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Probing the Arenium-Ion (ProtonTransfer) versus the Cation-Radical (Electron Transfer) Mechanism of Scholl Reaction Using DDQ as Oxidant

Linyi Zhai, Ruchi Shukla, Shriya H. Wadumethrige, and Rajendra Rathore*
Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

rajendra.rathore@marquette.edu

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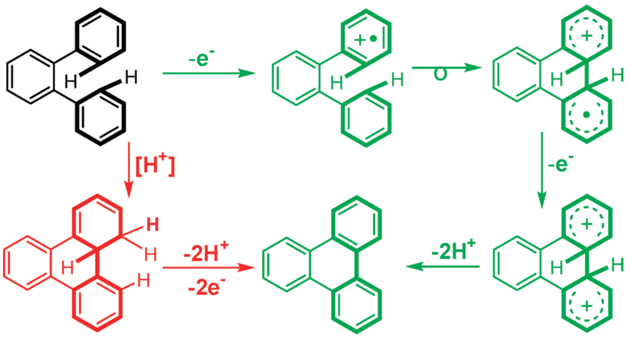
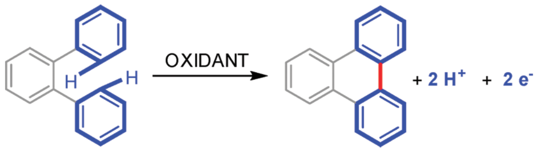


DDQ/H^+ system readily oxidizes a variety of electron donors with oxidation potential as high as ~1.7 V to the corresponding cation radicals. A re-examination of the controversial arenium-ion versus cation-radical mechanisms for Scholl reaction using DDQ/H^+ together with commonly utilized $FeCl_3$ as oxidants led us to demonstrate that the reaction proceeds largely via a cation-radical mechanism. The critical experimental evidence in support of a cation-radical pathway for the Scholl reaction includes the following: (i) There is no reaction in Scholl precursors in a mixture of dichloromethane and various acids (10% v/v). (ii) The necessity to use powerful oxidants such as ferric chloride ($FeCl_3$) or DDQ/H^+ for Scholl reactions is inconsistent with the arenium-ion mechanism in light of the fact that aromatization of the dihydro intermediates (formed via arenium-ion mechanism) can be easily accomplished with rather weak oxidants such as iodine or air. (iii) Various Scholl precursors with oxidation potentials ≤ 1.7 V vs SCE undergo ready oxidative C−C bond formation with DDQ/H^+ as oxidant, whereas Scholl precursors with oxidation potentials greater than >1.7 V vs SCE do not react. (iv) Finally, the feasibility of the dicationic intermediate, formed by loss of two electrons, has been demonstrated by its generation from a tetraphenylene derivative using DDQ/H^+ as an oxidant.

Introduction

The Scholl reaction[1] is one of the oldest C−C bond-forming reactions and has been extensively utilized for intramolecular (oxidative) cyclodehydrogenation of a variety of *o*-terphenyls and hexaarylbenzenes to produce the corresponding planar polycyclic aromatic hydrocarbons (PAHs) such as triphenylenes, hexa-*peri*-hexabenzocoronenes (HBCs), etc.[2] In its simplest form, the Scholl reaction can be represented as intramolecular oxidative C−C bond formation between the two benzenoid rings to produce a biaryl linkage, i.e., eq 1.



(1)

The Scholl reaction in eq 1 can be accomplished by using a variety of oxidants such as $FeCl_3$,[3] $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$,[4] $Tl(O_2CCF_3)_3$ in CF_3CO_2H or $BF_3 \cdot OEt_2$,[5] $Pb(OAc)_4/BF_3 \cdot Et_2O$ in MeCN,[6] triethyloxonium hexachloroantimonate ($Et_3O^+SbCl_6^-$),[7] $SbCl_5$,[8] $MoCl_5$,[9] etc. Moreover, the

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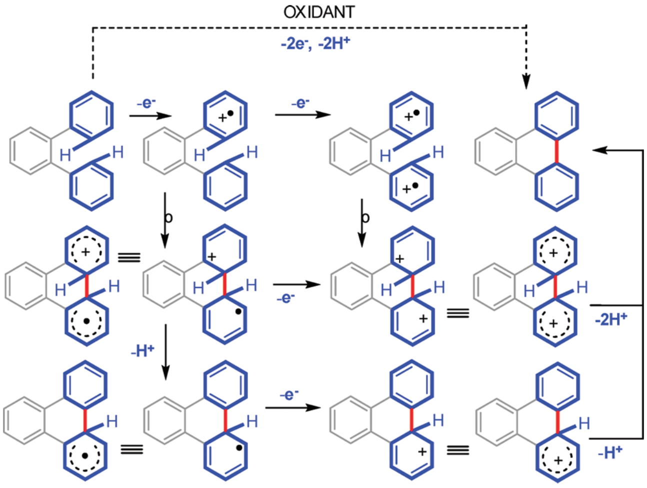
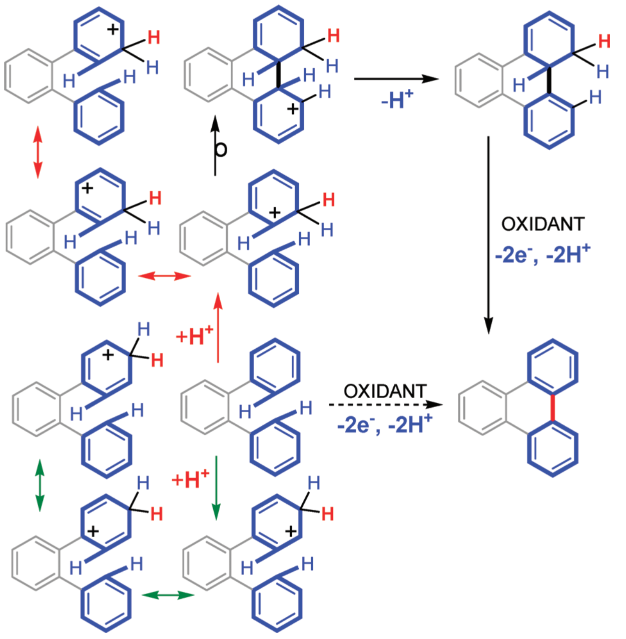
SCHEME 1. Cation Radical (or Electron Transfer) Mechanism for the Scholl Reaction



reaction in eq 1 can also be effected by electrochemical oxidation.[10] The involvement of cation radical intermediates (formed by 1-e$^-$ oxidation) in biaryl synthesis has been carefully probed by Parker and co-workers.[11] A detailed mechanism of oxidative biaryl synthesis involving cation radical intermediates is presented in Scheme 1.

A recent series of papers by King and co-workers[12,13] have advocated that Scholl reaction occurs via diamagnetic arenium ion intermediates (see Scheme 2) owing to the presence of adventitious acids in various oxidizing systems[3−9] utilized for Scholl reaction. It is further suggested by King and co-workers[12] that these reactions are accelerated as they proceed because of the formation of 2 equiv of acid per C−C bond formation. Interestingly, however, no evidence has been forthcoming for such a time-dependent acceleration which, if true, can be taken advantage of by added acids (see Scheme 2).

SCHEME 2. Arenium Ion (or Proton Transfer) Mechanism for the Scholl Reaction



The arenium-ion mechanism, depicted in Scheme 2, demands that C−C bond formation be accomplished only if the protonation occurs at a least preferred site, i.e., *meta* to an electron-releasing phenyl substituent (i.e., red arrow in Scheme 2) and finally producing a nonaromatic cyclohexadiene derivative.[12,13] Furthermore, the mechanism of aromatization of the cyclohexadiene derivative is overlooked in these studies[12,13] and supposedly is rapid and proceeds via an ECEC mechanism (vide infra).[10,11] It is further noted that no experimental evidence is available from these studies for the time-dependent acceleration of the Scholl reaction or the acid-catalyzed formation of the nonaromatic cyclohexadiene derivatives.[12,13]

Reactions involving proton transfers differ from electron transfer reactions in that the reactive intermediates are diamagnetic cations as opposed to paramagnetic cation radicals, and such a traditional (ionic versus radical) dichotomy continues to chronicle these mechanistic processes in separate, discrete mechanistic categories. Interestingly, however, the most favored method for generating paramagnetic cation radicals from electron-rich aromatic donors for ESR spectroscopic studies[14] involves their exposure to strong acids such as sulfuric or trifluoroacetic acids, where the conjugate acid (DH$^+$), formed by protonation of an aromatic donor (D), acts as an oxidant.[15,16] It is important to

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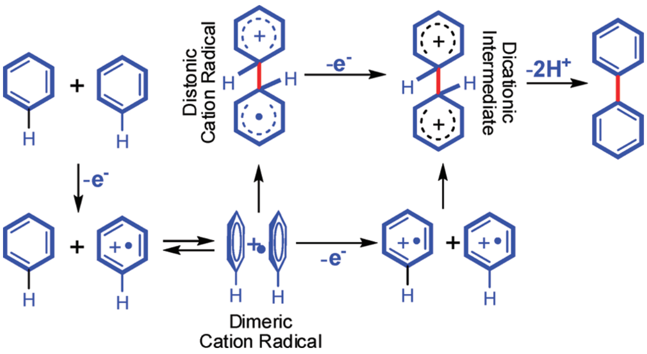
SCHEME 3. Two Pathways for Radical Cation Coupling To Form the Dicationic Intermediate



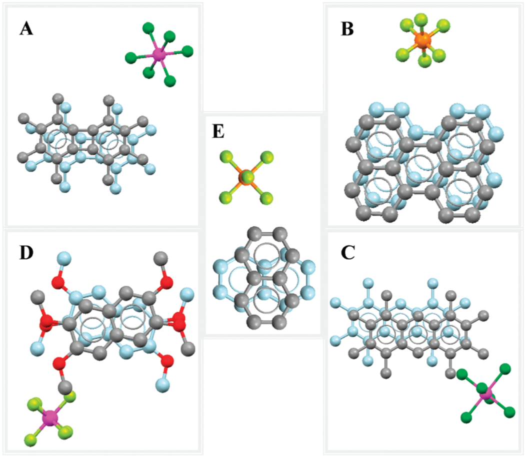


FIGURE 1. Representative X-ray structures of dimeric cation radicals showing the sandwich-like geometry: (A) $[\text{octamethylbiphenylene}]_2^{+\bullet}\text{SbCl}_6^-$,[22] (B) $[\text{perylene}]_2^{+\bullet}\text{PF}_6^-$,[24] (C) $[\text{octamethylanthracene}]_2^{+\bullet}\text{SbCl}_6^-$,[22] (D) $[\text{tetramethoxynaphthalene}]_2^{+\bullet}\text{SbF}_6^-$,[25] (E) $[\text{naphthalene}]_2^{+\bullet}\text{SbF}_6^-$.[26]

note that, generally, only a very small fraction of the donor molecules are oxidized to the corresponding cation radical (i.e., $\ll$1%) even upon extended exposure to the strongly acidic media.[14,17] It is a daunting task to clearly distinguish the arenium-ion (H^+ transfer) versus cation-radical (e^- transfer) pathways in a given reaction owing to the similar chemical reactivities of paramagnetic cation radicals and arenium ions. This distinction is especially difficult in the Scholl reaction because of the coexistence and ready interchangeability of these reactive intermediates. However, despite these difficulties, ample experimental evidence has been accumulated for the cation-radical pathway[7,10,11,18,19] for the Scholl reaction (or biaryl synthesis) as opposed to the arenium-ion mechanism.[12,13]

For example, according to theoretical calculations by King and co-workers,[12] a key contentious step in the cation-radical pathway for the Scholl reaction (see Schemes 1 and 3) is the intermediacy of the dicationic intermediate arising from either the coupling of two benzenoid cation radicals or via a coupling of the cation radical with its neutral counterpart (i.e., via a dimeric cation radical) followed by 1-e^- oxidation, i.e., Scheme 3.

First, the existence of dimeric cation radicals via a spontaneous association of a cation radical with its neutral counterpart in a sandwich-like geometry from a variety of aromatic electron donors has been established not only by spectroscopic methods by the observation of doubling of the hyperfine lines in their ESR spectra[20−22] and by the presence of intense intervalence transitions in near-IR region of their electronic spectra[22,23] but also by isolation and X-ray crystallography of crystalline dimeric cation-radical salts from a variety of aromatic electron donors (e.g., see Figure 1).[22,24−26]

It is also noted that formation of the dimeric cation radicals in Scheme 3 is exothermic by ~200−300 mV (or 4−7 kcal/mol), and lowering of the redox potentials owing to the stabilization of the cationic charge within a stabilized dimer formation is observed for both intermolecular as well as intramolecular pairs.[27] Second, the feasibility of the dicationic intermediate, which results in biaryl formation by loss of two protons (see Scheme 3), has also been demonstrated by isolation and X-ray crystallographic characterization of a robust dicationic intermediate from a tetraphenylene derivative, i.e., Scheme 4.[28]

For example, octamethoxytetraphenylene (OMT) undergoes a rapid single C−C bond formation ($C_1{-}C_5$ = 1.56 Å) between the *ipso*-carbons C_1 and C_5 of opposite phenylene rings upon a 2-electron oxidation either chemically (using $NO^+BF_4^-$, triethyloxonium hexachloroantimonate, or a stable hindered naphthalene cation-radical salt) or electrochemically to produce a magenta red (λ_{max} = 610 nm) solution of dicationic OMT^{+2}.[28] The structure of highly robust OMT^{+2} was established by X-ray crystallography (see Scheme 4).[28] It is also noted that the neutral OMT can be regenerated quantitatively by a 2-electron reduction of OMT^{+2} (Scheme 4) using zinc dust.[28]

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(17) The most likely explanation for formation of only a small amount of cation radical from various aromatic donors in strong acids is that the production of cation radical is accompanied by the formation of reduced dihydro-aromatic compound (see Rathore et al. in ref 15a), which in turn is reoxidized to the corresponding aromatic donor by cation radicals, thereby maintaining a small concentration of the cation radicals suitable for EPR spectroscopic measurments.

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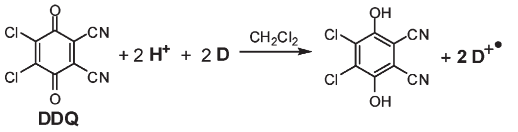
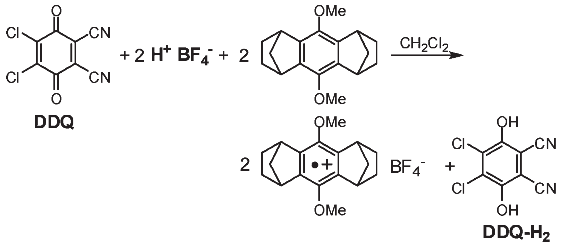
We[16] and others[29] have recently shown that quinones [such as tetrachloro-*p*-benzoquinone (chloranil, E_{red} = −0.02 V vs SCE) or dichlorodicyano-*p*-benzoquinone (DDQ, E_{red} = +0.60 V vs SCE)] in the presence of an added acid readily oxidize a variety of aromatic electron donors (such as naphthalene, anthracene, hexaalkylbenzenes, 1,4-dialkoxybenzenes, biphenyl, etc.), with oxidation potentials as high as ~1.7 V vs SCE, to the corresponding cation radicals according to the stoichiometry shown in eq 2.



(2)

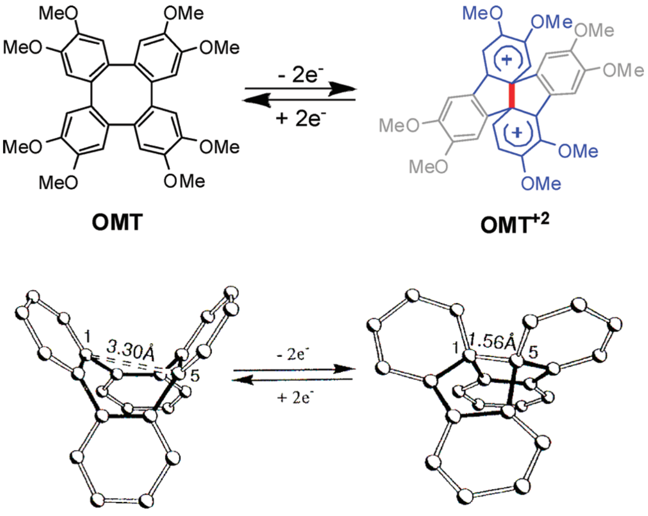
It is important to emphasize that in the absence of an added acid both chloranil and DDQ form vividly colored electron donor−acceptor (EDA) complexes with various aromatic donors,[30] and the highly *endothermic electron transfer* reaction in eq 2 is dramatically accelerated in the presence of an added acid.[16,29] The electron-transfer stoichiometry in eq 2 was independently confirmed by a quantitative isolation of a stable hydroquinone ether cation radical according to eq 3.[16]



(3)

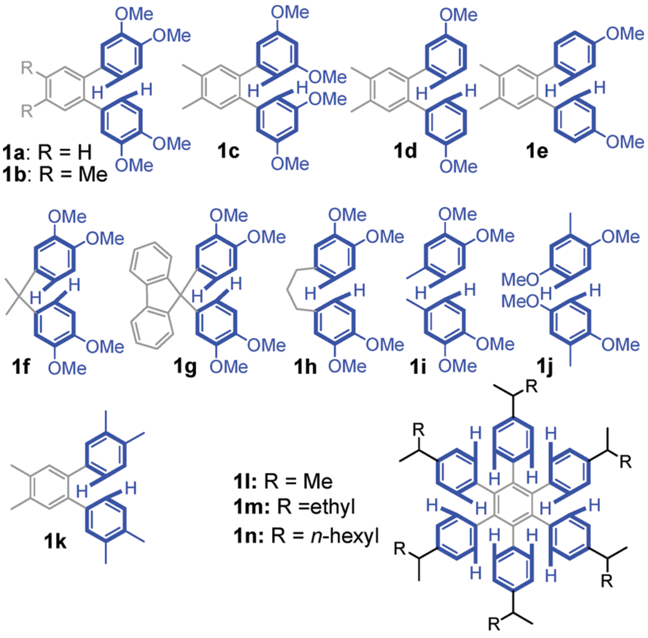
Herein, we will show that the DDQ/acid system (which readily oxidizes a variety of aromatic donors to the corresponding cation radicals) can be employed for Scholl reactions (or biaryl synthesis) as demonstrated by the preparation of a number of triphenylenes and hexa-*peri*-hexabenzocoronenes under mild conditions.[31] Moreover, we will show that a number of highly reactive (electron-rich) Scholl precursors including hexarylbenzenes (see Chart 1) do not undergo cyclodehydrogenation or produce nonaromatic cyclohexadiene derivatives (Scheme 2) when exposed to strong acids (such as HCl, CF_3CO_2H, CH_3SO_3H, HBF_4) or Lewis acids (such as $BF_3{\cdot}OEt_2$ or $AlCl_3$) alone for extended periods (1 to 24 h). Interestingly, however, various Scholl precursors in Chart 1 do undergo efficient oxidative cyclodehydrogenation within minutes if the above mixtures are treated with one equiv. of DDQ per C−C bond formation. Herein, the details of these findings are discussed in the context of arenium-ion versus cation-radical mechanisms of the Scholl reaction (or oxidative biaryl synthesis) by utilizing both DDQ and commonly utilized ferric chloride ($FeCl_3$) as oxidants and a variety of Scholl precursors including hexa-arylbenzenes.

SCHEME 4. X-ray Crystallographic Evidence for the Existence of the Dicationic Intermediate Formed by a 2-Electron Oxidation[a]



[a] Methoxy groups are omitted from X-ray structures for the sake of clarity.

CHART 1. Structure and Numbering Scheme for Various Scholl Precursors Used in This Study



Results and Discussion

Synthesis of various Scholl precursors. The Scholl precursors (Chart 1), employed in this study were synthesized using standard synthetic procedures.

For example, the *o*-terphenyl derivatives (**1a**−**1e** and **1k**) were obtained by standard *Suzuki* reactions[32] while the

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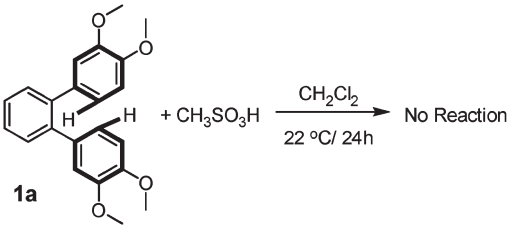
diarylmethane derivatives **1f** and **1g** were prepared by an acid-catalyzed condensation of 1,2-dimethoxybenzene with acetone and fluorenone,[33] respectively. The hexaarylbenzenes **1l**−**1n**,[34] the diarylpropane **1h**[35] and other precursors (i.e., **1i** and **1j**)[36] were available from published literature procedures from our laboratory. The synthetic details for various Scholl precursors in Chart 1 and the spectral data together with the $^{1}H/^{13}C$ NMR spectra are presented in the Supporting Information Section.

Reaction of Various Scholl Precursors with Various Protic/Lewis Acids. When a 0.01 M solution of *o*-terphenyl **1a** in a mixture of dichloromethane and methanesulfonic acid (10% v/v) was stirred under an argon atmosphere at 22 °C, it turned pale yellow. The reaction was monitored during a course of 24 h by ^{1}H NMR spectroscopy as follows. Thus, periodically an aliquot was removed and treated with solid sodium carbonate to neutralize the acid followed by filtration and removal of the solvent in vacuo. The ^{1}H NMR spectroscopic and thin-layer chromatographic analysis of the resulting residue showed that **1a** remained completely unchanged during a course of 24 h, i.e. eq 4.



(4)

Similarly, *o*-terphenyl **1a** did not undergo any reaction when it was exposed to other protic acids such as CF_3CO_2H, HBF_4, a saturated solution of gaseous HCl in dichloromethane or Lewis acids such as $BF_3 \cdot OEt_2$ and anhydrous aluminum trichloride ($AlCl_3$) in dichloromethane for up to 24 h at ambient temperatures. Furthermore, all Scholl precursors (i.e., **1a**−**1n**) in Chart 1 similarly did not undergo any reaction when treated with a 1:9 mixture of methanesulfonic acid in dichloromethane according to the eq 4 or with a saturated solution of HCl in dichloromethane for up to 24 h. It is also important to emphasize that hexakis(4-isoalkylphenyl)benzene derivatives **1l**−**1n**, precursors to planar HBCs, remained unchanged even when reacted with either a protic acid or a Lewis acid for up to 72 h.

Oxidative Cyclodehydrogenation of 1a with Various Protic/Lewis Acids and DDQ. Interestingly, when a 0.01 M solution of *o*-terphenyl **1a** in a mixture of dichloromethane and methanesulfonic acid (10%, v/v) was treated with 1 equiv of dichlorodicyano-*p*-benzoquinone (DDQ) under an argon atmosphere at ~0 °C, the solution immediately turned dark green. Upon stirring for 5 min at 0 °C, the reaction mixture took on a dark brown coloration. The reaction was quenched by the addition of a saturated aqueous solution of sodium bicarbonate (20 mL) followed by a standard aqueous workup, which afforded the corresponding triphenylene **2a** in quanttative yield (i.e., eq 5). Note that the reduced hydroquinone ($DDQ\text{-}H_2$) dissolves well in the aqueous sodium bicarbonate layer and can be recovered quantitatively by an acidification followed by extraction with ether. The identity of recovered $DDQ\text{-}H_2$ was confirmed by comparison of the ^{13}C NMR spectrum and melting point with an authentic sample.[37]

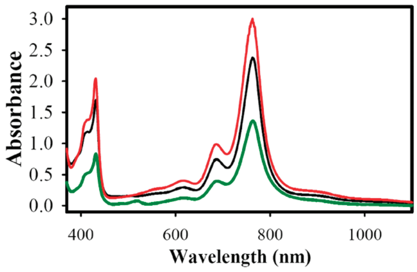
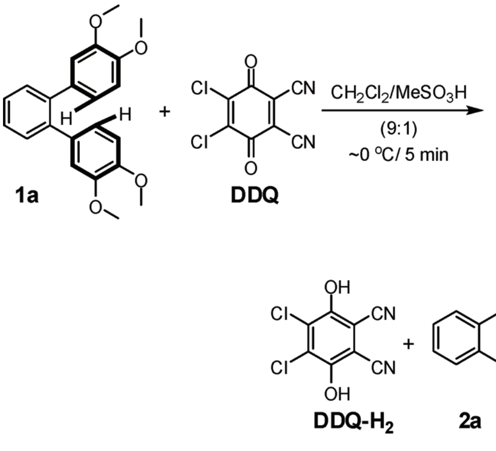


FIGURE 2. Comparison of the UV−vis absorption spectra of tetramethoxytriphenylene cation radical $2a^{+\bullet}$ generated using DDQ/H^{+} (black line) and $MA^{+\bullet}SbCl_6^{-}$ (red line) in dichloromethane. The green spectrum was obtained from an aliquot removed after 30 s from the reaction in eq 5.



(5)

The instantaneous appearance of green coloration in the reaction in eq 5 was determined to arise owing to the formation of the cation radical of tetramethoxytriphenylene **2a**. For example, when a solution of **2a** in a 9:1 mixture of dichloromethane−methanesulfonic acid was exposed to 0.5 equiv of DDQ, the solution immediately took on the characteristic green coloration. The UV−vis spectral analysis of the green solution (see Figure 2) together with a spectral comparison of an authentic spectrum of the $2a^{+\bullet}$ [generated using 9,10-dimethoxy-octahydro-[1,4:5,8]-dimethanoanthracenium hexachloroantimonate,[38] $MA^{+\bullet}SbCl_6^{-}$ (E_{red} = 1.14 V vs SCE), as a robust 1-electron oxidant] confirmed the formation of the tetramethoxytriphenylene cation radical $2a^{+\bullet}$ (λ_{max} = 410, 613, 684, and 762 nm), i.e., Scheme 5.

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[33] Apel, S.; Nitsche, S.; Beketov, K.; Seichter, W.; Seidel, J.; Weber, E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1212.

[34] Chebny, V. J.; Gwengo, C.; Gardinier, J. R.; Rathore, R. *Tetrahedron Lett.* **2008**, *49*, 4869.

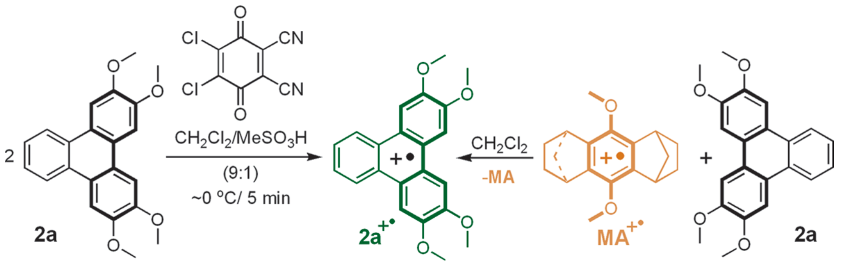
[35] Shukla, R.; Rathore, R. *Synthesis* **2008**, 3769.

[36] Sun, D.; Lindeman, S. V.; Rathore, R.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1585.

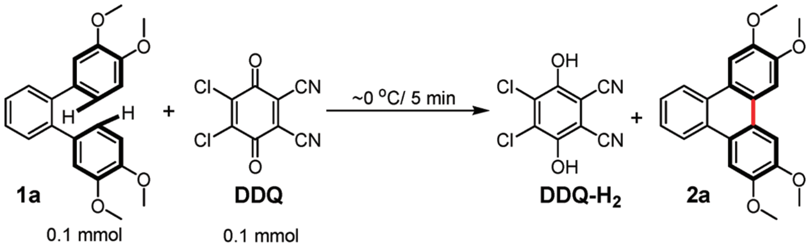
[37] Hageman, L.; McNelis, E. *J. Org. Chem.* **1975**, *40*, 3300. Note that DDQ can be regenerated quantitatively from $DDQH_2$ by oxidation using dinitrogen tetraoxide (Brook, A. G. *J. Chem. Soc.* **1952**, 5040) or conc nitric acid (Newman, M. S.; Khanna, V. K. *Org. Prep. Proc. Int.* **1985**, *17*, 422).

[38] (a) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Synth.* **2005**, *82*, 1. (b) Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399.

SCHEME 5. Generation of Tetramethoxytriphenylene Cation Radical ($2a^{+\bullet}$) Using DDQ/H^+ and $MA^{+\bullet}$ in CH_2Cl_2 at 22 °C



SCHEME 6. Formation of Tetramethoxytriphenylene 2a Using a Combination of DDQ and Various Protic Acids and Lewis Acids in CH_2Cl_2 at 22 °C

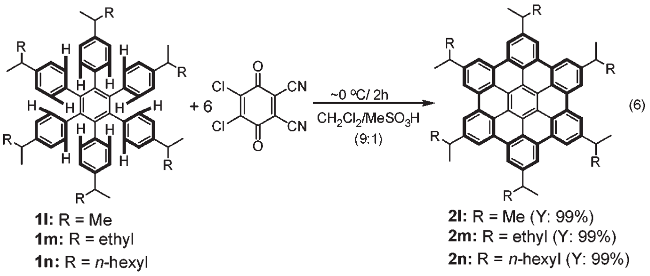


CH_2Cl_2 (9 mL)/$MeSO_3H$ (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/CF_3CO_2H (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/HBF_4-OEt_2 (1 mL)	Yield: 100%
CH_2Cl_2 (9 mL)/BF_3-OEt_2 (10 equiv.)	Yield: 100%
CH_2Cl_2 (9 mL)/$AlCl_3$ (10 equiv.)	Yield: 100%

As summarized in Scheme 6, the oxidative cyclodehydrogenation of *o*-terphenyl **1a** can be accomplished using DDQ as an oxidant in the presence of either a protic acid (such as methanesulfonic acid, trifluoroacetic acid, or tetrafluoroboric acid) or a Lewis acid in quantitative yields. Note that DDQ or acid alone is not sufficient to carry out the transformation in Scheme 6. It is further emphasized that a combination of both DDQ and an acid is necessary to accomplish the transformation in Scheme 6 (also see eq 5).

Oxidative Cyclodehydrogenation of Various Scholl Precursors Using CH_3SO_3H/DDQ. Using the protocol developed in eq 5 (or Scheme 6), a variety of Scholl precursors (Chart 1) were subjected to the reaction with DDQ in the presence of readily available and cheap methanesulfonic acid, under the standard conditions described in eq 5, to afford the corresponding cyclodehydrogenated products in excellent yields (see Table 1). It is noteworthy that the Scholl reactions using DDQ/acid oxidation system were equally effective with substrates undergoing both *intramolecular* and *intermolecular* aryl−aryl C−C bond formations (see entries **1f** and **1i** in Table 1).

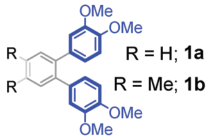
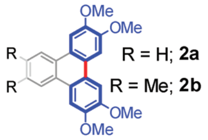
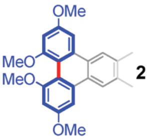
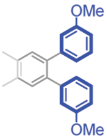
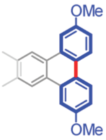
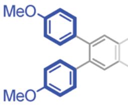
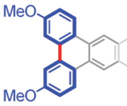
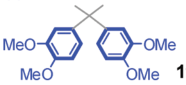
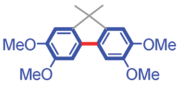
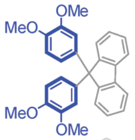
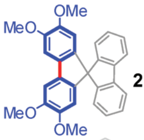
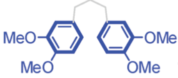
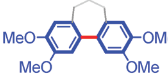
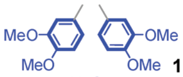
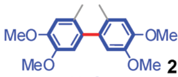
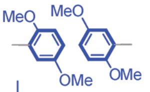
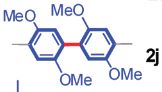
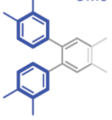
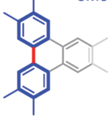
The versatility of the DDQ/acid system for the oxidative cyclodehydrogenation is further demonstrated by the preparation of soluble hexa-*peri*-hexabenzocoronenes (HBCs) from hexakis(4-isoalkylphenyl)benzenes **1l**−**1n**, where 6 new C−C bonds are formed in one step, in excellent yields. Thus, a reaction of a 0.01 M solution of hexaarylbenzene **1l** in a mixture of dichloromethane and methanesulfonic acid (10%, v/v) was treated with 6 equiv of DDQ under an argon atmosphere at ~0 °C. The resulting dark-colored mixture was stirred for 2 h, and a standard aqueous workup afforded pure HBC **2l** in a quantitative yield (eq 6).



The quantitative transformations of **1l**−**1n** to the corresponding HBC derivatives **2l**−**2n** require the formation of six C−C bonds and thus 6 equiv of DDQ is necessary for the complete conversion (eq 6). However, when the oxidation of a hexaphenylbenzene derivative (such as **1m**) was carried out with substoichiometric amounts of DDQ (e.g., 2 equiv), it afforded 33% of HBC **2m** and 66% unreacted **1m** with a quantitative mass balance, as determined by ^{1}H NMR spectroscopy (see Figure 3) as well as by the separation of **1m** and **2m** by chromatography. As such, this finding simply confirms that partially cyclized (planarized) intermediates of hexaarylbenzenes have relatively lower oxidation potentials as compared to the corresponding hexaarylbenzenes and therefore are far more reactive toward additional C−C bond formation as compared to the corresponding hexaarylbenzenes.[39]

Arenium Ion versus Cation Radical Mechanism of the Scholl Reaction. In order to facilitate the discussion of the arenium-ion versus cation-radical mechanism of Scholl

TABLE 1. Scholl Reaction and Products Obtained under the Standard Set of Conditions Using DDQ/$MeSO_3H$ in Dichloromethane at ~0 °C

reactant	product	time	% conversion (% yield)[a]
 R = H; **1a** R = Me; **1b**	 R = H; **2a** R = Me; **2b**	5 min 5 min	100 (99) 100 (99)
 **1c**	 **2c**	10 min	100 (50)[b]
 **1d**	 **2d**	30 min 5 min	66 (98)[c] 100 (99)[d]
 **1e**	 **2e**	30 min	100 (60)[d,b]
 **1f**	 **2f**	5 min	100 (99)
 **1g**	 **2g**	5 min	100 (99)
 **1h**	 **2h**	5 min	100 (98)
 **1i**	 **2i**	5 min	100 (99)
 **1j**	 **2j**	5 min	100 (99)
 **1k**	 **2k**	10 min	100 (99)

[a] Percent conversions were determined by ^1H NMR, and the yields refer to isolated products. [b] Approximately 30−40% of an unidentified compound was also formed. [c] NMR of crude reaction mixture showed that it contained 2:1 ratio of **2d** and **1d**. [d] 1.5 equiv of DDQ was used.

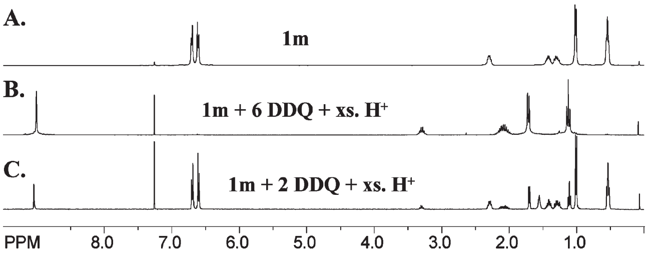


FIGURE 3. (A) ^1H NMR spectrum of hexakis(4-isobutylphenyl)-benzene (**1m**) in $CDCl_3$. (B) ^1H NMR spectrum of the crude product obtained after a reaction of **1m** with 6 equiv of DDQ in CH_2Cl_2 in the presence of CH_3SO_3H showing the quantitative formation of the corresponding HBC **2m**. (C) ^1H NMR spectrum of the crude product obtained after a reaction of **1m** with 2 equiv of DDQ in CH_2Cl_2 in the presence of CH_3SO_3H showing that only one-third of **1m** is transformed to corresponding HBC **2m**.

TABLE 2. Electrochemical Oxidation Potentials of Various Scholl Precursors (SP) and the Corresponding Cyclodehydrogenated Products (CD)[a]

Scholl precursor	$E_{ox(SP)}$ V vs SCE[b]	cyclized donor	$E_{ox(CD)}$ V vs SCE[c]	$E_{ox(SP)} - E_{ox(CD)}$
1a	1.20	**2a**	1.15	0.05
1b	1.11	**2b**	1.08	0.03
1c	1.20	**2c**	0.89	0.31
1d	1.68	**2d**	1.18	0.50
1e	1.56	**2e**	1.28	0.28
1f	1.26	**2f**	0.85	0.41
1g	1.27	**2g**	0.86	0.41
1h	1.32	**2h**	1.11	0.21
1i	1.35	**2i**	1.24	0.11
1j	1.27	**2j**	1.11	0.16
1k	1.33	**2k**	1.41	−0.08
1l	~1.6	**2l**	1.00	0.48
1m	~1.6	**2m**	1.00	0.48
1n	~1.6	**2n**	1.00	0.48

[a] Experimental conditions: a 1.0 mM solution of the substrate and 0.1 M nBu_4NPF_6 (as the supporting electrolyte) in dichloromethane at a scan rate of 200 mV s^{-1} and at 22 °C. [b] Irreversible cyclic voltammograms, $E_{ox(SP)}$ were determined from square-wave voltammograms. [c] Reversible cyclic voltammograms.

reaction, the redox potentials of various Scholl precursors (**1a**−**1n**) and the corresponding cyclodehydrogenated polyaromatic hydrocarbons (**2a**−**2n**) were determined by cyclic voltammetry. Electrochemical oxidations were performed at a platinum electrode as 1×10^{-3} M solutions in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Various Scholl precursors showed irreversible cyclic voltammograms, and therefore the oxidation potentials of **1a**−**1n** were determined by square-wave voltammetry[40] and are listed in Table 2. In contrast, the cyclized polyaromatic hydrocarbons **2a**−**2n** showed reversible cyclic voltammograms (CV) at scan rates between 25 and 400 mV s^{-1} with anodic/cathodic peak current ratios of $i_a/i_c = 1$ (theoretical) at ambient temperatures. The calibration of the CV peaks of **2a**−**2n** with ferrocene as an internal standard provided the reversible oxidation potentials that are compiled in Table 2.

Before examining the viability of the arenium-ion verses cation-radical mechanism for the Scholl reaction, it is important to add the caveat that diamagnetic arenium ions and paramagnetic cation radicals can coexist under the experimental conditions employed for Scholl reactions.[15,16,9] With this fact in mind, let us first consider the arenium-ion pathway for the Scholl reaction in light of the experimental facts described above. The arenium-ion pathway requires the protonation of a benzenoid ring of the Scholl precursor (**SP**) at a carbon *meta* to an electron-releasing group (see

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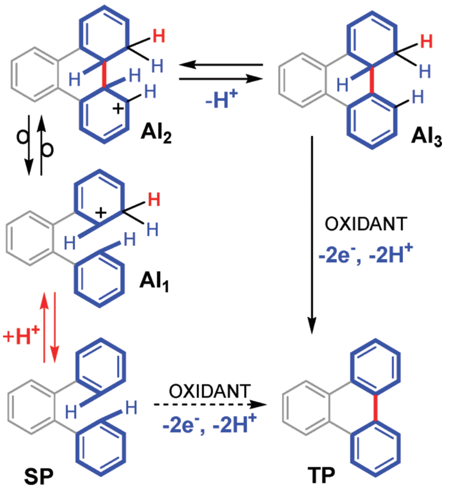
(39) The calculated structures (DFT at B3LYP/6-31G* level) of various polyaromatic intermediates and their energies during the transformation of a representative hexaarylbenzene to the corresponding HBC clearly show that introduction of and increasing number of C−C bonds in a hexaarylbenzene leads to planarized polycyclic aromatic hydrocarbons with increasing aromaticity and thus decreased redox potentials and in turn leads to their increased reactivity towards the Scholl reaction.

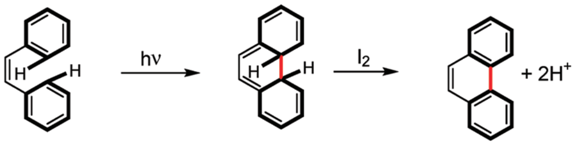
(40) Osteryoung, J. G.; Osteryoung, R. A. *Anal. Chem.* **1985**, *57*, 101A.

SCHEME 7. Arenium Ion Mechanism for the Scholl Reaction

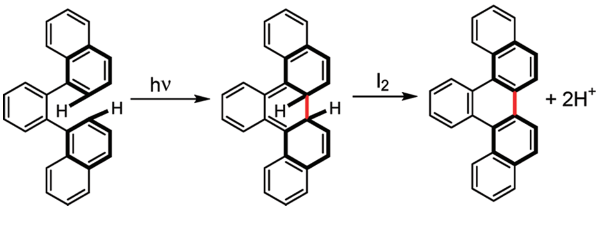


Scheme 2) to form an arenium ion intermediate (**AI$_1$**), which then undergoes an intramolecular Friedel–Crafts-type C–C bond formation (**AI$_2$**) followed by a rapid proton loss to produce a nonaromatic cyclohexadiene derivative (**AI$_3$**),[12,13] i.e., Scheme 7. The role of various oxidants [such as $FeCl_3$,[3] $CuCl_2$ or $Cu(OTf)_2$ and $AlCl_3$,[4] $Tl(O_2CCF_3)_3$ in CF_3CO_2H or $BF_3 \cdot OEt_2$,[5] $Pb(OAc)_4/BF_3$-Et_2O in MeCN,[6] triethyloxonium hexchloroantimonate ($Et_3O^+SbCl_6^-$),[7] $MoCl_5$[9]] in Scholl reactions, according to the arenium-ion mechanism, is limited to aromatization of the dihydroaromatic intermediate **AI$_3$** to complete the Scholl synthesis.

Interestingly, the necessity to use powerful oxidants such as ferric chloride ($FeCl_3$), the most commonly utilized oxidant for the Scholl reactions, would be unnecessary owing to the fact that aromatization of the dihydro intermediates of type **AI$_3$** can be easily accomplished with rather weak oxidants such as iodine (I_2) or oxygen, e.g., eqs 7 and 8.[41]



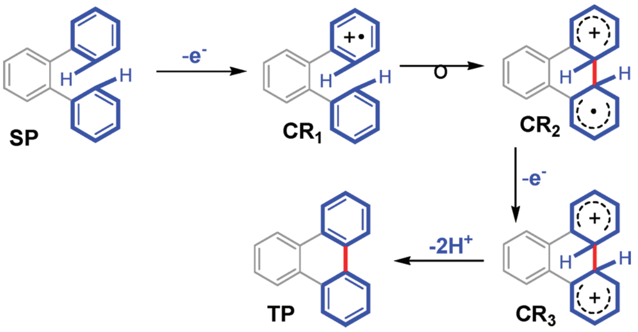
(7)[41c]



(8)[41a]

The cation-radical pathway for the Scholl reaction requires an initial 1-electron oxidation of the Scholl precursor to its cation radical (i.e., Scheme 8). The cation radical (**CR$_1$**) then undergoes an intramolecular C–C bond formation to yield a distonic radical cation (**CR$_2$**).[42] It is the distonic nature of this rearranged radical cation that facilitates the removal of a second electron at a much lower potential[43] and leads to the formation of a dicationic intermediate (**CR$_3$**) which upon the loss of two protons completes the Scholl synthesis, i.e., Scheme 8.

SCHEME 8. Cation Radical Mechanism for the Scholl Reaction



The following are the important considerations based on the experimental facts in support of the cation-radical mechanism in Scheme 8 for the Scholl reaction:

(1) The first evidence for the cation-radical mechanism for the Scholl reaction in Scheme 8 is the simple fact that most commonly employed oxidants including $FeCl_3$ for Scholl synthesis are powerful enough oxidants to effect the 1-electron oxidation of various Scholl precursors including various hexaarylbenzene derivatives to the corresponding cation radicals.[44] The DDQ/acid system described above as another efficient oxidant for the Scholl reaction is known to effect the 1-electron oxidation of a variety of electron donors, with oxidation potentials as high as ~1.7 V vs SCE, to the corresponding cation radicals.[16,29] Furthermore, various Scholl precursors in Table 1 as well as most of the hexaarylbenzenes excluding parent hexaphenylbenzene have oxidation potentials lower than 1.7 V vs SCE (see Table 2).

In this context it is important to note that highly electron-poor hexakis(4-bromophenyl)benzene[45] (E_{ox} > 2.1 V vs SCE) fails to undergo oxidative cyclodehydrogenation even upon prolonged exposure (1 week) to a large excess of $FeCl_3$.[46] As such this observation simply suggests that the inability of $FeCl_3$ to oxidize electron donors to their cation radicals with oxidation potentials beyond ~2 V prevents it from carrying out the oxidative cyclodehydrogenation of electron-poor hexakis(4-bromophenyl)benzene (Scheme 9). In order to further corroborate the thesis that 1-electron oxidation is a

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[41] (a) Tang, X.-Q.; Harvey, R. G. *J. Org. Chem.* **1995**, *60*, 3568. (b) Blackburn, E. V.; Timmons, T. J. *Quart. Rev. Chem. Soc.* **1969**, *23*, 482. (c) Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, *56*, 3769. (d) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed; Marcel Dekker: New York, 1989; Vol. 10, p 163. (e) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509. (f) Sudhakar, A.; Katz, T. J.; Yang, B. W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.

[42] The distonic cation radicals (Kiminkinen, L. K. M.; Stirk, K. G.; Kenttamaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 2027 and Bauld, N. L.; Gao, D. *J. Chem. Soc., Perkin 2* **2000**, 931) have ample literature precedent in the syntheses of a variety of biaryls, see: Hammerich, O.; Parker, V. D. in ref 11.

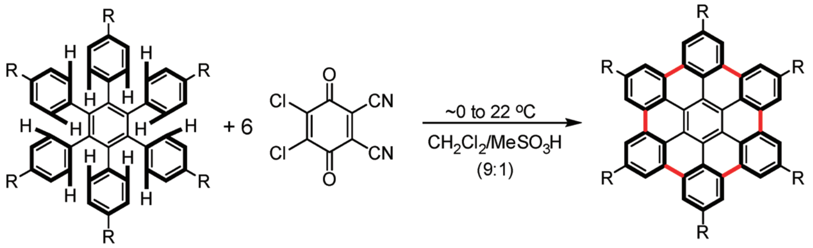
[43] Cyclohexadienyl-type radicals are known to undergo oxidation at ~0 V (vs SCE); see: Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

[44] $FeCl_3$ is known to affect oxidation of variety of electron donors to their cation radicals; see: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877 and references therein.

[45] Rathore, R.; Burns, C. L. *Org. Synth.* **2005**, *82*, 30.

[46] (a) Wu, J.; Fechtenktter, A.; Gauss, J.; Watson, M. D.; Kastler, M.; Fechtenktter, C.; Wagner, M.; Muellen, K. *J. Am. Chem. Soc.* **2004**, *126*, 11311. (b) Wu, J.; Watson, M. D.; Zhang, L.; Wang, Z.; Muellen, K. *J. Am. Chem. Soc.* **2004**, *126*, 177 and references therein.

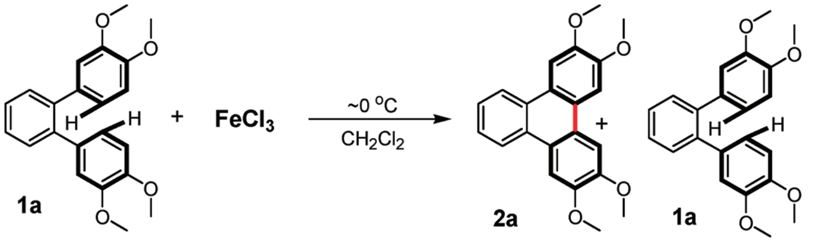
SCHEME 9. Effect of Redox Potentials on the Oxidative Cyclodehydrogenation of Various Hexaarylbenzenes



1o: R = *tert*-butyl; E_{ox} ~ 1.6 V SCE
1p: R = Br; E_{ox} > 2.1 V SCE
1q: R = H; E_{ox} >1.8 V SCE

2o: R = *tert*-butyl (Y: ~99%/2h)
2p: R = Br (Y: 0%/72h)
2q: R = H (Y: 0%/72h)

SCHEME 10. Formation of Tetramethoxytriphenylene 2a Using Varying Equivalents of $FeCl_3$ as Oxidant in CH_2Cl_2 at ~0 °C



0.1 mmol	0.2 mmol	30 min	0.05 mmol	0.05 mmol
0.1 mmol	0.4 mmol	30 min	0.09 mmol	0.01 mmol
0.1 mmol	0.6 mmol	30 min	0.1 mmol	0.00 mmol
0.1 mmol	0.2 mmol	8 h	~0.099 mmol	~0.001 mmol

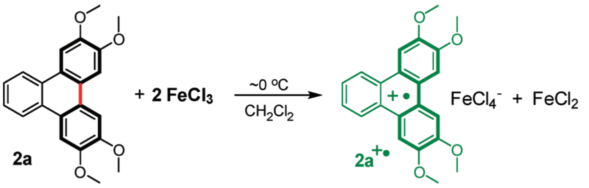
necessary step in Scholl reaction, we carried out the following tell-tale experiment.

As reiterated above, the DDQ/H^+ system fails to oxidize donors to their cation radicals with oxidation potentials beyond ~1.7 V vs SCE. Furthermore, parent hexaphenylbenzene[51] with E_{ox} > 1.8 V vs SCE is known to undergo oxidative cyclodehydrogenation using $FeCl_3$ as an oxidant.[12] Expectedly, however, a reaction of hexaphenylbenzene (**1q**) with DDQ/H^+ system for 72 h did not afford the corresponding parent HBC (**2q**) but allowed a quantitative recovery of both hexaphenylbenzene and DDQ (Scheme 9). Furthermore, only a slightly electron-rich derivative of hexaphenylbenzene **1o**[47] undergoes a quantitative conversion to the corresponding HBC **2o** when reacted with DDQ/H^+ (Scheme 9) or $FeCl_3$.[34]

The experimental facts presented in Scheme 9 are not readily reconciled on the basis of the arenium-ion mechanism presented in Scheme 7 but are completely consistent with the cation-radical pathway depicted in Scheme 8.

(2) In many reported procedures,[48-50] it is suggested that yields of Scholl reactions can be dramatically improved if a large excess of $FeCl_3$ (3-6 equiv per C-C bond formation) is employed, despite the fact that only 2 equiv of $FeCl_3$ is needed per C-C bond formation. For example, a 0.01 M solution of *o*-terphenyl **1a** in dichloromethane at ~0 °C was treated with varying equivalents of $FeCl_3$ to immediately produce a characteristic dark-green solution (vide infra). After 30 min, the reactions were quenched with excess dry methanol, and the products were isolated by a standard aqueous workup. The results are summarized in Scheme 10.

The incomplete transformation of **1a** to **2a** with 2 equiv of $FeCl_3$ in Scheme 10 can be reconciled by the fact that the cyclized product **2a** undergoes an efficient oxidation to its green-colored cation radical (**2a**$^{+\bullet}$) according to the stoichiometry in eq 9. The identity of **2a**$^{+\bullet}$ in eq 9 was confirmed by UV-vis spectral comparison with the spectrum of authentic **2a**$^{+\bullet}$ generated using either DDQ/acid system or $CRET^{+\bullet}SbCl_6^-$ as an oxidant (see Figure 2, vide supra).



(9)

In addition, $FeCl_3$ also forms a complex with hydrochloric acid, generated during the course of C-C bond

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[47] Hexakis(4-*tert*-butylphenyl)benzene (**1o**) can also be prepared by $Co_2(CO)_8$-catalyzed trimerization of the bis-4,4(di-*tert*-butylphenyl)-acetylene[48] or by $FeCl_3$-catalyzed *tert*-butylation of hexaphenylbenzene.[49]

(48) Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Muellen, K. *Chem.—Eur. J.* **2000**, *6*, 1834.

(49) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, *68*, 4071–4074.

(50) (a) Zhou, Y.; Liu, W.-J.; Zhang, W.; Cao, X.-Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Org. Chem.* **2006**, *71*, 6822–6828. and references therein. (b) Liu, W.-J.; Zhou, Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *Org. Lett.* **2008**, *10*, 2123. (c) Zhou, Y.; Liu, W.-J.; Zhang, W.; Cao, X.-Y.; Zhou, Q.-F.; Ma, Y.; Pei, J. *J. Org. Chem.* **2006**, *71*, 6822.

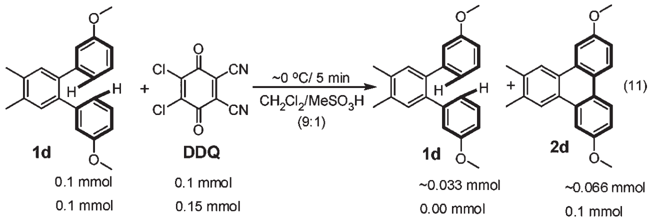
(51) (a) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, *13*, 2719. (b) Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Org. Chem.* **1976**, *13*, 155. (c) We also thank one of the reviewer for the suggestion to utilize magic blue as an oxidant to provide additional credence for the cation-radical mechanism for Scholl reaction.

formation, and thereby renders it to be a less efficient oxidant, i.e., eq 10.

$$FeCl_3 + HCl \underset{CH_2Cl_2}{\rightleftharpoons} HFeCl_4 \qquad (10)$$

The cation-radical mechanism demands that Scholl precursor **1a** undergo oxidation to its cation radical. Unfortunately, the oxidation of **1a** to **1a**$^{+\bullet}$ in Scheme 10 is hampered owing to the lowered oxidizing abilities of both H^+ $FeCl_4^-$ and **2a**$^{+\bullet}$ $FeCl_4^-$ (both of which are formed during the course of the reaction in Scheme 10) in comparison to the $FeCl_3$. Note that if **1a** was allowed to react with 2 equiv of $FeCl_3$ for an extended period (8 h) with a slow flow of argon to remove gaseous hydrochloric acid, it affords a nearly quantitative yield of **2a** (see Scheme 10, last entry). Interestingly, this observation serves to contradict the conjecture by King and co-workers[12] that Scholl reactions are accelerated as they proceed because of the formation of 2 equiv of acid per C−C bond formation.

(3) It is apparent from the examination of Tables 1 and 2 that the Scholl precursors with oxidation potentials as high as ~1.7 V (entry **1d** in Table 2) can be successfully subjected to the oxidative cyclodehydrogenation using the DDQ/acid system (eqs 5 and 6 and Scheme 6). Although, most Scholl precursors (see Table 1) produced nearly quantitative yields of the cyclodehydrogenated products in the presence of 1 equiv DDQ (per C−C bond formation), interestingly, however, 1,2-bis(3-methoxyphenyl)benzene (**1d**) afforded only ~66% of the cyclized 2,7-dimethoxytriphenylene (**2d**) together with ~33% of unreacted **1d**. However, if precursor **1d** was subjected to the same reaction conditions with 1.5 equiv of DDQ, it afforded a quantitative yield of methoxytriphenylene **2d** after aqueous workup, i.e., eq 11.



Moreover, it was independently confirmed that dimethoxytriphenylene **2d** (E_{ox} = 1.18 V vs SCE) undergoes a ready oxidation to its cation radical **2d**$^{+\bullet}$ (λ_{max} = 620, 687, and 760 nm) in the presence of DDQ and methanesulfonic acid according to the stoichiometry in eq 12 (compare eqs 2 and 3) and Figure 4.

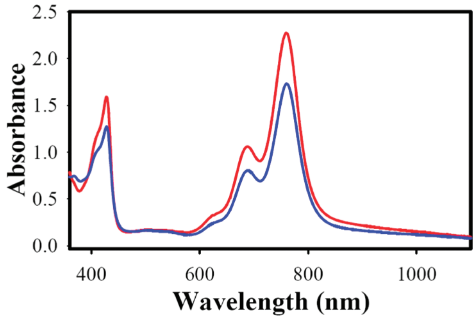
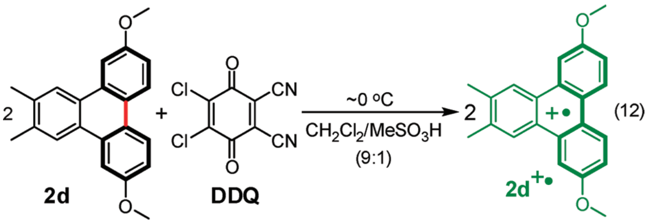
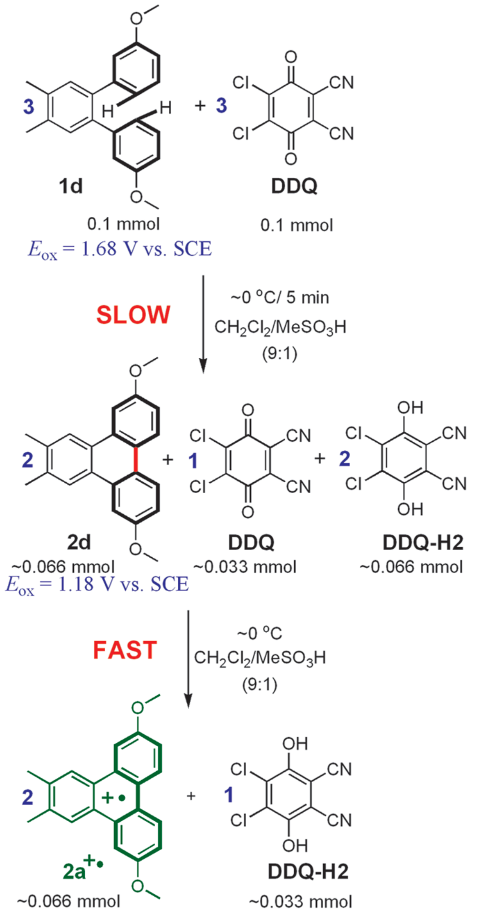


FIGURE 4. Comparison of the UV−vis absorption spectra of dimethoxytriphenylene cation radical **2d**$^{+\bullet}$ generated using DDQ/H^+ (red line) and $NO^+SbCl_6^-$ (blue line) in dichloromethane.



As summarized in Scheme 11, the formation of **2d** from **1d** in critical yield of 66% in eq 11 is readily reconciled by the fact that 1 equiv of DDQ is required to convert 1 equiv of **1d** to **2d**, whereas the oxidation of relatively electron-rich **2d** to its cation radical, under same conditions, requires only 0.5 equiv of DDQ (i.e., eq 12). A relatively low oxidation potential of **2d** (E_{ox} = 1.18 V vs SCE) as compared to **1d** (E_{ox} ~ 1.68 V vs SCE) ensures that it undergoes relatively fast oxidation to its cation radical as compared to **1d**. Furthermore, a highly endothermic (ΔE_{ox} ~ +500 mV) electron transfer from **1d** (E_{ox} ~ 1.68 V vs SCE) to **2d**$^{+\bullet}$ (E_{ox} = 1.18 V vs SCE) prevents the remaining **1d** (i.e., 0.33 equiv) from undergoing the Scholl cyclodehydrogenation (Scheme 11). Also, note that, owing to the high oxidation potential of **1d** (E_{ox} ~ 1.68 V vs SCE), its oxidation to cation radical by **2d**$^{+\bullet}$

SCHEME 11. Rationalization of the Observation of 2:1 Stoichiometry in Equations 11 and 12

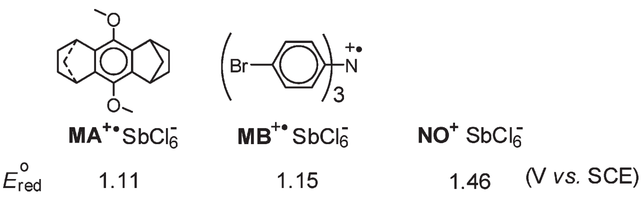


(E_{ox} = 1.18 V vs SCE) is further hampered by the presence of DDQ-H2, which effectively competes with **1d** for electron transfer equilibrium with $\mathbf{2d}^{+\bullet}$

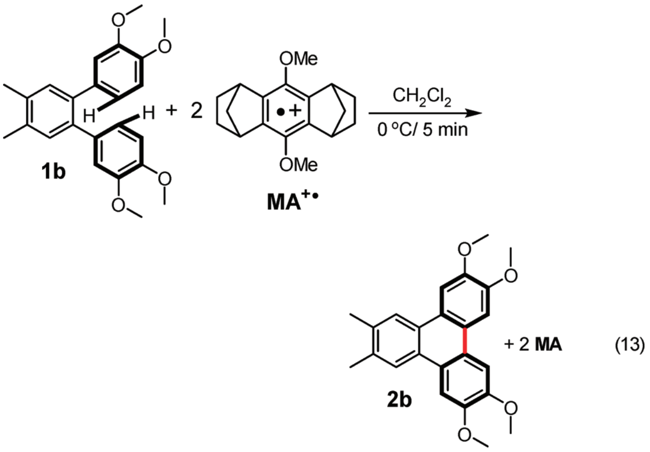
Importantly, the rationale in Scheme 11 further disfavors the arenium-ion pathway as the predominant mechanism for the Scholl reaction. It is re-emphasized that $\mathbf{2d}^{+\bullet}$ (E_{red} = 1.18 V vs SCE) could have easily served as an effective oxidant for the aromatization of the dihydro-aromatic intermediate (**AI$_3$**) in an arenium-ion pathway and thus would have led to a quantitative conversion of **1d** to **2d** in eq 11.

(4) Although we have earlier demonstrated[16,29] that DDQ in the presence of either a protic acid or a Lewis acid can affect the oxidation of a variety of aromatic donors to the corresponding cation radicals quantitatively (e.g., see eq 3), the need of an acid in the usage of DDQ as an oxidant in the Scholl reaction remains a source of concern as to the validity of the electron-transfer mechanism of Scholl reaction. Accordingly, herein we utilize three well-known 1-e$^-$ oxidants (see Chart 2) for the oxidative cyclodehydrogenation of an electron-rich precursor **1b** as follows.

CHART 2. Structures of Various Well-Known 1-e$^-$ Oxidants for the Oxidative Cyclodehydrogenation of Electron-Rich Precursor 1b



Thus, a 0.01 M solution of **1b** in dichloromethane was treated with 2 equiv of $\mathbf{MA}^{+\bullet}$ (E_{red} = 1.11 V vs SCE),[38] under an argon atmosphere at ~0 °C, which immediately afforded a characteristic green-colored solution identical to that obtained with DDQ/H$^+$. The resulting mixture was stirred for 5 min and was subjected to standard aqueous workup to afford **2b** together with neutral hydroquinone ether **MA** in a quantitative yield (eq 13).



Similarly, a reaction of Scholl precursor **1b** with either magic blue $\mathbf{MB}^{+\bullet}$ (E_{red} = 1.15 V vs SCE)[51] or nitrosonium hexacloroantimonate $\mathbf{NO}^+$ (E_{red} = 1.46 V vs SCE),[52] under the reaction conditions depicted in eq 13, afforded a quantitative yield of **2b**. The successful usage of clean 1-e$^-$ oxidants (Chart 1) for the Scholl reaction in eq 13 further provides the credence to the cation-radical pathway for Scholl reaction.

(5) The feasibility of a dicationic intermediate (**CR$_3$**) in the cation-radical mechanism (see Scheme 8) for the Scholl reaction has been questioned by King and co-workers.[12] Herein, we provide conclusive evidence, using DDQ/H$^+$ as oxidant, that dicationic intermediate **CR$_3$** is a viable intermediate in the cation-radical pathway of the Scholl reaction as follows. A dichloromethane solution of ocatmethoxytetraphenylene (OMT), which forms a stable dicationic salt upon 2-electron oxidation akin to the dicationic intermediate **CR$_3$** (see Scheme 8),[28] was treated with 1 equiv of DDQ in the presence of methanesulfonic acid to afford a characteristic magenta-red solution of OMT^{+2} in quantitative yield (see Figure 5) according to the stoichiometry depicted in Scheme 12.

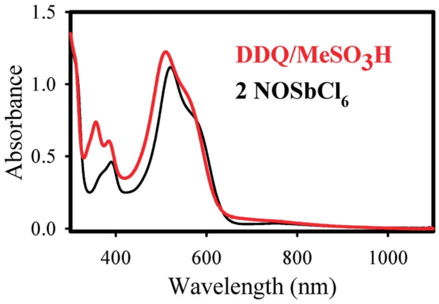


FIGURE 5. Comparison of the UV−vis absorption spectra of dicationic OMT^{+2} obtained by addition of 1 equiv of OMT to a 3 mL solution of 2.5 × 10^{-5} M DDQ in 9:1 mixture of dichloromethane and CH_3SO_3H (red line) or 5.0 × 10^{-5} M $NO^+SbCl_6^-$ (black line)[28] in dichloromethane.

The minor differences in the absorption spectra of **OMT^{+2}** when generated using DDQ/H$^+$ [λ_{max} = 510 and 561 (shoulder) nm] and NO$^+$ [λ_{max} = 521 and 576 (shoulder) nm][28] are attributed to different counteranions, i.e., $CH_3SO_3^-$ and $SbCl_6^-$, which differ significantly in their nucleophilicities.

It is noted that in above tetraphenylene OMT, the formation of dicationic intermediate OMT^{+2} is possible because of the fact that that the cyclized cation radical intermediate (such as CR$_2$) in the case of OMT does not have a proton that can be lost and therefore undergoes a second oxidation to produce the dicationic intermediate. However, at this juncture, one cannot easily distinguish whether a Scholl reaction proceeds via the pathway of a dicationic intermediate (see Scheme 8).

Summary and Conclusions

In summary, we have demonstrated that the DDQ/H$^+$ oxidation system (which is known to oxidize a variety of electron donors with oxidation potential as high as ~1.7 V to the corresponding cation radicals) can be effectively employed for the preparation of a variety of oxidative cyclodehydrogenation reactions. The procedure described herein with DDQ/H$^+$ rather than most commonly utilized oxidants such as $FeCl_3$, $MoCl_5$, or $SbCl_5$ for the Scholl reaction

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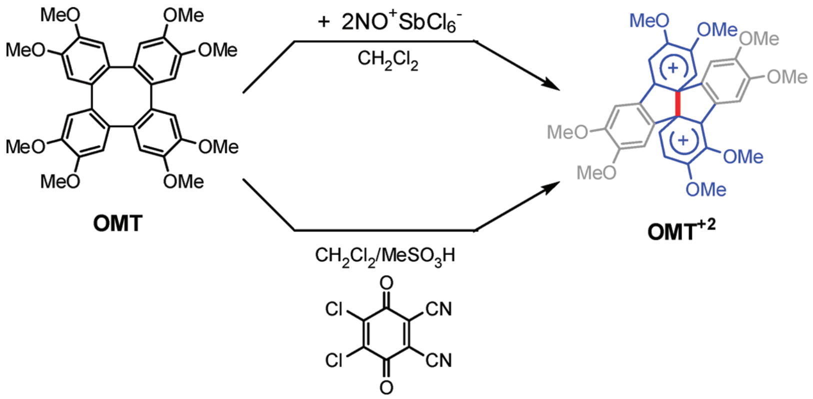
(52) Rathore, R.; Abdelwahed, S. H.; Guzei, I. A. *J. Am. Chem. Soc.* **2004**, *126*, 13582 and references therein.

SCHEME 12. **Oxidation of OMT to OMT^{+2} Using DDQ/H^+ in CH_2Cl_2**



obviates problems such as chlorination of the polyaromatic products and the usage of a large excess of oxidants.

The arenium-ion versus cation-radical pathways for the Scholl reaction involves diamagnetic carbocations and paramagnetic cation radicals as different types of reactive intermediates. Unfortunately, however, both of these intermediates are known to coexist and can undergo facile interchange under the conditions of the Scholl reaction. Herein we list critical experimental evidence in support of the cation-radical pathway for the Scholl reaction: (i) The necessity to use powerful oxidants such as ferric chloride ($FeCl_3$) for Scholl reactions is inconsistent with the arenium-ion mechanism. Note that the role of oxidant in the arenium-ion mechanism is to aromatize the dihydro intermediates (**AI_3**), which can be easily accomplished with rather weak oxidants such as iodine or air. (ii) Various Scholl precursors in Table 1 as well as most hexaarylbenzenes have oxidation potentials lower than 1.7 V vs SCE and thus can be readily oxidized to the corresponding cation radicals using either DDQ/H^+ or $FeCl_3$ as oxidants. Moreover, relatively electron-poor hexakis-(4-bromophenyl)benzene ($E_{ox} > 2.0$ V vs SCE) has an oxidation potential higher than 1.7 and does not undergo cyclodehydrogenation with $FeCl_3$ or DDQ/H^+. (iii) The observation that Scholl reaction using $FeCl_3$ can be driven to completion by removal of gaseous hydrochloric acid, by bubbling nitrogen or argon through the reaction mixture, clearly contradicts the conjecture of King and co-workers[12] that Scholl reactions are accelerated as they proceed because of the production of 2 equiv of acid per C−C bond formation. (iv) The experimental observation of 66% conversion of an *o*-terphenyl **1d** to **2d** in Scheme 11 is readily reconciled by the cation-radical pathway and helps to disfavor the arenium-ion pathway as the predominant mechanism for the Scholl reaction.

The experimental evidence presented herein together with the electrochemical studies by Parker and co-workers[11] strongly favor the cation-radical pathway for the Scholl reaction. However, a caveat is added that the involvement of a parallel arenium-ion mechanism for the Scholl reaction (however minor it may be) cannot be ruled out owing to the coexistence and interchangeability of the arenium ions and cation radicals under conditions of the Scholl reaction.

Experimental Section

The Suzuki coupling[32] provided a general route for the preparation of various substituted *o*-terphenyls (**1a**−**e** and **1k**). The hexaarylbenzene derivatives (**1l**−**1n**) were synthesized according to a previously known literature procedure.[34] Bichromophoric 2,2-bis(3,4-dimethoxyphenyl)propane (**1f**),[33] 9,9-bis(3,4-dimethoxyphenyl)fluorene (**1g**),[33] 1,3-bis(3,4-dimethoxyphenyl)propane (**1h**),[35] **1o**,[47] **1p**,[45] **1q**,[53] and octamethoxytetraphenylene[28] were prepared by literature procedures. The details of the synthesis and spectral data for various Scholl precursors, utilized in this study, are described in Supporting Information.

General Procedure for the Oxidative Cyclodehydrogenation with DDQ and Methanesulfonic Acid. Under an argon atmosphere, a protic acid (such as CH_3SO_3H, CF_3CO_2H, or HBF_4; 10% v/v, 1 mL) or a Lewis acid (such as $BF_3 \cdot Et_2O$ or $AlCl_3$; 5−10 equiv) was added to a solution of *o*-terphenyl **1a** (0.1 mmol) in dichloromethane (9 mL) at 22 °C. The reaction was stirred under an argon atmosphere for 30 min to 24 h. Under the argon flow, a 1-mL aliquot of the reaction mixture was removed and poured onto solid Na_2CO_3 to neutralize the added acid. The solution was then filtered and evaporated in vacuo to afford the starting *o*-terphenyl **1a** quantitatively, as judged for ^1H NMR spectroscopy and thin-layer chromatography. It is noted that various Scholl precursors in Chart 1 did not produce any cyclized products when exposed to protic acids or Lewis acids for extended periods of time (i.e., ~24 h) as described above. This conclusion was confirmed by a quantitative recovery of the starting materials in each case.

When a solution of *o*-terphenyl **1a** (0.1 mmol) in dichloromethane (10 mL) containing protic acid (10% v/v) or Lewis acid (~10 equiv) at ~0 °C was exposed to DDQ (1 equiv per C−C bond formation, i.e., 0.1 mmol), the solution immediately took on a dark-green coloration. [Note that the solution colors varied depending on the Scholl precursors used; see Chart 1.] The progress of the reaction was monitored by TLC and ^1H NMR spectroscopy. After the completion of the reaction (~5 min), it was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The dichloromethane layer was separated, washed with water and brine solution, dried over anhydrous $MgSO_4$, and filtered. Removal of the solvent in vacuo afforded the crude product, which by $^1H/^{13}C$ NMR analysis was shown to be 2,3,10,11-tetramethoxytriphenylene (**2a**). Various Scholl precursors were subjected to similar reaction conditions, and the characterization data for the oxidative cyclodehydrogenation products are summarized in Supporting Information.

General Procedure for the Oxidative Cyclodehydrogenation Using $FeCl_3$. To a solution of *o*-terphenyl **1a** (0.1 mmol) in 10 mL of dichloromethane at 0 °C was added $FeCl_3$ (2−6 equiv) under an argon atmosphere. The resulting mixture was stirred at 0 °C for 30 min. The reaction was quenched by addition of dry

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[53] Fieser, L. F.; Ramey, C. E.; Boekelheide, V. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 604; 1966, 46, 44.

methanol (5 mL). The reaction mixture was washed with water (40 mL), and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with brine solution, dried over anhydrous MgSO$_4$, and filtered. Removal of the solvent in vacuo afforded the crude product, which was further purified through recrystallization or column chromatography. Various Scholl precursors were subjected to similar reaction conditions, and the characterization data for the oxidative cyclodehydrogenation products are summarized here:

2a: yield quantitative; mp 215−216 °C; ^{1}H NMR (CDCl$_3$) δ 4.11 (s, 12H), 7.59 (q, 2H), 7.71 (s, 2H), 7.94 (s, 2H), 8.46 (q, 2H); ^{13}C NMR (CDCl$_3$) δ 56.1, 56.2, 104.1, 104.6, 123.0, 123.5, 123.9, 126.2, 128.9, 148.8, 149.4. **2b:** white crystals, yield quantitative; mp 282−283 °C; ^{1}H NMR (CDCl$_3$) δ 2.51 (s, 6H), 4.09 (s, 6H), 4.11 (s, 6H), 7.68 (s, 2H), 7.88 (s, 2H), 8.14 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 20.5, 56.1, 104.2, 104.5, 123.4, 123.5, 123.6, 127.2, 135.1, 148.8, 149.0. **2c:** white solid, yield 50%; mp 193−194 °C; ^{1}H NMR (CDCl$_3$) δ 2.49 (s, 6H), 3.97 (s, 6H), 4.01 (s, 6H), 6.68 (s, 2H), 7.51 (s, 2H), 8.16 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 20.5, 55.8, 56.0, 97.0, 98.1, 112.9, 124.3, 128.7, 132.3, 136.4, 158.8, 158.9. Note that the triphenylene **2c** undergoes decomposition under the reaction conditions, and thus the pure **2c** was isolated by column chromatography on silica gel using 5% ethyl acetate in hexanes as eluent. **2d:** yield 99%, mp 208−211 °C; ^{1}H NMR (CDCl$_3$) δ 2.52 (s, 6H), 4.02 (s, 6H), 7.21 (dd, J_1 = 8.91 Hz, J_2 = 2.58 Hz, 2H), 7.99 (d, J = 2.58 Hz, 2H), 8.28 (s, 2H), 8.44 (d, J = 8.91 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 20.5, 55.7, 105.7, 115.5, 123.9, 124.2, 124.5, 128.2, 130.3, 136.4, 158.3. **2e:** yield 60%; mp 214−215 °C; ^{1}H NMR (CDCl$_3$) δ 2.49 (s, 6H), 4.02 (s, 6H), 7.25 (dd, J_1 = 8.83 Hz, J_2 = 2.56 Hz, 2H), 7.94 (d, J = 2.56 Hz, 2H), 8.26 (s, 2H), 8.53 (d, J = 8.83 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 20.5, 55.7, 106.3, 115.7, 123.5, 124.4, 125.0, 127.2, 130.8, 135.4, 158.6. **2f:** white solid, yield 100%; mp 178−180 °C; ^{1}H NMR (CDCl$_3$) δ 1.65 (s, 6H), 3.77 (s, 6H), 3.86 (s, 6H), 6.69 (d, 2H, J = 2 Hz), 6.76−6.84 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 27.4, 46.7, 56.2, 56.3, 102.5, 106.1, 131.8, 146.1, 148.2, 148.7. **2g:** white solid, yield 100%; mp 242−244 °C; ^{1}H NMR (CDCl$_3$) δ 3.61 (s, 6H), 4.03 (s, 6H), 6.18 (s, 2H), 6.75 (d, J = 7.6 Hz, 2H), 7.14 (t, J = 7 Hz, 2H), 7.26 (d, J = 5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 56.2, 56.3, 65.9, 102.3, 107.0, 120.0, 124.2, 127.8, 128.0, 134.7, 141.0, 141.7, 148.6, 149.1, 149.3. **2h:** white solid, yield 100%; mp 152−153 °C (lit.[10b] mp 158−159 °C); ^{1}H NMR (CDCl$_3$) δ 2.11−2.20 (m, 2H), 2.43 (t, J = 7 Hz, 4H), 3.92 (s, 12H), 6.77 (s, 2H), 6.89 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 31.2, 34.0, 56.1, 56.3, 111.7, 112.0, 132.2, 133.1, 147.6, 147.9. **2i:** white solid, yield 100%; mp 113−114 °C; ^{1}H NMR (CDCl$_3$) δ 2.02 (s, 6H), 3.83 (s, 6H), 3.91 (s, 6H), 6.65 (s, 2H), 6.77 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 19.5, 56.0, 56.2, 112.9, 113.1, 128.36, 133.5, 146.7, 147.9. **2j:** white solid, yield 100%; mp 129−130 °C; ^{1}H NMR (CDCl$_3$) δ 2.29 (s, 6H), 3.75 (s, 6H), 3.81 (s, 6H), 6.79 (s, 2H), 6.83 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 16.6, 56.2, 56.8, 114.0, 115.1, 125.7, 126.7, 150.9, 151.9. **2k:** pale yellow crystals, quantitative yield, mp 303−306 °C; ^{1}H NMR (CDCl$_3$) δ 2.51 (s, 18H), 8.33 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 20.5, 123.8, 127.8, 135.6. **HBC 2l:** yellow/orange solid, yield qunatitative; mp >300 °C; ^{1}H NMR (CDCl$_3$) δ 1.73 (d, 36H), 3.58 (m, 6H), 8.9 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 25.0, 35.5, 120.0, 120.3, 124.2, 130.5, 146.6. **HBC 2m:** yellow/orange solid, yield quantitatve; mp >300 °C; ^{1}H NMR (CDCl$_3$) δ 1.11 (s, 18H), 1.69 (s, 18H), 2.07 (s, 12H), 3.29 (s, 6H), 9.03 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 12.1, 22.4, 31.3, 44.4, 120.1, 120.1, 124.9, 131.1, 146.8. **HBC 2n:** yellow/orange solid, yield quantitatve; mp 110−112 °C; ^{1}H NMR (CDCl$_3$) δ 0.84 (t, 18H), 1.06 (d, 18H), 1.33 (m, 60H), 2.38 (m, 6H), 6.59 (s, 12H), 6.67 (d, 12H); ^{13}C NMR (CDCl$_3$) δ 14.3, 23.0, 28.3, 29.8, 32.0, 32.1, 39.2, 41.3, 120.7, 120.8, 124.9, 130.6, 146.3. **HBC 2o:** yellow/orange solid, yield quantitatve; mp >320 °C (lit.[34] mp >300 °C) ; ^{1}H NMR (CDCl$_3$) δ 1.83 (s, 54H), 9.32 (s, 12H); ^{13}C NMR (CDCl$_3$) δ 32.3, 36.0, 119.1, 120.7, 124.2, 130.7, 149.2.

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Supporting Information Available: Synthetic details and ^{1}H and ^{13}C NMR data of various compounds. This material is available free of charge via the Internet at http://pubs.acs.org.