2,3-Dichloro-5,6-dicyano-*para*-benzoquinone (DDQ)/Methanesulfonic Acid (MsOH)-Mediated Intramolecular Arene-Alkene Oxidative Coupling

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Abstract: An efficient intramolecular arene-alkene oxidative coupling of 1,4-diaryl-1,3-butadienes has been developed involving the use of a 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ)/acid catalyst. The reaction involves the generation of a radical cation by abstraction of an electron from the substrate with DDQ, an intramolecular Friedel–Crafts-type reaction, and the loss of hydrogen radical.

Keywords: arene-alkene oxidative coupling; 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ); intramolecular Friedel–Crafts reaction; radical cations

Intramolecular oxidative cross-coupling between an arene and an alkene is an important transformation. Various aromatic and heteroaromatic compounds could be formed directly from their acyclic precursors using oxidative cross-coupling.^[1,2] Stoltz and co-workers reported a palladium-catalyzed oxidative cyclization of arylalkenes (intramolecular Fujiwara–Moritani reaction) for the synthesis of functionalized benzofurans from aryl allyl ethers.^[1a] Glorius and co-workers developed a palladium-catalyzed oxidative cyclization of *N*-arylenamines to open an efficient way to indoles from anilines.^[1b,c] Such transition metal-catalyzed oxidative annulations of arylalkenes has received continuing interest^[1d–k] and has also been used for the synthesis of some natural products.^[11–n]

Very recently, Niphakis and Georg reported a novel VOF₃-mediated arene-alkene oxidative coupling during the synthesis of phenanthroindolizidines.^[2] They successfully applied vanadium oxytrifluoride, which has been widely used for the intramolecular Scholl-type arene-arene coupling,^[3] to their intramolecular arene-alkene oxidative coupling. As a formal intramolecular oxidative coupling between an arene and an alkene, the intramolecular Friedel–Crafts (IMFC) alkylation of arylalkenes and a following aromatization (*via* oxidation or elimination) has also been reported.^[4] IMFC alkenylation can provide such annulation products directly; however, the reaction required arylalkynes instead of arylalkenes.^[5] As another formal intramolecular oxidative bond-formation between an arene and an alkene, a 6π -electrocyclization (thermal or photochemical) of 1-aryl-1,3-butadiene and a following aromatization has been used effectively in some cases.^[6]

DDQ (2,3-dichloro-5,6-dicyano-*para*-benzoquinone) is readily available oxidizing reagent and has been used as an effective dehydrogenation reagent. Recently, the synthetic applications of DDQ have been thoroughly investigated for the cross-dehydrogenative coupling (CDC)^[7a-g] and intramolecular dehydrogenative coupling (IDC) reactions.^[7h,i] In addition, DDQ has been used extensively in intramolecular Scholl-type arene-arene coupling reactions.^[8]

In these contexts, a direct and efficient intramolecular arene-alkene oxidative coupling method is highly required. In addition to the intramolecular oxidative arene-alkene coupling, $VOF_3^{[3]}$ and $Pd(II)/oxidant^{[1k,9]}$ have also been used for the intramolecular Scholltype arene-arene coupling reaction as well. However, DDQ has not been applied for the intramolecular oxidative arene-alkene coupling, to the best of our knowledge. Thus, we decided to examine the feasibility of an intramolecular arene-alkene oxidative coupling reaction mediated by DDQ.

We selected methyl 1,4-diphenyl-1,3-butadiene-2carboxylate **1a** as a model compound, which can be easily prepared from the Morita–Baylis–Hillman (MBH) adduct *via* three steps.^[10] We assumed that the reaction between a styryl moiety of **1a** and DDQ would produce a radical cation intermediate **I** which could be converted to naphthalene **2a** *via* an oxidative cyclization, as shown in Scheme 1.

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Scheme 1. Rationale of intramolecular arene-alkene oxidative coupling.

The reaction of **1a** in the presence of DDQ in 1,2dichloroethane (DCE) did not produce **2a** in any trace amount at room or even at reflux temperature. However, when we used an acid catalyst – methanesulfonic acid (MsOH) – as in the reported intramolecular Scholl-type reactions,^[8] naphthalene **2a** was obtained albeit in low yield. Encouraged by the result, we examined various conditions for the conversion of **1a** to **2a**, and the results are summarized in Table 1. A severe decomposition of **1a** was observed in the presence of one equivalent of MsOH even at room temperature (entry 1).

Table 1. Optimization of reaction conditions.

Entry	Oxidant ^[a]	Additive ^[b]	Solvent	$T/t^{[c]}$	2a [%] ^[d]
1	DDQ	MsOH (1.0)	DCE	25/5	13 ^[e]
2	DDQ	MsOH (0.1)	DCE	25/20	5 ^[f]
3	DDQ	MsOH (0.1)	DCE	60/5	80
4	DDQ	MsOH (0.1)	benzene	60/7	74
5	DDQ	MsOH (0.1)	toluene	60/7	0 ^[g]
6	none	MsOH (1.0)	DCE	60/5	0 ^[g]
7	DDQ	MsOH (0.05)	DCE	83/4	66
8	DDQ	MsOH (0.05)	DCE	60/7	77
9	DDQ	AcOH (0.1)	DCE	83/7	0
10	DDQ	TFA (0.1)	DCE	60/7	35
11	DDQ	$FeCl_{3}(0.1)$	DCE	60/7	64
12	DDQ	$FeCl_{3}(0.1)$	DCE	25/10	65
13	none	$FeCl_{3}(0.1)$	DCE	83/5	0
14	DDQ	$LiClO_{4}(0.1)$	DCE	83/5	0
15	BQ	MsOH (0.1)	DCE	83/5	0
16	<i>p</i> -chloranil	MsOH (0.1)	DCE	83/5	0

^[a] Oxidant was used in 1.1 equiv.

^[b] The equiv. of additive in parenthesis.

- ^[c] Temperature T [°C] and time t [h].
- ^[d] Isolated yield.
- ^[e] Complete decomposition of **1a**.

^[f] 65% of **1a** was recovered.

^[g] 95% of **1a** was recovered.

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Thus we reduced the amount of the acid catalyst; however, the reaction was sluggish at room temperature (entry 2). When we carried out the reaction at 60°C (entry 3), 2a was obtained in high yield (80%).^[11] The reaction in benzene (entry 4) showed a similar result, while no reaction was observed in toluene (entry 5, vide infra).^[12] Without DDQ no reaction was observed (entry 6) and 1a was not decomposed as compared to the result of entry 1. The reaction at refluxing temperature (entry 7) or in the presence of 5 mol% of MsOH (entry 8) did not show a better result. The use of AcOH was completely ineffective (entry 9) and CF₃COOH was less effective than MsOH (entry 10). It is interesting to note that the use of $FeCl_3$ produced **2a** in moderate yields at 60°C (entry 11) or even at room temperature (entry 12). However, the yield of 2a was slightly lower than that of the entry 3. No reaction was observed without DDQ (entry 13) and the use of $LiClO_4$ was not effective (entry 14). Replacement of DDQ with other oxidants such as benzoquinone (BQ) and p-

As noted above, the reaction of 1a in the presence of MsOH did not produce 2a without DDQ (entry 6 in Table 1). From the result, the following two routes for the formation of 2a would be regarded as less probable; (i) thermal 6π -electrocyclization/oxidation and (ii) IMFC alkylation/oxidation. In order to check the possibility of 6π -electrocyclization of 1a under more drastic conditions, the reaction was examined in *ortho*-dichlorobenzene (ODCB) at reflux temperature (180 °C); however, no reaction was observed as shown in Scheme 2. The reaction even in the presence of DDQ did not produce 2a at all. In addition, the reaction of 1a was examined in refluxing benzene (20 h)

chloranil was totally ineffective (entries 15 and 16).



Scheme 2. Trials of indirect route toward 2a.

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in the presence of H_2SO_4 (2.0 equiv.) in order to examine the possibility of IMFC alkylation. However, no reaction was observed. When we used stronger acid TfOH (2.0 equiv.), we could obtain **3a** in low yield (33%) by the IMFC alkylation pathway along with its acid derivative **4a** (37%). The acid **4a** was not formed by the hydrolysis of **3a**. As also shown in Scheme 2, **4a** must be formed *via* the lactone intermediate, as in our previous paper.^[13] DDQ-mediated dehydrogenation of **3a** afforded **2a** in good yield (95%). From the results, both 6π -electrocyclization and IMFC alkylation accompanying DDQ-mediated dehydrogenative aromatization pathway could be excluded.

Encouraged by the results, various 1,3-diene derivatives **1b–t** were prepared from the corresponding MBH bromides *via* the Wittig reaction according to the reported methods.^[10] The DDQ/MsOH-mediated intramolecular arene-alkene oxidative couplings of **1b–t** were examined under the standard condition (entry 3 in Table 1), and the results are summarized in Table 2 and Table 3. Table 2 summarizes the results of

 Table 2. DDQ/MsOH-mediated arene-alkene coupling of 1a-j.



^[a] DDQ (1.1 equiv.), MsOH (0.1 equiv.), DCE, 60 °C, 5 h. ^[b] **1a** (R=Ph), **1b** (R=4-ClC₆H₄), **1c** (R=4-MeOC₆H₄), **1d** (R=4-NO₂C₆H₄), **1e** (R=4-PhC₆H₄), **1f** (R=1-naphthyl), **1g** (R=Ph, E=COMe), **1h** (R=styryl), **1i** (R=5methyl-2-thienyl), **1j** (R=*n*-pentyl).

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Table 3. DDQ/MsOH-mediated arene-alkene coupling of1k-t.



- ^[a] DDO (1.1 equiv.), MsOH (0.1 equiv.), DCE, 60°C, 5 h.
- ^[b] **1k** (R^1 =3-MeOC₆H₄, R^2 =Ph), **1l** (R^1 =3,4-Cl₂C₆H₃, R^2 =Ph), **1m** (R^1 =3-NO₂C₆H₄, R^2 =Ph), **1n** (R^1 =2-BrC₆H₄, R^2 =Ph), **1o** (R^1 =4-MeC₆H₄, R^2 =Ph), **1p** (R^1 =2-furyl, R^2 =Ph), **1q** (R^1 =2-naphthyl, R^2 =Ph), **1r** (R^1 =1-naphthyl, R^2 =Ph), **1s** (R^1 =1-naphthyl, R^2 =1-naphthyl), **1t** (R^1 =2-naphthyl, R^2 =1-naphthyl).
- ^[c] Carried out in the presence of 0.05 equiv. of MsOH (7 h), and the yield of **20** decreased to 47% in the presence of 0.1 equiv. of MsOH (2 h).

1,3-dienes **1a**–j, which were prepared by the Wittig reaction between various aldehydes and the MBH bromide of benzaldehyde. Table 3 includes the results of 1k-t that were prepared from diversely-modified MBH bromides. As shown in Table 2, the reactions of 4-chlorophenyl derivative 1b and 4-methoxyphenyl derivative 1c provided 2b and 2c in good yields (81%) and 78%). However, the reaction of 4-nitrophenyl derivative 1d did not produce any trace amount of 2d. An electron abstraction from 1d by DDQ would be difficult due to the presence of an electron-withdrawing 4-nitro group, and the corresponding radical cation cannot be formed. The reactions of 4-biphenyl derivative 1e and 1-naphthyl derivative 1f afforded 2e and 2f in good yields (82% and 78%). The acetyl derivative 1g also produced 2g without a problem in slightly lower yield (75%). Even the styryl derivative

1h provided **2h** in moderate yield (72%). Unfortunately, the reaction of 2-thienyl derivative **1i** failed, and many intractable side products were observed.^[14] The reaction of *n*-pentyl derivative **1j** also failed presumably due to the instability of the alkyl radical cation.

As shown in Table 3, the reactions of 3-methoxyphenyl derivative 1k and 3,4-dichlorophenyl derivative 11 produced 2k and 2l in good yields (84% and 81%). A single regioisomer was obtained in the reactions, and the other possible regioisomer was not observed at all. The reaction of 3-nitrophenyl derivative **1m** showed no conversion. The failure of **1m** strongly suggested that the cyclization would be a cationic mechanism involving either an IMFC alkylation of a radical cation or an IMFC alkenylation of a vinyl cation (vide infra). The reactions of 1n and 1o afforded 2n and 2o in good yields (79% and 68%), while 2furyl derivative 1p was decomposed under the reaction condition as in the reaction of **1i** (vide supra).^[14] It is interesting to note that the benzofulvene derivative was prepared from 2-bromo derivative 1n under palladium-catalyzed Mizoroki-Heck reaction conditions.^[10c] Four phenanthrene derivatives 2q-t were synthesized from 1q-t in good to high yields (78-86%). For the synthesis of 2q and 2t, bond formations proceeded at the 1-position of the naphthalene ring regioselectively.

As a next entry, we examined the reaction of bisbenzylidenesuccinimide **5a**,^[6b,15] as shown in Scheme 3. The substrate 5a is different with 1a-t in that both alkenes of 5a are connected to electronwithdrawing carbonyl groups. The HOMO energy of the double bond of 5a would be lowered by conjugation with a carbonyl group, and the abstraction of an electron from 5a with DDQ would be difficult as compared to 1a-t.^[16] As expected, the formation of a trace amount (<5%) of benzo[*f*]isoindole-1,3-dione **6a**^[15b] was observed under the standard conditions employing MsOH (0.1 equiv.) in refluxing DCE even after 20 h. The reaction of 5a in the presence of FeCl₃ (0.2 equiv.) also showed a sluggish reactivity, and **6a** was obtained in low yield (36%) even after a long



results under other conditions:

 $\begin{array}{l} \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{MsOH} \ (0.1 \ equiv.), \ \mathsf{DCE}, \ \mathsf{reflux}, \ 20 \ \mathsf{h} \ (\mathbf{6a:} < 5\%) \\ \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{FeCl}_3 \ (0.2 \ equiv.), \ \mathsf{DCE}, \ \mathsf{reflux}, \ 80 \ \mathsf{h} \ (\mathbf{6a:} \ 36\%) \\ \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{FeCl}_3 \ (2.0 \ equiv.), \ \mathsf{DCE}, \ \mathsf{reflux}, \ 16 \ \mathsf{h} \ (\mathbf{6a:} \ 95\%) \\ \mathsf{no} \ \mathsf{DDQ}, \ \mathsf{MsOH} \ (2.0 \ equiv.), \ \mathsf{DCE}, \ \mathsf{reflux}, \ 0_2 \ \mathsf{balloon}, \ 20 \ \mathsf{h} \ (\mathsf{no} \ \mathsf{reaction}) \\ \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{MsOH} \ (2.0 \ equiv.), \ \mathsf{totene}, \ \mathsf{reflux}, \ 20 \ \mathsf{h} \ (\mathsf{no} \ \mathsf{reaction}) \\ \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{MsOH} \ (2.0 \ equiv.), \ \mathsf{totene}, \ \mathsf{reflux}, \ 20 \ \mathsf{h} \ (\mathsf{no} \ \mathsf{reaction}) \\ \mathsf{DDQ} \ (1.1 \ equiv.), \ \mathsf{MsOH} \ (2.0 \ equiv.), \ \mathsf{totene}, \ \mathsf{reflux}, \ 20 \ \mathsf{h} \ (\mathsf{no} \ \mathsf{reaction}) \\ \mathsf{MsOH} \ (2.0 \ equiv.), \ \mathsf{totene}, \ \mathsf{reflux}, \ 20 \ \mathsf{h} \ (\mathsf{no} \ \mathsf{reaction}) \\ \mathsf{MsOH} \ (\mathsf{ho} \ \mathsf{reaction}) \ \mathsf{ho} \ \mathsf{h$

Scheme 3. Synthesis of benzo[*f*]isoindole-1,3-dione 6a.

time (80 h). To our delight, **6a** could be isolated in an excellent yield (95%) in the presence of 2.0 equiv. of FeCl₃ for 16 h. The reaction in the presence of MsOH (2.0 equiv.) gave the best result to give **6a** in a quantitative yield (98%) in a short time (12 h). The result clearly implied that the use of an excess amount of MsOH is helpful to the electron abstraction by DDQ. In order to check the possibility of an acid-catalyzed IMFC alkylation pathway, the reaction of **5a** was examined in the presence of MsOH without DDQ under an O₂ balloon atmosphere. The reaction did not show the formation of **6a** or its dihydro intermediate. It is interesting to note that the reaction in toluene was completely ineffective as in the case of **1a** (*vide supra*, entry 5 in Table 1).^[12]

Thus, the reactions of similar 1,4-diaryl-1,3-butadienes 5b-f were examined, as shown in Table 4. The reaction of 4-methoxyphenyl derivative 5b afforded **6b** in good yield (86%). The regioisomeric compound **6b'** was not formed at all (*vide infra*, Scheme 4), and the result implied that an electron abstraction by DDQ occurred at the 4-methoxybenzylidene moiety selectively. In contrast to 5b, the reaction of 4-chlorophenyl derivative 5c produced an inseparable mixture of 6c and 6c' (ca. 1:1) in an excellent yield (98%). The reaction of a symmetrical bis(4-methoxybenzylidene) derivative 5d gave 6d in moderate vield (56%) in the presence of 0.1 equiv. of MsOH at 60 °C. The reaction of 5d produced many side products in the presence of 2.0 equiv. of MsOH at reflux temperature. The reaction of **5e** gave **6e** in an excellent yield (98%). The reaction of anhydride derivative 5f required a long reaction time (50 h) for the completion,^[16] and compound 6f was isolated in moderate yield (61%).

The selective formation of **6b** has proven that a radical cation **IV** was formed selectively instead of **III**, as shown in Scheme 4. The cation at the 4-methoxybenzylic position of **IV** could be stabilized by the methoxy group to form a resonance-stabilized distonic radical cation form **VI**. In addition, the radical at the homobenzylic position of **IV** could be isomerized to a benzylic position to make the electrophilic cyclization more facile. The results stated that the reaction would be controlled not by the electronic nature of attacking arene moiety but by the formation of more stable radical cation intermediate.

As a next entry, we examined the reaction of 2-styrylbiphenyl derivative **7a**, as shown in Scheme 5. The starting material **7a** was prepared by Catellani-type reaction from 2-iodotoluene and styrene, as reported.^[17a] The reaction of **7a** did not afford the phenanthrene derivative **8a** in reasonable yield under the standard condition employing MsOH. No reaction was observed even at refluxing temperature with 20 mol% of MsOH. Only 5% of **8a** was formed with 2.0 equiv. of MsOH accompanied with severe decomposition. Fortunately, **8a** was obtained in moderate

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 Table 4. Synthesis of benzo[f]isoindole-1,3-diones.^[a]

^[a] Carried out in DCE in the presence of DDQ (1.1 equiv.).

yield (48%) by using FeCl₃ (0.1 equiv.) at 60 °C for 2 h (*vide supra*, entry 11 in Table 1). The best yield of **8a** (63%) was obtained under the influence of 5 mol% of FeCl₃. Analogously, the synthesis of **8b** from **7b** was ineffective. Among the many trials, the reaction of **7b** afforded **8b** in reasonable yield (45%) when we used 20 mol% of FeCl₃. Although the reason for the low yield of **8b** is not clear at this stage, there has been reported a similar example for the failure in FeCl₃/DDQ-mediated CDC/benzoannulation between 1,2-diarylpropene and styrene bearing a methoxy substituent.^[7g] In order to eliminate a plausible harmful effect of a methyl^[12] or methoxy group^[7g] in the reaction, 2-styrylbiphenyl (**7c**, R=H) was prepared from 2-bromobiphenyl and styrene by



Scheme 4. Selective formation of 6b.



Scheme 5. The reaction of 2-styrylbiaryls.

Mizoroki–Heck reaction.^[17b] However, the reaction of **7c** in the presence of 5.0 mol% of FeCl₃ afforded **8c** in a similar yield (65%) to that of **8a**. The radical cation intermediates **VII** and **VIII** (corresponding to **I** and **X** in Scheme 6, *vide infra*) cannot be stabilized by delocalization, as shown in Scheme 5. This might be one of the reasons for the low yields of **8a–c**.

Based on the experimental results, we proposed a plausible reaction mechanism for the formation of **2a** as an example, as shown in Scheme 6. An electron abstraction of **1a** by DDQ produced a radical cation **I.** An IMFC-type alkylation of either **I** or its distonic benzylic radical cation **IX** would produce a cyclic radical cation **X**, which loses a proton and hydrogen radical to give **2a** (*a*-route). However, another plausible mechanism cannot be ruled out involving an initial loss of hydrogen radical from **I** to form a vinyl cation **XI** and a subsequent IMFC-type alkenylation process (*b*-route).^[5] The role of an acid catalyst is not clear at



Scheme 6. Proposed reaction mechanism.

this stage; however, it might facilitate the electron transfer process between the substrate and DDQ.^[8a-c]

In summary, we have disclosed an efficient intramolecular arene-alkene oxidative coupling of 1,4-diaryl-1,3-butadienes using DDQ in the presence of an acid catalyst. The widely-used DDQ/acid-catalyzed intramolecular Scholl-type reaction conditions are successfully applied to an intramolecular arene-alkene oxidative coupling for the first time. The reaction involved a generation of radical cation by abstraction of an electron from the substrate with DDQ, an intramolecular Friedel–Crafts-type cyclization, and a loss of hydrogen radical. Further studies on the reaction mechanism and scope of the reaction are currently underway.

Experimental Section

Typical Procedure for the Synthesis of 2a

To a stirred green solution of 1a (132 mg, 0.5 mmol) and DDQ (125 mg, 1.1 equiv.) in DCE (1.5 mL) at room temperature was added MsOH (5 mg, 10 mol%). Instantaneously the green color changed to dark green on addition of MsOH. The dark green reaction mixture was heated to 60 °C for 5 h. The color of the reaction mixture slowly turned to brown. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/ether, 30:1), product **2a** was obtained as a white solid; yield: 105 mg (80%).

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