in light of the fact that they form rather stable dications (i.e., **9a**$^{+2}$ and **10a**$^{+2}$) owing to the effective quinoidal delocalization of a pair of cationic charges (Figure 1). Moreover, the high stability of dicationic **9a**$^{+2}$ and **10a**$^{+2}$ was further demonstrated by their isolation and structural characterization by X-ray crystallography.[11]

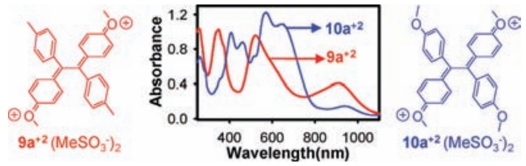
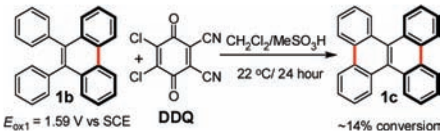


Figure 1. UV−vis absorption spectra of dicationic **10a** (blue) and **9a** (red) formed quantitatively from the reactions of the corresponding TAEs with 1 equiv of DDQ in CH_2Cl_2/$MeSO_3H$ at 22 °C.

Surprisingly, the oxidative transformations of various TAEs to DAPs using 1 equiv of DDQ, according to Scheme 3, did not show any indication of the formation of corresponding dibenzochrysenes. However, a reaction of isolated 9,10-diphenylphenanthrene (**1b**) with DDQ/H$^+$ for an extended period at 22 °C showed a partial conversion of **1b** to dibenzochrysene (**1c**) (Scheme 4).

Scheme 4. Oxidative Transformation of a **1a** to **1b** Using DDQ as Oxidant

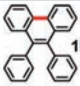
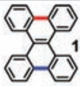
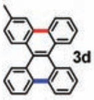
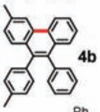
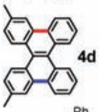
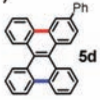


As noted above, the reaction times for the oxidative conversion of various TAEs to the corresponding DAPs increased with increasing oxidation potentials of TAEs, and therefore, the slow reactivity of **1b** toward the DDQ/H$^+$ oxidation system suggested that its oxidation potential must be relatively high as compared to tetraphenylethylene. Indeed, a cyclic voltammetric analysis of **1b** showed that its oxidation potential (E_{ox1} = 1.59 V vs SCE) was ~230 mV higher than the tetraphenylethylene (E_{ox1} = 1.36 V vs SCE) and was comparable to tetrakis(4-bromophenyl)ethylene (E_{ox1} = 1.51 V vs SCE) whose (partial) oxidative conversion to the corresponding DAP required 96 h (see Table 1).

Encouraged by the partial oxidative conversion of **1b** to dibenzochrysene (**1d**) in Scheme 4, we subjected various isolated **DAPs** to reaction with DDQ/H$^+$, according to Scheme 4, and found that they can be transformed to the corresponding dibenzochrysenes with excellent to moderate conversions depending on their redox potentials (see Table 2).

Table 2 shows that DAP **2b** with the lowest oxidation potential (i.e., E_{ox1} = 1.37 V) undergoes an efficient and quantitative conversion to the corresponding tetramethyldibenzochrysene **2d** while electron-poor bromo-substituted

Table 2. Oxidative Transformation of DAPs to DBCs Using DDQ/H^+ Oxidant System in Dichloromethane at 22 °C

reactant	E_{ox1}/E_{ox2} (V vs SCE)[b]	product	time (h)	% conversion (% yield)[a]
 **1b**	1.59/>2.0	 **1d**	24.0	14 (98)
 **2b**	1.37/~1.7	 **2d**	0.5	100 (98)
 **3b**	1.53/~1.9	 **3d**	9.0	100 (76)
 **4b**	1.46/~1.8	 **4d**	1.0	100 (94)
 **5b**	1.48/~1.8	 **5d**	6.0	100 (80)[c]
6b	1.64/>2.0	-none-	24.0	--
7b	1.66/>2.0	-none-	24.0	--
8b	1.80/>2.0	-none-	96.0	–

[a] Conversion percentages were determined by ^{1}H NMR spectroscopy and yields refer to the isolated dibenzochrysenes based on recovered DAPs. [b] The E_{ox1} and E_{ox2} values were determined by cyclic voltammetry in CH_2Cl_2 containing 0.1 M $n$$Bu_4PF_6$ at a scan rate of 200 mV s^{-1}. [c] An isomeric mixture of **5b**/**5c** was used.

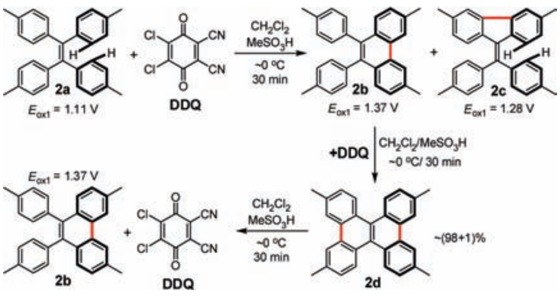
DAPs **6b**, **7b**, and **8b** with E_{ox1} values ≥1.64 V, expectedly, do not react under these conditions.[17]

Synthesis of various substituted dibenzochrysenes in Table 2 can also be accomplished directly from tetraarylethylene using 2 equiv of DDQ under otherwise identical conditions listed in Scheme 4 (see Scheme 5). A one-pot sequential oxidative transformation of **2a** to **2d** was also carried out, and it showed that an ~2:1 mixture of **2b** and diarylmethylidenefluorene **2c** formed after the addition of the first equivalent of DDQ was cleanly transformed into a single dibenzochrysene **2d** upon addition of a second equivalent of DDQ (Scheme 5).[18]

Similarly, tetraarylethylene **3a**, **4a**, and **5a** were converted to the corresponding dibenzochrysenes **3d**, **4d**, and **5d**, respectively, in yields comparable to those in Table 2, using 2 equiv of DDQ in a one-pot procedure. Note that bromo-substituted TAEs (i.e., **6a**, **7a**, and **8a**) even with excess DDQ (3−5 equiv) afforded only the DAP derivatives (see Tables 1 and 2).

The observation of the *selective oxidative transformation of various TAEs to DAPs without the contamination forming DBCs with 1 equiv of DDQ* warrants further explanation, especially in light of the fact that the conversion of the TAE **2a** to DAP **2b** or DAP **2b** to DBC **2d**, under identical conditions, occurs on a similar time scale (e.g., see Scheme 5). As such, the explanation for this remarkable selectivity may lie in the fact that both of the oxidative transformations (i.e., TAE→DAP and DAP→DBC) proceed via an electron transfer mechanism.

Scheme 5. Sequential Oxidative Transformation of TAE **2a** to DAP **2c** and DBC **2d** Using 1 and 2 equiv of DDQ, Respectively



As noted above the oxidation potentials of DAPs are considerably higher than TAEs, and therefore in the presence of TAE, the concentration of the DAP cation radical is expected to be insignificant. For example, based on the oxidation potential difference of 260 mV between **2a** and **2b**, one can easily estimate that, even in a 1:1 mixture of $\mathbf{2a}^{+\bullet}$ and **2b**, the concentration of $\mathbf{2b}^{+\bullet}$ will be negligible (see eq 1).[11] Therefore the oxidative transformation of **2b** to corresponding dibenzochrysene **2d** via a cation radical mechanism will not occur while **2a** is present in the reaction mixture.

$$\mathbf{2a}^{+\bullet} + \mathbf{2b} \xrightleftharpoons{K = 2.8 \times 10^{-5}} \mathbf{2a} + \mathbf{2b}^{+\bullet} \qquad (1)$$

$$\Delta G = +260 \text{ mV or} \sim 6 \text{ kcal/mol}$$

In summary, we have shown that substituted 9,10-diarylphenanthrenes and dibenzochrysenes can be easily accessed from readily available symmetrical and unsymmetrical tetraarylethylenes by sequential oxidative transformation using 1 and 2 equiv of DDQ, respectively, in dichloromethane in the presence of methanesulfonic acid. The selective formation of 9,10-diarylphenanthrenes, without contamination from dibenzochrysenes, with 1 equiv of DDQ strongly suggests that these sequential oxidative transformations proceed via paramagnetic cation radicals as reactive intermediates. The detailed mechanisms of these oxidative transformations of tetraarylethylenes to 9,10-diarylphenanthrenes and dibenzochrysenes are currently under investigation and will be presented in due course.

Acknowledgment. We thank the National Science Foundation (Chemsitry) for financial support.

Supporting Information Available. Experimental procedures, $^1H/^{13}C$ NMR data, X-ray structure data for representative DAPs and spectra of various compounds. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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(17) Note that DDQ (E_{red} = +0.60 V vs SCE), in the presence of an acid, oxidizes a variety of aromatic donors with oxidation potentials as high as ~1.6 V vs SCE to the corresponding cation radicals; however, the rate of formation of these cation radicals decreases with the increasing oxidation potential of donors; see: Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114 and references cited therein.

(18) The bifluorenylidene formed from **2a**, after oxidative C−C bond formation, can easily be isomerized to DBC **2d** by an acid or electron-transfer catalysis; see: Suzuki, K.; Yamaguchi, U. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 735 and references cited therein.