Green Chemistry

Sterically Driven Metal-Free Oxidation of 2,7-Di-tert-butylpyrene

Journal:	*Green Chemistry*
Manuscript ID	GC-COM-06-2020-002000.R1
Article Type:	Communication
Date Submitted by the Author:	20-Jul-2020
Complete List of Authors:	El-Assaad, Tarek; University of Arizona Department of Chemistry and Biochemistry, CBC Parida, Keshaba; University of Arizona Department of Chemistry and Biochemistry, CBC Cesario, Marcello; University of Arizona Department of Chemistry and Biochemistry, CBC McGrath, Dominic; University of Arizona Department of Chemistry and Biochemistry, CBC

COMMUNICATION

Sterically Driven Metal-Free Oxidation of 2,7-di-*tert*-butylpyrene

Tarek El-Assaad,[a] Keshaba N. Parida,[a] Marcello F. Cesario,[a] and Dominic V. McGrath*[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

We disclose an unprecedented single-step metal-free green oxidation of 2,7-di-*tert*-butylpyrene selectively into either the corresponding 4,5-dione or 4,5,9,10-tetraone, two key building blocks used for organic optoelectronic applications using hypervalent iodine oxyacids. This new method results in dramatic improvements in terms of yield, selectivity (dione *vs*. tetraone), ease of workup, cost and toxicity.

Pyrene (**1a**), the fruit fly of photochemists,[1] is a versatile polycyclic aromatic hydrocarbon (PAH), having been used extensively as a fluorescent probe[2,3] and a molecular building block of organic electronic applications such as organic light-emitting diodes (OLEDs),[4-8] organic field effect transistors (OFETs),[9,10] organic photovoltaics (OPVs).[11] In particular, *ortho*-quinones of pyrene such as pyrene-4,5-dione (**2a**) and pyrene-4,5,9,10-tetraone (**3a**), and 2,7-disubstituted derivatives **2b** and **3b**, are useful building blocks for larger organic semiconductors as they enable the extension of the π-conjugated system via simple condensation reactions with *ortho*-diamines.[12] This strategy enables the synthesis of imine-rich *N*-heteroacene chains known as pyrene-fused pyrazaacenes (PPAs), exceedingly stable compounds[13-15] that exhibit a wide range tunable semiconducting properties (p-type[16] to n-type[17]) unlike their nitrogen-free acene counterparts.[12,17,18]

Despite the critical nature of pyrene-based *ortho*-quinone building blocks for the synthesis of PPAs and other organic semiconductors,[12] they have been challenging to obtain via direct oxidation of the 4,5,9,10-positions in pyrene (known as the *K*-region) [1,19-21] Osmium and ruthenium tetroxides have been among the few oxidants that do oxidize pyrene at the *K*-region resulting in the 4,5-dione, albeit in poor yield (ca. < 22%) with several byproducts.[21]

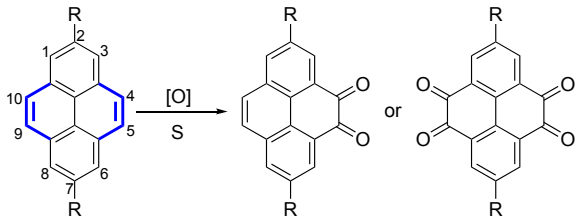
Indirect multistep pathways were regarded as the first-line option to make the **2a/2b** and **3a/3b** until 2005,[1,12] when Harris employed the ruthenium-ion-catalyzed oxidation (RICO)[22] method for a one-pot oxidation of the *K*-region of **1a** and 2,7-di-*tert*-butylpuyrene (**1b**) in a DCM/MeCN/H_2O solvent mixture.[23] This broadly enabling contribution provided gram quantities of compounds **2a/2b** and **3a/3b** in a single step for the first time, and was responsible for the resurgence of interest in PPAs as organic semiconductors throughout the past decade.[12] However, this synthesis suffered from relatively poor yield (< 50%)[23] and difficult workup exacerbated by the formation of large amounts of dark green and black intractable material (presumably Ru-based), the removal of which contributes to a substantial loss of the desired product and an increase in the amount of solvent used in the process.[24]

In 2011 and 2016, Bodwell reported improvements to the Harris method that included using THF as co-solvent instead of MeCN, which results in shorter reaction times (from 16 h to 2.5 h),[25] and using the additive *N*-methylimidazole (NMI) which helps clean up the workup by minimizing the formation of the troublesome intractable material.[24] However, neither of these improvements significantly changed the isolated yield of the desired product, and both improvements addressed the synthesis of diones **2a** and **2b** without the tetraones **3a** and **3b**. Despite the relative success of the Harris/Bodwell methods, all three procedures[23-25] remain ruthenium-mediated (i.e. RICO), require chlorinated solvents, suffer from low yields, are sensitive to variation in the reaction time or temperature[24] which frequently results in an unavoidable mixture of 4,5-dione, 4,5,9,10-tetraone, and several by-products such as biphenyl and phenanthrene aldehydes, according to a mechanistic study on the RICO of pyrene in 2018.[22]

Herein, we report the discovery of new *K*-region oxidation conditions that use hypervalent iodine oxyacids in ethanol or acetic acid (Fig. 1), eliminating the need for transition metal catalysts, additives, and solvents ranked as hazardous according to the CHEM21 (Chemical Manufacturing Methods for the 21st Century Pharmaceutical Industries)[26] in both the reaction and the workup procedure. These conditions are exceedingly

[a] *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721. *To whom correspondence should be addressed. Email: mcgrath@arizona.edu*

Electronic Supplementary Information (ESI) available: Detailed synthesis procedure for all reactions and characterization of all compounds. Green Chemistry Metrics evaluation and comparison with previous methods. See DOI: 10.1039/x0xx00000x



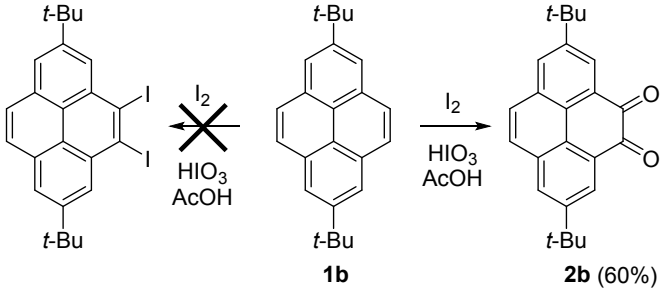
J. Org. Chem., 2005, **70**, 707-708.	[O] = $RuCl_3$, $NaIO_4$ S = DCM, MeCN, H_2O	**1a** → **2a** (45%) **1a** → **3a** (46%) **1b** → **2b** (36%) **1b** → **3b** (47%)
Eur. J. Org. Chem., 2016, **2016**, 5933-5936.	[O] = $RuCl_3$, $NaIO_4$, NMI S = DCM, THF, H_2O	**1a** → **2a** (52%) **1b** → **2b** (44%)
This work	[O] = H_5IO_6 S = EtOH, H_2O	**1b** → **2b** (75%)
	[O] = HIO_3 S = AcOH, H_2O	**1b** → **3b** (56%) **2b** → **3b** (74%)

Fig. 1 Our method compared to the original ruthenium-catalyzed method of Harris and subsequent modifications by Bodwell (***K*-region in blue**, changes in red).

effective for the oxidation of 2,7-di-*tert*-butylpyrene **1b** into the corresponding 4,5-dione **2b** and 4,5,9,10-tetraone **3b** with an unprecedentedly high selectivity for dione *vs*. tetraone dictated by the molar ratio of hypervalent iodine to starting material and the acidity of the reaction mixture. Our conditions completely eliminate the formation of the intractable byproducts associated with the ruthenium method (Fig. S2), resulting in increased reaction yield, improved Green Chemistry Metrics (atom economy, reaction mass efficiency, EcoScale Table S9-S10), and a much easier workup.

Our present discovery of the hypervalent iodine oxyacid mediated oxidation of **1b** resulted from an attempt to iodinate **1b** at the *K*-region carbons in a similar fashion to the sterically-driven *K*-region bromination[27] of **1b** that would typically occur at the electron-rich 1,3,6,8-carbons in the absence of the bulky *tert*-butyl groups.[1] *Tert*-butyl can serve as a protecting group to bias regioselectivity since it can be removed via Nafion-H mediated *trans*-*tert*-butylation.[28-30] Our first attempt to iodinate **1b** employed a recently reported aromatic iodination method using elemental iodine and iodic acid (I_2/HIO_3),[31,32] carried out in refluxing AcOH, which gave satisfactory results in our lab for the iodination of several aromatic compounds, including **1a**. However, compound **1b**, under the same conditions, yielded 4,5-dione **2b** in 60% yield after purification (Scheme 1). The ^{1}H NMR spectrum of the crude product exhibited peaks attributable to only dione **2b** and unreacted **1b**.

Although unexpected, we recognized the significance of a surprisingly clean, metal-free oxidation leading to a useful intermediate such as **2b**. Despite the simplicity of this method, we were surprised to find scant mention in the literature of oxidation of PAHs with hypervalent iodine reagents. In 1921, Williams reported oxidation of phenanthrene to 9,10-phenanthraquinone with HIO_3 in refluxing glacial AcOH.[33]



Scheme 1. The unexpected oxidation of **1b** using iodination conditions.

Subsequent citations of this report were few.[34-36] In a more extensive report on PAH oxidation by Fatiadi in 1968,[37] H_5IO_6 is used as the oxidizing agent, again in AcOH, but radical homo-coupling of pyrene to 1,1'-bipyrene in 70% yield was the result.[38,39] Interestingly, many recent oxidation examples of various organic substrates using the combination of hypervalent iodine reagents and Green solvents have been reported to provide better selectivity with often no or little workup required, unlike the metal-mediated methods.[40-42]

After verifying that the RICO conditions for oxidizing **1b** to **2b** did not proceed in the absence of ruthenium either at room temperature or at reflux (i.e. 4 eq. $NaIO_4$ in both DCM/MeCN/H_2O[23] and in DCM/THF/H_2O,[24] with and without I_2), we surveyed many solvents (Table S3). With $NaIO_4$ (alone or with I_2), conversion of **1b** to **2b** was only observed in refluxing AcOH, but in only <10% yield after 16 h at reflux. Noting the apparent necessity of acidic media for this oxidation reaction, we focused our search for effective oxidation conditions on acidic hypervalent iodine oxyacids HIO_3 (pK_a = 0.80)[43] and H_5IO_6 (pK_a = 3.29),[44] carrying out oxidations of **1b** (100 mg scale) in a similar variety of solvents as above using 4 equivalents of each oxidizing agent alone and with I_2, at room temperature and at reflux (or 110°C for DMSO) (Table S4). Successful oxidations of **1b** with H_5IO_6 or HIO_3 were observed in ethanol and in acetic acid. In the less polar isopropanol, H_5IO_6 was found to be less reactive than HIO_3 despite its higher oxidation state and oxidation potential.[45] We attribute this fact to the greater acidity of HIO_3 in comparison with H_5IO_6. The addition of I_2 did not seem to have any effect on the reaction outcome. Hence, our investigation of the solvent, medium and reagent indicated that successful oxidation requires an acidic oxidizing agent (iodine oxyacids, not their conjugate bases) and a polar protic solvent that dissolves the starting material at the reaction temperature.

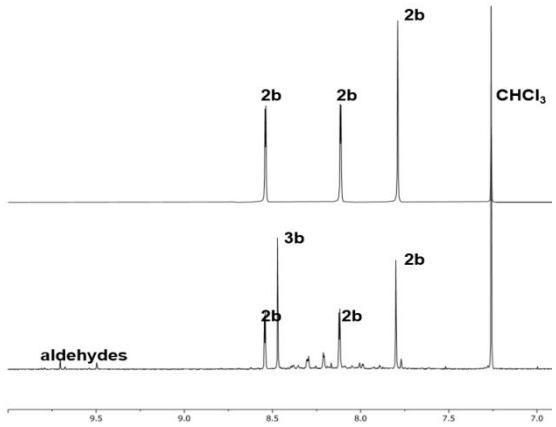


Fig. 2 ^{1}H NMR of crude **2b** prepared (top) by oxidation of **1** with H_5IO_6/EtOH on 1 g scale and (bottom) using the original RICO method.

To optimize the oxidation of **1b** to both **2b** and **3b**, we carried out the oxidation of **1b** on 100 mg scale in EtOH, ^{i}PrOH and AcOH at reflux temperature using different molar ratios of H_5IO_6 and HIO_3 (Table S5). Two oxidant/solvent combinations, H_5IO_6/EtOH and HIO_3/^{i}PrOH, seemed to be the most promising for a selective **1b→2b** oxidation. Both conditions yielded **2b** without any over-oxidation (**1b→3b**), even with increased molar ratios of oxidant to starting material. Using these combinations, the best yields of **2b** on 100 mg scale were obtained using 2 equivalents of H_5IO_6 and 3 equivalents of HIO_3. All reactions were complete within 3 h. Longer reflux time after reaction completion did not appear to affect the yield.

Even though both sets of condition were successful, H_5IO_6/EtOH was found to be the better option in terms of yield, reaction completion, ease of workup, and lower oxidant molar ratio on larger reaction scale. Use of HIO_3/EtOH resulted in some over-oxidization of **1b** to **3b**, which decreases the yield of isolated **2b**. The crude product using the H_5IO_6/EtOH conditions exhibited a surprisingly clean NMR spectrum when compared to an oxidation of **1b** using the RICO conditions (Fig. 2). As a result, we were able to carry out a minimal work-up procedure (precipitation, filtration, silica plug) to isolate highly pure **2b**, without the need of a challenging chromatographic separation,

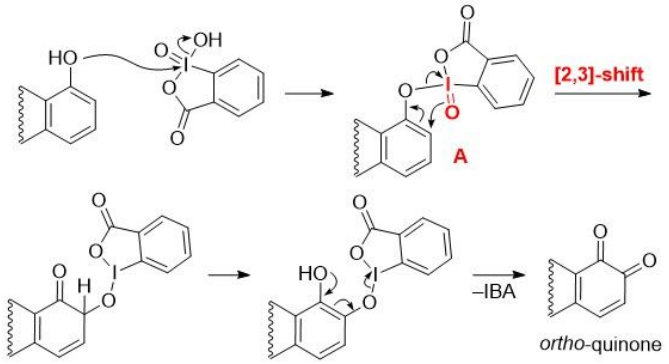
Table 1. Conditions to make **2b** selectively in EtOH at reflux within 5h.

Mass **1b**	Equiv. H_5IO_6	Time	Mass **2b**	Yield
100 mg	2.0	1.5 h	84 mg	76%
1.0 g	2.5	3 h	0.82 g	75%
5.0 g	3.0	4 h	3.9 g	72%
10 g	4.0	5 h	7.3 g	69%

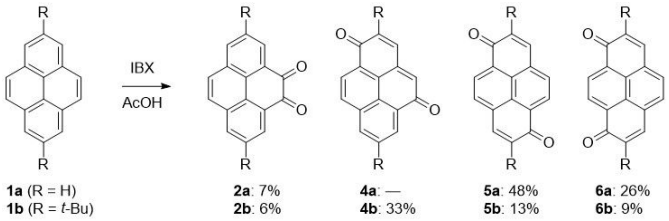
Table 2. Conditions to make **3b** selectively using HIO_3 in 10 vol % H_2SO_4 in AcOH.

Mass **1b**	[H_2SO_4] (aq) [a]	Temp.	Time	Mass **3b** (yield)
100 mg	18.4 M	Reflux	3 h	33 mg (28%)
100 mg	1.84 M	Reflux	3 h	57 mg (48%)
100 mg	0.184 M	Reflux	3 h	64 mg (54%)
100 mg	0.184 M	50 °C	16 h	71 mg (60%)
1.0 g	0.184 M	50 °C	16 h	0.67 g (56%)

[a] Aqueous H_2SO_4 stock solution concentration that was used as 10 vol% in AcOH.



Scheme 2. Mechanism of the *ortho*-oxidation of phenols and PAPs by IBX.[46-48]

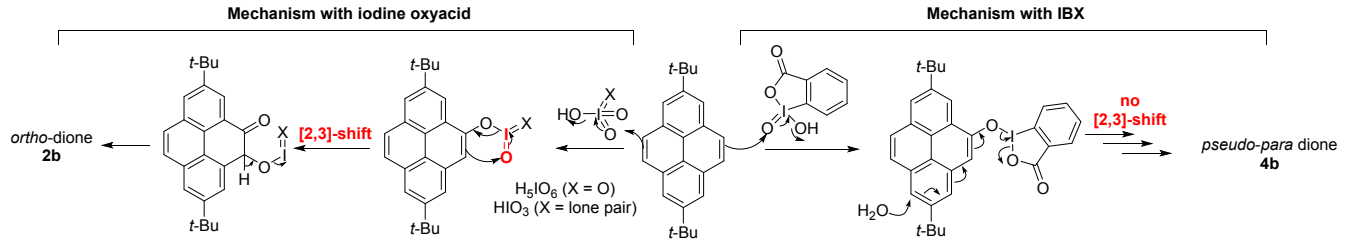


Scheme 3. Oxidation of **1a** and **1b** with IBX.

in yields consistently around 70-75% after complete consumption of **1b**. Yields decreased only slightly on increasing the scale to 10 g, although complete conversion on a larger reaction scale required higher oxidant ratio and longer reaction time. Optimized conditions for different scale conversions (within 5h reaction time) are shown in Table 1.

We found that oxidation of **1b** to **3b** was best carried out in the more acidic reagent/solvent combination HIO_3/AcOH, and selectivity for **3b** over **2b** required either a large excess of HIO_3 (10 equiv.) or the addition of a catalytic amount of H_2SO_4 in AcOH (Table 2). The use of 10 vol% in AcOH of a 1% aqueous H_2SO_4 stock solution (i.e. 0.184 M) with longer reaction time at moderate temperature (16 h at 50 °C) gave the best results. We were able to perform the synthesis of tetraone **3b** from **1b** on a 1 g scale in a 56% yield. Interestingly, we achieved the oxidation of dione **2b** to tetraone **3b** under these optimized reaction conditions in a 74% yield, making the overall yield of 56% for **1b** to **3b** consistent with the yields for the two individual oxidations performed separately.

Formulation of a plausible mechanism for the iodine oxyacid mediated oxidation of **1b** benefits from consideration of the mechanism proposed by Pettus,[46] Quideau[47] and Harvey[48] for the oxidation of phenols with the organic hypervalent iodine reagent 2-iodoxybenzoic acid[49] (IBX, p*K*a = 2.40),[50] and our own observations on the results of oxidation of **1a** and **1b** with IBX (vide infra). A [2,3]-sigmatropic shift was proposed[46,47] for the observed *ortho*-oxidation of phenols to quinones by IBX and further validated[48] to account for a regioselective *ortho*-oxidation of polycyclic aromatic phenols (PAPs), including pyren-1-ol and pyren-2-ol (Scheme 2). This [2,3]-shift is only possible if an I=O bond is present on the hypervalent iodine moiety in the mechanistic intermediate after condensation with the phenol (intermediate **A**, Scheme2). In the absence of I=O, as



Scheme 4. Plausible oxidation mechanisms of **1b** with(left) the iodine oxyacids and (right) IBX.

is the case when (bis(trifluoroacetoxy)iodo)benzene (BTI) is used as oxidant,[48] nucleophilic attack of water leading to a *para*-oxidation product predominates.

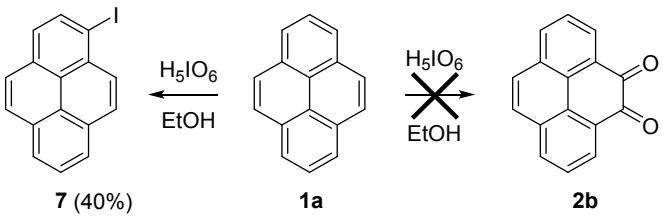
Based on these results, we investigated the oxidation of **1a** and **1b** with IBX, reasoning that the single I=O bond in this reagent would result in an intermediate lacking an I=O bond, leading to oxidation products from water attack. Indeed, *pseudo-para*-diones were the major products from treatment of both **1a** and **1b** with IBX (diones **5a** and **4b**, respectively, Scheme 3). The steric influence of the *tert*-butyl groups in **1b** led to previously unknown 1,5-dione **4b** as the major product, presumably through initial oxidation of the 4,5,9,10-carbons. Although IBX seems to be a strong enough oxidant to yield appreciable amounts of **5b** and **6b** through oxidation of the more sterically shielded 1,3,6,8-carbons, the relative lack of *ortho*-oxidation (i.e. **2a** and **2b**) is consistent with the role of an I=O bond in the *ortho*-oxidation of **1b** with the iodine oxyacids.

Accordingly, we postulate the mechanism in Scheme 4 for the oxidation of **1b** with iodine oxyacids and IBX. Iodine oxyacid oxidation leads to an intermediate with an I=O bond, enabling the subsequent [2,3]-shift pathway. IBX oxidation proceeds via an intermediate lacking an I=O bond, precluding the [2,3]-shift pathway and allowing for nucleophilic attack of water that yields **4b**. Compounds **5b** and **6b** can form by this latter pathway via initial oxidation of carbon-1 of **1b**.

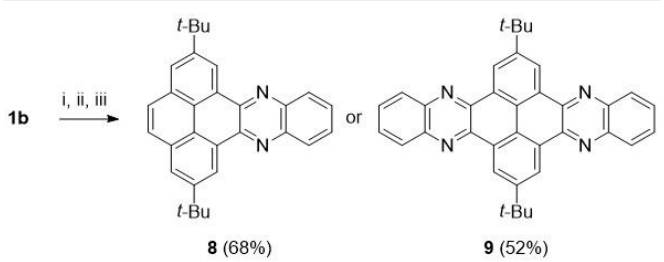
Despite the successful oxidation of unsubstituted pyrene (**1a**) with IBX, when we attempted to use the optimized iodine oxyacid conditions (H_5IO_6/EtOH) for the oxidation of **1a**, surprisingly, we obtained 1-iodopyrene (**7**)[51] in 40% yield, without formation of dione **2a** (Scheme 5). This result offers a Green direct mono-iodination method of pyrene **1a** into **7**, since such transformation has only been reported using the highly toxic cyanogen iodide (ICN)[52] as iodinating reagent or through indirect methods(through 1-bromopyrene[51] or 1-amino-pyrene[53] intermediates). Precedent for this elemental iodine-free iodination exists in two reports by Skulski on the iodination of aromatics in varied yields (27-88%) using $NaIO_4$ under highly acidic conditions ($AcOH/Ac_2O/H_2SO_4$), proceeding via a postulated periodylarene ($ArIO_3$) intermediate that is reduced to the corresponding iodoarene (ArI) through the reductive reaction workup,[54] and HIO_3-mediated aromatic iodinations that proceed presumably via iodylarene ($ArIO_2$) intermediates.[55]

The iodination of **1a**, as opposed to the oxidation of **1b** using the same reaction conditions, highlights the ability of iodine oxyacids to act as both O-electrophiles[37] and I-electrophiles[38,54,55] via two available mechanistic pathways with different pyrene carbons: (i) addition of carbon-4 to the I=O at the oxygen with a change of oxidation state (e.g. Scheme 4);[37] or (ii) addition of carbon-1 to the I=O at the iodine without any change in oxidation state.[54,55] This is an interesting regioselective feature of different pyrene carbons towards H_5IO_6: the I-selectivity at the more nucleophilic 1,3,6,8-positions *vs*. the O-selectivity at the more susceptible to oxidation 4,5,9,10-positions. Once access to the nucleophilic sites is impeded by the steric effect of the *tert*-butyl groups, the less aromatic, more alkene-like sites, which are more prone to oxidation, react preferentially.

To demonstrate the utility of our oxidation method, we performed a direct synthesis of *N*-heteroacenes (**8** and **9**)[56] from **1b** without purification of intermediate dione **2b** or tetraone **3b** (Scheme 6). We carried out the oxidation reaction leading to **2b** and **3b** under the optimized conditions, quenched with water, extracted using ethyl acetate, washed with sodium thiosulfate to neutralize any leftover oxidizing agent, and then crude dione/tetraone was immediately used for the subsequent condensation with *o*-phenylenediamine. Following condensation, the reaction mixture was allowed to cool and the corresponding *N*-heteroacene **8** and **9** was isolated by vacuum filtration as yellow solid (Fig. S3). The absence of side products



Scheme 5. Result of the H_5IO_6/EtOH reaction with **1a**.



Scheme 6. Direct synthesis of *N*-heteroacenes **8** and **9** from **1b**. Reagents: (i) H_5IO_6/EtOH (for **8**) or HIO_3, H_2SO_4, AcOH (for **9**); (ii) $EtOAc/Na_2S_2O_3$; (iii) 1,2-benzenediamine (50% excess), EtOH/AcOH.

was confirmed by NMR illustrating the cleanliness and high selectivity of our method.

In conclusion, we have demonstrated a new metal-free method to oxidize **1b** into **2b** or **3b** with superior selectivity based on the oxidant molar ratio and the acidity of the reaction mixture. The new method is more time and resource efficient in comparison with the transition metal mediated methods. Our method adheres to the 12 Principles of Green Chemistry and results in significant improvements in atom economy, reaction mass efficiency and EcoScale (see ESI) in comparison with the previous methods. We demonstrated the cleanliness and selectivity of the new method via direct synthesis of *N*-heteroacenes. We also introduced the use of IBX as oxidant for non-hydroxylated PAHs and highlighted the role of the I=O in forcing an *ortho*-oxidation and the regioselectivity of different pyrene carbons towards the hypervalent iodine reagent as I-electrophile (iodinating reagent) or O-electrophile (oxidant).

Procedure for the synthesis of **2b** and **3b** on 1 g scale:

2,7-Di-*tert*-butylpyrene-4,5-dione (2b). A mixture of **1b** (1.00 g, 3.18 mmol, 1.0 equiv.) and H_5IO_6 (1.81 g, 7.95 mmol, 2.5 equiv.) and EtOH (50 mL, 95%) was maintained at reflux for 3 h. The reaction color changed from colorless to yellow to orange to red over that period (Fig. S1). After complete conversion was confirmed by TLC, the homogenous dark red reaction mixture was allowed to cool to RT. Compound **2b** slowly crystallized upon cooling. Water (50 mL) and aqueous sodium thiosulfate (50 mL, 10%) were successively added and the mixture was stirred in an ice bath for 2 h. The orange precipitate was collected by vacuum filtration and washed with cold water (3 x 100 mL). The crude solid was purified by filtration through a silica plug (9:1 heptane/EtOAc) to remove inorganic contaminants. Solvent was removed under reduced pressure to provide dione **2b** (0.820 g, 2.38 mmol, 75%) as orange solid: mp 240–242 °C (lit.[23] 241–244 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ8.54 (d, *J* = 2.0 Hz, 2H), 8.12 (d, *J* = 2.0 Hz, 2H), 7.79 (s, 2H), 1.49 (s, 18H); 13C NMR (CDCl3, 100 MHz): δ181.0 (C_q), 151.1 (C_q), 131.9 (C_q), 131.8 (CH), 129.7 (C_q), 128.35 (CH), 127.3 (CH), 126.5 (C_q), 35.2 (C_q), 31.2 (CH_3) (NMR data were identical to reported literature.[23,24]); IR (KBr, ν_{max}) 1672 cm^{-1}; UV-Vis (EtOH, λ_{max}) 440 nm; HRMS (ESI/Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}O_2$ 345.1849; Found 345.1835.

2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone (3b). A mixture of **1b** (1.00 g, 3.18 mmol, 1.0 equiv.), HIO_3 (3.36 g, 19.1 mmol, 6.0 equiv), AcOH (45 mL, 95%), and aqueous H_2SO_4 (0.184 *M*; 5 mL, 0.92 mmol, 0.3 equiv.) was maintained at 50 °C for 16 h. After complete conversion was confirmed by TLC, the dark orange reaction mixture was allowed to cool to RT and poured in water (ca. 100 mL). The mixture was then cooled in an ice bath for 2 h, and the resultant orange precipitate was collected by vacuum filtration and washed with cold water (3 x 100 mL) and aqueous sodium thiosulfate (100 mL, 10%). The collected precipitate was purified by filtration through a silica plug (4:1 heptane/EtOAc) to remove inorganic contaminants. Solvent was removed under reduced pressure to provide **3b** (0.670 g, 1.79 mmol, 56%) as an orange solid: mp > 300 °C (lit.[29] > 300 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ8.48 (s, 4H), 1.43 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ178.2 (C_q), 154.8 (C_q), 133.9 (CH), 132.2 (C_q), 130.5 (C_q), 35.4 (C_q), 30.7 (CH_3) (NMR data were identical to reported literature.[23]); IR (KBr, ν_{max}) 1676 cm^{-1} (lit.[29] 1670 cm^{-1}); UV-Vis (EtOH, λ_{max}) 421 nm (lit.[29] 420 nm); HRMS (ESI/Orbitrap) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}O_4$ 375.1591; Found 375.1580.

Acknowledgments

This work was supported by the National Science Foundation (CHE-1464530 and DMR-1708443).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1. T. M. Figueira-Duarte and K. Müllen, *Chem. Rev.*, 2011, **111**, 7260-7314.
2. F. M. Jradi, M. H. Al-Sayah and B. R. Kaafarani, *Tetrahedron Lett.*, 2008, **49**, 238-242.
3. A. Mohr, P. Talbiersky, H.-G. Korth, R. Sustmann, R. Boese, D. Bläser and H. Rehage, *J. Phys. Chem. B*, 2007, **111**, 12985-12992.
4. X. Yang, Z. Zhao, H. Ran, J. Zhang, L. Chen, R. Han, X. Duan, H. Sun and J.-Y. Hu, *Dyes Pigments*, 2020, **173**, 107881.
5. D. Chercka, S.-J. Yoo, M. Baumgarten, J.-J. Kim and K. Müllen, *J. Mater. Chem. C*, 2014, **2**, 9083-9086.
6. B. R. Kaafarani, T. H. El-Assaad, W. A. Smith, S. M. Ryno, F. Hermerschmidt, J. Lyons, D. Patra, B. Wex, E. J. W. List-Kratochvil, C. Risko, S. Barlow and S. R. Marder, *J. Mater. Chem. C*, 2019, **7**, 5009-5018.
7. T. H. El-Assaad, M. Auer, R. Castañeda, K. M. Hallal, F. M. Jradi, L. Mosca, R. S. Khnayzer, D. Patra, T. V. Timofeeva, J.-L. Brédas, E. J. W. List-Kratochvil, B. Wex and B. R. Kaafarani, *J. Mater. Chem. C*, 2016, **4**, 3041-3058.
8. M. Jung, J. Lee, H. Jung, S. Kang, A. Wakamiya and J. Park, *Dyes Pigments*, 2018, **158**, 42-49.
9. X. Zhan, J. Zhang, S. Tang, Y. Lin, M. Zhao, J. Yang, H.-L. Zhang, Q. Peng, G. Yu and Z. Li, *Chem. Commun.*, 2015, **51**, 7156-7159.
10. Z.-H. Wu, W.-J. Sun, H.-H. Tian, Z.-F. Yu, R.-X. Guo, X. Shao and H.-L. Zhang, *Advanced Electronic Materials*, 2019, **5**, 1800598.
11. O. P. Lee, A. T. Yiu, P. M. Beaujuge, C. H. Woo, T. W. Holcombe, J. E. Millstone, J. D. Douglas, M. S. Chen and J. M. J. Fréchet, *Adv. Mater.*, 2011, **23**, 5359-5363.
12. A. Mateo-Alonso, *Chem. Soc. Rev.*, 2014, **43**, 6311-6324.
13. J. K. Stille and E. L. Mainen, *J. Polym. Sci. B*, 1966, **4**, 665-667.
14. J. K. Stille and E. L. Mainen, *Macromolecules*, 1968, **1**, 36-42.
15. K. Imai, M. Kurihara, L. Mathias, J. Wittmann, W. B. Alston and J. K. Stille, *Macromolecules*, 1973, **6**, 158-162.
16. B. Wex, A. a. O. El-Ballouli, A. Vanvooren, U. Zschieschang, H. Klauk, J. A. Krause, J. Cornil and B. R. Kaafarani, *J. Mol. Struct.*, 2015, **1093**, 144-149.
17. B. Gao, M. Wang, Y. Cheng, L. Wang, X. Jing and F. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 8297-8306.
18. M. Winkler and K. N. Houk, *J. Am. Chem. Soc.*, 2007, **129**, 1805-1815.
19. X. Feng, J.-Y. Hu, C. Redshaw and T. Yamato, *Chem. Eur. J.*, 2016, **22**, 11898-11916.

20. R. S. Tipson, *Oxidation of polycyclic, aromatic hydrocarbons: a review of the literature*, National Bureau of Standards. Institute of Materials Research, 1965.
21. F. G. Oberender and J. A. Dixon, *J. Org. Chem.*, 1959, **24**, 1226-1229.
22. E. Nowicka, N. W. Hickey, M. Sankar, R. L. Jenkins, D. W. Knight, D. J. Willock, G. J. Hutchings, M. Francisco and S. H. Taylor, *Chem. Eur. J.*, 2018, **24**, 12359-12369.
23. J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, **70**, 707-708.
24. J. C. Walsh, K.-L. M. Williams, D. Lungerich and G. J. Bodwell, *Eur. J. Org. Chem.*, 2016, **2016**, 5933-5936.
25. G. Venkataramana, P. Dongare, L. N. Dawe, D. W. Thompson, Y. Zhao and G. J. Bodwell, *Org. Lett.*, 2011, **13**, 2240-2243.
26. D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chemistry*, 2016, **18**, 288-296.
27. X. Feng, J.-Y. Hu, H. Tomiyasu, N. Seto, C. Redshaw, M. R. J. Elsegood and T. Yamato, *Org. Biomol. Chem.*, 2013, **11**, 8366-8374.
28. G. A. Olah, G. K. S. Prakash, P. S. Iyer, M. Tashiro and T. Yamato, *J. Org. Chem.*, 1987, **52**, 1881-1884.
29. T. Yamato, M. Fujimoto, A. Miyazawa and K. Matsuo, *Journal of the Chemical Society, Perkin Transactions 1*, 1997, 1201-1208.
30. A. Miyazawa, A. Tsuge, T. Yamato and M. Tashiro, *J. Org. Chem.*, 1991, **56**, 4312-4314.
31. B. R. Patil, S. R. Bhusare, R. P. Pawar and Y. B. Vibhute, *Tetrahedron Lett.*, 2005, **46**, 7179-7181.
32. A. T. Shinde, S. B. Zangade, S. B. Chavan, A. Y. Vibhute, Y. S. Nalwar and Y. B. Vibhute, *Synth. Commun.*, 2010, **40**, 3506-3513.
33. A. G. Williams, *J. Am. Chem. Soc.*, 1921, **43**, 1911-1919.
34. M. Bücker, H. R. Glatt, K. L. Platt, D. Avnir, Y. Ittah, J. Blum and F. Oesch, *Mutation Research/Genetic Toxicology*, 1979, **66**, 337-348.
35. V. Prelog and S. Polyák, *Helv. Chim. Acta*, 1957, **40**, 816-830.
36. J. I. Levin and S. M. Weinreb, *J. Org. Chem.*, 1984, **49**, 4325-4332.
37. A. J. Fatiadi, *J Res Natl Bur Stand A Phys Chem*, 1968, **72A**, 341-350.
38. A. J. Fatiadi, *J. Org. Chem.*, 1967, **32**, 2903-2904.
39. A. J. Fatiadi, *Chem. Commun.*, 1967, 1087-1088.
40. M. Solas, S. Suárez-Pantiga and R. Sanz, *Green Chemistry*, 2019, **21**, 213-218.
41. Y.-B. Kang, X.-M. Chen, C.-Z. Yao and X.-S. Ning, *Chem. Commun.*, 2016, **52**, 6193-6196.
42. S. Kafka, K. Proisl, V. Kašpárková, D. Urankar, R. Kimmel and J. Košmrlj, *Tetrahedron*, 2013, **69**, 10826-10835.
43. L. Hui and D. G. Leaist, *Can. J. Chem.*, 1990, **68**, 1317-1322.
44. *Inorganic Reactions in Water*, Springer, Berlin, 2007.
45. R. Parsons, *Handbook of Electrochemical Constants*, Butterworths Scientific, London, 1959.
46. D. Magdziak, A. A. Rodriguez, R. W. Van De Water and T. R. R. Pettus, *Org. Lett.*, 2002, **4**, 285-288.
47. N. Lebrasseur, J. Gagnepain, A. Ozanne-Beaudenon, J.-M. Léger and S. Quideau, *J. Org. Chem.*, 2007, **72**, 6280-6283.
48. A. Wu, Y. Duan, D. Xu, T. M. Penning and R. G. Harvey, *Tetrahedron*, 2010, **66**, 2111-2118.
49. A. Duschek and S. F. Kirsch, *Angew. Chem. Int. Ed.*, 2011, **50**, 1524-1552.
50. M. J. Gallen, R. Goumont, T. Clark, F. Terrier and C. M. Williams, *Angew. Chem. Int. Ed.*, 2006, **45**, 2929-2934.
51. T. Stark, M. Suhartono, M. W. Göbel and M. Lautens, *Synlett*, 2013, **24**, 2730-2734.
52. F. Radner, *Acta Chem. Scand.*, 1989, **43**, 481-484.
53. S. Preciado, L. Mendive-Tapia, F. Albericio and R. Lavilla, *J. Org. Chem.*, 2013, **78**, 8129-8135.
54. P. Luliński, M. Sosnowski and L. Skulski, *Molecules*, 2005, **10**, 516-520.
55. B. Krassowska-Swiebocka, G. Prokopienko and L. Skulski, *Molecules*, 2005, **10**, 394-400.
56. P. K. Sahoo, C. Giri, T. S. Haldar, R. Puttreddy, K. Rissanen and P. Mal, *Eur. J. Org. Chem.*, 2016, **2016**, 1283-1291.