



Carbon–carbon cleavage of aryl diamines and quinone formation using sodium periodate: a novel application

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ABSTRACT

A first novel synthetic utility of sodium periodate for aryl diamine carbon–carbon cleavage is described. Aryl 1,2-diamine compounds were successfully converted into corresponding nitriles, while the developed method is also useful for the preparation of quinones from corresponding aryl 1,4-diamine compounds. The advantages of this protocol are shorter reaction time and mild reaction conditions to obtain moderate to good yields.

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Sodium periodate (NaIO_4) is useful in certain synthetic chemistries due to the oxidative power of the periodate ion. Recently, sodium periodate in combination with other reagents has been effectively used in dihydroxylations,¹ as well as oxidative cleavage of styrene, olefins, and terminal olefins to carbonyl compounds.² Sodium periodate is best known for carbon–carbon cleavage. We hypothesized that exposure of sodium periodate to *ortho*, *para*, and *meta* aryl diamines would result in the formation of corresponding nitriles by oxidative cleavage of carbon–carbon diamine bond.

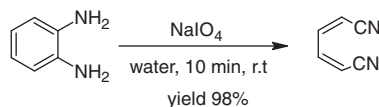
Oxidative carbon–carbon cleavage of 1,2-diaminobenzene is still an issue because there are only three systems available, that involved molecular oxygen in the presence of CuCl in pyridine, however this reaction suffers from several drawbacks: the reactions are performed using pyridine and it involves tedious work-up.^{3a} In another method 1,2-diaminobenzene has been oxidized using stoichiometric amount of nickel peroxide or lead tetraacetate.^{3b} Here too there are drawbacks: the necessary use of toxic lead tetraacetate and less than 50% yield.

We initially selected 1,2-diaminobenzene as a model substrate, which on exposure to sodium periodate resulted in the formation of *cis,cis*-mucononitrile. The *cis,cis* configuration of the mucononitrile was established by comparison of the infrared spectrum, proton spin–spin coupling constant, and melting point with a reported literature.⁴ Further screening of the reaction conditions revealed that water as the solvent and 2 equiv of sodium periodate

are required to furnish *cis,cis*-mucononitrile in 98% yield (Scheme 1). When 1 mol of sodium periodate was used, the reaction did not go to completion and almost 50% 1,2-diaminobenzene was recovered. The reaction does not take place in dry organic solvents (EtOAc , CH_2Cl_2 , CHCl_3 , and CH_3CN) but in 50% aqueous organic solvents (water/organic solvent, 1:1) it gives *cis,cis*-mucononitrile without affecting the yield and reaction time. Thus water-insoluble aryl diamine substrates can be converted into corresponding nitriles using 50% aqueous organic solution.

We have also examined KMnO_4 , CAN , NaCl_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$, for oxidative carbon–carbon cleavage of 1,2-diaminobenzene, but no reaction was observed even at higher temperature and longer reaction time.

As part of our studies on the development of novel methodology using iodine reagents,⁵ herein we describe a new approach using NaIO_4 to bring about direct oxidative carbon–carbon cleavage of aryl diamines under mild conditions.⁶ Next, to evaluate the scope of this new method, these conditions were applied to a variety of aromatic electron-donating or electron-withdrawing-substituted 1,2-diaminobenzenes (Table 1, entries 1–8). In each case, good to excellent yields of the desired nitrile products were observed in short reaction time, while no reaction was observed in case of

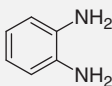

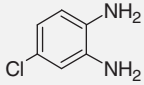

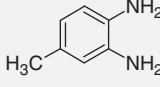
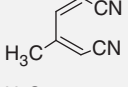
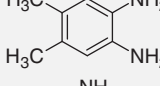
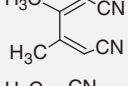
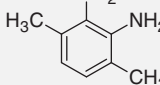
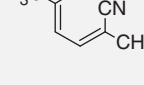
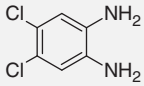

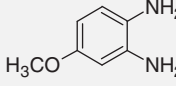
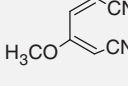
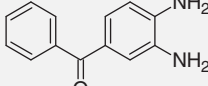
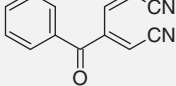
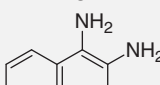
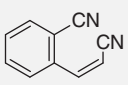
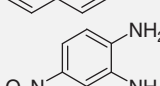
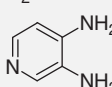


Scheme 1. Oxidative carbon–carbon cleavage of 1,2-diaminobenzene using NaIO_4 .

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Table 1
Carbon–carbon cleavage of aryl diamino compounds using sodium periodate^a

Entry	Substrate	Product	Time (min)	% Yield ^b
1			10	98
2			15	95
3			10	95
4			15	98
5			10	97
6			15	92
7			15	92
8			20	90
9			15	97
10		—	120	NR ^c
11		—	120	NR ^c

^a Reaction conditions: substrate (4.62 mmol), NaIO₄ (2 equiv) in 10 mL EtOAc/water (1:1), room temperature.

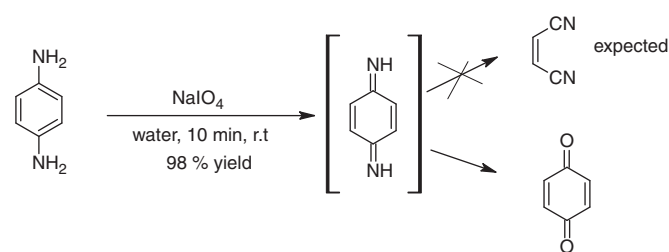
^b Isolated yields after column chromatography and structures were confirmed by comparison of IR and ¹H NMR with authentic materials.

^c NR: no reaction.

strong electron-deficient aromatic diamine (Table 1, entry 10) even after longer reaction time. Heterocyclic diamine does not undergo this transformation (Table 1, entry 11). Aqueous organic solvents (1:1) were used when diamines were insoluble in water (Table 1, entries 2–7).

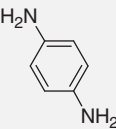
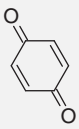
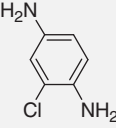
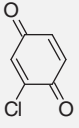
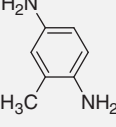
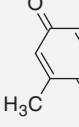
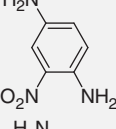
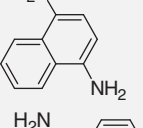
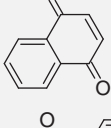
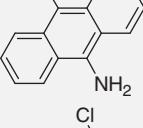
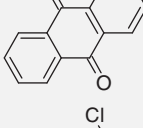
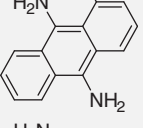
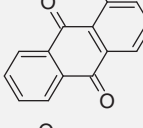
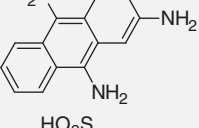
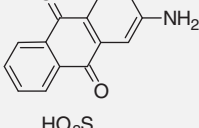
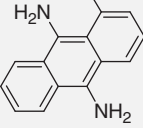
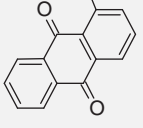
Under these reaction conditions, 1,3-diaminobenzene was unaffected while 1,4-diaminobenzene showed unexpected results and provided an interesting route to quinones which are key structural components in many bioactive compounds.⁷ 1,4-diaminobenzene reacted with 1 equiv of NaIO₄ in water and got converted into benzoquinone rather than the expected fumarodinitrile which may be due to the hydrolysis of intermediate rather than breaking of two sigma bonds (Scheme 2). Even the use of more than 1 equiv of sodium periodate and different temperature conditions resulted only in the conversion of 1,4-diaminobenzene into benzoquinone.

Considering this fact we studied various substituted 1,4-aryl diamines to get the corresponding quinones in short reaction time in water and the results are presented in Table 2. In the case of water-insoluble diamines, 50% aqueous organic solution as mentioned above can be used. Generally quinones are prepared

**Scheme 2.** Quinone formation using NaIO₄.

from the oxidation of phenols or hydroquinones with high yield.⁸ There are only a few methods reported on the preparation of quinones from 1,4-diaminobenzenes which includes metal oxides in combination of H₂O₂, where a lower yield and *p*-nitro aniline as a major side product were observed, while in another method, K₂Cr₂O₇ and FeCl₃ were successfully used for the preparation of quinones in high yield.⁹

Table 2
Reaction of sodium periodate with aryl diamino compounds^a

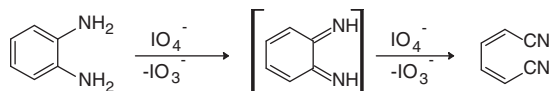
Entry	Substrate	Product	Time (min)	% Yield ^b
1			10	98
2			10	98
3			10	98
4		—	120	NR ^c
5			15	98
6			10	95
7			20	95
8			20	98
9			25	96

^a Reaction conditions: substrate (4.62 mmol), NaIO₄ (1 equiv) in 10 mL EtOAc/water (1:1), room temperature.

^b Isolated yields after column chromatography and structures were confirmed by comparison of IR and ¹H NMR with authentic materials.

^c NR: no reaction.

No quinone formation was observed when 1,4-diaminobenzene was substituted with electron-withdrawing group (Table 2, entry 4). The method was also successfully applied to the synthesis of naphthaquinones and anthraquinones from corresponding diamino compounds at room temperature (Table 2, entries 5–9). In all the cases, yields were found to be higher in short reaction time.¹⁰



Scheme 3. Plausible reaction mechanism for oxidative carbon-carbon cleavage of 1,2-diaminobenzene.

A plausible mechanism³ for oxidative carbon-carbon diamine cleavage has been proposed in Scheme 3. Sodium periodate oxidizes diamine to give unstable imine and itself gets reduced to iodate. However, iodate form does not oxidize further imine to muconitrile as we have not observed any product when NaIO₃/HIO₃ was used for the reaction. Hence 2 equiv of NaIO₄ was required for 100% conversion of 1,2-diaminobenzene to muconitrile. The *cis,cis* configuration of protons is retained during the reaction. An attempt to isolate the imine was unsuccessful due to its unstable nature.

In conclusion, we have exploited a novel application of NaIO₄ for the oxidative cleavage of carbon-carbon aryl diamines to nitriles as well as a novel route for the synthesis of quinones in short

reaction time. Both these applications are general, practical, economical, and efficient.

Acknowledgements

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- Representative procedure for the oxidation of 1,4-diaminobenzene (Table 2, entry 1): NaIO₄ (1 g, 4.62 mmol) in H₂O (10 mL) was stirred at room temperature for 2 min, then 1,4-diaminobenzene (0.5 g, 4.62 mmol) was added to the stirred solution, and after completion of the reaction, the product benzoquinone was isolated as mentioned above (486 mg, 98%) as a yellow solid. Mp: 115 °C (lit.¹¹ 115 °C); IR (KBr, cm⁻¹): 3050, 1658, 1650, 1573, 1301, 896; ¹H NMR (300 MHz, CDCl₃): 6.70 (s, 4H); ¹³C NMR (75 MHz, CDCl₃): 136.51, 187.23.
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